



SPE 93273

## Foams for Controlling Water Production

Vikram Bhide, SPE, George Hirasaki, SPE, Clarence Miller, SPE, and Maura Puerto, Rice University; Ian Robb, SPE, and Lewis Norman, SPE, Halliburton

Copyright 2005, Society of Petroleum Engineers Inc.

This paper was prepared for presentation at the 2005 SPE International Symposium on Oilfield Chemistry held in Houston, Texas, U.S.A., 2 – 4 February 2005.

This paper was selected for presentation by an SPE Program Committee following review of information contained in a proposal submitted by the author(s). Contents of the paper, as presented, have not been reviewed by the Society of Petroleum Engineers and are subject to correction by the author(s). The material, as presented, does not necessarily reflect any position of the Society of Petroleum Engineers, its officers, or members. Papers presented at SPE meetings are subject to publication review by Editorial Committees of the Society of Petroleum Engineers. Electronic reproduction, distribution, or storage of any part of this paper for commercial purposes without the written consent of the Society of Petroleum Engineers is prohibited. Permission to reproduce in print is restricted to a proposal of not more than 300 words; illustrations may not be copied. The proposal must contain conspicuous acknowledgment of where and by whom the paper was presented. Write Librarian, SPE, P.O. Box 833836, Richardson, TX 75083-3836, U.S.A., fax 01-972-952-9435.

### Abstract

There is a great interest in the oil production industry in relative permeability modifiers (RPM) that can preferentially reduce water production without significantly affecting oil production. Various hydrophilic polymers have been studied for their RPM properties. This paper shows the potential of foam as RPM. Foams stable for a long time in presence of flowing water were developed using polymeric surfactants. Scale-up calculations show foam lifetimes long enough in field geometries for the process to be practicable. Foam tolerance to residual oil in water producing zones was produced by adding anionic surfactant to a nonionic polymeric surfactant. Resistance to flowing oil was, however, found to be unexpectedly high due to stable emulsion generation in porous medium. A process modification is shown to reduce the severity of this problem.

### Introduction

Reducing water production during oil production in a mature oilfield is an important objective for the oil producing industry. Produced water has a significant impact on the profitability of the field. Producing water involves a waste of drive energy in pumping water rather than oil, in addition to loss of oil production. Also, water production can lead to other problems such as corrosion of surface equipment, need for more separator capacity, and other disposal and handling concerns.<sup>1-3</sup>

Several techniques have been developed to overcome this problem. The most popular involve injection of polymer<sup>1-3, 6-9</sup> or gel<sup>4,5</sup> into the production wells. These materials preferentially reduce water permeability relative to oil and are, hence, referred to as relative permeability modifiers (RPM). Various mechanisms have been proposed to explain their RPM property such as swelling/shrinkage, fluids partitioning and wall effects.<sup>6</sup> Though none of them is universally

applicable, the hydrophilic polymers, in particular, are accepted to exhibit RPM behavior due to the wall effect, in which a hydrated layer of polymer adsorbs on the rock surface along pore throats and inhibits water flow.

In this paper, we show the potential of foam for use as RPM in oil-producing wells. Aqueous foam has properties that make it suitable for use as a RPM. Foam reduces water permeability in the regions where it is present by trapping gas in the pore spaces. In addition, foam is not expected to impede flowing oil as aqueous foam usually collapses in presence of large amount of oil.<sup>10, 11</sup> However, foams from conventional low molecular weight surfactants are unsuitable for this application as they tend to collapse rapidly in presence of flowing water,<sup>12</sup> presumably, due to surfactant desorption from the air-water interfaces of foam. Hence polymeric surfactants were studied for foam generation, as these are not expected to desorb as easily. In addition, for water-control application, foam has to be stable to residual oil present in the water producing zones and foam has to collapse in presence of flowing oil in the oil zones. These properties were examined in this study and are addressed in the following sections.

### Foam washout stability with polymeric surfactants

**Screening tests.** To test foam stability in presence of flowing water in a short amount of time, a screening test was developed. The experimental setup (Fig 1) consisted of a foot-long glass column, about an inch in diameter equipped at the bottom with a perforated metal plate fitted with a 360-mesh screen. Air was blown at 10 ml/min from the bottom through a fixed amount of surfactant solution until foam was generated to fill the glass column. About 15 ml of surfactant solution was used. The excess surfactant was drained and water (or brine) was injected at a fixed rate of 3 ml/min from the top. The injected water flowed through the plateau border regions of the foam (where three foam films meet at 120°), carrying off the surfactant present in those regions. This eventually caused the foam films to rupture, giving rise to foam collapse from the top to the bottom of the column. The time required for the foam height to decrease from the upper to the lower mark in Fig 1 was denoted as the washout time. The distance between the two marks was about 9.5 inches and the volume between the marks was approximately 120 ml.

Some of the conventional and polymeric surfactants (triblock copolymers from BASF and Dow Chemical, and hydrophobically modified polymers supplied by Halliburton) that were tested in the above setup are listed in Tables 1

through 3. In Table 1, SDS and C<sub>16</sub>TAB are pure materials and the rest are commercially available surfactant solutions that may contain ingredients other than active materials. Two types of triblock copolymers were tested (Table 2) – ethylene oxide-propylene oxide-ethylene oxide (EO-PO-EO) and ethylene oxide-butylene oxide-ethylene oxide (EO-BO-EO), wherein BO is more hydrophobic than PO. The hydrophobically modified (HM) polymers listed in Table 3 (HMPA1 and HMPA3) have some randomly distributed hydrophobic chains attached to a relatively hydrophilic backbone. However, their exact composition and molecular weight are not known.

The foam washout times in the screening test are shown in Fig 2. Most conventional surfactants produced foam that washed out quickly (< 10 min) except for CS-330. The triblock copolymers, in general, showed much better washout resistance than conventional surfactants. In presence of salt (5% NaCl), the triblocks were even better foamers and also better foam washout stabilizers. F108, with the highest molecular weight of ~15,000, also had the highest washout time of ~150 min. In presence of salt, the HM polymers also showed excellent foam washout stability. Foam produced from HMPA1 required washout time close to 300 min. This demonstrates that polymeric surfactants are more suited than conventional surfactants for producing foams in reservoirs that can last for a long time in flowing water.

**Sand pack experiments.** Foam was generated with some of the above polymeric surfactants in a porous medium to evaluate the water blocking property of foam. The experimental setup that was used is shown in Fig 3. The porous medium consisted of a 2-ft long, 5 to 7 darcy sand pack. Pressure drops could be measured across four equal sections of the pack. Foam was generated in-situ by injecting air and surfactant solution through the sand pack. Strong foam generation, i.e. foam with high resistance to flow, and simultaneous propagation of foam has been observed to be difficult to achieve in porous medium in several studies including this one.<sup>13-16</sup> A procedure of alternating injection of surfactant and air into an initially surfactant saturated sand pack was used to achieve both strong foam generation and propagation. This sequence of air and surfactant injection was continued till a sufficiently high resistance to flow was developed.

Foam generation in the sand pack is shown in Fig 4a using the example of B20-5000 polymeric surfactant. In this case, after three cycles of air and surfactant injection, an average mobility reduction factor (MRF, defined below) of greater than 100 was developed.

$$\text{MRF} = \frac{\text{pressure drop with foam present}}{\text{pressure drop for brine flow without foam}} \quad (1)$$

Note that the corresponding MRFs reported in the studies of polymers as RPM are generally only about 5 to 10.<sup>6</sup> Due to some entrance and exit end effects,<sup>13, 15</sup> MRF during foam generation was usually lower than average in the first section and higher in the fourth section as seen in Fig 4a.

