Spontaneous Imbibition of Seawater Into Preferentially Oil-Wet Chalk Cores—Experiments and Simulations

L. Yu, S. Evje*, H. Kleppe, T. Kårstad, I. Fjelde*, and S.M. Skjaeveland

Faculty of Science and Technology, Department of Petroleum Engineering University of Stavanger, N-4036, Norway * International Research Institute of Stavanger (IRIS), Prof. Olav Hanssensvei 15, N-4068, Norway

Abstract

Spontaneous imbibition is an important IOR process, especially for fractured carbonate reservoirs with low permeability matrix blocks. If the chalk is oil-wet, the process will not take place. Previous studies have shown that seawater may increase the water-wetness. The sulphate ions in seawater may alter the wetting conditions of the chalk surface, especially at high temperatures.

One-dimensional imbibition tests of water into vertically placed, preferentially oilwet chalk cores were performed, with non-sulphate formation water as a reference. The cores were sealed and only open to flow at one or both end faces. For core plugs with both ends open, a delay period was observed if the core initially was 100% oil saturated, and the difference in oil recovery from top and bottom was about 2-4% of OOIP. For core plugs with initial water saturation, the difference was increased to 14% of OOIP with higher oil production from the top. For cores with only the upper end face open to flow, only countercurrent imbibition takes place. Higher oil recovery was observed with seawater than with formation water as imbibing brine. Cleaned core plugs can be more easily rendered partially oil-wet. A numerical model was developed to describe the seawater imbibition process, including the effect of wettability alteration, and used to simulate the experiments. The model includes molecular diffusion and adsorption of salts (sulphate), and gravitational and capillary forces. The salts in the seawater diffuse into the formation water initially present in the core, absorb onto the rock surface and induce wettability alteration.

Two measured capillary pressure curves are used in the simulation. The curve with seawater is taken as the water-wet extreme, and the curve with non-sulphate formation water is taken as the oil-wet extreme. The capillary pressure curve is dynamically shifted from oil-wet to water-wet conditions proportionally to the absorb amount of salt. The simulation results match the experimental data well. The inclusion of the dynamic shift of the wettability condition controlled by molecular diffusion results in delayed oil recovery, in line with the experimental results.

The model can easily be extended to include different types of ion concentration, e.g. of magnesium and calcium, to include more of the chemical reactions taking place.

Key words: Spontanesou Imibibition; Wettability Alteration; Modelling/Simulation;

E-mail: LIPY@statoilhydro.com (Liping Yu, Corresponding author, started working in StatoilHydro, Norway after August 2008. Tel.: +47-47712058.)

1. Introduction

About half the world's discovered oil reserves are in carbonate reserviors and many of them are naturally fractured (Roehl and Choquette, 1985). Spontaneous imbibition of water from the fractures into the matrix takes place if the reservoir is water-wet. However, up to 65% of carbonate rocks are oil-wet and 12% are intermediate-wet (Chillingar and Yen, 1983).

Wettability affects fluid distributions and flow in the reservoir during production (Anderson 1986b), and it affects almost all types of core analyses (Anderson, 1986a). And for fractured carbonate reservoirs, wettability has widely been described as an important factor to consider for waterflooding to increase oil recovery (Tong et al, 2002; Morrow and Mason, 2001; Zhou et al., 2000; Hirasaki et al, 2004).

There are published many papers on wettability alteration by surfactants (Spinler et al, 2000; Seethepalli et al, 2004), but for practical application the cost may be prohibitive. However, seawater has been injected into the naturally fractured Ekofisk chalk reservoir in the North Sea for nearly 20 years with great success (Sylte et al. 1988). And recent laboratory studies indicate that seawater helps to improve oil recovery from moderately water-wet fields such as the Ekofisk field (Austad et al., 2005; Høgnesen et al., 2005; Zhang and Austad, 2005a; Zhang and Austad, 2006). It was observed that high temperature and the presence of sulphate ions from the injected seawater were the key factors for wettability modifications towards more water-wet conditions. The water-wetness of the chalk material increased with increasing temperature and concentration of sulphate in the seawater. The mechanism for the increased water-wetness was interpreted as caused by desorption of carboxylic materials from the chalk surfaces. This was caused by the chalk surface becoming less positively charged due to adsorption of SO4²⁻ and complexing the carboxylic group by Ca²⁺ on the chalk surface.

Imbibition may take place by both cocurrent and countercurrent flow, but for fractured reservoirs countercurrent imbibition is often the only possible mechanism for oil production especially when the matrix is surrounded by water in the fractures (Pooladi-Darvish and Firoozabadi, 2000; Najurieta et al, 2001; Tang and Firoozabadi, 2001). Countercurrent, spontaneous capillary imbibition and molecular diffusion of surfactant into chalk plugs have been studied recently (Stoll et al, 2007). It was concluded that diffusive surfactant transport was limited, while both gravity and viscous forces were neglected. Some works (Adibhatla et al, 2005; Delshad et al, 2006) about spontaneous imbibition of surfactant solutions into oil-wet reservoirs has been done with wettability change and interfacial tension as functions of surfactant concentration. Høgnesen et al (2006) did an experimental and numerical study of seawater imbibition into preferentially oil-wet, cylindrical chalk cores, but wettability alteration was not considered.

