

# Development of Defoamers for Confinement Foam

*D. Mark Hoffman and Alexander R. Mitchell  
High Explosives Application Facility  
Lawrence Livermore National Laboratory  
Livermore, CA 94550*

Final Report  
Project #: LLNL-02-010

## Manuscript Date

*U.S. Department of Energy*

Lawrence  
Livermore  
National  
Laboratory

November 20, 2003

## DISCLAIMER

This document was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor the University of California nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or the University of California, and shall not be used for advertising or product endorsement purposes.

This is a preprint of a paper intended for publication in a journal or proceedings. Since changes may be made before publication, this preprint is made available with the understanding that it will not be cited or reproduced without the permission of the author.

This work was performed under the auspices of the U.S. Department of Energy by the University of California, Lawrence Livermore National Laboratory under Contract No. W-7405-Eng-48.

# Development of Defoamers for Confinement Foam

D. Mark Hoffman and Alexander R. Mitchell  
L-282 Lawrence Livermore Labs  
Livermore, CA 94550

## Abstract

Aqueous foam concentrate (AFC) 380 foam was developed by Sandia National Laboratory as a blast mitigation foam for unexploded ordnance (UXO) and its “engineered foam structure” is reported to be able to “envelop chemical or biological aerosols” [1]. It is similar to commercial fire-fighting foams, consisting mostly of water with small amounts of two alcohols, an ether and surfactant. It also contains xanthan gum, probably, to strengthen the foam film and delay drainage. The concentrate is normally diluted in a 6:94 ratio with water for foaming applications. The diluted solution is normally foamed with air to an expansion factor of about 100 (density 0.01 g/cc), which is called “dry” foam. Higher density foam ( $0.18 > \rho > 0.03$  g/cc) was discovered which had quite different characteristics from “dry” foam and was called “wet” foam. Some characterization of these foams has also been carried out, but the major effort described in this document is the evaluation, at the small and medium scale, of chemical, mechanical and thermal approaches to defoaming AFC 380 foam. Several chemical approaches to defoaming were evaluated including oxidation and precipitation of the xanthan, use of commercial oil-emulsion or suspension defoamers, pH modification, and cation exchange with the surfactant. Of these the commercial defoamers were most effective. Two mechanical approaches to defoaming were evaluated: pressure and foam rupture with very fine particles. Pressure and vacuum techniques were considered too difficult for field applications but high surface area silica particles worked very well on dry foam. Finally simple thermal techniques were evaluated. An order-disorder transition occurs in xanthan solutions at about 60°C, which may be responsible for the effectiveness of hot air as a defoamer. During defoaming of 55 gallons of foam with hot air, after about 70% of the AFC 380 foam had been defoamed, the effectiveness of hot air was dramatically reduced. Approximately 15 gal of residual foam containing mostly small bubbles was resistant to further defoaming by methods that had been effective on the original, dry foam. In this paper the residual foam is referred to as “wet” and the original foam is referred to as “dry”. Methods for generating “wet” foam in small to moderate quantities for defoaming experiments have been developed. Methods for defoaming wet foam are currently under study.

## Introduction

AFC 380, developed by Sandia National Laboratory and marketed by Chemguard Inc., is diluted with water in a 6/94-weight ratio and foamed with conventional foam generating equipment (such as the Intelagard back pack foam generator). It has been used with a tent cover to mitigate shock and contain fragments of UXO when such ordnance cannot be moved to safer locations [1]. The foam thus generated is stable for

between 1.5 and 2 hours or longer depending on the scale of the experiment. Diluted AFC-380 foam contains 98% water with a sodium olefin sulfonate surfactant (Bio-Terge AS-40), Xanthan gum, 2-methyl-1-propanol, and EPAL 1214 making up the other ingredients. A general discussion of foams can be found in reference 2. It is sometimes necessary to rapidly access an area covered by the foam. To do this as safely as possible, aqueous foam in this area needs to be defoamed. A defoamer that would collapse large volumes of the confinement foam in a few minutes was one of the highest priority technology short falls listed under the containment effort.

In order for foam to be stable the following conditions must be met[3]:

1. The media must be liquid and composed of at least two substances.
2. A soluble surfactant must be present.
3. The Marangoni effect must occur.
4. A gelatinous surface layer must form.

The defoamer should remove one of the 4 requirements for stable foam. Then like a chair with one of its legs removed, the foam should collapse.

At least three approaches to destroying existing foam are available for evaluation and possible implementation [4]. Mechanical defoaming has been investigated by evacuating or pressurizing foam [5]. Vacuum is used routinely to degas adhesives and moderately viscous mixtures. Alternately, when all components except air are homogeneous, centrifugal force can be used. Since the mechanical strength of the gelatinous surface is less than 1 atmosphere, the foam should easily be destroyed. This is easily demonstrated on a small scale, but is often not portable or convenient to field.

Thermal defoaming depends on the phase diagram of the surfactant/solution or the effect of temperature on the Marangoni effect. In some surfactant solutions, there are lower critical solution temperatures where the surfactant separates from the solution causing the foam to destabilize.[6] The Marangoni effect in foams is the tendency of surfactant-solution to migrate into areas where the foam film is being deformed and prevent rupture of the foam cells. In some instances the temperature dependence of the Marangoni effect reduces the recovery rate substantially so that the foam collapses more easily. Xanthan also undergoes an order/disorder transition with increasing temperature [7]. If either of these mechanisms are applicable to AFC-380, rapidly heating aqueous containment foam should cause its collapse.

A wide variety of chemical defoaming agents are available commercially. These defoamers are typically emulsions of oil, surface-active agents and colloidal particles that destroy foam after it has formed [4]. One postulated mechanism of chemical defoamers is displacement of the adsorbed foaming surfactant by a more active surface layer that does not support foaming. This simplified mechanism cannot explain the relative effectiveness of defoamers in different foaming systems. It also cannot explain the improved performance associated with incorporation of low levels of hydrophobic colloidal particles into the chemical defoamer formulation. For a chemical defoamer to

work, it must enter and spread through the foam. The dynamic surface tension of the foam and the defoamer are, therefore, of interest. Commercial defoamers evaluated in this effort are listed in Table 1.

Table 1. Typical Defoamer active ingredients.

| Defoamer | Supplier   | Oil                 | solid                | Type           |
|----------|------------|---------------------|----------------------|----------------|
| TS-10    | Tiarco     | PDMS <sup>†</sup>   | T-SiO <sub>2</sub> * | Aq emulsion    |
| FB 235   | Ross       | PDMS                |                      | Emulsion       |
| AF9030   | GE         | PDMS                | T-SiO <sub>2</sub>   | Emulsion       |
| RD-71    | RD         | PDMS                |                      | Emulsion       |
| C2010    | New London | PDMS                |                      | Nonionic emuls |
| C2290    | New London | N-PDMS <sup>‡</sup> |                      |                |

\*T-SiO<sub>2</sub> – treated silica; <sup>†</sup>PDMS – polydimethylsiloxane; <sup>‡</sup>N-PDMS – non silicone oil

Alternatively, the chemistry of the foaming agents may be attacked directly. If the surfactant could be altered chemically so that it became ineffective or was removed, the foam should be destroyed. Several approaches to this have been tried. The thickener, xanthan gum, is known to be susceptible to oxidation [8,9] and to precipitate from solution with the addition of alcohols [10-14]. If these can be exploited, defoaming should be possible.

## Experimental

**1. Foam concentrate:** The composition of the foam concentrate used to prepare AFC 380 is given in Table 2. Chemguard Corporation prepares this concentrate for the DOE. This concentrate was diluted 94:6 with water and foamed through various techniques to an expansion factor of approximately 100. Bio-Terge AS-40 is 14 to 16 carbon  $\alpha$ -olefin sodium sulfonate general purpose anionic surfactant manufactured by Stepan Company and used extensively in detergents for foam rinsing and cleaning [15]. Epal 1214 is a long chain alcohol, which is no longer manufactured by Emery. Comparable alcohols are available from Pilot Chemical Corporation, Chemcentral Corporation or Brenntag Chemicals. The original xanthan gum, K9A48 by Kelco Polymer is no longer manufactured and Kelco has replaced this gum with “Kelzan” industrial grade xanthan gum [16]. Generic alcohols such as isobutyl and diethylene glycolmonobutyl ether are available from Aldrich or many other chemical suppliers.

Table 2. Composition of AFC 380 foam concentrate.

| Component        | %     | Chemistry   | Purpose               |
|------------------|-------|---|-----------------------|
| Bio-Terge AS-40  | 19.9  | Na-SO <sub>3</sub> -(CH <sub>2</sub> ) <sub>14-16</sub> | Surfactant            |
| EPAL 1214        | 0.8   | HO-(CH <sub>2</sub> ) <sub>12</sub>                     | Alcohol 1             |
| Xanthan Gum      | 1.8   | $\alpha$ -glycoside side chain                          | Rheology modification |
| Isobutyl Alcohol | 4.0   | HO-(CH <sub>2</sub> ) <sub>2</sub> -(Me) <sub>2</sub>   | Alcohol 2             |
| DEGMBI ether*    | 6.2   | HOEt-OBu  | Alcohol 3             |
| Deionized water  | 67.3% |   | Solvent               |

\* DEGMB ether – diethylene glycol monobutyl ether

**2. Foaming and defoaming procedures.** The 96/4: water/AFC 380 diluted solution was foamed in small quantities using a sparging technique illustrated in Figure 1 to make a representative dry foam. Low-pressure air was blown through a polyethylene mesh cylinder 25 mm in diameter by 25 mm high immersed in a beaker of foam solution. When the vessel was full of foam, the sparger and stainless steel beaker were removed. Sufficient foam was added using the sparger to completely fill the vessel and then the residual fluid was weighed. The density of the foam was estimated from the foam weight divided by the volume of the vessel.

Once the dry foam completely filled the vessel, liquid defoamer was sprayed into the vessel. The amount of liquid defoamer was determined by difference. For the 4 liter vessel, a simplex sprayer was used to apply the defoamer. Because of the nozzle and limited pressure, the viscous defoamers were applied as a cylindrical stream. Defoaming in a mid-scale vessel (5 gal) was performed using a high-pressure sprayer. This sprayer produced extensive atomization and a mist covered the foam surface. In both cases the approximate time required to defoam was measured. The amount of residual foam, which was not defoamed, was estimated by marking the outside of the vessel in 0.1 liter increments, shaking down the foam on the sides of the vessel and approximating its volume. In some instances the amount of liquid drained from the foam was measured during the defoaming operation. Usually however, defoaming occurred very rapidly and no estimate of drainage could be made.

Wet foam (density above 0.03 g/cc) was made in several different ways once inadvertently and then on purpose. One approach to making a wet/dry foam generator is shown in Figure 2. This consisted of two interconnected 3-necked round bottom flasks. Flask I contains the sparger and when used alone, generates dry foam at volume flow rates of about 1 l/m. Flask II contains a large Teflon stirrer. When dry foam from flask I was fed into flask II and stirred vigorously, wet foam is produced as shown in the figure. This process can produce 4-20 liters but is slow and cumbersome and produces variable cell size when some dry foam flows around the impeller. For rapid generation of 15-20 cc of wet foam, 2-4 cc of diluted AFC 380 solution in a 40-cc capped vial was mixed for approximately 30 - 60 s in a Vortex mixer. Wet foams of reasonable consistency with densities between 0.15 and 0.18 g/cc are quickly produced in this way. These wet foams were used to screen prospective defoamers by adding the defoamer directly to the wet foam or by spraying on the foam surface. Two to three and a half liters of wet foam can be prepared from 80 - 150 g of diluted AFC 380 in a 4-liter, polyethylene container by shaking for 5 minutes on a commercial paint shaker. This wet foam had lower density (0.03-0.06 g/cc) than the vortex mixer foam, but was still quite persistent.

**3. Chemical Defoaming.** Six commercial chemical defoamers, listed in Table 1, were evaluated. Although the exact formulations of most of the defoamers were proprietary, there are common characteristics associated with them [3, 17-21]. All are emulsions of oil in water with some surfactant. Usually the oil is all or partly poly(dimethyl siloxane). All contain hydrophobic silica filler. Some of the specifications are given in Table 3. All these defoamers were used as received.

Table 3. Physical properties of Commercial Chemical Defoamers.

| Sample | % Solids | Surfactant | pH    | Viscosity<br>(cps) | Density<br>g/cc |
|--------|----------|------------|-------|--------------------|-----------------|
| TS-10  | 10.5     |            | 8 ± 1 | 3000               |                 |
| FB-235 | 9.6      | nonionic   | 8.5   | 2000               | 1.00064         |
| AF9030 | 40       | nonionic   |       |                    | 0.982           |
| RD-71  | 15.4     |            |       |                    | 1.00            |
| C-2010 |          |            |       |                    | 1.00025         |
| C-2290 | 15       |            | 7.7   | 1800               |                 |

Because of the susceptibility of xanthan to oxidation, solutions of five different oxidizing agents were evaluated as defoamers. The concentration of oxidizer varied depending on its solubility in water or availability. Ammonium persulfate (3N), oxone (1N,  $2\text{KHSO}_5 \cdot \text{KHSO}_4 \cdot \text{K}_2\text{SO}_4$ ), sodium hypochlorite (9.5% Cl) and hydrogen peroxide (30%) were sprayed onto the foam using the technique described above. Deionized water was used in all solution preparations. Sodium hypochlorite and hydrogen peroxide were kept cold and used as received. Typical properties of these oxidizing agents are given in Table 4. To enhance the reactivity of the oxidizing agents, especially sodium perborate, the accelerators listed in the table were evaluated.

Table 4. Some properties of the oxidizers used in defoaming experiments

| Oxidizer type       | Oxidizer            | Formula                                       | N or %  | Accelerators                    |
|---------------------|---------------------|---|---------|---------------------------------|
| <i>Persulfate</i>   |                     |   |         |                                 |
|                     | Ammonium persulfate | $\text{NH}_4\text{S}_2\text{O}_8$             | 3N      | ketones, $\text{NH}_4\text{Cl}$ |
|                     | Oxone               | $\text{K}_5\text{H}_3\text{S}_4\text{O}_{18}$ | 1N      | ketones, $\text{NH}_4\text{Cl}$ |
| <i>Hypochlorite</i> |                     |   |         |                                 |
|                     | Sodium              | $\text{NaClO}$                                | 9.5% Cl | cyanuric acid                   |
| <i>Peroxide</i>     |                     |   |         |                                 |
|                     | hydrogen            | $\text{H}_2\text{O}_2$                        | 30%     |                                 |
| <i>Perborate</i>    |                     |   |         |                                 |
|                     | Sodium              | $\text{NaBO}_3$                               | 2.7%    | ethylacetoacetate               |

**4. Mechanical Defoaming.** Eight different hydrophobic and hydrophilic silicas were evaluated as defoamers by sprinkling them onto the dry and wet foams described above. Cab-o-Sil T-530 and EH-5 fumed silicas from Cabot Corporation [22]; Aerosil 200, R-812 and R-792 fumed silicas from DeGussa Corporation [23] and Hi Sil T-700 precipitated silica from PPG [24] were evaluated in this way. Alumina C, fumed alumina and COK 84, a physical mixture of fumed silica and fumed alumina available from DeGussa corporation were also evaluated. Table 5 lists some properties of these silicas. All silicas were used as received.