Following foam generation, surfactant solution was injected to displace any flowing air and leave behind only

trapped air in the sand pack. Water (or brine) was then injected in the pack and collapse of foam monitored with pore volumes (PV) of water throughput. Washout of foam from B20-5000 is shown in Fig 4b. Foam was observed to collapse almost sequentially in the first three sections of the sand pack. However, MRF in the 4<sup>th</sup> section actually increased initially during washout. This is again believed to be due to a capillary end effect which causes foam generation near the exit by the mechanism of snap-off and traps some of the air from foam washed out in the preceding sections near the exit. MRF in 4<sup>th</sup> section decreased somewhat after foam in 3<sup>rd</sup> section washed out but never collapsed completely. The reason for this slow washout in 4<sup>th</sup> section had to do with slow desorption of polymeric B20-5000 and air compressibility effects and will become clearer later in the section on causes of foam washout. The end effect length is, however, not significant in field length scales and can be neglected for the purpose of measuring foam washout. So, PV for foam washout for only the first three sections is considered. It required about 22 PV of 5% NaCl throughput to wash out foam from first three sections.

A practical problem with carrying out foam washout at constant rate of 6 ft/d, as in Fig 4b, was that it required long time durations (~6 days in Fig 4b). Hence, for most experiments washout was switched to a high rate pump from time to time to accelerate washout. This is shown in Fig 4c for B20-5000. Gaps in washout in the Fig are periods when flow was switched to higher rates and when pressure transducers were isolated to keep them from going out of range. In this case, about 16 PV were required for foam washout. Thus, though changing flow rate had some effect on number of PV, it was not very substantial and did not affect any meaningful comparison of surfactants.

In contrast to polymeric surfactants, washout of foam with pure conventional surfactants such as C<sub>16</sub>TAB was quite rapid. In Fig 5, foam from C<sub>16</sub>TAB collapsed in all sections of the sand pack (including 4<sup>th</sup>) in ~2.5 PV. Washout of foam from commercial surfactants such as CS-330 required larger throughput (~10 PV) because of some impurities in the formulation, as described in the following section. Fig 6 summarizes the foam washout results for several conventional and polymeric surfactants. Again, foam from F108 required the largest number of PV of brine for washout. The HM polymers tested in this study were found to be relatively poor foamers in sand pack experiments, with maximum MRF during brine flow of 50 or lower. The foam films from HMAP1 and HMPA3 appeared to be unstable at the higher capillary pressures in the sand pack in contrast to the screening test where capillary pressures are lower. Yet, the HM polymers show very good foam washout stability as seen in Fig 6. The reason that PV for foam washout for HMPA1 was not higher than F108 (as in screening test) was because of foam dissolution limitation in sand pack as explained in the next section.

The foam washout experiments in sand pack show that the screening test developed was a good qualitative indicator of foam washout in sand pack. The foam washout experiments demonstrate that the polymeric surfactants can produce foams with much higher foam washout resistance than most conventional surfactants. A little later, the section

on scale-up will estimate washout times for field applications.

**Reasons for foam washout stability.** As mentioned earlier, the reason foam from conventional surfactants is unstable to washout is because of desorption of surfactants from air-water interface into the flowing water which destabilizes foam films. The desorption of conventional and polymeric surfactants from air-water interface was measured in our research in the following manner: A pendant bubble was created initially in a surfactant solution and then the surfactant solution was replaced with water. The surface tension of the bubble was monitored as a function of surfactant concentration around the bubble. The experimental setup is shown in Fig 7. More detailed description can be found elsewhere.<sup>17</sup> A similar principle has also been used by Svitova et al.<sup>18</sup> to measure desorption of surfactants from air-water and oil-water interfaces. The desorption results are summarized in Fig 8. The surface tension of the bubble as a function of replaced cell volumes of surfactant solution (and hence surfactant concentration) is shown in the Fig. It is observed that pure conventional surfactants, such as SDS desorbed easily from the air-water interface as the surfactant solution was diluted and eventually the surface tension reached that of pure water, indicating that all the surfactant was removed from the air-water interface. For commercial surfactant CS-330, though the surfactant desorbed rapidly, there were other surface active impurities in the surfactant formulation (probably solubilized long chain alcohols) that did not desorb from the air-water interface. This is represented in the Fig by a final surface tension significantly lower than that of pure water (~ 55 mN/m). This explains the higher washout time for foam from CS-330 in the screening test. As opposed to the conventional surfactants, most polymeric surfactants did not desorb significantly from the air-water interface. For example, the change in surface tension of the bubble initially generated in F108 solution was only about 5 mN/m. This explains why polymeric surfactants such as F108 and HMPA1 produce such long lasting foams in presence of flowing water.

However, it was found that dissolution of gas from foam into the flowing water was a limiting factor on foam lifetime in sand pack for foam from polymeric surfactants. In the sand pack experiments described in the previous section, the water that was injected during foam washout was under-saturated with air at the inlet pressures of the sand pack (approximately 2 to 3 atm). This can cause foam collapse due to gas dissolution. Using the method of characteristics and ideal gas law, the following expression for PV required for foam dissolution in completely unsaturated water was derived.<sup>17</sup>

$$PV = 1 + S_g \left(0.018 \frac{H}{RT} - 1\right) \quad (2)$$

where,  $S_g$  is the initial gas saturation before washout and  $H$  is the Henry's constant for the gas in foam. Using this equation, one gets ~30 PV for foam dissolution in 3 sections for initial gas saturation of 70%. The observed PV for many polymeric surfactants was ~16-25, indicating that foam dissolution has a very important role in foam washout for many polymeric surfactants. This was further verified from the following two observations: 1) foam from polymeric surfactants collapsed

even when surfactant solution was injected instead of water in a similar number of PV, and 2) when additional air was dissolved into the injected liquid, foam washout was slowed considerably.

Therefore, foam dissolution can explain why foam from HMPA1 does not last longer than foam from F108 as may be expected from the screening test. This also explains why very little washout of foam was observed in the 4<sup>th</sup> section with polymeric surfactants as described earlier. Near the exit pressure (atmospheric), the flowing water was always either saturated or oversaturated with air and no washout occurs by gas dissolution.

It must be noted that the above expression for foam dissolution is independent of pressure (provided Henry's law and ideal gas law hold) and foam lifetime is not expected to be a function of depth of the reservoir. The expression describes the worst case scenario of unsaturated water. In oilfield reservoirs, one may expect dissolved gases, particularly hydrocarbon gases such as methane, to be present in the produced water. Thus, if foam is generated with N<sub>2</sub> but reservoir brine contains CH<sub>4</sub>, some CH<sub>4</sub> will be transferred to foam as N<sub>2</sub> dissolves, thereby prolonging foam lifetime. The expression also highlights the importance of the type of gas used to generate foam. Hence, N<sub>2</sub> rather than CO<sub>2</sub> would be preferable to produce foam because of its lower solubility in brine.

**Scale-up to field geometries.** From the above experimental observations in one dimensional sand packs, the time scales for foam washout in radial oilfield geometries can be calculated. A parameter  $m$  is defined as follows,

$$m = v_f/v,$$

where  $v_f$  is the velocity of foam front during washout and  $v$  is the interstitial water velocity when no foam is present. It can be shown that for 1-D sand pack experiments

$$m = 1/(PV \text{ for foam washout}).$$

This can be computed from Fig 6 after taking into account that PV for washout in Fig 6 is for three sections only for polymeric surfactants.