In this paper we report results from one-dimensional spontaneous seawater imbibition experiments with both countercurrent and cocurrent flow. Countercurrent imbibition occurs when only the top surface is open to flow. Salt ions in water will diffuse into the core and surface conditions will change to more water-wet conditions. The capillary pressure will increase and drive the imbibition process. Note that the progress of the water imbibition front will at all times depend on diffusion and wettability alteration ahead of the front. In the model, the wettability change is proportional to the ion concentration.

A 1D numerical model is constructed including molecular diffusion, salt adsorption, gravitational, and capillary forces to simulate the dynamic wettability alteration process.

Dynamic change of capillary pressure and relative permeability curves from oil-wet to water-wet condition is made dependent on salt concentration. The modelling results show that it is necessary to include wettability alteration to correctly simulate the oil recovery versus time.

2. Experimental

2.1. Fluids

Oil: The crude oil, with AN=3.01 mgKOH/g and BN=0.95 mgKOH/g, was diluted with heptane in the volume ratio of 40/60 heptane/crude oil. It was filtered through 5 μ m Millipore filter and no precipitation of asphaltenes was observed. It is denoted oil type A with an AN about 2.07 mgKOH/g. It was added 10 weight % silica and the mixture was stirred for 3 days. Another10 weight % silica was added again and the mixture was stirred for 2 days to get oil B with AN about 0.17 mgKOH/g. Oil A and B was then mixed in the weight ratio A/B=1:5 to finally arrived at oil C with AN=0.49 mgKOH/g.

Brines: Components of the artificial formation water and seawater are listed in Table 1. The EF-brine has a model composition close to formation brine in the Ekofisk field. It was used as initial water present in core plugs. The brine SSW is artificial seawater. They were used as the imbibing fluids in the experiments.

2.2. Porous medium

The core material is outcrop Stevns Klint chalk from a quarry nearby Copenhagen, Denmark. This chalk has a high porosity (45-50%), low permeability (2-5 mD) and a specific surface area about 2.0 m^2/g (Frykman, 2001; Røgen and Fabricius, 2002).

2.3. Core preparation

The cores were prepared according to the method described by Standnes and Austad (2000):

- The cores without initial water present were dried at 90°C to constant weight and then evacuated and saturated with oil C. Afterwards they were flooded with 2PV of the same oil in each direction to ensure homogeneous wettability condition. Then they were aged at 50°C for 5 days.
- The cores with initial water present were saturated with EF-brine after having been dried at 90°C to constant weight and evacuated. They were then flooded with 2PV of oil A or C in each direction to get water saturations of about 25%. Lower water saturations around 10% was achieved by porous plate desaturation using strongly non-wetting nitrogen before flooding with oil. The cores were then aged at 90°C for different time periods or aged at 50°C for 5 days.
- A large amount of surface-active components from the oil may adsorb onto the outermost surfaces of the cores. Hence, after aging, the outermost 2 mm of each core was shaved off prior to the imbibition test to ensure a more uniform wettability of the core. Now imbibition tests could be performed after sealing the core plugs with epoxy to get different boundary conditions.

Before they were dried to constant weight, core plugs LY2-4–LY2-9 were flooded at 50°C with 4PV distilled water from each direction while in the Hassler core holder. After this cleaning procedure, they were prepared following the procedures described

above. No attempts were made to separately determine the wettability. We assume that the cores are either slightly water-wet or slightly oil-wet. Even if a core is slightly water-wet, the influence of salt water is expected to improve spontaneous imbibition and oil recovery.

2.4. Imbibition tests

Epoxy was used to seal the core plugs to vary the boundary conditions. For all tests the cylindrical surface of the core was sealed to ensure one-dimensional flow. The imbibition tests on core plugs with two ends open to flow were performed at 50°C with modified cells that can realize oil collection separately from top and bottom ends, Figure 1. Shrink tube was used to connect the core plug with the cell. The core plug was immersed by SSW. The produced oil was sucked out through the holes at the top of the cell by a syringe at selected time intervals.

High temperature imbibition tests were carried out at 130°C on core plugs with only top end open. The schematic diagram of the experimental setup is shown in Figure 2. During the whole test in order to keep the fluids inside the cell below the bubble point, a back pressure was maintained by a piston cell with imbibing fluid on top and nitrogen gas on bottom with 10 bars pressure. Core plugs were put into the steel imbibition cells in the oven, with only top end surface exposed to imbibing fluid in the cell. At selected points in time the valve was opened slowly and the produced oil was collected into the burette and measured.

2.5. Experimental results

2.5.1. Spontaneous imbibition at 50°C, two ends open, Swi = 0

Oil recovery in the range of 40-50% was reached, Figure 3-4. The relative permeability concept is not applicable since there is no initial water inside the core. In the startup period, perhaps seawater moves into the core by film flow along the internal surfaces near the end faces exposed to seawater. And when the water saturation is increased up to the so-called critical water saturation, ordinary Darcy flow takes over, firstly close to the end surfaces and gradually into the core. This could perhaps explain the initial delay observed in the oil recovery curves. When initial water saturation is present, there will be pressure continuity in the water phase from top to bottom, and if the oil pressure inside the core is high, production of oil should start immediately.