**5. Superabsorbers.** In earlier experiments on large volumes of foam, it was observed that during defoaming operations about 25% of the foam would not defoam with conventional silicone emulsion defoamers or calcium chloride [25]. No further information about this phenomenon was given. As is well known [26, 27], lightly

crosslinked poly(acrylic acid) sodium and potassium salts will absorb several hundred times their weight in water. The five superabsorbing polymers listed in Table 6 were purchased from Aldrich Chemical Company and evaluated as clean up aids. Superabsorbers based on lightly crosslinked polyacrylic acid potassium (PAA-K) and sodium (PAA-Na) salts and two superabsorber copolymers: the potassium salt of polyacrylic acid and polyethylene oxide (PAA-co-EO-K), the sodium salt of polyacrylic acid and polyacrylamide (PAA-co-AC-Na) were coarse powders. The superabsorber based on the sodium salt of poly(maleic acid) and polyisobutylene (PIB-co-MA-Na) was fibrous. Two methods were used to estimate the uptake of solution by each polymer. Small amounts of polymer (2-5 mg) were deposited on a stainless steel screen and immersed in about 40 ml of foam solution. Samples were removed and patted dry and weighed as a function of log time for 5 days. After this time the sample was removed and dried on the stainless steel screen and reweighed to determine sol and gel content. The foam/defoamer solutions were tested using 0.1 g of polymer inside a 9-mm Whatman 42 filter paper funnel immersed in the fluid. Samples were removed from the solution and the solvent removed with a Buchner funnel and vacuum. Then the filter paper and sample were weighed and the weight of the wet filter paper subtracted. These measurements were made after 5 and 15 minutes and approximately 24 h.

Table 5. Properties of colloidal silicas evaluated in defoaming experiments.

| Colloid          | Particle size (nm) | Aggregate size ( $\mu\text{m}$ ) | Surface area ( $\text{m}^2/\text{g}$ ) | pH  |
|------------------|--------------------|----------------------------------|--|-----|
| Cab-o-sil EH5    | 7                  | 0.3                              | 380                                    | 4   |
| Aerosil 200      | 12                 | 0.4                              | 200                                    | 4   |
| HiSil T700       | 21                 | 1.9                              | 210                                    | 7   |
| Cab-o-sil TS 530 |                    | 0.2-0.3                          | 205-245                                |     |
| Aerosil R-812    | 7                  |                                  | 260                                    | 7.5 |
| Aerosil R 792    | 16                 |                                  | 110                                    | 4   |
| COK 84           |                    |                                  | 170                                    | 4   |
| Alumina C        | 13                 |                                  | 100                                    | 7   |

Table 6. Some properties of superabsorbing polymers evaluated used to imbibe residual defoamed solution.

| Absorbent Polymer | Morphology | Size <d> | Absorption characteristics |
|-------------------|------------|----------|----------------------------|
| PAA-K salt        | powder     | 1-mm     | 27 g/g 1% saline           |
| PAA-Na salt       | powder     | 1-mm     | 45 g/g 1% saline           |
| PAA-co-EOK        | granules   | 0.2mm    | Many times its wt          |
| PAA-co-AC-Na      | granules   | 0.1mm    | Many times its wt          |
| PIB-co-MA-Na      | Fiber      | 24 mm    | 65 g/g 1% saline           |

**6. Surface tension measurements.** Two different types of surface tensiometers were used to measure the surface tension of the foam solution and mixtures of the foam solution with two commercial antifoams. The SensaDyne PC-500L uses the dynamic



bubble method to determine the surface tension of a fluid [28]. The First Ten Angstroms FTA 200 surface tensiometer was used to measure the surface tension of the same materials using the pendent drop technique [29]. Both instruments were calibrated against pure water prior to the measurements on foam solutions and antifoams.

## Results and Discussion

### A. Characterization of AFC 380 Foam solution and its foams.

**1. Surface tension.** The dynamic surface tension of the 94/6 dilution of AFC 380 foam was measured using the maximum bubble pressure method on the SensaDyne PB-500L. After a water calibration run ( $71.6 \pm 0.2$  dy/cm), approximately 60 ml foam solution was placed under 2 tubes of large and small orifice. The flow rate of air was varied to give different bubble periods. The longer the time required for the bubble to release from the orifice, the lower the surface tension. The "surface age" on the bubble from this technique varied from 0.03 to 1.3 sec. This "surface age" gives some idea of the dynamic surface tension associated with surfactant migration to the air/water interface. [30] The initial surface tension based on second order polynomial extrapolation to zero time was  $40.5 \pm 0.2$  dy/cm. Within 1 second "surface age" the dynamic surface tension had decreased to  $33.6 \pm 0.2$  dy/cm. Close examination of this data indicates that the surfactant (C12-14 sodium sulfonate) begins to migrate to the surface within the first 0.1 sec and continues to aggregate there for some time. The "equilibrium" surface tension was estimated using the pendent drop experiments. The First Ten Angstroms surface tensiometer model 200 analyzed a video of a drop of solution for temporal variation in the surface tension. The drop takes about 6 seconds to become large enough to apply the Laplace-Young [29] equation. After that with a time resolution of 0.5 s, the surface tension decreases as the surfactant absorbs on the drop's surface. The initial value from the drop measurements averaged about  $28.2 \pm 0.8$  dy/cm. The "equilibrium" value of the surface tension was 23.5 dy/cm. The surface tension continued to change until after about 43 seconds. The surface tension of both measurements was plotted as a function of "time" in Figure 3. As can be seen in the figure, substantial changes in surface tension occur in the first 10 to 20 s. The dip and recovery from the FTA 200 data was only seen in this run and may be an artifact. The effect of xanthan, alcohols and ether in the AFC-380 foam solution dynamic surface tension is not known, but may be important [31, 32].

**2. Foam Drainage.** The drainage characteristics of the 94/6 AFC 380 foam depend upon the ability of the liquid in the foam to flow through the Plateau borders under the force of gravity, capillary pressure due to the liquid pressure in the Plateau borders being lower than the pressure of the gas in the surrounding bubbles, and viscous resistance to flow. A second order nonlinear drainage equation, requiring uniform bubbles, has been developed and used to estimate drainage [2, 33,34]. In general the 4-l foams did not contain uniform bubbles. Figure 4 shows the drainage characteristics of a typical 4-liter sample of freshly prepared 94/6 AFC 380 dry foam. The foam in this figure had an initial density of 0.015 g/cc. Approximately 61.55 g of foam solution filled the 4 l vessel. This gave an expansion factor of about 65, which is somewhat lower than

the 100 value given by Sandia when using the Intelgard foam generator. The drainage is measured as the weight of liquid poured off in a given time increment. Initially it was zero and in the first 10 minutes about 30% of the AFC-380 had drained off. Some of this may be associated with spillage from the foaming solution in the bottom of the vessel. Subsequently, drainage slowed down and became nearly constant after about 20 minutes. This dry foam drained down from 4 liters to about 0.5 liters in 2 hours. Note that the volume reduction rate does not correlate with drainage but appears to be nearly constant at about -0.0336 liters/minute. This implies that the foam film and Plateau borders can shrink from loss of fluid without substantial bubble coalescence or cell collapse. The result was typical of foam generated by the sparger.

Wet foam drainage is very different from dry foam. Wet foam tends to thin, but not collapse over several days. Figure 5 shows the drainage measured on 4 samples 7-8 cc's of wet foam with average density of 0.18. As can be seen in the figure almost 75% of the liquid has drained out after one day. However the volume of the foam is only reduced by about 40%. This implies significant thinning of the foam film and Plateau borders has occurred without comparable collapse of the foam or coalescence of foam bubbles.

**3. Foam density.** Dry foams made by sparging were polydisperse. Densities of  $0.021 \pm 0.006$  were obtained for 16 trials by weighing the 4 L container after removing the sparging apparatus. This gives an expansion factor of about 50. Sandia typically obtains an expansion factor of 100 (density 0.01). Within about 10 minutes, foams made in this way tended to drain without significant volume change. Densities averaged 0.0096 after the first drainage of liquid, more representative of the Sandia foam. Some of the weight in the initial measurements may be from spillage. A photo of dry foam prepared by sparging is shown in Figure 6a.

Wet foam generated by the apparatus in Figure 2 had densities between 0.28 and 0.037 g/cc. This foam tended to have some dry foam in it causing its density to be low. Wet foam made on the paint shaker had densities from 0.032 to about 0.5 g/cc depending on the amount of diluted AFC 380 added to the vessel. Wet foam produced from the vortex mixer had the highest densities varying from about 0.1 to 0.3 g/cc. The higher densities prepared by this method tended to lose about 1/3 of their liquid rapidly until their densities approached 0.1 g/cc. A photo of wet foam made on the paint shaker is shown in Figure 6b.

**4. Bubble size and foam film thickness.** A schematic representation of bubble size and foam film thickness for wet and dry foams is shown in Figure 7. As shown in the figure, most of the surfactant is believed to be near the liquid/air interface. Ideally, as the amount of fluid increases, the bubbles in the foam transform from polyhedral to more spherical [2]. The bubbles in the dry foams produced by the Integrand foam generators used by Sandia for the confinement foam have a broad distribution of sizes from 2.5cm across to relatively small (50  $\mu$ m) bubbles often trapped along the Plateau borders. The largest bubbles generated in the sparger described above were 2.5 cm as measured by photographs of dry foam on the surface of a glass plate. Smaller bubbles have higher internal pressure and tend to be absorbed by larger bubbles [3]. Larger bubbles also tend

to burst and the as produced foam is quite dynamic. Larger bubbles also tend to rise to the surface leaving their smaller counterparts further down in the foam. Foam film thickness was measured using a Zeiss transmitted light microscope by depositing dry foam on the bottom of the glass stage and focusing on sections of the bubble film between bubbles that were at least 1 cm across. Optical micrographs of the bubble films were calibrated against a stage micrometer. Dry foam film thicknesses were between 600 and 750  $\mu\text{m}$ .

A polarized light micrograph of wet foam generated by the vortex mixer ( $\rho = 0.154 \text{ g/cc}$ ) is shown in Figure 8. This micrograph shows the largest bubble sizes are about 420  $\mu\text{m}$  or less. The foam films tend to be between 10-25  $\mu\text{m}$  thick and they do not appear to be shared by adjacent bubbles. Here each bubble appears to have an individual film and an interstitial film exists between adjoining bubbles. Finally the Plateau borders appear to contain air bubbles as well as liquid and often contain bubbles above or below them. Apparently the AFC 380 wet foam is not simply an expansion of the liquid boundaries to accommodate the increase in liquid volume as presumed in the schematic of wet foam in Figure 7. The order of magnitude difference in foam film dimensions should produce a  $10^4$  or more difference in flow rate, which would explain the low drainage rate in wet foams.

## **B. Chemical defoaming.**

**1. Commercial Defoamers.** As might be expected, a substantial amount of information is available on commercial defoamers [4, 35-43]. These types of defoamers are formulated as emulsions of an oil, often a silicone oil, a proprietary surfactant to emulsify the oil, and hydrophobic silica[3]. A substantial increase in defoaming rate occurs with the addition of particulate silica and/or other insoluble suspended material to these emulsions. There is disagreement regarding the exact defoaming mechanism for these types of defoamers and different formulations are more or less effective against different foams, but it is generally accepted that “oil lenses” insert themselves into the film portion of the foam as shown schematically in Figure 9a. Because of the incompatibility of the oil lens with water, the inserted “oil lens” tends to form a bridge across the foam film (see Fig. 9b) and thin. Without the presence of hydrophobic silica or other insoluble suspended matter, the thinning process takes considerable time. With suspended particulate, however, the foam film is abraded and ruptures very quickly (as shown schematically in Figure 9c).

Following the manufactures recommendations, the six commercial defoamers listed in Table 3 were sprayed into 4 liters of ‘dry’ foam generated as described above and shown schematically in Figure 1 using a simplex sprayer. Because of the relatively high viscosities of the defoamers, straight streams were sprayed into the foam rather than an aerosolized dispersion. Never the less, all six defoamers collapsed 80% or more of the foam. Table 7 shows the results. Relative ratings between 1 and 5 based on the extent of foam collapse are given in the table with 5 being complete collapse of the foam and 2 being 50% collapse. The amount of defoamer used was estimated from the increase in

weight of the container after defoaming and the relative percentage of defoamer to foam was calculated.

Table 7. Commercial Emulsion defoamer results

| Chemical         | wt (g) | % defoamer used |        | Eff | Refoam<br>ml/100ml | $\eta$ (Pa-s) |
|------------------|--------|-----------------|--------|-----|--------------------|---------------|
|                  |        | 4 liter         | 5 gal  |     |                    |               |
| Octosperse TS 10 | 16.68  | 8.79%           | 5.93%  | 5   | 3.5                | 3             |
| NL C-2010        | 6.76   | 7.23%           | --     | 3   | --                 | med           |
| NL C-2290        | 12.1   | 11.80%          | 15.51% | 5   | 1                  | 1.8           |
| GE AF 9030       | 6.65   | 7.38%           | 9.40%  | 5   | 6                  | high          |
| Foam Blast 235   | 6.72   | 7.47%           | 10.33% | 4   | 5                  | 2             |
| RD-71            | 8.72   | 8.89%           | 18.27% | 4   | 4                  | high          |
| Water            | 7.25   | 8.44%           |        | 2   |                    | low           |

Some observations on use of these defoamers are given below. All defoamers sprayed a straight stream of thick solution into 4 liters of foam. Within 3 minutes with 12 sprays, Octosperse TS-10 reduced the volume of foam to 0.1 L. NL C-2010 knocked down about half the foam in 3 minutes. After another 2 minutes a second spray of this defoamer reduced the volume of foam to 0.5 L and within 2 more minutes to 0.1L. With 12.1 g of NL C-2290, the 4 L foam sample was reduced to less than 0.5 L in 2 minutes. GE AF 9030 reduced the 4 L sample to 0.1 L within 2 minutes. The GE antifoam stuck to the edges of the polypropylene vessel, but defoamed very well. Foam blast 235 required about 5 minutes to reduce the foam from 4 to 1 L. Subsequent spraying reduced the foam down to 0.1 L after 7 minutes. Approximately 8.7 g of RD -71 reduced the foam to 0.1 L in about 5 minutes. Figure 10 is a bar graph of the relative effectiveness of each commercial emulsion against 4 liters of AFC dry foam. Five of the chemical defoamers were used on larger foam samples (5 gallon) with similar results.

It may be necessary to refoam over a defoamed area with AFC 380. After defoaming with emulsion type chemical defoamer (5 gal level) small quantities of AFC 380 was bubbled over the defoamed surface liquid. The foam collapsed almost immediately. If after some period of time, the effectiveness of the defoamer dissipated, refoaming might then be possible. Preliminary estimates of the time dependence of commercial emulsion defoamers in AFC-380 foam solutions was evaluated with a simple shake test[38,44]. In this test 10 ml of residual fluid from 5 gallon defoaming experiment were added to a 100 ml graduated cylinder and shaken by hand for 100 shakes. The concentrations of the defoamer in the AFC 380 foaming solution are given in Table 7. The maximum amount of foam generated in 100 shakes is also given. The results are very low considering the foam expansion factor is usually about 100. None of the defoamers gave more than 6 ml of regenerated foam. FB 235, AF 9030 and RD 71 gave weakly increasing amounts of regenerated foam with increasing number of shakes (between 0.015 and 0.004 ml/shake). This is typical of some silicone-based defoamers where the oil emulsifies with the surfactant in the foam [38]. However, TS-10 gave a very slight decrease in foam concentration with number of shakes and C-2290 gave generated no foam at all during the shaking. Figure 11 is a plot of foam volume as a

function of the number of shakes for all 5 commercial emulsion defoamers. As can be seen, the scatter is large and the amount of foam generated in the tests was very small. Attempts to refoam over defoamed solutions were unsuccessful, consistent with the continued activity of the antifoam based on shake testing results. When paper or other barrier material was placed over the defoamed solution, then new foam could be generated over defoamed liquid.

