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Capillary and Gravity Dominated Flow Regimes in Displacement of Oil from an Oil-Wet Chalk Using Cationic Surfactant

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Oil can be displaced from preferentially oil-wet low permeability chalk by spontaneous imbibition of seawater containing a cationic surfactant, C12TAB, as wettability modifier. In the presence of the cationic surfactant, the capillary forces are decreased due to lowering of the IFT, but at the same time, the capillary forces are also increased due to increased water wetness. The relative impact of capillary and gravity forces on the fluid flow is experimentally studied by comparing the fractional oil production rate per area unit from the top surface and the other core surfaces. The cores used had a dimension of height ≈ 5 cm and diameter ≈ 3.5 cm. For IFT values in the range of 1.10 mN/m, the displacement of oil was dominated mainly by capillary forces at the start, but a crossover to gravity dominated flow was observed at a later stage. The impact of gravity forces decreased as the height of the core decreased. For IFT values below 0.63 mN/m, the oil displacement was mainly dominated by gravity forces (i.e., the oil was recovered mostly from the top surface of the core). In a fractured carbonate reservoir with significant capillary continuity in vertical direction, it is therefore expected that the oil displacement using the cationic surfactant is totally dominated by gravity forces.

Introduction

Reservoir modeling of highly fractured carbonate reservoirs is often performed using a dual porosity model, which is based on a fluid exchange term between the fractures and the matrix blocks.[1,2] If the permeability contrast between the matrix and the fractures is large, the displacement of oil from the matrix blocks usually takes place due to capillary forced spontaneous imbibition, provided that the rock is preferentially water-wet. The fluid exchange term can be calculated using scaling laws, which determine the imbibition in terms of dimensionless time.[3] Since the pioneering work by Mattax and Kyte,[4] who scaled capillary forced imbibition under very specific conditions, several modifications of the scaling formula have appeared in the literature.[5] The scaling law defined by Ma et al.[6] has been frequently used to scale capillary forced imbibition:

$$t_d = \frac{\sqrt{\frac{k}{\phi}}\sigma}{\sqrt{\mu_o \mu_w} L_a^2} t \tag{1}$$

where t_d is the dimensionless time, k is the rock permeability, ϕ is the porosity, σ is the interfacial tension between the wetting and the nonwetting phase, μ_o and μ_w are the viscosities of oil and water, respectively, and t is the actual time. L_a is the characteristic length defined by:

$$L_a = \sqrt{\frac{V_b}{\sum \frac{A_i}{d_i}}} \tag{2}$$

where V_b is the bulk volume, A_i is the different production areas, and d_i is the distance from A_i to the no-flow boundary. Also in this case, limitations concerning the wetting conditions, initial fluid saturation, and, of course, gravity forces must be neglected.

Schechter et al.[7] discussed the relative contribution of capillary and gravity forces on the fluid flow in terms of the inverse Bond number defined by:

$$N_B^{-1} = C \frac{\sigma \sqrt{\frac{\phi}{k}}}{\Delta \rho g H} \tag{3}$$

where C is a dimensionless constant equal to 0.4 for a cylindrical capillary tube model, $\Delta \rho$ is the density difference between oil and water, σ is the interfacial tension between water and oil, g is the gravity constant, H is the height of the core, ϕ is the porosity of the core, and k is the permeability. Model solvent systems were used as fluids with well-defined wetting and nonwetting phases, and the IFT was varied by using corresponding fluids along different tie lines (0.10−38.1 mN/m). For this well-defined water-wet model system, the relative impact of capillary and gravity forces on the spontaneous imbibition process could be related to the value of the inverse Bond number.

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(1) Gilman, J. R.; Kazemi, H. *SPEJ* **1983**, *23* (August), 695−707.
(2) Thomas, L. K.; Dixon, T. N.; Pierson, R. G. *SPEJ* **1983**, *23* (February), 42−54.
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(6) Ma, S.; Zhang, X.; Morrow, N. R. *J. Can. Pet. Technol.* **1999**, *38*, 25−30.
(7) Schechter, D. S.; Zhou, D.; Orr, F. M. *J. Pet. Sci. Eng.* **1994**, *11*, 283−300.