Oil recovery from the top and bottom surfaces is recorded separately. For both core plugs LY1-1 and LY1-2, higher oil recovery (about 2-4 percentage points) from the top surface is observed, caused mainly by gravity. Only countercurrent flow takes place at the bottom surface, oil and water flow in opposite directions, and gravity must be overcome to produce oil. For the top surface, both countercurrent and cocurrent flow contribute to oil recovery, and gravity improves the oil production.

2.5.2. Spontaneous imbibition at 50°C, two ends open, Swi = 0.257

The core plug LY1-3 with initial water saturation of 25.7%, was aged at the same temperature 50°C for the same time period of 5 days. Imbibition test was carried out at the same condition as for the core plugs without initial water saturation, and different behaviour was observed.

Spontaneous imbibition took place immediately without any delay. Initially oil and water exist together inside the core and both phases are continuous. Oil is expelled and produced immediately due to a positive capillary pressure.

The oil recovery difference between top and bottom surfaces was enhanced for core plugs LY1-3 with initial water saturation, Figure 5. Compared to the core plugs without initial water saturation, the oil recovery from top surface is increased (from 22-24% to 30%), and oil produced from bottom surface is decreased (from 20-22% to 16%). With an initially mobile and continuous water phase gravity has more influence and cocurrent flow more important. Only minor differences in final oil recovery were observed for core plugs with and without initial water saturation.

The recent experimental results of Karimaie and Torsaeter (2007) also show the influence of the initial water saturation on the imbibition process. Induction time, the time before oil was produced, decreased with increasing initial water saturation. Their results also show an initial delay period and faster recovery with higher initial water saturation, in line with our results.

2.5.3. Spontaneous imbibition at 130°C, only top end open, different Swi-values

Different water saturations were established for several core plugs and they experienced different aging time at 90°C. When these cores were exposed to SSW at 50°C, no oil production was observed. Then they were put into a steel cell filled with SSW at 130°C with back pressure at 10 bars for an imbibition test. Figure 6 shows the oil recovery difference for core plugs with low water saturation about 10%, and long aging time. About 30% oil recovery was reached for the long core, while 15%-20% recovery was observed for the core plugs half the length. The crossover point is at about 4 days. In the initial period, oil recovery rate for the shorter cores was higher than that of long core. Afterwards, oil production for the long core kept increasing until about 10 days. It is the balance between gravitational and capillary forces that determines the difference. A similar result was found by Karimaie and Torsaeter (2007) for slightly water-wet core with almost the same dimensions.

The comparison between EF-brine imbibition and SSW imbibition, Figure 7, confirms that SSW may contribute to increased oil recovery. The ion strength of EFbrine and SSW is the same but SSW contains sulphate ions, and this may be the reason for higher oil recovery at high temperature. It is also shown in the paper of Zhang and Austad (2006) that higher sulphate concentration in SSW leads to higher oil recovery.

Figure 8 shows the oil recovery for core plugs with initial water saturation of about 25% and with aging time of 35 days. The characteristics of curves are almost the same as Figure 7. The initial fast increase during the first day is due to thermal fluid expansion and probably some heterogeneity in the wetting conditions during the core preparation. The oil recovery afterwards increases slowly and seems to reach a plateau after 30 days. The slow increase thereafter is probably caused by gravity forces.

Lower water saturation is supposed to lead to more oil-wet conditions (Zhou et al, 2000), but as can be seen from Figure 6 to 8, oil recovery for the core plugs with 10% water saturation and 220 days aging was higher than core plugs with about 25% initial water saturation and 35 or 100 days aging, indicating a less oil-wet trend with lower initial water saturation and longer aging time. Recent experimental results (Puntervold, 2007) show that there initially is sulphate present in the core plugs, a condition which could lead to a more water-wet state after aging. In the present work, the core plugs with lower initial water saturation at 10% did not experience cleaning procedures and proved to be more water-wet. And even longer aging time can not change them to be more oil-wet. Hence a cleaning procedure is recommended to prepare for more oil-wet core plugs.

For the core plugs subjected to a cleaning procedure, aging time for core plug LY2-4–LY2-7 was three times longer than for LY 2-8 and 2-9, but oil recovery after seawater imbibition for 30 days almost arrived at the same plateau value of 18%-20%. After 35 days aging at 90°C with oil A core plugs will achieve the same wetting state as those with longer aging times (100 days). During aging the wettability of a core plug is supposed to be changed by adsorption of polar components from crude oil onto the rock surface (Buckley et al., 1998; Madsen and Lind, 1998). Clearly, for oil A, an aging time of 35 days at 90°C is sufficient.

3. Numerical Model Description

Seawater can contribute to an increase oil recovery from the initial, preferentially oilwet cores, and sulphate ions in the seawater are the salt causing the oil recovery increase. We assume that the spontaneous imbibition is initiated by diffusion of the Wettability Alteration [WA] agent or salt into the preferentially oil-wet cores. Adsorption of these ions onto core surface, renders the wettability more water-wet. Capillary pressure and relative permeabilities are considered to be functions of the salt concentration. We have programmed a 1D simulator to study the dynamic wettability alteration process of seawater imbibition into preferentially oil-wet cores. A brief description of the model given below, the details can be found in a paper by Yu and Evje et al (2007).