Two of the defoamed solutions were evaluated using surface tensiometers. Short time surface tensions were measured using SensaDyne PC-500L and long times were measured using the FTA 200. Comparison of the dynamic surface tensions of the foam solution with and without 7% defoamer, are shown as a function of surface age in Figure 12. At least two runs of each solution were measured. At short times the foam solution approaches a limiting surface tension, probably associated with the amount of surfactant dissolved in the bulk solution. This value decreases with surface age ( $\sim 1/\text{bubble frequency}$ ), ie, as the surfactant migrates to the surface of the air/water interface. On addition of the defoamer, the initial surface tension flattens out. Since the Marangoni effect is caused by the gradient in surface tension when new surface is generated, the reduction in this gradient on addition of defoamer should tend to reduce foam film stability and formation. On addition of  $\sim 4$  g of FB-235 at early time  $\Delta\gamma/\Delta t$  was negative providing no driving force for the Marangoni effect. Both GE 9030 and FB-235 gave  $\gamma_0 \approx 35.7$  dy/cm. The dynamic surface tension of FB-235 defoamer solution passed through a maximum at about 37 dy/cm. AF 9030 defoamer tended to cause the solution surface tension to remain nearly constant at 35.7 dy/cm for bubble frequencies up to about 5 bubbles/sec, and then fall off to slightly lower surface tension than the foam solution itself. In both cases, after the defoamers had been added to the AFC 380 94/6 solution, no foam was observed on the surface of the liquid as the bubbles rose.

The sessile drop method requires approximately 6-7 seconds for the drop to become sufficiently large to observe the effect of gravity and allow the Laplace-Young equation to be solved. The FTA 200 analyzes video of each drop and calculates the surface tension as a function of time. Figure 13 shows the surface tension of the foam solution based on sessile drop and the change associated with the addition of  $\sim 9\%$  of the same defoamers used previously. The data from the previous plot is also shown. The 'equilibrium' surface tension extrapolated to long times was unchanged when the FB-235 was added, but was increased to  $\sim 27$  dy/cm on addition of AF 9030 defoamer. Two runs of the FB-235 defoamer superimposed very well. However both the foam and the AF 9030 defoamer gave somewhat different results at times in the neighborhood of from 10-25 sec on second runs in the FTA 200.

Tests of five of the six defoamers against 2.5-3.5 liters of wet foam gave similar results to dry foam tests except that more defoamer and longer times were required. Within about 3 minutes GE AF 9030, C-2290, and TS-10 had defoamed 3 liters of wet foam down to 0.5 liters or less. RD-71 required almost 12 minutes with agitation of the vessel to defoam 2 liters of wet foam to 0.5 liters. FB-235 only reduced a volume of 3 liters of wet foam down to 2 L after 1 minute of spraying. This foam remained stable for minutes after the spraying stopped. These experiments tend to indicate that 3 defoamers

will defoam any type of AFC 380 foam. However, when experimenting with 55 gal of foam using a hot air blower (discussed below), about one fourth of the volume was converted to wet foam after about 5 minutes. The remaining “wet” foam could not be defoamed thermally. About 15 gallons of wet foam was sprayed with almost 100 g of TS-10 only about 1 gallon of this foam was destroyed. 100 g of TS 10 should have removed at least 7 gal of foam. After this about 150 g of RD-71 was sprayed into the “wet” foam with similar results. Clearly further large scale testing of the most promising formulations would be of interest.

Based on results to date, the most promising of the chemical defoamers was Tiarco’s Octosperse TS-10. Although GE’s AF 3090 and New London’s C-2290 performed as well in all the head-to-head testing, the GE and New London antifoams show definite aging effects, so they would have limited shelf life. The GE antifoam turned yellow and became more viscous over 2 years. The New London antifoam tended to phase separate with visible evidence of solids in the bottom of the container. This is not a significant problem if the jar can be shaken, but large quantities might tend to produce spurious results.

**2. Oxidation of xanthan.** Assuming that xanthan gum used in AFC 380 helps stabilize the foam’s gelatinous surface, reducing this stability should enhance drainage and accelerate the collapse of the foam. Xanthan gum is a high molecular weight heteropolysaccharide whose main chain consists of  $\beta$ -glycoside linkages, which are chemically very inert. The xanthan structure is shown in Figure 14. Xanthan has a trisaccharide side chain which contains the anions which make it soluble and an  $\alpha$ -glycoside linkage that is susceptible to oxidation.[8, 9] These side chains are also believed to be responsible for the order/disorder transition which give xanthan solutions their unique rheology and yield stress[7].

The four oxidizing agents evaluated in aqueous solution are listed in Table 4. When sprayed, these oxidizers were not as effective as the commercial defoamers against 4 l of dry foam as shown in Figure 15. Oxone ( $2\text{KHSO}_5 \cdot \text{KHSO}_4 \cdot \text{K}_2\text{SO}_4$ ) was the most reactive in preliminary foam tests, leaving about 0.5-l of residual foam and was more effective when used warm. It is known that the oxidation rate of persulfates can be accelerated with ketones, which react to form dioxirane ring structures, which are very reactive [45-47]. These catalysts must be added just prior to treatment [8]. Oxone is also acidic which may influence the oxidation of xanthan. Ammonium persulfate, which tends to be basic, was ineffective (comparable to water). Sodium hypochlorite (12% active chlorine) was the second most effective oxidizer in the foam tests. Lithium or Calcium hypochlorite can be prepared at 30 and 65%, respectively, so they should be more reactive. Hydrogen peroxide ( $\text{H}_2\text{O}_2$  in water at 30% was used) generates oxygen during application, which caused more foaming after some defoaming had occurred. Needless to say, this was ineffective.

Experiments on the degradation of the xanthan backbone with acid and hydrogen peroxide [48, 49] have shown that this reaction can reduce the molecular weight of xanthan by up to 2 orders of magnitude. However, the rates are relatively slow requiring

about 1 hour to reduce the xanthan molecular weight from 2,000,000 to 10,000. Since the persulfate anion has a higher oxidation potential than hydrogen peroxide [50], it should be more effective at oxidizing xanthan and hence defoaming, as seen in the table. The effect of increasing the pH in the persulfates by going from oxone ( $K^+$  ion and pH ~ 3) to ammonium persulfate ( $NH_4^+$  ion and pH ~ 7) was to reduce the effectiveness of the oxidizing agent ( $S_2O_8^{2-}$ ) even though ammonium persulfate had higher solubility in water. Although it is known that oxone oxidations can be enhanced by adsorption on silica [51-53], addition of silica to 1N oxone solutions was less effective at defoaming than using the solution by itself.

Table 8. Oxidizing agent defoamer results for dry foam.

| Chemical   | wt (g) | % defoam | Eff | $\eta$ (Pa-s) |
|--|--------|----------|-----|---------------|
| Oxone / EH 5 gel   | 10.62  | 12.26%   | 4   | thix          |
| 9.5% NaClO   | 5.95   | 6.56%    | 3   | Low           |
| 3N (NH <sub>4</sub> ) <sub>2</sub> S <sub>2</sub> O <sub>8</sub> | 5.97   | 6.27%    | 2   | low           |
| 30% H <sub>2</sub> O <sub>2</sub>                                | 23.02  | NA       | 2   | Low           |
| 1N Oxone @70C  | 14.1   | 12.13%   | 4.5 | low           |
| Water  | 7.25   | 8.44%    | 2   | low           |

The reaction rates of these aqueous oxidizers may be accelerated by catalysis in some instances [8, 9]. Metal salts, iron (+3) is often used, can be used to generate the sulfate radical ( $SO_4^{\cdot-}$ ) which has an even higher oxidation potential than the persulfate anion. The addition of ketones to persulfates should generate four-membered dioxirane ring structures in situ [45], which are very strong oxidizing agents. Hypochlorites have reportedly been accelerated with ammonium chloride or cyanuric acid [8]. Ammonium chloride and sodium hypochlorite probably generate monoamines [54,55]. This approach produces hydroxyl amines which can generate toxic gasses (Ammonia) during oxidation reactions. Cyanuric acid is known to stabilize free radical formation during chlorine oxidation, which tends to increase the effectiveness of hypochlorites. Sodium perborate is not effective as an oxidizing agent below 40°C [56], but can be catalyzed with ethyl acetoacetate or tetraacetylenediamine [57] to generate the peracetate ion which is an excellent oxidizing agent at ambient. It is also known that the residual borate can form complexes with saccharides, which might enhance xanthan oxidation or render it incapable of sustaining the foam.

Attempts to defoam wet foam using accelerated oxidizing solutions listed in Table 4, were not successful. Stoichiometric amounts of acetone and methylethyl ketone, were added to 1.75N oxone (almost the solubility limit of the oxidizer in water) and sprayed onto 15-20 ml of wet foam. Assuming the dioxirane forms under these conditions, it was ineffective as a defoamer. At the 2% level, ammonium chloride was effective as a catalyst for 1.75 N oxone solutions against wet foam. This reaction released gas (probably ammonia) and the sprayer had to be punctured to relieve the pressure. Initially the solution remained clear, but within minutes a crystalline precipitate formed. At 1% levels of  $NH_4Cl$ , no defoaming was observed, but the foam dissipated on shaking. The use of cyanuric acid or ammonium chloride to generate hydroxylamines with sodium

hypochlorite was also ineffective as a defoamer for wet foam. Finally, Acceleration of monohydroxy sodium perborate with ethyl acetoacetate in an attempt to oxidize xanthan via the acetate radical, was unsuccessful. Figure 16 shows the results of these experiments.

**3. Precipitation of xanthan.** An alternate approach to destabilizing the AFC 380 foam by attacking the xanthan gum is to precipitate it with alcohol. This method is used to recover the gum from fermentation broths [10-14, 58]. Considerable difference in the required amount of alcohol has been observed depending on which is chosen for the precipitation. Fermentation broth contains monovalent cations so that the ionic strength should be similar to foam. Preliminary evaluation of methyl, ethyl, isopropyl alcohols against 4-l of dry foam showed good results in about 15-s with isopropanol. However the amount required for defoaming wet foam at the 15-20 ml scale was 3:4 alcohol to foam and the rate was about 1 liter/min. Figure 17 shows 0, 20, 33, and 50% by weight of IPA in about 20 ml of wet foam. Note how the foam tends to adhere to the sides of the glass vial, making estimates of the amount of defoaming difficult. In the 50% photo, a white, gel-like precipitate can be seen. This is characteristic of the beginning of phase separation of the xanthan [10].

Table 9: Results of xanthan precipitation experiments with alcohols.

| Alcohol              | defoam    | Amt (g) | wt/wt Ratio | Comments                  |
|----------------------|-----------|---------|-------------|---------------------------|
| 2-Propanol           | Y         | 3.15    | 0.905:1     |                           |
| Ethyl Alcohol        | Y         | 5.245   | 0.462:1     |                           |
| tert-Amyl Alcohol    | Y         | 3.45    | 6.8:1       |                           |
| Butyl Alcohol        | Y         | 2.4     | 13.11:1     |                           |
| Methyl Alcohol       | N         | 5.96    | -           |                           |
| Benzyl Alcohol       | N         | 5.38    | 3.95:1      |                           |
| Glycerol             | too thick | -       | -           | Formed 5-10 ml foam       |
| Anisyl Alcohol       | N         | 5.74    | 4.27:1      |                           |
| 2-Butanol            | Y         | 2.4     | 2.98:1      |                           |
| 2-Methoxyethanol     | N         | 3.38    | -           |                           |
| tert-Butyl Alcohol   | Y         | 2.43    | 0.95:1      |                           |
| 2-Ethyl-n-butanol    | Y         | 6.19    | 9.52:1      | shaken by vortex machine. |
| 1-Propanol           | Y         | 2.55    | 0.967:1     |                           |
| Decyl Alcohol        | N         | 5.62    | 16.27:1     |                           |
| Cyclohexanol         | Y         | 3.71    | 9:1         | shaken by vortex machine. |
| 2-Methylcyclohexanol | Y         | -       | 30.25:1     | shaken by vortex machine. |
| 1,4-Butanediol       | N         | 4.11    | -           |                           |
| Ethylene Glycol      | N         | 4.84    | -           | Formed 6 ml foam          |
| Propylene Glycol     | N         | 4.49    | -           |                           |
| Triethylene Glycol   | N         | 5.66    | -           |                           |
| 1,2,6-hexanetriol    | too thick | -       | 2:1         |                           |



Although precipitation of xanthan worked well as a method of defoaming, the amount of alcohol was considered excessive and the rate of defoaming wet foam needs to be better. Salts have been used to enhance the precipitation of xanthan[23] but the concentrations per g of xanthan are less than the concentration of ions in the surfactant, so this approach was not considered. It is known that polyvalent salts are more effective at precipitation than sodium, but this was not evaluated. Twenty one different alcohols were sprayed onto approximately 20 ml of wet foam, to see if improvement in defoaming was possible. The amount of alcohol required to defeat 20 ml of ACF-380 foam solution was recorded. Subsequently, alcohol was added dropwise until evidence of precipitation of xanthan was observed. The weight ratio of alcohol/AFC 380 solution required to observe xanthan precipitation was recorded in Table 9.

Results indicated that the three butyl alcohols were the most effect as defoamers requiring only 37.5% or roughly 2 parts to 5 parts by weight of foam to defoam wet foam. Isopropyl alcohol may also be useful. Higher alcohols worked in some cases, Cycloaliphatic alcohols had to be shaken to defoam. Di- and trifunctional alcohols were also ineffective. Owing to the relatively large quantities required, the precipitating alcohols would not be used until wet foam was the major constituent to be defoamed. Rates of defoaming wet foam using different butanols should be determined.

### **C. Mechanical defoaming.**

When mechanical agitation by rotating wires, stirrers, whisks, etc. was tried as a method for defoaming AFC-380, the foam either shifted away from the stirrer or its volume was reduced by up to 50% with the commensurate reduction of cell size. Apparently what happens is the bubbles are being subdivided into smaller bubbles with more foam film and plateau borders being generated. The foam density of increased by a factor of 2. This higher density foam did not drain rapidly as was observed in the case of the dry foam and tended to be stable for several days. This was the first wet foam formulation and led to the wet foam generator shown in Figure 2.

The second approach to mechanical defoaming was to sprinkle the foam with particles. If the particle has sufficient mass, the yield stress of the foam film will be exceeded and the foam film should rupture. It is also possible for high surface area particles to absorb surfactant on the surface where they land and rupture the foam film surface in this way. If the shear modulus of the foam is 10 Pa and deformations are 0.8, a particle of the order of 100  $\mu\text{m}$  should penetrate the foam film. On the other hand, if absorption of the foam on the surface of the particle is important, high surface area particles should be more effective defoamers. Since silica with nearly 400  $\text{m}^2/\text{g}$  surface area is available commercially, six different silicas were tested. Since hydrophobic silica is effective in commercial emulsion based defoamers, three hydrophobic silicas were evaluated. One commercial, precipitated silica and two fumed silicas were used as indicated in Table 5. To determine if other absorbing surfaces would be effective fumed alumina and a blend of alumina and silica were tried.