Table 1. Molar Concentration of the Ions in the Imbibing Seawater, SSW, and Solutions Used for the Chromatographic Wettability Test, SSW-U and SSW-M

ion	SSW mole/L	SSW-U mole/L	SSW-M mole/L
Ca^{2+}	0.013	0.013	0.013
K^+	0.010	0.010	0.034
Mg^{2+}	0.045	0.045	0.045
Na^+	0.45	0.500	0.450
Cl^-	0.525	0.623	0.525
HCO_3^-	0.002	0.002	0.002
SO_4^{2-}	0.024	0	0.024
SCN^-	0	0	0.024

Recently, Li and Horne[8] derived a general analytical scaling model for spontaneous imbibition, which incorporated both capillary and gravity forces. The model also contained general parameters such as mobility and capillary pressure. They tested the scaling model by using the experimental data published by Schechter et al.,[7] and the fit was surprisingly good when the normalized oil recovery was plotted versus the dimensionless time. The scaling was, however, performed without testing the shape or the height of the cores. It appeared as the authors used the shape factor L_a, which is normally used for capillary forced imbibition.

In a recent article, Høgnesen et al.[9] tested the scaling model of Li and Horne[8] by using data from spontaneous imbibition of a water-based surfactant solution into neutral to preferential oil-wet chalk. The imbibition took place by means of a wettability alteration process, which was described in detail in previous articles.[10,11] Thus, in addition to decreasing the IFT and thereby activating the gravity forces, the capillary forces are also enhanced by the wettability alteration. It was of great interest to note that the imbibition data, also in this case, were fitted with the new dimensionless time formula suggested by Li and Horne[8] provided that the height of the core was used as shape factor. The dimension of the core was not scaled by using the shape factor L_a (eq 2), which is mainly related to countercurrent flow. A fluid flow model involving a crossover from countercurrent flow dictated by capillary forces to a more gravity dominated flow was suggested.[9]

The objective of the present work is to perform laboratory experiments to monitor the oil production rate from the various surfaces of the core sample. A special imbibition cell was constructed to isolate and monitor the oil production by spontaneous imbibition from the top surface of the core and the rest of the core surface, using a cationic surfactant as wettability modifier.

Experimental Section

Oil. The oil used was a crude oil diluted with 40 vol % heptane. No precipitation of asphaltenic materials was observed during storage. The oil mixture had an acid number, AN, of 1.7 mg KOH/g. The density and viscosity at 20 °C was 0.805 g/cm³ and 2.5 cP, respectively.

Water. Artificial seawater (SSW) was used as the imbibing fluid, and modifications of SSW were used in the wettability test. The brine compositions are given in Table 1.

Surfactant. The cationic surfactant dodecyltrimethylammonium bromide, abbreviated C12TAB, was used as the wettability modifier.

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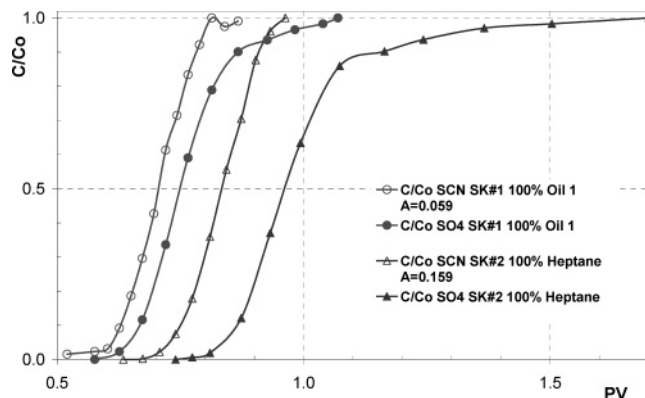
Figure 1. Wettability tests on Stevns Klint chalk without initial brine during aging. WI = (0.059/0.159) = 0.37.

