

Paper 4

Comparing the static and dynamic foam properties of a fluorinated and an alpha olefin sulfonate surfactant

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Abstract

To improve the understanding of the influence of oil type and of oil saturation on foam stability and foam generation, core flooding experiments and static foam tests have been conducted using three different North Sea oils. The experiments were performed using two surfactants - an alpha olefin sulfonate (AOS) and a fluorinated surfactant (FS-500) - both with and without oil.

Foam was generated by both surfactants in all core flooding experiments both with and without oil.

The experiments showed that the surfactants generated foam with similar strengths and stability in both dynamic foam experiments and static foam tests without oil. In the core flooding experiments with residual oil saturation, the AOS surfactant generated a weaker foam than that of the FS-500 surfactant, although foam propagated more rapidly with the AOS.

The static experiments showed that foam generation with FS-500 seemed to be independent of the presence of oil. Furthermore, the FS-500 foam generation in core flood experiments seemed independent of the presence of residual oil saturation with respect to foam strength. Foam propagation was significantly delayed, however, in the presence of oil.

For the AOS surfactant, the foam generated using 2 of 3 North Sea oils was destabilized in static foam tests. AOS generated foam with differing foam strengths for the different crude oils in the core flooding experiments. The correlation between the static and dynamic foam experiments was poor for the AOS surfactant. AOS showed more rapid foam propagation with, than without oil.

Keywords: Foam, foam-oil interactions, core flooding experiments, alpha olefin sulfonate, fluorinated surfactant

Introduction

Gas is the discontinuous phase in a foam system, separated by thin liquid films (Schramm, 1994, Holm, 1968). Foam formation in a porous media reduces gas mobility. In Enhanced Oil Recovery (EOR) foam has been used both to improve gas sweep efficiency and to shut off gas production in production wells. Foam can improve results in situations of, for example, poor area sweep, gas channeling and gravity override (Rossen, 1996, Schramm, 2005). Several field applications are discussed in: Hanssen et al., 1994, Aarra et al., 1996 and 2002, Blaker et al., 2002, and Skauge et al., 2002. In many of these North Sea field tests an alpha olefin sulfonate surfactant was used to generate foam.

A great number of core flooding experiments have been conducted to evaluate the properties of foam generation in the presence of oil (Nikolov et al., 1986, Jensen and Friedmann, 1987, Chou, 1991, Dalland et al., 1992, Kristiansen and Holt, 1992, Aarra et al., 1994 and 1997, Holt et al., 1996, Vassenden et al., 1998, Mannhardt and Svorstøl, 1999, Mannhardt et al., 2000). Usually, foam is used to reduce gas mobility in zones already flooded by gas. Thus, it is important to perform the core flooding experiments at residual oil saturation (Aarra et al., 1997 and 2002, Mannhardt and Svorstøl, 1999, Mannhardt et al., 2000).

From the literature, most data suggest that oil may limit the efficiency of foams in reducing gas mobility. Some define a critical oil saturation above which foam does not form (see discussion by Schramm, 1994), but several studies show that it is possible to generate strong foams at relatively high oil saturations (Aarra et al., 1997 and 2002, Mannhardt and Svorstøl, 1999, Mannhardt et al., 2000). Another suggests that a high concentration of light hydrocarbons in the oil appears to be the main reason for reduced foam stability (Kuhlman, 1990). In our earlier work (Vikingstad et al., 2005), we include the results for alkanes in static bulk foam tests. Lower molecular weight alkanes provided a less favorable environment for foam than alkanes with a higher molecular weight, as indicated by others (Suffridge et al., 1989, Meling and Hanssen, 1990).

Oil in the core during foam experiments has been reported to reduce the propagation velocity of foam through the core (Jensen and Friedmann, 1987, Arra et al., 1997, Vassenden et al., 1998, Mannhardt and Svorstøl, 1999). Chou (1991) reports that foam propagation without oil depends on the initial condition of the core material. Pre-saturating the core with surfactant solution prior to foam generation seemed beneficial for both foam generation and foam propagation.

To characterize the strength of the generated foam, the mobility reduction factor (MRF) is often defined (Schramm, 1994, Mannhardt et al., 2000):

$$MRF = \frac{\Delta P_{foam}}{\Delta P_{no-foam}} \quad \text{Eq. [1]}$$

ΔP_{foam} and $\Delta P_{no-foam}$ are the measured differential pressure across the porous medium with and without foam respectively. A high MRF corresponds to a strong foam.