Two of the three treated silicas were ineffective as defoamers for dry foam but one was quite effective. Both TS-530 and R-812 are made by hydrolysis of hydrophilic silica surface hydroxyls and surface moisture with hexamethylenedisilazane[22]. This results in a single trimethyl silanoxane group replacement for each silanol[23]. When these silicas were sprinkled on the surface of the foam, the volume was reduced to 1 to 1.5 liters. This is slightly more effective than spraying the foam with water. On the other hand, R-972 hydrophobic silica is prepared using dichlorodimethyl silane, which reacts with 2 silanol groups on the surface and should have somewhat different surface energetics. This relatively small change in surface characteristics has a dramatic effect on the foam stability. With very small amounts of R-972, the foam collapsed almost completely.

Unexpectedly, all of the hydrophilic silicas caused dry foam to collapse with very small concentrations of silica. These results seem to scale with the surface area of the silica particles. This might be associated with the ability of the high surface area silica to repel the surfactant at the surface of the foam film. This would alter the electrolytic interactions of the bilayer that forms the film and cause water to wet the silica and collapse the film. This idea was discussed with P. Garrett and he felt that behavior might be associated with a xanthan gum - silica filler interaction. In any event, all three hydrophilic silicas made very effective defoamers for dry foams.

Cok 84 is a blend of 82% silica and 18% Alumina C which has excellent colloidal properties in water. This blend also defoamed the dry foam very well. When Alumina C was used alone, its effectiveness against dry foam was considerably lower than the precipitated silicas or the blend, but better than the TS-530 or R-812 treated silicas. Sandia found that calcium oxide as a defoamer was effective except for larger quantities of foam where wet foam would not collapse [20]. They also considered colloidal clays, but these were deemed too slippery after adsorption to be effective.

Table 9. Silica particle defoamer results

| <b>Chemical</b>    | <b>wt (g)</b> | <b>% defoamer</b> | <b>used</b>     | <b>Effectiveness</b> |
|--------------------|---------------|-------------------|-----------------|----------------------|
|                    |               | <b>In 4 liter</b> | <b>In 5 gal</b> |                      |
| <i>hydrophobic</i> |               |                   |                 |                      |
| Cab-o-sil TS-530   | 2.3           | 2.52%             |                 | 2                    |
| Aerosil R-812      | 0.222         | 0.26%             |                 | 2                    |
| Aerosil R-972      | 0.596         | 0.66%             | 0.38%           | 5                    |
| <i>hydrophilic</i> |               |                   |                 |                      |
| Cab-o-sil EH5      | 0.237         | 0.27%             |                 | 5                    |
| Aerosil 200        | 0.314         | 0.38%             |                 | 5                    |
| HiSil T700         | 0.555         | 0.64%             | 0.65%           | 5                    |
| COK 84             | 0.41          | 0.42%             |                 | 5                    |
| Alumina C          | 2.5           | 2.67              |                 | 4                    |
| Water              | 7.25          | 8.44%             |                 | 2                    |

Fumed silica, alumina and precipitated silica were ineffective against wet foam generated at 15-20 cc levels with the vortex mixer. Wet foam has enough strength to

prevent the silica from migrating through the system. The low bulk density silicas all sit benignly on top of the wet foam. Higher bulk density solids such as talc were evaluated as well. In this case, the talc was able to penetrate the air/foam interface and work through the wet foam, but as it worked down through about 20 cc's of foam, voids were formed in the powder through which the foam could move. Within about 2 minutes most of the talc had settled to the bottom of the vial without effecting the wet foam.

#### **D. Thermal Defoaming**

Four and 20 l samples of AFC 380 were defoamed with a heat gun. One possible mechanism for this might involve the order-disorder transition in xanthan water solutions that is observed at about 50°C [7]. Thermal defoaming required about 15 seconds with 4 l samples and was relatively rapid in 20 l samples. Reinserting a sparger into the defoamed liquid could regenerate foam. The temperature approximately 2 cm away from the end of the heat gun was approximately 500°C. The temperature of the foam approximately 1" below the surface during heat defoaming was close to ambient. The success of this approach prompted a 55 gal scale up experiment. During this experiment the problem that had been observed in very large-scale experiments [25] was reproduced. Initially the heat gun defoamed rapidly and well, but after about 35-40 gal of foam had been defoamed, the process began to slow down. The last 10-15 gal of foam could not be defoamed with the heat gun. About 160 g of RD-71 and 90 g of Tiarco TS-10 emulsion defoamers were ineffective were sprayed onto the surface of this foam. This was the first small scale validation of the wet foam defoaming problem observed with large quantities of AFC 380 foam. Subsequent testing on wet foam with Tiarco TS-10 showed that at least 4 times this amount was required to defoam wet foam at the 4-l scale.

#### **E. Superabsorbers:**

Even when a large scale defoaming operation is successful residual liquid will produce very slippery surfaces that would pose a hazard to operators working in the defoamed area. Assuming an 8'x 8'x 8' office filled with foam, of which 25% was defoamed, defoaming would generate 36-40 liters of fluid over the floor. As a possible method of mitigation, super absorbent polymers were evaluated. Super absorbent polymers are usually produced from an acrylic acid monomer that is partially converted to its sodium or potassium salt. Often a second comonomer is added [26,27]. This polymer is usually lightly cross-linked to prevent complete dissolution. Preparative procedures for a wide variety of super absorbing polymers have been described [59-65]. The repulsion of the monovalent cations causes these polymers to swell and absorb water to several hundred times their original weight [66-74]. The presence of ions in the water can affect the swelling characteristics significantly [75-78]. We evaluated five different commercially available polymers listed in Table 6 in solutions of defoamed AFC 380 where T-700 or R-974 silica had been used. Approximately 0.1 g of polymer was placed on a Watmann # 41 filter and immersed it in the defoamed solution. After 5, 15, and 1440 minutes the filter was removed and drained over a Beuchner funnel with vacuum, then weighed. The weight of the wet filter and the dry polymer were subtracted and the increase assumed to be that of the imbibed solution. Comparison of the dry and wet

weight of the filter paper showed that about  $12.0 \pm 0.2$  g of solution was absorbed by the paper. No accounting was made for any soluble fraction of polymer, which would be lost into the liquid. Figure 19 shows the results for Hi-Sil 700 precipitated silica measurements.

As can be seen from the figure, between 80 and 120 times the weight of the polymer has been absorbed for solutions defoamed with silica nanoparticles. Assuming that time was of the essence, the rates of absorption should be rapid. Comparison of the polyacrylic acid sodium and potassium salts is consistent with the literature, ie, the potassium salt has higher rates of absorption but absorbs less solution [27, 59, 60]. The amount and rate of solution absorbed by the graft copolymer of ethylene oxide and the random copolymer of acrylamide with acrylic acid salts were very similar to the acrylic acid homopolymer. The potassium salt in the acrylic acid/acrylamide copolymer did not accelerate the rate of absorption. The fibrous poly(isobutylene-co-maleic acid) sodium salt performed best in this test. Comparison of absorption of defoamed solutions when the DeGussa R972 treated fumed silica was used gave very similar results to those shown in Figure 19. Only the fibrous sample absorbed significantly more defoamed solution with the R-972 silica (about 23%). Differences between absorption of solutions defoamed with silica are not expected to change since the electrolytic nature of the solution should not be affected when such small amounts of solid silica are added. For the commercial chemical defoamers, where 7 to 11% of the defoamer is added to the foam, the electrolytic makeup of the solution could change substantially and absorption by the different superabsorbers is expected to change.

When AFC 380 was defoamed with emulsion defoamers from Table 7, the best super-absorbing polymer depended on which defoamer was used. Figure 20 shows the results for the 5 polymers tested with 5 commercial defoaming emulsions. What is not shown in Figure 20 is the rates of absorption. For a 5.93% solution of Otospense TS-10 in defoamed AFC380 (shown in the first row of Fig. 20), after 1 hour the copolymer of poly(acrylic acid-co-acrylamide) potassium salt and the fibrous poly(isobutylene-co-maleic acid) sodium salt look comparable, but after 5 minutes, the fibers have absorbed 75 g/g of polymer while the acrylamide copolymer has not quite absorbed 50 g/g. The potassium salt of polyacrylic acid absorbs at a comparable rate to the polyacrylamide copolymer in the first 5 minutes, but will only absorb 40 g/g. Both the sodium polyacrylic acid salt and the ethylene oxide copolymer absorb slowly and only about 30 g/g.

For a 15.5% solution of C-2290 defoamer in AF-380 foam solution, in the second row of Figure 20, the potassium salt of polyacrylic acid worked best, but the maximum amount absorbed in 1 hour was only 74%. The rate of absorption for the potassium salt of PAA in this case was almost double that of the other superabsorbers after 15 minutes (60 g/g compared to between 25-35 g/g for all 4 other polymers). So for C-2290 cleanup the clear choice would be PAA-K. Interestingly, the PAA-K absorption curve is S shaped, but this may be a measurement error.

For an 18.27% solution of RD-71 defoamer in AFC 380 foam solution, the third row in Figure 20, the graft copolymer of polyacrylic acid and polyethylene oxide absorbed more than twice the amount of the other superabsorbers in 5 minutes (65.7 compared to 24-30 g/g of polymer). After 1 day the Acrylamid copolymer and the fibrous copolymer of isobutylene and maleic acid have almost absorbed as much solution, but for our purposes the graft copolymer is the clear choice for RD-71 defoamer.

For a 9.40% solution of GE AF-9030 defoamer in AF 380 foam solution, the fourth row in Figure 20, the most rapidly absorbing polymers were the PIB-co-MA fiber and the PAA – K salt which absorbed (66.7 and 60 g/g, respectively in 5 minutes). After 15 minutes however, the PAA-Na salt has absorbed more than the K salt (78.8 versus 67.4 g/g) and the fiber has absorbed 80 g/g. So the fiber is slightly superior to the polyacrylic acid salts, which are superior to the other copolymers with the GE antifoam.

For a 10.33% solution of FB 235 defoamer in AF 380 defoamed solution, the last column in Figure 20, remarkably rapid and large absorption occurred with the polyacrylic acid sodium salt. The fibrous copolymer PIB-MA absorbs almost as much as PAA-Na in the first 5 minutes (78.2 and 80.8 g/g), but after 15 minutes the PAA-Na has absorbed almost 140 g/g while the fiber only 104 g/g. The other superabsorbers only absorb about 50 g/g. Again the potassium PAA salt showed an induction time similar to that seen with C-2290 defoamer.

When superabsorbing polymers were added to dry foam, they would defoam the area in which they landed, but substantially more was required than with fumed silica. When superabsorbing polymers were added to wet foam, the granular samples fell to the bottom of the vessel and the drainage was imbibed but the volume of wet foam made with the Vortex mixer remained virtually unchanged.

Three tests of superabsorbing polymers as clean up aids were performed. Approximately 60 g of 94/6 AFC 380 was added to a 4-l container. To this solution 3.6 g of TS-10 or 6 g of AF 6030 was added to emulate residual defoamed solution on the floor. Approximately two grams (about twice that required) of fibrous poly(isobutylene-co-maleic acid) sodium salt, which was a good absorber for both defoamers, was spread over the liquid mix. Within 1.5 – 2 minutes the fibers had thickened into a gelatinous mass. This gel was still quite slippery but could be handled relatively easily. Clean up should be much simplified using the fibrous super-absorbing polymer. Another useful feature of gelled material was that it mitigated the effect of the defoamer. In both cases fresh foam could now be reapplied over the gelled defoamed solution. The third test used granular poly(acrylic acid-co-acrylamide) potassium salt instead of the fibrous superabsorber. This copolymer worked effectively with TS-10 defoamer. The granular polymer is easier to distribute in the liquid than the light, fluffy fiber. For 60 g of solution with 4.2-g of TS-10 defoamer, 2.2 g of superabsorber imbibed the liquid in two to three minutes. In the first minute the consistency was similar to cream of wheat cereal, but after three minutes, a gelled solid, which would not flow on shaking or tilting the 4-

liter vessel, had formed. Again the solid was slippery, but could be removed more easily than the defoamed liquid alone.

## **Conclusions**

Chemical, mechanical and thermal approaches to defoaming AFC 380 foam have been evaluated at the small and medium scale. Some characterization of this foam has also been carried out. Several chemical approaches to defoaming were evaluated including oxidation and precipitation of the xanthan, use of commercial oil-emulsion or suspension defoamers, pH modification, and cation exchange with the surfactant. Of these the commercial defoamers were most effective.

The most promising of the chemical defoamer was Tiarco's Octospense TS-10. Although GE's AF 3090 and New London's C-2290 performed as well in all our head to head testing, the GE and New London antifoams show definite aging effects, so they would have limited shelf life. The GE antifoam turned yellow and became more viscous over about 2 years. The New London antifoam tended to phase separate with visible evidence of solids in the bottom of the container.

Hot air blowers, high surface area particulate such as fumed silica, and super absorbing polymers were very effective against dry foam, but ineffective against wet foam. Fumed silica was especially efficient requiring less than 1% silica to defoam the dry AFC 380. A method for dispensing powder would be required to implement this defoaming approach. Fumed silica is amorphous and therefore not hazardous. Of the silicas tested the precipitated Hi Sil 700 was the least expensive. Hi Sil 700, Aerosil 200 and Cab-o-Sil EH-5 all required very low levels to defoam dry foam.

Butyl alcohols, which cause the xanthan to precipitate, were effective against wet foam. Butyl alcohols could be used when wet foam is generated in a large defoaming operation, especially if the preliminary defoamer becomes ineffective. Flammability issues may have to be addressed for these organic alcohols. The amounts of butyl alcohol required to defoam wet foam were less than any other alcohol tested, typically 3-5 %.

Super absorbing polymers could play an important role in removing defoamed liquid and mitigating the effect of the defoamer so that the area could be refoamed. It might be feasible to make a thin woven sheet of fibrous absorbing polymer, which could be laid down over the defoamed fluid if the area needed to be refoamed.

## **Suggestions for Future Work**

Clearly, a large-scale evaluation of Tiarco's TS-10 defoamer perhaps combined with super absorbing polymer should be of interest. It is not known whether this defoamer will be effective against wet foam generated in large-scale operations. If it is not, butyl alcohol should be evaluated as a second stage defoamer. The defoamer could be sprayed on with a commercial paint sprayer such as a Grayco XM-7 electric high-pressure sprayer or comparable sprayer capable of handling at least 5 gallons of

defoamer. Evaluation of the effectiveness of a clean up procedure involving an absorbing polymer should be done on this scale as well.

More detailed evaluation of wet foam should be done. Does the mechanism by which this foam is generated at the operational scale correspond more closely to any of the 3 different methods of preparation of wet foam on a small scale? Further evaluation of butanols as defoamers for wet foams would be of interest.

The effectiveness of shock mitigation as a function of foam density might be of interest. Since shock velocity impedance mismatch is effective at shock mitigation, higher density wet foam may out-perform the currently used dry foam.

### **Acknowledgements**

Helpful discussions with and the loan of a foam generator from Paul Johnson of Sandia National Laboratory in Albuquerque are gratefully acknowledged. Doug Goyer of CP Kelco provided a sample of xanthan gum, useful discussions and information on oxidation. Shannon Bays worked two summers at LLNL on this project. Roger Woodward made the Sessile Drop surface tension measurements and Rod Eberwein made the arrangements for us to use the First Ten Angstrom facilities in Portsmouth, Virginia. Victor Janule made the bubble surface tensiometer measurements at Sensodyne Labs in Phoenix, AZ. Thanks also to the commercial defoamer representatives for supplying samples of their company's products. Special thanks to Mike Larson, who provided the opportunity to propose this work, for his encouragement during our efforts to complete it.