3.1. Phase behaviour

We assume that fluids and rock are incompressible, and that the dissolution of WA agent into water does not cause any volume change. We consider two phases, an oil phase and an aqueous phase, and the three components are distributed between the two phases in the following manner:

- The oil component only exists in oil phase.
- The water component only exists in aqueous phase.
- The WA agent exists as a component only in aqueous phase. Its concentration does not affect density and viscosity of the aqueous phase and the interfacial tension. The WA agent can adsorb onto the rock surface and the adsorption process does not affect rock permeability and porosity.

3.2. Constraints

The contraints are:

 $p_o - p_w = p_c$, capillary pressure, $S_o + S_w = 1$, saturation, $c_a + w_a = 1$, mole fraction, $c_r = f(c_a)$, adsorption,

where f is a function expressing how the absorption depends on the concentration of WA in the water phase.

3.3. Molecular diffusion and adsorption

Molecular diffusion initiates the wettability change from oil-wet to water-wet conditions followed by spontaneous imbibition. In the mass balance equation the

molecular diffusion coefficient is written as $D_a^{s,e} = \phi S_a D_a^s$. The molecular diffusion coefficient D_a^s of WA agent in water is a constant given by the input data.

The change of wettability is caused by adsorption of the WA agent onto the rock surface. The amount of WA agent adsorbed is accounted for in the mass balance equation by the adsorption term $(1-\varphi)M_Dc_r$, where the mass density of rock M_D is constant. A Langmuir type (Lake, 1989; John et al, 2004) isotherm relation is used, $c_r = a_1c_a/(1+a_2c_a)$ with constants $a_1, a_2 > 0$.

3.4. Effects of the WA agent on flow functions

We use a measured capillary pressure curve for the simulation, and a modified Corey type model to describe the relative permeability, $k_{rl} = k_{rl}^0 (S_l^*)^{N_l}$, where k_{rl}^0 is the endpoint of the relative permeability k_{rl} and N_l is the exponential parameter that determines the curve shape. Normalized phase saturation S_l^* is defined as $S_l^* = (S_l - S_{lr})/(1 - S_{or} - S_{wr})$.

The effects of wettability alteration on capillary pressure and relative permeability are given by interpolation, $k_{rl} = Fk_{rl}^{ow} + (1-F)k_{rl}^{ww}$, $p_c = Fp_c^{ow} + (1-F)p_c^{ww}$, where $F(c_r) = (a^* - c_r)/a^*$, and $a^* = a_1/a_2$.

A single set of oil-wet curves, k_{rl}^{ow} , p_c^{ow} corresponds to oil-wet condition, and another set, k_{rl}^{ww} , p_c^{ww} corresponds to water-wet conditions. The actual relative permeability or capillary pressure used in the simulator model is computed the weighted average, where $F(c_r) = 1$ corresponds to the oil-wet extreme, and F(c) = 0 the water-wet extreme.

3.5. Boundary conditions

For a core plug with only the top end open to imbibing fluid, seawater with a certain concentration c_a of WA agent, we use the Dirichlet condition $S(1^+,t) = 1.0$, $c_a(1^+,t) = c^*$, where c^* is the concentration of WA agent in the seawater. Here 1^+ denotes just outside the plug, and we have $p_c(t)|_{x=1^+} = 0$, which implies that only when $p_c(t)|_{x=1^-} > 0$ there will be flow of seawater into core plug, and 1⁻ denotes just inside the core plug.

The simulation of countercurrent imbibition is limited to the cases of just top end open plugs, and then the total fluid flux is zero.

3.6. Numerical Formulation

The discrete mass balance differential equations for each component are

$$\frac{\partial}{\partial x} \left[\frac{kk_{ro}\rho_o}{\mu_o} \left(\frac{\partial p_o}{\partial x} - \rho_o g_x \right) \right] + q_o = \frac{\partial}{\partial t} (\varphi S_o \rho_o)$$

$$\frac{\partial}{\partial x} \left[\frac{kk_{rw}\rho_w w_a}{\mu_w} \left(\frac{\partial p_w}{\partial x} - \rho_w g_x \right) \right] + q_w = \frac{\partial}{\partial t} (\varphi S_w \rho_w w_a)$$

$$\frac{\partial}{\partial x} \left[\frac{kk_{rw}\rho_w c_a}{\mu_w} \left(\frac{\partial p_w}{\partial x} - \rho_w g_x \right) \right] + \frac{\partial}{\partial x} \left(D_w^{s,e} \frac{\partial c_a}{\partial x} \right) + q_s = \frac{\partial}{\partial t} (\varphi S_w \rho_w c_a + (1 - \varphi) M_D c_r)$$

The convection-diffusion system is solved by the relaxed scheme proposed by Jin and Xin (1995) for the numerical discretization of convective fluxes, and the "central in space-explicit in time" type of discretization is used for the discretization of the fluxes. The programming is done in Matlab.