Other methods used to describe foam strength in porous media include reporting the differential pressure of the full core and in parts of the core (Chou, 1991, Mannhardt et al., 1996, Svorstøl et al., 1996, Arra et al., 1997, Mannhardt and Svorstøl, 1999 and 2001, Siddiqui et al., 2002), or to observe the time needed for foam to propagate throughout the core.

In this paper we have examined foam generation capability for an alpha olefin sulfonate and a fluorinated surfactant in cores with residual crude oil saturation. The results from core experiments are compared to results from static foam tests (Vikingstad et al., 2005 and 2006, Arra et al., 2006). The spreading coefficient (S), entering coefficient (E), lamella number (L), and bridging coefficient (B) have been calculated using the measured surface and interfacial tension values for the oil and surfactant solution. The aim has been to try to find correlations that can elucidate and improve the understanding of foam generation and foam stability in porous media. Dynamic core experiments were conducted at high pressure and temperature. Three

different North Sea crude oils were used in separate experiments, as well as trials without oil, for each surfactant.

Dalland et al. (1992) and Mannhardt et al. (2000) found that fluorinated surfactants formed foams that were very stable in the presence of oil. Mannhardt et al. (2000) added a fluorinated surfactant to different types of surfactants. The addition of a fluorinated surfactant enhanced the oil tolerance of some, but not all, foams. Further, Dalland et al. (1992) categorized four of eight fluorinated surfactants as creating oil-tolerant foams. In their experiments, they observed foams with properties ranging from effective gas blocking foams to oil sensitive foams. Chukwueke et al. (1998) studied the AOS surfactant and two fluorinated surfactants for foam generation for use in gas shut-off. Core flooding experiments showed that gas-blocking performance under reservoir conditions was poor for one of the fluorinated surfactants. AOS combined with a polymer showed good gas blocking, as also reported by Aarra et al. (1997).

Methods and Materials

The core material used in the experiments was outcrop Berea sandstone. Each core was one piece, about 30 cm in length, and around 3,5 cm in diameter. The permeability of the cores varied between 260 mD and 310 mD. The porosity was approximately 20%, pore volume ~ 65 ml.

Two different surfactants were used: an anionic C₁₄-C₁₆ alpha-olefin sulfonate surfactant, AOS, with a molecular weight of 324 g/mole; and a fluorinated surfactant. The fluorinated surfactant was a Perfluoroalkyl betaine, FS-500, supplied by DuPont. The surfactant was zwitterionic, and, according to the vendor, the molecular weight was comparable to the AOS surfactant. The surfactant concentration was 0,5wt% in all experiments. First reference experiments without oil were conducted for the two surfactants. Experiments with three different crude oils, oil 1-3, from the North Sea for both of the surfactants followed. Two parallel experiments were done with oil 1 using FS-500. The Gas Oil Ratio (GOR), viscosity and density for the three crude oils

are presented in Table 1. The oil formation volume factor, B_o , was close to 1 for each of the oils.

Table 1: Different properties of the oils.

	GOR (Sm ³ /Sm ³)	Viscosity of STO*, 50°C (cp)	Density of STO*, 25°C (g/cm ³)
Oil 1	10	6,8	0,843
Oil 2	11	4,6	0,842
Oil 3	4	63,8	0,934

*STO= stock tank oil

The experiments were conducted at 50°C (45°C for oil 2 using AOS) and an outlet pressure of 120 bar on a horizontally oriented core. In the core flood experiments the foam quality was 80%; that is, the gas volume fraction was 0,8 and constant at the inlet throughout each experiment. The N₂-gas and the surfactant solution were injected simultaneously at a total flow rate of 40 ml/h; injection rates were controlled directly by two high pressure Quizix pumps. A visual cell was placed at the outlet of the core to observe the texture of the foam and to try to find the approximate time for foam propagation through the core. The pressure was measured at the inlet, the outlet and at the pressure tab located 17,8 cm from the inlet, that is, about 3/5 of the core length from the inlet (Figure 1). This allowed comparing pressure development through the core during foam generation and evaluation of foam propagation.