A schematic of foam in the water producing zone is shown in Fig 9. Let  $r_w$  be the well radius and  $r_e$  be a position deep enough the formation such that change in pressure at that position ( $P_e$ ) is not very large at the time scales of washout. Let  $r_i$  be the initial position of foam front and  $r_t$  the position at time  $t$  during washout. Let  $P_w$  be the pressure at the well and  $P_t$  be the pressure at the foam front at time  $t$ . Let the mobility reduction factor be  $MRF_f$  in the foam region and  $MRF_{nf}$  in the remaining region where foam has washed out.

$$\text{Thus, } r_i - r_t = \int_0^t v_f dt \quad (3)$$

$$= \int_0^t \frac{m\lambda(P_e - P_w)}{r_t \phi MRF_{mean} \ln \frac{r_e}{r_w}} dt \quad \text{using Darcy's law} \quad (4)$$

Here,  $\lambda$  ( $= k/\mu$ ) is the water mobility in formation,  $\phi$  is the porosity and  $MRF_{mean}$  is the harmonic average of MRFs from  $r_w$  to  $r_e$  at any given time  $t$ . A couple of simplifying assumptions can be made to get an analytical solution of (4).

In 1-D experiments, the foam washout front was observed to travel with approximately constant speed (hence, constant  $m$ ) from inlet to outlet. This is shown for the foam washout of B20-5000 for the first three sections in Fig 10 (from MRF versus PV data from Fig 4b). In addition, only a weak dependence of  $m$  on flow rate was observed from experiments in Figs 4b and 4c. So,  $m$  can be considered independent of flow rate and time, and values from 1-D experiments can be used. In addition, for a deep enough  $r_e$ ,  $P_e - P_w$  can be considered approximately constant (in any case, this will only underestimate foam washout time). These assumptions give the following expression for foam washout time ( $\Delta t$ ):

$$\frac{m\lambda(P_e - P_w)}{\phi} \Delta t = \left( \frac{r_w^2 - r_i^2}{2} \right) (MRF_f \ln r_w - MRF_{nf} \ln r_e) + (1/4)(MRF_{nf} - MRF_f) \left[ r_w^2 (2 \ln r_w - 1) - r_i^2 (2 \ln r_i - 1) \right] \quad (5)$$

Since,  $r_w \ll r_i$ , we get:

$$\frac{\Delta t}{r_i^2 \phi / 2m\lambda(P_e - P_w)} = \left[ (MRF_{nf} \ln r_e - MRF_f \ln r_w) + (MRF_f - MRF_{nf})(\ln r_i - 1) \right] \quad (6)$$

Foam washout time as a function of initial foam penetration ( $r_i$ ) is plotted for F108 in Fig 11 for two values of  $MRF_f$  with the following typical parameter values:  $k = 100$  mD,  $\phi = 0.3$ ,  $r_w = 0.5$  ft,  $r_e = 1000$  ft,  $P_e - P_w = 1000$  psi,  $m = 0.03$ ,  $MRF_{nf} = 1$ ,  $MRF_f = 50$  or  $100$ . The plot shows an approximately quadratic dependence of washout time on foam penetration length. Foam lifetime of the order of years can be seen for initial foam penetration of 20 ft or more with  $MRF_f \geq 50$ . What is more important for field application is the foam lifetime in relation to time for foam generation. Equation (6) can also be used to compute time for fluid front propagation using appropriate values for front velocity ( $m$ ) and resistance factor ( $MRF_f$ ). To compute time for foam generation, it is assumed that foam is generated in the field by injecting one slug of surfactant followed by one slug of gas. It can be shown that time for surfactant solution injection is negligible compared to gas injection. Hence time for foam generation ( $\Delta t_{fg}$ ) equals time for gas injection to distance  $r_i$ . That is,

$$\Delta t_{fg} \approx \Delta t \text{ from (6) with } m = 1 \text{ and } MRF_f = 100/n \quad (7)$$

In 2-ft sand pack experiments, MRF during air injection was about 50% of MRF during liquid flow after foam generation (i.e.  $n \approx 2$  or  $MRF_f \approx 50$  in (7)). Hence, it can be shown that

$$\text{Time for foam washout } (\Delta t_{fw}) \approx (2/m) \times \Delta t_{fg} \quad (8)$$

For F108,  $\Delta t_{fw} \approx 66 \times \Delta t_{fg}$ . That is, in the case of F108, for every day of production downtime in generating foam one may expect at least 2 months of reduced water production. Thus, with a few days of foam treatment, water production can be reduced for several months using foam from F108.

The MRF of foam in 3-D has been observed to be less than that in 1-D<sup>19, 20</sup> because of more avenues to bypass a channel blocked by a foam lamella. The maximum MRF achievable due to foam at 20 ft or more in radial geometries may have to be studied further, but there is some evidence in literature that it is possible to have high MRF in field conditions.<sup>21, 22</sup> In the use of foam for gas blocking,<sup>22</sup> for example, Blaker et al. have estimated maximum foam MRF of 400 for a foam zone longer than 280 ft.

### Foam stability to residual oil

The water producing zones in an oilfield may also contain residual amounts of oil from past history. Hence, for the use of foam as RPM, it must have tolerance for residual oil. Foam stability to residual oil in porous medium was tested using the experimental set-up shown in Fig 12. Foam was generated in a short sand pack (about 1.5" long) by co-injecting air and surfactant (80% air fraction at 1 atm). The texture of foam generated could be observed in the transparent plastic tubing at the outflow end. The pressure drop across the short pack was measured at steady state and is an indicator of foam stability in the short sand pack. Pressure drop across the pack when no oil was present was compared to pressure drop when residual oil was present. To prepare the pack at residual oil saturation, oil was flowed through a water saturated pack and then followed by water injection. Residual oil saturation of about 30% was observed in the pack.

Fig 13 shows the steady state pressure drop across the short pack at 80% foam quality (gas fraction) for the cases with and without residual oil for non-ionic triblock copolymers and anionic surfactants. Hexadecane was used as oil in these experiments. It can be seen that the two polymeric surfactants tested - F108 and B20-5000 - show little foam tolerance to residual oil and hardly any foam was produced with residual oil. In contrast both anionic surfactants CS-330 and SDS produced stable foams with residual oil. This indicated that the charged surfactants are better for producing foams tolerant to oil than uncharged surfactants. This was further supported by the entering (E), spreading (S) and bridging (B) coefficients for these oil-water-surfactant systems as listed in Table 4. The various interfacial tensions listed were measured using a pendant drop apparatus. The thermodynamic theories of foam stability predict that foam is likely to be destabilized when any of these coefficients is positive and a higher magnitude of a coefficient indicates greater tendency for destabilization by a particular mechanism.<sup>23, 10, 11</sup> The positive values of all the coefficients for all the surfactants in the Table show that all are expected to form foam intolerant to oil. In addition, the magnitudes of the coefficients for SDS are comparable to those of F108 or B20-5000. The only difference between the stable and unstable sets of surfactants is that the stable set is negatively charged. The charged surfactants produce an electrostatic barrier for the entry of an oil droplet into an air-water interface and prevent foam destabilization by spreading or bridging mechanisms.

