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Developing Stable Foams from Polymeric Surfactants for Water Production Control

by

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ABSTRACT

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This research explores a new method using foams for water production control in an oilfield. Reducing water production during oil production is an important objective impacting the profitability of a mature oilfield. Currently practiced methods using gel or polymer based systems either offer inadequate water flow reduction or suffer problems of proper placement in the field.

Because of its properties, foam has the potential for use in water control. In this study, foams stable in presence of flowing water (washout stability) were developed using polymeric surfactants. A screening test was developed to measure the washout resistance of various conventional and polymeric surfactants. Foam from several polymeric surfactants such as triblock F108 and hydrophobically modified HMPA1 exhibited remarkable improvement in washout stability over conventional surfactants. Strong foam that offered a large resistance to flow of water was generated in a two-foot long sand pack with some of these polymeric surfactants. Again, the polymeric surfactants exhibited higher foam washout resistance than the conventional surfactants as predicted by the screening tests.
Investigation of surfactant desorption from an air-water interface using bubble shape analysis showed that this improved foam washout resistance was due to almost irreversible adsorption of polymeric surfactants. Collapse of foam from polymeric surfactants at long times in the screening test was determined to be due to hydrodynamic effects and not desorption. Also, foam washout stability with polymeric surfactants in sand pack was found to be limited by air dissolution into flowing water. Scale-up calculations for oilfield geometries showed that foam from F108 can be stable for a long enough time, even with gas dissolution, for the process to be practicable.

Foam stable to residual oil, expected in the water producing zones, was created by mixing an anionic surfactant CS-330 with nonionic F108. This is because ionic surfactants produce an electrostatic barrier that prevents entry of oil droplets into the air-water interface. Flowing oil, however, produced a stable emulsion with this surfactant combination which offered a large resistance to flow. This was undesirable and was minimized by a brine flush to remove surfactant from the aqueous phase of the foam region before contact with flowing oil.
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CHAPTER 1

INTRODUCTION

Reducing water production during oil production in a mature oilfield is an important objective for the oil industry. Produced water has a significant impact on the profitability of the field [Dalrymple et al., 1998; Eoff et al., 2001]. Producing water involves a waste of drive energy in pumping water rather than oil, in addition to loss of oil production. Also, water production leads to other problems such as sand production, corrosion of tubulars and surface equipment, need for more separator capacity, and disposal and handling concerns.

Current methods used to reduce water production involve using polymer or gel based systems that either block flow through certain zones completely or reduce permeability of water relative to oil. This study follows the latter approach and develops foams that can be used to reduce water production by reducing the relative permeability to water much more than to oil.

1.1 Current methods of controlling water production

The chemical systems used to reduce water production fall into two broad categories -

1) Sealing systems: These completely block the flow of fluids in the porous medium by filling in the pores. These are useful only when a water producing zone can be
mechanically or chemically isolated. However, in many situations, the water zone cannot be isolated and the sealing system then can penetrate zones that should not be treated [Eoff et al., 2001]. Also, it is very difficult to remove sealants from a porous matrix once they are in place because their resistance to extrusion is significant [Dalrymple et al., 1998]. Thus it is very risky to pump sealants without zonal isolation and proper placement techniques.

2) Relative permeability modifiers (RPM): The high cost of placement techniques and the risks involved in using a sealing system have focused research towards development of non-sealing relative permeability modifiers (RPMs). RPMs have physical/chemical properties that help reduce water flow from the treated areas of the water producing zones and yet they do not affect the flow of oil significantly. In other words, RPMs reduce the relative permeability to water but not to oil and hence the name.

Gels are often used as sealants. There are reports [Liang and Seright et al., 1995, 1997] that gels reduce the permeability to water more than to oil. However, Eoff et al. [2001] claim that the pressure required for the oil to break through the gel sealants may be so high that oil production after treatment is highly unlikely. Dalrymple et al. [1998] say that since these gels are water based, they achieve deeper penetration into the water regions of the zone leading to RPM-like behavior but that it is incorrect to refer to them as RPMs. However, in many papers gels have been referred to, along with other polymers, as RPMs.
Dilute solutions of water soluble polymers such as polyacrylamide (PAM) or hydrolyzed polyacrylamide (HPAM) have been commonly used as RPMs [Zaitoun et al., 1988, 1989]. At higher temperatures and salinities biopolymers (e.g., xanthan and scleroglucan) [Kohler and Zaitoun, 1991] and synthetic copolymers [Ranjbar et al., 1995] have been used. There are several theories in the literature on how the polymers and gels work in reducing relative permeability to water more than to oil, but none seem to be universally accepted [Zaitoun et al., 1998]. High molecular weight polymers are known to adsorb irreversibly on mineral surfaces and are believed to contribute to the relative permeability modification by the wall effect, wherein the polymer adsorption on pore walls induces three effects:
(a) steric effect - inhibits water flow by reducing effective pore sizes and hence permeability,
(b) lubrication effect - induced by the polymer layer covering the pore walls and makes the flow of oil layer easier,
(c) wettability effect – adsorption of hydrophilic polymer renders the oil-wet parts of the rock water-wet, thus improving oil mobility and reducing water mobility.

Generally, a reduction of water permeability ranging from a factor of about 2 to 50, but rarely above 10, has been reported in laboratory corefloods with these RPMs. The corresponding oil permeability reduction factor could be as high as 5. If they are placed in homogeneous zones producing both water and oil, they will tend to decrease both water and oil production as they adsorb on pore walls of both water and oil producing
regions. Hence, the main application of these RPMs is in layered, heterogeneous reservoirs.

1.2 Foam for controlling water production

A new approach is proposed to address the problem of water production via the relative permeability modification route. Instead of using adsorption of polymers, foam can be used to reduce relative permeability to water. Foam is a dispersion of a gas in liquid where the lamellae are stabilized by a surfactant. Foam can be either generated in-situ in the porous medium or injected after pre-generation. The water relative permeability reduction is achieved by trapping of the non-wetting gas phase in the pores of a porous medium, which reduces the water saturation in the pores. This reduces the water relative permeability as it is a function of the water saturation. In this study, foam has been observed to reduce the permeability to water by a factor of 100 or more in laboratory tests in sand packs. In addition, most aqueous foams have been observed to be destabilized in the presence of oil [Wasan et al., 1994; Schramm, 1994]. Hence foam should not significantly affect the oil permeability in the oil producing zones near the well.

Before foam can be used for water control application, it has to satisfy the following criteria: 1) Foam should be stable and last for a long time so that the well does not have to be treated frequently, 2) Foam should have tolerance for small amounts of oil that may be present in the water producing zones, and 3) Foam should collapse with
flowing oil in the oil zones without causing any other associated problems like emulsion formation.

Foams have been used in the oil industry for reducing mobility of steam and CO₂ during improved oil recovery processes. It has also been used in near-well applications like diversion and gas blocking to reduce gas-oil ratio [Schramm, 1994 b]. However, the foams used in these applications are unlikely to perform well in reducing water production. This is because foams stabilized by conventional low molecular weight surfactants have been observed to collapse easily in the presence of water, probably due to desorption of the surfactant from the air-water interface [Szafranski, 1997]. Hence this research focused on using suitable polymeric surfactants to generate foams since one may expect polymeric surfactants to produce foams stable to washout with water because of their stronger adsorption at air-water interface than conventional surfactants. This idea for using polymeric surfactants originates from the wide use of proteins to stabilize food emulsions and foams [Dickinson, 1987]. Some groups have also found stable foam films with polymeric surfactants (tri-block copolymers by the group of Sedev and Exerowa) or polymer-surfactant combinations [for example: Folmer and Kronberg, 2000; Goddard and Ananthapadmanabhan, 1993]. In this study, polymeric surfactants were tested for foam washout stability, in bulk as well as in porous media, and several promising candidates were identified. Thereafter, foam with tolerance to small amounts of oil - necessary for oilfield applications - was developed.
The following chapters give the details of development of foams suitable for water control in an oil producing well. The next chapter gives the background on relevant foam properties, especially in porous media. Chapter 3 describes the properties of the various polymeric surfactants studied in this research. A screening test was developed to test foam washout stability quickly outside of the porous medium. Chapter 4 describes this test and the results with several conventional and polymeric surfactants. Promising surfactants were then tested in a porous medium (sand pack). In chapter 5, the procedure developed to generate stable foam in the sand pack is described, and then the results of foam washout experiments in the sand pack are given. Chapter 6 examines desorption of conventional and polymeric surfactants from an air-water interface and the role it plays in foam washout stability. Then foam stability to oil is described in chapter 7. The chapter describes the development of foam stable to residual oil in the sand pack and the steps taken to minimize emulsification in the sand pack with flowing oil. Scale-up of foam washout time to oil field conditions is also described. Chapter 8 summarizes the findings of this study and gives recommendations for future work.
CHAPTER 2
FOAM BACKGROUND

This chapter serves as an introductory background on foam, especially foam in porous media. The following sections describe the mode of foam flow in porous media, mechanisms of foam generation and collapse, and effect of oil on foam stability. But first the bulk foam (defined below) structure is described, which will introduce terminology that is used in later sections and chapters.

Foam is a dispersion of gas in liquid. Bikermann [1973] describes foam as an "agglomeration of gas bubbles separated from each other by thin liquid films". The films are stabilized by surfactants adsorbed at the gas-liquid interface and are generally very thin (order of 10-100 nanometers). However a distinction must be made between bulk foam and foam in porous media. According to Rossen [1996] - a foam 'in bulk' is a foam in a container much larger than individual bubbles. Falls et al. [1988] defined foam in porous media as a dispersion of gas in liquid such that the liquid phase is interconnected and at least some of the gas flow paths are blocked by lamellae. In a porous medium the size of the pores is comparable to or smaller than the diameter of an individual bubble. Therefore, foam cannot be treated as a homogeneous phase. Interaction between the solid walls and the liquid films is very important.
2.1 Bulk foam structure

The structure of a typical foam formed in a vessel, say by shaking a surfactant solution, is described here [Garrett, 1993; Kornev et al., 1999]. The foam structure is bounded on the bottom by the bulk liquid phase and on the top by gas phase. In the lower part of the foam, the bubbles are spherical and of small size with relatively low gas volume fraction (also called wet foam or kugelschaum). As the liquid drains out of the foam, the bubbles distort to form polyhedral structures. The gas fraction here is relatively high (dry foam or polyederschaum) and the density low. The polyhedra first form at the top of the foam column. When the foam becomes very dry and polyhedral, the structure begins to look like the schematic in fig 2.1.

![Diagram of foam structure](image)

**Fig 2.1: Bulk foam structure [From Schramm and Wassmuth, 1994]**

A two-dimensional slice of a bulk foam system is shown in fig 2.1. Within the magnified region, the various parts of the foam structure are clarified. The gas phase is separated from the thin liquid film by an interface. A lamella is defined as the region that encompasses the thin film, the two interfaces on the either sides and part of the junction
to the other lamellae [Schramm & Wassmuth, 1994]. The connection of three lamellae, at
an angle of 120°, is referred to as the Plateau border. The Plateau border extends
perpendicularly out of the page. In three dimensions, four Plateau borders meet at a point
at the tetrahedral angle (~ 109°).

Throughout the foam there are differences in the sizes of adjacent bubbles. Thus
the differences in capillary pressure between adjacent bubbles (given by Young-Laplace
equation, see section 2.3.2) will cause gas diffusion from the small to the large bubbles.
Also, if there is free space above the foam column the upper surface will consist of films
of curved section. This will mean diffusion of gas out of the upper layers of bubbles
because of the capillary pressure implied by the curved top surface.

As the films at the top of the foam column thin, they become more susceptible to
rupture by mechanical shock or vibration. In some foams, the rupture of films at a certain
thickness is spontaneous. The films at the top of the column tend to break first and the
foam collapses from the top downwards.

2.2 Foam flow in porous media

As described earlier, foam in porous media is a dispersion of gas in liquid where
the liquid is continuous and at least some of the gas is made discontinuous by thin liquid
films called lamellae. The lamellae are stabilized by surfactant molecules adsorbed at the
air-water interface. Flowing foam is not a separate phase by itself, but consists of separate
flows of gas and liquid. Fig 2.2 shows a schematic picture on the mechanisms of foam flow in porous media. Some of the gas is flowing either as a continuous or discontinuous phase, while the rest is trapped. The increase in trapped gas saturation is crucial to the behavior of foam flow as it results in the blockage of gas pathways, hence reducing the effective permeability of gas. The amount of gas trapped during a foam flood has been observed to be as high as 80% to almost 100% [Radke and Gillis, 1990]. Bernard and Holm [1964] found that the trapped gas saturation depends on surfactant concentration but is independent of permeability. Kovszcek and Radke [1994] found no consistent trend of trapped gas saturation with gas or liquid velocity in the literature.

Fig 2.2: Pore level schematic of foam in porous media [From Tanzil, 2001]
Weak foams – defined as foams that cause only small reduction in mobility – consist of a small fraction of gas that is trapped while the rest flows in continuous gas paths. For strong foams, that is, foams causing a large reduction in mobility, the flowing gas is also discontinuous because of the lamellae. Consequently, the gas bubbles flow in the so-called bubble trains, as shown in the central portion of fig 2.2. Flow of the bubble trains faces much higher resistance compared to regular gas flow and hence, the discontinuous foam has a much higher effective viscosity compared to regular gas. The higher apparent viscosity is due to the following contributions [Hirasaki and Lawson, 1985]- that resulting from slugs of liquid between bubbles, the resistance to deforming the bubble interface, and the surface tension gradients along the bubble surface. It is the combined effect of the reduction of gas permeability and the increase in apparent gas viscosity that gives rise to the gas mobility-reduction effect of foam.

While foam lowers gas mobility partly by lowering its effective permeability, the effective permeability of water or the wetting liquid for a given saturation remains unchanged from its permeability in regular multiphase flow. This is because the wetting liquid occupies essentially the same pore spaces as in the absence of foam [Bernard et al., 1965]. Only a very small amount of liquid flows in the foam lamellae, so that the wetting-liquid relative permeability curve is not altered. Thus, the reduction in relative permeability to water due to foam is only because of the decreased saturation of water arising from trapped gas occupying the pore space.
Trapped gas and bubble trains exist only in a time-averaged sense. Once the lamellae are mobilized, none of the discontinuous gas is always trapped or always moving. Bubbles may switch to flowing or blocking a channel because of changes in the flow path [Kovscek and Radke, 1994]. In addition, increasing the pressure gradient opens up new flow channels that were originally filled with trapped gas, creating new bubble trains. Therefore, foam is non-Newtonian and shear thinning [Kornev et al., 1999]. Several investigators [e.g. Hirasaki and Lawson, 1985; Falls and Ratulowski, 1989] have experimentally confirmed the shear-thinning nature of foam.

2.3 Foam generation and collapse in porous media

Foam texture in porous media is determined by foam formation and decay [Kovscek and Radke, 1994]. Researchers have identified three mechanisms for foam generation: (1) leave behind, (2) capillary snap-off, and (3) lamella division. Foam destruction occurs through two mechanisms: (1) film rupture due to capillary suction, and (2) gas diffusion through the lamellae.

2.3.1 Foam generation

2.3.1.1 Leave-behind

When two gas fingers enter adjacent liquid filled pores [Kovscek and Radke, 1994], a lamella is left behind (fig 2.3). The left-behind lamella will be stable as long as
the capillary pressure is not too high and the pressure gradient is not too large. The left-behind lamella is oriented parallel to the direction of flow and does not make the gas discontinuous. Therefore, the leave-behind mechanism results only in a weak foam.

![Diagram of foam formation by leave-behind process](image)

(a) Gas fingers entering adjacent pores  
(b) Left-behind lamella

**Fig 2.3: Foam formation by leave-behind process [From Tanzil, 2001]**

2.3.1.2 Capillary snap-off

Snap-off was first identified by Roof [1970] to explain the origin of residual oil. Fig 2.4 shows a gas finger invading a pore constriction initially filled with the wetting phase. As the bubble front enters the downstream pore body (flow is from left to right in the figure), the local capillary pressure at the bubble front falls with the expansion of the interface. When the capillary pressure at the bubble front ($P_{cf}$) falls below that at the throat ($P_{ct}$), the liquid will flow into the pore throat where it will accumulate and form a collar. Under certain conditions, the collar will grow till snap-off occurs (as in fig 2.4(b))
and a lens is formed. This will occur when the radius of curvature of the downstream bubble front is at least twice the inscribed radius at the pore throat and provided that the constriction is not too sharp. Lamellae will be created downstream where the newly formed bubbles collide with the previously created bubbles.

![Diagram](image)

**Fig 2.4: Schematic of the snap-off process [From Tanzil, 2001]**

(a) Gas bubble entering a water filled pore
(b) Water lens formed by snap-off when $P_{GF} < P_{CT}$

Snap-off depends on several parameters such as capillary pressure (hence saturation), pore geometry, and wettability of the porous medium. Snap-off is a mechanical process; therefore it occurs independent of surfactant presence. The surfactant, however, plays an important role in stabilizing the lamellae formed.

An interesting phenomenon observed during foam generation experiments of this study (see appendix A and chapter 5) was that of foam generation by snap-off at the
outflow end of a porous medium. A capillary end effect arises because the porous medium retains water near the outflow end in order to maintain continuity in capillary pressure across the outlet where the capillary pressure is zero or near zero. Snap-off occurs because the capillary pressure, in order to satisfy the capillary pressure continuity, drops below the critical capillary pressure for snap-off near the exit. Tanzil et al. [2000] demonstrated that foam generation by snap-off takes place when foam flows from low permeability sand to high permeability sand with sufficient permeability contrast. Similarly, snap-off is also exhibited near the exit of a sand pack due to the permeability contrast and will lead to stronger foam generation near the outlet.

2.3.1.3 Lamella division

Another mechanism of foam generation is by lamella division (fig 2.5). Division occurs after some foam lamellae have been generated and the pressure gradient becomes large enough to mobilize the lamellae. When a moving lamella train encounters a branch in the flow path, it may split into two, one in each branch of the path. Lamella division depends on the pore geometry and bubble size. When the bubble size is smaller than the pore sizes, lamella division does not occur. Moreover, if the flowing lamella train is surrounded by stationary lamellae, i.e. when there is only a single isolated lamella train, then there will be no branching and thus no division. Lamella division depends on pressure gradient and is proportional to gas velocity [Falls et al., 1988]. Like snap-off, lamella division can result in the generation of fine discontinuous-gas foam, or strong foam.
According to Tanzil et al. [2002] strong foam generation takes place only when one or a few lamellae are mobilized which then leads to their division. They explain their strong foam generation results in terms of a normalized pressure drop defined as follows

\[ N_{\Delta p} = \frac{\Delta p}{\gamma / \sqrt{k / \phi}} \]

where, \( \Delta p \) is the differential pressure, \( \gamma \) is the surface tension of surfactant, \( k \) is the permeability of the porous medium, \( \phi \) is the porosity. They assert that to mobilize a single lamella this pressure drop must exceed a critical value \( N^*_{\Delta p} \). Thus, \( N_{\Delta p} > N^*_{\Delta p} \sim 1 \) is a necessary, but not sufficient condition, for lamella mobilization and hence strong foam generation. Tanzil [2002, 2001] observed strong foam generation in a homogeneous sand pack whenever \( N_{\Delta p} \) exceeded \( \sim 2 \) over a foot-long column.
Among the three foam generation mechanisms, only snap-off and lamella division can result in large reduction in gas mobility, or strong foam. Kovscek and Radke [1994] asserted that snap-off is the dominant mechanism especially when water saturation is sufficiently high such as during gas and surfactant co-injection. Even when more lamellae are generated by leave-behind than snap-off, only the snap-off lamellae make the gas discontinuous and determine the foam strength. Lamella division is likely to be important under high velocity or high pressure-gradient.

2.3.2 Foam decay

Gas diffuses from bubbles with larger curvatures to bubbles with smaller curvatures because of the pressure difference according to the Young-Laplace equation –

\[ P_g - P_l = -2H\gamma \]

where, \( P_i \) is the pressure in the \( i \) phase (\( g = \text{gas} \); \( l = \text{liquid} \)), \( H \) is the mean curvature of the interface, and \( \gamma \) is the interfacial tension. Because of this, bulk foams coarsen with the large bubbles growing at the expense of small bubbles which eventually disappear. However, the curvature of foam in porous media is governed by the pore dimension and lamellae location in the pore space, not by bubble size. Foam disappearance by gas diffusion takes place only when two lamellae happen to reach the same pore throat. Therefore, gas diffusion is relatively unimportant for foam in porous media.

The more important destruction mechanism for foam in porous media is coalescence by capillary suction. The existence and destruction of the lamellae are
governed by the combined effect of repulsive and attractive forces within a lamella represented by the disjoining pressure ($\Pi$) isotherm (fig 2.6) [Chambers and Radke, 1990]. The disjoining pressure can be defined as the additional pressure that a film exerts on the gas and liquid phases as the film is thinned [Hirasaki, 1991]. When this pressure is positive, it tends to disjoin the two interfaces and when it is negative, it tends to contract the film. The disjoining pressure is significant only when the film is sufficiently thin. In the absence of surfactant, the attractive van der Waals forces are dominant, resulting in negative disjoining pressure and collapse of the thin film. The lamella is stabilized by surfactant adsorption at the gas-liquid interface. The electrical double-layer produced by adsorption of ionic surfactants is responsible for the repulsive forces that stabilize the thin film. The magnitude of the stabilizing forces depends on the surfactant concentration, surfactant structure, and the ionic content of the aqueous solution [Kovscek and Radke, 1994]. Fig 2.6 shows a typical disjoining pressure isotherm where the van der Waals forces and the electrical forces are in play. The isotherm will be somewhat modified from this particular shape at concentrations in far excess of CMC (critical micelle concentration) of the surfactant or in the case of adsorbed polymers on the air-water interfaces which lead to steric effects.

At concentrations in excess of the CMC, more undulations may be observed in the curve with the distance between two adjacent peaks of the order of the micellar size [Wasan et al., 1994]. Steric interactions between surfaces can be important when a polymer is adsorbed at the interface. The forces are usually repulsive due to the overlapping of chains from each surface. Some attractive forces can also arise if the
solvent is poor or if bridging of the opposite surfaces occur due to the polymer [Miller and Neogi, 1985]. Also, the steric forces arising from the polymer brush interactions are of longer range compared to the van der Waals or the electrostatic forces. Irrespective of the exact shape of the isotherm as in the above-mentioned cases, the following discussion is still applicable.

For a static film in equilibrium, the disjoining pressure is equal to the capillary pressure. Consider a thin film of some thickness $h$ (see fig 2.6). During gas injection, wetting-liquid saturation decreases and the capillary pressure increases. The increase in capillary pressure causes the film thickness to decrease. The film thins until it reaches the critical film thickness $h_{cr}$ that corresponds to the maximum disjoining pressure, $\Pi_{\text{max}}$. 
When the capillary pressure exceeds $\Pi_{\text{max}}$, the static film ruptures because the film is unstable in the region where $d\Pi/dh$ is positive [Chambers and Radke, 1990].

The collapse of flowing lamellae is more complicated [Singh et al., 1997]. A moving thin film undergoes squeezing and stretching as it travels through the pore throats and pore bodies (fig 2.7). This causes film thickness to oscillate about the equilibrium film thickness established for the static film. A thin film with mobile surface would rupture during stretching if its thickness falls below the critical film thickness $h_{cr}$. Therefore, a moving thin film could rupture at a limiting capillary pressure that is less than the maximum disjoining pressure $\Pi_{\text{max}}$. In other words, moving lamellae are even less stable than static ones.

![Fig 2.7: A mobile foam lamella passing through a periodically constricted tube](image)

Coalescence occurs at $t_3$. From Kowseck and Radke [1994]

The lamella stability also depends on the film restoration process. The Marangoni effect helps the restoration process. Lamella stretching causes a reduction in surfactant concentration and an increase in the local surface tension. The surface tension gradient
produced works against the thinning. Surface flow from the low surface tension area at the plateau border to the high-tension regime drags liquid along with it and helps to restore the film thickness. Surfactant formulation is therefore a very important factor in foam stability. It stabilizes the lamella through both the disjoining pressure and the Marangoni effect.

2.4 Foam-oil interactions

For foam applications in the petroleum industry, as in this study, the effect of oil on foam stability is very important. The volume fraction of oil present has been observed to be important for the bulk foam stability [Wasan et al., 1994]. In a porous medium, the magnitude of residual oil saturation has also been observed to be a significant factor for the success of full-scale steam-foam process [from Schramm, 1994]. This section discusses some of the important issues regarding foam stability in presence of oil. More detailed discussions on foam sensitivity to oil in porous media and on antifoam action of oil can be found in a review articles by Schramm [1994] and Garrett [1993] respectively.

According to Schramm, some possibilities for the mechanisms of foam destabilization by an oil phase include:

- Foam forming surfactant may be absorbed or adsorbed by the oil, causing depletion in the aqueous phase.
- Surfactants from the oil may be adsorbed by the foam lamellae and destabilize a stable film.
• Components from oil may be adsorbed by the porous medium altering the wettability of the solid phase and this alteration makes it more difficult for foam to be generated.

• The oil may spread spontaneously on foam lamellae and displace the foam stabilizing interface.

• The oil may emulsify spontaneously and allow drops to breach and rupture the stabilizing interface.

The last two mechanisms of foam destabilization are more relevant to this study and can be described in terms of the spreading and entering coefficients and the stability of the pseudo-emulsion film.

2.4.1 Entering, spreading and bridging coefficients

The various configurations that an oil droplet can adopt in foam as described by Wasan et al. [1994] are depicted in fig 2.8. For an oil droplet to emerge into the air-water surface as in fig 2.8 (c) the entering coefficient (E) must be positive. The entering coefficient is defined as-

\[ E = \gamma_{a-w} + \gamma_{o-w} - \gamma_{o-a} \]

where,

\( \gamma \) is the interfacial tension and the subscripts refer to the air-water (a-w), oil-water (o-w) and oil-air (o-a) interfaces respectively. A positive entering coefficient corresponds to a favorable free energy change. If the oil is to spread at the surface of the foaming
liquid (fig 2.8 (d)), then the spreading coefficient (S) must also be positive. The spreading coefficient is defined as-

\[ S = \gamma_{a-w} - \gamma_{o-w} - \gamma_{o-a} \]

---

**a.**

**b.**

**c.**

**d.**

**Fig 2.8: Oil configurations at air-water interface (adapted from Wasan et al., 1994)**

- a. oil drop inside the solution
- b. oil drop separated by pseudoemulsion film from the gas phase
- c. oil lens
- d. spread oil layer at the solution surface

According to Garrett [1993], Robinson and Woods [1948] observed that whenever \( E < 0 \), no antifoam effect was observed. This is a clear evidence that a positive value of the entering coefficient is a necessary for antifoam action. Ross [1950], however,
postulated that oil breaks the foam film by spreading on both sides of the foam film, thereby driving out the original film liquid and leaving an oil film that is unstable. Thus Ross claims that foam rupture requires $S > 0$ and $E > 0$. However, several examples have been observed in which antifoam behavior is seen even when $E > 0$ but $S < 0$. Thus, $S > 0$ does not seem a necessary condition for foam destabilization by oil.

According to Garrett, antifoam action of oils spreading at the air-water interface can occur via two mechanisms. One is when the spreading oil eliminates surface elasticity, i.e. produces a surface which has a constant surface tension when subjected to expansion. The other mechanism involves the spreading droplet dragging the underlying liquid due to shear and will lead to film thinning and rupture.

