



**SPE 113304**

## **Analysis of the Wettability Alteration Process during Seawater Imbibition into Preferentially Oil-Wet Chalk Cores**

L. Yu, U. of Stavanger, S. Evje, IRIS, H. Kleppe, T. Kårstad, U. of Stavanger, I. Fjelde, IRIS, and S.M. Skjaeveland, U. of Stavanger

Copyright 2008, Society of Petroleum Engineers

This paper was prepared for presentation at the 2008 SPE/DOE Improved Oil Recovery Symposium held in Tulsa, Oklahoma, U.S.A., 19–23 April 2008.

This paper was selected for presentation by an SPE program committee following review of information contained in an abstract submitted by the author(s). Contents of the paper have not been reviewed by the Society of Petroleum Engineers and are subject to correction by the author(s). The material does not necessarily reflect any position of the Society of Petroleum Engineers, its officers, or members. Electronic reproduction, distribution, or storage of any part of this paper without the written consent of the Society of Petroleum Engineers is prohibited. Permission to reproduce in print is restricted to an abstract of not more than 300 words; illustrations may not be copied. The abstract must contain conspicuous acknowledgment of SPE copyright.

### **Abstract**

Improved oil recovery from fractured oil-wet carbonate reservoirs is a great challenge. The water-flooding efficiency will be low because of higher permeability in fractures than in matrix, and negative capillary pressure retains oil inside the matrix blocks. Studies of oil-wet chalk have shown that sulphate ions in the seawater may alter the wettability towards increased water-wetness.

One-dimensional spontaneous imbibition tests of seawater into preferentially oil-wet chalk cores are performed. To get a better understanding, a numerical model has been developed which includes effects of wettability alteration.

The experiments are carried out on cylindrical, sealed core plugs with only top open or with both ends open. Only countercurrent imbibition takes place for cores with top end open. For cores with both ends open, both countercurrent and cocurrent imbibition take place, and oil recovery rate is obviously accelerated. Taking formation water as the base case, higher oil recovery is observed with seawater imbibition. To simulate the wettability alteration process caused by seawater, a model is developed which includes molecular diffusion, adsorption of wettability alteration (WA) agent, gravity and capillary pressure. The WA agent diffuses into the formation water initially present in the core, adsorb onto the rock surface and induce wettability alteration. Consequently, the capillary pressure curve is shifted to higher values. In particular, the capillary pressure at the initial water saturation changes from negative to positive values and seawater is imbibed into the core. The shapes of relative permeability curves also depend on the wettability. The simulation results can fairly well match the experimental data.

With the experimental and modeling work we explore the interplay between capillarity and gravity, and especially the importance to consider wettability alteration process is again confirmed.

### **Introduction**

Spontaneous imbibition is a process where a wetting phase displaces the non-wetting phase in a porous media by capillary action. It is important for fractured reservoirs to produce oil from the rock matrix. Many carbonate reservoirs are naturally fractured but often preferentially oil-wet (Roehl and Choquette, 1985; Chillingar and Yen, 1983). Water can enter the oil-wet matrix block to displace oil only if it overcomes the entry pressure or capillary barrier. The goal can be achieved by several mechanisms, altering the wetting state of the rock surface, lowering interfacial tension, or making use of viscous or gravitational forces. With the first approach the capillary pressure can be changed from negative to positive value which then leads to spontaneous imbibition.

Many literatures have reported the wettability alteration towards water-wetness caused by surfactants (Spinler and Baldwin, 2000; Seethepalli et al., 2004; Standnes and Austad, 2000b). Usually the surfactant will also reduce the interfacial tension quite a lot, but at the same time it decreases the capillary pressure, and then spontaneous imbibition process will be negatively influenced. On the other side, the commercial feasibility of surfactant should be further studied.

Strand *et al.* (2003) studied the spontaneous imbibition of aqueous surfactant solutions into oil-wet carbonate cores. They observed that sulphate in the imbibing fluid had a positive effect to improve spontaneous imbibition behavior. Recent laboratory studies indicated that seawater could improve oil recovery from moderately water-wet chalk reservoir such as the Ekofisk field (Austad et al., 2005; Høgenesen and Standnes, 2006; Zhang and Austad, 2005; Zhang and Austad, 2006). It was observed that high temperature and the presence of sulphate ions in 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.

Rezaei and Hamouda (2006) concluded that presence of sulphate ions during adsorption process reduced the surface density of fatty acids. This was due to high affinity of sulphate ions for the calcite surface, which was evidenced by their

ability to change the surface charge sign of calcite. Moreover, it was shown that sulfate solutions are possible to partly displace pre-adsorbed acids from the calcite surface.