This phenomenon has also been observed by other researchers.<sup>24</sup>

Because of the above observations, a mixture of F108 and CS-330 was tested to produce foam with both residual oil tolerance and good washout resistance. The amount of CS-330 added had to be kept to a minimum to prevent displacement of F108 at the air-water interface by the faster adsorbing CS-330. But because of binding of CS-330 molecules to F108 molecules in solution, a larger amount of CS-330 had to be used for CS-330 to be available at the surface. Finally, a 1:1 ratio by weight of CS-330 and F108 was used. This 0.5% F108 + 0.5% CS-330 mixture did produce foam that was tolerant to residual oil as seen in Fig 13. In addition, foam washout resistance was comparable to F108 in both screening test and 2-ft sand pack experiment. In the screening test, both F108 + CS-330 mixture and F108 alone required close to 150 min for foam washout with 5% NaCl. In the 2-ft sand pack experiment, foam from F108 + CS-330 mixture washed out in 18-19 PV which was only slightly lower than 21-25 PV required for F108.

### Foam stability to flowing oil

Another criterion for the use of foam as RPM is that it should not offer significant resistance to oil flow. For this to happen, foam should collapse with flowing oil. When oil was injected through a glass column containing foam, foam was observed to collapse rapidly within a few minutes. Table 5 shows the time for foam collapse with flowing hexadecane in the screening test compared with foam washout time with brine. For all the surfactants tested – anionic as well as non-ionic - foam collapsed in a very short time compared to washout time with water, as desired for the application.

In the porous media (2-ft sand pack), however, the surfactant present in the foam led to a very stable oil-in-water emulsion when oil was flowed through the foam region. This emulsion produced a large resistance for flow of oil (MRF >1000). The F108 + CS-330 combination, in particular, turned out to be a much better emulsifier than a foamer. Since the flow resistance was due to presence of surfactant which produced emulsions, the flow resistance can also be tested when oil is flowed through a surfactant solution saturated sand pack, even without the presence of foam. This is depicted in Fig 14. The F108+CS-330 combination gave higher flow resistance (MRF/viscosity) than F108 itself, because the combination produced a more stable emulsion. This stable emulsion is undesirable for the RPM application of foam.

One way to reduce emulsion stability is by modification of oil + water + surfactant phase behavior. It has been observed by several researchers that the rate of emulsion coalescence increases as one approaches the 3-phase region and is maximum in the Winsor III system.<sup>25, 26</sup> F108+CS-330 combination is very hydrophilic. Hydrophilic-lipophilic balance (HLB) closer to intermediate values could be obtained by increasing salt concentration or by replacing CS-330 by a more lipophilic surfactant. This is also shown in Fig 14 for a couple of cases. Adding salt shifts the HLB of the system to more lipophilic values. However, for F108+CS-330 combination, adding even a large amount of salt did not produce a Winsor II or Winsor III system because of the very hydrophilic nature of surfactants. But when the solution was

saturated with CaCl<sub>2</sub>, the rate of emulsion coalescence increased substantially in bottle tests. Hence, as shown in Fig 14, this produced lower resistance to flowing oil than the system with 5% NaCl. Also, when CS-330 was replaced with more lipophilic TDA-4PO (which has a branched C13 hydrocarbon chain), emulsion coalescence was very rapid at 20% NaCl and very little resistance was offered to flowing oil in Fig 14. Unfortunately, in each of these cases foam stability was also affected adversely. Thus, there is some trade-off between foam stability and emulsion coalescence in using this approach.

Hence, a process modification is proposed to address this problem. The modification would involve application of a pre-flush of brine before foam generation in the field. The idea is that when the well is brought back to production, this brine from the pre-flush will flow through the foam regions and remove most of the surfactant present in the aqueous phase, and this in turn, will reduce the amount and stability of emulsion generated. This concept was tested in the 2-ft sand pack as shown in Fig 15. Unlike in field conditions, the flow direction was not changed in the laboratory experiments. So, foam was generated first and then brine was injected. When oil was flowed through the sand pack after brine flush, some emulsion was still generated, probably due to the presence of some polymeric surfactant at the air-water interfaces of foam. But this emulsion flowed out or coalesced over time. For oil flow amounting to 4-5 PV of the initial foam region, resistance factor was reduced to less than 10. This remaining resistance appears not to be due to emulsion, but instead due to some air trapped in the porous media. One may expect this air to dissolve into the flowing oil over time and offer even lower resistance to flow.

In summary, this paper demonstrates the principle of using foam as RPM. A combination of non-ionic polymeric F108 and anionic CS-330 was shown to produce foam that would satisfy many of the important criteria required of a RPM. But different types of polymeric surfactants will have to be developed for particular field conditions. For example, polymeric F108 is not suitable for reservoirs where temperatures exceed its cloud point (about 90 °C). Also, a single anionic polymeric surfactant can be developed to generate foam instead of using a combination of non-ionic and anionic surfactants.

### Conclusions

1. The potential of foam as a RPM for reducing water production is shown. Mobility reduction factors greater than 100 were achieved in 1-dimensional sand pack experiments.
2. Foams stable to washout with water were produced by using polymeric surfactants such as triblock F108 and hydrophobically modified HMPA1. The washout stability was due to almost irreversible adsorption of polymeric surfactants at the air-water interface.
3. Foam dissolution into flowing water was observed to be a factor limiting the foam lifetime of polymeric surfactants. Foam lifetime for field conditions will depend on dissolved gas content in produced water and type of gas in foam, but not on the pressure in the formation, to a first

approximation.

- Even accounting for the gas dissolution, scale-up of foam washout of polymeric F108 to field geometries showed large enough time between re-treatment of production well for the process to be practically feasible.
- Foam tolerance to residual oil was produced by a mixing anionic CS-330 with non-ionic polymeric F108. The increased tolerance was due to electrostatic repulsion between the air-water and oil-water interfaces produced by the charged surfactant.
- Flowing oil in the porous medium, however, produced a stable emulsion that did not flow out easily. The resistance to flowing oil was minimized by a process modification involving a pre-flush of brine before foam generation.

### Acknowledgements

The authors would like to thank Halliburton for funding this project and for providing some of the surfactants used in this study.

### Nomenclature

- $H$  = Henry's constant,  $m/Lt^2$ , atm  
 $k$  = absolute permeability,  $L^2$ , darcy  
 $m$  = ratio of foam front to interstitial water velocity, dimensionless  
MRF = mobility reduction factor, dimensionless  
 $MRF_f$  = MRF in foam region  
 $MRF_{nf}$  = MRF in region without foam  
 $MRF_{mean}$  = mean MRF  
 $P_w$  = well pressure for water zone,  $m/Lt^2$ , psi  
 $P_t$  = pressure at foam front at time  $t$ ,  $m/Lt^2$ , psi  
 $P_e$  = pressure deep inside the formation,  $m/Lt^2$ , psi  
PV = pore volumes, dimensionless  
 $R$  = gas constant,  $mL^2/t^2K$ , 0.082 lit-atm/K-mol  
 $r_w$  = well radius, L, ft  
 $r_i$  = radial distance of initial foam front, L, ft  
 $r_t$  = radial distance of foam front at time  $t$ , L, ft  
 $r_e$  = radial distance where pressure is  $P_e$ , L, ft  
 $S_g$  = gas saturation, dimensionless  
 $T$  = temperature, K, °K  
 $v_f$  = foam front velocity, L/t, ft/day  
 $v$  = interstitial water velocity, L/t, ft/day
- $\Delta t_{fg}$  = time for foam generation, t, days or months  
 $\Delta t_{fw}$  = time for foam washout, t, days or months  
 $\phi$  = porosity, dimensionless  
 $\lambda$  = mobility,  $L^3/tm$   
 $\mu$  = viscosity,  $m/Lt$ , cp

### SI Metric Conversion Factors

- |                          |                  |
|--------------------------|------------------|
| cp $\times$ 1.0*         | E-03 = Pa.s      |
| darcy $\times$ 9.869 233 | E-01 = $\mu m^2$ |
| day $\times$ 8.64*       | E+04 = s         |
| ft $\times$ 3.048*       | E-01 = m         |
| in $\times$ 2.54*        | E+00 = cm        |
| psi $\times$ 6.894 757   | E-00 = kPa       |

\*Conversion factor is exact.