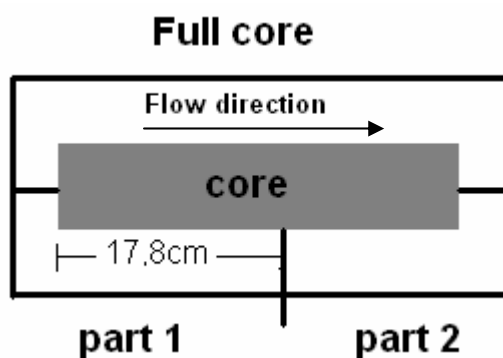


Figure 1: Illustration of pressure measurements configuration on the core.

The water-filled core was drained by Marcol (~11 cP) to irreducible water saturation. The Marcol was then exchanged by one of the nitrogen-saturated North Sea oils. A gravity stable water flooding was conducted to bring the cores to residual oil

saturation after water flooding (Sorw). Prior to foam generation, two pore volumes of surfactant were injected. The synthetic seawater had the following composition: 2,489wt% NaCl, 0,173wt% CaCl₂, 1,112wt% MgCl₂, 0,019wt% NaHCO₃, 0,406wt% Na₂SO₄, and 0,067wt% KCl. The procedure for static foam experiments is described in Vikingstad et al., 2005 and 2006, and Arra et al., 2006.

Results and Discussion

We discuss here the results of foam core flooding experiments and static experiments. Results are compared against our earlier static bulk foam experiments (Vikingstad et al., 2005 and 2006, Arra et al., 2006). The role of similarity or lack thereof between static and dynamic foam tests is a subject of ongoing debate in the literature. Mannhardt et al. (2000) reports a large number of experiments and finds it difficult to correlate foam performance in core floods with bulk foam stability, etched-glass micro model observations or interfacial parameters. The same result is reported by Dalland et al. (1992).

Overview of static foam experiments

One of the main findings of the static bulk experiments was that, in the presence of oil, the fluorinated surfactant (FS-500) generated more stable foam over time than the AOS. FS-500 seemed nearly unaffected by oil as foam tests with and without oil showed equal stability for this surfactant (Vikingstad et al., 2005 and 2006, Arra et al., 2006). The FS-500 generated 16-18 cm foam for all the foam tests.

For the AOS surfactant, results for the three North Sea oils used in this study are shown in Figure 2. Two of three oils destabilized foam. Foam stability was good for several other of the crude oils investigated (Vikingstad et al., 2005 and 2006, Arra et al., 2006). Further, foam tests with decane and alkanes with lower molecular weights destabilized the foam. The ionic strength of the brine also influenced the stability of AOS foams in the presence of oil.

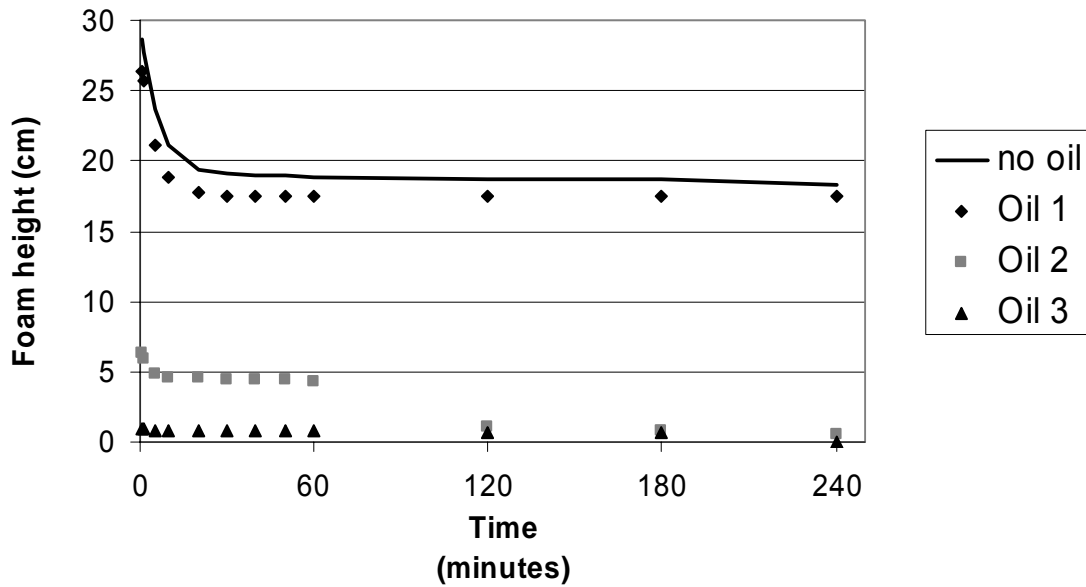


Figure 2: Foam column height as a function of time for static foam experiments with 1wt% of oil using a 0,5wt% AOS solution for the three crude oils. The same experiment without oil is indicated with a line.