In the absence of spreading, the mechanism by which rupture of a foam film can occur with oil is by bridging. Garrett [1993] has shown that if an oil lens (fig 2.8 (c)) bridges a foam film by entering into both air-water surfaces then no configuration of stability is available to the lens if the angle formed by tangents to the air-water and oil-water surfaces is $> 90^\circ$. This condition expressed in terms of the bridging coefficient ($B$) leads to the following criterion:

$$B = \gamma_{a-w}^2 + \gamma_{o-w}^2 - \gamma_{o-a}^2 > 0$$

When the above condition is satisfied, the capillary forces cause enhanced drainage in the aqueous film away from the oil lens. Since, in general, $\gamma_{o-w} << \gamma_{o-a}$ and $\gamma_{a-w}$, essentially all that is required for $B > 0$ is that the oil-air surface tension be less than the air-water surface tension.
2.4.2 Importance of the pseudo-emulsion film

The above theories based on the spreading and entering coefficients have been tested widely by several researchers. The classical spreading-entering theories (i.e. foam destabilized if $E$ or $S > 0$ and stable if $E < 0$), however, have not always been able to predict experimental observations of foam stability. In foam flooding for enhanced oil recovery, Schramm and Novosad [1990], and Manlowe and Radke [1990] did not find a correlation between $E$, $S$, and the effect of oil on foam stability. This highlights the importance of the pseudo-emulsion film stability (fig 2.8 (b)). The spreading and entering theories do not take into account the role of the pseudo-emulsion film as an intermediate metastable state. Thus if this film is stable, it provides an energy barrier that prevents the entry of an oil droplet, even if the spreading and entering coefficients are positive.
CHAPTER 3

CONVENTIONAL AND POLYMERIC SURFACTANTS

This chapter lists and describes the structures and relevant properties of the various surfactants (especially polymeric surfactants) used in this study – both for the screening tests and sand pack experiments described in the following chapters. The surfactants studied can be broadly put into two categories – (1) conventional surfactants: these are low molecular weight (< 500 daltons) surfactants commonly used in foaming and other applications commercially and in research laboratories and (2) polymeric surfactants: these are much higher molecular weight (> 3500 daltons) molecules which show some surface activity.

3.1 Conventional surfactants

The various low molecular weight surfactants used are listed in table 3.1 along with their active components. The table includes a mix of non-ionic (C_{12}E_{8}, Foamer1), cationic(C_{16}TAB), and anionic surfactants. SDS, C_{16}TAB and C_{12}E_{8} are relatively pure laboratory reagents. The rest are commercially available surfactants and are expected to contain other unknown surface active impurities (also see Chapter 6). Foamer1, Foamer2 and Foamer3 were supplied by Halliburton and are commercial foamers used in oilfield applications. The rest were obtained as follows - SDS from Aldrich, CS-330 from Stepan, AOS 16/18 from Shell Chemicals, C_{16}TAB from TCI and MA-80I from Cytec. MA-80I had been used previously in this laboratory [Szafranski, 1997; Tanzil, 2001] for aquifer
remediation work and hence it was used extensively for the initial foam tests in the sand pack.

<table>
<thead>
<tr>
<th>Surfactant</th>
<th>Active components</th>
</tr>
</thead>
<tbody>
<tr>
<td>SDS</td>
<td>Sodium dodecyl sulfate (98%) ([\text{CH}_3(\text{CH}<em>2)</em>{11}-\text{OSO}_3\text{Na}])</td>
</tr>
<tr>
<td>C(_{12})E(_8)</td>
<td>n-Dodecyl octa-oxyethylene ether ([\text{CH}_3(\text{CH}<em>2)</em>{11}-(\text{EO})_8])</td>
</tr>
<tr>
<td>C(_{16})TAB</td>
<td>n-Hexadecyltrimethylammonium bromide ([\text{CH}_3(\text{CH}<em>2)</em>{15}-\text{N}(\text{CH}_3)_2\text{Br}])</td>
</tr>
<tr>
<td>CS-330</td>
<td>Sodium laureth sulfate ([\text{CH}_3(\text{CH}<em>2)</em>{11}(\text{OCH}_2\text{CH}_2)_3-\text{OSO}_3\text{Na}])</td>
</tr>
<tr>
<td>AOS 16/18</td>
<td>(\text{C}_{16-18}) alpha olefin sulfonate</td>
</tr>
<tr>
<td>Foamer1</td>
<td>Alkyl polyoxyethylene ether</td>
</tr>
<tr>
<td>Foamer2</td>
<td>Alpha olefin sulfonate + ethylene glycol monobutyl ether</td>
</tr>
<tr>
<td>Foamer3</td>
<td>Alkyl ether sulfate + ethylene glycol monobutyl ether</td>
</tr>
<tr>
<td>MA-80I</td>
<td>Sodium dihexylsulfosuccinate ([((\text{CH}_2\text{COOCH(\text{CH}_3)CH}_2\text{CH(\text{CH}_3)CH}_3)_2 -\text{SO}_3\text{Na}])</td>
</tr>
</tbody>
</table>

**Table 3.1: Conventional surfactants studied**

3.2 Polymeric surfactants

The emphasis of this study is on using polymeric surfactants for stabilizing foam to washout with water. The idea of using polymeric surfactants for stabilizing foams originates from the use of proteins in food emulsions and foams [Dickinson, 1987 & 1993]. Proteins are known to adsorb spontaneously at a variety of solid and liquid interfaces. Proteins at interfaces give rise to very stable emulsions & foams with stabilities often far in excess of surfactant foams [Clark et al., 1987]. A major driving force for adsorption of proteins is the entropic change due to displacement of ordered water molecules from near a hydrophobic surface. Due to proteins’ strong affinity for
hydrophobic surfaces and their unfolding at the interface (denaturation), they normally
cannot be desorbed by diluting with water. This type of behavior may also be
countered by synthetic polymers which are surface active. A molecule with a long
hydrophobe would be difficult to desorb (i.e., require more energy for desorption) from
an air-water interface and even more so if there are multiple adsorbing groups on a single
molecule. Various synthetic polymers which show sufficient surface activity to form
foams were investigated in this study.

Combinations of surfactant and polymer have been studied widely for some time
because of the applications of such systems in rheology control, gels, solubilization,
controlled drug delivery and surface conditioning among others [Goddard and
Ananthapadmanabhan, 1993]. Associative interactions in several polymer-surfactant
systems have shown synergistic lowering of air-water tension and hence these
combinations can be considered equivalent to polymeric surfactants. Foam stabilization
has been observed on addition of a polymer to surfactant in, among others, SDS (Sodium
dodecylsulfate)-PEO (poly ethyleneoxide) [Lionti-Addad and di Meglio, 1992], SDS-
PVP (poly vinylpyrrolidone) [Folmer and Kronberg, 2000] and C12TAB
(dodecyltrimethylammonium bromide)-PAMPS (copolymer of acrylamide and
acrylamidomethyl propanesulfonate) [Bhattacharyya et al., 2000] systems. In all these
systems the stabilization arose from the interaction between the surfactant and polymer.
Unlike proteins, the polymer itself is not very surface active in these combinations but
goes to the interface mainly due to the interaction with the surfactant. Increased foam
stability in sand packs has also been observed by Sydansk [1993 a & b] on addition of
partially hydrolyzed polyacrylamide (HPA) to C_{14-16} alpha olefin sulfonate (AOS), both in the presence and absence of crude oil. However, it appears that the foam stabilization was due to the increased viscosity of the foaming solution by the polymer, as PHPA and AOS, both being negatively charged, are not expected to show any significant synergistic interaction. In any case, however, one must note that in all the above combinations stabilization refers to the ‘intrinsic’ stabilization of either foam columns or foam films, which does not necessarily mean higher washout stability. But it still gives a starting point for the search of polymer-surfactant combinations. However, Folmer and Kronberg [2000] show that for the SDS-PVP system, the polymer is present at the air-water interface only at low surfactant concentrations. On increasing the surfactant concentration, the polymer desorbs from the interface and goes into the bulk solution where it forms a complex with the surfactant. Similar behavior can be expected for other systems of charged surfactant and uncharged polymer as they show similar surface tension curves as that of the SDS-PVP system. This might be expected to be detrimental for foam stabilization. In addition, there is also a likelihood of the surfactant washing out from surfactant-polymer systems and hence reducing the washout stability of foams as the polymer itself is not very surface active. Because of these reasons it was decided to use a single polymeric surfactant molecule, rather than combinations of surfactant and polymer, for studying foam washout stability.

Later on, some surfactant was added to a polymer (ethylene oxide-propylene oxide copolymer F108 in chapter 7) for other reasons. But in that case the polymer itself was surface active unlike in above combinations. Associative interactions between the
EO-PO copolymers and surfactants such as SDS or C₁₆TAB have also been observed by various researchers (Jansson et al. [2004], Hecht and Hoffmann [1994]). Hecht and Hoffmann [1994] observed somewhat similar surface tension behavior with F127 (EO₉₉-PO₆₉-EO₉₉) - SDS system as with PVP-SDS combination. But in this case, when the conventional surfactant washes out, the polymer can still adsorb at the air-water interface and provide washout resistance.

The following two sections describe two types of polymeric surfactants that were studied – the block copolymers and the hydrophobically-modified polymers.

3.2.1 Block copolymers

One class of polymeric surfactant(s) studied for its effect on foam washout stability was that of the block copolymers. These are a class of polymers of considerable interest in recent years for a wide variety of applications like detergency, dispersion stabilization, foaming, emulsification, lubrication, cosmetic products, ink formulation, drug solubilization and delivery, bioprocessing and separations [Nace, 1996 a; Alexandridis and Lindman, 2000]. Variations of molecular characteristics like the molecular weight, geometry (diblock, triblock or random) and the EO to PO or BO ratio during synthesis can lead to molecules with optimum properties for a particular application. Here EO stands for ethylene oxide group, PO for propylene oxide and BO for butylene oxide. Two structures of tri-block copolymers were considered in this study – EOₘ-POₙ-EOₘ and EOₘ-BOₙ-EOₘ polymers. Tri-block non-ionic macromolecular
surface active agents are available commercially under various names like Pluronics, Poloxamers or Synperonics.

3.2.1.1 Surface properties of EO-PO copolymers

The surface tension versus concentration curve for several tri-block EO-PO-EO copolymers shows two breaks in the curve, unlike that for pure surfactants which shows a single break at the CMC. The first break usually occurs around 0.001 w% and a surface tension of 40-50 mN/m. The second break is usually at surface tensions of 35-40 mN/m. Some researchers [Wanka et al., 1994; Hecht and Hoffmann, 1994] have attributed this to polydispersity of the copolymer and to presence of impurities. However, Alexandridis et al. [1994 a] argued against this explanation and offered another explanation. They hypothesized that after the first break in the surface tension-concentration curve, a change in the configuration of the copolymer layer occurs and that the layer becomes more compact by expelling water and EO segments protrude more into the aqueous solution. This allows more molecules to fit on the surface and surface tension continues to decrease, though at a slower rate, till CMC (second break) is reached.

Surface coverage: Alexandridis et al. [1994 a] also observed that the area per molecule at surface increases with number of EO units and shows a similar scaling relationship (exponent ~ 0.5) with the number of EO units as non-ionic [(octylphenoxy)-ethoxy] ethanol surfactants. In addition, they observed that an increase in PO units results in a decrease in area per molecule at the surface. Also, at complete surface coverage, an
increase in temperature results in decreased area per molecule either due to decreased hydration of EO groups or increased hydrophobicity of the PO groups or both.

**CMC:** The CMC of triblock EO-PO-EO copolymers decreases exponentially with the number of PO units [Alexandridis et al., 1994 b; Wanka et al., 1994]. An increase in EO units increases the CMC. However, the influence of number of EO units on CMC is less pronounced than PO units. For a constant PO to EO ratio, the CMC decreases with total molecular weight of the copolymer surfactants. An important property of the triblock copolymers is that the self-assembly is very strongly influenced by temperature, much more than for conventional non-ionic surfactants. A 10 °C change in temperature can change the CMC of the triblocks by a factor of 10 to 100, whereas Chu and Zhou [1996] observed that for non-ionic surfactants C_{10}(EO)_{8} and C_{14}(EO)_{8}, the change in CMC is less than 50% for a 25 °C temperature change.

The four EO-PO copolymer structures used in this study are summarized in table 3.2. These EO-PO-EO copolymers were obtained from BASF (known by the name Pluronics).

<table>
<thead>
<tr>
<th>Product name</th>
<th>Average molecular weight</th>
<th>% EO</th>
<th>Average molecular formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>F108</td>
<td>14,600</td>
<td>80</td>
<td>EO_{132}-PO_{56}-EO_{132}</td>
</tr>
<tr>
<td>F88</td>
<td>11,400</td>
<td>80</td>
<td>EO_{103}-PO_{39}-EO_{103}</td>
</tr>
<tr>
<td>F68</td>
<td>8,400</td>
<td>80</td>
<td>EO_{76}-PO_{30}-EO_{76}</td>
</tr>
<tr>
<td>P85</td>
<td>4,600</td>
<td>50</td>
<td>EO_{26}-PO_{39}-EO_{26}</td>
</tr>
</tbody>
</table>
According to both Nace [1996 a] and the BASF literature, in general, the higher EO content polymers are supposed to be better foamers. Hence all but one of the polymers chosen have 80% EO content but have varying molecular weight. These molecules belong to the category designated as foamers by BASF among the Pluronics. Some of the relevant properties for the four molecules studied in this thesis are summarized in table 3.3. There is a lot of discrepancy in the literature on the surface properties like CMC reported by different groups. This is believed to be due to variety of reasons such as polydispersity, variations in different batches (from same or different sources) and lack of proper temperature control (as these properties are very sensitive to temperature). The properties reported in the following table are mainly from the group of Alexandridis et al. as some of the properties measured in the lab by Meier [2001] match those reported by that group.

Thin film and foam stability:

The group of Exerowa and Sedev in Bulgaria has studied the surface forces in foam films formed from aqueous solutions of tri-block copolymers. Exerowa et al. [1997] and Khristov et al. [2001] observed a small electrostatic component to the disjoining pressure (similar to non-ionic surfactants) at large film thickness. This is believed to be due to preferential adsorption of the OH⁻ ions at the air-water interface. On increasing electrolyte concentration a transition to steric stabilization was observed. Sedev at al. [2000] observed that even at concentrations below the CMC, the EO chains are squeezed out from the surface and protrude into the aqueous solution. Thus the tri-blocks form a brush (‘Π’ configuration) at the surface. At lower capillary pressures steric repulsion
occurs due to coiled polymers in the film core and at high capillary pressures brush to brush contact is observed. Khristov et al. [2001] also observed that foam from F108 was more stable than foam from P85 and that this result agreed with film stability of the single films formed by the two copolymers.

Table 3.3: Properties of EO-PO copolymers

<table>
<thead>
<tr>
<th></th>
<th>F108</th>
<th>F88</th>
<th>F68</th>
<th>P85</th>
</tr>
</thead>
<tbody>
<tr>
<td>c.m.c. at 25 °C (g/L)</td>
<td>45</td>
<td>100</td>
<td>190</td>
<td>40</td>
</tr>
<tr>
<td>$\gamma$ at 0.1% (25 °C) in dynes/cm</td>
<td>41.2</td>
<td>48.5</td>
<td>50.3</td>
<td>42.5</td>
</tr>
<tr>
<td>$\Gamma_{\text{sat}}$ (mol/m$^2$)</td>
<td>$1.09 \times 10^{-6}$</td>
<td>$1.51 \times 10^{-6}$</td>
<td>$1.15 \times 10^{-6}$</td>
<td>$1.36 \times 10^{-6}$</td>
</tr>
<tr>
<td>(25 °C)</td>
<td>(20 °C)</td>
<td>(20 °C)</td>
<td>(25 °C)</td>
<td></td>
</tr>
<tr>
<td>Area/molecule (Å$^2$) at the corresponding temperature</td>
<td>150</td>
<td>110</td>
<td>145</td>
<td>120</td>
</tr>
<tr>
<td>Foam height in mm (0.1% at 26 °C)</td>
<td>27</td>
<td>37</td>
<td>40</td>
<td>19</td>
</tr>
<tr>
<td>HLB</td>
<td>27</td>
<td>28</td>
<td>29</td>
<td>16</td>
</tr>
</tbody>
</table>

a. From Chu and Zhou [1996]
b. From BASF website on Pluronics

3.2.1.2 Surface properties of EO-BO copolymers

Amphiphilic block copolymers containing the more lipophilic hydrophobe BO have also been widely studied. The research group of Booth and Attwood has done extensive studies on association and gelation properties of the EO-BO block copolymers. The trends in solution properties are similar to those of EO-PO copolymer (described in
the previous section) in many respects. For example, BO groups have a stronger influence than EO groups on micellization, and the CMC decreases with increasing temperature and increasing number of BO units. More details can be found in the review article by Booth, Yu and Nace [2000]. But since the BO group is more hydrophobic than the PO group, the EO-BO block copolymers are more surface active and have lower CMCs than corresponding EO-PO block copolymers. In terms of free energy of micellization 1 BO unit is equivalent to 1 CH2 group or 4 PO units [Bedells et al., 1993]. Nace [1996 b] reported that surface tensions were as much as 40% lower and interfacial tensions (with n-dodecane) were as much as 90% lower for EO-BO copolymers than analogous EO-PO copolymers. EO-BO copolymers also have smaller areas per molecule at the air-water interface. In addition, Nace also found that they produce higher foam heights and exhibit greater foam stability than analogous EO-PO copolymers.

Other than the work by the group of Booth and Nace, the group of Szymanowski [Myszkowski et al., 1982; Szymanowski et al., 1982, 1983 a & b] has described and mapped various performance-oriented properties for a range of molecular weights and compositions (EO to BO ratio) for diblock and triblock (EO-BO-EO and BO-EO-BO) copolymers. Some of the properties mapped as a function of EO content and total molecular weight were- wetting power, foaming power, emulsifying properties and washing properties. They observed that foam height (Ross-Miles method) increases with the EO content in the copolymer and also that it passes through a maximum (at ~1200 daltons) with increasing molecular weight for a given composition. Rippner et al. [2002] observed that, similar to EO-PO copolymers, foam films from EO-BO copolymers have
an electrostatic component at large thickness and a strong steric component at short thickness.

Table 3.4: Tri-block EO-BO copolymers studied

<table>
<thead>
<tr>
<th>Product name</th>
<th>Average molecular weight</th>
<th>% EO</th>
<th>Average molecular formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>B20-5000</td>
<td>5,000</td>
<td>80</td>
<td>EO_{45}-BO_{14}-EO_{45}</td>
</tr>
<tr>
<td>B20-3800</td>
<td>3,800</td>
<td>80</td>
<td>EO_{34}-BO_{11}-EO_{34}</td>
</tr>
</tbody>
</table>

The EO-BO-EO polymers used in this study were obtained from Dow Chemical, though they are not available commercially. Though the EO-BO copolymers have been shown to be better foamers than the structurally analogous EO-PO copolymers [Nace, 1996 b], there was a limited range of structures and molecular weights available for selecting the EO-BO copolymers as compared to the EO-PO copolymers. Table 3.4 describes the two copolymers selected for this study.

Table 3.5: Properties of EO-BO copolymers

<table>
<thead>
<tr>
<th></th>
<th>B20-5000</th>
<th>B20-3800</th>
</tr>
</thead>
<tbody>
<tr>
<td>c.m.c. at 25 °C (g/L)</td>
<td>0.28</td>
<td>4.3</td>
</tr>
<tr>
<td>γ at (25 °C) in dynes/cm 0.1%</td>
<td>36.3</td>
<td>38.4</td>
</tr>
<tr>
<td></td>
<td>1.0%</td>
<td>33.7</td>
</tr>
<tr>
<td>Ross miles foam height, t = 0/t = 5 min. (mm)</td>
<td>101/95</td>
<td>96/59</td>
</tr>
</tbody>
</table>
Some of the relevant properties for the two polymers used, obtained from the Dow product brochure, are summarized in the table 3.5. The foam height and stability after 5 minutes, for the two polymers selected were among the best for the EO-BO copolymers in the Dow product brochure.

3.2.2 Hydrophobically modified polymers

Hydrophobically modified (HM) polymers are polymers in which, usually in small amounts, strongly hydrophobic groups have been introduced. The main significance for many applications is their self-aggregation from hydrophobic interactions which leads to interesting rheological behavior, such as a strongly shear-rate dependent viscosity. These molecules are usually referred to as associative thickeners and are used to produce consistency. Thus, they are extensively used in coatings and paints. They have also been studied for use in enhanced oil recovery processes for mobility control and also as model molecules for studying the behavior of natural macromolecules in biological processes [Glass, 2000, Strauss, 1993; Lindman & Thalberg, 1993]. Depending on the distribution of hydrophobic groups there can be different structures such as comb or end-substituted.

Because of their associative tendencies they can also have a strong tendency to produce foams [Goddard and Braun, 1985] though this property has not been as widely explored in the literature as their rheological or solubilizing properties. However, some have not observed significant surface activity with HM polymers. For example-
Jorgensen and Strauss [1961] found that surface activity was minimal for a set of poly-4-vinlypyridine derivatives in the absence of electrolytes. They equate it to the case of micelles of ordinary surfactants which have very little surface activity. Addition of KBr produced surface activity for derivatives containing dodecyl groups. Emulsan (polyionic lipopolysaccharide), a biologically produced surface active polymer, is only moderately surface active and not an efficient emulsifying agent. But it is an extremely good emulsion stabilizer for specific oil-in-water emulsions [Jonsson et al., 1998].

Sodium salts of hydrophobically-modified polyacrylic acids have also been found to be very effective oil-in-water emulsion stabilizers. The group of Millet et al. has extensively studied [2002, 1999 a & b] the influence of structure and concentration of HM poly(sodium acrylates) on thin film structures. For molecular weights ranging from 18,000 to 525,000, they observed that above a certain concentration threshold, film thickness increased rapidly with concentration and a physical gel formed which was a key factor in emulsion stabilization [1999 a]. They also observed that HM poly(sodium acrylates) behaved like small surfactant molecules with surface tension leveling off after a critical aggregate concentration [1999 b]. For the case of HM poly(sodium acrylate) with molecular weight of 120,000 and C12 to C18 hydrophobe, the CAC ranged from 1 to 10 w% when the hydrophobe content ranged from 10 to 1 mol%. Also, these molecules were quite surface active as, above the CAC, the surface tensions of several of the HM poly(sodium acrylates) were below 40 mN/m. However, the kinetics of surface adsorption & relaxation were quite slow because of the slow penetration of the hydrophobic grafts through the initially adsorbed polymer layer. Also, the kinetics of
adsorption at long times were observed to be independent of polymer structure or concentration and depended only on polymer molecular weight [2002].

However, in most studies with these HM polymers, the polymers were synthesized in-house. One major hurdle in studying these polymers for foaming and washout stability was in finding commercially available HM polymers according to required specifications. The HM polymers available commercially were mainly designed for rheological and not foaming applications and many had largely proprietary compositions. Table 3.6 lists the various HM polymers used in this research along with the available description of the polymers. Except for the keratin, all HM polymers are believed to have a comb like structure.

Pemulen TR-1 was obtained from BF Goodrich and the rest were obtained through Halliburton. Of the cationic HM polymers (HMPCs), because of the different methods of syntheses, HMPC1 and HMPC2 are believed to have a random distribution of the hydrophobes attached to the backbone whereas HMPC3 is believed to have a more blocky distribution of the hydrophobes.
Table 3.6: HM polymers studied

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pemulen TR-1</td>
<td>Polyacrylic acid with $C_{10-30}$ alkyl acrylate hydrophobe, partially crosslinked</td>
</tr>
<tr>
<td>CP</td>
<td>Acrylamide + cationic monomer, no hydrophobe</td>
</tr>
<tr>
<td>HM1</td>
<td>Acrylamide with $C_9$ hydrophobe + cationic monomer</td>
</tr>
<tr>
<td>HM2</td>
<td>Acrylamide/Acrylic acid copolymer with $C_{12-14}$ hydrophobe</td>
</tr>
<tr>
<td>HM3</td>
<td>Acrylic acid polymer + $C_{12}$ methacrylate</td>
</tr>
<tr>
<td>FP</td>
<td>Hydrolyzed keratin</td>
</tr>
<tr>
<td>HMPC1</td>
<td>Polydimethylaminoethyl methacrylate (polyDMAEMA) reacted with 6% $C_{16}$Br + 0.23% benzylcocodimethyl ammonium chloride</td>
</tr>
<tr>
<td>HMPC2</td>
<td>PolyDMAEMA reacted with 6% $C_{16}$Br + 0.17% cocoamidopropyl betaine</td>
</tr>
<tr>
<td>HMPC3</td>
<td>DMAEMA reacted with $C_{16}$Br and then copolymerized with DMAEMA in 6:94 ratio</td>
</tr>
<tr>
<td>HMPA1</td>
<td>Copolymer of methacrylic acid and ethyl methacrylate + small amount of methyl methacrylate, $C_{18}$ hydrophobe; partially crosslinked</td>
</tr>
<tr>
<td>HMPA2</td>
<td>Copolymer of methacrylic acid and ethyl methacrylate + small amount of methyl methacrylate, $C_{16}$ hydrophobe; partially crosslinked</td>
</tr>
<tr>
<td>HMPA3</td>
<td>Polyacrylate based HM polymer similar to above two</td>
</tr>
</tbody>
</table>

For easy reference, the chemical structure of some of the monomers mentioned in the above table are given below:

Acrylic acid: \( \text{CH}_2=\text{CHCOOH} \)

Acrylamide: \( \text{CH}_2=\text{CHCONH}_2 \)

DMAEMA: \( \text{CH}_2=\text{C(CH}_3\text{)COOCH}_2\text{CH}_2\text{N(CH}_3\text{)}_2 \)
Methacrylic acid: \[ \text{CH}_2\text{C} (\text{CH}_3)\text{COOH} \]
Ethyl methacrylate: \[ \text{CH}_2\text{C} (\text{CH}_3)\text{COOCH}_2\text{CH}_3 \]
Methyl methacrylate: \[ \text{CH}_2\text{C} (\text{CH}_3)\text{COOCH}_3 \]

In the case of the HMPA polymer series, the hydrophobe is believed to be attached to the backbone by the esterification of the carboxylic acid group, based on similar HM polyelectrolytes described by Vorobyova and Winnik [2000]. For the HMPC polymers, the hydrophobe is attached by the quaternization reaction of the tertiary amine (DMAEMA) with the alkyl bromide.

The following chapter describes the results of screening the conventional as well as the polymeric surfactants for washout stability.
CHAPTER 4

FOAM WASHOUT IN SCREENING TEST

This chapter describes a screening test that was developed to test foam washout stability and the results of the test with conventional and polymeric surfactants. Since the time involved for doing the washout experiments in a sand pack was very long and since the procedure was complex (see the next chapter), a need was felt to design a screening test. The screening test had to be simple and relatively quick, so that a large number of surfactants could be screened in a relatively short period of time. Yet it had to be reliable enough to demonstrate the washout resistance of foam. The following section describes the screening test developed for this purpose.

4.1 Screening test setup and procedure

The screening test setup is shown in Fig 4.1. It consisted of a foot-long glass column, about an inch in diameter fitted at the bottom with a perforated metal plate fitted with a 360-mesh screen. Air was blown 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 from the top. The injected water flowed through the plateau border regions of the foam generated, 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. The time required for the foam height to decrease from the upper to the lower
mark is denoted as the washout time. The distance between the two marks is about 9.5 inches and the volume between the marks is approximately 120 ml. Comparing the washout time for different surfactants gives an idea of the foam washout resistance.

Fig 4.1: Schematic diagram of the screening test setup
Initially, foam was generated by blowing air in from a constant pressure source. Even at approximately 1-2 psig pressure, the air rate was very high and the column was filled with foam within a few seconds. As a result, the bubbles generated were not uniform in size – the sizes ranged over several orders of magnitude and the results with this foam weren’t very reproducible. Later on, foam was generated by injecting air at a constant rate slow enough to generate uniformly sized bubbles. Generally, an air injection rate of 10 ml/min was used. Bubble sizes of about 1 mm were generated in most cases. The volume of air required to fill the column with foam was also recorded and is summarized in section 4.4. The quality of foam (i.e., gas fraction) generated was generally quite high - over 97% in most cases (when solution viscosity was similar to that of water) except for viscous solutions in which case the quality could go as low as 75% for the very viscous ones. Flowing water through the foam column would cause the column to swell and decrease the foam quality. For flow rates ranging from 1 ml/min to 10 ml/min the foam quality would change from ~ 95% to ~ 80%. In the following discussion the water flow rate for washout is fixed at 3 ml/min unless mentioned otherwise.