### References

- Dalrymple, E.D., and Brown, D.: "Effect of Relative-Permeability Modifier Treatments in a Sandstone-Layered System and in a Sandstone-Homogeneous System", paper SPE/DOE 39636 presented at the 1998 SPE/DOE Improved Oil Recovery Symposium, Tulsa, April 19-22.
- Eoff, L., Dalrymple, E.D., Reddy, B.R., and Everett, D.: "Structure and Process Optimization for the Use of a Polymeric Relative-Permeability Modifier in Conformance Control", paper SPE 64985 presented at the 2001 SPE International Symposium on Oilfield Chemistry, Houston, February 13-16.
- Eoff, L., Dalrymple, D., Reddy, B.R., Morgan, J., and Frampton, H.: "Development of a Hydrophobically Modified Water-Soluble Polymer as a Selective Bullhead System for Water-Production Problems", paper SPE 80206 presented at the 2003 SPE International Symposium on Oilfield Chemistry, Houston, February 5-7.
- Liang, J., Sun, H., and Seright, R.S.: "Why Do Gels Reduce Water Permeability More Than Oil Permeability", *SPE* (1995) 282.
- Liang, J., and Seright, R.: "Further Investigations of Why Gels Reduce kw More Than ko", paper 1997 SPE 37249 presented at the SPE International Symposium on Oilfield Chemistry, Houston, February 18-21.
- Zaitoun, A., and Bertin, H.: "Two-Phase Flow Property Modifications by Polymer Adsorption", paper SPE/DOE 39631 presented at the 1998 SPE/DOE Improved Oil Recovery Symposium, Tulsa, April 19-22.
- Zaitoun, A., and Kohler, N.: "Improved Polyacrylamide treatments for Water Control in Producing Wells", paper SPE 18501 presented at the 1989 SPE International Symposium on Oilfield Chemistry, Houston, February 8-10.
- Zaitoun, A., and Kohler, N.: "Two-Phase Flow through Porous Media: Effect of an Adsorbed Polymer Layer", paper SPE 18085 presented at the 1988 SPE Annual Technical Conference and Exhibition, Houston, October 2-5.
- Zitha, P., Chauveteau, G., and Zaitoun, A.: "Permeability Dependent Propagation of Polyacrylamides Under Near-Wellbore Flow Conditions", paper SPE 28955 presented at the 1995 SPE International Symposium on Oilfield Chemistry, San Antonio, February 14-17.
- Schramm, L.L.: "Foam Sensitivity to Crude Oil in Porous Media", in *Foams: Fundamentals and Applications in the Petroleum Industry*, L.L. Schramm (ed.), American Chemical Society, Washington, D.C. (1994).
- Wasan, D.T., Koczo, K., and Nikolov, A.D.: "Mechanisms of Aqueous Foam Stability and Antifoaming Action with and without Oil", in *Foams: Fundamentals and Applications in the Petroleum Industry*, L.L. Schramm (ed.), American Chemical Society, Washington, D.C. (1994).

12. Szafranski, R.: "Laboratory Development of the Surfactant/Foam Process for Aquifer Remediation", Ph.D. thesis, Rice University, 1997.
13. Myers, T.J., and Radke, C.J.: "Transient Foam Displacement in the Presence of Residual Oil: Experiment and Simulation Using a Population-Balance Model", *Ind. Eng. Chem. Res.* (2000) **39**, 2725.
14. Gauglitz, P.A., Friedmann, F., Kam, S.I., and Rossen, W.R.: "Foam Generation in Porous Media", paper SPE 75177 presented at the 2002 SPE/DOE Improved Oil Recovery Symposium, Tulsa, April 13-17.
15. Apaydin, O.G., and Kovscek, A.R.: "Transient Foam Flow in Homogeneous Porous Media: Surfactant Concentration and Capillary End Effects", paper SPE 59286 presented at the 2000 SPE/DOE Improved Oil Recovery Symposium, Tulsa, April 3-5.
16. Persoff, P., Radke, C.J., Pruess, K., Benson, S.M., and Witherspoon, P.A.: "A Laboratory Investigation of Foam Flow in Sandstone at Elevated Pressure", *SPE* (1991) 365.
17. Bhide, V.V.: "Developing Stable Foams from Polymeric Surfactants for Water Production Control", Ph.D. thesis, Rice University, 2004.
18. Svitova, T.F., Wetherbee, M.J., and Radke, C.J.: "Dynamics of Surfactant Sorption at the Air/Water Interface: Continuous-Flow Tensiometry", *J. Colloid and Interface Science* (2003) **261**, 170.
19. Hirasaki, G.J., Miller, C.A., Szafranski, R., Tanzil, D., Lawson, J.B., Meinardus, H., Jin, M., Londergan, J.T., Jackson, R.E., Pope, G.A., and Wade, W.H.: "Field Demonstration of the Surfactant/Foam Process for Aquifer Remediation", paper SPE 39292 presented at the 1997 SPE Annual Technical Conference and Exhibition, San Antonio, October 5-8.
20. Hirasaki, G.J., Jackson, R.E., Jin, M., Lawson, J.B., Londergan, J., Meinardus, H., Miller, C.A., Pope, G.A., Szafranski, R., Tanzil, D.: "Field Demonstration of the Surfactant/Foam Process for Remediation of a Heterogeneous Aquifer Contaminated with DNAPL", in *NAPL Removal: Surfactants, Foams and Microemulsions*, S. Fiorenza, C.A. Miller, C.L. Oubre, C.H. Ward (eds.), CRC Press LLC, Boca Raton (2000).
21. Hanssen, J.E., and Dalland, M.: "Gas-Blocking Foams", in *Foams: Fundamentals and Applications in the Petroleum Industry*, L.L. Schramm (ed.), American Chemical Society, Washington, D.C. (1994).
22. Blaker, T., Celius, H.K., Lie, T., Martinsen, H.A., Rasmussen, L., and Vassenden, F.: "Foam for Gas Mobility Control in the Snorre Field: The FAWAG Project", paper SPE 56478 presented at the 1999 SPE Annual Technical Conference and Exhibition, Houston, October 3-6.
23. Garrett, P.R.: "The Mode of Action of Antifoams", in *Defoaming: Theory and Industrial Applications*, P. R. Garrett (ed.), Marcel Dekker, Inc.; New York (1993).
24. Zhang, H., Miller, C.A., Garrett, P.R., and Raney, K.H.: "Mechanism for Defoaming by Oils and Calcium Soap in Aqueous Systems", *J. Colloid and Interface Science* (2003) **263**, 633.
25. Baldauf, L.M., Schechter, R.S., Wade, W.H., and Graciaa, A.: "The Relationship between Surfactant Phase Behavior and the Creaming and Coalescence of Macroemulsions", *J. Colloid and Interface Science* (1982) **85**, 187.
26. Aveyard, R., Binks, B.P., Fletcher, P.D.I., Ye, X., and Lu, J.R.: "The Resolution of Emulsions, Including Crude Oil Emulsions, in Relation to HLB Behavior", in *Emulsions – A Fundamental and Practical Approach*, J. Sjoblom (ed.), Kluwer Academic Publishers, Dordrecht (1991).