In general the spreading coefficient (S), entering coefficient (E), and lamella number (L) indicated stable foam for the FS-500 (Table 2). The bridging coefficients (B) were negative in most cases. This is consistent with the results of the static foam experiments. No such correlation between S, E, L, and B, and static foam stability was evident for the AOS surfactant (Table 3 and Figure 2).

Table 2: Spreading coefficient (S), Entering coefficient (E), Lamella number (L) and Bridging coefficient (B) at equilibrium for FS-500 using different crude oils.

	Spreading Coefficient (mN/m)	Entering Coefficient (mN/m)	Lamella number	Bridging Coefficient (mN/m)
Oil 1	-15,0	-5,4	0,5	-403
Oil 2	-14,8	-7,6	0,7	-477
Oil 3	-21,9	-10,1	0,4	-776

Table 3: Spreading coefficient (S), Entering coefficient (E), Lamella number (L) and Bridging coefficient (B) at equilibrium for AOS using different crude oils.

	Spreading Coefficient (mN/m)	Entering Coefficient (mN/m)	Lamella number	Bridging Coefficient (mN/m)
Oil 1	-3,2	-0,4	2,5	-85
Oil 2	-0,2	0,6	11,6	13
Oil 3	-5,9	-5,0	9,5	-337

In these static foam tests the stability of the pseudo-emulsion film was not investigated but may be important for foam stability.

Another important results of these earlier studies was that foam generated below cmc for both surfactants, and that both reached a constant maximum foam height at 0,1-0,5wt% surfactant. In the presence of oil FS-500 generated stable foam at lower surfactant concentrations than the AOS surfactant.

Core flooding experiments

In Figure 3 the differential pressure (dP) during foam generation in the core experiments without oil is shown for the two surfactants, with a surfactant concentration of 0,5wt%. Based on dP measurements, both surfactants generated strong foams without oil in the core. Without oil the AOS surfactant generated even stronger foam than the fluorinated surfactant (compared after 2,5 PV fluid injected).

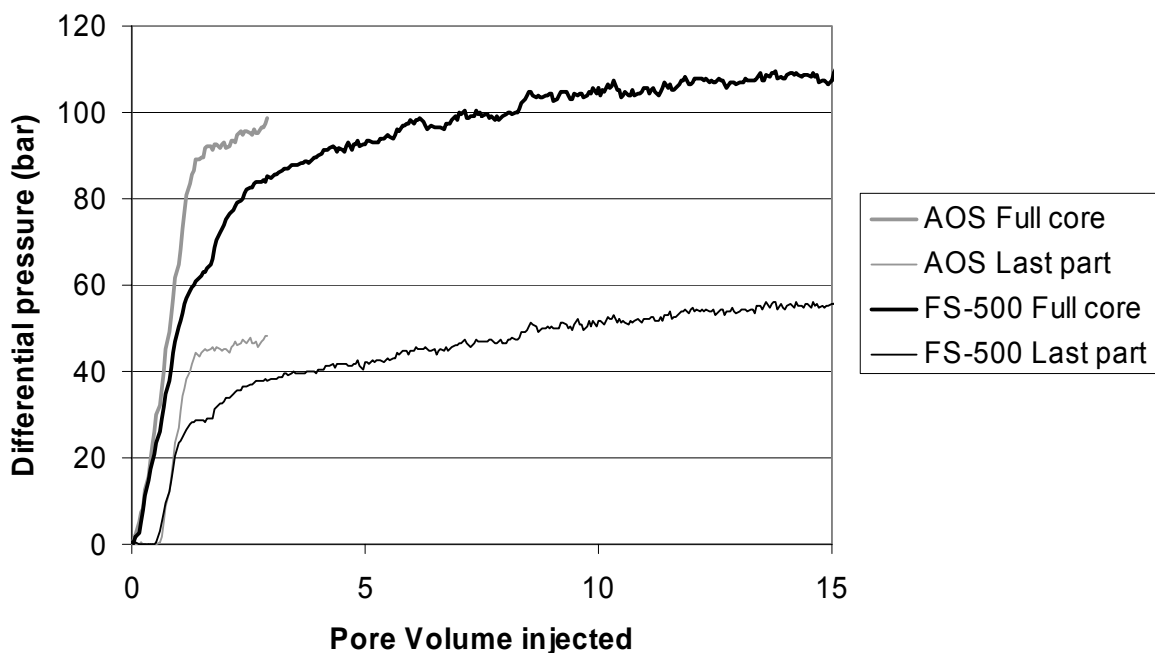


Figure 3: Differential pressure (dP) as a function of pore volumes injected fluid for core flooding experiments without oil with AOS and FS-500 surfactants. The thicker line represents the full core dP: the thinner line represents dP over the last part of the core.