Karoussi and Hamouda (2007) studied the composition of initial fluid in contact with carbonate rock before the drainage process. Ion-free water and water containing  $\text{Mg}^{2+}$  and  $\text{SO}_4^{2-}$  were investigated. The carbonate rocks were initially saturated with ion-free water, and then modified by stearic acid oil. During the spontaneous imbibition process, the water containing  $\text{Mg}^{2+}$  or  $\text{SO}_4^{2-}$  was taken as imbibing fluid, and the ions concentration was the same as that in seawater. The highest oil recovery was observed when  $\text{Mg}^{2+}$  was present in the imbibing fluids. When the initially saturated fluid and imbibing fluid contained  $\text{SO}_4^{2-}$ , an inconsiderable difference between the oil recovery factor with  $\text{SO}_4^{2-}$  and that for the ion-free water was observed. While if  $\text{Mg}^{2+}$  existed both in initial saturation fluid and imbibing fluid, the lowest oil recovery was observed.

In the reservoir, spontaneous imbibition can take place both in countercurrent and cocurrent flowing modes (Bourbiaux and Kalaydjian, 1988; Tavassoli et al., 2005; Zhou et al., 2001). Moreover, countercurrent imbibition is a very important recovery mechanism during water injection for fractured reservoirs, because water flows through fractures to quickly surround the matrix. All the above experiments that studied the influence of sulphate were performed with cylindrical core plugs, which have all the surfaces exposed to imbibing fluids, both countercurrent and cocurrent imbibition took place and it is difficult to analyze their separate performance to oil production.

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. Here only sulphate ions in the seawater are taken as WA agent. They 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 always depend on diffusion and wettability alteration ahead of the front. In the model, the wettability change is proportional to the WA agent concentration.

A 1D numerical model is constructed including molecular diffusion, WA agent 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 WA agent concentration. The experimental results are simulated and the performance by considering dynamic wettability alteration is investigated.

## Experiments

### Fluids.

#### Oils.

Two types of oils, oil A and oil C with different acid numbers were used.

- Oil A: 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  $\mu\text{m}$  Millipore filter and no precipitation of asphaltenes was observed. It is denoted oil type A (AN=2.07 mgKOH/g).
- Oil C: oil A was treated with silica gel to get the oil B with low AN about 0.17 mgKOH/g. Oil A and B was then mixed in the weight ratio A/B=1:5 to obtain 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 the formation water in the Ekofisk field. It was used as initial water present in core plugs, also as a referred imbibing fluid. The brine SSW is artificial seawater, and SSW-4S is the modified seawater with four times  $\text{SO}_4^{2-}$  containing compared to SSW. They were used as the spontaneous imbibing fluids in the experiments. The ionic strength of SSW and SSW-4S is the same by adjusting the amount of NaCl.

### 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  $\text{m}^2/\text{g}$  (Frykman 2001; Røgen and Fabricius, 2002).

### Core Preparation.

The cores were prepared according to the method described by Standnes and Austad (2000a). The cores without initial water present were dried to constant weight, 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. To get the initial water saturation the cores were saturated with EF-brine after having been dried 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%. 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. Then spontaneous imbibition tests were performed after sealing the core plugs with epoxy to get different boundary conditions.

Before they were dried to constant weight, the core plugs used for 130°C imbibition tests were flooded at 50°C with 4PV distilled water in the Hassler core holder (Puntervold et al., 2007). After this cleaning procedure, they were prepared following the procedures described above. No attempts were made to 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 sulphate containing water is expected to improve spontaneous imbibition and oil recovery.

### Spontaneous Imbibition tests.

For all tests the cylindrical surface of the core was always sealed to ensure one-dimensional flow. Different boundary conditions were achieved by leaving only top end open, or both top and bottom ends open, see **Fig. 1**. Epoxy was used to seal the required surfaces. The parameters for the core plugs are shown in **Table 2**.

The spontaneous 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, **Fig. 2**. Shrink tube was used to connect the core plug with the cell. The core plug was immersed in 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 two different boundary conditions, top open, both top and bottom open. The schematic diagram of the experimental setup is shown in **Fig. 3**. A back pressure for the imbibition cell was maintained by a piston cell with imbibing fluid on top and nitrogen gas on bottom. Here 10 bars pressure was used to keep the fluids above the bubble point. Core plugs were put into the steel imbibition cells in the oven, with only top end surface or both top and bottom ends exposed to imbibing fluid. Three brines, EF-brine, SSW and SSW-4S were taken as imbibing fluids. At selected times the valve was opened slowly and the produced oil was collected into the burette and measured.

## Experimental Results

### Spontaneous Imbibition Test at 50°C for the Core Plugs with Two Ends Open.

#### *Effects of $S_{wi}$ .*

For the core plug without initial water, a startup time period was observed, but for the core plugs with initial water saturation, immediate oil recovery was recorded, shown by **Figs. 4, 5 and 6**. One explanation could be that in the startup period, seawater may move into the core by film flow along the internal surfaces near the end faces exposed to seawater. When the water saturation has 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 of oil recovery observed by core plug without initial water. Moreover, 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.