### **References:**

1. J. German, Sandia Lab News, 54, No. 23, (November 15, 2002).
2. D. Weaire and S. Hutzler, "The Physics of Foams" Clarendon Press, (Oxford) 19992.
3. J.J. Bikerman, "Foams", Springer-Verlag (New York) 1973
4. P. R. Garrett, ed, Defoaming: Theory and Industrial Applications, Marcel Dekker; New York, 1993
5. H-G. Miller, "Rupture of foam and emulsion films at a critical pressure", presented at Eurofoam 2002, Manchester UK , July 7-14, 2002.
6. J. O. Carnali, "(Polymer/polymer)-like phase behavior in the system tetradecyltrimethylammonium bromide/sodium polyacrylate/water ", Langmuir **9**, 2933(1993).
7. E. Pelletier, C. Viebke, J. Meadows and P. A. Williams, "A Rheological Study of the Order-Disorder Conformational Transition of Xanthan Gum", Biopolymers, 50, 39 (2001).
8. CP Kelco Tech Bull. "Breaker Applications" Kelco Oil Field Group, Houston, Tx (December 1997).
9. RT Vanderbilt Tech.Bul. VAS1469, "Vanzan, Xanthan gum, the Natural choice for thickening, stabilizing and suspending formulations", R.T. Vanderbilt Co., Inc Norwalk CT. (2000)

10. F. Garcia-Ochoa, J.A.Casas and A.F. Mohedano, "Xanthan Precipitation from Solutions and Fermentation Broths", *Sep. Sci. Technol.*, 28, 1303 (1993).
11. J.J. Flahive III, A. Foufopoulos, M.R. Etzel, "Alcohol precipitation of xanthan gum from pure solutions and fermentation broths", *Sep. Sci. Technol.*, 29 1573 (1994).
12. E. Galindo and V. Albiter, "High-yield recovery of xanthan by precipitation with isopropyl alcohol in a stirred tank", *Biotechnol. Prog.*, 12, 540 (1996).
13. R. Gonzales, M.R. Johns, P.F. Greenfield, and G.W. Pace, "Xanthan precipitation using ethanol", *Process Biochem.*, 24, 200, (1989).
14. R. Gonzales, M.R. Johns, P.F. Greenfield, and G.W. Pace, "Phase equilibria for xanthan gum in ethanol-water solutions, *Carbohydr. Polym.* 13, 317 (1990).
15. Stepan Product Bulletin "Bio-Terge AS-40 (2/01) Stepan Co, Northfield, IL
16. Kelzan Xanthan Gum, Tech Bull. DB-15, C.P. Kelco Co, Inc, Chicago, IL (1991)
17. New London Chemicals Tech. Bull., "C-2290 Industrial Antifoam", (2000); New London Chemicals Tech. Bull., "C-2000 Series Silicone Antifoam Emulsions for the Food Industry"
18. Tiarco Chem. Tech. Data Sheet, "Octospense TS-10 Defoamer (9/8/95) Tiarco Chemical Co, Dalton, GA
19. Ross Chem, Inc Tech. Data Sheet "Foam Blast 235" (8/18.98) Ross Chem, Fountain Inn, SC.
20. GE Silicones MSDS "AF9030" (2/26/99) GE Silicones Waterford NY
21. RD Chemical Data Sheet "RD-71" (4/5/00) RD Chemical Mountain View, CA.
22. Cabot Tech. Bull. "Cab-o-Sil untreated fumed silica Properties and Functions", Cabot Corp.(1993)
23. DeGussa Tech Bull., "Aerosil Fumed Silica" PT6-35-3-688H and PT 6-15-8-1297H; Tech. Bull. Pigments No 11, "Basic Characteristics of Aerosil" DeGussa Corp, Teterboro NJ.
24. PPG Tech Bul.
25. E. Ryder, Memo: 'Results of Defoaming Investigations Performed through March 19 Sandia National Laboratories, Albuquerque, NM (1999)
26. F.L. Bucholz and N.A. Peppas, eds, "Superabsorbent polymers: Science and Technology", ACS Symposium Series # 573, American Chemical Society, Washington DC, (1993)
27. F.L. Bucholz and A.T. Graham, "Modern Superabsorbent Polymer Technology, Wiley-VCH (New York) 1998.
28. J.P. Klus, EW.E. Gibbons, E. L. Brodsky and V. P Januel, US Patent 4,416,148, "Surface Tensiometer,(Nov. 22, 1983)
29. R. P. Woodward, First Ten Angstroms Tech Bulls. "FTA200 Measurement Capabilities"; Surface Tension Measurement using the Drop Shape Method" and "Dynamic Surface Tension and Dilational Stress Measurements using the Drop Shape Method"
30. V.P. Januel, "Molecular "fingerprinting of surfactant-containing formulations", *Chimica Oggi/Chemistry Today*, **20**, 60 (2002).
31. J. Schwartz, "The importance of low dynamic surface tension in waterborne coatings" *J. Coat. Technol.*, **64** 654 (1992).
32. W. R. Dougherty, "Acetylenic diol surfactants cut foaming and wetting problems", *Adhesives Age*, p. 26 (September, 1989).



33. S.A. Koehler, H.A. Stone, M.P. Brenner, and J. Eggers, *Physical Review E*, **58**, 2097 (1998).
34. G. Verabist, D. Weaire and A.M. Kraynik, *J. Phys.: Condens. Matter*, **8**, 3715 (1996).
35. R.P. Garrett, "A Simple Statistical Theory for the Effect of Changes in Antifoam Concentration on Foamability", *Langmuir* 11, 3576 (1995).
36. V. Bergeron, P. Cooper, C.Fischer, J. Giermanska-Kahn, D. Langevin, and A. Poouchelon, "Polydimethylsiloxane (PDMS)-based antifoams" *Coll. & Surfaces A: Physicochemical and Eng. Aspects* 122, 103 (1997).
37. N.D. Denkov, P. Cooper, and J-Y Martin, "Mechanisms of Action of Mixed Solid-Liquid Antifoams. 1. Dynamics of Foam Film Rupture and 2. Stability of Oil Bridges in Foam Films", *Langmuir* 15, 8514, 8542 (1999).
38. G. Racz, K. Kocz, and D.T. Wasan, "Mechanisms of Antifoam Deactivation" *J. Colloid Interface Sci.*, 181, 124 (1996).
39. G. Wang, R. Pelton, A. Hrymak, N. Shawafaty, and Y.M. Heng, "On the Role of Hydrophobic Particles and Surfactants in Defoaming", *Langmuir* 14, 2202 (1999).
40. B. K. Jha, S. P. Christiano, and D.O. Shah, "Silicone Antifoam Performance: Correlation with Spreading and Surface Monoayer Packing", *Langmuir*, 16, 9947 (2000)
41. T. Tamura, M. Kageyama, Y. Kaneko, T. Kishino, and M. Nikaido, "Direct Observation of Foam Film Rupture by Several Types of Antifoams using a Scanning Laser Microscope", *J. Colloid and Interface Sci.* 213, 179 (1999)
42. A. Bonfillon-Colin and D. Langevin, "Why do Ethoxylated Nonionic Surfactants not Foam at High Temperatures", *Langmuir* 13, 599 (1997).
43. L. Arnaudov, N.D. Denkov, I. Surcheva, P. Durbut, G. Groze and A. Mehreteab, "Effect of Oily Additives on Foamability and Foam Stability 1. Role of Interfacial Properties" *Langmuir* 17 6999 (2001).
44. K.G. Marinova, S. Tcholakova, N.D. Denkov, S. Roussev, and M. Deruelle, "Model Studies on the Mechanism of Deactivation (Exhaustion) of Mixed Oil-Silica Antifoams", *Langmuir* 19, 3084 (2003).
45. R.W. Murray, "Dioxiranes" *Chem. Rev.* 89, 1187 (1989).
46. P.J. Kropp, G.W. Breton, J.D. Fields, J.C. Tung and B.R. Loomis, "Surface-Mediated Reactions. 8. Oxidation of Sulfides and sulfoxides with tert-butyl hydroperoxide and Oxone", *J. Am. Chem. Soc.*, 2003, 125 7596
47. M-Y. Chen, L. N. Patkar, H-T. Chen, and C-C. Lin, "An efficient and selective method for preparing glycosyl sulfoxides by oxidizing glycosyl sulfides with oxone or t-buOOH on SiO<sub>2</sub>" *Carbohydrate Res.* 338, (2003), 1327.
48. B.E. Christensen, O. Smidsrad, A. Elgsaeter, and B. T. Stokke, "Depolymerization of Double-stranded Xanthan by acid hydrolysis: Characterization of Partially Degraded Double stranded and Single-Stranded Oligomers Released from the Ordered Structures", *Macromol.* 1993, 26, 6111.
49. B.E. Christensen, M. H. Myhr, and O. Smidsrod, "Degradation of double-stranded xanthan by hydrogen peroxide in the presence of ferrous ions: comparison to acid hydrolysis", *Carbohydrate Research* 280 (1996) 85.
50. FMC Tech. Bul. FMC9487-2500 (12/01) "Persulfates, Technical Information"
51. V.K Aggarwal, C. Lopin and F. Sandrinelli, "New Insights in the Mechanism of amine catalyzed epoxidation: Dual Role of Protonated Ammonium salts as both

- Phase Transfer Catalysts and Activators of Oxone”, *J. Am. Chem. Soc.*, 2003, 125 7596.
52. P.J. Kropp, G.W. Breton, J.D. Fields, J.C. Tung and B.R. Loomis, “Surface-Mediated Reactions. 8. Oxidation of Sulfides and sulfoxides with tert-butyl hydroperoxide and Oxone”, *J. Am. Chem. Soc.*, 2003, 125 7596
  53. M-Y. Chen, L. N. Patkar, H-T. Chen, and C-C. Lin, “An efficient and selective method for preparing glycosyl sulfoxides by oxidizing glycosyl sulfides with oxone or t-buOOH on SiO<sub>2</sub>” *Carbohydrate Res.* 338, (2003), 1327.
  54. D.L. Harp, “Specific Determination of Inorganic Monochloramine in Chlorinated Wastewaters, *Water Env. Res.*, 72, 706 (2000).
  55. P.C. Pertorius and W.A. Pertorius, “Disinfection of purified sewage effluent with monochloramine”, *Water SA*, 25, 463 (1999).
  56. Bleaching with Sodium Perborate”, in *Borax Detergent Book*, <http://www.borax.com/detergentbook/bleaching.html> (2003)
  57. J.F. Cooper, G. Bryan Balazs, P. Lewis and M. Adamson, “Direct Chemical Oxidation Using Peroxydisulfate” in *Handbook of Mixed Waste Management Technology*, H.O. Chang, Ed., Lewis Publishers, Inc (June 2001)/
  58. S. Parija, M. Misra and A.K. Mohanty, “Studies of Natural Gum Adhesive Extracts: An overview”, *J. Macromol. Sci.- Polymer Reviews*, C41(3), 175 (2001).
  59. U. Sdayal, S. K. Mehta, M.S. Choudhary, and R.C. Jain, “Synthesis of Acrylic Superabsorbents”, *JMS-Rev. Macromol. Chem. Phys.*, **C39(3)** 507 (1999).
  60. W-J. Zhou, K-J. Yao and M.J. Kurth “Synthesis and swelling properties of the copolymer of acrylamide with anionic monomers”, *J. Appl. Poly. Sci.*, 62, 911 (1996).
  61. Z.S. Liu and G.L. Rempel, “Preparation of superabsorbent polymers by crosslinking acrylic acid and acrylamide copolymers”, *J. Appl Poly. Sci.*, 64, 1345 (1997).
  62. K. Kabiri, H. Omidian, S.A. Hashemi, M.J. Zohuriaan-Mehr, “Synthesis of fast-swelling superabsorbent hydrogels: effect of crosslinker type and concentration on porosity and absorption rate” *European Polym. J.*, 39 (2003) 1341.
  63. M. P. Raju and K.M. Raju, “Design and synthesis of superabsorbent polymers, *J. Appl. Polym. Sci.*, 80, 2635 (2001).
  64. D.J. Arriola, S.S. Cutie, D.E. Henton, C. Powell, and P.B. Smith, “Crosslinker reactivity and the structure of superabsorbent gels”, *J. Appl Polym. Sci.*, 63, 439 (1997).
  65. H. Omidian and M.J. Zohuriaan-Mehr, “DSC studies on synthesis of superabsorbent hydrogels”, *Polym.* 43, 269 (2002).
  66. E. Karadag, O. B. Uzum, and D. Saraydin, “Swelling equilibria and dye adsorption studies of chemically crosslinked superabsorbent acrylamide/maleic acid hydrogels”, *European Polym. J.*, 38 (2002) 2133.
  67. W. Xue S. Champ, and M.B. Huglin, “Network and swelling parameters of chemically crosslinked thermoreversible hydrogels”, *Polym.* **42** (2001) 3665.
  68. J.P. Baker, D.R. Stephens, H.W. Blanch and J.M. Prausnitz, “Swelling Equilibria for Acrylamide based Polyampholyte hydrogels” *Macromol.* 1992, **25**, 1955.
  69. A.K. Bajpai and M. Shrivastava, “Dynamic swelling behavior of polyacrylamide based three component hydrogels”, *J.M.S.-Pure Appl. Chem.*, A37(9), 1069 (2000).

70. M. Liu and T. Guo, "Preparation and Swelling properties of crosslinked sodium polyacrylate", *J. Appl. Poly. Sci.*, 82, 1515 (2001).
71. M. Bakass, A. Mokhlisse, M. Lallemand, "Absorption and desorption of liquid water by a superabsorbent polyelectrolyte: Role of polymer on the capacity for absorption of a ground", *J. Appl. Polym. Sci.*, 82, 1541 (2001).
72. H. Omidian, S.A. Hashemi, G.P. Sammes and I. Meldrum, "A model for the swelling of superabsorbent polymer", *Polym.* 39 6697 (1998).
73. R. Skouri, F. Schosseler, J.P. Munch and S.J. Candau, "Swelling and Elastic Properties of polyelectrolyte gels", *Macromol.*, 1995, 28, 197.
74. J. Chen and J. Shen, "Swelling behaviors of polyacrylate superabsorbent in the mixtures of water and hydrophilic solvents, *J. Appl. Polym Sci.*, 75, 1331 (2000).
75. W-F. Lee and P-L Yeh, Superabsorbent polymeric materials. IV. Swelling behavior of crosslinked poly(sodium acrylate-co-N,N-dimethyl(acrylamidopropyl) ammonium propane sulfonate) in aqueous salt solutions:, *J. Appl Polym. Sci.*, 66, 499 (1997).
76. W-F. Lee and R-J Wu, Superabsorbent polymeric materials. I. Swelling behaviors of crosslinked poly(sodium acrylate-co-hydroxyethylmethacrylate) in aqueous salt solutions:, *J. Appl Polym. Sci.*, 62, 1099 (1996).