Table 2. Core Data for the Imbibition Experiments

test	core	length (cm)	diameter (cm)	ϕ	pore volume (cm³)	permeability (mD)
1	E5a	5.86	3.495	0.48	27.25	1−3
2	E5b	2.62	3.495	0.48	12.19	1−3
3	M3	5.06	3.50	0.47	22.66	1−3
4	M5	4.52	3.50	0.47	20.38	1−3
5	M1	5.53	3.50	0.48	25.25	1−3

Porous Medium. Outcrop chalk from Stevns Klint near Copenhagen was used as porous medium. The core data are given in Table 2.

Core Pretreatment. To obtain uniform wetting conditions, the cores were treated according to the procedure previously described by Standnes and Austad[12] for chalk cores without initial water present. The cores were first dried at 90 °C to constant weight. They were then evacuated and saturated with oil before being flooded with the same oil, about 2 PV in each direction, to ensure homogeneous saturation. The porosity was calculated by weight differences and the density of the oil. The residual water saturation, S_{wr}, was then calculated on the basis of the initial pore volume and displaced water. The cores were aged in the oil in a closed container at 50 °C for 5 days. During the aging process, the cores were surrounded with fresh crude oil, and a large amount of surface-active components from the oil adsorbed onto the outermost surfaces of the cores.[12] Since this is not representative for the general wetting state of the rest of the core surface, the outermost 2 mm of each core was shaved off in a lathe prior to the imbibition test. The volume of oil, V_o, present was then calculated according to the formula:

$$V_o = V_{bulk}\Phi(1 - S_{wr}) \qquad (4)$$

where V_{bulk} is the new bulk volume of the core, Φ is the porosity, and S_{wr} is the residual water saturation after flooding the core with oil.

Wettability Test. The principle of the test was based on the chromatographic separation of the nonadsorbing tracer thiocyanate, SCN^-, and the adsorbing species SO_4^{2-} at water-wet sites in the porous system. The chromatographic test was identical to the method described by Strand et al.[13] The wetted core was flooded to residual oil saturation, S_{or}, with seawater without sulfate and tracer (SSW-U), and then the core was flooded at constant rate with seawater with sulfate and tracer (SSW-M). The compositions of the brines used are listed in Table 1. Small fractions of the effluent were collected using a fraction collector and analyzed for the concentration of SCN^- and SO_4^{2-}. The relative concentration of the ions was plotted against the PV injected. The area (*A*)

(12) Standnes, D. C.; Austad, T. *J. Pet. Sci. Eng.* **2000**, *28*, 111−121.

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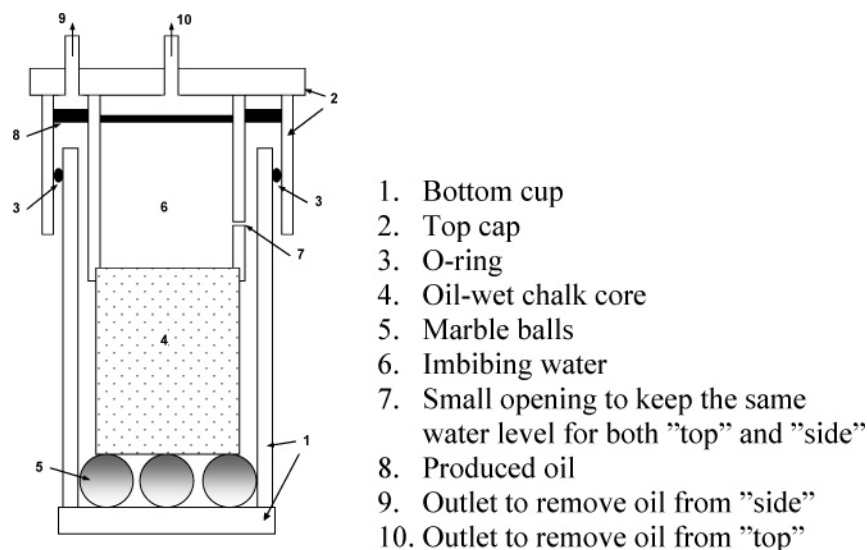
Figure 2. Schematic illustration of the imbibition cell used.