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.

The water saturation also influences the flowing modes. Higher oil recovery from top end was observed, moreover, the gap between top end and bottom end was increased for higher water saturation, from 3% OOIP in **Fig. 4** to about 13% OOIP in **Fig. 5** and 6% OOIP in **Fig. 6**. With initial water present in the core plug, the water phase becomes continuous, which leads to stronger cocurrent flow.

#### *Effects of Gravity.*

Oil recovery from the top and bottom surfaces was recorded separately. For all the core plugs LY1-1, LY1-2 and LS1-1 higher oil recovery from the top surface was observed, which is 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.

For core plug LY1-1 with  $S_{wi}=0$  and core plug LY1-2 with  $S_{wi}=25.7\%$ , the core length for both of them was about 7cm, the difference of oil recovery from top surface and bottom surface was enhanced when initial water exists inside the core, see **Figs. 4 and 5**. The explanation can be that with an initially mobile and continuous water phase gravity has more influence and cocurrent flow becomes more dominated. For core plugs LY1-2 and LS1-1 with similar initial water saturations about 25% while different core length about 7cm and 4cm separately, the gap of oil recovery from top surface and bottom surface was decreased for the short core plug LS1-1, see **Figs. 5 and 6**. This again confirms the important influence of gravity on cocurrent flow during this spontaneous imbibition process.

### Spontaneous Imbibition at 130°C.

#### *Effects of Sulphate Concentration.*

Water saturation about 25% was established for several core plugs and they were aged at 90°C. After aging 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 or SSW-4S at 130°C with back pressure at 10 bars for an imbibition test. **Figs. 7 and 8** show the oil recovery curves. The initial fast production increase during the first day is due to thermal fluid expansion and probably some heterogeneity in the wetting conditions during the core preparation.

The comparison between EF-brine imbibition and SSW imbibition, **Fig. 7**, confirms that SSW may contribute to increased oil recovery. Compared to EF-brine, SSW contains sulphate ions. 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.

The spontaneous imbibition test with imbibing fluid SSW-4S gave high oil recovery compared to those results taking SSW as imbibing fluid, **Fig. 8**. No matter for the case with only top end open or the case with both top and bottom ends open, high sulphate containing water enhanced the imbibition process. The oil production was correspondingly high for SSW-4S. Imbibition fluid SSW-4S showed higher potential for wettability alteration towards more water-wetness.

The sulphate concentration also influences the spontaneous imbibing rate, see **Figs. 9** and **10**, taking SSW-4S as the imbibing fluid the production rate was increased and the peak value is almost doubled compared to SSW, the high sulphate containing water can modify the wetting state faster. Moreover the peak production rate for high concentration imbibing fluid SSW-4S appeared earlier, see **Fig. 9**, after 8 days imbibition for SSW-4S while about 11 days for SSW. It seems SSW-4S can change the core plug to be more water-wet.

#### **Effects of Boundary Conditions.**

It is obvious that when larger area of the core plug was open to imbibing fluid, more oil was produced out fast, **Figs. 9** and **10**. With only the top surface open, the oil recovery does not increase much in the starting time period about 5 days. It is the same even for the imbibing fluid SSW-4S, which has four times sulphate content in SSW. This could be explained by the time delay due to ion diffusion to into the core plug to modify the wettability condition towards more water-wet. However, if the core plugs had two ends open, the effect of this phenomenon is not obvious, because more oil can be produced out due to double area open to imbibing fluids.

The imbibing rate is influenced by the boundary condition of core plugs. With only the top surface open, the production rate was relatively high in a wide range, from 10<sup>th</sup> to 27<sup>th</sup> day for SSW and 13<sup>th</sup> to 25<sup>th</sup> day for SSW-4S, see **Fig. 9**. It is a relatively slow process for the SSW to imbibe into the core plug until it reaches the bottom of the core plug and during this process the continuous wettability modification takes place from the top surface further into the core plug. For the core plugs with both top and end surfaces open, see **Fig. 10**, high production rate continues in a shorter time period, from 6<sup>th</sup> to 9<sup>th</sup> day for SSW-4S and 8<sup>th</sup> to 12<sup>th</sup> day for SSW, but both takes place earlier compared to the results with only top surface open. With both ends open, more imbibing fluid enters the core plug to displace oil, which leads to higher oil recovery and imbibition rate. For all the cases, the final wetting state caused by SSW or SSW-4S is approximately the same, but the speed to arrive at the final wetting state is increased for the case with two ends open.