During washout, water distribution through the foam column was observed by dyeing the injected water in some runs. It was seen that the color was distributed uniformly across the cross-section of the foam column and the color front moved like a piston down the column. This shows that there is no significant fingering of water through certain regions of the foam column during washout.
4.2 Conventional vs. tri-block copolymer surfactants

To test the hypothesis that polymeric surfactants are more stable to washout than most conventional surfactants, several conventional surfactants and tri-block copolymers were screened using the procedure described above. The washout times (at 3 ml/min water injection) for each of these surfactants are presented in table 4.1. The descriptions of the various surfactants tested here are given in the previous chapter. Generally, a 2 wt% active concentration of each surfactant was used in the screening test and washout was carried out with de-ionized (DI) water. The variation in washout times between several runs was within 20% (also see section 4.5 on reproducibility). It can be seen that in general the conventional surfactants show much shorter washout times (< 10 min) than the tri-block copolymers despite the fact that they are all better foamers (see section 4.4) than the tri-blocks. (Note: MA-80I was a poor foamer. In the case of MA-80I, the foam collapsed so rapidly during generation that it was difficult to generate more than couple of inches of foam in the column. This foam washed out very quickly on injecting water). The exceptions were CS-330 and C12E8, which showed longer washout times. In contrast, most of the tri-block copolymers showed much better washout resistance. As explained later (chapter 6) this is due to the fact that polymeric surfactants are very difficult to desorb from the air-water interface whereas conventional surfactants desorb almost reversibly. The longer washout times of some conventional surfactants can be attributed to their large concentrations (w.r.t. CMC) and/or to the presence of some strongly adsorbing impurities, as discussed further in chapter 6.
That foam collapse was due to flow of water and not due to inherent foam instability was verified by comparing with static foam column stability without flow of water. For example, static foam column from CS-330 was stable for more than 48 hours and only 50% of the foam from F108 had collapsed in 300 min - thus confirming that foam collapse was indeed due to water flowing through the column (also, see chapter 6).

Table 4.1: Washout times for surfactants with DI water

<table>
<thead>
<tr>
<th>Surfactant (2wt% in DI water)</th>
<th>Washout time with DI water (in minutes)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MA-80I</td>
<td>-</td>
</tr>
<tr>
<td>SDS</td>
<td>2</td>
</tr>
<tr>
<td>C16TAB (0.5%)</td>
<td>3</td>
</tr>
<tr>
<td>C12E8 (0.13 %)</td>
<td>40</td>
</tr>
<tr>
<td>CS-330</td>
<td>63</td>
</tr>
<tr>
<td>AOS 16/18</td>
<td>13</td>
</tr>
<tr>
<td>Foamer1</td>
<td>4</td>
</tr>
<tr>
<td>Foamer2</td>
<td>10</td>
</tr>
<tr>
<td>Foamer3</td>
<td>5</td>
</tr>
<tr>
<td>F108</td>
<td>150</td>
</tr>
<tr>
<td>F88</td>
<td>23</td>
</tr>
<tr>
<td>F68</td>
<td>120</td>
</tr>
<tr>
<td>P85</td>
<td>20</td>
</tr>
<tr>
<td>B20-5000</td>
<td>93</td>
</tr>
<tr>
<td>B20-3800</td>
<td>60</td>
</tr>
</tbody>
</table>

Among the EO-PO copolymers, F108 (m.w. = 14,600) and F68 (m.w. = 8,400) show the best washout stability. In general, it seems that higher molecular weight of EO-
PO polymer leads to a higher washout time with the exception of F88. Actually, F88 and P85 were also poor foamers, requiring larger amounts of air to fill the column than other triblocks. This may explain their poor washout resistance. B20-5000 and B20-3800 with molecular weights of just 5000 and 3800 are still among the best washout resistant surfactants. The fact that the EO-BO copolymers with lower molecular weights show comparable washout resistance to the higher molecular weight EO-PO copolymers suggests that EO-BO copolymers are better foam washout stabilizers than EO-PO copolymers for a given molecular weight. This is likely due to the fact that BO is more hydrophobic than PO and hence is more difficult to desorb from the air-water interface. In addition, the EO-BO copolymers are better foamers than EO-PO copolymers [Nace, 1996]. However, due to unavailability of higher molecular weight EO-BO copolymers, this could not be studied further. But it would be interesting to see the washout times of higher molecular weight EO-BO copolymers.

4.2.1 Effect of water flow rate

The effect of water flow rate on washout time was tested with two surfactants - the polymeric F108 and the conventional anionic AOS 16/18. For the case of F108, water injection rates of 2-3 ml/min, 6 ml/min and 9 ml/min gave washout times of 163 min, 133 min and 151 min respectively, which correspond to total volumes of 372 ml, 786 ml and 1350 ml respectively. Thus an increase in flow rate of injected water by ~3-4 times increased the volume required by ~3.6 times i.e. the volume required scales roughly by the same factor as change in flow rate. This implies that the washout time can be
considered fairly independent of the flow rate within acceptable error. In contrast, for the AOS 16/18 surfactant the washout times at 3 ml/min, 6 ml/min and 9 ml/min were 12.5 min, 8.5 min and 6.5 min respectively. That is, increase in flow rate by a factor of 3 causes washout time to decrease by a factor of ~2. Considering the errors at small times, it could mean that the washout volume is almost constant for AOS 16/18.

These results already hint at the importance of surfactant desorption in foam washout stability. The rate of desorption of surfactant from an air-water interface is not influenced by flow rate when the bulk phase surfactant concentration is negligible, as during washout. Since, for foam from F108, washout time is independent of flow rate of injected water, the washout appears to be limited by desorption from air-water interfaces rather than mass transfer of surfactant from air-water interface to the bulk aqueous region. As will be seen later (chapter 6), this is confirmed by the desorption experiments which show that F108 desorbs very slowly (and very little) from an air-water interface. Whereas for AOS 16/18, the washout time decreases with flow rate indicating that mass transfer of the surfactant is rate limiting rather than desorption.

4.2.2 Effect of salt

In practical applications i.e. in the oil reservoirs, there are always some salts present like NaCl, MgCl₂, CaCl₂ etc. Hence it was decided to test all surfactants with salt in the sand pack experiments. Therefore to get the washout times in the screening tests at the same conditions as the sand pack experiments, the above mentioned screening tests were also carried out with some salt in the solution. The actual salt concentrations can
vary widely from reservoir to reservoir. It was decided to use 5% NaCl solution as brine in the screening tests and the sand pack experiments for consistency. However, to keep things simple it was also decided not to include any multivalent ions at this stage. Another change that was made was that 0.5 wt% concentration was used for all surfactants in the screening tests as this may be a more reasonable value for field application and was the concentration used in most of the sand pack experiments (see chapter 5). The results of the screening test with salt are shown in table 4.2.

Table 4.2: Washout times in presence of 5% NaCl

<table>
<thead>
<tr>
<th>Surfactant (0.5wt% in 5% NaCl solution)</th>
<th>Washout time with brine (minutes)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Foamer3</td>
<td>6</td>
</tr>
<tr>
<td>CS-330</td>
<td>61</td>
</tr>
<tr>
<td>F108</td>
<td>132</td>
</tr>
<tr>
<td>F88</td>
<td>70</td>
</tr>
<tr>
<td>F68</td>
<td>88</td>
</tr>
<tr>
<td>P85</td>
<td>49</td>
</tr>
<tr>
<td>B20-5000</td>
<td>108</td>
</tr>
<tr>
<td>B20-3800</td>
<td>55</td>
</tr>
</tbody>
</table>

It can be seen that though the actual washout times of the surfactants differ from the case without salt, the general ranking of the surfactants is relatively unchanged. With the addition of salt, the triblock copolymer solutions were better foamers than without. F88 and P85, especially, showed much better foamability (as defined in section 4.4) with salt and this is also reflected in their improved washout stability.
The results of the screening tests for the conventional and the tri-block copolymeric surfactants are summarized in figure 4.2 below—both with and without salt.

![Graph showing washout time (min) for various surfactants]

Fig 4.2: Screening test for conventional and tri-block surfactants

4.2.3 Effect of surface cohesiveness

To check the effect of cohesive interaction of a surfactant on foam washout stability, washout tests were carried out with SDS and SDS + dodecanol systems. With addition of dodecanol, the SDS molecules pack more closely at the air-water interface due to screening of charges of SDS. At 100:1 molar ratio of SDS to dodecanol, maximum surface shear viscosity was observed by Djabbarah [1978] at SDS concentration of 1.15 g/L i.e. about 0.1%. This indicates that maximum amount of SDS molecules are packed at the interface at 0.1% SDS with 100:1 SDS to dodecanol. Hence the washout was
carried out with 0.1% SDS with and without addition of dodecanol. It was observed that the washout time increased from about 2 min for SDS alone to about 4 min for SDS-dodecanol system. Thus, it suggests that surface cohesiveness does increase foam washout stability. However for the case of SDS, the increased washout time is still too small to be of any practical benefit.

4.3 Screening of hydrophobically modified polymers

Another class of polymeric surfactants that was studied was the hydrophobically modified (HM) polymers. As described in the previous chapter, these are polymers with a hydrophilic backbone with several hydrophobes branching out from the backbone. The reason for using these polymers was that since they had multiple hydrophobic chains on a single molecule, it would be extremely difficult to desorb these molecules once the hydrophobes anchored at the air-water interface. Most of these polymers were supplied by Halliburton except for Pemulen TR-1 which was obtained from BF Goodrich. Table 4.3 summarizes the results of the screening tests. It can be seen that only three sets of HM polymers showed significant washout resistance comparable to or exceeding that of the tri-block copolymers. These are the Pemulen TR-1, the HMPA polymers and some of the HMPC polymers. The HMPC1 and HMPC2 samples (without salt) were tested for washout for ~120 minutes. In this time HMPC2 foam height had decreased by a mere 10% whereas that of HMPC1 had decreased by about 40%. This shows the very high washout times that can be expected from these polymers. This is even more obvious from figure 4.3a. It can also be seen that the foam from HMPA polymers is more resistant to washout in the presence of salt (after neutralization) whereas, foam from the HMPC &
TR-1 polymers is more resistant in the absence of salt. In fact, TR-1 precipitates on addition of 5% NaCl. It is likely that more molecules of HMPA polymers adsorb per unit area at the air-water surface when salt is added, just as is the case for conventional ionic surfactants, because of decreased electrical repulsion between charges. This may explain the increased washout stability of foam from these polymers.

Table 4.3: Screening test for HM polymers

<table>
<thead>
<tr>
<th>Polymer (0.5 %)</th>
<th>Washout time (min) with DI water</th>
<th>5% NaCl</th>
<th>Solution in 5% NaCl; washout with 5% NaCl</th>
</tr>
</thead>
<tbody>
<tr>
<td>CP</td>
<td>11</td>
<td>3</td>
<td></td>
</tr>
<tr>
<td>HM1</td>
<td>10</td>
<td>2</td>
<td></td>
</tr>
<tr>
<td>HM2</td>
<td>18</td>
<td>15</td>
<td></td>
</tr>
<tr>
<td>HM3</td>
<td>1*</td>
<td>4*</td>
<td></td>
</tr>
<tr>
<td>FP (0.5%) (1.5%)</td>
<td>10**</td>
<td>16**</td>
<td></td>
</tr>
<tr>
<td>Pemulen TR-1 (0.1%)</td>
<td>187</td>
<td>~2</td>
<td>precipitates</td>
</tr>
<tr>
<td>HMPC3</td>
<td>18**</td>
<td>10**</td>
<td></td>
</tr>
<tr>
<td>HMPC2</td>
<td>&gt;&gt; 120 min</td>
<td>-</td>
<td>90</td>
</tr>
<tr>
<td>HMPC1</td>
<td>&gt;&gt; 120 min</td>
<td>-</td>
<td>55</td>
</tr>
<tr>
<td>HMPA1, Neutralized with NaOH</td>
<td>17**</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>HMPA2, Neutralized with NaOH</td>
<td>7**</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>HMPA3 (neutralized with NaOH)</td>
<td>28</td>
<td>-</td>
<td>170</td>
</tr>
</tbody>
</table>

* - hardly foams (just a couple inches of foam generated)

** - foams with difficulty (i.e. large amount of air required) and forms a very coarse foam
Surface tension of HMPA1 without neutralization was compared with HMPA1 after neutralization and addition of 5% NaCl by Meier [2001]. It was observed that the surface tension of the non-neutralized sample was about 40 mN/m and that of the neutralized sample with 5% NaCl was about 37 mN/m after 20 min of adsorption. It must be noted that some amount of a conventional surfactant is expected to be present in the solution due to its use in the polymer synthesis, and this can explain the low tension of the non-neutralized solution even though it does not foam very well. The slight lowering of surface tension of the latter sample perhaps indicates adsorption of the polymer molecules at the interface. The difference between the washout times of HMPA1 and HMPA2 can probably be attributed to the fact that HMPA1 has a higher percentage of the hydrophobe which is also of a longer chain length ($C_{18}$) than in HMPA2 ($C_{16}$).

With regard to the HMPC samples, it was observed that C3 sample does not foam well whereas C1 and C2 do so easily. This is perhaps due to some surfactant present in both C1 and C2 (See chapter 3, table 3.6). Adding the same amount of the surfactant (betaine) as present in C2 sample to the C3 sample (which does not contain surfactant) resulted in the solution foaming easily. However, the foam still washed out in ~28 min, much faster than C2. This indicates that block versus random distribution of hydrophobes may be important for washout stability (C3 has blocky structure whereas C1 and C2 have a more random hydrophobe distribution). Also, there may be some synergism between the polymer and surfactant present in C1 and C2 samples as the washout times observed for the samples are much higher than for surfactants or for the polymer (i.e., in C3) itself.
For example, the betaine by itself at the concentration at which it is present in the C2 solution shows a washout time of only ~25 min.

The results of the screening tests for the better among the HM polymers are compared with those of the tri-block F108, with and without salt, in figures 4.3a and 4.3b. Both HMPA and HMPC samples show higher foam washout times compared to Pluronic F108 in one or the other case. However, the cationic HMPC polymers are not suitable for practical applications as they will adsorb much more than anionic HMPA polymers in sandstone reservoirs. In addition, their washout times are reduced significantly in presence of salt which is the condition of interest for oilfield applications.

Figure 4.3a: Comparison of washout times of F108 and HM polymers (Washout with DI water) Concentration of F108 = 2%, TR-1 = 0.1%, all others = 0.5%. All HMPA polymers are in neutralized form. The arrows on top of HMPC2 and HMPC1 indicate that the total washout time for these is expected to be much longer than the values shown.
Figure 4.3b: Comparison of washout times of F108 and HM polymers with salt (Washout with 5% NaCl)

All concentrations 0.5% surfactant in 5% NaCl. All HMPA polymers are in neutralized form.

4.4 Foaming efficiency

Foaming efficiency or foamability can be described in terms of volume of air it takes to generate a fixed volume of foam. For the washout tests described before, air was injected till the foot-long glass column was filled with foam before washout was commenced. The amount of air it took to fill the column with foam was, however, different for different surfactants and polymers. The reason for this could either be due to the ‘intrinsic’ stability of the foam films or due to the dynamic effects in the foam films during generation of foam.
Figure 4.4 shows the volume of air required to fill the column with foam for various surfactants and polymers. The conventional surfactants show good foamability i.e. all the injected air is retained in the foam (100% efficiency). Among the polymeric surfactants, the HM polymers HMPA and HMPC also have close to 100% efficiency. However, for the triblock copolymers some of the foam collapses during generation and foaming efficiency is less than 100%. There is also a variation in volume required for foam generation in different runs with the triblocks. This is because during foam generation, foam fingers or holes in the foam column were observed to develop with these surfactants. This causes the exposed foam surface area to increase and as the rate of foam coalescence is related to the exposed area [Nishioka et al, 1996], this leads to faster foam collapse and gives irreproducible results. This is the reason why conical, and not cylindrical, vessels are used to measure reproducible dynamic foam heights [Ross and Suzin, 1985].

However, despite the poor reproducibility in the amount of air required when efficiency is lower than 100%, it can be observed that the EO-BO-EO triblock copolymers have better foamability than the EO-PO-EO triblocks (Pluronics). Among the Pluronics, F108 appears to be the best foamer. The presence of some conventional surfactants appears to be the reason why HMPA and HMPC show better foamability than the triblock copolymers. These conventional surfactants would adsorb at the surface faster than the higher molecular weight polymeric surfactants, so that the dynamic surface tension would be lower at short times. This would be favorable to foam stability
during the generation step. The triblock copolymers, in contrast, don’t contain any conventional surfactant.

![Diagram showing foaming efficiencies of various surfactants and polymers](image)

**Figure 4.4: Foaming efficiencies of various surfactants and polymers**

### 4.5 Reproducibility and sources of error

Reproducibility of the screening test can be gauged by looking at the washout times of F68 at different times. A 2% F68 solution exhibited the following washout times with DI water at various instances: 100 min, 120 min, 150 min and 132 min. Hence the error range is about 20% around the average for F68. Similar error range was also
observed with another Pluronic- F108. This is quite acceptable as the main purpose of the screening test is to identify surfactants that are significantly more stable to washout than conventional surfactants; which then can be tested in the sand pack. The range of error in the washout times of conventional surfactants like CS-330 was more narrow than for Pluronics.

One of the reasons for this variation may be the fact that the commercially available copolymers have a large distribution of molecular weights. Chu and Zhou [1996] have observed variations in the data on association characteristics reported by the same labs with these types of copolymers. Another source of error could be the bubble size distribution in the foam column. Though the bubble sizes generated in the foam column are fairly uniform - with the maximum size variation about a factor of two - there is further size variation caused by coalescence and/or collapse of bubbles as the foam column grows. And this is more important for the Pluronics as shown in section 4.4.

4.6 Foam height vs. time

In the tables above for the results of the screening tests, only the washout times for the complete collapse of the foam column are given. In addition, for several conventional and polymeric surfactants, the washout times for collapse to different levels were also measured. These are summarized in figs 4.5 a & b.
**Fig 4.5a: Washout progression with DI water.**

Concentration of AOS 16/18, F68, F108 and B20-3800 is 2%. Concentration of TR-1 is 0.1%.

All other concentrations are 0.5%.

**Fig 4.5b: Washout progression with 5% NaCl.**

All surfactant concentrations are 0.5%.
It can be seen from figs 4.5a and 4.5b that foam collapse becomes more rapid with time for all surfactants. This is discussed further in chapter 6, where the reasons for foam collapse are examined. However, this effect appears to be more pronounced in the case of the tri-block and the HMPA polymers than with CS-330 i.e., more with the polymeric surfactants. The figures again highlight the fact that the HMPA polymers exhibited the best washout stability of all surfactants screened in the presence of salt whereas the HMPC polymers did so in the absence of salt.

In summary, the screening test developed and the results of the screening tests were presented in this chapter. In general it was observed that the foam from tri-block copolymers did show better washout stability than from most of the conventional surfactants. F108 was observed to be the best among the tri-block copolymers. Some of the HM polymers also showed good washout stability exceeding that of the tri-blocks in some cases. Notable among them are HMPA1, HMPA3, HMPC1 and HMPC2. Thus, the general concept that foam from polymeric surfactants is more resistant to washout than foam from conventional surfactants was demonstrated in the screening tests. Chapter 6 further discusses the reasons for foam washout stability. The washout stability also depended on the presence or absence of salt especially in the case of the HM polymers, which are polyelectrolytes. F108 and HMPA1 represent the best among their respective categories with respect to washout resistance and these will be studied further in the following chapters. The next chapter describes foam washout experiments in sand pack to test these polymeric surfactants in a porous medium.
CHAPTER 5

FOAM WASHOUT IN SAND PACK

The previous chapter showed that polymeric surfactants produced foams stable to washout in the screening test. The next step was to test them for washout in a porous medium. This chapter describes the sand pack setup for conducting experiments and the results of foam washout experiments using a method developed for generating foam in sand pack. It was observed that generating both strong foam and uniform air saturation through the pack was non-trivial. An alternating air and surfactant injection scheme was developed to overcome the problems with other foam generation methods. This method allowed foam washout to be tested with several conventional and polymeric surfactants.

5.1 Materials and experimental setup

Sand for preparing the pack (unground silica from Ottawa, Illinois) was obtained from the U.S. Silica Company. Two grades of sand—F-110 and F-95—were used in preparing the sand pack. The size distribution for each as given by the supplier is shown in table 5.1. The actual distribution, though, varies between samples depending on the different degree of settling of sand in the drum. Only for a few initial experiments was unsorted F110 or F95 sand used as received. For the rest of the experiments only the 100-140 std sieve size cut was used for packing the column. This gave an average permeability between 5.5 and 7.5 darcy for various packs.
Table 5.1: Size distribution of sands

<table>
<thead>
<tr>
<th>USA std sieve size</th>
<th>millimeters</th>
<th>% retained on sieve</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>F-95</td>
</tr>
<tr>
<td>40</td>
<td>0.425</td>
<td>0.2</td>
</tr>
<tr>
<td>50</td>
<td>0.300</td>
<td>1.0</td>
</tr>
<tr>
<td>70</td>
<td>0.212</td>
<td>9.0</td>
</tr>
<tr>
<td>100</td>
<td>0.150</td>
<td>30.0</td>
</tr>
<tr>
<td>140</td>
<td>0.106</td>
<td>42.0</td>
</tr>
<tr>
<td>200</td>
<td>0.075</td>
<td>15.0</td>
</tr>
<tr>
<td>270</td>
<td>0.053</td>
<td>2.5</td>
</tr>
<tr>
<td>pan</td>
<td></td>
<td>0.3</td>
</tr>
</tbody>
</table>

5.1.1 Sand pack arrangement

Figure 5.1 shows the schematic arrangement of the setup for the sand pack experiments. A stainless steel column, 2 feet long with 0.9 inch inner diameter, was used to pack the sand. The steel column had three equi-spaced pressure taps so that pressure drops could be measured across the four equal sections of the pack. Five Validyne pressure transducers were used - four to measure the pressure drops across each of the four sections and one to measure the overall pressure drop across the whole pack. The transducers were hooked to a computer so that pressure drops could be recorded at specified intervals. All the connecting tubing used in the arrangement was 1/8” stainless steel tubing. All the valves and tube fittings used were stainless steel Swagelok fittings.
The pumps used for fluid injection were either Harvard syringe pumps (for high rates but injection pressures < 20 psig) or Isco pumps (for higher injection pressures or higher volumetric capacities but lower flow rates). The effluent from the pack was collected in measuring cylinders arranged in a pneumatically operated auto collector.

Fig 5.1: Schematic of sand pack setup
In the steel column, a 200 mesh size screen was used at both ends to prevent sand from coming out of the sand pack. A 60 mesh size screen and perforated metal plate were used behind it to provide mechanical support. In addition, at the inlet end a section of a rubber stopper was used to compress the sand in the column. The section was about 0.5 cm in thickness (uncompressed) with holes to allow for flow of fluids but a screen was put in front to prevent sand from passing through. Fig 5.2 shows a detailed schematic diagram of the inlet end of the column.

![Diagram of inlet end of sand pack](image)

**Fig 5.2: Inlet end of the sand pack (unassembled)**

After a few initial experiments, it was observed that there was a significant dead volume (~ 20 ml for inlet and outlet) between the reducing unions at the ends and the Swagelok connectors on the column. This volume was greatly reduced by filling the gap concentrically with sections of rubber stoppers and plastic tubes.
5.1.2 Packing and characterization of the sand column

Most of the sand packs were prepared by dry packing of the sand in the steel column. 100-140 mesh sand was poured into the vertical steel column accompanied by continuous vibration or tapping of the column to settle the sand. Then a screen was placed on top followed by the section of a rubber stopper to compress the sand and finally the column was closed with the Swagelok end fitting. CO₂ was blown through the pack to displace all the air with CO₂. Then a vacuum was applied to remove most of the CO₂ and this was followed by injection of several pore volumes of de-ionized water to dissolve the remaining CO₂ and saturate the pack with water. The difference in the weight of the dry column and the water saturated column gave the weight of water in the saturated pack (in grams) which corresponded to the pore volume plus any dead volume in milliliters. The permeability was calculated for the pack by measuring the steady state pressure drops at various water flow rates and using the Darcy’s law-

\[ u = \frac{k \Delta P}{\mu L} \]

where,

- \( u \) = superficial velocity of injected fluid
- \( k \) = permeability of pack
- \( \mu \) = viscosity of injected fluid
- \( \Delta P/L \) = average pressure gradient over length \( L \).

The measured average permeability for various sand packs prepared ranged from about 5.5 to 7.5 darcy.
The column was re-packed with fresh sand after every experiment involving a polymeric surfactant as there could be some amount of the adsorbed polymer left in the pack. When low molecular weight surfactants were used, the same column could be reused for the next experiment. To do so, the pack was first flushed with alcohol (ethanol or isopropanol) to remove any surfactant left, and then followed by several pore volumes of DI water. Then, as before, CO₂ was injected to displace any air in the pack and this was followed by application of vacuum and then re-saturating the sand pack with DI water.

5.2 Experiments with air

Before generating foam in the sand pack, resistance to flow of air was measured in a water saturated pack. Fig 5.3 shows the plot for a experiment in which air is injected into a sand pack saturated with de-ionized water. Air was injected at a superficial rate of ~ 24 ft/day which corresponded to a flow rate of 2 ml/min. Initially, till ~ 10 min of air injection (~0.2 apparent PV), the pressure drops across all the four sections were equal and rising. This represents the region where air is entering the dead volume near the entrance of the sand pack and compressing simultaneously. After this the pressure drops across all but the 1st section drop suddenly as the air flow is halted at the sand pack entrance. Pressure across the 1st section rises until it reaches the entry pressure for the sand pack and then it enters the sand pack. This is when the pressure drops across sections 2, 3 and 4 start rising again. Pressure drop across the 2nd, 3rd and the 4th sections increase sequentially as air passes through those sections before air breakthrough is observed at ~ 0.6 PV of apparent air injection. The actual volume injected is even less (~
0.3 PV) because of air compressibility. This premature breakthrough is due to the gravity override of air in the sand pack. Gravity segregation of air means there are actually two regions of single phase flow- one of air flow and another of water flow. The apparent viscosities in all but the 1<sup>st</sup> section are about 0.2 to 0.4 cP. The pressure drop across the 1<sup>st</sup> section stays at the value of ~1.25 psi which would be the entry pressure for the sand pack. This is confirmed by the calculation of the capillary entry pressure from the Leverett J function for unconsolidated sandstone which gives a value of ~1.13 psi for the entry pressure. Two other observations confirm that this indeed is the entry pressure for the sand pack. Injection of air in the reverse direction (i.e. from the outlet) also gives a similar pressure drop in the 4<sup>th</sup> section indicating that the arrangement at the entrance of 1<sup>st</sup> section is not a barrier to flow. Also, when the sand pack was saturated with surfactant
(MA-801) the pressure at which air starts entering the pack was reduced roughly by half. This would be expected for the entry pressure as the surface tension of the surfactant solution is also roughly half that of water.