3.7. Simulated examples

Capillary pressure curves were measured on core plugs from a North Sea carbonate field at reservoir conditions (Webb et al, 2005), Figure 9. The capillary pressure characteristics were compared between the cases of sulphate-free formation water and sulphate-containing seawater as injection fluids. We choose the capillary pressure curve for sulphate-free formation water to represent the oil-wet extreme and capillary pressure curve for sulphate-containing seawater the water-wet extreme.

The correspondingly relative permeability curves are calculated from equations in Sec. 3.4 and the parameters in Table 3, see Figure 10. The simulated oil recovery matches the experimental oil recovery data quite well for core plug LY2-5, Figure 11. The simulation produces the distribution of water saturation and ion concentration along the core as a function of time. Water saturation distribution as a function of time is shown in Figure 12. The dimensionless distance from the top of the core is taken as x-axis with 0 at the bottom end and 1 at the top. The water saturation increases almost uniformly from top to bottom. The water saturation at the top reaches 0.38 quickly, where the capillary pressure is 0. After 30 days, the water saturation through the core is close to 0.38, only very slightly higher on the bottom position, caused by the gravity influence. Later, the imbibition process continues, driven by gravity. This slow process will end when the balance between gravitational and capillary forces is reached.

Diffusion of WA agent or salt into the core is shown in Figure 13, corresponding to the water distributions in Figure 12. The x-axis is the dimensionless distance from the bottom, where x=0, to the top of the core plug, x=1. After the salt starts to diffuse into the core plug, the concentration is decreasing from top due to diffusion rate and loss of salt caused by adsorption onto the rock surface. With diffusion taking place, the rock surface that has been exposed to salt can be rendered partially water-wet. This will increase the imbibition rate and bring more salt into the plug. Finally, at equilibrium, the salt concentration inside the core plug will attain the same value as that of the imbibing fluid surrounding the core plug.

During the imbibition process, further progress of the waterfront inside the core depends on available salt ions in the water at the front. And these ions have to be brought up to the front by diffusion. The imbibition process of water will therefore be controlled by diffusion. Flow of SSW into the core in combination with diffusion will eventually render the core with a uniform water saturation determined by the capillary curve, and a uniform salt concentration.

In Figure 14 the simulated oil recovery curves for the two cases of fixed and dynamic wettability alteration are shown. For the fixed case, during the simulation the final wettability-altered capillary pressure curve is used directly inside the core, independent of salt concentration. For the dynamic wettability alteration case, the capillary pressure depends on the salt concentration adsorbed onto rock surface and gradually changes from oil-wet to water-wet. In Figure 14, for the case with fixed wettability, the oil recovery reaches its maximum after a couple of days. Compared to the result considering dynamic wettability alteration, which will arrive at the oil recovery plateau after about 20 days, the oil recovery is overestimated in the earlier production period if we use the model with fixed wettability through the core. This shows that considering dynamic wettability alteration is very important to predict the production period.

4. Discussions

4.1. Wettability of prepared core plugs

The wettability condition of core plugs was not determined by measurements. Observed from imbibition test results, the core plugs prepared with oil C (with lower acid number) and aged only 5 days seem preferentially water-wet. Core plugs prepared with oil A, at low initial water saturation around 10% and aged for 220 days, still seem slightly water-wet. Through the cleaning treatment to get rid of possible WA agent initially present inside the cores, they seem to become preferentially oil-wet. With only the top end open to flow, countercurrent imbibition will cause a lower recovery (Zhou et al, 2001; Bourbiaux and Kalaydjian, 1988). Separate measurements of wettability should be done to investigate this point more in detail.

Wetting heterogeneity caused by core preparation is neglected, as is also thermal expansion of fluids which leads to a fast oil recovery increase step initially for the imbibition cases at high temperature.

4.2. Limited rate controlled by diffusion

Seawater imbibition will increase the water-wetness of chalk cores, but, the wettability alteration is still controlled by diffusion, both through the water inside the core and from salty water into formation water up front.

4.3. Model improvement

The simulated example in this paper is for a core plug with only the top end open to flow which is the case for countercurrent imbibition. If both ends are open to flow, both countercurrent and cocurrent flows take place and capillary pressure and relative permeability curves should reflect this to get more realistic and accurate simulation results.

WA agent adsorbs onto rock surface and then chemical interaction takes place, probably time delayed. The alteration process should possibly depend on both amount of adsorb material and a time-dependent chemical reaction.

Hysteresis in capillary pressure and relative permeability curves is not included. We have demonstrated, however, that it is possible to achieve a reasonable match by the simplified numerical model presented here.

It is very time consuming to accurately measure capillary pressure curves and we have therefore applied the curves published by Webb et al. (2005) for a similar situation. Of course, actual measured p_c -curves would be preferable, but the core material, the preparation of the cores and the test conditions are fairly similar to Webb et al. (2005).

5. Conclusions

One-dimensional seawater spontaneous imbibition tests have been done on vertically placed chalk core plugs with and without initial water saturation, with different aging periods and different crude oils. A startup, delayed time period is observed for core plug without initial water saturation to establish Darcy flow conditions.

Countercurrent imbibition leads to oil recovery from the bottom end, while both countercurrent and cocurrent flows exist at the top surface exposed to the imbibing fluid. Oil recovery is highest from the top end. Initial water saturation leads to much higher oil recovery from the top surface since cocurrent flow then is enhanced. Comparing the experiments on core plugs with different length, only open at top end, the importance of gravity is obvious even for small core plugs.