### **Simulation of Spontaneous Imbibition Experiments**

To better understand the imbibition process of seawater into preferential oil-wet chalk core plugs, the experimental results are investigated with a 1-D simulator developed in the previous work (Yu et al., 2007a; Yu et al., 2007b). We assume that sulphate ions are WA agent that will adsorb onto chalk surface and render the wettability more water-wet. The capillary pressure and relative permeability are functions of the WA agent concentration, and they are dynamically changing due to WA agent concentration change in the core plug.

Capillary pressure curves measured by Webb *et al.* (2005) were used as input data, **Fig. 11**, taking the capillary pressure curve with sulphate-free formation water for the initial wettability condition after the core plugs finish aging. The capillary pressure curve with SSW was used for the final wettability condition after SSW imbibition.

Relative permeability curves are calculated with the Corey type equation  $k_{rl} = k_{rl}^0 (S_l^*)^{N_l}$ , 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,  $l$  is either oil or water phases, which are then substituted by  $o$  or  $w$ . Normalized phase saturation  $S_l^*$  is defined as  $S_l^* = (S_l - S_{lr}) / (1 - S_{or} - S_{wr})$ . The values are given in **Table 3**.

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

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

### **Simulation Results.**

Taking the measured capillary pressure as input data for the simulator, we run the simulation and get the oil recovery curves for two cases, fixed wettability and dynamic wettability. For the case with fixed wettability, only the capillary pressure curve for the final wetting state (red curve in **Fig. 11**) is used, and it is independent of WA agent concentration, which means the capillary pressure is only changing with water saturation. For the dynamic wettability alteration case, the capillary pressure depends on the WA agent concentration adsorbed and gradually changes from oil-wet (blue curve in **Fig. 11**) to water-wet (red curve in **Fig. 11**). The capillary pressure is not only the function of water saturation, it is also changing the value to be more positive towards the direction of more water-wetness which is dependent on the sulphate concentration entering the core plug.

The oil recovery curves are shown in **Fig. 12**, for the case with dynamic wettability, the oil recovery increases slowly until it reaches the plateau value after 20 days production, and it produces the similar production profile as the experimental result for core plug LY2-2. For the case with fixed wettability, the oil recovery reaches its maximum value after a couple of days and the result clearly over estimates the recovery. This shows that the simulation of the improved recovery caused by sulphate water injection in the lab scale must include the dynamic wettability alteration.

## Conclusions

1. Comparing imbibition tests for core plugs with and without initial water saturations, a startup time period is observed for core plug without initial water saturation to establish flow conditions.
2. If both top and bottom surfaces are open, countercurrent imbibition takes place at the bottom end, while both countercurrent and cocurrent flows take place at the top surface exposed to the imbibing fluid. Oil recovery is higher 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, the importance of gravity is observed.
3. It is shown that SSW may increase the oil recovery compare to EF-brine as a reference. From the result taking high sulphate containing seawater as imbibing fluid, the positive contribution of sulphate ions on improving oil recovery is confirmed.
4. Boundary conditions of core plugs have a great effect on the imbibition rate. With only top end open, higher imbibition rate range is widened. An explanation is that the wettability change is slow because the alteration is taking place by WA agent diffusion into the core plug and with only one surface open the area exposed to imbibing is small.
5. The core scale simulated oil recovery shows marked differences between dynamic wetting state and fixed wettability condition. The wettability alteration is controlled by diffusion, as reflected by the initially limited recovery rate. Wettability alteration is observed to be an important factor that must be accounted for in simulation studies.

## Nomenclature

$a_1, a_2$	=	Constants to calculate adsorption isotherm, $a_1 = 1$ , $a_2 = 5000$
$c_r$	=	Adsorption isotherm of WA agent onto rock
$F$	=	Weighting function to interpolate relative permeability and capillary pressure
$k_{rl}^0$	=	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
$N_l$	=	Exponential parameter to calculate relative permeability for phase $l$
$p_c^{ow}$	=	Capillary pressure at oil-wet condition
$p_c^{ww}$	=	Capillary pressure at water-wet condition
$S_l$	=	Saturation of phase $l$
$S_{lr}$	=	Residual saturation of phase $l$
$S_{or}$	=	Residual oil saturation
$S_{wr}$	=	Irreducible water saturation

## Acronyms

AN	=	Acid number
EF-brine	=	Ekofisk Formation Brine
OOIP	=	Original oil in place
SSW	=	Synthetic seawater
SSW-4S	=	Synthetic seawater with four times the sulphate content in SSW
TDS	=	Total dissolved solid
WA	=	Wettability alteration