**Table 1: Conventional surfactants tested for foam washout stability**

Surfactant	Active components
SDS	Sodium dodecyl sulfate [CH <sub>3</sub> (CH <sub>2</sub> ) <sub>11</sub> -OSO <sub>3</sub> Na]
C <sub>16</sub> TAB	n-Hexadecyltrimethylammonium bromide [CH <sub>3</sub> (CH <sub>2</sub> ) <sub>15</sub> -N(CH <sub>3</sub> ) <sub>3</sub> Br]
CS-330	Sodium laureth sulfate [CH <sub>3</sub> (CH <sub>2</sub> ) <sub>11</sub> (OCH <sub>2</sub> CH <sub>2</sub> ) <sub>3</sub> -OSO <sub>3</sub> Na]
AOS 16/18	C <sub>16-18</sub> alpha olefin sulfonate
Foamer1	Alkyl polyoxyethylene ether
Foamer2	Alpha olefin sulfonate
Foamer3	Alkyl ether sulfate

**Table 2: Triblock copolymers tested for foam washout stability**

Product name	Average molecular weight	% EO	Average molecular formula
F108	14,600	80	EO <sub>132</sub> -PO <sub>56</sub> -EO <sub>132</sub>
F88	11,400	80	EO <sub>103</sub> -PO <sub>39</sub> -EO <sub>103</sub>
F68	8,400	80	EO <sub>76</sub> -PO <sub>30</sub> -EO <sub>76</sub>
P85	4,600	50	EO <sub>26</sub> -PO <sub>39</sub> -EO <sub>26</sub>
B20-5000	5,000	80	EO <sub>45</sub> -BO <sub>14</sub> -EO <sub>45</sub>
B20-3800	3,800	80	EO <sub>34</sub> -BO <sub>11</sub> -EO <sub>34</sub>

**Table 3: Hydrophobically modified polymers tested for foam washout stability**

HM polymer	Description
HMPA1	Copolymer of methacrylic acid and ethyl methacrylate + small amount of methyl methacrylate, C <sub>18</sub> hydrophobe; partially crosslinked
HMPA3	Similar to above with lower molecular weight and lower fraction of crosslinking

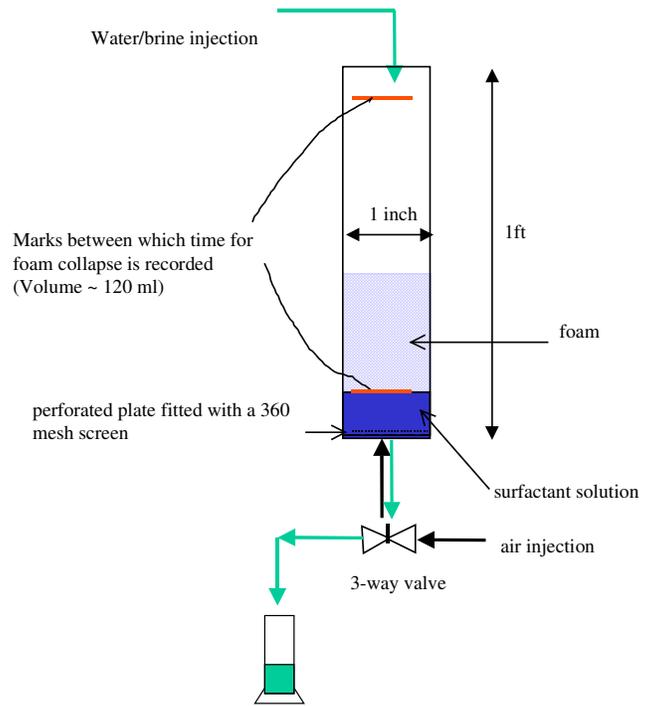
**Table 4: Entering, spreading and bridging coefficients**

Surfactant	$\gamma_{a-w}$	$\gamma_{o-w}$	$\gamma_{o-a}$	E	S	B
F108	37.2	6.9	23.5	20.6	6.8	879.2
B20-5000	33.7	5.2	23.5	15.4	5.0	610.5
CS-330	28.0	0.5	23.5	5.0	4.0	232.0
SDS	36.8	4.8	23.5	18.1	8.5	825.0

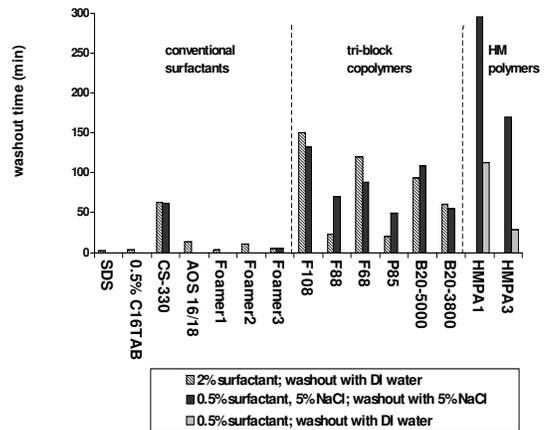
All surfactants 0.5%. All except SDS contain 5% NaCl.  
 $\gamma$  = Interfacial tension of a-w (air-water), o-w (oil-water), o-a (oil-air) interfaces in mN/m.  
 $E = \gamma_{a-w} + \gamma_{o-w} - \gamma_{o-a}$      $S = \gamma_{a-w} - \gamma_{o-w} - \gamma_{o-a}$      $B = \gamma_{a-w}^2 + \gamma_{o-w}^2 - \gamma_{o-a}^2$

**Table 5: Foam collapse time with flowing oil compared to washout with brine in the screening test**

Surfactant	Foam collapse time with hexadecane (3 ml/min)	Washout time with 5% NaCl (3 ml/min)
0.5% F108, 5% NaCl	3 min	160 min
0.5% CS-330, 5% NaCl	3.5 min	60 min
0.5% F108, 0.5% CS-330, 5% NaCl	6 min	161 min



**Fig. 1–Setup used for foam washout screening test**



**Fig. 2–Foam washout times for conventional and polymeric surfactants in the screening test**  
 HMPA1 and HMPA3 neutralized with dil. NaOH to pH ~7