The cleaning procedure will lead to more oil-wet conditions, and it may compensate for the effect of long aging time and low water saturation. With the cleaning procedure, a more oil-wet condition can be achieved with shorter aging time and higher initial water saturation.

It is shown that seawater may increase the oil recovery compare to EF-brine as a reference.

The core scale simulated oil recovery matches the experimental result fairly well. Wettability alteration is confirmed to be an important factor to be considered for inclusion in simulation studies. Flowing parameters are changing with the wettability alteration from oil-wet to water-wet by conditions according to the amount of adsorbed salt.

Marked differences in simulation behavior are observed in the simulated results from dynamic and fixed wettability conditions. The wettability alteration is controlled by diffusion, as reflected by the initially limited recovery rate.

More studies should be done on the dynamic wettability alteration process and its importance for full scale reservoir applications.

Nomenclature

 a_1, a_2 : Constants to calculate adsorption isotherm, $a_1=1, a_2=5000$

 c_a : Mass fraction of salt component in aqueous phase

 c_r : Adsorption isotherm of salt onto rock

 c^* : Mass fraction of salt in seawater is 0.001

- $D_a^{s,e}$: Effective diffusivity
- D_a^s : Molecular diffusion coefficient
- F: Weighting function to interpolate relative permeability and capillary pressure

g : Gravity acceleration = $9.8 m / s^2$

k : Absolute permeability

- k_{rl}^{0} : End point relative permeability of phase l
- k_{rl} : Relative permeability of phase l
- k_{rl}^{ow} : Relative permeability at oil-wet condition
- k_{rl}^{WW} : Relative permeability at water-wet condition
- M_D : Mass density of the rock
- N_l : Exponential parameter to calculate relative permeability for phase l
- p_l : Pressure of phase l
- p_c : Capillary pressure
- p_c^{ow} : Capillary pressure at oil-wet condition
- p_{c}^{WW} : Capillary pressure at water-wet condition
- q_l : Source/sink term of phase l
- S_l : Saturation of phase l

 S_{wi} : Initial water saturation

 S_{wr} : Irreducible water saturation

 S_{ar} : Residual oil saturation

- T_l : Phase transmissibility
- w_a : Mass fraction of water component in aqueous phase
- V : Grid block bulk volume
- ϕ : Porosity
- ρ_l : Density of phase l
- ψ_l : Phase potential
- $\Delta_t(A) = A^{n+1} A^n$: Operator for standard backward difference approximation of time derivative

 Δt : Time step length

Abbreviations

EF: Ekofisk Formation Water SSW: Sea Water WA: Wettability Alteration

References

- Adibhatla, B., Sun, X. and Mohanty K. K., 2005. Numerical studies of oil production from initially oil-wet fracture blocks by surfactant brine imbibition. Paper SPE 97687 presented at the SPE International Improved Oil Recovery Conference hold in Kuala Lumpur, Malaysia, 4-6 December.
- Anderson, W.G., 1986a. Wettability literature survey part 1: rock/oil/brine interactions and the effects of core handling on wettability. Journal of Petroleum Science and Engineering: 1125-1144.
- Anderson, W.G., 1986b. Wettability literature survey part 2: wettability measurement. Journal of Petroleum Science and Engineering: 1246–1262.