In the FS-500 experiment 15 PV of surfactant solution and N₂-gas were injected. Considering the position of the pressure tabs, the dP/cm in the last part of the core was about 1,5 times higher than in the first part of the core, indicating generation of

even stronger foam. This is consistent with core experiments performed by Mannhardt et al., 2000, Mannhardt and Svorstøl, 1999 and 2001. They report a lower pressure drop in the first part of the core than over other sections both with (Mannhardt et al., 2000, Mannhardt and Svorstøl, 1999) and without oil (Mannhardt and Svorstøl, 2001). Foam propagation velocity was similar for the two surfactants in these experiments.

Core flooding experiments with residual oil saturation

Three core flooding experiments in 30 cm Berea core material were conducted for both surfactants with North Sea crude oils (1, 2, 3) at residual oil saturation after water flooding, see Table 4.

Table 4: S_{wi} and S_{orw} for the different core experiments

Core experiment:		S_{wi} (frac. PV)	S_{orw} (frac. PV)
Oil	Surfactant		
Oil 1	AOS	0,28	0,40
Oil 2	AOS	0,31	0,41
Oil 3	AOS	0,31	0,35
Oil 1	FS-500	0,30	0,39
Oil 2	FS-500	0,26	0,49
Oil 3	FS-500	0,32	0,33

Oil 1 generated a foam with equal strength and propagation rate in the two parallel experiments using FS-500. The results of the core flooding experiments are shown in Figure 4 (AOS) and Figure 5 (FS-500). Foam quality was always 80% at the inlet end of the core. Foam was visually observed at the outlet end of the core for all experiments.

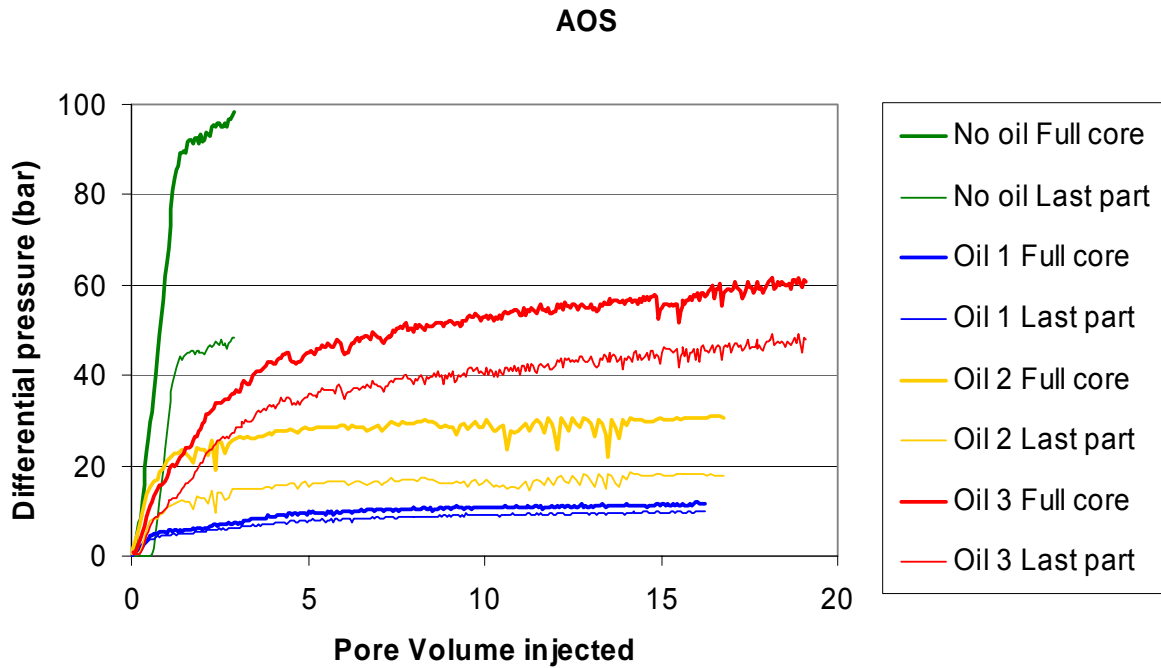


Figure 4: Differential pressure (dP) as a function of pore volumes injected fluid for the core flooding experiments using the AOS surfactant. The thicker line represents the full core dP: the thinner line represents dP over the last part of the core.