5.3 Foam generation in sand pack

The first step before comparing the washout stabilities of foam from various surfactants in a porous medium, was to place foam in the sand pack. Foam can be generated in situ in the sand pack. The aim of the foam generation experiments was to create equivalent foam (i.e. similar trapped gas saturation) with different surfactants. This meant generating foam so as to get the same relative permeability reduction for the surfactant solution used which would imply similar trapped gas saturation in the sand pack, provided the gas distribution was uniform throughout the sand pack. A target relative permeability reduction factor (RPRF) of 100 was specified for the surfactant during foam generation i.e.

\[
\frac{\text{pressure drop for surfactant flow with foam present}}{\text{pressure drop for surfactant flow without foam}} = 100
\]

Since, in the oil industry a common way of expressing results is in terms of a mobility reduction factor (MRF), the results of the foam generation (and washout tests) were also expressed in terms of mobility reduction factor defined as follows-

\[
\text{MRF} = \frac{\text{pressure drop with foam present}}{\text{pressure drop for brine flow at same rate when no foam present}}
\]
The difference between MRF and RPRF is that RPRF factors out the contribution of the surfactant (or polymer) solution viscosity to the mobility reduction. However, the results are presented in terms of the more commonly used MRF in this study. Thus, the target for foam generation expressed in terms of MRF becomes:

\[ \text{Target MRF} = 100 \times \frac{\mu_{\text{surfactant}}}{\mu_{\text{brine}}} \]

\[ \approx 100 - 130 \text{ for most surfactants (except for HM polymers) used in the study} \]

Some of the experiments tried to generate strong foam (MRF \~{}100) with uniform distribution are described in appendix A. The problem in generating foam arises due to existence of two states – strong foam and weak foam – at same flow rates in the porous media. Here ‘weak foam’ refers to foam with high gas mobility because of failure to create lamellae and ‘strong foam’ refers to foam with low gas mobility due to high lamella density usually by process of division (see chapter 2, section 2.2). In a homogeneous porous medium, the transition from weak foam to strong foam occurs when either a critical pressure drop [Tanzil et al., 2002] or a pressure gradient [Gauglitz et al., 2002] is exceeded. The transition is accompanied by a very large and rapid increase of pressure drop due to foam generation. In the foam experiments described in appendix A, when air and surfactant were injected at low rates, the pressure drop/gradient was small and weak foam was generated. The trapped gas saturation was close to residual gas saturation in that case. However, at higher injection rates (resulting in higher pressure gradients), the foam became so strong (generally in the 1\textsuperscript{st} or 2\textsuperscript{nd} section) that it was very difficult to propagate it through the rest of the pack (at least with the available equipment
and the safety considerations in the laboratory). Another complicating factor was the end effect in the sand pack (see chapter 2). With many surfactant solutions, even at low rates when foam was weak in most of the pack, due to the end effect, foam generation by snap-off would occur near the exit and the pressure drop would increase. Beyond a critical pressure drop, strong foam generation with rapidly rising pressure drop was observed in the 4th section of the pack. Propagating this foam throughout the pack would have required very high injection pressures and a large amount of time as observed by other researchers [Mannhardt et al., 1998; Aronson et al., 1994; Persoff et al., 1991; Bergeron et al., 1993]. It is, thus, clear from the experiments in appendix A that simply co-injecting air and surfactant at varying rates or fractional flows through the pack cannot produce the desired foam strength and distribution.

**Foam generation procedure:**

The foam generation method eventually adopted to generate foam in the sand pack is described here. The idea was to inject alternate pore volumes of air and surfactant through a sand pack that was initially saturated with the surfactant solution. The air rate should be low enough so that the foam can be propagated easily throughout the pack in the 1st pass. Injecting surfactant after air would wash out the weak foam (i.e. longer air bubbles with very few lamellae along its path) and leave a trapped gas saturation. Subsequent passes of air and surfactant would increase the resistance to flow with each cycle throughout the pack as more and more air gets trapped in the pack. This should generate strong enough foam i.e. a relative permeability reduction (RPRF) of over 100,
after a few cycles. In terms of the commonly used MRF, this translates to a MRF of approximately 100 with most surfactant solutions as their viscosity is close to that of water. Also, one may expect a much more uniform gas saturation distribution in the pack if the foam propagates throughout the pack. However, the entry and the end effects may still cause lower and higher pressure drops in the 1st and the 4th section respectively.

5.4 Foam washout tests in sand pack

The foam generation method described above is shown for the Pluronic F108 in fig 5.4a. The pack was first saturated with 0.5% F108 in 5% NaCl solution. Air was then injected at a superficial velocity of 12 ft/day. When the weak foam generated in the sand pack broke through, the gas saturation was 82%. Flushing with surfactant at 12 ft/day (superficial) removed the continuous foam and produced a trapped gas saturation of 44% and MRF of ~ 11. With the subsequent cycles of air and surfactant injection the trapped gas saturation increased to 57%, 61% and 68% after the 2nd, 3rd and 4th cycles respectively. The overall mobility reduction factor after the 4th cycle was ~75.
Fig 5.4a: Foam generation using the new procedure (F108)

Fig 5.4b: Foam washout for F108
At this point, brine injection at a superficial velocity of 12 ft/day was started to study the foam washout in the sand pack (fig 5.4b). After some time when the flow rate was reduced to 6 ft/day, it was observed that the pressure drops did not decrease by a factor of 2, as would have been expected, but by a much smaller factor. Hence the MRF in fig 5.4b at 6 ft/day increased to ~130. This can be explained by the compressibility of air in the sand pack at the experimental conditions. Decrease in the flow rate caused an expansion of gas in the sand pack because the injection pressure for the pack was about four times the exit (atmospheric) pressure. This increase in MRF due to gas expansion is confirmed by the fact that when the brine rate was reduced from 12 to 6 ft/day, the gas saturation increased from ~64% to ~69%. Also, in fig 5.4b, on changing the rate back to 12 ft/day, the original pressure drops were attained. Because of this dependence of the MRF on the flow rate due to the air compressibility, it was decided for consistency to achieve the target MRF (of $100 \mu_{\text{surfactant}}/\mu_{\text{brine}}$) for each surfactant at the flow rate of 6 ft/day before measuring washout of the foam.

One concern in carrying out the foam washout in the sand pack experiments was the very long time required to complete the washout. For instance, the initial 14 PV of brine injection required about two days at the rate of 6 ft/day. This was clearly too slow a rate to complete the washout experiments in a reasonable time. The washout time was reduced considerably by using a FMI fluid metering pump to inject brine at high rates (> 100 ft/day). This was achieved by switching from the Isco pump injecting at 6 ft/day to the metering pump from for a short period. Since the pressure drops during the high flow rate could have exceeded the transducer ranges, the transducers were isolated during this
time by closing various valves. This region is represented by the gaps in the washout curves in fig 5.4b. After injecting a few PV of brine at high rate, the rate was again reduced to 6 ft/day to monitor any changes in the pressure drops across the various sections. Brine was injected at such high rates several times to speed up the washout process.

During washout, the pressure drop in each section (except in the 4th) decreased sequentially before leveling out at MRF of ~20 or lower. It must be noted that this is slightly higher than the MRF expected at residual air saturation (since at residual oil saturation of 25-30%, MRF was ~3-4; see chapter 7). This is supported by final air saturation of ~35-40% which is higher than residual air saturation. This may be partly explained by the higher pressure drop and hence higher gas saturation in the 4th section. But it also indicates that there is a small amount of foam that does not wash out from the pack.

A peculiar thing that can be observed in the figure is that while the pressure drops across the initial three sections decreased as the washout progressed, the pressure drop across section 4 actually increased! This may be explained by the previously described capillary end effect. As the foam lamellae in the preceding sections of the sand pack collapse as the surfactant is washed out of the air/water interfaces, the resulting continuous gas is pushed out towards the outlet. Near the outlet, due to the end effect snap-off occurs and some of the air is trapped as foam near the outlet region. This causes the pressure drop across the 4th section to rise. Further strengthening of foam can be
expected from higher gas flow rates due to gas expansion near the outlet. This can be expected to continue till the capillary pressure near the outlet exceeds the limiting capillary pressure for F108 surfactant at which point the foam in the 4th section collapses before starting to build up again. As can be seen later on, this behavior has been observed in almost all washout experiments with different surfactants. Since the pressure drop across the 4th section keeps on rising most of the time during washout, the PV required to washout foam (i.e., till pressure drops level out) from only the first three sections of the sand pack were recorded. By this measure, it took about 26 PV of brine (PV based on the whole pack, not just the first three sections) to washout F108 from the first three sections. In a real reservoir, the exit region is a much smaller fraction of the reservoir length and considering the smaller air compressibility at reservoir pressures, this effect would be negligible.

In summary, with this new procedure of foam generation it was possible to generate as well as propagate strong foam throughout the sand pack. The key for the successful use of this method seems to be to inject air at a sufficiently low rate so as to propagate weak foam throughout the pack. Starting at high rates will produce strong foam and cause plugging at the entrance region as observed in some experiments with MA-80I (appendix A). But too low a rate would require a long time for foam generation. Hence, to strike an optimum balance some amount of initial trial and error for each surfactant formulation is inevitable. Each subsequent cycle of air injection at this low rate makes the foam stronger. This can be continued till sufficient mobility reduction is achieved.
5.4.1 Washout tests for other surfactants/tri-block copolymers

Several surfactants/polymers which were screened earlier were then tested for foam washout stability in the sand pack using the procedure described above. Their washout tests are discussed in this section.

a) P85 (0.5%, 5% NaCl):

For the case of P85, air and surfactant were injected alternately at superficial velocity of 12 ft/day (fig 5.5a) after saturating the pack with the surfactant solution. Foam breakthrough in the first pass gave a $S_g$ of ~93%. On injecting surfactant, the trapped gas saturation was ~53%. After 3 cycles of air and surfactant injection and stepping down of the surfactant rate to 6 ft/day, an overall MRF of ~95 was observed with a trapped gas saturation of ~67%. Washout was commenced with 5% brine at the rate of 6 ft/day at this point (fig 5.5b). As before, flow was switched to the high rate pump in between to reduce the time for washout. It can be seen that it required between 3.5 to 5.5 PV of brine to complete the washout of P85 (first three sections) from foam in the sand pack.
Fig 5.5a: Foam generation with P85

Fig 5.5b: Foam washout for P85
b) F88 (0.5%, 5% NaCl):

As with P85, foam was generated by alternately injecting air and surfactant at 12 ft/day. After 4 cycles of injection and then decreasing the surfactant rate to 6 ft/day, an overall MRF of ~ 95 was observed (fig 5.6a). It can be seen that the overall pressure drop (and hence MRF) decreases during surfactant injection because of the decrease in pressure drop across the 1st section and unlike the previous cases this is not compensated by a corresponding increase in 4th section. It required between 6.5 to 9 PV of brine for washout of foam (fig 5.6b) from the first three sections of the sand pack.

c) B20-5000 (0.5%, 5% NaCl):

Washout was also carried out with one of the EO/BO copolymers in the sand pack (Figs 5.7a & b). Again, foam was generated by injecting air and surfactant alternately at superficial velocity of 12 ft/day. After 3 cycles of injection and then decreasing the surfactant rate to 6 ft/day, an overall MRF of ~120 was observed with a trapped gas saturation of ~71%. Washout was carried out with brine at 6 ft/day with periodic switching to high rate to accelerate the washout. PV of brine for washout of B20-5000 from all but the last section was between 13 to 15 PV.
Fig 5.6a: Foam generation with F88

Fig 5.6b: Foam washout for F88
d) CS-330 (0.5\%, 5\% NaCl):

One of the conventional surfactants tested was CS-330. After saturating the sand pack with 0.5 \% CS-330 in 5\% NaCl solution, air was injected at superficial rate of 3 ft/day (fig 5.8a). Note that a lower rate was required to generate strong foam with CS-330 compared to the triblocks. Soon after foam breakthrough, surfactant was injected at 3 ft/day which resulted in a trapped gas saturation of \(~57\%\). Subsequently, air and surfactant were injected at 4 ft/day for 2 more cycles till overall MRF of \(~145\) and trapped gas saturation of 76\% was obtained at 4 ft/day. For consistency with other experiments, surfactant rate was increased to 6 ft/day resulting in an overall MRF of \(~100\) due to air compression. This was followed by washout with 5\% brine at 6 ft/day (fig 5.8b). It can be seen that it took between 7 to 12 PV of brine to complete the washout of foam from CS-330 from all sections of the sand pack which is considerably less than the \(~26\) PV required for the first 3 sections with F108. This is consistent with the observations from the screening test (chapter 4).
Fig 5.7a: Foam generation with B20-5000

Fig 5.7b: Foam washout for B20-5000
e) $C_{16}$TAB (0.5%):

Another conventional surfactant tested was the $C_{16}$TAB. In this case, the pack was saturated with the surfactant solution containing no salt. Air was injected at 12 ft/day (fig 5.9a). This led to strong foam generation in the 3<sup>rd</sup> and 4<sup>th</sup> sections delaying foam breakthrough considerably. The second cycle of air injection led to strong foam generation in the 1<sup>st</sup> section. Thus after 2 cycles and at surfactant injection rate of 6 ft/day overall MRF was ~150, though the trapped air distribution was not as uniform as with other surfactants. A slower injection rate would have produced a more uniformly distributed foam. In any case, this foam washed out rapidly from all four sections in ~ 2.5 PV of DI water injection (fig 5.9b) and the high rate pump was not required at all.
Fig 5.8a: Foam generation with CS-330

Fig 5.8b: Foam washout for CS-330
Fig 5.9a: Foam generation with C_{16}TAB

Fig 5.9b: Foam washout for C_{16}TAB
The observations from the foam generation and washout experiments above are summarized in the following table.

<table>
<thead>
<tr>
<th></th>
<th>Air/Surfactant injection rate (ft/day)</th>
<th>Number of cycles required</th>
<th>MRF due to foam generated at 6 ft/day</th>
<th>PV for foam washout in first 3 sections</th>
</tr>
</thead>
<tbody>
<tr>
<td>CS-330</td>
<td>3-4</td>
<td>3</td>
<td>100</td>
<td>7 - 12</td>
</tr>
<tr>
<td>C\textsubscript{16}TAB</td>
<td>12</td>
<td>1-2</td>
<td>150</td>
<td>2</td>
</tr>
<tr>
<td>F108</td>
<td>12</td>
<td>3-4</td>
<td>130</td>
<td>21 - 26</td>
</tr>
<tr>
<td>P85</td>
<td>12</td>
<td>3</td>
<td>95</td>
<td>3.5 - 5.5</td>
</tr>
<tr>
<td>F88</td>
<td>12</td>
<td>4</td>
<td>95</td>
<td>6.5 - 9</td>
</tr>
<tr>
<td>B20-5000</td>
<td>12</td>
<td>3</td>
<td>120</td>
<td>13 - 15</td>
</tr>
</tbody>
</table>

Thus, the washout results agree qualitatively with the results from the screening test (chapter 4). Foam from polymeric surfactants F108 and B20-5000 was more stable to washout than foam from conventional surfactants.

5.4.1.1 Effect of rate/switching pumps

In the experiments described above, the time for the washout part was reduced considerably by injecting brine using a high rate pump. A natural question arising from this is - what is the effect of changing rate and switching pumps on the washout of surfactant from foam in the sand pack? This is addressed in this section by looking at the
washout of foam from polymeric B20-5000 in the sand pack at low rate and comparing to the washout with the high rate pump.

Figs 5.10a & b show the foam generation and washout of 0.5 w% B20-5000 in 5% NaCl. During the experiment, effluent from the sand pack was collected from time to time and analyzed in Halliburton labs for copolymer concentration using the TOC (total organic carbon) method. This gives the total concentration of copolymer B20-5000 in the effluent. This was done to gauge if the polymer adsorption on the sand particles has any adverse effect on foam generation. The effluent concentration of B20-5000 was 0.45 % after saturating the sand pack with ~1 PV of the copolymer solution. From fig 5.6a it can be seen that the effluent concentration reaches 0.5 % by 2 cycles of air/surfactant injection. This demonstrates that injection of even 1 PV of copolymer is sufficient to satisfy most of the adsorption for the copolymer on the sand particles and that the copolymer solution in the sand pack is not depleted so much as to affect the foam generation in the pack.

As before, foam was generated in the pack by injecting air and surfactant alternately at 12 ft/day. After 3 cycles of injection and then reducing surfactant rate to 6 ft/day, an overall MRF of ~ 125 was observed with a trapped gas saturation of 72%. These values are very close to those observed with the earlier experiment with B20-5000 (fig 5.7) and thus confirms the reproducibility of the foam generation method. Washout was commenced by injecting brine (5% NaCl) at a superficial velocity of 6 ft/day. However, unlike the earlier experiment, the rate was kept constant at 6 ft/day throughout
without switching to the high rate pump. The small periodic jumps in the data represent the refilling/switching of the Isco pumps. It can be observed that the general trends and the shape of the washout curves seem unchanged from the case where the high rate pump was used. The sequential nature of the washout is more clearly evident in the fig 5.10b. Again, it can be seen that pressure drop across the 4th section keeps on rising until foam in the first three sections has collapsed after which it starts decreasing gradually. The amount of brine required to wash out the foam from the first three sections was about 22 PV. This is about 7 PV more than the approximately 15 PV required when flow was switched to a higher rate from time to time. Thus, the decrease in PV for washout is by a factor of ~0.3 when the rate is increased by a factor of ~50 indicating a weak influence of flow rate on washout. The decrease could be due to the mobilization and displacement of a small fraction of the trapped gas at the higher pressure gradients during the higher rate. Also some destabilization of bubbles may have occurred due to their stretching and compressing when flow was switched from one rate to another.

Since the time required to carry out washout at a constant rate in the above example is very large (~ 7 days), it is not feasible to test each surfactant at low rate. Although the throughput of brine required for washout is reduced somewhat when high rate injection was used, one would expect similar reduction with all the surfactants/polymers tested. Hence even when flow is switched to a higher rate during washout, it is still reasonable to compare different surfactants/polymers for their washout stability while keeping in mind that actual amount of brine required would be somewhat higher.
Fig 5.10a: Foam generation with B20-5000

Fig 5.10b: Foam washout for B20-5000 (at constant brine rate)
5.4.2 Hydrophobically modified polymers

This section describes the washout tests of some of the hydrophobically modified polymers screened earlier. Of the three types of HM polymers which showed good washout resistance in the screening tests – TR-1, the HMPA polymers and the HMPC polymers – TR-1 precipitated in presence of NaCl and was not studied further. Cationic HMPCs also showed decreased foam washout stability in the screening tests. In addition, because of stronger adsorption of cationic polymers in sandstone reservoirs, they are not suitable for oilfield applications. Therefore, this section discusses the washout tests of only the HMPA polymers. Two types of the polymers were tested – HMPA1 and HMPA3. From the screening tests (chapter 4) it is clear that only the neutralized polymers show good washout resistance. Addition of salt resulted in even better washout resistance in addition to reducing the viscosity of the solution tremendously. Both the HM polymers were neutralized with 0.1N NaOH till the solution became clear and then 5% NaCl was added to the solution.

HMPA1:

Figs 5.11a & b show the foam generation and washout steps for foam generated with 0.5% HMPA1 (after neutralization and adding salt). Air and surfactant were injected alternately at a superficial velocity of 12 ft/day for foam generation. It was observed that the MRF in the different sections rose less rapidly than in the earlier experiments with the block copolymers and were reaching a plateau by the third cycle. Overall MRFs after the
3rd, 4th and 5th cycles were 44, 50 and 53 respectively, with not much change in the trapped gas saturation indicating approach towards a steady state. Injecting the HMPA1 solution at the reduced rate of 6 ft/day, after the 5 cycles of injection, gave an overall MRF of ~89. However, it must be noted that the viscosity of the HMPA1 solution was about twice that of brine, so it really corresponds to a relative permeability reduction (RPRF) of only ~45. This is supported by the observation that the trapped gas saturation at this stage was only ~59% compared to the trapped gas saturations of ~72-77% for the other surfactants.

This was followed by washout with 5% brine. It can be seen from fig 5.11b that the number of PV required to wash out the foam from the first three sections was between 15 to 20. Thus, even though HMPA1 did not give rise to as strong a foam as with the tri-block copolymers in the sand pack, it still showed good washout stability- ranking only behind F108.
Fig 5.11a: Foam generation with HMPA1

Fig 5.11b: Foam washout for HMPA1
Before the foam generation experiment in fig 5.11, the pack was flushed with ~4 PV of the HMPA1 solution to satisfy adsorption on sand particles. Effluent concentration was measured for TOC (total organic carbon) at various points during foam generation and washout. It was observed that the effluent was not depleted of the polymer solution before foam generation. So, depletion of polymer from solution is also not a cause for low foaming. To make sure that there was no problem with the packing of the sand pack that could cause channeling of air, the experiment was repeated after repacking the column with fresh sand. Nearly identical results were obtained in the repeated experiment. The number of PV of brine for washout in this case was observed to be ~18. Another test was carried out with a higher concentration of HM polymer as described next with HMPA3.

HMPA3:

HMPA1 has some degree of cross-linking present which also could have made foam generation difficult. Hence another HM polymer, HMPA3, was tested which is supposed to contain little cross-linking and have a lower molecular weight than HMPA1 but is supposed to be chemically similar to HMPA1. Again the polymer was used after neutralizing with 0.1N NaOH and adding 5% NaCl. But in this case, a higher concentration of polymer was used (2%) to make sure that lower concentration of polymer did not cause poor foam generation.
Fig 5.12a: Foam generation with HMPA3

Fig 5.12b: Foam washout for HMPA3
Again, it was observed (figs 5.12a & b) that foam generated was not as strong as with the Pluronics. After 4 cycles of air and surfactant injection, an overall MRF of only about 51 was observed. In this case the solution viscosity was about four times that of brine and therefore the relative permeability reduction (RPRF) due to foam was only ~13. The trapped gas saturation at this stage was only ~51%. It, however, still did show good washout stability. The throughput of brine required for foam washout was between 12 and 17 PV.

The reason for low foaming of HMPA polymer solutions in the pack appears to be due to their lower film stability at higher capillary pressures. In the screening tests HMPA1 did foam easily – in fact required lesser amount of air to generate the same volume of foam compared to the Pluronics. Whereas in the sand pack, the trapped gas saturation and pressure drops did not increase above a certain level. A lower critical disjoining pressure for the HMPA1 films can explain why it foams readily in the screening test since the capillary pressures are much smaller than in the sand pack experiments. In the glass column the maximum capillary pressure is approximately the hydrostatic head of the column, which is ~ 0.4 psi. Whereas in the sand pack, with total pressure drop of ~ 40 psi and gas saturation > 50%, one may expect the capillary pressures to be of the order of a few psi. In the sand pack, it appears that the limiting capillary pressure for foam collapse is exceeded at higher gas saturations for the HMPA solutions unlike for conventional surfactants or Pluronics. Aronson et al. [1994], for example, have shown that the steady state pressure gradients in porous media at various concentrations of SDS depend on the rupture pressures for the films from that solution.
The behavior of foam in the 4th section of the sand pack during washout also supports this. It can be seen from fig 5.11b that the MRF across the 4th section does not rise as much as observed with other surfactants and block copolymers. In fact, foam in the 4th section collapses whenever the MRF reaches about 140. This suggests that the limiting capillary pressure for foam collapse is exceeded in the 4th section whenever the MRF exceeds about 140.

Increasing the polymer concentration (e.g.: 2% HMPA3) does not appear to have increased the film stability and in fact, decreased foam stability. Two other methods were tried to improve film stability – increasing pH and mixing with conventional surfactants. Detailed observations from the experiments can be found in appendix B. When pH of HMPA1 was increased from 7 to 10, the solution containing 5% NaCl became more clear in appearance and also more viscous (viscosity was found to increase gradually over time), indicating that more of the carboxylic acid groups had been neutralized. The surface activity, however, was not affected though the rate of adsorption at the air-water surface decreased (as observed during surface tension measurements) probably due to increased viscosity. The foam stability, however, decreased further in the porous medium compared to HMPA1 solution at pH 7.

When HMPA1 at pH 7 was mixed with anionic CS-330 or amphoteric C14DMAO (C14- dimethyl amine oxide), there was little or no increase in foam stability in porous medium even though the conventional surfactants adsorbed at the surface (appendix B). Surface tensions of the mixtures had the same value as the conventional surfactants
indicating sufficient quantities had adsorbed at the surface. Also, washout in screening tests showed decreased washout time for the mixtures indicating that some of the polymeric surfactant had been displaced from the surface. Yet, there was no improvement in foam stability.

The above observations lead one to believe that the low film stability is not because of some surface properties (such as high dynamic surface tension) but because of bulk properties of the films. The HMPA molecules have molecular weights in hundreds of thousands plus some amount of cross-linking. The molecular sizes are therefore quite large – the solutions at pH 7 containing 5% NaCl were bluish/whitish indicating large sized aggregates. Hence, one possible explanation could be that these molecules cause

![Bar chart](image)

**Fig 5.13: Washout tests in sand pack**
All surfactant concentrations 0.5% in 5% NaCl (except C_{16}TAB, which is in DI water). The * on top of HMPA1 and HMPA3 indicate that the foam generated before washout was carried out was not as strong as with the other surfactants.
bridging of the opposite air-water interfaces of foam films, just as some polymers cause flocculation of colloidal particles by bridging.

In summary, several conventional and polymeric surfactants were tested for foam washout stability in a sand pack after generating foam using a method of alternating air and surfactant injection. The number of PV required for foam washout of conventional, tri-block copolymers and HM polymers are summarized in fig 5.13. In general, as predicted by the screening test, the polymeric surfactants produced foam that is more resistant to washout than conventional surfactants. There is remarkable similarity in the ranking of foam washout with tri-block copolymers observed in the screening test (fig 4.2) and sand pack experiments (fig 5.13). However, the HM polymers tested were found to be low foamers in porous media compared to the Pluronics due to lower foam film stability, possibly due to bridging by the HM polymers. But they still they showed good washout resistance.

The next chapter examines the role of surfactant desorption in foam washout stability in both screening tests and sand pack experiments. An important reason for the observed foam washout in porous media when using polymeric surfactants is also discussed in chapter 6.
CHAPTER 6
SURFACTANT DESORPTION AND FOAM WASHOUT

The previous two chapters showed foam from polymeric surfactants to be more stable to washout with water than foam from conventional surfactants. This chapter examines the role of desorption of surfactants in foam washout stability. A modification was made to a traditional pendant bubble apparatus, used to measure interfacial tensions, to measure desorption of surfactants during washout. The following section describes the modified setup and the experimental results for various surfactants. It will be seen that desorption is the critical parameter distinguishing washout of conventional and polymeric surfactants. However, desorption alone cannot explain the differences in foam washout of polymeric surfactants. It will be shown that hydrodynamic factors and gas solubility are also important for explaining foam washout in the screening tests and the sand pack experiments respectively.

6.1 Desorption of surfactants

This section describes the experimental setup for measuring desorption and presents the results for several conventional and polymeric surfactants. A similar setup has also been developed by the group of Radke [Svitova et al., 2003] to measure desorption of surfactants from air-water and oil-water interfaces. In this study, a pendant bubble is used instead of a sessile drop/bubble used in their experiments.
6.1.1 Experimental setup

To study the role of desorption of conventional and polymeric surfactants in foam washout, a pendant bubble setup as described below was used. The principle behind the experiment is as follows: a pendant bubble was created in a cell containing surfactant solution and the solution was then replaced with water or brine. The surface tension was monitored using bubble shape analysis during the removal of surfactant to determine the ease of desorption of surfactant molecules from the air-water interface as a function of surfactant dilution in the cell.