- Austad, T., Strand, S., Høgnesen, E. J., and Zhang, P., 2005. Seawater as IOR Fluid in Fractured Chalk. Paper SPE 93000 presented at the SPE International Symposium on Oilfield Chemistry held in Houston, Texas, U. S. A., 2-4 February.
- Bourbiaux, B.J. and Kalaydjian, F.J., 1988. Experimental Study of Cocurrent and Countercurrent Flows in Natural Porous edia. Paper SPE 18283 presented at the SPE Annual Tech. Conf. And Exh, Houston, TX, 2-5 October.
- Buckley, J.S., Liu, Y., and Monsterleet, S., 1998. Mechanisms of Wetting Alteration by Crude Oils. SPEJ (March): 54-61.
- Chilingar, G.V. and Yen, T.F., 1983. Some notes on wettability and relative permeability of carbonate rocks. II. Energy and Sources, 7: 67-75.
- Delshad, M., Najafabadi, N.F., Anderson, G.A., Pope, G.A., and Sepehrnoori, K., 2006. Modeling wettability alteration in naturally fractured reservoirs. Paper SPE 100081 presented at the SPE/DOE Symposium on Improved Oil Recovery held in Tulsa, Oklahoma, U.S.A., 22-26 April.
- Frykman, P., 2001. Spatial variability in petrophysical properties in Upper Maastrichtian chalk outcrops at Stevns Klint, Denmark. Marine and Petroleum Geology, 18: 1041-1062.
- Hirasaki, G. and Zhang, D. L., 2004. Surface Chemistry of Oil Recovery from Fractured, Oil-Wet, Carbonate Formations. SPE Journal, 9(2): 151-162.
- Høgnesen, E. J. Strand, S. and Austad, T., 2005. Waterflooding of preferential oil-wet carbonates: Oil recovery related to reservoir temperature and brine composition. Paper SPE 94166 Presented at the 14th Europec Biennial Conference held in Madrid, Spain, 13-16 June.
- Høgnesen, E. J. and Standnes, D.C., 2006. Experimental and numerical investigation of high temperature imbibition into preferential oil-wet chalk. Journal of Petroleum Science and Engineering, 53(1-2): 100-112.
- Jin, S. and Xin, Z., 1995. The relaxation schemes for systems of conservation laws in arbitrary space dimensions. Comm. Pure Appl. Math., 48: 235-276.
- John, A., Han, C., Delshad, M., Pope, G. A., Sepehrnoori, K., 2004. A new generation chemical flooding simulator. Paper SPE89436 presented at the 2004 SPE/DOE 14th Symposium on Improved Oil Recovery, Tulsa, OK, 17-21 April.
- Karimaie, H. and Torsaeter, O., 2007. Effect of injection rate, initial water saturation and gravity on water injection in slightly water-wet fractured porous media. Journal of Petroleum Science and Engineering, (In press).
- Lake, L. W., 1989. Enhanced oil recovery. Prentice-Hall Inc. Upper Saddele River, New Jersy, 600 pp.
- Madsen, L. and Lind, I., 1998. Adsorption of carboxylic acids on reservoir minerals from organic and aqueous phase. SPE Reservoir Evaluation & Engineering, 47-51 (February).
- Morrow, N. R, and Mason, C., 2001. Recovery of Oil by Spontaneous Imbibition. Current opinion in Colloid and Interface Science, 6: 321-337.
- Najurieta, H.L., Galacho, N., Chimienti, M.E., Illiano, S.N., 2001. Effect of temperature and interfacial tension in different production mechanisms. Paper SPE 69398 for Latin American and Caribbean Petroleum Engineering Conference, Buenos Aires, Argentina.
- Pooladi-Darvish, M., Firoozabadi, A., 2000. Experiments and modelling of water injection in water-wet fractured porous media. J. Can. Pet. Technol., 39(3): 31-42.

- Puntervold, T., Strand, S. and Austad, T., 2007. New method to prepare outcrop chalk cores for wettability and oil recovery studies at low initial water saturation. Energy & Fuels, (under review).
- Roehl, P. O. and Choquette, P. W., 1985. Carbonate Petroleum Reservoirs. Springer-Verlag, New York, 622 pp.
- Røgen, B. and Fabricius, I. L., 2002. Influence of clay and silica on permeability and capillary entry pressure of chalk reservoirs in the North Sea. Petroleum Geoscience, 8: 287-293.
- Seethepalli, A.; Adibhatla, B. and Mohanty, K. K., 2004. Wettability Alteration During Surfactant Flooding of Carbonate Reserviors. Paper SPE 89423 presented at SPE/DOE 14th Symposium on Improved Oil Recovery, Tulsa, OK, 17-21 April.
- Spinler, E. A and Baldwin, B. A., 2000. Surfactant Induced Wettability Alteration in Porous Media. In: L. L. Schramm (Editor), Surfactant Fundamental and Application in the Petroleum Industry. Cambridge University Press, pp. 159-202.
- Standnes, D.C. and Austad, T., 2000. Wettability alteration in chalk 1: Preparation of core material and oil properties. Journal of Petroleum Science and Engineering, 28(3): 111-121(November).
- Stoll, W.M., Hofman, J.P., Ligthelm, D.J., Faber, M.J., and van den Hoek, P.J., 2007 Filed-Scale wettability modification-The limitations of diffusive surfactant transport. Paper SPE 107095 presented at the SPE Europec/EAGE annual conference and exhibition held in London, United Kingdon, 11-14 June.
- Sylte, J. E., Hallenbeck, L. D., and Thomas, L. K., 1988. Ekofisk Formation Pilot Waterflood. Paper SPE 18276 presented at the 63th Annual Technical Conference and Exhibition held in Houston, TX, U. S. A., 2-6 October.
- Tang, G.Q., Firoozabadi, A., 2001. Effect of pressure gradient and initial water saturation on water injection in water-wet and mixed-wet fractured porous media. SPE Reserv. Evalu. Eng. A, 516-524.
- Tong, Z. X.; Morrow, N, R. and Xie, X., 2002. Spontaneous Imbibition For Mixed-Wettability States In Sandstone Induced By Adsorption From Crude Oil. Presented at the 7th International Symposium on Reservior Wettability, Tasmania, Australia, 12-14 March.
- Webb, K.J., Black, C.J.J., and Tjetland, G., 2005. A laboratory study investigating methods for improved oil recovery in carbonates. Paper IPTC 10506 presented at the International Petroleum Technology Conference held in Doha, Qata, 21-23 November.
- Zhang, P. and Austad, T., 2005. The Relative Effects of Acid Number and Temperature on Chalk Wettability. Paper SPE 92999 presented at the International Symposium on Oilfield Chemistry held in Houston, TX, U. S. A., February 2-4.
- Zhang, P. and Austad T., 2006. Wettability and Oil recovery from Carbonates: Effects of Temperature and Potential Determining Ions. Colloids and Surfaces A: Physicochem. Eng. Aspects, 279: 179–187.
- Zhou, X., Morrow, N. R. and Ma, S., 2000. Interrelationship of Wettability, Initial Water Saturation, Aging Time and Oil Recovery by Spontaneous Imbibition and Waterflooding. SPE Journal, 5(2): 199-207(June).
- Zhou, D., Jia, L., and Kovscek., 2001. An investigation of counter-current imbibition processes in diatomite. Paper SPE68837 presented at the Western regional meeting held in Bakersfield, CA.

