

## WETTABILITY ALTERATION DUE TO RETENTION OF CO<sub>2</sub>-FOAMING AGENTS ONTO CHALK ROCK

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### ABSTRACT

Reservoir rocks can undergo significant alterations in wettability upon retention of CO<sub>2</sub>-foaming agents on them. This paper presents a wettability characterisation study based on the retention of CO<sub>2</sub>-foaming agents on outcrop Liege chalk core samples at 55°C. Wettability characterisations were done using a sulphate wettability test which determines the water-wet fraction of a chalk rock. Two branched ethoxylated (EO) sulphonates with different ethoxylation degrees; S1 (EO=7) and S2 (EO=12) were used. The aim was to investigate the effect of foaming agent retention on wettability alterations of chalk core samples after aqueous CO<sub>2</sub>-foaming agent flooding. The wettability alterations were measured on chalk core samples saturated with 100% formation water and at residual oil saturation after waterflooding. Wettability indices were found to be altered from less water-wet to more water-wet with increasing ethoxylation degree of the CO<sub>2</sub>-foaming agents on core samples saturated with 100% formation water. In the presence of residual oil after waterflooding, increasing the ethoxylation degree shifted the wettability from more water-wet to less water-wet.

Results also show that increasing the ethoxylation degree of the CO<sub>2</sub>-foaming agent decreases the retention onto chalk cores saturated with formation water at 55°C. The presence of residual oil saturation after waterflooding ( $S_{orw}$ ) decreased the retention of S1 (EO=7) and increased the retention of S2 (EO=12) when compared to the absence of residual oil.

### INTRODUCTION

Field tests using high-pressure CO<sub>2</sub>-foam injection show that it is a feasible process for improved oil recovery (IOR) (Hoefner et al 1995). An evaluation of candidate reservoirs for possible CO<sub>2</sub>-foam application therefore requires a fundamental understanding of CO<sub>2</sub>-foam behavior under varying test conditions. The effects of parameters such as surfactant type, surfactant concentration, surfactant retention and reservoir rock type on the behaviour of CO<sub>2</sub>-foam mobility are still studied. Fjelde et al (2008) observed high retention of CO<sub>2</sub>-foaming agents with different ethoxylation degree on chalk reservoirs. Le et al (2008) proposed a new injection strategy which involved dissolving the surfactant in the CO<sub>2</sub> phase. This lowered the loss of surfactants due to adsorption and improved in-situ foam generation in carbonate cores.

During CO<sub>2</sub>-foam flooding, adsorption of surfactants on rock surface can change the wettability of the rock. Information on wetting characteristics of reservoir rocks and changes in them is of much use for studying the performance of oil recovery systems.

The wettability of a rock surface has been found to strongly influence foam generation through its functional relation with capillary pressure variation (Nguyen et al 2000). Rock surface rheological properties due to surfactants in relation to retention mechanisms of surfactants, such as adsorption, partitioning, thermal degradation, and cation exchange can significantly affect microscopic mechanisms of foam generation. Sanchez and Hazlet (1992) in a laboratory experiment compared the flow characteristics of foam in oil-wet and water-wet media. Their results showed that at similar surfactant concentrations, gas permeability reduction in both systems were approximately equal. The formation of stable foam in-situ in the oil-wet porous medium was attributed to the alteration of the initially hydrophobic surface to hydrophilic by two mechanisms; oil-water interfacial tension reduction and surfactant adsorption.

Wettability, water or oil-wetness, is usually defined in terms of the method used to determine the wetting state of a porous media. Reservoir rock wettability states are inherently difficult to ascertain as the precise wetted state of most reservoirs is largely unknown (Sanchez and Hazlet, 1992). The two most frequently used methods to quantify the wettability of core samples are the Amott-Harvey and the United States Bureau of Mines (USBM). Both methods measure the average wettability of the core sample and may be sensitive to the location of water-wet and oil-wet areas (Strand et al 2006). Measurement of wettability alterations based on dynamic adsorption on porous media has been reported in literature. Bryant et al (2006) observed wettability changes induced by adsorption and removal of polyethoxylated coconut and tallow amines on mica surfaces.