The setup (schematic shown in fig 6.1) consisted of a glass cell with inner dimensions of 2 cm (W) x 4 cm (L) x 8 cm (H), containing 30 ml of a given surfactant solution. A bubble was created in this solution using a steel U-shaped needle (1.66 mm diameter) connected to a glass micro-syringe through a steel valve. Two metal tubes (1/8 inch diameter) were inserted into the solution to inject and withdraw water (or brine) to replace the surfactant solution in the cell. The tip of the tube injecting water was near one top corner and the tip of the tube withdrawing water was near the opposite bottom corner. The metal tubes were connected to Isco pumps (model 2350) through polyethylene tubing and the pumps were operated at the maximum flow rate of 10 ml/min during washout experiments. The cell was mounted on a goniometer stage (Rame-Hart, Inc.) between a lamp and a video camera. An image grabber card (DT3955) was used to capture images at various times and drop shape analysis software was used to calculate the surface tension from the bubble shape.
The valve connecting the U-shaped needle to the syringe was closed after creating a bubble to prevent air leak and the consequent decrease in bubble size that was observed when the valve was open or absent. Also, surfactant solutions tended to wet the inside of the metal needle which caused bubble size to increase with time. Hence, the inside of the metal needle was coated with teflon to make it non-wetting. The coating was carried out by dipping the needle in 6% teflon solution (AF1601S from DuPont) and then heating it above the glass transition temperature of the polymer (160 °C). This significantly reduced the increase in bubble size with time.
A note on the error in measurements due to needle size:

For accurate measurement of surface tensions the bubble size had to be close to maximum. In these experiments, the surface tensions ranged from \(\sim 30\) mN/m for surfactant solutions to 72 mN/m for water. The maximum possible bubble size was dictated by the surface tension of the starting surfactant solution which made the bubble size less than optimum for measuring water surface tension after surfactant washout. It was observed that bubble size affected accuracy quite strongly (much more than needle size). When a 2.4 mm needle was used, it gave large errors of \(\sim 10-20\) mN/m with water surface tensions because of the under-optimum bubble sizes (which made the shape of the bubble close to hemispherical). A smaller needle size (1.66 mm) had to be used to get more accurate measurement of surface tensions of water even though both 1.66 mm and 2.4 mm needles gave accurate measurements at the lower surface tensions of surfactant solutions. This dependence of the measured water surface tension on needle size is illustrated in fig 6.2.

\[\text{Fig 6.2: Surface tension of water with different needle sizes}\]
Concentration profile in the cell

To estimate the concentration and determine the extent of mixing in the glass cell during surfactant replacement (washout), an experiment was performed in which brine in the glass cell was replaced with water and the concentration of brine in the exiting liquid determined by measuring conductance (using a Beckman conductivity bridge). A 1% NaCl solution was initially taken in the cell and replaced by 1% sucrose solution of the same density. Fig 6.3 shows the normalized conductance (or concentration) of the samples taken from the pump used for withdrawing fluid from the cell. There appears to be no change in the concentration in the cell for a while initially. This time lag was estimated to be the time it would take the liquid to flow from the cell to the pump where samples were collected. So, the curve was shifted to remove the time lag as depicted by the curve ‘CV-0.37’ in the figure. This profile is compared to the exit concentration profile expected from a well-mixed cell of 30 ml volume in the figure. It can be seen that the concentration decreases exponentially in the cell similar to the ideal mixing curve and the slight deviation may be explained by the lack of additional agitation (such as by a stirrer) in the cell. This shows that the agitation produced by flow is sufficient to produce close to ideal mixing conditions.
6.1.2 Desorption during surfactant washout

The aforementioned setup was tested by measuring desorption of a pure non-ionic \( \mathrm{C}_{12}\mathrm{E}_8 \) surfactant during washout. In fig 6.4 the surface tension is plotted against the number of cell volumes of de-ionized water injected. The initial surfactant concentration (0.002\%) was below the CMC of the surfactant. It can be seen that surface tension rises rapidly with cell volumes and reaches \( \sim71 \) mN/m after 15 cell volumes, which is close to the surface tension of de-ionized water. This shows that the surfactant molecules desorb from the air-water surface as concentration in the bulk decreases and eventually almost all the molecules desorb from the surface. A new bubble was created in the solution.
present at the end of the experiment and its surface tension was measured to be \( \sim 74 \) mN/m (shown by the big circle at the end of the washout in fig 6.4) confirming that there is insignificant amount of surfactant present in the cell.

![Graph showing desorption of C_{12}E_4 from air-water interface](image)

**Fig 6.4: Desorption of C_{12}E_4 from air-water interface**

Washout with DI water. Initial concentration = 0.002 w%.

The program for capturing images does so only in logarithmic scale with time- as can be seen by the increasing distances between the points. Because of this, the surfactant removal and image capture was stopped after a while (30 min or 10 cell volumes in this case), the images processed to calculate surface tensions and then flow and image capture resumed to again capture images at higher frequency for a while. This new run is shown with unfilled squares in fig 6.4. This scheme of image capture was followed for all the
washout experiments described below and the consecutive runs are distinguished in the following figures by using filled and unfilled squares.

The surface tension during desorption of \( C_{12}E_8 \) is also compared to the expected equilibrium surface tension at that surfactant dilution in fig 6.4. The Langmuir isotherm is the best fit to experimental data by Lin et al. [1996]. Thus, the figure shows that surface tension during desorption matches the equilibrium surface tension within experimental error. The apparent deviation between 6 to 10 cell volumes is likely due to lack of experimental data in that region. This shows that there is no desorption rate or mass transfer rate limitation, at least on the time scales of washout, for pure conventional \( C_{12}E_8 \) surfactant during surfactant washout.

6.1.2.1 Desorption of other conventional surfactants

Some other conventional surfactants were also tested using the procedure described above. These experiments are shown in figs 6.5 to 6.7. Desorption of another pure surfactant, SDS, is shown in fig 6.5. The initial surfactant concentration (0.5%) was slightly higher than its CMC (0.2%). Hence, for a short while initially the surface tension remained constant till concentration in cell dropped to the CMC and then surface tension increased rapidly to reach \( \sim 73 \) mN/m in 6-8 cell volumes. A fresh bubble created in the solution showed the same surface tension, thus demonstrating that all the SDS molecules had desorbed from the air-water surface.
Fig 6.5: Desorption of SDS from air-water interface
Washout with DI water. Initial concentration = 0.2 w%.

Again, a comparison with the equilibrium surface tension of SDS (Frumkin fit by Lin et al. [2002]) in fig 6.5 shows that there is no observable desorption barrier or significant mass transfer resistance during desorption of SDS from the air-water interface.

The commercial surfactants showed a slightly different behavior. Fig 6.6 shows the washout of 0.5% CS-330 surfactant (in 5% NaCl) with a 5% NaCl solution. This concentration is well above the CMC of CS-330. Hence, initially there was no change in the surface tension of the bubble even as the concentration in the cell was dropping. Only after several cell volumes did the surface tension start increasing. The surface tension
increased rapidly for the next 10 cell volumes but then leveled out around 58 mN/m. Surface tension of a newly created bubble was 72 mN/m, which showed that the reduced surface tension at long times is due to some molecules at the air-water surface that do not desorb rather than due to any surfactant present in solution. This deviation from the surface tension of pure brine may be due to some insoluble impurities present in CS-330 such as long chain alcohols. These would be solubilized in the surfactant micelles at higher concentrations but would remain adsorbed irreversibly on the surface once surfactant concentration dropped below the CMC.

Fig 6.6: Desorption of CS-330 from air-water interface
Washout with 5% NaCl. Initial concentration = 0.5 % in 5% NaCl.
Another commercial surfactant, foamer3 (described in chapter 3), also showed similar desorption characteristics as CS-330, though the surface tension leveled out at a higher value of ~66 mN/m than for CS-330. This is shown in fig 6.7.

![Desorption Graph](image)

**Fig 6.7: Desorption of foamer3 from air-water interface**

Washout with 5% NaCl. Initial concentration = 0.5% in 5% NaCl.

6.1.2.2 Desorption of polymeric surfactants

Desorption of polymeric surfactants was also measured using the above procedure and compared to conventional surfactants. Polymeric surfactants required much longer times to achieve equilibrium surface tensions during adsorption, so the bubble was equilibrated for a longer period of time (at least 20 min) till the rate of change of surface tension was very small, before washout of surfactant was commenced. The desorption of polymeric surfactants is depicted in figs 6.8 to 6.11.
Tri-block copolymers:

Fig 6.8 shows the washout of 0.5% B20-5000 in 5% NaCl with a 5% brine solution. This concentration of B20-5000 is well above its CMC. So, for about 10 to 15 cell volumes, the surface tension hardly increased and then rose slightly before leveling again at 39-40 mN/m. The rate of increase was very slow compared to conventional surfactants observed in the earlier sections. The surface tension increased only by ~ 5-6 mN/m in 25 cell volumes after the surface tension started increasing, compared to, say, 35 mN/m in 6 cell volumes for SDS.

![Graph showing desorption of B20-5000 from air-water interface](image)

**Fig 6.8: Desorption of B20-5000 from air-water interface**

Washout with 5% NaCl. Initial concentration = 0.5 % in 5% NaCl.

Not only is the rate of desorption slow compared to conventional surfactants but the adsorption of polymeric surfactant is also irreversible as indicated by leveling of surface tensions near the end of the experiment around 40 mN/m. In fact, after the
experiment, the bubble was kept in the still solution for 17 hours (equivalent to 340 cell volumes) and the surface tension increased by only about 1 mN/m. This is within the experimental error of the setup, especially considering the changes in bubble size, and represents negligible increase in surface tension over long periods of time. Again, the negligible surfactant presence in the solution was verified by measuring the surface tension of a fresh bubble in the solution as shown in the figure.

Fig 6.9 shows a similar behavior during desorption of Pluronic F108 (0.5% in 5% NaCl) into 5% brine. Surface tension started increasing immediately after washout commenced, indicating that initial concentration was less than the CMC of F108. However, the change in surface tension was very small, in fact, smaller than with B20-5000. The increase in surface tension by only by ~3-4 mN/m in the first 25 cell volumes.

Fig 6.9: Desorption of F108 from air-water interface
Washout with 5% NaCl. Initial concentration = 0.5 % in 5% NaCl.
of washout and even after 40 cell volumes the change in surface tension was less than 6 mN/m.

Desorption of a more hydrophobic triblock copolymer, P85, is shown in fig 6.10. This copolymer also had the lowest molecular wt (4600 daltons) among the Pluronics tested. Starting with a concentration of 0.5% P85 in 5% NaCl, the surface tension did not increase till its CMC was reached and then rose rapidly. Desorption of P85 was still slower than any of the conventional surfactants but was more rapid than that of F108 or B20-5000. Surface tension increased by ~ 8-9 mN/m in about 15 cell volumes and then leveled off around 40 mN/m. Again, when the bubble was kept in the still solution (no flow) overnight for ~14 hours (≈ 280 cell volumes), there was little increase in surface tension (~ 2 mN/m) of the bubble.

![Figure 6.10: Desorption of P85 from air-water interface](image)

Washout with 5% NaCl. Initial concentration = 0.5 % in 5% NaCl.
Hydrophobically modified polymer:

Desorption of the hydrophobically modified HMPA1 (0.5% in 5% NaCl, pH~7) was also measured as shown in fig 6.11. Again, as with the triblock copolymers, the desorption was very slow and surface tension increased by ~9 mN/m in 40 cell volumes and leveled at ~ 41 mN/m.

![Graph showing desorption of HMPA1 from air-water interface.](image)

**Fig 6.11: Desorption of HMPA1 from air-water interface**

Washout with 5% NaCl. Initial concentration = 0.5 % in 5% NaCl, pH~7.

6.1.3 Comparison with foam washout

From the observations in the preceding section and in chapter 4, some conclusions can be drawn regarding the role of desorption of surfactants in foam washout stability (in the screening test, at least). All of the above desorption experiments are summarized in a single plot in fig 6.12. It is clear that there is a marked distinction between desorption of
conventional and polymeric surfactants. Conventional surfactants desorb easily from the air-water surface into the bulk solution and in the case of pure surfactants desorb completely whereas polymeric surfactants adsorb almost irreversibly at the air-water surface. This explains the difference in foam washout stability of conventional and polymeric surfactants seen in chapter 4. When water flows down the plateau border network in bulk foam, conventional surfactant molecules desorb from the air-water interface and transport to the plateau border regions where they are carried away by flowing water leading to foam collapse. Whereas for polymeric surfactants, very few molecules desorb from the interface and the foams are much more stable.

Fig 6.12: Summary of desorption of conventional and polymeric surfactants from air-water interface
Among conventional surfactants, pure reagents like SDS and C_{12}E_{8} desorb completely from the air-water interface. Foam washout times for these two can be related to their time (cell volumes) for desorption. SDS (0.5%) desorbed completely in 6-8 cell volumes (fig 6.5) and foam from SDS washed out in \(~3\) minutes in the screening test. C_{12}E_{8} (0.002%) required about 15 cell volumes to desorb completely (fig 6.4) and foam from C_{12}E_{8} (0.13%) washed out in \(~40\) minutes. Thus for pure conventional surfactants, the more surface active surfactant (i.e. one with higher initial concentration with respect to CMC) takes longer to desorb and also gives higher foam washout time. But commercial foamers like CS-330 and foamer3 do not desorb completely and leave some impurities at the surface. This can also affect their foam washout stabilites in addition to their surface activities. Surface tension of CS-330 (0.5%, \(>100\) times CMC) leveled off in \(~20-25\) cell volumes (fig 6.6) whereas foamer3 (0.5%, \(~20\) times CMC) leveled off in \(~15\) cell volumes (fig 6.7). Their foam washout times were 60 mins and 6 mins respectively. The large number of cell volumes for CS-330 is mainly due to its large concentration with respect to the CMC. Starting from the CMC of CS-330 (see fig 6.6), it required \(~15\) cell volumes to reach the level of \(~57\) mN/m. When a lower concentration of CS-330 closer to CMC was used (0.01%) foam washout time was 40 min. Surface activity cannot explain the difference between this washout time and that of foamer3. One must also consider that even after surfactant desorption, the surface tension of a bubble initially loaded with CS-330 was \(~57\) mN/m whereas for foamer3 it was \(~66\) mN/m. Thus, one also has to take into account the type and amount of impurities adsorbed on the surface too though it is difficult to quantify the effect these impurities will have.
In the case of polymeric surfactants, adsorption of surfactants is almost irreversible and hence foam washout cannot be correlated to time/cell volumes for desorption. In fact, it raises the question – what causes washout of foams made from polymeric surfactants if they do not desorb? The following sections shed more light on this question. Interestingly, it was observed that for the triblock copolymers, foam washout stability can be ordered on the basis of extent of increase and/or rate of increase of surface tension during the desorption experiments. The ranking of surfactants in order of larger (and faster) increase in surface tension is P85 > B20-5000 > F108 and ranking of foam washout times is in the order F108 > B20-5000 > P85. As discussed in next section, this may be because foam washout time in the screening tests for polymeric surfactants relates to the foam film stability and more desorption leads to greater weakening of these foam films.

6.2 Other factors affecting foam washout stability

From the above discussion, it is apparent that desorption alone cannot explain either the washout of foam from polymeric surfactants or the differences in washout stabilities for foam from different polymeric surfactants. Other factors, such as hydrodynamic effects, may influence foam washout too. Influence of other factors on foam washout was investigated using the screening test setup described in chapter 4.

First of all, to determine any influence of flow on foam washout, bulk foam washout with brine was compared with foam washout with surfactant solution in the
screening test. This is shown for conventional SDS and polymeric F108 and P85 in fig 6.13. With flow of surfactant, foam from anionic SDS was seen to be stable for a long time. But foam from non-ionic polymeric F108 and P85 collapsed even with flowing surfactant though it took longer than for foam collapse with brine. This shows that flow itself has an effect on foam collapse. The difference between SDS and other surfactants was intriguing. A more complete picture emerged by varying the flow rate for SDS and F108 as shown in fig 6.14. When surfactant flow rate was decreased to 0.05 ml/min with SDS, foam did eventually collapse. Also, when flow rate was increased with F108 to 11 ml/min, the foam was observed to be stable with flow for a long time. This shows that there is a particular flow rate for each surfactant below which foam collapses even with
surfactant flow. This actually has more to do with foam quality than flow rate. Depending on the flow rate, the foam quality was observed to change – from ~80% gas fraction at 11 ml/min to ~95% at 1 ml/min. Lower the quality of foams, thicker the plateau borders and thicker the foam films. Hence, for foam from SDS the critical film thickness below which foam collapses with flow was lower than that for foam from F108. This leads to the idea that foam stability to flow with surfactant may be related to inherent film stability as foam films from anionic SDS are expected to be more stable than from non-ionic F108. This is evident from the greater foaming efficiency of SDS (chapter 4).

![Graph showing effect of surfactant flow rate on foam collapse](image)

**Fig 6.14:** Effect of surfactant flow rate on foam collapse

Concentrations: SDS = 0.2% in DI water, F108 = 0.5% in 5% NaCl.
Foam washout times with brine were also compared for a few polymeric surfactants with their inherent foam stabilities. One measure of inherent foam stability is the rate of foam collapse of a static (i.e. no external imposed flow) foam column under gravity drainage.

**Fig 6.15 a: Foam washout with brine (5% NaCl)**

Flow rate = 3 ml/min. Concentration = 0.5% in 5% NaCl.

**Fig 6.15 b: Foam collapse under gravity drainage**

Concentration = 0.5% in 5% NaCl.
This is compared in fig 6.15 a & b for F108, P85 and HMPA1. These figures demonstrate that foam washout stability with brine is related to the inherent foam stability in addition to desorption. That is, for conventional surfactants desorption is the dominant effect, whereas for polymeric surfactants inherent film stabilities are more important.

One effect flow can have is generation of surface tension gradients in plateau borders of the foam due to shear of flow. Surface tension gradients in the plateau border will produce gradients in the foam films too. An estimate of surface tension gradients in the plateau borders can be made using the following treatment of Weaire and Hutzler [1999] regarding the geometry and drainage in polyhedral foam. The number of plateau borders \( N_p \) over area of cylindrical tube, \( A_{cyl} \), is given by

\[
N_p = A_{cyl} * l_v
\]  

(6.1)

where \( l_v \) is the edge length per unit volume. For a Kelvin structure (tetrakaidecahedron), it is related to bubble volume \( (V_b) \) as follows

\[
l_v \equiv 5.35/V_b^{2/3}
\]  

(6.2)

The cross-sectional area of the plateau borders \( (A_p) \) is related to the liquid fraction \( (\phi_L) \) by

\[
\phi_L = l_v * A_p
\]  

(6.3)

The observed liquid fraction during washout was \( \sim 5\% \) when liquid flow rate was \( \sim 1-3 \) ml/min. Thus, for a bubble size of \( \sim 1 \) mm, \( N_p \sim 4224 \) and \( A_p \sim 5.9 * 10^{-5} \) cm\(^2\). Assuming a circular cross-section and Poiseuille flow, the estimated shear stress is about 1.9 dynes/cm\(^2\) at 3 ml/min of liquid flow. This will be balanced by the surface tension gradients along the walls of the plateau borders. For a plateau border length \( (L_{PB}) \) of \( \sim 1 \)
mm, the change in surface tension will, thus, be $\sim 0.2$ mN/m. The viscous drag in a plateau border is roughly twice that in a cylindrical pipe, so the change in surface tension will be somewhat higher than above value, especially in the corner regions.

The relation between liquid flow rate and liquid fraction is given by

$$\frac{Q}{A_{cyl}} = \frac{\rho g f \phi_i^2}{150 \mu l_v}$$

(6.4)

where, $f$ is a factor to account for surface mobility, $\rho$ and $\mu$ are the density and the viscosity of the draining liquid respectively. Using liquid fraction of 0.05 and 1 mm bubble diameter, this equation gives the value of $Q \sim 0.6$ ml/min for $f = 1$ (immobile surface) and $Q \sim 3.6$ ml/min for $f = 6$ (value used by Monin et al. [2000]). The experimentally observed flow rates fall in this range and hence, this justifies the applicability of the equations 6.1 to 6.3 to estimate the various flow parameters.

The estimated change in surface tension of $\sim 0.2$ mN/m in plateau border regions due to flow is quite small. In some regions the local flow rates and hence gradients may be higher. But this surface tension variation is still an order of magnitude smaller than surface tension increase observed due to desorption of some of the polymeric surfactant molecules from the air-water interface. Therefore, it is unlikely that flow shear will have a significant influence over foam collapse during washout.

To estimate if the small increases in surface tensions produced by desorption of polymeric surfactants can explain the difference between foam washout stability with brine versus washout stability with surfactant solution, the following experiment was
performed- A bubble was created using a U-shaped needle in a vessel containing surfactant solution and time for the bubble to collapse at the top surface of the liquid in the container was measured. Bubble coalescence times were measured for different concentrations of F108 with equilibrium surface tensions ranging from ~38 to 42 mN/m.

![Bar graph showing coalescence time with different surface tensions](image)

**Fig 6.16: Bubble coalescence time with different surface tensions**

At each concentration, about 10 bubble coalescence events were recorded and the average coalescence time computed. The results are depicted in fig 6.16. In the first two experiments, the top surface was at equilibrium surface tension whereas the bubble surface was aged till rate of surface tension change was very slow (up to ~ 20 min). About 40% reduction in coalescence time was observed when the change in surface tension was from ~38 (0.5% F108) to 42 mN/m (0.02% F108). In the third experiment the bubble surface was not aged and the coalescence time was shorter by 80% for an
estimated bubble surface tension of ~50-55 mN/m. Note that foam washout time with brine was only ~50% shorter than foam washout time with F108 (fig 6.13). In addition, the films in above bubble coalescence experiments are not identical to foam films during washout with brine – aqueous region of foam films will be depleted of surfactant during washout. Hence, it appears quite feasible that the small surface tension changes due to desorption (≤ 6mN/m) can account for this reduction in washout time.

The preceding discussion has shown that there exists a critical capillary pressure \( (P_c^*) \) or film thickness \( (h^*) \), that depends on the surfactant, which determines transition from stable to unstable foam during washout. \( P_c^* \) can be estimated from fig 6.14, equations 6.2 and 6.3 and using the following relations

\[
A_p = 0.161 r^2; \quad P_c = \gamma / r \tag{6.5}
\]

where \( r \) is the curvature of the plateau borders and \( \gamma \) is the surface tension. This gives \( P_c^* \) for SDS as ≥ 193 Pa and \( P_c^* \) for F108 as ≥ 96 Pa. It must be noted that these values are significantly lower than the rupture pressures of greater than 10^4 Pa reported for single films from these surfactant solutions in the literature (Aronson et al. [1994], Khrystov et al. [2001]). However, it is in line with observations by other researchers that bulk foams rupture at much lower capillary pressures than single films (for example, by Monin et al. [2000]). The preceding discussion also demonstrated the dependence of foam washout stability on inherent foam or film stability in the case of polymeric surfactant. In addition, faster foam collapse with brine, compared to foam collapse with flow of surfactant, could be explained by the small increases in surface tension due to desorption.
The above experiments do not explain the mechanism for foam collapse or the shape of washout curve (i.e. increasing rate of collapse with time). In the case of foam under gravity drainage, as the liquid drains from top to bottom through the plateau border network, the films thin under the influence of capillary pressure in the plateau borders. The films are the thinnest at the top of the foam column because of higher capillary pressure at the top. The films thin till some critical film thickness is reached at which point the films rupture. Hence foam collapse propagates from top to bottom of the foam column. As the foam height decreases, the drainage slows down and so does film thinning. Thus the rate of foam collapse decreases with decreasing height, and after a certain height the foam column would be stable for an indefinite time were it not for foam coalescence by gas diffusion. This can be seen in the inherent foam stabilites depicted in fig 6.15 b.

On the other hand, in the case of foam washout, liquid flows down the plateau border network of the foam column under an externally applied flow rate (forced drainage). Under steady drainage, it can be shown that liquid fraction at any cross-section is the same throughout the column height [Verbist et al., 1996]. This has also been observed in experiments of forced drainage [Carrier and Colin, 2003; Monin et al., 2000]. Assuming monodisperse bubbles and negligible foam collapse, the capillary pressure in the plateau borders can thus be assumed uniform throughout the foam height. Hence films will thin under the same capillary pressure throughout and reach the same film thickness at equilibrium. This can explain why at higher flow rates (as with F108 and SDS), when the equilibrium film thicknesses are large enough, foam is stable indefinitely.
(fig 6.14), in theory. Below a critical flow rate corresponding to some critical film thickness, the films are more susceptible to rupture perhaps due to the mechanical perturbations of falling drops or flow of liquid. But, it does not explain why the foam collapses from top to bottom or why the rate of collapse increases with time.

One important factor is the coarsening of foam over time. It had been observed that foam bubble (polyhedral cells) sizes increased over time during washout, from ~1 mm initially to ~3-4 mm after 2 hours, presumably by gas diffusion (but could be by foam coalescence). The effect of bubble size on foam washout stability was determined by measuring the washout of foam made of larger bubble sizes. Foam was generated by passing air through a 60-mesh screen to produce bubbles of 2-3 mm initial size. Fig 6.17 compares the foam washout with brine for foam from F108 for the two different bubble sizes. It is clear that larger bubble sized foam collapses faster and this can explain the increasing rate of collapse with time. In addition, due to increasing bubble size, the same frequency of film collapse will lead to a larger rate of foam volume collapse.

Increasing bubble size could potentially lead to larger increase in surface tensions in the upstream part of a plateau border due to surface tension gradients produced by shear. But this increase is still too small (~ 0.6-0.8 mN/m after 2 hours) to account for any significant change. Also, from equations 6.2 to 6.5, it can be shown that for a given flow rate, $\phi_L \propto (L_{PB})^{-1}$ and $A_p \propto L_{PB}$ (or $P_c \propto (L_{PB})^{-1/2}$). That is, with increasing bubble size (increasing plateau border length, $L_{PB}$), the liquid fraction decreases but the plateau border area increases and hence capillary pressure decreases. Thus, this should lead to
thicker films (in the stable region of disjoining pressure curve, where $d\Pi/dh$ is negative; see section 2.3.2) with coarsening of foam which, if anything, will be expected to be more stable.

![Graph showing foam washout as a function of bubble size and flow mode](image)

Fig 6.17: Foam washout as a function of bubble size and flow mode
Washout of foam from F108 (0.5% in 5% NaCl) with brine (5% NaCl) at 3 ml/min. ‘1 mm, drop-wise’ refers to foam of initial bubble size of $\sim$ 1 mm and washout with brine flowing drop-wise.

Hence, non-equilibrium factors must be of importance in explaining the decreased stability of larger bubble-sized foam. The role of falling drops of liquid is essential in explaining this behavior. In the foam washout experiments described so far, liquid (water or surfactant) was injected drop-wise from the top of the foam column. The mechanical disturbances produced by these drops hitting the foam column may contribute to foam collapse. A comparison was made of foam washout when liquid was injected as falling
drops and when liquid flow was along the glass wall. This is also shown in fig 6.17 for washout of F108 with brine. It can be observed that the rate of foam washout is reduced significantly when water flows along the wall before entering the foam column. In the experiment where foam bubble sizes were ~ 2-3 mm, when flow was switched for a while to falling-drops mode the rate of foam collapse increased appreciably. This demonstrates that the mechanical perturbations produced by the falling drops are an important cause of collapse of foam from polymeric surfactants and when these perturbations are minimized, foam from polymeric surfactants are stable to washout with brine for a long time even at low flow rates. In addition, in fig 6.17 there does not appear to be significant difference in rate of foam collapse for different bubble-sized foam when flow was along the sidewalls. This indicates that foam of larger bubble sizes is more susceptible to collapse with the perturbations produced by the falling drops than foam of smaller bubble sizes and this can explain the faster foam collapse of foam with time during washout.

6.3 Foam washout with surfactant in sand pack

In view of the observation of foam collapse with surfactant flow in the screening test, one may wonder if factors other than desorption may be responsible for foam collapse in the sand pack too. There was some indication of foam collapse in the first section during surfactant flow even before washout with water was commenced in the experiments described in chapter 5 (for example, figs 5.10a and 5.11a). Foam washout with surfactant was tested with triblock copolymer B20-5000 in the sand pack and is shown in fig 6.18 a & b.
Fig 6.18 a: Foam generation with B20-5000 in 2-ft sand pack

Fig 6.18 b: Foam washout with surfactant solution (0.5% B20-5000, 5% NaCl)
Fig 6.18a shows foam generation using the procedure described in chapter 5. Foam with average MRF of ~80 was generated in the pack and this was followed by injection of surfactant solution. Fig 6.18b shows that even with surfactant flow the foam washes out in 15-17 PV. This is a similar number of PV as for foam washout with brine in chapter 5 (fig 5.7b) indicating that factors other than desorption are responsible for foam washout. Thus, as with bulk foam, flow has an effect on foam washout in porous media. But the foam structure in porous medium is quite different from that of bulk foam and the mechanism for foam collapse is also expected to be different. An evidence of this is that while washout time of bulk foam from polymeric surfactants in the screening test does not depend on water throughput, the foam washout in the sand pack is, to a large extent, a function of water throughput and not time. For example, washout time for F108 foam in screening test was ~150 min for water flow rates ranging from 2 to 9 ml/min, i.e. 370 to 1350 ml of throughput (see sec 4.2.1). On the other hand, for B20-5000 foam in sand pack, the PV for washout ranged only between 16 to 22 PV when average flow rate ranged from 300 ft/day to 6 ft/day respectively (see figs 5.7 and 5.10). The actual time for washout in this case ranged from <1 day (16 PV) to ~3 days (22 PV).

To test if inherent foam stability has any role in foam washout in the sand pack, as in the screening test, washout of foam from CS-330 (which forms very stable foam films) with the surfactant solution was compared with washout of B20-5000. The foam generation and washout of foam from CS-330 is shown in fig 16.19 a & b. Fig 16.19b shows that foam washes out in ~16 PV of surfactant throughput. This is comparable to
that observed with B20-5000 in the previous figure and does not indicate any apparent
relation between inherent foam stability and foam washout in sand pack. Of course, the
CS-330 surfactant PV for washout was more than PV of brine for washout (\sim 10), unlike
that with B20-5000, which confirms that desorption of surfactant is primarily responsible
for foam collapse with brine for foam from CS-330.