## References

- Austad, T., Strand, S., Høgenesen, 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 Media. Paper SPE 18283 presented at the SPE Annual Tech. Conf. And Exh, Houston, TX, 2-5 October.
- Chillingar, G.V. and Yen, T.F., 1983. Some Notes on Wettability and Relative Permeability of Carbonate Rocks. II. *Energy and Sources* 7: 67-75.
- Frykman, P., 2001. Spatial Variability in Petrophysical Properties in Upper Maastrichtian Chalk Outcrops at Stevns Klint, Denmark. *Marine and Petroleum Geology* 18: 1041-1062.
- Høgenesen, 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.
- 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* 58(1-2): 293-308.
- Karoussi, O., Hamouda, A. A., 2007. Imbibition of Sulfate and Magnesium Ions into Carbonate Rocks at Elevated Temperatures and Their Influence on Wettability Alteration and Oil Recovery. *Energy & Fuels* 21: 2138-2146.
- Punternvold, 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* 21(3): 1606-1616.
- Rezaei, Gomari, K.A., Hamouda, A.A., Denoyel, R., 2006. Influence of Sulphate Ions on the Interaction between Fatty Acids and Calcite Surface. *Colloids Surf. A* 287: 29-35.
- 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.
- Seethapalli, A., Adibhatla, B. and Mohanty, K.K., 2004. Wettability Alteration During Surfactant Flooding of Carbonate Reservoirs. 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., 2000a. Wettability Alteration in Chalk 1: Preparation of Core Material and Oil Properties. *Journal of Petroleum Science and Engineering* **28**(3): 111-121.
- Standnes, D.C. and Austad, T., 2000b. Wettability Alteration in Chalk 2. Mechanism for Wettability Alteration from Oil-Wet to Water-Wet Using Surfactants, *Journal of Petroleum Science and Engineering* **28**: 123-143.
- Strand, S., Standnes, D.C. and Austad, T., 2003. Spontaneous Imbibition of Aqueous Surfactant Solutions into Neutral to Oil-Wet Carbonate Cores: Effects of Brine Salinity and Composition. *Energy & Fuels* **17**: 1133-1144.
- Tavassoli, Z., Zimmerman, R.W. and Blunt, M.J., 2005. Analysis of Counter-current Imbibition with Gravity in Weakly Water-Wet Systems. *Journal of Petroleum Science and Engineering* **48**: 94-104.
- 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.
- Yu, L., Evje, S., Fjelde, I., Kleppe, H., Kårstad, T., and Skjaeveland, S.M., 2007a. Modeling of Wettability Alteration Processes in Carbonate Oil Reservoirs. Accepted for publication in *Network and Heterogeneous Media*.
- Yu, L., Evje, S., Kleppe, H., Kårstad, T., Fjelde, I., and Skjaeveland, S. M., 2007b. Spontaneous Imbibition of Seawater into Preferentially Oil-wet Chalk Cores-Experiments and Simulations. Submitted to *Journal of Petroleum Science and Engineering*.
- 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, D., Jia, L., and Kovscek, 2001. An Investigation of Counter-current Imbibition Processes in Diatomite. Paper SPE 68837 presented at the Western regional meeting held in Bakersfield, CA.

**Table 1. Molar compositions of the brines used. Table 3. Parameters for relative permeability calculation.**

Ion	EF-brine (mol/l)	SSW (mol/l)	SSW-4S (mol/l)
Na <sup>+</sup>	0.684	0.450	0.419
K <sup>+</sup>	--	0.010	0.010
Mg <sup>2+</sup>	0.025	0.045	0.045
Ca <sup>2+</sup>	0.231	0.013	0.013
Cl <sup>-</sup>	1.196	0.525	0.350
HCO <sub>3</sub> <sup>-</sup>	--	0.002	0.002
SO <sub>4</sub> <sup>2-</sup>	--	0.024	0.096
TDS, g/l	68.01	33.39	33.39

Water-wet	$k_{rw}^0$	0.4
	$k_{ro}^0$	0.9
	$N_w$	3.0
	$N_o$	2.0
Oil-wet	$k_{rw}^0$	0.7
	$k_{ro}^0$	0.75
	$N_w$	2.0
	$N_o$	3.0

**Table 2. Experimental information of cores for spontaneous imbibition tests.**

Core#	Oil type	Aging Temp. (°C)	Aging time (days)	Core properties				Spontaneous imbibition		
				Diameter (cm)	Length (cm)	Porosity (%)	Swi (%)	Boundary	Temp. (°C)	Imbibing fluid
LY1-1	C	50	5	3.80	7.04	47.8	0	Two Ends Open	50	SSW
LY1-2	C	50	5	3.80	7.04	50.1	25.7	Two Ends Open	50	SSW
LS1-1	C	50	5	3.80	4.05	50.2	24.9	Two Ends Open	50	SSW
LY2-1	A	90	100	3.70	4.38	51.0	26.5	Top End Open	130	SSW
LY2-2	A	90	100	3.70	4.40	50.0	25.6	Top End Open	130	SSW
LY2-3	A	90	100	3.70	4.34	49.0	24.3	Top End Open	130	EF-brine
LY2-4	A	90	30	3.70	4.34	47.9	25.3	Top end Open	130	SSW-4S
LY2-5	A	90	30	3.70	4.54	50.7	25.6	Top end Open	130	SSW
LT1-1	A	90	30	3.70	5.03	51.2	26.1	Two ends Open	130	SSW-4S
LT1-2	A	90	30	3.70	4.98	50.3	25.6	Two ends Open	130	SSW