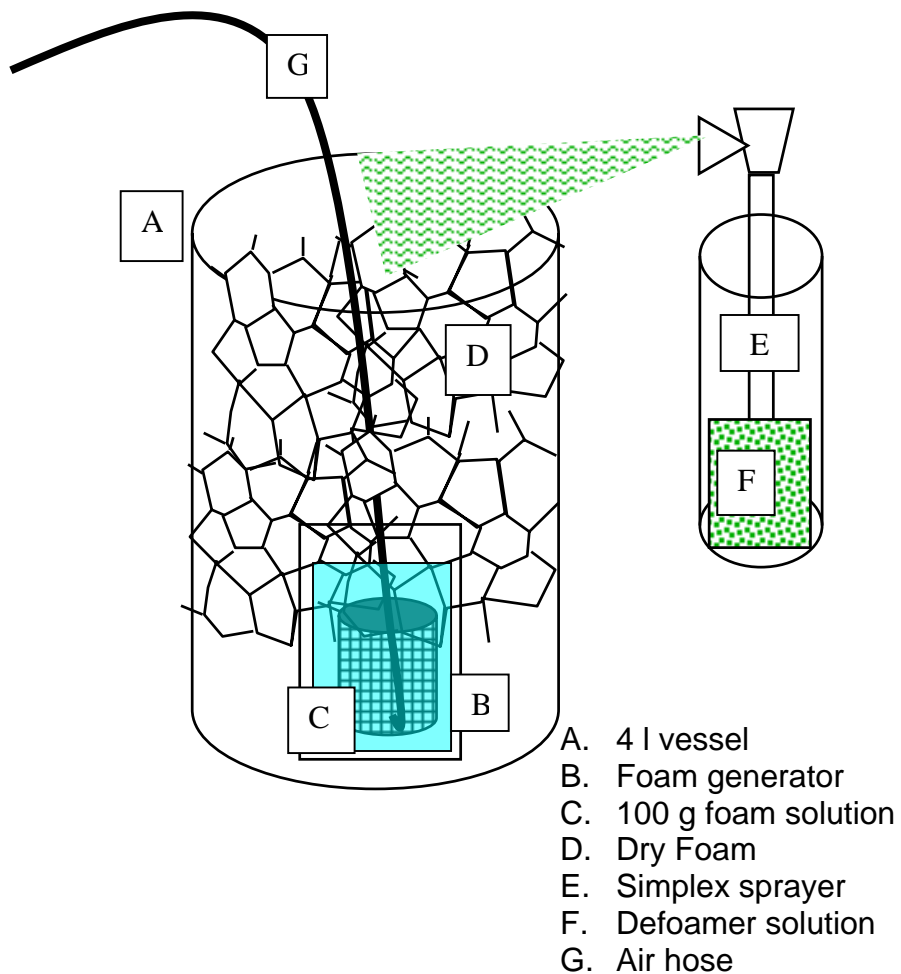


Figure 1. Small-scale foam generator set up consisted of approximately 100 g of 94/6 water/AFC 380 solution, sparger, 4 liter vessel, and air hose. Chemical defoamers were sprayed into the foam after the residual solution was removed.

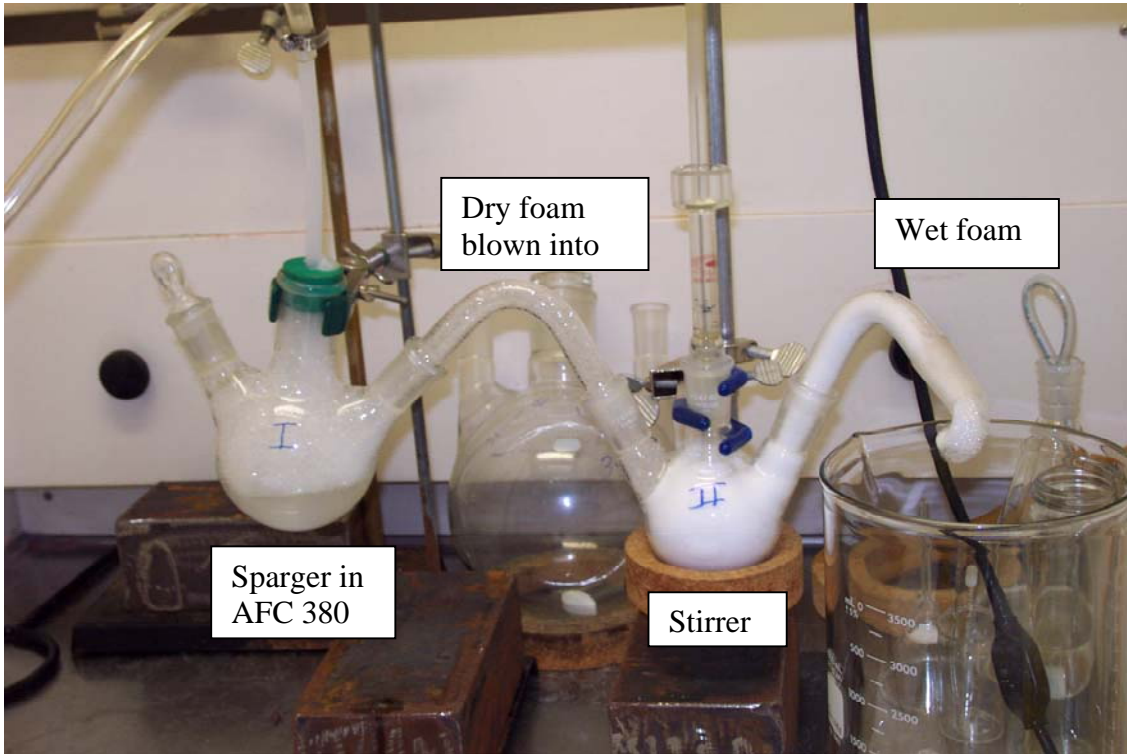


Figure 2. The first attempt at a wet or dry foam generator consisted of two 3 necked flasks with sparger, stirrer and interconnecting glass tubing. If dry foam were desired flask I was opened. For wet foam (as shown) flask II was opened.

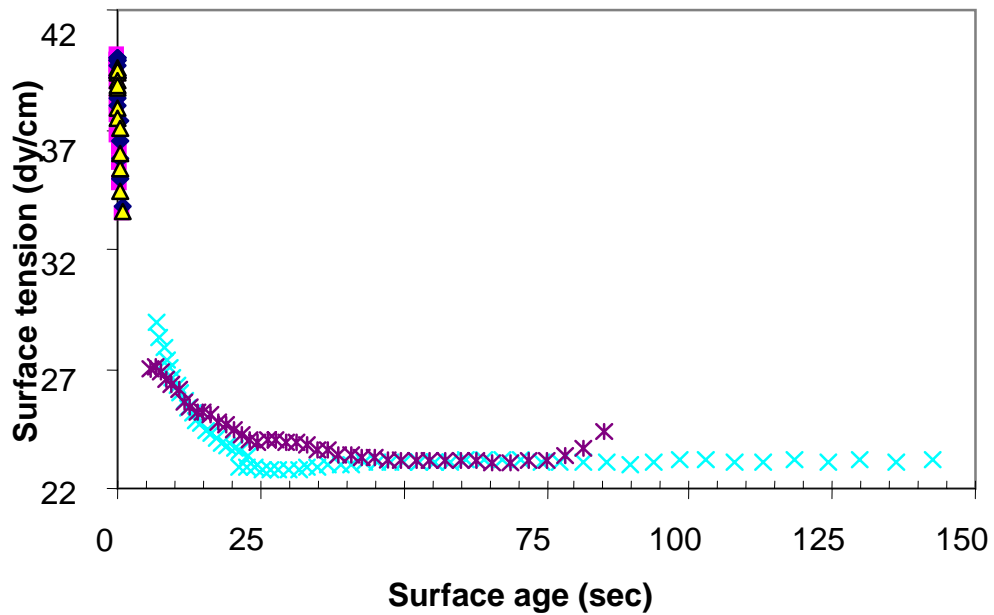


Figure 3. Foam solution surface tension as a function of time from bubble (short time) and pendent drop data.

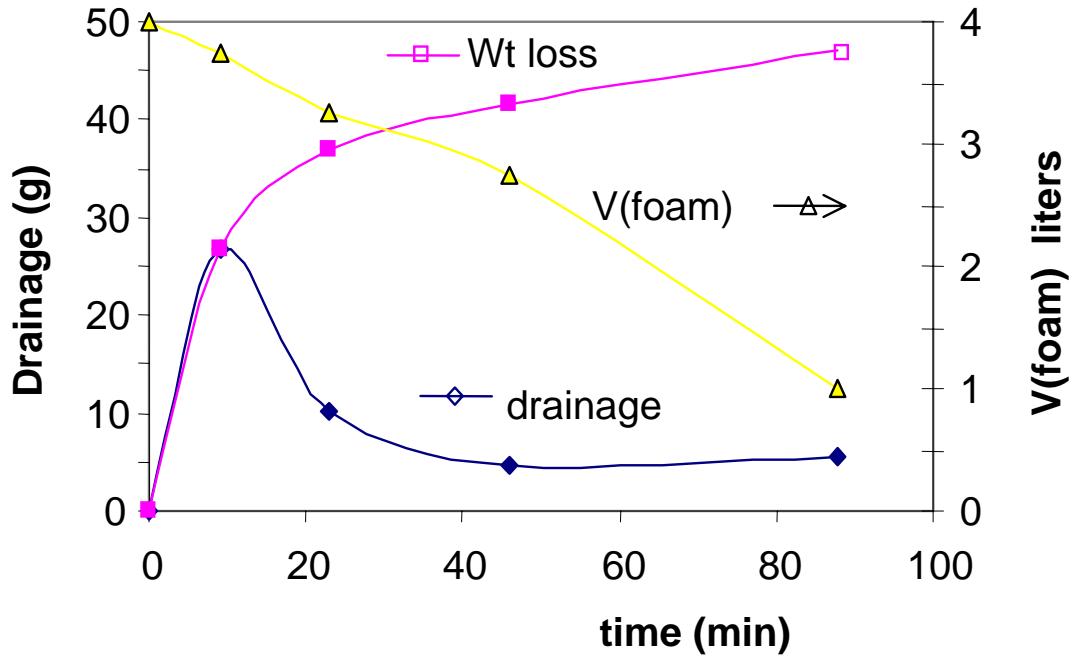


Figure 4. Drainage characteristics of four liters of dry foam show most of the solution drains out in 30 minutes but about half of the foam volume remains for twice that long.

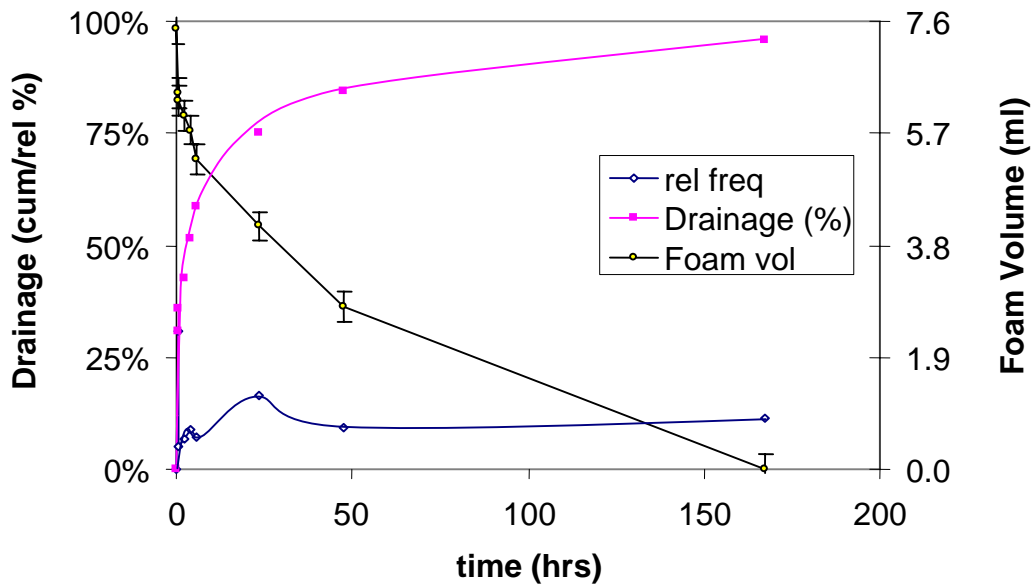
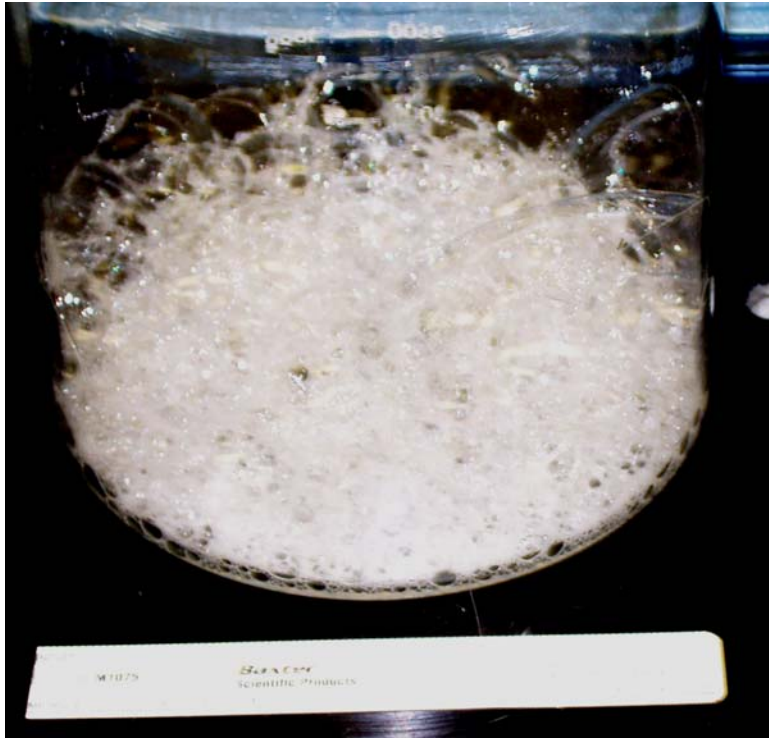


Figure 5. Drainage characteristics of 8 cc of wet foam show solution drains to be logarithmic with about half of the solution having drained out in 2 hrs but 60% of the foam volume remained for 24 h.



a.



b.

Figure 6. Examples of dry (a) and wet (b) foam produced from AFC-380 show a broad distribution of bubbles and lower density compared to small bubbles and higher density.

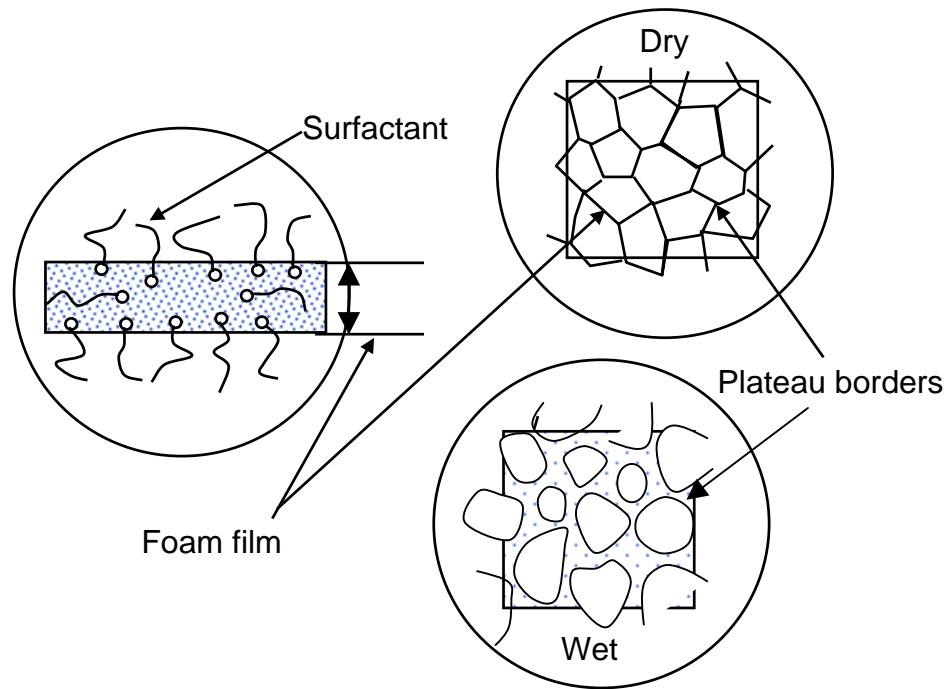


Figure 7. Structure of foam film and Plateau borders in dry foams [after ref. 2].