The group of Rossen at University of Texas had earlier observed slow foam
collapse during liquid flow [Zeilinger et al., 1995; Kibodeaux et al., 1994] in their studies
of foam diversion process for matrix acidization. They attributed this to dissolution of
nitrogen from foam into the flowing liquid. Hence, gas dissolution as a possible reason
for foam washout was explored. At 1 atm and 25 °C, solubility of air in water is 0.017
ml/ml. With 70% gas saturation in pack before washout, the PV of water to dissolve air in
the foam would be 0.7/0.017 = 41 PV (see appendix C for a more rigorous theoretical
analysis). For washout of 3 sections only, PV required would be \sim 31 PV. This
calculation ignores the effects of pressure change in the pack (not insignificant). While
the liquid (brine or surfactant solution) injected into the pack is expected to be saturated
with air at atmospheric pressure, the liquid would be under-saturated at the inlet pressures
in the washout experiments (\sim 2-3 atm). So, it is quite conceivable that gas dissolution can
explain foam washout observed in the sand pack even with flow of surfactant solution.
Fig 6.19 a: Foam generation with CS-330

Fig 6.19 b: Foam washout with surfactant solution (0.5% CS-330, 5% NaCl)
The role of gas dissolution was tested in the experiment shown in fig 6.20 a & b. After foam generation with CS-330, surfactant solution was injected at 6 ft/day as before. But this time, air was co-injected at a slow rate in order to saturate the liquid with air before it entered the pack. Initially, air fraction was ~0.017 ml/ml of water (Note: the increased solubility and the reduced volume at higher pressures tend to cancel each other. So, solubility can be considered to be ~0.017 ml/ml irrespective of the pressure). Air bubbles were seen entering the pack occasionally, so air fraction was decreased to ~0.007 ml/ml later on. Fig 6.20b shows that foam washout is much slower than in fig 6.19b. In fig 6.19b, foam from first section washes out in ~3-4 PV whereas in this case only ~30% MRF reduction in first section is observed even after 5-6 PV. The liquid injected is still suspected to be undersaturated and may explain the slow foam collapse. Air injection was stopped around 8.3 PV. This led to an increase in the washout rate. This is quite clear in the rapid washout of foam in section 2 after a while. This rate of collapse was comparable to that observed in fig 6.19b confirming that gas dissolution was responsible for this behavior. Again around the 15.5 PV mark, air was co-injected to saturate the water entering the pack. This time a slightly higher rate (air fraction of 0.017 ml/ml of water) was used to make sure that liquid was saturated. A slight increase in the pressure drop in section 1 occurred because of some air entering into the pack during equalizing of pressures in the air and the liquid lines. Thereafter, almost no foam collapse was observed for next 4 PV of liquid injection.
The above observations prove that this foam collapse during surfactant flow was mainly due to gas dissolution. The gradual increase in pressure drops in downstream sections during flow can be explained by supersaturation of liquid with air at the lower downstream pressures, which causes some air release. This also explains why foam in 4th section was difficult to washout for foams from polymeric surfactants (chapter 5) – at exit pressures, the flowing liquid will always be saturated, if not super-saturated, with air and no foam collapse by dissolution is expected. Gas dissolution puts an upper bound on PV for foam washout. For foams from polymeric surfactants that do not desorb much from an air-water interface, such as F108, B20-5000 and HMPA1, throughput of brine for
washout was in the range 16 to 25 PV. This indicates that gas dissolution rather than desorption was the controlling factor in foam washout with these polymeric surfactants.

![Graph showing MRF vs PV for different sections with air injection](image)

**Fig 6.20 b: Foam washout with surfactant solution saturated with air**

This finding also shows the importance of the gas that is used to generate foam. Assuming incompressible gas (reasonable at field pressures), the pore volumes for foam dissolution into flowing water containing no dissolved gases is given by the following expression (see appendix C for derivation):

\[
PV = 1 + S_g \left(0.018 \frac{H}{RT} - 1\right)
\]
where, \( S_g \) is the initial gas saturation and \( H \) is the Henry's constant for the gas. Hence, if methane is used instead of nitrogen, the foam will wash out faster (about twice as fast) because of higher solubility of methane (at 25 \(^{\circ}\)C, \( H(\text{CH}_4) = 4.13 \times 10^4 \) atm, \( H(\text{N}_2) = 8.65 \times 10^4 \) atm). Also, in the above expression, PV for foam washout is independent of pressure as long as Henry's law is applicable. So, reservoir pressure is not expected to affect the PV for foam washout. In many real reservoirs, the produced water contains some dissolved hydrocarbon gases that will reduce the dissolution of gas into flowing water and extend - sometimes greatly - the foam lifetime.

The following chapter looks at the polymeric surfactants' foam stability to residual and flowing oil that are important considerations for oilfield applications. In addition, the scale-up of foam washout times to reservoir geometries is evaluated.
CHAPTER 7
DEVELOPING FOAM FOR OILFIELD APPLICATION

The earlier chapters showed that foam stable to washout can be produced using polymeric surfactants. Chapter 5 showed that it is possible to generate stable foam in porous media using some of these polymeric surfactants such as Pluronic F108. This chapter explores the suitability of these polymeric surfactants in oilfield reservoirs with respect to a critical consideration – presence of oil in the reservoir. The water producing regions of the reservoir near the producing well are expected to contain oil at residual saturations. So, foam stability to residual amounts of oil is desired. Also, for effective treatment, the foam placed in the oil producing regions of the reservoir should collapse with flowing oil when the well is brought back to production after treatment. The following sections describe the stability of foam from various polymeric surfactants to oil and a way to improve the foam stability of Pluronic surfactants. Another aspect that is explored is how the foam washout time would scale-up from 1-D sand pack experiments (chapter 5) to the radial geometry in a field. This is described in section 7.4.

7.1 Effect of residual oil on foam stability

To test the foam stability to residual oil in porous medium, a short sand pack setup was constructed. This was done to cut down on the long periods of time that would have been required to test various surfactants in the 2-ft long pack.
Fig 7.1 shows the schematic of the short porous medium apparatus, hereafter referred to as the short pack arrangement. The porous medium consisted of an approximately 1.5 inch long and about 0.5 inch diameter cylinder (from a Swagelok filter body) packed with 50-mesh size sand. Pore volume in the short pack was approximately 5 ml. Foam was generated by co-injecting air and surfactant from the bottom of the pack. Surfactant was injected using an Isco pump (model 2350) and air was injected from the lab air source through a pressure regulator. The other end of the pack was connected to a 50-inch long, 1/8-inch diameter plastic (semi-transparent) tubing that allowed observation of the texture of foam exiting the pack. Two pressure transducers measured the injection
pressure to the sand pack and the pressure drop across the tubing. The difference of the injection pressure and the pressure drop across the tubing gave the pressure drop across the pack. Foam quality, i.e. air fraction, was measured by passing foam from the tubing through an inverted burette containing isopropanol-water mixture which collapsed the foam. The ratio of the volume of air collected to the amount of liquid displaced gave the quality of foam. The surfactant injection rate was fixed at 1 ml/min (~25 ft/day) and the air rate was manipulated using the pressure regulator to obtain a foam quality (gas fraction) of 80% at the outlet.

The pressure drop across the pack for a given foam quality is then a measure of the foamability of the surfactant solution in the porous medium. This is because good foamers will produce more foam lamellae per unit length and will offer more resistance to foam flow than poor foamers. Fig 7.2 shows a typical experimental run for foam generation using F108 in the short pack. Surfactant flow rate was constant at 1 ml/min and air flow rate was manipulated by changing the injection pressure of air using a pressure regulator. The figure shows the injection pressure and the pressure drop across the tube as the air pressure was increased stepwise. Foam quality was measured at the outlet at various steps after steady state was achieved. Eventually, when the injection pressure was 30 psi and pressure drop across tubing was 8 psi, 80% foam quality was observed. Thus the corresponding pressure drop across the pack was 22 psi. This method was used to determine the foam stability to residual oil by comparing the pressure drop across a pack containing residual oil to a pack containing no oil. To prepare the pack at residual oil saturation, the water-saturated pack was first flushed with oil (hexadecane).
The pack was then flushed with water and surfactant solution to achieve residual oil saturation (~30%) in the pack. Foam was then generated by co-injecting air and surfactant so as to obtain 80% foam quality at the outlet. The pressure readings of the transducers were recorded and compared with foam generation experiments without any oil in the pack. Table 7.1 compares the pressure drop for several surfactants across the short pack with residual amounts of hexadecane to packs in which no oil was present.
Table 7.1: Foam stability at residual oil saturation in the short pack

<table>
<thead>
<tr>
<th>Surfactant</th>
<th>Pressure drop across short pack (psi) at 80% quality</th>
<th>No oil</th>
<th>Residual hexadecane</th>
</tr>
</thead>
<tbody>
<tr>
<td>F108 (0.5%, 5% NaCl)</td>
<td></td>
<td>22</td>
<td>2</td>
</tr>
<tr>
<td>B20-5000 (0.5%, 5% NaCl)</td>
<td></td>
<td>18</td>
<td>2</td>
</tr>
<tr>
<td>CS-330 (0.5%, 5% NaCl)</td>
<td></td>
<td>20</td>
<td>20</td>
</tr>
<tr>
<td>SDS (0.5%)</td>
<td></td>
<td>22</td>
<td>18</td>
</tr>
</tbody>
</table>

It can be seen from the table that foam from CS-330 was much more stable to residual oil than foam from triblock F108 or B20-5000. In the case of the triblocks, when air and surfactant were co-injected through the pack hardly any foam was produced and mostly slugs of air and surfactant solution were seen exiting the pack. This showed that foam from anionic CS-330 was significantly more stable than from non-ionic F108 or B20-5000. To test whether ionic surfactants produce more stable foam with oil, foam stability to oil was tested with another anionic surfactant SDS (without salt). Table 7.1 shows that foam from SDS is indeed quite stable to residual oil. This demonstrates that, in general, foam from anionic surfactants is more stable in presence of oil than foam from non-ionic surfactants (as observed earlier by Zhang et al. [2003] for bulk foam).

To understand this further, the entering (E), spreading (S) and bridging (B) coefficients (see chapter 2) were calculated for the different surfactant systems and are listed in table 7.2. The interfacial tensions were measured using the pendant drop/bubble apparatus described in section 6.1. The entering, spreading and bridging coefficients are all positive for the surfactants listed in the table indicating a strong likelihood of foam destabilization with oil according to thermodynamic considerations. The E, S and B
values for F108 and B20-5000 are comparable to that of SDS. Thus the reason foam from SDS is more stable to oil must be due to the ionic charge of SDS. The presence of anionic surfactant at the air-water and oil-water interfaces can provide an additional kinetic barrier for the entry of an oil droplet through the air-water interface that is not included in the thermodynamic quantity E and thus is capable of producing stable foam films. The E, S and B values for CS-330 are smaller than for SDS and the triblocks, but they still are all positive. CS330-hexadecane interfacial tension was also smaller by about a factor of 10 than for other surfactant-hexadecane interfaces which means more oil may be displaced by the CS-330 solution than others (capillary number \( \sim 5 \times 10^4 \)). But this was not observed to be a very significant factor in the long sand pack experiments (described later). In those experiments, very little additional oil was produced when CS-330 solution was flowed through a pack that was earlier brought to residual oil saturation with water. Hence, foam from CS-330 must also be stable to oil because of the ionic charge of the surfactant at the interface.

Table 7.2: Entering, spreading and bridging coefficients

<table>
<thead>
<tr>
<th>Surfactant</th>
<th>( \gamma_{a-w} )</th>
<th>( \gamma_{o-w} )</th>
<th>( \gamma_{o-a} )</th>
<th>E</th>
<th>S</th>
<th>B</th>
</tr>
</thead>
<tbody>
<tr>
<td>F108</td>
<td>37.2</td>
<td>6.9</td>
<td>23.5</td>
<td>20.6</td>
<td>6.8</td>
<td>879.2</td>
</tr>
<tr>
<td>B20-5000</td>
<td>33.7</td>
<td>5.2</td>
<td>23.5</td>
<td>15.4</td>
<td>5.0</td>
<td>610.5</td>
</tr>
<tr>
<td>CS-330</td>
<td>28.0</td>
<td>0.5</td>
<td>23.5</td>
<td>5.0</td>
<td>4.0</td>
<td>232.0</td>
</tr>
<tr>
<td>SDS</td>
<td>36.8</td>
<td>4.8</td>
<td>23.5</td>
<td>18.1</td>
<td>8.5</td>
<td>825.0</td>
</tr>
</tbody>
</table>

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.

\[
E = \gamma_{a-w} + \gamma_{o-w} - \gamma_{o-a} \\
S = \gamma_{o-w} - \gamma_{o-a} \\
B = \gamma_{a-w} + \gamma_{o-w} - \gamma_{o-a}
\]

Note: the surface tension of hexadecane was lower than literature value of around 26 mN/m. But similar values were obtained by two methods – spinning drop and pendant drop. Thus the oil may contain some impurity.
7.2 Improving foam stability to residual oil

One way to develop foam stable to residual oil would be to use an anionic polymeric surfactant. Unfortunately, the anionic polymeric surfactant that looked good in the washout tests, HMPA1, was not a very good foamer in the sand pack. Another way would be to mix non-ionic and anionic surfactant. A mixture of F108 and CS-330 was studied for this purpose.

The mixture should also produce foam with good washout stability in addition to foam stability to residual oil. One concern was that the low molecular wt. CS-330 would adsorb rapidly at the air-water surface preventing adsorption of F108. Thus, to determine the minimum amount of CS-330 required to produce stable foam with residual oil, the mixtures were first tested in the short pack. The F108 concentration was fixed at 0.5% in all formulations. Fig 7.3 shows the results for three mixtures containing 0.01%, 0.1% and 0.5% CS-330. Foam stable to oil was generated at CS-330 concentrations of 0.1% and 0.5%. At 0.1%, the time required for stable foam to be generated was longer, indicating lower oil tolerance than at 0.5%. Later, it was observed that the formulation with 0.1% CS-330 was not as stable as the one with 0.5% in the longer sand pack (2-ft) experiments. This shows that a large amount of CS-330 (compared to its CMC of <0.01%) is required to develop foam stable to oil.
CS-330 at 0.01% is a poor foamer itself even without oil (produced a pressure drop of ~ 8 psi compared to a pressure drop of ~ 20 psi for CS-330 at ≥ 0.1%) and can account for the lower pressure drop across the pack with residual oil at that concentration. But the large amount of CS-330 required (> 0.1%) can be explained by the aggregation of CS-330 on the F108 molecules in the bulk solution which reduces the amount available at the surface. Hecht and Hoffmann [1994] have observed aggregation between a Pluronic F127 (70% EO, MW = 12,600) and SDS (or C_{16}TAB) with about 6 molecules of SDS per molecule of F127 in the aggregation complex for 1-5 wt% of F127 in solution. CMC of SDS increased by about an order of magnitude when only 0.001 wt% F127 was present. The complex was not as surface active as SDS and increased the surface tension at
intermediate concentrations of SDS. One would expect similar aggregation behavior between F108 and CS-330. This was proved by comparing the surface tension of 0.01% CS-330 (> CMC) with a mixture containing F108. The surface tension of 0.01% CS-330, 5% NaCl solution was 28 mN/m whereas that for 0.01% CS-330 + 0.5% F108 mixture in 5% NaCl was 35 mN/m even after 15 min - confirming complexation between the F108 and CS-330 in solution and thus, a lower concentration of CS-330 monomer in solution.

Next, foam washout time was measured in the screening test for the F108+CS-330 mixtures to find out what effect the large concentration of CS-330 would have on the washout stability. Comparison of the washout time of 0.5% CS-330 + 0.5% F108 mixture with that other mixtures with smaller quantities of CS-330 is shown in table 7.3. The table shows that washout time is hardly affected even when a large quantity of CS-330 is present. This indicates that sufficient amount of F108 is able to adsorb at the air-water surface even in the presence of large concentration of CS-330 so as to produce foam with high washout stability. This was proved by observing desorption of the mixture from an air-water interface.

<table>
<thead>
<tr>
<th>Surfactant</th>
<th>Washout time with 5% NaCl (3 ml/min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5% F108, 0.5% CS-330, 5% NaCl</td>
<td>161 min</td>
</tr>
<tr>
<td>0.5% F108, 0.01% CS-330, 5% NaCl</td>
<td>168 min</td>
</tr>
<tr>
<td>0.5% F108, 5% NaCl</td>
<td>160 min</td>
</tr>
</tbody>
</table>
Fig 7.4 shows the desorption of the 0.5% F108 + 0.5% CS-330 mixture from the surface of a air bubble as a function of cell volumes replaced, using the pendant bubble setup described in the previous chapter. It is also compared with desorption of CS-330 and F108 individually. The surface tension of the mixture initially matches that of 0.5% CS-330. On replacing the surfactant solution surrounding the bubble, the surface tension does not change till the CMC of CS-330 is reached. At that point the surface tension rises rapidly because of desorption of CS-330 and plateaus at a value in between that of F108 and CS-330. This shows that some amount of F108 that is less than when only F108 is present in solution adsorbs at the interface and this adsorbed amount of F108 (plus insoluble impurities from CS-330) is sufficient to produce foam with good washout resistance.

![Graph showing desorption of F108 + CS-330 from an air bubble surface.](image)

*Fig 7.4: Desorption of F108 + CS-330 from an air bubble surface*
Finally, this mixture was tested for foam generation and washout in the 2-ft sand pack as shown in figs 7.5 a & b. To prepare the pack at residual oil saturation, oil was first flowed through a water-saturated pack till oil was produced at the exit. The oil saturation at this point was ~80%. Then water was injected to displace most of this oil and finally a residual oil saturation of ~25% was obtained. Then foam was generated in the pack by alternating injection of air and surfactant at 12 ft/day into the pack as shown in fig 7.5a. It required about 5 cycles to reach MRF of 100 compared to 4 cycles with F108 and 3 cycles with CS-330 (and at lower rate of 3 ft/day) when no oil was present. Hence it proves that the mixture of F108 and CS-330 can produce a strong foam with residual oil in the long sand pack, though the foam stability may be slightly reduced. Final trapped air saturation was only ~49% compared to ~70% air saturation obtained at MRF of 100 when no oil was present. This indicates that the oil saturation in the pack is about 70 - 49 = 21%. Thus, this shows that foam does not displace most of the residual oil in the pack but instead air is trapped in the pores not occupied previously by oil.
Fig 7.5a: Foam generation with residual oil in the pack for F108+CS-330 mixture

Fig 7.5b: Foam washout with 5% NaCl
The foam generation step was followed by brine injection to measure the PV for foam washout (fig 7.5b). It required about 18-19 PV to complete the washout. This was only slightly less than for F108 alone (about 21-25 PV) when no oil was present. This result was also compared with foam washout for CS-330 when residual oil was present as shown in figs 7.6 a & b. Sand pack was prepared at residual oil saturation as described before. Again, it required 5-6 cycles to generate strong foam in the pack. This foam washed out in ~10 PV of brine injection. This shows that foam from F108+CS-330 is more stable to washout than foam from CS-330 even in presence of residual oil.
Fig 7.6a: Foam generation with residual oil in the pack for CS-330

Fig 7.6b: Foam washout with 5% NaCl
7.3 Effect of flowing oil

As mentioned earlier, foam should be unstable in oil producing zones, where oil is flowing. Foam stability to flowing oil was first tested using the screening test setup. After generating foam, oil, instead of water, was injected from the top through the foam column and time for foam collapse was recorded. When oil was injected from the top it formed a thin layer at the top above the foam column and then flowed through a few channels to the bottom of the column. Because of its non-wetting nature, the horizontal distribution of oil was not uniform during flow. In any case, foam collapse was observed to be quite rapid compared to collapse with flowing water. This can be seen in table 7.4 for foam from CS-330, F108 and the combination of the two. Foam collapsed in a matter of minutes with flowing oil. Thus, during flow of oil, because of the positive E, S, and B coefficients, oil was able to penetrate the air-water interface and collapse foam by spreading or bridging mechanism even though the foam was stable to small amount of trapped oil (residual oil). It is possible that the flowing oil depletes the available CS-330 molecules by partitioning of the surfactant into the oil and thus reducing the electrostatic barrier. Flowing oil may also supply mechanical energy to overcome the kinetic barrier for entry of oil into the air-water surface. In any case, this shows that foam stability to oil is dependent on the quantity of oil present as has been reported in the literature [Wasan et al., 1994; Schramm, 1994 a].
Table 7.4: Foam stability to flowing oil in the screening test

<table>
<thead>
<tr>
<th>Surfactant</th>
<th>Foam collapse time with hexadecane (3 ml/min)</th>
<th>Washout time with 5% NaCl (3 ml/min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5% F108, 5% NaCl</td>
<td>3 min</td>
<td>160 min</td>
</tr>
<tr>
<td>0.5% CS-330, 5% NaCl</td>
<td>3.5 min</td>
<td>60 min</td>
</tr>
<tr>
<td>0.5% F108, 0.5% CS-330, 5% NaCl</td>
<td>6 min</td>
<td>161 min</td>
</tr>
</tbody>
</table>

However, when oil was injected into a porous medium in which foam was present, emulsification of oil was encountered. One may expect some emulsion formation when oil is injected in a porous medium because of oil droplet generation from a process similar to that of bubble generation. However, the emulsion produced was observed to be very stable and produced extremely large resistance to flow of oil. This can be seen in figs 7.7a and b where F108 + CS-330 mixture (0.5% F108, 0.5% CS-330, 5% NaCl) was used.

In this experiment, foam was generated only in the first section of the pack before oil was injected to simulate oil flow back in a well. This was due to the fact that in an earlier experiment, when foam was generated throughout the pack, the injection pressure for oil flow became too high to inject oil even at extremely low rates. Foam was generated only in the first section (fig 7.7 a) by injecting air and surfactant alternately. MRF of ~ 90 was obtained in the first section. Oil (hexadecane) injection was started after foam generation in the pack as shown in fig 7.7 b. The injection pressure rose
rapidly on injecting oil and injection rate had to be decreased several times to keep the pressure within limits of the syringe pump. Shear thinning behavior was observed due to presence of air and/or emulsion in the pack. The MRF in the first section was \( \sim 1690 \) near the end of the experiment. Since viscosity of hexadecane is \( \sim 3 \) cP, the resistance factor to flow of oil was \( \sim 560 \) at 0.12 ft/day. That this huge resistance to flow was due to the emulsion formed in the pack was confirmed when eventually a very viscous oil-in-water emulsion was produced at the exit. The collected emulsion layer was also observed to be stable for months, at least.
Fig 7.7a: Foam generation in section 1 of 2-ft sand pack with F108+CS-330

Fig 7.7b: Oil flow in sand pack containing foam
The experiment shows that the F108 + CS-330 mixture which is a good foamer is also a very good, if not better, emulsifier. When a mixture of this surfactant solution with an equal volume of hexadecane was shaken in a glass vial (called the shake test from here on) it produced a very stable oil-in-water emulsion by emulsifying all of the oil in the vial. The viscosity of the emulsion produced by shaking was ~500 cP at a shear rate of 5 s\(^{-1}\) and did not coalesce even after several months similar to the emulsion produced from the sand pack. This is undesirable since, the surfactant injected to produce foam would block the flow of oil too in an oil field due to emulsion formation.

It has been observed in the literature that the macro-emulsion stability is related to the equilibrium phase behavior of the oil + water + surfactant system [Baldauf, Schechter et al., 1982; Aveyard et al., 1991]. Depending on the hydrophile-lipophile balance (HLB) of the surfactant, one observes an oil-in-water microemulsion (Winsor I system) at high HLB, water-in-oil microemulsion (Winsor II system) at low HLB, and a 3-phase system (Winsor III) at intermediate HLB values. Rate of emulsion coalescence has been observed to increase as one approaches the 3-phase boundaries. Dramatically higher rates of emulsion coalescence have been observed at the intermediate HLB values (Winsor III system). Hence, by changing the HLB of the system to near Winsor III type system, one may reduce the emulsion stability.

One way of changing the HLB of the system is to add salt to make surfactant more lipophilic. The salinity which produces a middle layer microemulsion, i.e. a Winsor III system, is called the optimal salinity. When additional NaCl was added to the F108 +
CS-330 system, the system was found to be Winsor I even with 20% NaCl and formed a very stable oil-in-water macro-emulsion in a shake test with hexadecane (fig 7.8) – indicating a very hydrophilic surfactant (indeed, the reported HLB value of F108 is 25). When, instead of NaCl, the system was saturated with CaCl$_2$ ($\sim$36%) to shift the system closer to optimum, the macro-emulsion stability decreased significantly as observed by the much faster rate of coalescence of emulsion – after a few hours only a thin layer of emulsion was observed near the water-oil interface. This can be seen from the photo in fig 7.8. However, at such high salinities the foam stability of the surfactant solution was also very poor as was observed by shaking the solution and in short pack experiments.

Fig 7.8: Phase behavior of F108+CS-330 and hexadecane with
(a) 5% NaCl – Winsor I, top layer is a stable macroemulsion
(b) 20% NaCl – Winsor I, still stable macroemulsion
(c) 36% CaCl$_2$ – Winsor I, very thin macroemulsion layer
In addition to the hydrophilic surfactant system (CS-330+F108), the high carbon number of the oil used (hexadecane) was probably also responsible for the high salinities required to reach optimum. It has been observed that higher the alkane or the equivalent alkane carbon number (EACN) of the oil, higher the optimum salinity (For example, by Puerto and Reed [1982]). Most crude oils have EACN of less than 12. Hence the phase behavior of the system with 20% NaCl was also observed with octane instead of hexadecane as the oil as shown in fig 7.9. The stability of the emulsion had decreased compared to the case where hexadecane was used, though the system was still Winsor I. When toluene (EACN = 0) was used, indeed a Winsor II system was produced at 20% NaCl, which proved that higher EACN of hexadecane was partly responsible for the high optimal salinity. This indicates that for some oils with EACN lower than 16, the system will be closer to Winsor III and emulsion stability would be lower with the surfactant used.

Another way to shift the system closer to optimum is by using a more lipophilic anionic surfactant instead of CS-330 to mix with F108. TDA-4PO (ammonium salt of a branched C_{13\text{-}}(PO)_{4\text{-}}SO_{4}^{-}) by itself had an optimum salinity between 10-15% NaCl with hexadecane. When it was mixed with F108 at 20% NaCl, again rapid coalescence of emulsion was found and almost all the emulsion coalesced in a few hours. This system is also shown in fig 7.9. But even this surfactant combination was found to be a poor foamer at 20% NaCl. A similar behavior at 20% NaCl was observed when another lipophilic surfactant, AOT (sodium bis(2-ethylhexyl)-sulfosuccinate) with a double carbon chain, was used instead of TDA-4PO.
In summary, it was observed that shifting the surfactant system closer to Winsor III for the oil used increases emulsion coalescence rate. Only increasing the salt concentration did not produce a Winsor III system. In addition, a more lipophilic surfactant (than CS-330) or lower EACN oil (than hexaecane) had to be used which led to decreased emulsion stability. But since F108 is so hydrophilic, a large amount of salt was still required which affected foam stability adversely. Hence another polymeric surfactant that is more lipophilic than F108 may be required to produce stable foam but a less stable emulsion with oil.