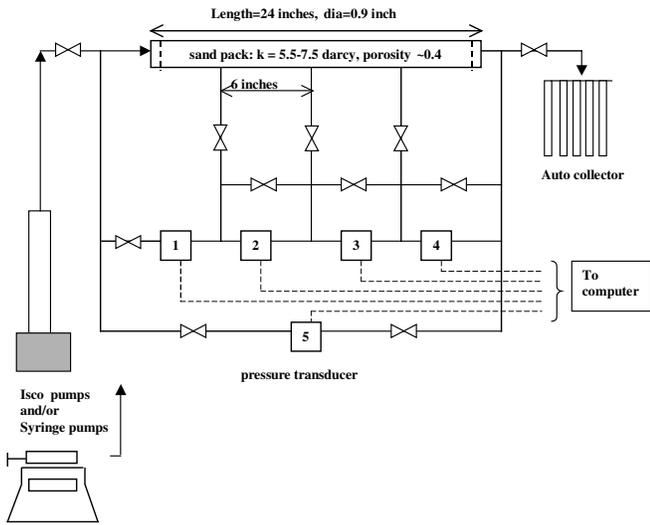


Fig. 3—Experimental setup for the foam washout in sand pack

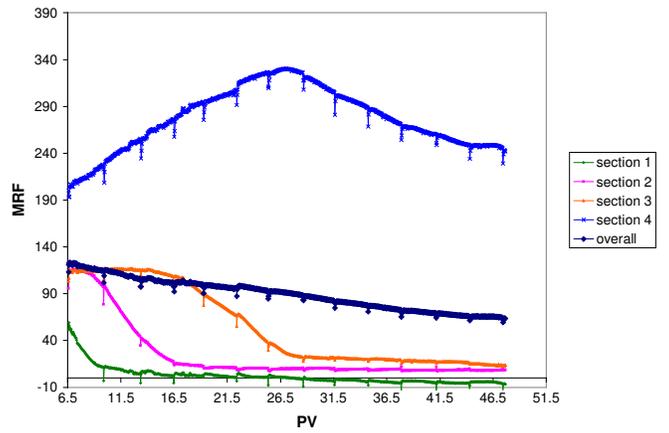


Fig. 4b—Foam washout for B20-5000 (at constant brine rate)

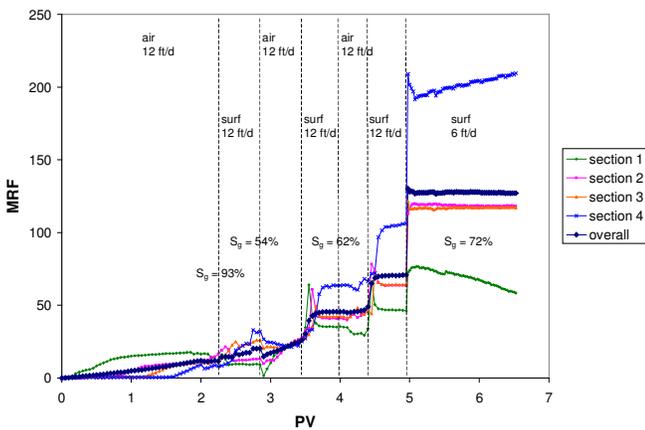


Fig. 4a—Foam generation with B20-5000 in 2-ft sand pack

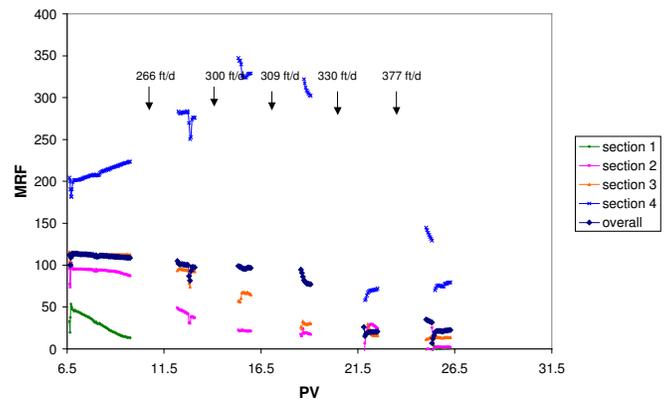


Fig. 4c—Foam washout of B20-5000 using high rate pump (in gaps)

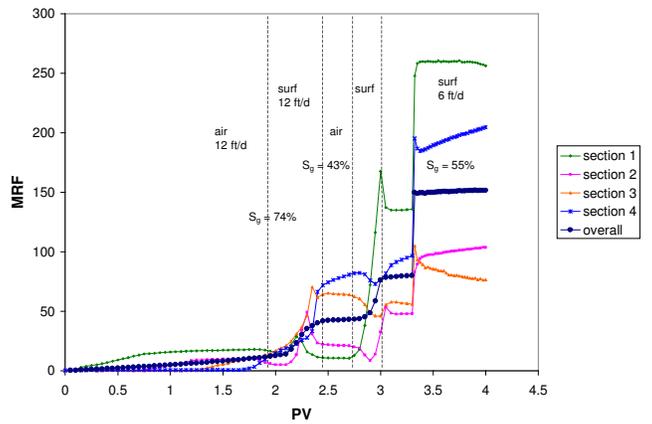


Fig. 5a—Foam generation with C<sub>16</sub>TAB

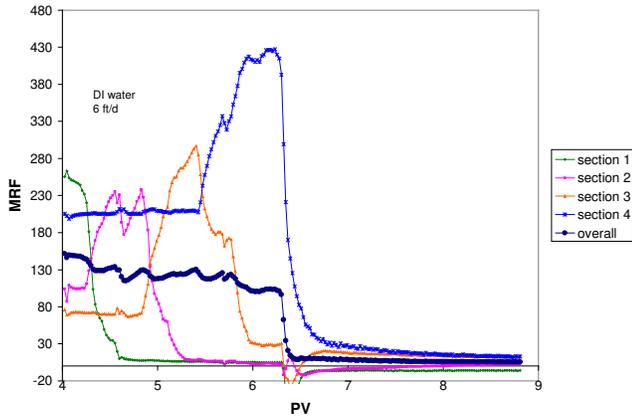


Fig. 5b–Foam washout for C<sub>16</sub>TAB with DI water

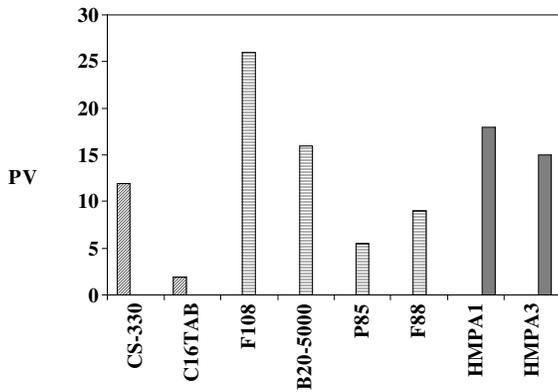


Fig. 6–Pore volumes for foam washout in 2-ft sand pack for conventional and polymeric surfactants

Surfactant concentrations: HMPA3 = 2%, rest = 0.5%, all in 5% NaCl (except C<sub>16</sub>TAB). HMPA1 & HMPA3 neutralized with dil. NaOH to pH ~7. HMPA1 and HMPA3 were relatively poor foamers compared to others.