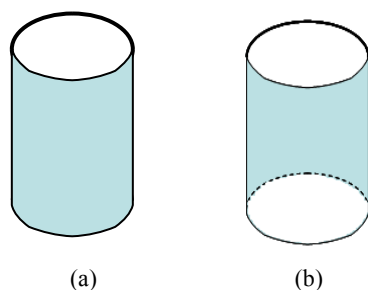


Figure 1. Schematic diagram of boundary conditions for the core plugs. (a) only top end open, (b) both top and bottom ends open.

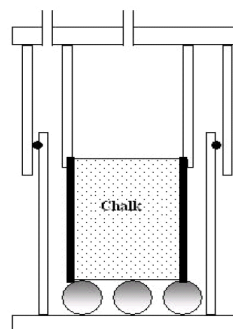


Figure 2. Schematic diagram of experimental setup for imbibition tests at 50°C. Oil is collected separately from top and bottom end.

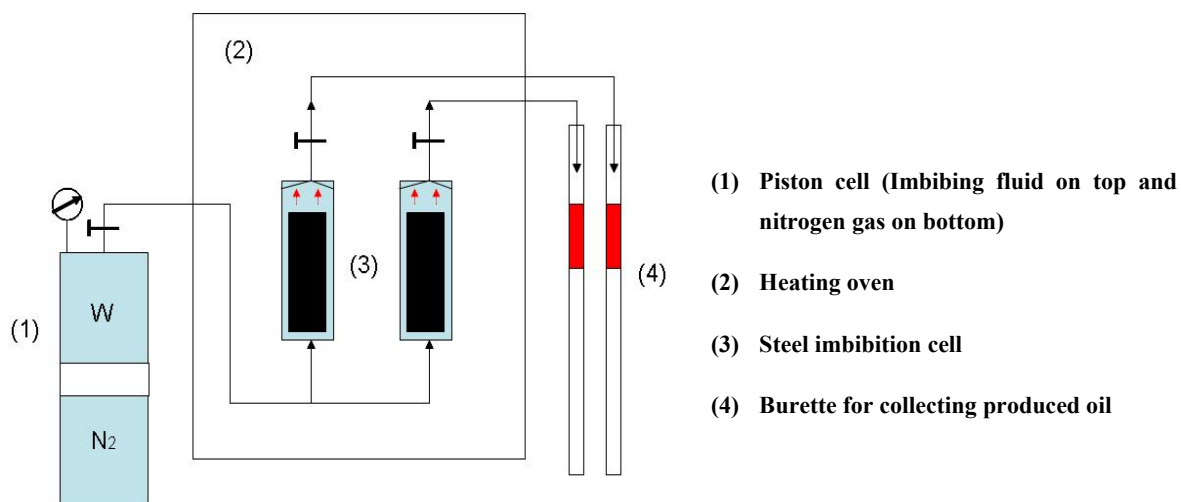


Figure 3. Schematic diagram of experimental setup for imbibition test at 130°C.