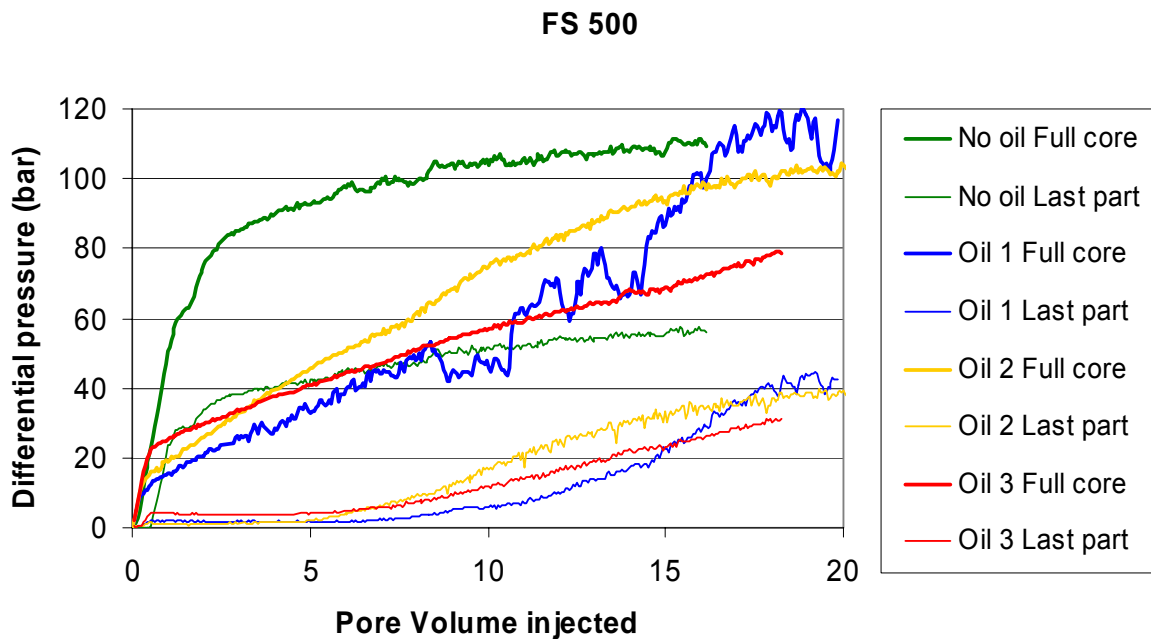


Figure 5: Differential pressure (dP) as a function of pore volumes injected fluid for the core flooding experiments with the FS-500 surfactant. The thicker line represents the full core dP: the thinner line represents dP over the last part of the core.

In the core flooding experiments with residual oil 1 and oil 2 the pressure gradient was significantly lower for the AOS surfactant than for FS-500 (Table 5). With oil 3

used as residual oil saturation, foam with nearly the same foam strength was generated for the two surfactants, it even generated stronger foam in the last part of the core for the AOS surfactant than for the FS-500, see Table 5. The pressure drop over the full core in trials with the different crude oils was 10-60 bar for the AOS and 75-115 bar for the FS-500.

Table 5: Pressure gradients for each the experiment (15 PV injected):

	Pressure gradient (bar/m)			
	AOS		FS-500	
	part 1	part 2	Part 1	part 2
No oil	271*	385*	294	457
Oil 1	9	80	366	183
Oil 2	67	151	340	351
Oil 3	56	378	255	198

*2,5 PV injected

The core experiments with FS-500 showed that the foam generated has equal strength throughout the core (oil 2) or stronger foam in the first part of the core (oils 1 and 3; calculated pressure gradients for the two parts of the core are shown in Table 5). The AOS surfactant again showed stronger foam in the last part of the core, similar to the experiment without oil (Table 5).

For the AOS surfactant the differential pressure was significantly lower with oil 1 present than with the other North Sea oils (Figure 4, Table 5). The dP was almost similar in the last part as over the full core, thus, indicating generation of high mobility foam in the first part of the core for oil 1.