**Fig 7.9: Phase behavior of systems containing 20% NaCl**
(a) F108+CS-330 with hexadecane – Winsor I, stable macroemulsion
(b) F108+CS-330 with octane – Winsor I, reduced macroemulsion stability
(c) F108+TDA-4PO with hexadecane – Winsor I, no emulsion
(d) F108+AOT with hexadecane – Winsor I, thin macroemulsion layer
Many of the systems described above in the phase behavior/shake tests were also evaluated for emulsion stability in the 2-ft long sand pack. Since the emulsion was produced because of the surfactant and not because of the foam itself, for simplicity, the flow resistance due to emulsion was measured without any foam in the pack. Surfactant was injected to saturate section 1 of the pack, and this was followed by oil injection into the pack. The resistance to oil flow (i.e., MRF divided by oil viscosity) in only the first section was monitored to save time. It was observed that the resistance to flow increased linearly till about a pore volume of oil was injected after which it leveled out at a certain level. The experiments are summarized in fig 7.10 and the results tabulated in table 7.5. These results match very well with the observations made from the simple shake tests.
Fig 7.10: Resistance to oil flow in 2-ft sand pack for various surfactant-oil systems

Table 7.5: Resistance to oil flow due to emulsion formation with various surfactants

<table>
<thead>
<tr>
<th>Surfactant</th>
<th>Salt</th>
<th>Oil</th>
<th>Resistance factor to oil flow</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5% F108 + 0.5% CS-330</td>
<td>5% NaCl</td>
<td>hexadecane</td>
<td>128</td>
</tr>
<tr>
<td>0.5% F108</td>
<td>5% NaCl</td>
<td>hexadecane</td>
<td>45</td>
</tr>
<tr>
<td>0.25% F108 + 0.25% CS-330</td>
<td>20% NaCl</td>
<td>octane</td>
<td>43</td>
</tr>
<tr>
<td>0.25% F108 + 0.25% CS-330</td>
<td>36% CaCl₂</td>
<td>hexadecane</td>
<td>9</td>
</tr>
<tr>
<td>0.25% F108 + 0.25% TDA-4PO</td>
<td>20% NaCl</td>
<td>hexadecane</td>
<td>2</td>
</tr>
</tbody>
</table>
Another approach – process modification

It is clear from the above discussion that reducing emulsion formation without affecting foam stability is difficult for oils with high EACN using the very hydrophilic polymeric surfactant F108. Another approach was tried to reduce the problem of emulsion formation with oil. Since the presence of surfactant is the reason for strong emulsion formation, if the surfactant is removed or at least minimized in the foam regions before oil comes in contact with the foam, then the emulsion formed won’t be very stable. Flushing the foam region with brine for a while will remove most of the surfactant in the foam regions except for that present in foam films. To do this would require a change in the foam application process in the reservoir. If, before injecting surfactant and air in the formation to generate foam, a pre-flush of brine is injected in the formation, then on resuming production after foam generation, the water would remove most of the surfactant solution as it flows out before the oil. Some amount of surfactant may still remain in the foam films. Thus one may expect the emulsion coalescence to be faster with the smaller amounts of the surfactant present.

This concept was tested in the 2-ft sand pack as shown in fig 7.11. Foam was generated in the first section of the sand pack by alternate air and surfactant (0.5% F108 + 0.5% CS-330) injection till MRF of ~100 was achieved. This was followed by brine injection to remove most of the surfactant, especially CS-330 which was a better emulsion stabilizer. About 6 PV of brine was injected to remove as much of CS-330 as possible. This was followed by hexadecane injection into the pack. Initially, for a while,
MRF similar to that during brine flow was observed, but later on MRF started dropping (unlike in fig 7.10 where the high resistance to oil flow stayed constant) and finally leveled at ~29 after ~5 PV of oil injection. This indicated that the flowing oil was breaking foam in the pack. Taking into account the oil viscosity, the final resistance to flow of oil was really only about a factor of 9. Though, this was slightly higher than resistance to oil flow with irreducible water (resistance factor of ~2), it was orders of magnitude lower than the case where the surfactant was not washed out prior to oil injection (fig 7.7). The fact that it took longer than 1 PV to achieve the final low resistance to flow may indicate that some emulsion was formed in the pack which eventually coalesced or flowed out. Some emulsion was produced at the outlet of the pack later on confirming that stable emulsion was produced in the pack even with the small quantities of surfactant (mostly F108) available. Some trapped emulsion may be partly responsible for the final resistance factor of ~9. However, it is suspected that presence of some trapped air in the pack is mainly responsible for this resistance. This is because, later on, even after any emulsion present in the pack was collapsed using isopropanol, the pack was still compressible, which confirms the presence of air. Since it was observed earlier in foam experiments with residual oil (fig 7.5 a) that foam did not displace most of the residual oil, one may expect that flowing oil will not displace all of the trapped air either.
Fig 7.11: Reduced emulsion formation during oil flow following a brine flush in 2-ft sand pack

In the above experiment ~6 PV brine was flowed since foam from CS-330 required fairly large amount of brine (7-12 PV) to wash out. The ratio of brine throughput to surfactant throughput (for foam generation) was 150 ml:47 ml i.e. ~3:1. In another experiment (fig 7.12), only ~2 PV of brine was injected after a foam with MRF of 60 (at 3ft/d) was generated. In this case the ratio of brine to surfactant was ~1:1. When oil was subsequently injected, an increase in MRF was observed due to emulsion formation and higher oil viscosity before it started decreasing. Again the MRF leveled out in 4-5 PV to ~20 (i.e., resistance to oil flow of ~6.5). This shows that the emulsion problem can be reduced even with a smaller brine flush of 2 PV instead of the 6 PV used in the previous experiment. The PV here refers to the foam region and will correspond to volume of a
region several feet deep in a producing well. Thus, one may be able to reduce the emulsion problem significantly by injecting a small amount of brine (comparable to amount of surfactant injected) before foam generation.

From the earlier discussion, emulsification with hexadecane represents the worst case. With another lower EACN oil, the resistance due to emulsion formation to flowing oil for a period of time may be further reduced.

![Graph showing oil flow and brine flush](image)

**Fig 7.12:** Another run of oil flow following shorter brine flush
7.4 Scale-up

So far, we have seen that stable foam can be generated using a combination of Pluronic F108 and CS-330 in the water producing zones (containing residual oil) of a oil producing well. Another aspect that is important is how long this foam is expected to last in the field before the well needs re-treatment. And how the time for foam washout compares to time for foam generation in the formation. This section answers these questions.

From 1-D foam washout experiments in the sand pack described in chapter 5, it can be seen that foam collapse is sequential from the first to the third section in most cases. MRF decreases from inlet to outlet as the foam collapses and can be approximated as a travelling foam washout front. This is best illustrated by the foam washout of B20-5000 by continuous injection of brine at 6 ft/day as seen in fig 5.10b. From chapter 6 (section 6.3), it is clear that this represents mainly a gas dissolution wave. If the MRF for the first three sections is plotted as a function of PV throughput (fig 7.13), one gets approximately a straight line. The slope actually decreases a bit with PV probably because of reduced air solubility at downstream pressures. Under reservoir conditions the pressure drop in the foam region will not be as significant compared to reservoir pressures and the solubility change would be negligible. Thus, the collapsing foam front can be assumed to be travelling at a constant velocity in the porous medium from inlet towards the outlet.
Fig 7.13: Washout of foam from B20-5000 (from fig 5.10b)

Thus, in 1-D experiments it can be observed that:

\[
\frac{V}{v} = \frac{1}{PV \text{ for washout}} = m
\]

where,

\( V \) = velocity of foam front

\( v \) = interstitial water velocity when no foam present

The above observations can be used to scale up foam washout time in the radial flow conditions near the producing well. The terms and notations used are defined in the following schematic of a water producing region-
Let,

\[ P_w = \text{bottom hole pressure in the producing well} \]
\[ r_w = \text{radius of the well} \]
\[ P_i, r_i = \text{pressure and radial distance from center of the well at the initial position of foam front} \]
\[ P_e, r_e = \text{pressure and radial distance of foam front at time } t \]
\[ P_{e\text{r}}, r_c = \text{pressure at distance } r_c \text{ deep inside the formation} \]
\[ MRF_f = \text{MRF in the foam region} \]
\[ MRF_{nf} = \text{MRF in the other regions (usually } = 1) \]

From Darcy's law in cylindrical coordinates,

\[ q(t) = \frac{2\pi \lambda h (P_i - P_w)}{MRF_f \ln \frac{r_i}{r_w}} \quad \text{or} \quad \frac{2\pi \lambda h (P_e - P_w)}{MRF_{\text{mean}}(t) \ln \frac{r_c}{r_w}} \quad (7.1) \]

where,

\[ q = \text{flow rate over interval } h \]
\[ \lambda = \text{mobility of a water in the formation } = \frac{k}{\mu_{\text{water}}}; k = \text{permeability of the formation} \]
\[ MRF_f = 1/k_{rw}(S_g) \]; \( k_{rw} \) is the relative permeability of water at trapped gas saturation \( S_g \)

\[ MRF_{mean} = \text{mean MRF at time } t \text{ depending on position of foam front} \]

Assuming that foam collapse front velocity scales with the interstitial water velocity as in 1-D experiments, that is, \( V/v = m \) for radial flow too and using (7.1),

\[
V = mV = m \frac{q}{2\pi \rho h \phi} = \frac{m \lambda (P_e - P_w)}{r \phi MRF_{mean} \ln \frac{r_c}{r_w}}
\]  

(7.2)

where, \( \phi \) = porosity

The position of the foam front at time \( t \) can be calculated from the following equation for the distance traveled by the front in time \( t \):

\[
r_f - r_i = \int_0^t V \, dt = \int_0^t \frac{m \lambda (P_e - P_w)}{r \phi MRF_{mean} \ln \frac{r_c}{r_w}} \, dt
\]  

(7.3)

Following simplifying assumptions can be made to get an analytical solution for (7.3).

Assumption 1: \( m \) is independent of \( t \)

From 1-D washout of foam from B20-5000 at different flow rates as in figs 5.7b and 5.10b,

\[
\frac{V}{v} = \frac{1}{15 \times 4/3}
\]  

at 6 ft/d superficial velocity, and
\[
\frac{V}{v} = \frac{1}{22 \times 4/3}
\] at 300 ft/d superficial velocity.

Since the PV for foam washout in chapter 5 are with respect to the PV for the whole pack (4 sections), the factor 4/3 is applied as the correction factor when considering three sections only. As can be seen the foam front velocity has a weak dependence on water velocity and part of the reason may be switching of flow rates between the two levels itself. So, as a first approximation, \( m \) is assumed independent of flow rate.

\[
\frac{V}{v} = m \quad \text{and } m = \text{constant}
\]

Assumption 2: \( P_c - P_w \) independent of \( t \)

The pressure differential \( P_c - P_w \) decreases over time with production. However, to estimate the time for foam washout, this differential may be considered constant over the period of foam washout for simplicity. In any case, this assumption will only underestimate and not overestimate foam washout time.

From the above assumptions and using

\[
MRF_{mean} = \frac{MRF_f \ln \frac{r_{wc}}{r_i} + MRF_{nf} \ln \frac{r_i}{r_e}}{\ln \frac{r_{wc}}{r_e}}
\]

(7.4)

in (7.3), one can solve to get the following analytical solution:
\[
\frac{m\lambda(P_e - P_w)}{\phi} \Delta t = \\
\left( \frac{r_i^2 - r_e^2}{2} \right) (MRF_f \ln r_w - MRF_{nf} \ln r_e) + \frac{1}{4}(MRF_{nf} - MRF_f) \left[ r_i^2 (2 \ln r_i - 1) - r_e^2 (2 \ln r_e - 1) \right]
\]

(7.5)

Equation (7.5) can be used to calculate the position of the foam front as a position of time using the appropriate values for the parameters. The time for washout is given by using \( r_i = r_w \) in (7.5). Also, since \( r_w \ll r_i \), the \( r_w^2 \) terms can be neglected. Thus,

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

(7.6a)

or, non-dimensionalizing both sides,

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

(7.6b)

The relative foam front velocities \( (m) \) during washout for various surfactants are computed from the washout experiments in chapter 5, and tabulated in table 7.6 after suitable correction factors. All these values are for air foam, and to a satisfactory approximation apply to nitrogen foam too.
Table 7.6: m values observed for various surfactants

<table>
<thead>
<tr>
<th>Surfactant</th>
<th>m</th>
</tr>
</thead>
<tbody>
<tr>
<td>C₁₆TAB</td>
<td>0.5</td>
</tr>
<tr>
<td>CS-330</td>
<td>0.08-0.14</td>
</tr>
<tr>
<td>P85</td>
<td>0.14-0.21</td>
</tr>
<tr>
<td>F88</td>
<td>0.08-0.12</td>
</tr>
<tr>
<td>F108</td>
<td>0.029-0.036</td>
</tr>
<tr>
<td>B20-5000 (high rate)</td>
<td>0.05-0.06</td>
</tr>
<tr>
<td>HMPA1</td>
<td>0.042</td>
</tr>
</tbody>
</table>

Using the following typical values of parameters, the front position versus time is plotted in fig 7.14 for two values of $MRF_f$:

\[ k = 100 \text{ mD}, \phi = 0.3, r_w = 0.5 \text{ ft}, r_l = 30 \text{ ft}, r_e = 1000 \text{ ft} \]

\[ P_e - P_w = 1000 \text{ psi}, MRF_f = 50 \text{ or } 100, MRF_{nf} = 1 \]

For foam from F108, \( m \sim 1/(25*4/3) = 0.03 \)

The figure shows that the foam washout becomes faster near the well due to higher interstitial velocities. Fig 7.14 shows that it will require 40 to 85 months to wash out foam from a distance of 30 ft depending on the MRF of foam. Also, deeper foam penetration will increase the foam washout time roughly quadratically. The equation can also be used to compute the foam washout time (or time for well re-treatment) as a function of foam penetration. This is shown in fig 7.15. It shows that for foam penetration of more than 10-15 ft and $MRF$ of 100, the foam would be expected to take years to wash out.
Fig 7.14: Position of foam front with time during washout

Fig 7.15: Time for foam washout as a function of foam penetration distance
But, the time of foam washout has to be considered in reference to the time required for foam generation to a particular distance. Assuming that foam generation requires a one slug of surfactant injection followed by a slug of air injection,

Time for foam generation ($\Delta t_{fg}$)

\[ = \text{time for surfactant injection} + \text{time for air injection to distance } r. \]

Equation (7.6) can also be used compute these times by setting $m = 1$, i.e. front velocity = water interstitial velocity, and suitable $MRF_j$ values. To generate foam of $MRF$ of say 100, and assuming the same magnitude of pressure differential (but opposite sign) for foam generation as during production, i.e. $P_w - P_e = 1000$ psi,

\[ \Delta t_{fg} = \Delta t \text{ from (7.6) with } (m = 1 \text{ and } MRF_j = 1) \]

\[ + \Delta t \text{ from (7.6) with } (m = 1 \text{ and } MRF_j = 100/n). \]

The factor $n$ accounts for the difference in resistance during flow of surfactant solution and flow of air when foam $MRF = 100$. In the foam generation experiments in sand pack in this study (chapter 5), $n \approx 2$. It can be shown that the time for surfactant injection ($1^{st}$ term) is negligible compared to the other term. For example, for penetration of 30 ft, $1^{st}$ term $\sim 0.05$ months and $2^{nd}$ term $\sim 1.3$ months for $n = 2$. So,

\[ \Delta t_{fg} = \Delta t \text{ from (7.6) with } m = 1 \text{ and } MRF_j = 100/n. \]

Thus for $n = 1$, it can be seen that,

Time for foam washout ($\Delta t_{fw}$) = $(1/m) \times \Delta t_{fg}$
For any other $n$ with a large enough $MRF_f$, it can be shown that,

\[
\text{Time for foam washout } (\Delta t_{\text{foam}}) \approx (n/m) \ast \Delta t_f
\]

That is, for foam from F108, it will take approximately $2/0.03 = 66$ times longer to washout foam than to generate foam or in other words, for every day of production downtime in generating foam about two months of reduced water production is achieved. Also, since the time for surfactant injection is negligible, so is the time for a brine pre-flush before foam generation and it will not disturb the above calculations.
CHAPTER 8

CONCLUSIONS AND RECOMMENDATIONS

The preceding chapters described the work done in this study in developing stable foams for water production control application. This chapter summarizes the main findings of this study and follows this by suggestions for the direction of future work.

8.1 Summary and conclusions

This study explored the suitability of using foam for reducing water production from a well that is producing both oil and water. Foam has the potential for use as a relative permeability modifier (RPM) i.e., in reducing water relative permeability without significantly affecting oil relative permeability. For foam to be used for such an application it has be stable for a long enough time in presence of flowing water. In addition, foam should have tolerance for small amounts of oil that may be present in the water producing zones. Finally, foam should collapse in the presence of flowing oil so that it will not hinder oil production. Each of these aspects was studied and is discussed below.

8.1.1 Foam stability to washout

Foams stable to washout with water were produced by using polymeric surfactants instead of commonly used low molecular weight surfactants. Two broad
classes of polymeric surfactants were used – the triblock copolymers and the hydrophobically modified (HM) polymers. The triblock copolymers tested had molecular weights in the range of 3,000 to 15,000, while some of the HM polymers, which were not well characterized, had molecular weights probably exceeding 100,000. A screening test was developed to test the foams for washout stability outside of the porous medium (chapter 4). In this test water was flowed through a vertical column of foam in a 1-ft glass column and the time for foam collapse was measured. Foam from polymeric surfactants exhibited much higher washout stability than foam from conventional surfactants like SDS or C_{16}TAB. The EO-PO-EO copolymer with molecular weight of 15,000 (F108) was seen to have the highest washout time among the triblock copolymers. The EO-BO-EO copolymer with molecular weight of only 5,000 (B20-5000) was close behind. Thus it appears that the EO-BO copolymers may be better for producing foams stable to washout than comparable molecular weight EO-PO copolymers, because of the more hydrophobic BO groups. In addition, the EO-BO copolymers are better foamers than the EO-PO copolymers.

Some of the HM polymeric surfactants screened also exhibited good foam washout stability – some of them, such as HMPA1 and HMPC2, exceeding the washout time of F108 in the screening tests. The cationic HM polymers, HMPC1 and HMPC2, however, showed a marked reduction in washout time in the presence of salt. The anionic HMPA1 and HMPA3, in contrast, showed an improvement in foam washout stability in presence of salt. The washout time of HMPA1 in the screening test was also the highest among all the surfactants used in this study.
To understand the mechanism of foam washout, desorption of surfactants was observed using a modified pendant bubble apparatus (chapter 6). Surface tension of an air bubble in a surfactant solution was monitored as a function of exponentially decreasing surfactant concentration to estimate the ease of desorption. The desorption experiments show that conventional surfactants desorb rapidly from an air-water interface, some with no observable mass transfer resistance, whereas the polymeric surfactants are very difficult to desorb. This largely explains the difference in the washout times of foam from conventional and foam from polymeric surfactants. Some commercial surfactants, like CS-330, contained some impurities that did not desorb from the air-water interface and may explain the longer washout times exhibited compared to pure conventional surfactants like SDS. Polymeric surfactants, such as F108 and HMPA1, adsorbed almost irreversibly at the air-water interface and the surface tension did not increase more than a few mN/m even after a long time in the desorption experiments. This indicates that these polymeric surfactants can produce foam that can be expected to last for a very long time in presence of flowing water. Foam collapse of these polymeric surfactants in screening test, hence, cannot be explained by desorption. In fact, below certain flow rates, foam collapse was observed even when surfactant solution was used instead of water. This shows that some hydrodynamic factors are involved in collapse of foam from polymeric surfactants. It was demonstrated that foam coarsening with time and mechanical perturbations of falling drops of liquid are two important factors in explaining foam collapse. This is because foam coarsening led to larger foam bubble sizes over time and a foam which collapsed faster due to the perturbations produced by the falling drops of
liquid. It was also observed that for the polymeric surfactants, foam washout time could be correlated with inherent foam film stability.

Some of the conventional and polymeric surfactants were tested for foam washout stability in a sand pack (chapter 5) also. Strong foam (mobility reduction factor of $\sim 100$) with uniform trapped gas saturation in the pack was generated using a method of alternating injection of air and surfactant. This method worked better than co-injecting air and surfactant in the sand pack (see appendix A) as it allowed for both strong foam generation and propagation of foam in the sand pack (Incidentally, the foam generation experiments using co-injection, described in appendix A, also supported the criteria for foam generation by lamella division developed by Tanzil et al. [2002]). Foam washout experiments in the sand pack again demonstrated that foam from polymeric surfactants like F108 was more resistant to washout than foam from conventional $C_{16}$TAB or CS-330. However, the HM polymer HMPA1 did not generate a very strong foam in the sand pack compared to the conventional surfactants or the triblock copolymers (maximum MRF of $\sim 50$). This is because foam films from HMPA1 appear to be less stable at the higher capillary pressures expected at the higher gas saturations in the sand pack. While the reason for this is not certain, the large molecular aggregates of HMPA1 observed in solution may be destabilizing foam films at smaller film thickness by mechanisms such as bridging of the two air-water interfaces.

The screening tests were found to be good predictors of foam washout resistance in a sand pack even though they were not always good indicators of foam stability. This
was because it was desorption of surfactants which differentiated the washout stabilities of foam from conventional and polymeric surfactants and this property could be captured in the screening test. However, the similarity in the ranking of foam washout of triblock surfactants observed between the screening test and the sand pack experiments must have been coincidental. This is because the reason for foam collapse with polymeric surfactants is different in sand pack and in screening tests. In the sand pack, it was observed that the washout stability of foam produced from some of the polymeric surfactants was limited by the dissolution of air in the flowing liquid (see chapter 6) and not due to foam destabilization. Because of this, the throughput of water/brine for foam washout with some of the polymeric surfactants in the absence of air dissolution is expected to be much higher than that reported in chapter 5. In oilfield reservoirs, presence of dissolved hydrocarbon gases in produced water may reduce or even eliminate gas dissolution from foam. In contrast, foam collapse during washout in the screening test was observed to be due to hydrodynamic factors and not due to air dissolution.

Chapter 7 shows how these foam washout times scale-up to oilfield geometries. Even with air dissolution, sufficient foam life is expected for foam from polymeric surfactants like F108. It was shown that for every day of foam generation, about a month or two of reduced water production can be expected. For sufficiently strong foam (MRF > 50), foam penetration of just 20 feet from the well can be expected to give reduced water production for several years. These scale-up results show that even in the case of foam washout due to air dissolution, foams from polymeric surfactants can last for a long enough time to be of practical benefit.
8.1.2 Foam stability in presence of oil

Another criterion that has to be satisfied for use of foams for water production control is that foam should be stable to small amounts of oil so that it can be placed in the water producing zones containing residual oil. It was observed that foam from the triblock polymeric surfactants was very unstable to presence of residual oil (hexadecane). In contrast, foams from ionic surfactants like CS-330 or SDS were quite stable to residual oil (chapter 7). This is because of the electrostatic barrier produced by the adsorption of charged surfactants at the air-water and oil-water interfaces, which prevents the entry of oil droplets into the air-water interface. Thus, even though the thermodynamic coefficients (entering, spreading and bridging) predicted foam destabilization with oil, the ionic surfactants produced foam stable to small amounts of oil. Foam stable to residual oil and with high washout stability was produced by using a mixture of polymeric F108 and anionic CS-330 surfactants (0.5% each).

Foam should also not hinder the oil production from a well and hence should be unstable in presence of flowing oil. Foam was observed to collapse rapidly with flowing oil in the screening test. However, in the sand pack, flowing oil was seen to form stable and viscous emulsions because of the surfactant present in the foam regions. F108 + CS-330 mixture, in particular, was a very good emulsifier and was observed to produce very stable emulsions that did not coalesce for a long time. Emulsion coalescence rates were enhanced significantly if the surfactant system was shifted closer to optimum (Winsor III). This was achieved by using a more lipophilic surfactant, TDA-4PO, instead of CS-
330 or by adding CaCl₂ to the F108 + CS-330 surfactant system. Use of a lower alkane number oil, octane, instead of hexadecane also reduced emulsion stability. However, the quantity of salt required in above cases was quite large (close to maximum solubility) and the foam stability was affected adversely.

Another approach is proposed to tackle the emulsion problem. In the foam application process, if some quantity of water or brine is injected into the formation before surfactant solution and air are injected for foam generation, then, on resuming production this water will flow through the foam and remove most of the surfactant present before flowing oil contacts the foam. In sand pack experiments, it was observed that this procedure significantly reduced the amount and stability of emulsion produced and in ~ 4 PV throughput (with respect to foam region), the resistance to oil flow was quite low – about a factor of 6-10. This is believed to be mainly due to the air trapped in the porous medium, which would eventually dissolve for oils undersaturated in gas.

Hence, this study shows that foams stable to washout with water for a long time can be produced using polymeric surfactants such as F108. Using a mixture of non-ionic polymeric and anionic conventional surfactants, or alternatively, anionic polymeric surfactant itself, can produce foams stable to residual oil. The surfactant combinations used in this study will, however, affect oil production because they are good emulsifiers too. This can be handled by a suitable process modification described above. More appropriate surfactant structures could probably be designed to further reduce emulsion stability.
8.2 Recommendations for future work

- Design of more optimal polymeric surfactant structures:

  In this study, commercially available polymeric surfactants were used. Only a limited choice of molecular architectures was thus available. In addition, these were not designed for foaming applications. The triblock copolymers studied here, while they proved the concept, may not be suitable for a range of oilfield conditions. They are known for their high sensitivity to temperature (see chapter 3) and may not work for many high temperature reservoirs. The reported cloud point for some of the Pluronics used in this study is around 90 °C. Since the ethoxylated groups are mainly responsible for the temperature sensitivity, surfactants containing fewer ethoxylated groups have to be developed for higher temperature applications. In addition, it is preferable to have anionic charge on surfactants because then they will be expected to show higher oil tolerance than non-ionics and will also be expected to be better foamers. Also, the adsorption of anionic surfactants is lower on rock surfaces, such as sandstone, that are negatively charged. This study shows that polymeric surfactants with molecular weights of thousands to tens of thousands are sufficient to adsorb irreversibly at the air-water interface and thus produce washout resistant foams. Higher molecular weights should be avoided as these can give rise to other problems such as higher loss of surfactants due to adsorption on the rock surfaces and reduced permeability of the formation. It would be interesting to investigate how much lower molecular weight can one use that will still adsorb irreversibly at the air-water interface.
Both block copolymer and randomly distributed hydrophobe architectures seem suitable for producing foams stable to washout. Hydrophobically modified polymers such as HMPA1, however, did not generate as strong a foam as with other surfactants in porous media. These types of polymeric surfactants are known for their intra-molecular and inter-molecular association, which may lead to large networks that could cause bridging. There is a need to study further, using well defined structures, if hydrophobically modified polymer architecture is suitable for use in porous media.

- Reducing stable emulsion formation:

The F108 + CS-330 combination developed in this study was found to be a good emulsifier too (mainly because of CS-330). The process modification proposed reduced this problem significantly. But, it will still lead to a decreased oil production for a short while after production is resumed. So, it would be preferable to design surfactant systems that will lead to faster emulsion coalescence rates without significantly affecting foam stability. For example, polymeric surfactants with lower HLB values than F108 can be developed or more lipophilic conventional surfactants than CS-330 can be added to shift the surfactant system closer to Winsor III. It needs to be seen if this can be done without adversely affecting foam stability significantly.

- Direct comparison with current technologies:

For wide use of this foam technology for water control applications, a direct economic comparison with currently used technologies is desired. This study mainly
proves the concept that foams can be used for reducing water production. Some estimates of time required between foam treatments and the downtime for treatment are also given in this study. Additional factors that will determine the economics of the process are surfactant price, amount of surfactant required, and the economic cost of reduced oil production for a while due to the emulsion formation. In addition, in 3-D geometries, mobility reduction factors as high as 100 may not be attainable with foams because, unlike in 1-D, when lamellae block flow in one direction there are other directions available for flow. This discrepancy between laboratory and field foam experiments has been observed in the aquifer remediation work done in the group [Hirasaki et al., 1997, 2000]. Appropriate MRF values for 3-D will have to be determined and their economic impact will have to be studied further.
BIBLIOGRAPHY


APPENDIX A

FOAM GENERATION IN SAND PACK

Some of the sand pack experiments attempted to achieve the objective of producing strong foam with a uniform trapped gas distribution are described here along with the problems encountered in each case. It can be seen from the following discussion that foam behaves like a complex fluid in the porous medium and generating strong foam as well as propagating it through the sand pack is difficult.