1. Bottom cup
2. Top cap
3. O-ring
4. Oil-wet chalk core
5. Marble balls
6. Imbibing water
7. Small opening to keep the same water level for both "top" and "side"
8. Produced oil
9. Outlet to remove oil from "side"
10. Outlet to remove oil from "top"

Table 3. Fluid Data for the Imbibition Experiments

test	core	ρ_o (g/cm^3)	ρ_w (g/cm^3)	surfactant concn (wt %)	IFT (mN/m)
1	E5a	0.808	1.04	3.5	1.10
2	E5b	0.808	1.04	3.5	1.10
3	M3	0.808	1.02	1.0	0.63
4	M5	0.808	1.02	1.0	0.63
5	M1	0.808	1.01	0.6	0.40

Figure 3. Interfacial tension versus surfactant (C12TAB) concentration at 40 °C.

between the effluent curves for the two components SCN$^-$ and SO$_4^{2-}$ is directly proportional to the water-wet area of the chalk surface. The area was calculated using the trapezoid method.

The wetting index (WI) is defined as the ratio between the adsorption area of the wetted core and the adsorption area for a completely water-wet core using heptane as the wetting fluid. The WI varies from 1.0 for a complete water-wet condition to 0 for a complete oil-wet condition. At neutral conditions, WI = 0.5. According to Figure 1, the wetting indexes were in the range of 0.37, which corresponded to a preferential oil-wet core. The chromatographic wetting test was performed at room temperature. No spontaneous imbibition of brine without surfactant was noticed at 40 °C.

Imbibition Procedure. The imbibition cell was designed to separate the oil leaving the core from the top surface from the oil leaving the core from the rest of the core surface, as illustrated in Figure 2. All the tests were performed at 40 °C, and the produced oil was removed from the cell through a hole in the top by a syringe at proper time intervals. The oil volume was recorded. The various test data are given in Table 3.

IFT. The IFT measurements were performed using a Krüss SITE04 spinning drop tensiometer with a small sample volume set installed. The fluids were equilibrated at 40 °C at a 1:1 ratio by volume.

Results and Discussion

The acid number of the crude oil used is relatively high, AN = 1.7 mg KOH/g. The carboxylic materials in the crude oil will act as surface active compounds, which make the interface between oil and water negatively charged.[14] From the chemical literature, it is well-known that cationic surfactants of the ammonium-type and carboxylic acids form strong 1:1 complexes, and the adducts are often described as cat-anionic
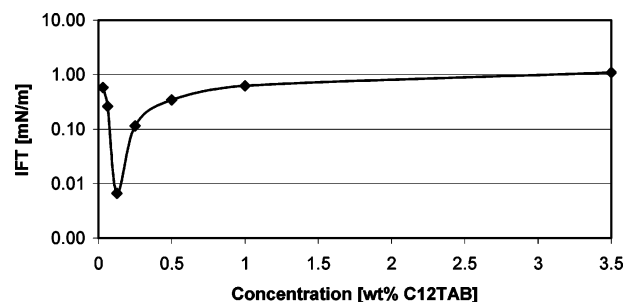
surfactants.[15] Strong synergism in the interfacial tension reduction efficiency is normal for binary surfactant systems of this type.[16] The naturally occurring carboxylic materials in the crude oil have a wide compositional range, and this may be the reason for the low IFT value at the minimum observed in Figure 3. In all cases, the IFT was determined using a 1:1 volume ratio between oil and water at different surfactant concentrations. The minimum in the IFT has often been related to the CMC of the surfactant system, and the CMC for C12TAB in distilled water has previously been determined to be about 0.4 wt %. In the case of a crude oil with a high AN, the minimum in the IFT appeared to occur at a much lower concentration of the surfactant, and furthermore, the minimum IFT value was much lower. It should be noted that a minimum in the IFT value would probably also be observed at constant surfactant concentration and varying the oil/water ratio.[14]

During a spontaneous imbibition process, the concentration of the surfactant at the waterfront may be somewhat different from the concentration in the initial bulk solution due to adsorption onto the rock or partitioning into the oil phase. For the first two experiments, it was decided to keep the concentration of surfactant high, 3.5 wt %, to have a fairly constant value of the IFT during the imbibition process, IFT = 1.10 mN/m. The core termed E5a from test 1 was 5.86 cm long, while the core E5b from test 2 was only 2.62 cm long. The wetting