The calculated mobility reduction factor (MRF) is presented in Table 6. In the calculation of the MRF values, the pressure drop across the core when flooding seawater at 40 ml/h at Sorw, has been used as a reference dP. This rate is equal to the total rate of gas and surfactant during foam generation. Using oil 3, the most viscous oil present, the MRF values are almost equal for the two surfactants. For oil 1 and oil 2 the MRF values are higher for the FS-500 than for the AOS. The AOS surfactant generated weaker foam than the FS-500 surfactant.

Table 6: The mobility reduction factor for each of the core experiments.

	Mobility reduction factor	
	AOS	FS-500
Oil 1	12	96
Oil 2	25	65
Oil 3	67	75

Foam propagation

The foam propagation rate for the two surfactants without oil present was similar. The rate was about 15 cm/h, consistent with the injection rate. With residual oil present the propagation rate was very different for the two surfactants. Foam was observed in the visual cell after about 1 hour with the AOS surfactant. In Figure 6 the differential pressure development for the last part of the core is shown, compared to the reference experiment without oil. For the AOS surfactant foam propagation was significantly more rapid with residual oil in the core than without oil. The pressure measurements revealed that the strength of the generated foam was higher without oil.

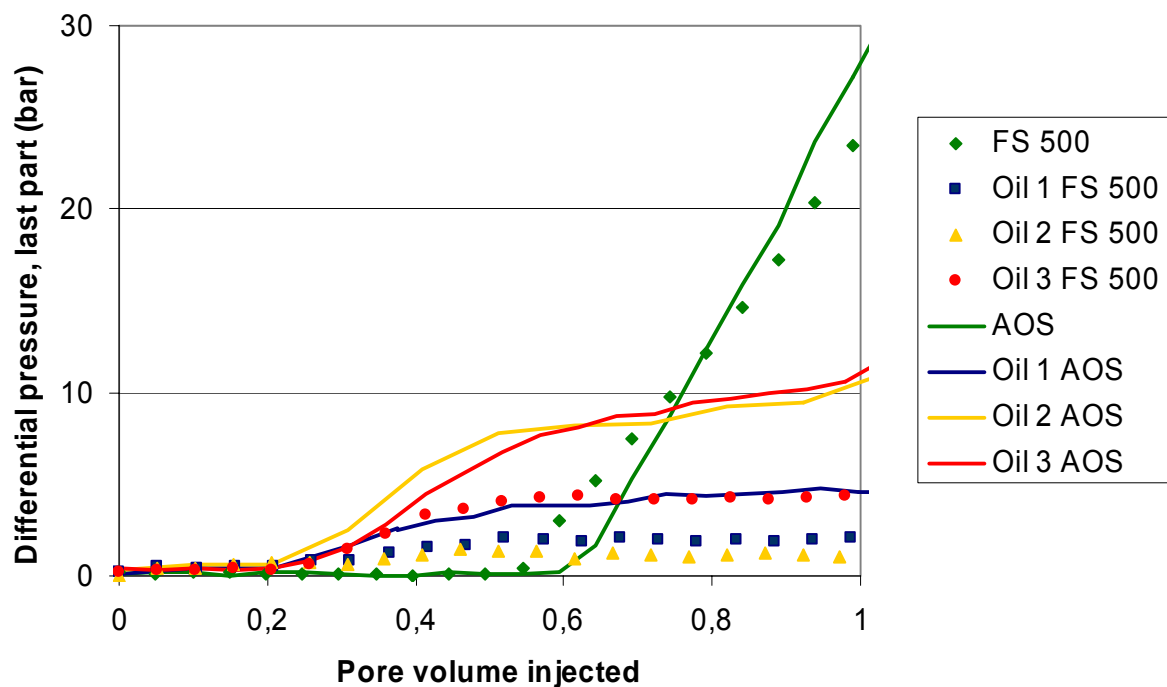


Figure 6: Differential pressure in the last part of the core as a function of pore volumes injected fluid.

It took more than 20 hours (~12 PV) for foam to propagate through the whole core using FS-500. In experiments without oil foam was observed in the visual cell after about 2 hours for both surfactants. The propagation rate was about 40 times faster without oil than with oil for FS-500 (Figure 5).

To compare foam strength and propagation Table 7 shows pore volumes injected to reach a differential pressure of 20 bar over the full core and in the last part of the core. These data, together with observations of foam in the visual cell at the core outlet shows, that the AOS generated weaker foams than the FS-500 surfactant but propagated more rapidly.