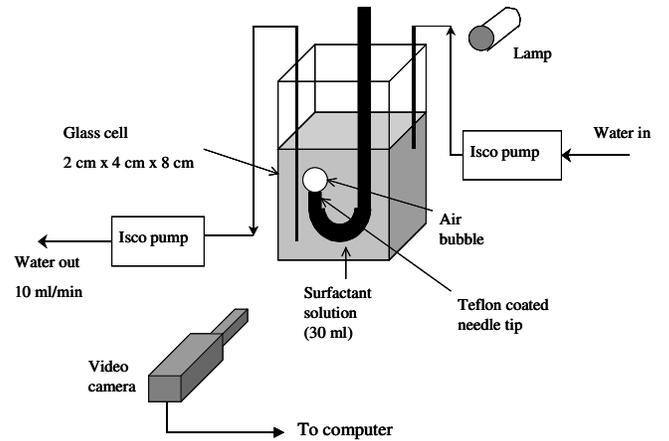


Fig. 7–Schematic of pendant bubble setup to measure surfactant desorption

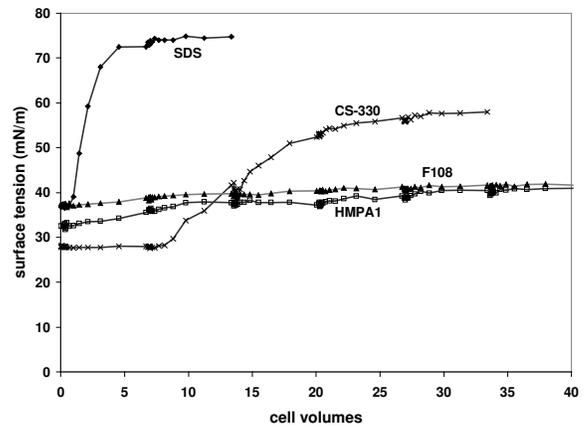


Fig. 8–Desorption of conventional and polymeric surfactants from air-water interface during washout

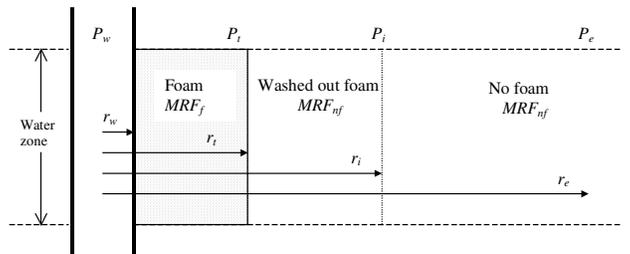


Fig. 9–Schematic of foam in water producing zone near production well

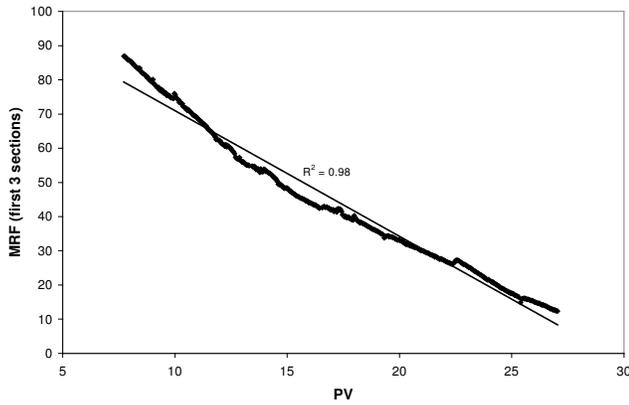


Fig. 10–Washout of foam from B20-5000 (data from fig 4b)

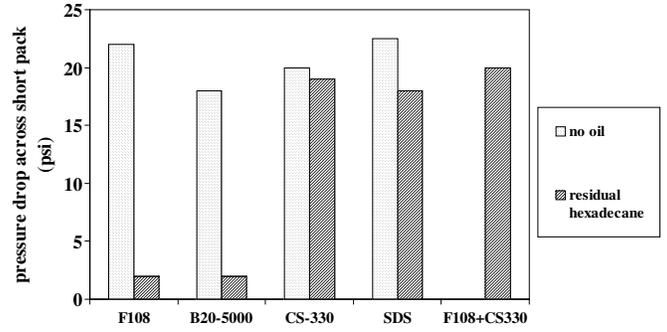


Fig. 13–Steady state pressure drops for foam flow in the short pack with and without residual oil

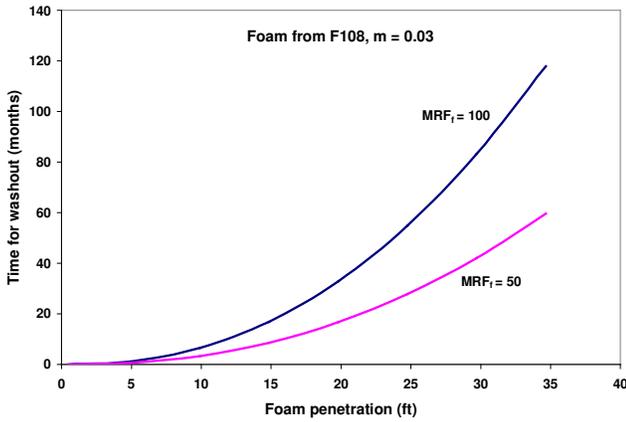


Fig. 11–Time for foam washout as a function of initial foam penetration distance

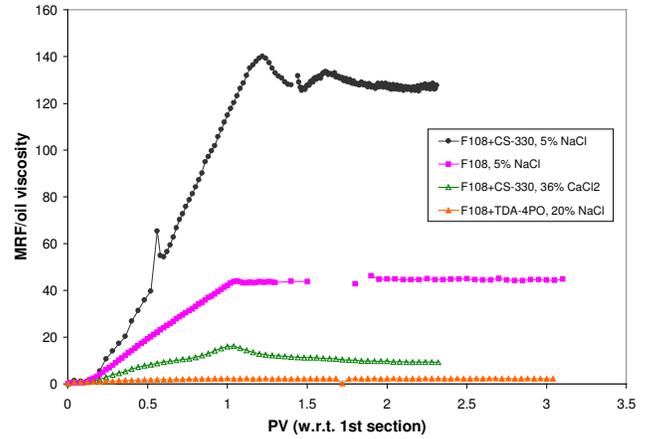


Fig. 14–Resistance to oil flow (MRF/oil viscosity) in 2-ft sand pack initially saturated with surfactant

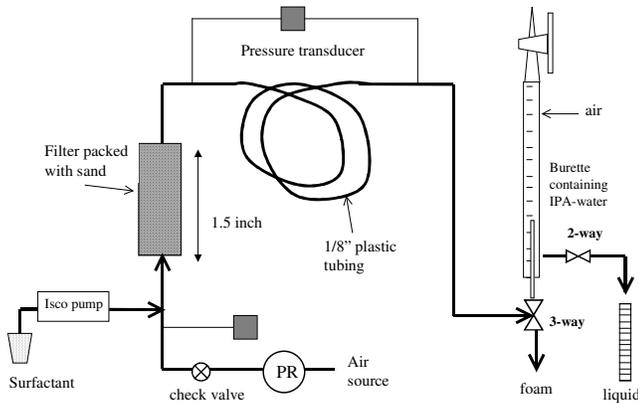


Fig. 12–Short sand pack arrangement used for testing foam stability to residual oil

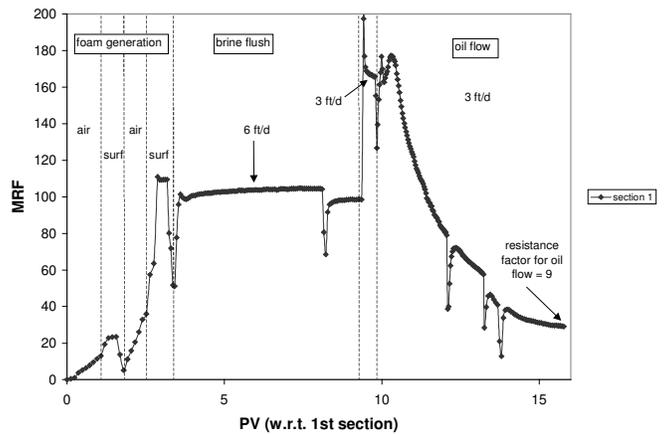


Fig. 15–Reduced emulsion formation for flowing oil after a foam process modification (oil flow following a brine flush in 2-ft sand pack)