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(16) Rosen, M. J. In *Phenomena in Mixed Surfactant Systems*; Scamehorn, J. F., Ed.; ACS Symposium Series 311; American Chemical Society: Washington, DC, 1986; pp 144−162.
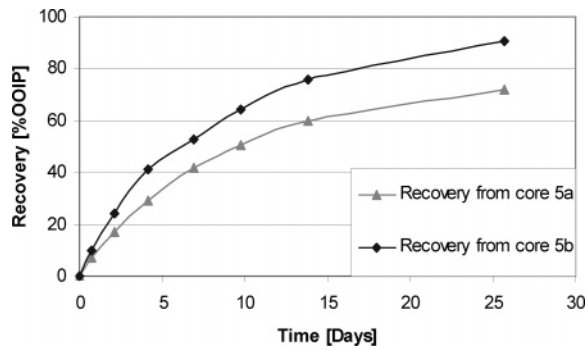
Figure 4. Recovery curves of the imbibition with 3.5 wt % C12TAB. IFT = 1.10 mN/m.
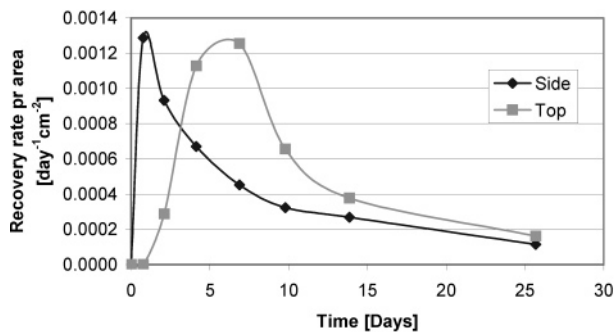

Figure 5. Fractional oil recovery rate per unit area for the core E5a from the top surface and the rest of the surface area. Temperature is 40 °C.

Figure 6. Fractional oil recovery rate per unit area for the core E5b from the top surface and the rest of the surface area. Temperature is 40 °C.

Figure 7. Spontaneous imbibition using 1.0 wt % C12TAB (IFT = 0.63 mN/m). Temperature is 40 °C.

Figure 8. Fractional oil recovery rate per unit area for the core M3 from the top surface and the rest of the surface area. Temperature is 40 °C.

Figure 9. Fractional oil recovery rate per unit area for the core M5. Surfactant concentration is 1.0 wt %, and temperature is 40 °C

conditions for the two cores should be quite similar since they were prepared from the same initial core. The oil recovery from the small core appeared to be faster than the oil recovery from the longer core (Figure 4), which may indicate a stronger impact of capillary forces for the small core. Displacement of oil by gravity forces in low permeable chalk in a spontaneous imbibition experiment is known to be very slow.[10]

To illustrate the relative production rate of oil from the top surface and the rest of the core surface, the oil recovery rate was calculated as fractional oil recovery per unit surface area (i.e., fractional oil recovery/day$_*$cm^2). The fraction was defined as recovery relative to oil initially in place. In the case of core E5a, the oil recovery rate from the bottom and side was high at the start, and it passed through a maximum after about 1 day (Figure 5). Then the recovery rate decreased with time. The oil production rate from the top surface was initially low, and it passed through a maximum after about 7 days. The difference in the oil production rate per unit area from the top surface and the other surfaces was obvious, and it confirmed that the imbibition process was governed by capillary forces at the start and by gravity forces at a later stage.

For the smaller core E5b (2.62 cm), the difference in the fractional oil recovery rate per unit area between the top surface and the other surfaces was smaller, but we can still see a similar trend (Figure 6). As expected, the impact of gravity forces will increase as the height of the core increases. The influence of gravity forces on the fluid flow in the E5a core suggests that even a small decrease in the IFT should increase the impact of gravity forces significantly. It was therefore suggested to perform imbibition experiments at lower surfactant concentrations (i.e., at 1.0 and 0.6 wt %) to obtain lower IFT values in line with Figure 3.