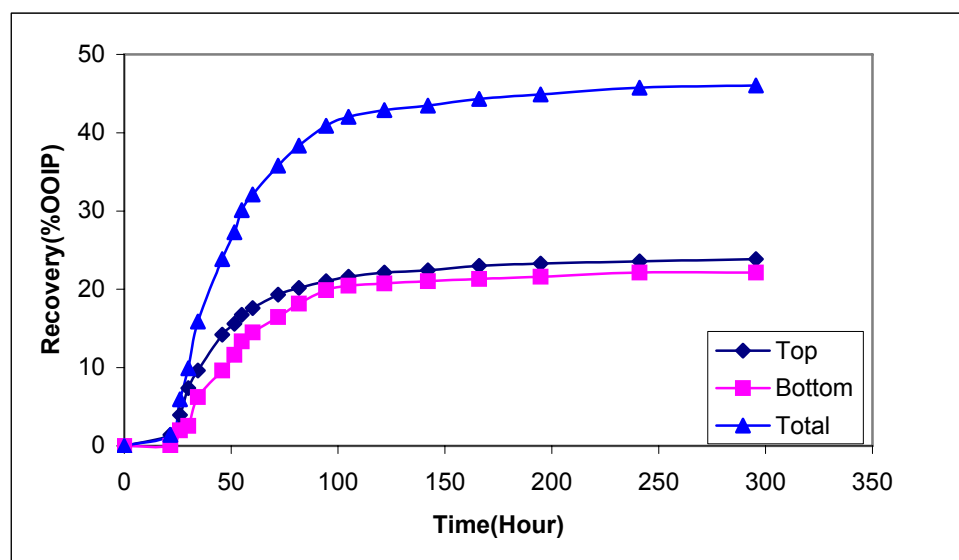


Figure 4. SSW spontaneous imbibition into core plug LY1-1 with two ends open,  $Sw_i=0$ . Oil recovery from top and bottom ends was recorded separately. Tests were performed at 50°C.

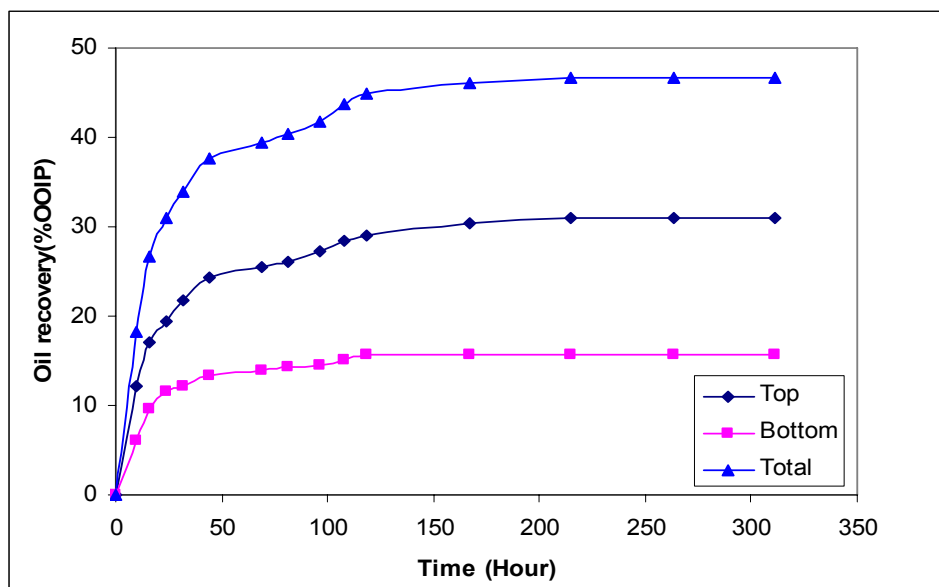


Figure 5. SSW spontaneous imbibition into core plug LY1-2 with two ends open,  $S_{wi}=25.7\%$ . Oil recovery from top and bottom ends was recorded separately. Tests were performed at  $50^{\circ}\text{C}$ .

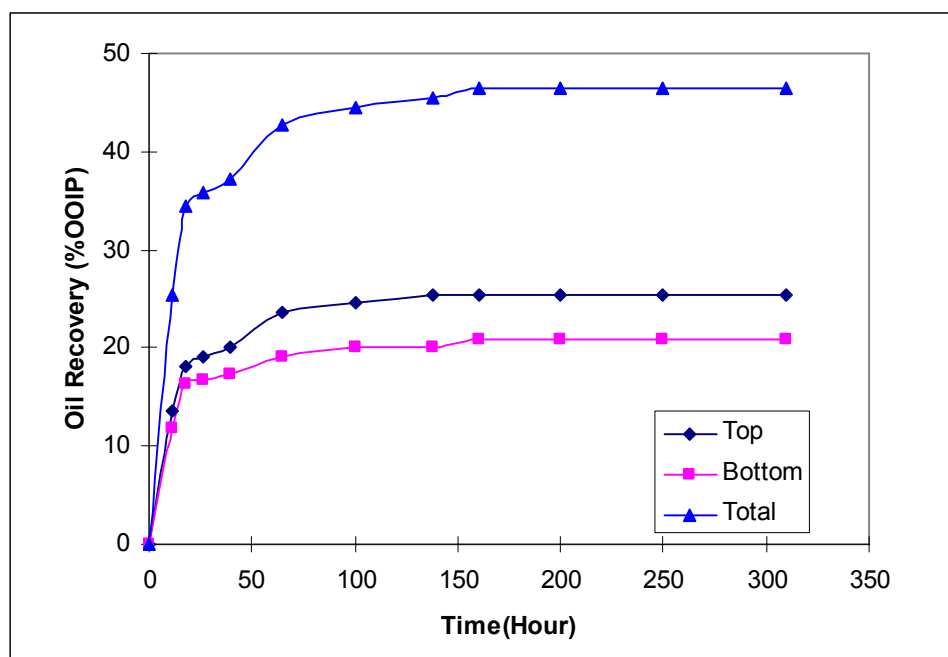


Figure 6. SSW spontaneous imbibition into core plug LS1-1 with two ends open,  $S_{wi}=24.9\%$ . Oil recovery from top and bottom ends was recorded separately. Tests were performed at  $50^{\circ}\text{C}$ .