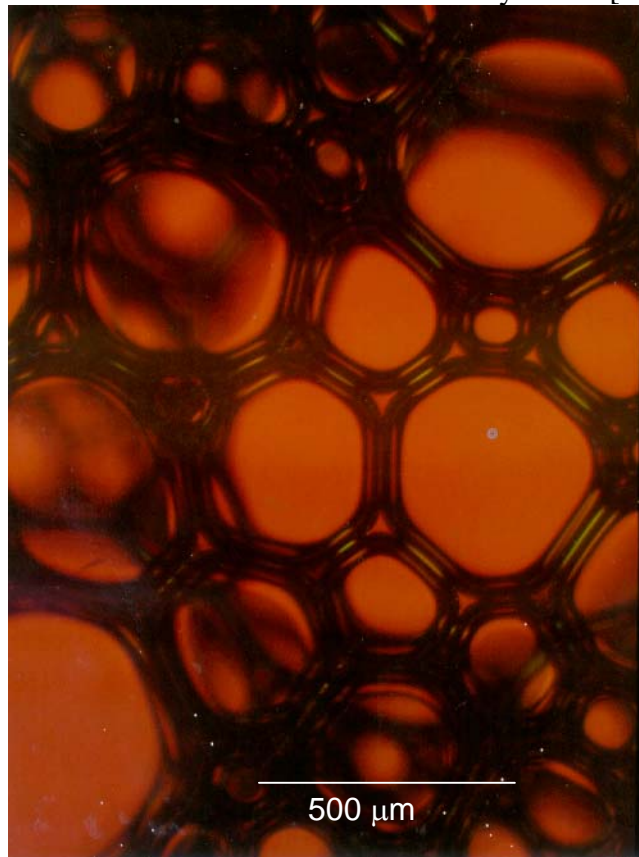


Figure 8. A polarized light micrograph of wet foam generated in the vortex mixer shows cells between 420 and 150 μm across for the largest bubbles.



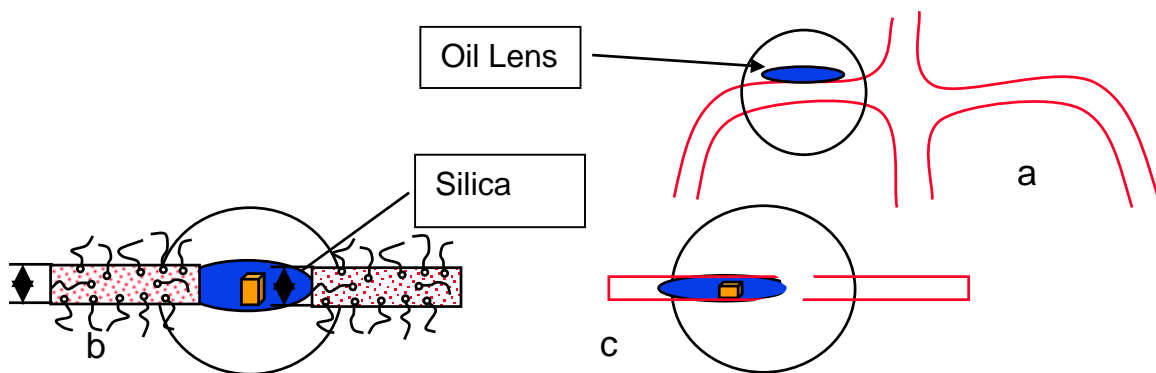


Figure 9. Proposed mechanism for commercial defoamers is: a. The circle in 4a shows an oil lens ready to insert into the foam film; b. The circle in 4a has been expanded to show an inserted oil lens with hydrophobic silica or other solid cutting the foam film; c. The foam film fails at the oil bridge and the bubble collapses.

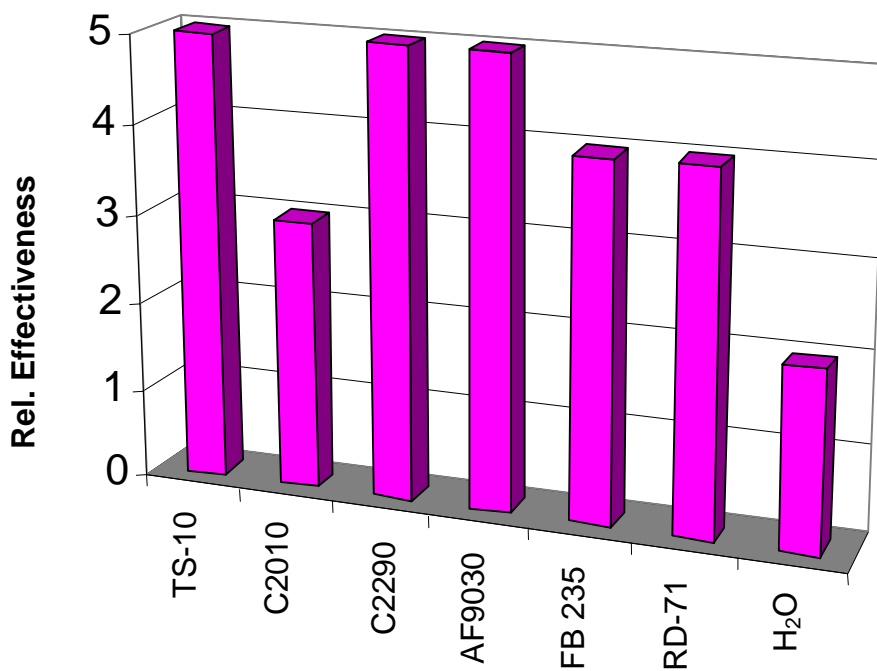


Figure 10 The effectiveness of commercial defoamers against AFC-380 dry foam in 1 liter vessel with a simplex sprayer was quite good in most cases.

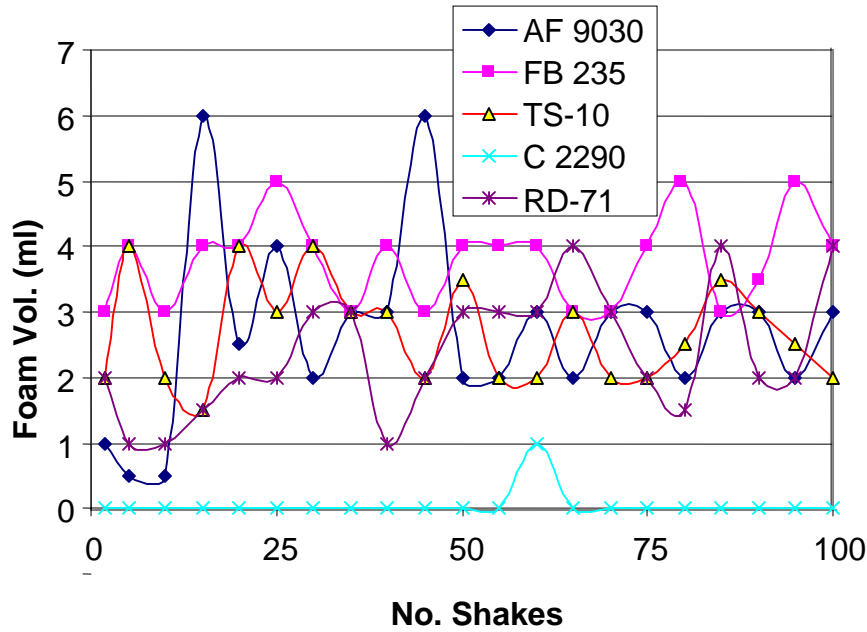


Figure 11. Foam volume as a function of the number of shakes of 10 ml of defoamed AFC-380 showed only small increases in foam during 100 shakes. This indicates that the defoamers are still active for a long time after defoaming.

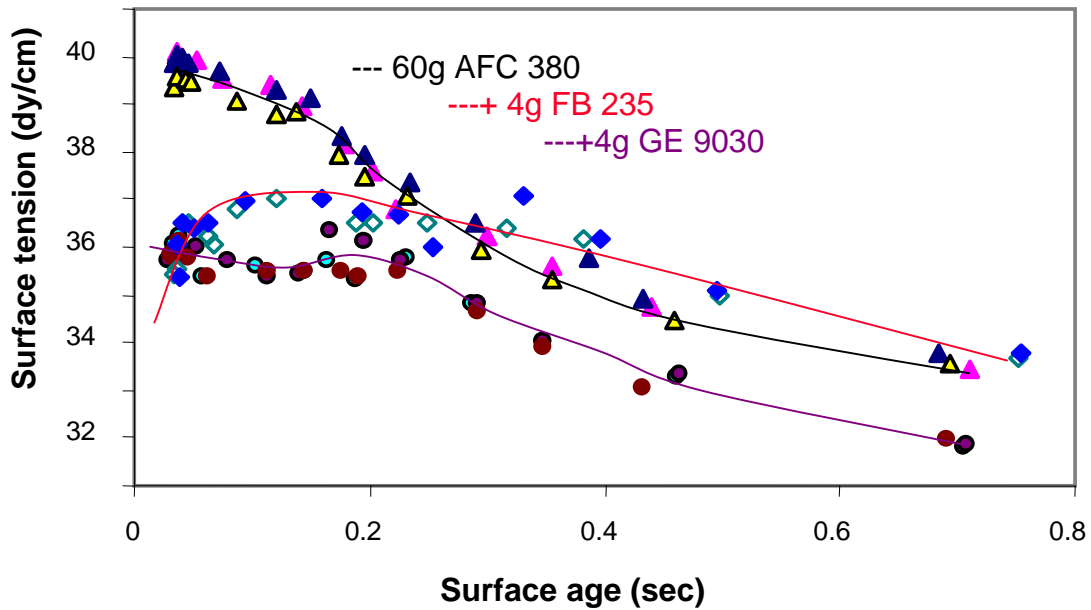


Figure 12. Short-term surface tension measurements using the dynamic bubble technique showed different degrees of reduction of the initial surface tension AFC 380 94/6 solution on addition of of about 9% FB 235 and GE 9030 defoamers.

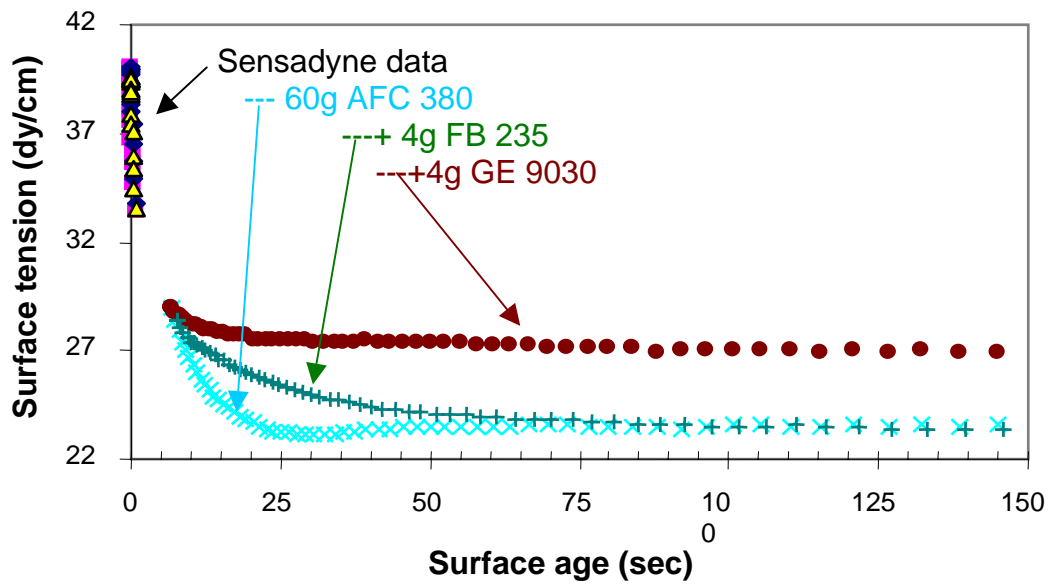


Figure 13. Longer term surface age as determined by sessile drop method using the FTA 200 surface tensiometer shows addition of 9% GE 9030 increases the equilibrium surface tension of the solution..

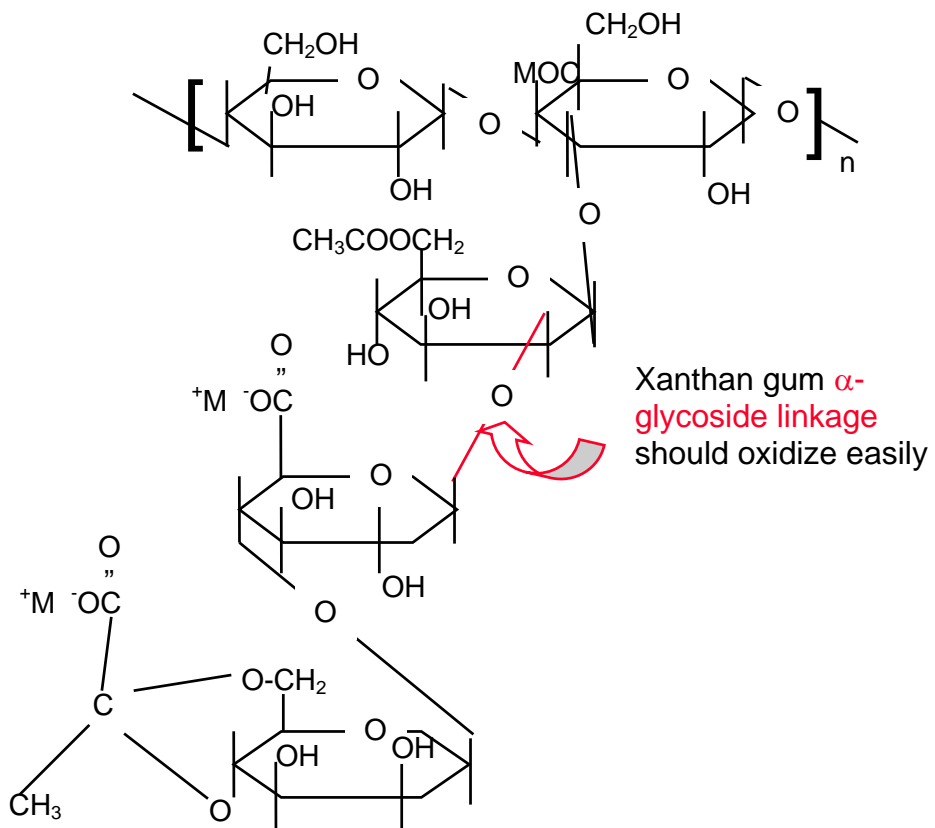


Figure 14. Xanthan gum is a b-glycoside polysaccharide with a unique 3 sugar side chain with a-glycoside linkage (in red) which is susceptible to oxidation.