The imbibition data for cores M3 (height 5.06 cm) and M5 (height 4.52 cm), when using 1.0 wt % C12TAB, are shown in Figure 7. At this surfactant concentration, the initial IFT between
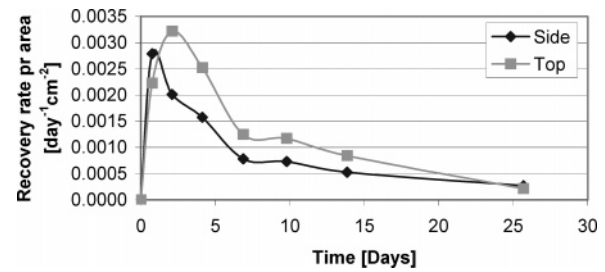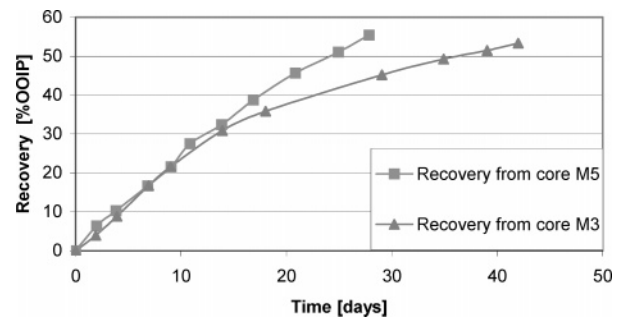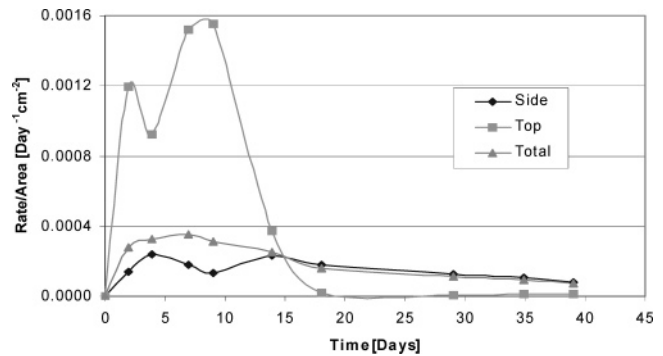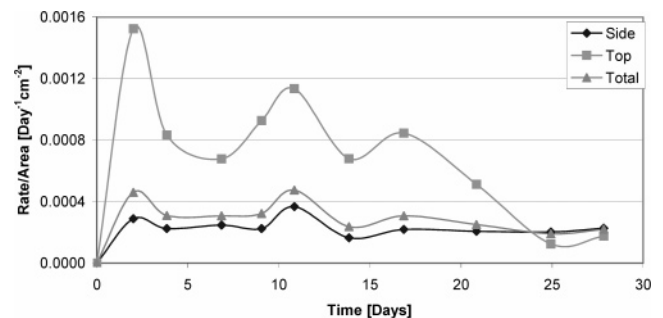
oil and water was about 0.63 mN/m. The fractional oil production rates per unit area are presented in Figures 8 and 9 for cores M3 and M5, respectively. Even though there is some scattering in the data, the oil production rate from the top surface was large from the start of the imbibition process and much higher than the oil displacement rate from the other surfaces. Thus, a decrease in IFT from 1.10 to 0.63 mN/m increased the impact of gravity forces drastically. The scattering in the data for the M5 core (Figure 9) must be related to the inaccuracy sampling technique used.
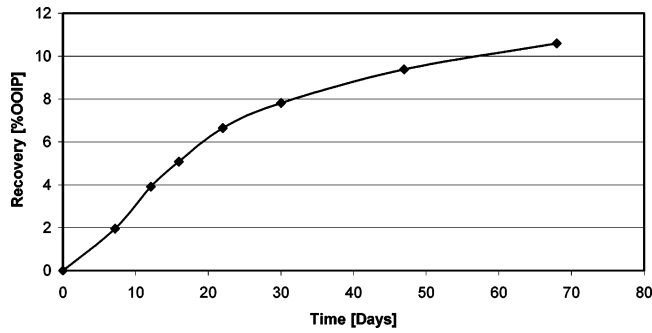
Figure 10. Spontaneous imbibition using 0.6 wt % C12TAB (IFT = 0.40 mN/m). Temperature is 40 °C.
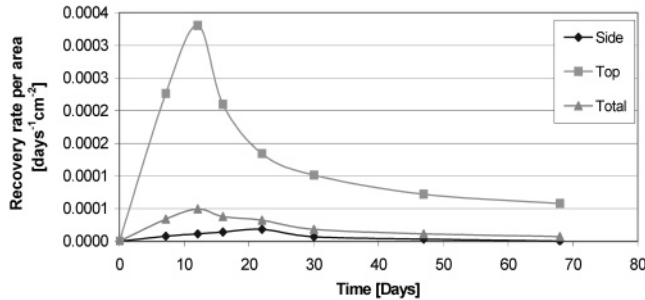