In this post presentation, the objective was to investigate the effect of aqueous CO<sub>2</sub>-foaming agent retention on wettability alterations of Liege outcrop chalk core samples at 55°C. A sulphate wettability test which determines the water-wet fraction of a chalk rock was used. It is based on the chromatographic separation of two water-soluble components, a non-adsorbing tracer, lithium, and sulphate a potential determining ion towards chalk (Strand et al 2006). The wettability changes were measured on core samples saturated with 100% formation water and at residual oil saturation after aqueous surfactant flooding.

**Table 1. Composition of brines**

Salt	Formation water (FW)	Seawater (SW)	Seawater without Sulphate (SWU)	Seawater with lithium (SWL)	Seawater with thiocyanate (SWT)
	g/l	g/l	g/l	g/l	g/l
NaCl	36.81	23.38	29.12	23.38	23.38
Na <sub>2</sub> SO <sub>4</sub>	-	3.41	-	3.41	3.41
LiCl	-	-	-	0.10	-
KSCN	-	-	-	-	2.33
NaHCO <sub>3</sub>	-	0.17	0.17	0.17	0.17
KCl	0.31	0.75	0.75	0.75	0.75
MgCl <sub>2</sub> *6H <sub>2</sub> O	4.48	9.15	9.05	9.15	9.15
CaCl <sub>2</sub> *2H <sub>2</sub> O	33.25	1.91	1.91	1.91	1.91

## **METHODOLOGY**

### **Materials**

The core samples used were outcrops of Liege chalk. They were sampled from the same block. All the plugs had a length of approximately 7.0 cm and a constant diameter of 3.8 cm. Liege outcrop chalk contains only minor amounts of clay and less than 2 % silica (Strand et al 2007). The core samples were cleaned using a procedure described elsewhere (Fjelde et al 2008). A cleaned chalk plug at initial water saturation was flooded with heptane to establish a water-wet reference plug (Strand et al 2006). Stock tank oil from a North Sea reservoir was used for the core preparations.

### **Fluids**

Brines used were synthetic formation water (FW) and seawater (SW) with the compositions as listed in Table 1. Active aqueous CO<sub>2</sub>-foaming agent solutions (1.0wt %) were prepared with synthetic seawater including a tracer (non-adsorbing chemical substance). Synthetic seawater with thiocyanate (SWT) as a tracer was used in the first set of retention experiments and later changed to synthetic seawater with lithium (SWL) in subsequent tests (because of in-consistent measurements with an in-house spectrophotometer). The sulphate wettability tests were done by water flooding the plugs with synthetic seawater without sulphate (SWU) followed by synthetic seawater with sulphate and lithium (SWL). All the fluids samples were filtered before use.

### **Core Preparations**

The core samples were prepared with either formation water or stock tank oil. Detail descriptions of the procedures are described in Fjelde et al (2008).

### **Flooding Procedures**

Retention and wettability experiments were done using a flow-through experimental set-up, and procedures used in the absence and presence of oil are described in Fjelde et al (2008). Aqueous solutions of the foaming agents and brines were injected upward at a constant rate of 0.2 ml/min at 55°C. Solutions were injected until the injected and effluent concentrations were the same. Five millilitre fractions of the effluent samples were collected and analysed for surfactant, sulphate and tracer concentrations.

### **Analytical Methods**

Analytical methods used for analyzing surfactants (S1 and S2), tracers (lithium and thiocyanate), and sulphate concentrations in effluent samples are described in Fjelde et al (2008). The amount of surfactant retained was determined by plotting the ratio ( $C/C_0$ ) of effluent surfactant/tracers concentrations ( $C$ ) to injected surfactant/tracer concentrations ( $C_0$ ) versus the cumulative pore volumes produced, and calculating the area between the effluent profiles using the trapezium method. Wettability indices (WI) were similarly determined by plotting the ratio ( $A/A_0$ ) of effluent sulphate/tracer concentrations ( $A$ ) to injected sulphate/tracer concentrations ( $A_0$ ) versus the cumulative pore volumes produced, and determining the area between the effluent profiles. Wettability indices in the absence of oil were calculated as normalized wettability indices based on a core sample saturated

with 100% FW and not exposed to any foaming agent solution. Wettability indices in the presence of oil were calculated as a ratio between the areas,  $A_{wett}$  and  $A_{heptane}$  as follows:

$$WI = \frac{A_{wett}}{A_{heptane}} \tag{1}$$

where:

$A_{wett}$  = area between the lithium and sulphate effluent profiles water flooding