Table 7: Number of pore volumes injected before the differential pressure exceeded 20 bar for the full core and the last part of the core in each experiment.

	Differential pressure exceed 20 bar (pore volume injected)			
	AOS		FS-500	
	Full core	part 2	Full core	part 2
No oil	0,7	1,1	0,5	1,0
Oil 1	-	-	1,8	14,0
Oil 2	0,9	-	1,2	11,8
Oil 3	1,3	2,0	0,5	12,1

Even if the foam propagation were rapid with and without oil for the AOS surfactant the dP became significantly higher without oil (Figure 4). Jensen and Friedmann (1987) found that pressure increased more rapidly without oil, but in their experiments the pressure drops were, in the end, the same with and without oil. For FS-500 the differential pressure also increased faster without oil, and consistent with Jensen and Friedmann (1987), it seemed that the pressure drops were almost equal with and without oil as shown in Figure 5 (the dP was still increasing for the experiment with oil 1 when the experiment was stopped).

Comparing static and dynamic foam experiments

In our previous work (Vikingstad et al., 2005 and 2006, Aarra et al., 2006) we found that the stability of static foam with AOS was dependent on oil type. Foam stability in presence of some of the oils was almost as stable as foam tests without oil, while other oils destabilized the foam completely; see Figure 2.

The FS-500 foam was clearly more stable in the presence of oil than the AOS surfactant; foam stability was the same with or without oil for the FS-500 in the static experiments. Strong foams were also generated by FS-500 in the core experiments. It was difficult to find any direct correlations between static and dynamic foam tests with the AOS surfactant. As shown in Figure 2 unstable foam was generated in the static experiments using oil 3. In the core flooding experiment, however, with oil 3 present, the AOS generated strong foam. In fact, foam was generated with all three North Sea oils in the dynamic experiments. That is, the AOS surfactant generated foam more easily in porous media than in the static foam tests. The results from the core flooding experiments for the AOS surfactant are more consistent with the calculated S and E values (Table 3) than are the static foam results.

Kristiansen and Holt (1992) reported that non-spreading oil systems resulted in higher flow resistance than spreading systems. The spreading coefficient values for the crude oil and surfactant systems used in this paper are reported in Table 2 and Table 3. The spreading coefficients in the AOS systems were negative for both oil 1 and oil 3 and slightly negative for oil 2. The entering and bridging coefficients also indicate stable foam for oil 1 and oil 3. In FS-500 systems all coefficients were negative. Kristiansen and Holt (1992) reported that the C₁₄ AOS surfactant they used resulted in spreading behavior while the fluorinated surfactant caused non-spreading characteristics for a dead reservoir oil and a nonane/xylene system.

Holt et al. (1996) discuss the effect of increased pressure on foam stability for a C₁₆ AOS and a fluorinated surfactant. The paper presents pressure effects on foam formed inside the porous media and measurements of interfacial tension and surface tension both at 20 bar and 290 bar. At 20 bar, the fluorinated surfactant gave both negative spreading and entering coefficients. As pressure increased, the spreading coefficient was slightly negative and the entering coefficient became positive. For the

AOS surfactant the S and E were positive at both pressures. The interfacial tension was almost constant with increasing pressure, whereas the surface tensions between oil and gas, σ_{go} , or water and gas, σ_{wg} , were reduced. In fact, the surface tension between water and gas were very similar for the two surfactants at higher pressure. Interestingly, the AOS indicated the best foam in core flooding at high pressure.

Conclusions

- Foam was generated in all the core flooding experiments, both with and without oil, for both surfactants.
- The AOS and FS-500 surfactants generated foam with similar strength and propagation rate in Berea core flooding experiments without oil.
- The AOS generated weaker foam than the FS-500, but the propagation rate was more rapid for the AOS in presence of residual oil saturation (Sorw).
- The AOS generated foam with different foam strength for the different crude oils in the core flooding experiments. The results from the dynamic experiments were different from the results using static foam tests.
- The strength of the FS-500 foam was similar in core flooding experiments with and without oil.
- Foam propagation rate was influenced by residual oil saturation. From observations in a visual cell and pressure measurements the AOS surfactant showed a faster propagation rate in comparison to the propagation rate with the FS 500 surfactant, which was significantly delayed in the presence of residual oil saturation.

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