Figure 11. Oil recovery rate per unit area for the core M1 from the top surface and the rest of the surface area. Temperature is 40 °C.

A final test at 0.6 wt % surfactant solution was performed on core M1 (height = 5.53 cm). In this case, the initial IFT was 0.40 mN/m. As seen in Figure 10, the oil recovery was low, about 10% after 50 days. Figure 11 also confirms that the oil was produced mainly from the top surface, and only traces of oil were produced from the other surfaces. Thus, in this case, the gravity forces dominate totally the mechanism of the fluid flow, and in line with previous studies, the fluid flow is very slow.

It should be noticed that no initial brine was present in the cores. Previous experiments have shown that chalk cores became more oil-wet compared to cores containing initial brine, otherwise they showed a similar behavior regarding spontaneous imbibition in the presence of the cationic surfactant. It is therefore hard to believe that the fluid flow pattern should be different for cores containing initial water.

In a spontaneous imbibition process using surfactant, it is difficult to relate the crossover from a capillary forced imbibition to a gravity dominated flow to a certain inverse Bond number in the way Schechter et al.[7] did for their model systems. The reason is that the core undergoes a wettability change during the imbibition process, and furthermore, the IFT is much lower in the flooded area compared to the noncontacted area.

In an actual fractured chalk reservoir, the capillary contact in the vertical direction is normally much larger than the size of the matrix blocks. Thus, if the cationic surfactant is injected into a field, the fluid flow would be completely governed by gravity forces.

Conclusion

Spontaneous imbibition experiments into small preferential oil-wet chalk cores have been performed using a cationic surfactant, C12TAB, as wettability modifier. The relative impact of capillary and gravity forces was studied by comparing the production rate from the top surface and the other surfaces of the core. The fluid flow was in line with a mechanism previously suggested by Høgnesen et al.[9] based on the scaling model proposed by Li and Horne.[8] The main conclusions from the work are:

(1) The IFT between a crude oil with a high AN (1.70 mg KOH/g oil) and an aqueous solution containing a cationic surfactant of the quaternary ammonium type (C12TAB) is very sensitive to the surfactant concentration, probably due to complex formation between carboxylic materials from the crude oil and the cationic surfactant.

(2) At IFT values in the range of 1.10 mN/m, the displacement of oil was dominated mainly by capillary forces at the start, but a crossover to gravity dominated flow was observed at later times. The impact of gravity forces decreased as the height of the core decreased.

(3) At IFT values below 0.63 mN/m, the oil displacement was mainly dominated by gravity forces, i.e., the oil was recovered mainly from the top surface.

(4) In a fractured carbonate reservoir with significant capillary continuity in the vertical direction, it is expected that the oil displacement using the cationic surfactant is totally dominated by gravity forces.

Nomenclature

A_i = area of surface i

AN = acid number

C12TAB = dodecyltrimethylammonium bromide, $C_{12}H_{25}N(CH_3)Br$

IFT = interfacial tension

k = permeability

L_a = characteristic length

l_i = distance from surface i to the nonflow boundary

PV = pore volume

RRA = recovery rate per area

SSW = synthetic seawater

S_{wr} = residual water saturation

t = time

t_d = dimensionless time

V_b = bulk volume

V_o = oil volume

WI = wetting index

σ = interfacial tension

Φ = porosity

μ_o = oil viscosity

μ_w = water viscosity

ρ_o = density of oil

ρ_w = density of water