MA-80I was used as the surfactant for the foam generation experiments initially, mainly because it had been used earlier extensively in the lab for aquifer remediation work [Szafranski, 1997; Tanzil, 2001]. In the first experiment, the sand pack was initially saturated with 2% MA-80I solution. Air was then injected into the pack at superficial velocity ($u_s$) of 3 ft/day. Fig A.1 shows the mobility reduction factor for the middle two sections of the pack as well as for the whole pack. It can be seen that air breakthrough was observed even as pressure drop across the 3rd section was increasing - which means the foam was very weak and there was some fingering or gravity override of air through the pack. Overall MRF of about 10 was obtained at breakthrough even though the gas saturation was very high at 70%. This indicates that the trapped gas saturation was much smaller than 70%. On injecting water, $S_g$ decreased to $\sim$ 30% within 1 PV of injection. This may actually be closer to the trapped gas saturation in the foam generated. Thus, air injection at 3 ft/day produced weak foam in the sand pack with 2% MA-80I.
To create stronger foam, it was decided to co-inject air and surfactant for future experiments to prevent foam from becoming too dry and then collapsing as may be the case with just air injection. It was also decided to inject surfactant after the foam generation step to measure the trapped gas before injecting water to observe the washout. In the next experiment, an increased superficial air velocity of 6 ft/day was used for foam generation after the pack was saturated with 2% MA-80I. In addition, surfactant was co-injected with air in the ratio 1:3 (surfactant to air). It can be seen from figure A.2 that the foam does not break through prematurely as before but only after the pressure drop in the fourth section approaches that in the other sections. The foam breakthrough was observed
around 1.3 PV of air injection even though gas saturation at breakthrough was ~57%. This is because of the compressibility of air which delays foam breakthrough. However, foam was still weak as MRF of ~10 and $S_g$ of only 57% was observed at foam breakthrough. Injecting surfactant following this gave $S_g$ of only 30% which represents the trapped gas saturation. This low trapped gas saturation explains why the foam was weak. Following with water injection at the same rate showed no change in MRF or $S_g$, which indicates that the residual gas saturation for the sand pack had been reached.

![Graph showing foam generation with 2% MA-80I](image)

**Fig A.2: Foam generation with 2% MA-80I**

In figures A.1 and A.2, the normalized pressure drops ($N_{\Delta p} = \frac{\Delta p}{\sigma / \sqrt{k / \phi}}$) across the 6-inch individual sections never exceeded 1. Hence, according to the criterion
developed by Tanzil et al. [2002] lamellae mobilization does not occur (see chapter 2, section 2.2) and strong foam generation is not observed.

Because of the inability to generate strong foam in the previous two experiments and based on other foam generation experiments with MA-80I in the lab [Tanzil, 2001] it was decided to use a higher concentration of the MA-80I surfactant. For the next experiment, depicted in figure A.3, after saturating the sand pack with 4% MA-80I, air and surfactant were co-injected in the pack in 5:1 ratio, with air rate at 9 ft/day. As can be seen from the figure, even after 1.8 PV of apparent air injection, all the pressure drop was still across the first two sections and there was hardly any flow in the 3\textsuperscript{rd} and 4\textsuperscript{th} sections. This was due to strong foam generation in the first half of the sand pack that would not propagate beyond the 2\textsuperscript{nd} section of the sand pack. All the air injected as well as the air in the pump was only compressing against this foam ‘plug’ as can be seen from the fact that $S_g$ in the pack was 34\% even when apparently 1.8 PV of air (at atmospheric pressure) was injected in the pack. It was also observed, near the inlet, that the air fraction that was entering the pack was much smaller than the set ratio (5:1) due to air compression in the pump. It can be seen that near the end of the plot pressure drop in 2\textsuperscript{nd} section was rising rapidly and injection had to be halted. The strong foam generation may be in part due to the increasing flow rate with time (as rate of compression decreases) which would lead to higher pressure gradients. The pressure drops in sections 1 and 2 do exceed the critical pressure drop of Tanzil et al. (i.e., $N_{Ap} > 1$). However, no sharp transition from weak foam to strong foam generation is evident from the plot in A.3. Air breakthrough could only be observed after keeping the column standing overnight which caused air in the
pack to expand due to decreasing pressure and/or some foam collapse in the pack. This shows that the rate of 9 ft/day was too high to propagate strong foam throughout the pack. In another run at 9 ft/d, strong foam generation was observed in the 1st section only. An experiment where the air rate was 12 ft/day also showed strong foam generation in section 2 which was again difficult to propagate.

Fig A.3: Foam generation with 4% MA-80I

The previous experiments show that injecting air at too high a rate will produce strong foam but it will be difficult to propagate the foam - at least with the available experimental setup. An alternative was to start air injection at low enough rate so that foam will be propagated throughout the sand pack and then increase the air rate in steps
to make that foam stronger. When air was injected at 3 ft/day through MA-80I saturated sand pack (fig A.4), it produced a weak foam that propagated easily through the pack. However, when the rate was stepped up to 6 ft/day, it again created a strong foam in the 1st section of the pack which made foam propagation difficult. In this experiment (fig A.4), strong foam generation in sections 3 and then in section 1 was observed when $N_{\Delta p}$ exceeded $\sim 1$. Hence the window of rates for propagating the foam in shortest possible time is probably between 3 to 6 ft/day.

![Diagram of foam generation with 4% MA-80I](image)

**Fig A.4: Foam generation with 4% MA-80I**

In another experiment, shown in fig A.5, the rate was stepped up more gradually in steps of 0.5 ft/day after foam breakthrough was observed at 3 ft/day. In this case, it was
observed that the pressure drop in the 4th section rises very rapidly after ~2 PV of air injection and when air rate was 4 ft/day. This seems to arise partly from the well known end effect also observed by other researchers [Apaydin et al., 2000; Myers and Radke, 2000]. Due to the end effect, foam generation by snap-off occurs near the exit of the pack (also, see chapter 2) which increases the pressure drop in the 4th section. However, in figure A.5 and in following experiments it can be observed that strong foam generation and rapid increase in pressure drop takes place when the \( N_{Ap} \) exceeds ~1. This indicates that when the pressure drop in 4th section increases due to snap-off and also higher rate near exit, the pressure drop exceeds the critical value for lamella mobilization and strong foam is generated.

Fig A.5: Foam generation with 4% MA-80I
When the pressure drop across 4\textsuperscript{th} section starts rising pressure drops in preceding sections start dropping somewhat because as the air compresses with rising pressure, the actual rate in the pack keeps dropping. This makes it very difficult, if not impossible, to generate stronger foam in the preceding sections once the pressure drop across the 4\textsuperscript{th} section starts to shoot up. This behavior was also observed in subsequent experiments where the end effect was seen. Following foam generation with surfactant injection at 4 ft/day, a trapped gas saturation of 54\% and an overall MRF of \sim 85 was observed. Note that MRF in section 4 levels off for some region in the plot because the pressure drop across section 4 exceeds the range of the transducer used. Following this with water injection, it was observed that most of the foam collapses within 1 PV of water injection. This indicates the poor foam washout resistance of MA-80I surfactant.

Figures A.4 and A.5 show that strong foam generation began when $N_{\Delta p}$ exceeded \sim 1 (over 6-inch interval). When injection rate was high enough (for e.g., in fig A.3 where rate > 9 ft/day), no transition from weak to strong foam was observed, as Tanzil et al. did, though the criterion for lamellae mobilization was satisfied. But when rate was increased in steps from a low value (e.g., from 3 ft/day to 6 ft/day) transition from weak to strong foam was observed.

At this point it was decided to use another surfactant, CS-330, for foam generation experiments. CS-330 is believed to be a much better foamer than MA-80I. In addition, it was decided to carry out future experiments with salt present in the surfactant solution and in the injected water as this would be the case in natural reservoirs. 5\% NaCl
solution was used as brine for preparing surfactant solution and for injected water. To test this surfactant, a foam generation experiment was carried out as follows. Air and surfactant were co-injected in 5:1 ratio into a sand pack saturated with 2% CS-330. The superficial air rate \( (u_a) \) was 3 ft/day. It was observed that shortly after foam breakthrough the pressure drop in the 4\(^{th} \) section started rising rapidly and within a short period of time the pressure drop exceeded the range of the transducer as can be seen from fig A.6. This is again believed to be due to the end effect described before. On injecting surfactant at 3 ft/day, a trapped gas saturation of 54% was obtained and an overall MRF of \( \sim 94 \) was obtained most of which was due to pressure drop across section 4. To propagate this strong foam throughout the pack, this was followed by a series of manipulations of air and surfactant flow rates (not shown in the figure), with the air rate never exceeding 4
ft/day, including shutting flow for some period of time. After which, it was observed that foam had propagated through most of the pack except for section 1 and an overall MRF exceeding 200 was obtained. This did demonstrate that CS-330 generates stronger foam much more easily (lower concentration & at lower rate compared to MA-80I) and hence is a better foamer than MA-80I.

A new strategy was tried to propagate strong foam throughout the sand pack. The idea was to generate a strong foam near the entrance by injecting air at high rate before the end effect produces very strong foam in the 4th section. This was to be followed by stepping down the air rate to a low value to push/expand the strong foam into the subsequent sections – thus propagating fairly strong foam throughout the sand pack. This is shown in figure A.7. In this figure pressure drops in psi are plotted instead of MRFs as the processes involved are much more clear in this format. Initially air and surfactant were co-injected in 5:1 ratio with air rate at 2 ft/day. As soon as foam broke through the sand pack, air rate was stepped up to 4 then 6 and then 12ft/day. The air rate is also plotted in figure A.7 with the rate indicated on the axis on the right. At this point it was observed that the pressure drop across the 1st section starts rising rapidly due to strong foam formation. After some time the rate was brought down in steps to 3 and then 2 ft/day. At this point the pressure drop across section 2 starts rising rapidly and foam generation in 1st section is reduced as more air is propagated to subsequent sections. This is accompanied by increase in the air flow rates in the subsequent sections because of air expansion due to lower pressures. Thus foam generation takes place in the 2nd and then 3rd section. When the pressures in various sections were more or less equal, surfactant was injected at 2 ft/day. After ~1 PV of surfactant injection, trapped gas saturation of
88% was observed and an average MRF of ~480 was observed. From the pressure drops it is apparent that the trapped gas saturation is fairly uniform in various sections.

![Graph](image)

**Fig A.7: Foam generation with 2% CS-330 in brine**

However, the disadvantage of this method of foam generation is that it is not possible to control the final strength of foam and hence would not aid easy comparison between different surfactants. Also, it is not readily extendable to other surfactants without some trial and error. Similar experiment with F108, for example, did not generate very strong foam near the inlet even when rate was increased to 30 ft/day, by which time the end effect had become so dominant that most of the pressure drop (~ MRF 400) was across the 4th section.
In figures A.6 and A.7, again, as in earlier examples, strong foam generation with co-injection of air and surfactant was observed in a particular section only after $N_{Ap}$ in that section exceeded $\sim 1$. For most experiments, foam generation could be observed anywhere in the pack as long as $N_{Ap}$ in that section exceeded $\sim 1$. Thus, the foam generation experiments so far support Tanzil et al.’s criterion of strong foam generation above a critical pressure drop. The critical $N_{Ap}$ was $\sim 1$ for a 6-inch interval in the experiments in this study. The critical $N_{Ap}$ in Tanzil’s experiments was, however, observed to be $\sim 2$ probably because the pressure drop was measured across a foot long column.

From above observations it becomes clear that generating strong and uniform foam in the sand pack by co-injecting air and surfactant is not feasible for the following reasons-

1. It would take a long time to propagate strong foam throughout the pack or for steady state to be reached. Other researchers have observed 10-100 PV, meaning several days to weeks to achieve steady state in the sand pack using co-injection.

2. There would be no control over the final gas saturation/foam strength. It would vary with the surfactant system used. Hence, a meaningful comparison is not possible for the washout of surfactant from foam for different surfactants.

3. The final overall pressure drops could be very high (several tens of atmospheres) going by the experiments by other researchers. This raises several safety and
procedural considerations and would not have been possible to achieve with the available equipment.

This explains the need to develop an alternative foam generation method which could be used to generate strong enough foam with uniform trapped gas saturation in the shortest possible time (preferably less than a day). After trying various methods for generating foam without much success, finally an approach was adopted which seemed to satisfy the various foam generation criteria reasonably well. In this new method instead of co-injecting air and surfactant, alternating pore volumes of air and surfactant were injected. More details on this new procedure can be seen in chapter 5.
APPENDIX B

FOAM STABILITY OF HMPA1

In chapter 5, it was observed that anionic HM polymer, HMPA1, did not produce as strong a foam in porous medium as did conventional surfactants or the Pluronics. Some of the methods attempted to improve foam stability of HMPA1 in a sand pack are discussed here. Two main methods were tried to improve the foamability of HMPA1 — 1) increasing pH and 2) mixing with conventional surfactants.

B.1 Effect of increasing pH

One possible way of increasing the film stability and hence foam stability of HMPA1 could be by increasing the pH of the solution. Increasing pH would neutralize more carboxylic acid groups and add more negative charge to the HMPA1 molecule. Even though the pKa for methacylic acid groups is < 7, the pH required for complete neutralization of the acid groups on the polymer would be higher. For a similar HM polymer, Vorobyova and Winnik [2000] observed full neutralization at pH ~9. Hence the pH was increased to >10 by adding an excess of dil. NaOH during neutralization. The solution with 5% NaCl became more clear in appearance than the solution at pH ~7. Viscosity also increased from ~ 2 to ~5 cP for freshly prepared solution containing 5% salt (viscosity was observed to increase gradually to ~13 cp after a few weeks). This indicates that indeed more negative charges were created which caused the polymer chains to become more stretched leading to higher viscosity and a clear appearance. This
HMPA1 solution at pH 10 foamed easily in the screening test (just as solution at pH 7) and the washout time with brine was comparable to that with pH 7 case.

Fig B.1 shows the foam generation in a 2-ft sand pack with this pH 10 solution. Air and surfactant were injected alternately at a superficial velocity of 12 ft/day into the surfactant saturated pack. As with the pH 7 case (chapter 5), there was not much increase in trapped gas saturation or MRF after a few cycles. After 5 cycles and at surfactant flow rate of 6 ft/day, the overall MRF was ~ 80. Factoring out the viscosity of the solution, the RPRF was only ~ 15 with a trapped gas saturation of 46%. The normalized pressure drop ($N_{dp}$) across each of the 6-inch section was ~4-5 and should have lead to strong foam
generation by Tanzil’s criterion. In another run with an aged solution, air was injected at higher rate (30 ft/d). But, it still produced weak foam with RPRF of ~5 and a trapped gas saturation of 31%.

**Sonication**

The very large viscosity of the HMPA1 solution, which forms a gel when neutralized without salt, indicates a very high molecular weight which is enhanced by presence of some cross-linking. Attempt was made to break molecule by sonicating the neutralized gel at pH 10 and then adding salt. After sonicating (using Branson sonifier) viscosity of the solution was reduced to values close to that of the pH 7 solution at 5% NaCl immediately after sonication. But, again, the viscosity would slowly increase over time (from 2.5 cP to 6.5 cP in ~2 weeks). This perhaps indicates that only a few cross-linking bonds may have been broken. But in the screening test the foam washout time was reduced from ~300 to ~200 min with 5% brine.

In the sand pack, the foamability was slightly improved over the unsonicated solution at pH 10 and approached values of HMPA1 at pH 7. Fig B.2 shows the foam generation in the long sand pack. In this case the air rate was increased from 12 ft/day to 30 ft/day after the first cycle to aid foam generation. Yet, the final MRF was ~90. The RPRF was ~30 with a trapped gas saturation of 54%. N_{sp} for each section was again ~4-6, which should have been sufficient for strong foam generation by lamella division.
Fig B.2: Foam generation with HMPA1 at pH 10 (sonicated)

To make doubly sure that the poor foamability is not due to insufficient pressure gradient, another experiment was performed where air was injected at a constant injection pressure of ~35 psi. Initially, most of the pressure drop would be across a small region close to the entrance and would aid strong foam generation by lamella division. Surfactant was also co-injected at 12 ft/day along with air. This is shown in fig B.3. Foam breakthrough was observed within 2 min of air injection with a gas saturation of ~35%. This indicated that foam was weak. After air injection was stopped and only surfactant was injected, the RPRF was ~ 2.5 with a trapped gas saturation of 24%. Another run with a higher surfactant flow rate to prevent foam from drying out also produced similar weak foam in the pack.
Fig B.3: Foam generation with HMPA1 (pH 10, sonicated) using high injection pressure

Thus, in summary, HMPA1 at pH 10 was an even poor foamer than at pH 7 in the sand pack. The surface tension of HMPA1 solution at pH 7 and at pH 10 after sonication was similar. But the rate of adsorption was slower for the pH 10 solution, probably due to its higher viscosity. But, since it foams readily in the screening test, this cannot explain the poor foamability in porous medium.

B.2 Foamability of HMPA1 mixtures

Another approach to improve foamability of the HMPA1 was to mix it with other conventional surfactants that would adsorb quickly at the air-water surface. (This
approach also was used in chapter 7 to increase foam stability of F108 to oil). HMPA1 at pH7 was mixed with varying amounts of either anionic CS-330 or amphoteric C\_14DMAO [C14- dimethyl amine oxide] which is a known foam booster.

<table>
<thead>
<tr>
<th>Table B.1: Foam stability of HMPA1 mixtures in short pack</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Surfactant flow (psi)</strong></td>
</tr>
<tr>
<td>---------------------------</td>
</tr>
<tr>
<td>CS-330</td>
</tr>
<tr>
<td>HMPA1</td>
</tr>
<tr>
<td>HMPA1 (0.5%) + CS-330</td>
</tr>
<tr>
<td>10:1</td>
</tr>
<tr>
<td>5:1</td>
</tr>
<tr>
<td>1:1</td>
</tr>
<tr>
<td>HMPA1 (0.5%) + C_14DMAO</td>
</tr>
<tr>
<td>10:1</td>
</tr>
<tr>
<td>5:2</td>
</tr>
<tr>
<td>1:1</td>
</tr>
<tr>
<td>B20-5000</td>
</tr>
</tbody>
</table>

A short sand pack (~ 1.5” long) was used to test foamability in porous medium instead of the long 2-ft pack so that several combinations could be tested quickly. The setup of this short pack arrangement and procedure for foam generation is described in chapter 7. Pressure drop across the pack was measured for surfactant flow, foam flow at 80% quality and for surfactant flow after foam generation. The results for mixtures of HMPA1 at pH 7 with CS-330 and C\_14DMAO are shown in table B.1. The HMPA1
concentration was kept constant at 0.5%. With CS-330, three mixtures in HMPA1:CS-330 ratios of 10:1, 5:1 and 1:1 were used. With C14DMAO, ratios of 10:1, 5:2 and 1:1 were used. The following table also lists the RPRF for surfactant flow after foam generation.

As can be seen from the RPRF in the tables, there was not much affect of CS-330 on foamambility of HMPA1. C14DMAO increased foamability slightly but not to the levels observed for CS-330 (or B20-5000). Surface tension measurements with a couple of mixtures did show that conventional surfactants adsorbed at the air-water surface in sufficient quantities. HMPA1+CS-330 mixture (1:1) had a surface tension of 28.5 mN/m and HMPA1+C14DMAO mixture (1:1) had a surface tension of 24 mN/m – i.e., surface tensions of conventional surfactants themselves at those concentrations. In addition, foam washout of the mixtures in the screening test (table B.2) show that washout times were reduced compared to the HMPA1, implying that some of the HMPA1 had been displaced from the surface. Yet, the foamability was poor in the porous medium.

Table B.2: Foam washout in screening test

<table>
<thead>
<tr>
<th>Surfactant (in 5% NaCl)</th>
<th>Washout time with 5% NaCl (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5% HMPA1 (pH ~7)</td>
<td>295</td>
</tr>
<tr>
<td>0.5% CS-330</td>
<td>60</td>
</tr>
<tr>
<td>0.5% HMPA1 + 0.5% CS-330</td>
<td>110</td>
</tr>
<tr>
<td>0.2% C14DMAO</td>
<td>20</td>
</tr>
<tr>
<td>0.5% HMPA1 + 0.2% C14DMAO</td>
<td>107</td>
</tr>
</tbody>
</table>
The mixture results show that conventional surfactants do adsorb at the surface and yet the foam is not as stable as with the surfactants themselves. Both the experiments at higher pH and with mixtures suggest that it is not the surface properties (charge density or rate of adsorption) that reduce foamability. This leads to the conclusion that bulk microstructure is somehow responsible for the poor foamability at higher capillary pressures in a porous medium. Perhaps the HM polymer causes lower foam stability by bridging of the two surfaces of the foam film.
APPENDIX C

FOAM DISSOLUTION IN FLOWING WATER

Foam washout due to gas dissolution in oilfield conditions can be investigated using the following theoretical analysis. In this analysis, the method of characteristics and the coherence theory developed by Helfferich and Klein [1970] and later applied by Helfferich [1981] and Hirasaki [1981] to multicomponent, multiphase flow in porous media is used.

The assumptions involved in the application of the theory are stated below [Helfferich, 1981]-

1) It applies to one-dimensional system.

2) The porous medium is uniform and isotropic with respect to all relevant properties.

3) The porous medium is considered as quasihomogeneous (i.e. effects of pore structure such as excluded volume, capillary imbibition etc are neglected and fractional flows are unique functions of composition).

4) All fluids are incompressible.

5) The effect of pressure on equilibrium and relative permeabilities is negligible.

6) The system is isothermal.

7) Partial molar volumes of components are constant (i.e. volume additivity of components in all phases; no change in total volume upon transfer of components from one phase to another).

8) The phases are in local equilibrium everywhere.
9) Effects of fluid dynamic dispersion and of dispersion through molecular diffusion are neglected.

At the pressures at the bottom of production wells, we can assume that pressure changes in the length scale of foam section are negligible compared to the absolute pressure. Hence we may consider the gas (i.e. foam) phase to be incompressible. But this is not realistic for laboratory experiments carried out in this study and the situation there is more complicated. Also, the partial molar volume of the gases will be different in the gas phase and the liquid phase unlike point 7 above, but this can be ignored with little error because of very small volume fractions of gas components in liquid phase (due to low solubility of air in water).

Suppose that a stable foam is present initially in a one-dimensional porous medium. Let the initial gas (say, nitrogen) saturation be uniform everywhere ($S_g$) and that all of the gas is trapped. Water with a constant nitrogen concentration (between zero to the saturation concentration) is injected in the porous medium at a constant rate.

Nomenclature:

\[ C_i = \text{overall concentration (volume fraction) of component } i \]

\[ F_i = \text{overall fractional flow of component } i \]

\[ y_i = \text{concentration (volume fraction) of component } i \text{ in the gas phase} \]

\[ \phi_i = \text{concentration (volume fraction) of component } i \text{ in the liquid phase} \]

\[ f_g \text{ (or } f_l) = \text{fractional flow of the gas phase (or liquid phase)} \]
\( S_g \) (or \( S_l \)) = saturation of the gas phase (or liquid phase)

\( v \) = interstitial velocity of the liquid phase

Material balance over species \( i \) gives the following-

\[
\frac{\partial C_i}{\partial t} + v \frac{\partial F_i}{\partial z} = 0, \quad i = 1, 2
\]

(C.1)

For a 2-phase (liquid and gas) and 2-component system (water and nitrogen) we have,

\[
C_i = y_i S_g + \phi_i S_l
\]

(C.2)

and,

\[
F_i = y_i f_g + \phi_i f_l
\]

(C.3)

It can be shown that concentration velocity of component \( i \) (which also equals composition velocity for 2-component system) is given by,

\[
v_{ci} = \frac{dF_i}{dC_i} \bigg|_{dr=0}
\]

(C.4)

Thus, for the nitrogen component, from (C.2) and (C.3) we have -

\[
C_{N_2} = y_{N_2} S_g + \phi_{N_2} S_l
\]

and

\[
F_{N_2} = y_{N_2} f_g + \phi_{N_2} f_l = \phi_{N_2}
\]

since \( f_g = 0 \) (all the gas is trapped)
At a given temperature and pressure, the liquid phase nitrogen fraction, $\phi_{N_2}$, is fixed and equals the saturation value in the foam region because of assumed local equilibrium. Hence in the foam region (2-phase region),

$$\frac{dF_{N_2}}{dC_{N_2}} = 0$$  \hspace{1cm} (C.5)

And in the water flowing region (1-phase region), $S_g = f_g = 0$ and

$$\frac{dF_{N_2}}{dC_{N_2}} = 1 \quad \text{since} \quad F_{N_2} = \phi_{N_2} = C_{N_2}$$  \hspace{1cm} (C.6)

The $F$ vs. $C$ curve then is as follows-

Thus, going from B.C. (boundary condition) to I.C. (initial condition) we have some compositions with velocity $= v$ and then some compositions ahead of it with velocity $= 0$. This is not permissible (as the faster waves will overtake the slower waves) and will lead to a shock wave from B.C. to initial nitrogen composition.
The velocity of this shock front can be calculated by mass balance across the step change as follows-

Here the front moves in the z direction from time $t_1$ to $t_2$. The $F$ and $C$ behind the front are denoted by superscript 2 and in front of the step are denoted by superscript 1.

Mass balance gives:

Accumulation = In – Out

i.e.

$$A\Delta z (C^{2}_{N_2} - C^{1}_{N_2}) \phi = F^{2}_{N_2} uA \Delta t \mid_{z} - F^{2}_{N_2} uA \Delta t \mid_{z+\Delta z}$$

where,

$u =$ superficial velocity injected fluid

$A =$ cross-sectional area

which gives,

$$\frac{F^{2}_{N_2} - F^{1}_{N_2}}{C^{2}_{N_2} - C^{1}_{N_2}} = \frac{\Delta z}{\Delta t}$$

(C.7)

where $v =$ interstitial velocity $= u/\phi$

Thus,

$$\frac{1}{v} \frac{\Delta z}{\Delta t} = \frac{\phi^{3}_{N_2} - \phi^{1}_{N_2}}{(\phi^{3}_{N_2}) - (S_{g}^{1} + \phi^{1}_{N_2} (1 - S_{g}^{1}))}$$

(C.8)
The number of PV required to dissolve foam equals \( \nu \Delta t / \Delta z \) and is the reciprocal of (C. 8).

Consider the extreme case where there is no nitrogen in the injected water. The velocity of the front (\( \Delta z / \Delta t \)) is then given by -

\[
\frac{1}{\nu} \frac{\Delta z}{\Delta t} = \frac{F_{N_2}^1}{C_{N_2}^1} = \frac{\phi_{N_2}^1}{S_g^1 + \phi_{N_2}^1 (1 - S_g^1)}
\]  

(C. 9)

Using Henry’s law for gas solubility in the form \( yP = H\phi \) and ideal gas law, and using consistent concentration units for numerator and denominator (instead of volume fractions) this becomes -

\[
\frac{1}{\nu} \frac{\Delta z}{\Delta t} = \frac{1}{S_g^1 (0.018 \frac{H}{RT}) + (1 - S_g^1)}
\]  

(C.10)

Note that in this form, the front velocity and hence pore volumes for dissolution is independent of pressure as long as Henry’s law is valid.

The number of pore volumes required for complete dissolution of foam is, therefore, given by-

\[
PV = 1 + S_g^1 (0.018 \frac{H}{RT} - 1)
\]  

(C.11)

For \( T = 298K, S_g = 0.7, H = 8.65 \times 10^4 \) atm (for nitrogen),

\[
PV = 45
\]
The above equation shows the importance of using the appropriate gas to generate foam. If air is used, then above equation can be used to calculate the number of PV for washout (assuming air as a single component) using appropriate value of $H$. Since air is slightly more soluble than nitrogen, the number of PV required will be smaller. Similarly, if natural gas (methane) is used to generate foam, because of its higher solubility in water ($H = 4.13 \times 10^4$ atm), the PV for washout at the above conditions would only be $\sim 23$ (using equation C.11).

Of course, if the injected water is partially saturated with nitrogen, the PV required will be larger and can be calculated using (C.8). If the injected water contains other dissolved gases (hydrocarbons) then there will be exchange between the gas in the foam and gas in the liquid, the result of which will be to increase the PV required for foam dissolution compared to the case where water does not contain any dissolved gases. It can also be shown, using a treatment similar to that described in this appendix, that in case flowing water is saturated with dissolved gases with higher solubility (such as methane) than that present in foam (such as nitrogen), then, gas saturation will increase in foam because of this exchange of gases.