Yu, L., Evje, S., Fjelde, I., Kleppe, H., Kårstad, T., and Skjaeveland, S. M., 2007. Modeling of wettability alteration processes in carbonate oil reservoirs. Accepted for publication in Network and Heterogeneous Media.

Ion	EF-brine	SSW
-	(mol/l)	(mol/l)
Na ⁺	0.684	0.450
K^+		0.010
Mg^{2+}	0.025	0.045
Ca ²⁺	0.231	0.013
Cl	1.196	0.525
HCO ₃ ⁻		0.002
SO_4^{2-}		0.024
TDS, g/l	68.01	33.39

Table 1. Molar compositions of the brines used

Table 2. Experimental information of cores for spontaneous imbibition tests

Oil Aging Aging		Core properties		Spontaneous imbibition						
Core#	type	Temp. (°C)	time (days)	Diameter (cm)	Length (cm)	Porosity (%)	S_{wi} (%)	Boundary	Temperature (°C)	Imbibing fluid
LY1-1	С	50	5	3.80	7.04	47.8	0	Two Ends Open	50	SSW
LY1-2	С	50	5	3.80	7.05	47.7	0	Two Ends Open	50	SSW
LY1-3	С	50	5	3.80	7.04	50.1	25.7	Two Ends Open	50	SSW
LY2-1	Α	90	220	3.80	7.06	48.9	10.4	Top End Open	130	SSW
LY2-2	А	90	220	3.80	3.50	48.8	10.8	Top End Open	130	SSW
LY2-3	Α	90	220	3.80	3.50	48.8	10.8	Top End Open	130	SSW
LY2-4	Α	90	100	3.70	4.38	51.0	26.5	Top End Open	130	SSW
LY2-5	А	90	100	3.70	4.40	50.0	25.6	Top End Open	130	SSW
LY2-6	Α	90	100	3.70	4.28	49.0	26.4	Top End Open	130	EF-brine
LY2-7	Α	90	100	3.70	4.34	49.0	24.3	Top End Open	130	EF-brine
LY2-8	Α	90	35	3.70	4.54	50.7	25.6	Top End Open	130	SSW
LY2-9	А	90	35	3.70	4.50	51.4	26.5	Top End Open	130	SSW

Table 3 Parameters used to calculate relative permeability

	k_{rw}^0	0.4
Water-wet	k_{ro}^0	0.9
	$N_{_W}$	3
	N_o	2
	k_{rw}^0	0.7
Oil-wet	k_{ro}^0	0.75
On-wet	$N_{_W}$	2
	N_o	3



Figure 1 Schematic diagram of experimental setup for imbibition tests at 50°C. Oil is collected separately from top and bottom end.



Figure 2 Schematic diagram of experimental setup for imbibition test at 130°C.



Figure 3 Seawater spontaneous imbibition into core plug LY1-1 with two ends open, S_{wi} =0. Oil recovery from top and bottom ends is recorded separately. Tests were performed at 50°C.



Figure 4 Seawater spontaneous imbibition into core plug LY1-2 with two ends open, Swi=0. Oil recovery from top and bottom end recorded separately. Tests performed at 50°C.



Figure 5 Seawater spontaneous imbibition into core plug LY1-3 with two ends open, S_{wi} =25.7%. Oil recovery from top and bottom ends recorded separately. Tests performed at 50°C.



Figure 6 Seawater spontaneous imbibition into core plugs LY2-1, LY2-2, and LY2-3 with only top end open to flow; S_{wi} about 10%. Tests performed at 130°C.



Figure 7 Spontaneous imbibition into core plugs LY2-4—LY2-7 with only top end open, S_{wi} about 25%. For LY2-4 and LY2-5, seawater was imbibing fluid, while EF-brine was imbibing fluid for LY2-6 and LY2-7. Tests performed at 130°C.



Figure 8 Seawater spontaneous imbibition into core plugs LY2-8 and LY2-9 with only top end open, S_{wi} about 25%. Tests performed at 130°C.



Figure 9 Reservoir condition measured capillary pressure (Webb et al, 2005).



Figure 10 Calculated relative permeability curves.



Figure 11 Oil recovery comparison of experimental results with simulation results for core plug LY2-5, dynamic wettability alteration used in the simulation.



Figure 12 Simulated water saturation along the core plug, the curves from right to left represent the spontaneous SSW imbibition after 0.5, 1, 5, 10, 30 days.



Figure 13 Simulated salt concentrations along the core plug, the curves from right to left represent the spontaneous SSW imbibition after 0.5, 1, 5, 10, 30 days.



Figure 14 Oil recovery results for simulation with dynamic wettability alteration and with same fixed wettability through the core during imbibition.