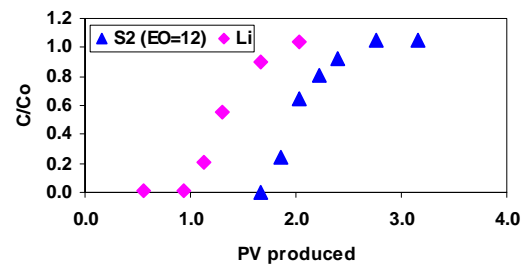
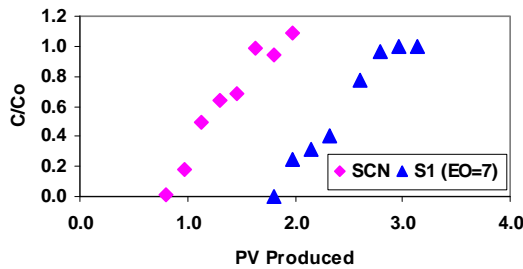
$A_{heptane}$  = reference area between lithium and sulphate profiles generated by flooding a chalk core sample at initial water saturation with heptane (Strand et al 2006).

### RESULTS AND DISCUSSIONS

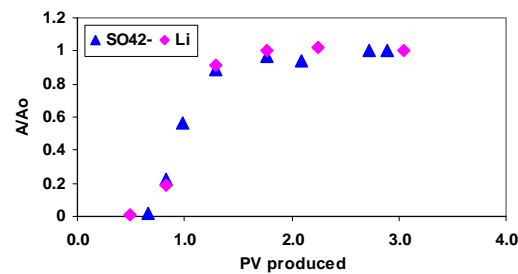
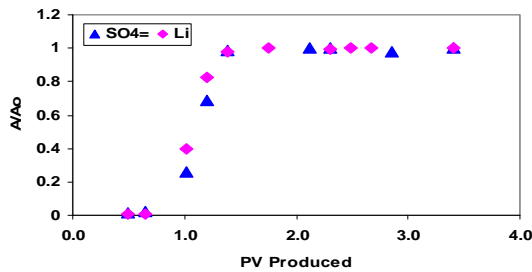
Table 2 presents an overview of the retention and wettability results on plugs saturated with 100% FW at 55°C. The retention of surfactants onto chalk were estimated as 2.7 mg S1 (EO=7) / g rock and 1.6 mg S2 (EO=12)/ g rock respectively (Figures 1 and 2).

**Table 2. Core properties and an overview of retention and wettability indices on plugs saturated with 100% formation water at 55°C**

Core sample #	Dry weight	$S_{wi}$	Fluid type	Retention	Area between profiles	Normalized Wettability Index
	[g]	[%]		[mg/g rock]	[ $A_{wett}$ ]	[WI]
2	123.6	100	SWL	-	0.12	1.0
3	130.1	100	S1 (EO=7)	2.7	0.07	0.6
4	124.9	100	S2 (EO=12)	1.6	0.12	1.0



**Figures 1 and 2—Normalized effluent adsorption profiles for S1 (EO = 7) and S2 (EO=12) at  $S_{wi} = 1$**



**Figures 3 and 4— Normalized effluent wettability profiles for S1 (left) and S2 (right) at  $S_{wi} = 1$**

The experiments show that the retention of surfactants onto 100% FW saturated chalk core

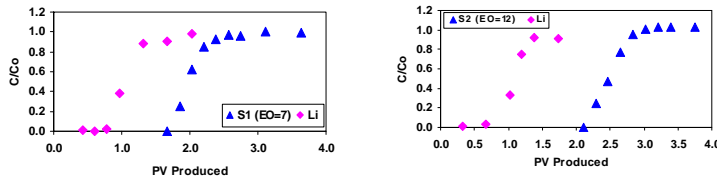
samples decreases as the number of ethoxylation degree increases. The foaming agents used were anionic surfactants, and they are thought to have rather large adsorption onto positively charged surfaces due to heavy electrostatic interactions. However, it has been suggested that increasing the ethoxylation degree might reduce the surfactant retention (Zhang and Somasundaran, 2006).