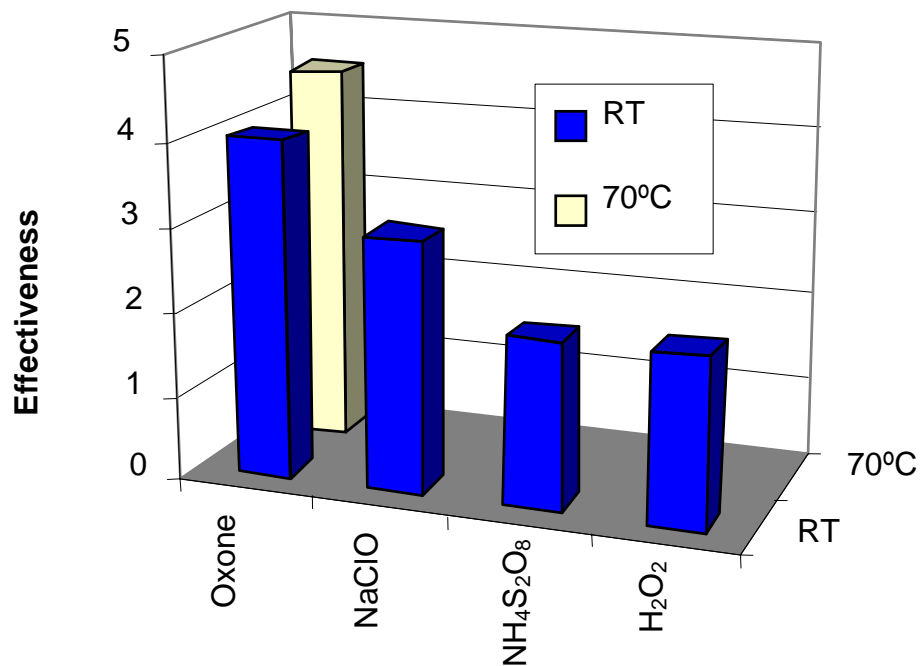


Figure 15. Effectiveness of various oxidizing agents on 4 l dry foam was lower than commercial defoamers and increased slightly with moderate heating.

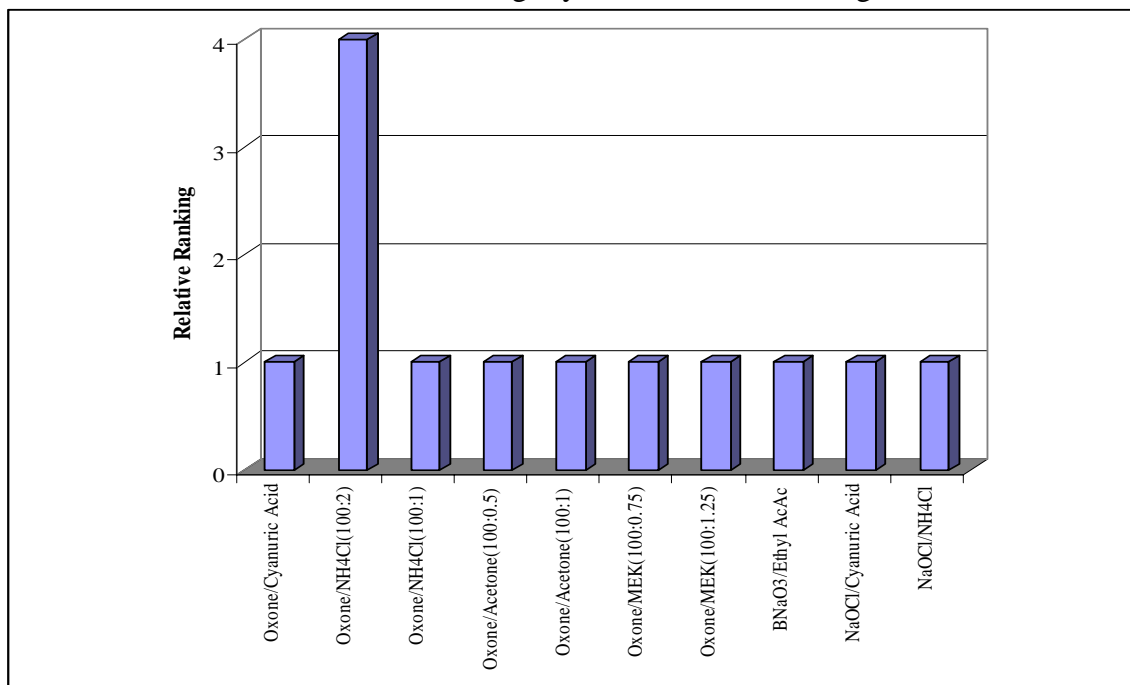


Figure 16. Even with accelerators oxidation of the xanthan inn wet foam was ineffective at defoaming.

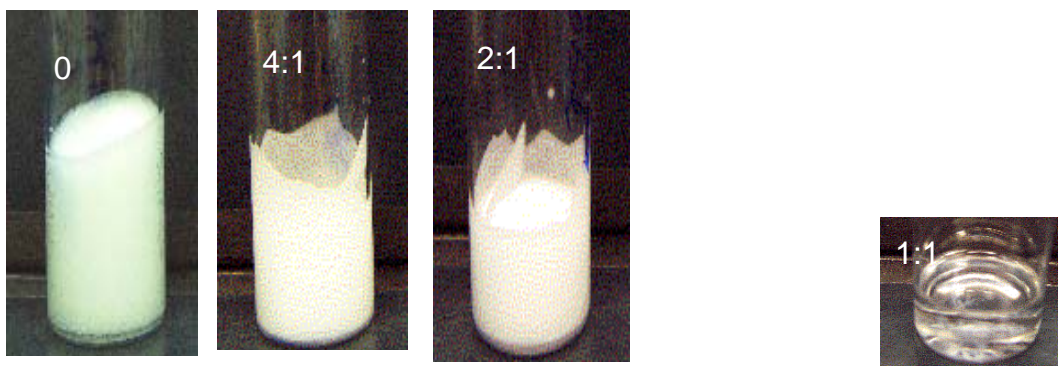


Figure 17. Wet foam made with the vortex mixer can be defoamed by precipitation of ethanol, isopropanol or other nonsolvent for xanthan, but at least a 4:3 weight ratio of foam to nonsolvent is required for complete defoaming.

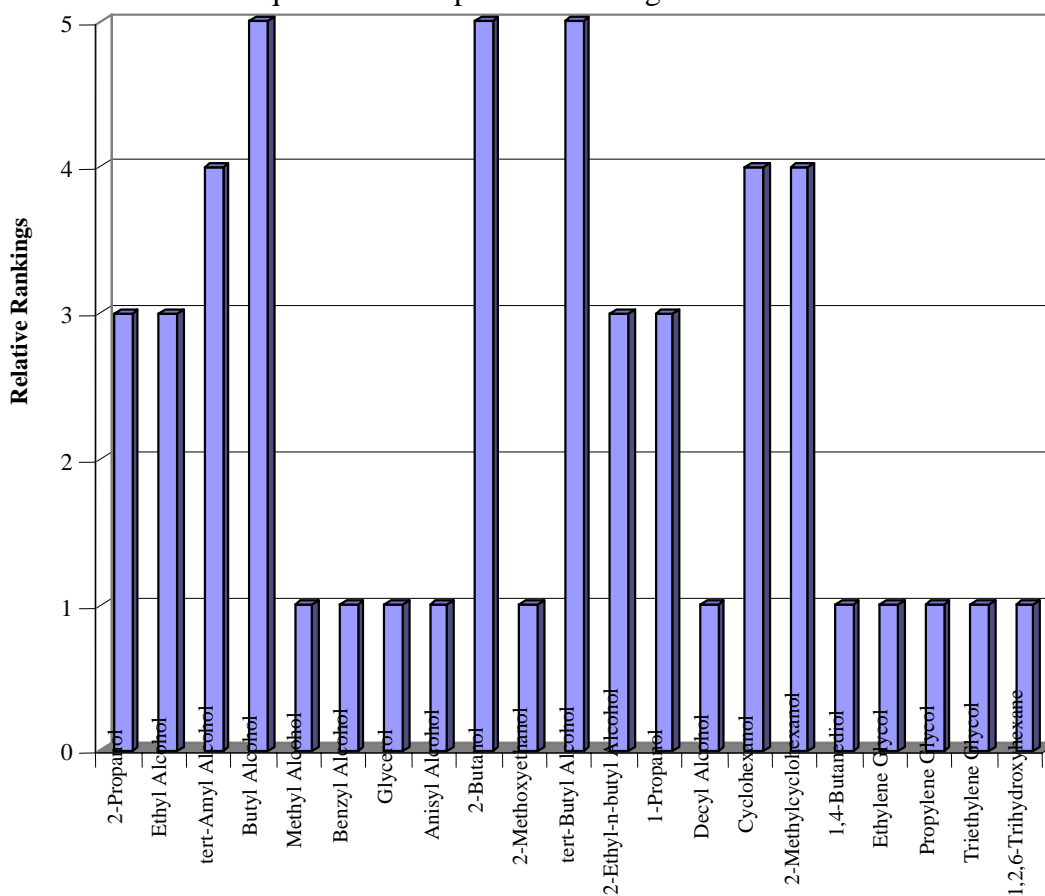


Figure 18. Relative ratings of alcohols as defoamers show butyl alcohols performed best.

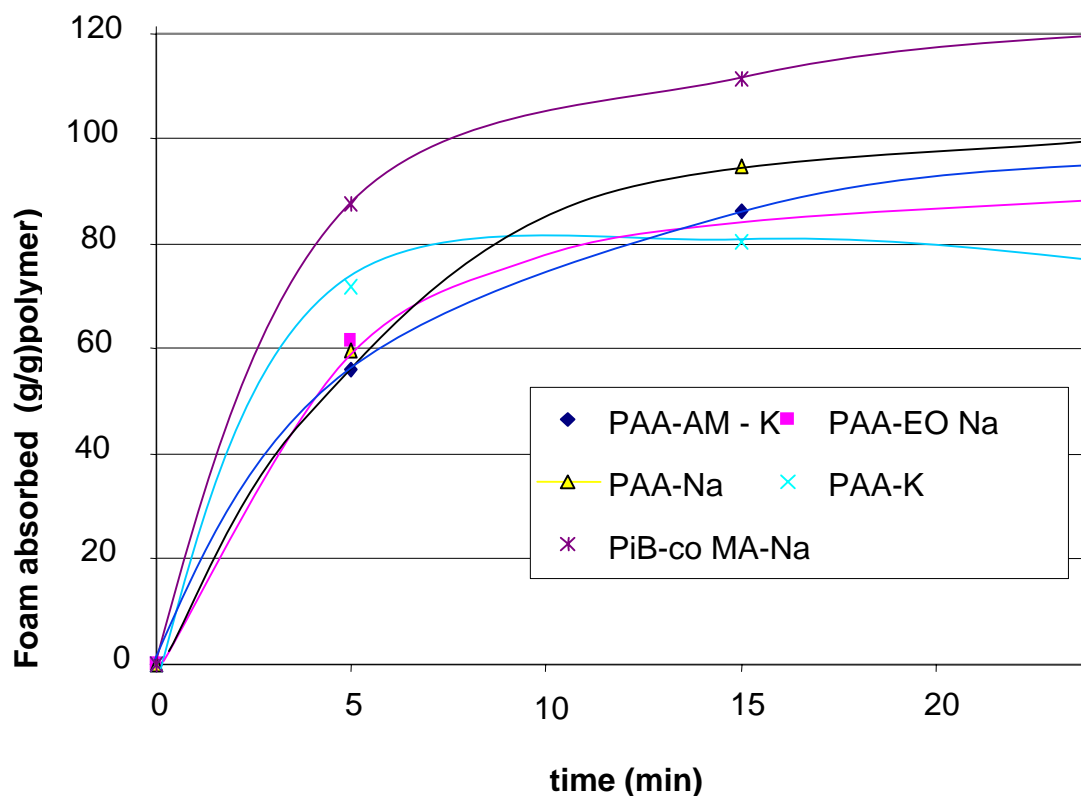


Figure 19. Poly(maleic anhydride-co-isobutylene) fiber absorbs about 115 times its weight in AFC-380 foam solution after being defoamed with precipitated silica (Hi-Sil 700).

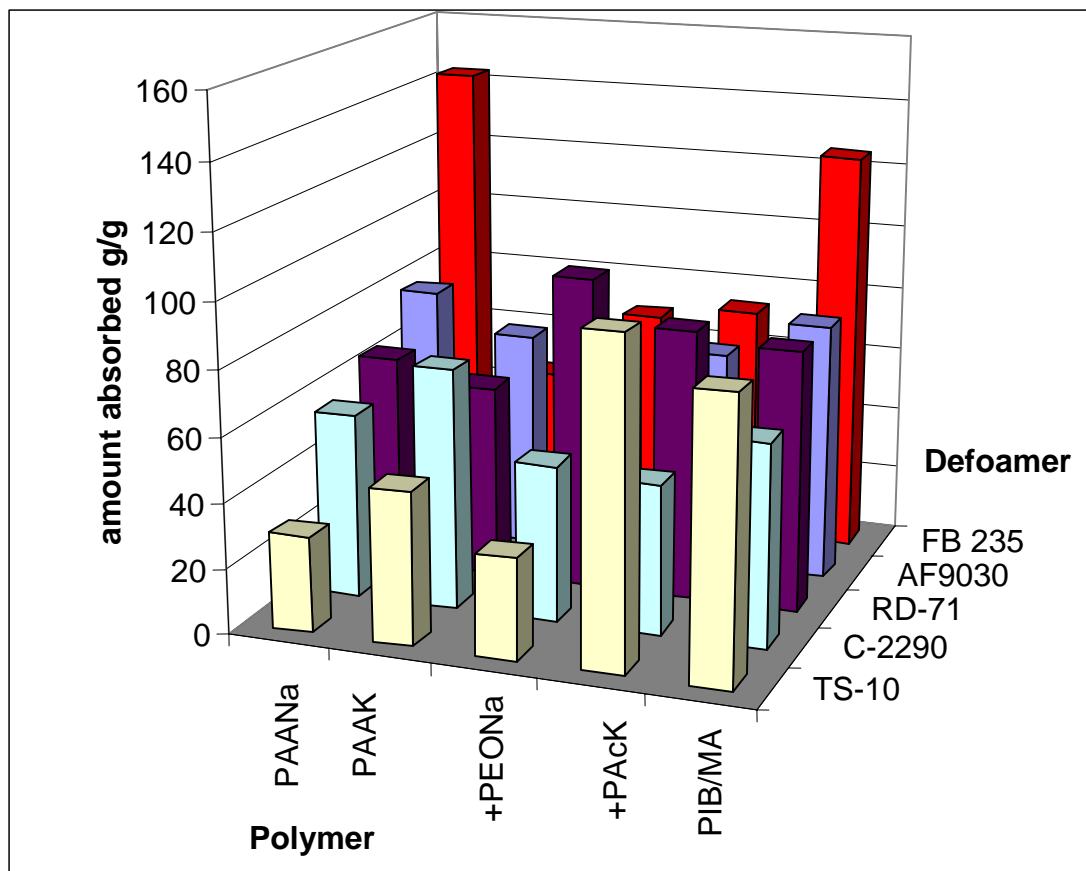


Figure 20. Comparison of the absorption characteristics of 5 super absorbing polymers in AFC-380 solution after it has been defoamed with one of the 5 commercial defoamers tested showed substantial variation in each polymer's ability to imbibe solution depending on which defoamer had been used.