Using the area between the effluent profiles, the normalized water-wetting indices (WI) were estimated to range between 0.6-1.0 depending on the amount of foaming agent retained (Table 2). The reference core sample #2 saturated with 100% FW and not exposed to any aqueous foaming agent solution was used to determine the initial WI of the core samples before aqueous foaming agent injection. Compared to core sample #2, the wettability of plugs saturated with 100% FW and flooded with aqueous foaming agent solutions were observed to shift from less water-wet to more water-wet with increasing ethoxylation degree of the CO<sub>2</sub>-foaming agent (Figures 3 and 4). Table 3 presents an overview of the retention and wettability results on plugs with residual oil saturations. The retention of S1 (EO=7) in the presence of oil was estimated as 2.2 mg/g rock (see Figure 5), approximately 19% lower than in the absence of oil (Figure 1).

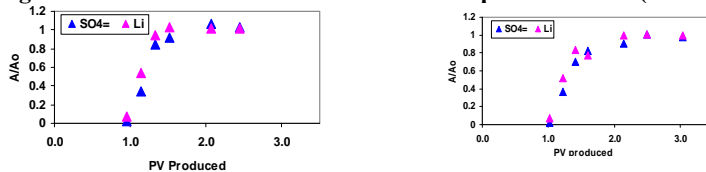
**Table 3. Core properties, retention and wettability indices for core plugs with  $S_{orw}$  at 55°C**

Core sample #	Dry weight	$S_{wi}$	$S_{orw}$	$S_{orc}$	Fluid type	Retention	Wettability index
	[g]	[%]	[%]	[%]		[mg/g rock]	WI
1	121.8	10.6	-	-	Heptane	-	1
5	121.3	13.5	24.8	24.5	SW	-	0.5
6	125.3	15.2	17.5	19.6	S1(EO=7)	2.2	0.8
7	126.3	15.2	30.6	9.8	S2(EO=12)	3.2	0.6

The reduction in retention in presence of oil may be due to the fact that residual oil could block some of the relevant adsorption sites for the surfactant. Similar behavior has been found by Austad *et al.* (1991) during similar studies with an ethoxylated sulphonate with 7 ethoxy groups.



**Figs. 5 and 6—Normalized effluent retention profiles for S1 (EO = 7) and S2 (EO=12) at  $S_{orw}$**



**Figs. 7 and 8— Normalized effluent wettability profiles for S1 (left) and S2 (right) at  $S_{orw}$**

The retention of S2 (EO=12) in the presence of residual oil was estimated as 3.2 mg/g rock (Figure. 6), 100% higher than in the absence of oil (Figure. 2). The increased loss of S2 (EO=12) may be attributed to both the surfactant and oil molecules having a high affinity

for the solid-liquid interface, and are both co-adsorbed. Celik et al. (1988) observed a similar relation when they investigated the adsorption of anionic surfactants with different ethoxylation degree onto limestone at 90°C.

The water-wetting indices (WI) in core samples with residual oil saturations were calculated as a ratio between  $A_{wett}$  of the tested core sample and  $A_{heptane}$  for the reference core at initial water saturation and flooded with heptane (as the non-wetting fluid) (Table 3). WI were classified as follows; between 0.0 for a completely oil-wet core, 0.5 for a neutral wettability to 1.0 for a completely water-wet core (Strand et al 2006). Comparing the wettability indices to core #5 (not exposed to any aqueous foaming agent solution) at  $S_{orw}$  before foaming agent injection, the wettability indices were observed to shift from 0.5 (neutral wettability) to 0.8 (more water-wet) and 0.6 (less water-wet) with increase in ethoxylation degree of the CO<sub>2</sub>-foaming agent. (Figures 7 and 8). Strand et al (2006) using the same wettability test observed wettability alterations of neutral to strongly oil-wet depending on the crude oil's acid number on Liege cores at 90°C.

## CONCLUSIONS

Based on the experimental results the following conclusions can be drawn:

- Increasing the number of ethoxylation degree decreased the retention on core samples saturated with 100% FW at 55°C.
- The retentions were estimated as 2.7 mg/g rock for S1 (EO=7) and 1.6 mg/g rock for S2 (EO=12) respectively on core samples saturated with 100% formation water.
- Sulphate wettability indices were observed to increase with increasing ethoxylation degree of the foaming agents on core samples saturated with 100% FW, i.e. more water-wet.
- The presence of residual oil increased and decreased retention. The retention of S1 (EO=7) decreased to 2.2 mg/g rock, whilst that of S2 (EO=12) increased to 3.2 mg/g rock.
- The presence of residual oil saturations shifted the wettability indices from more water-wet to less water-wet with increasing ethoxylation degree.

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