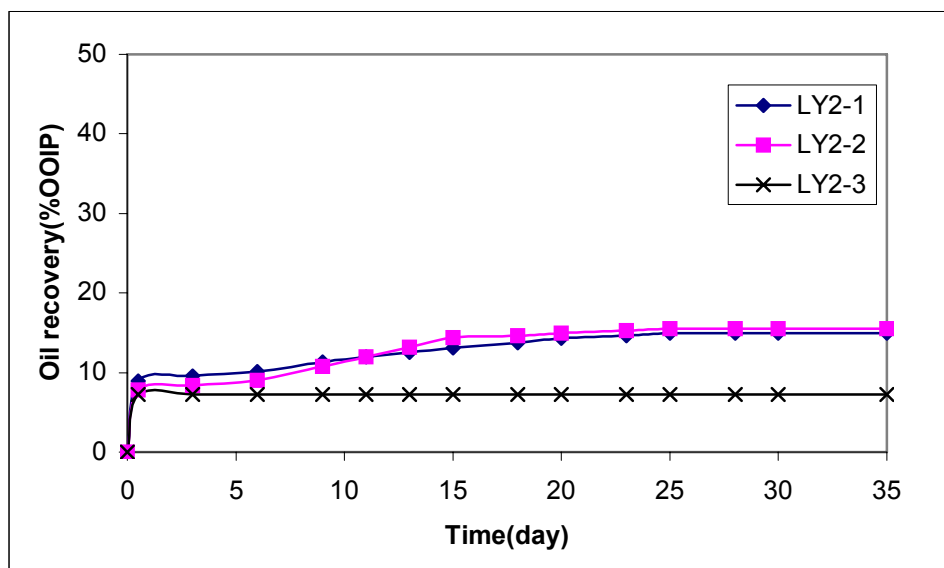


Figure 7. Spontaneous imbibition into core plugs LY2-1, LY2-2 and LY2-3 with only top end open,  $S_{wi}$  about 25%. For LY2-1 and LY2-2, SSW was imbibing fluid, while EF-brine was imbibing fluid for LY2-3. Tests were performed at 130°C.

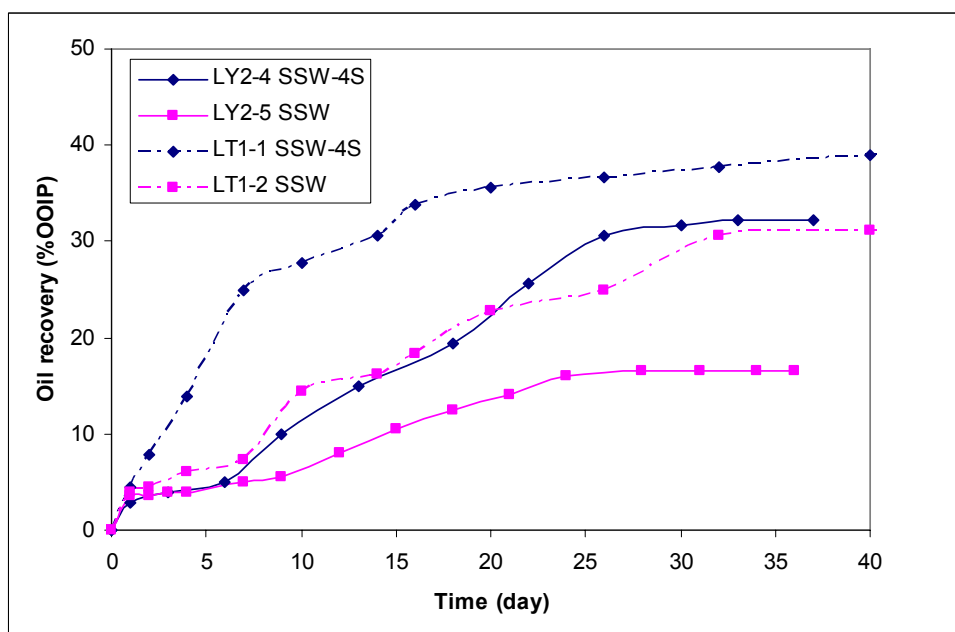


Figure 8. Spontaneous imbibition of SSW and SSW-4S into core plugs with different boundary conditions, LY2-4 and LY2-5 only top end open, LT1-1 and LT1-2 both top and bottom ends open,  $S_{wi}$  about 25%. Tests were performed at 130°C.

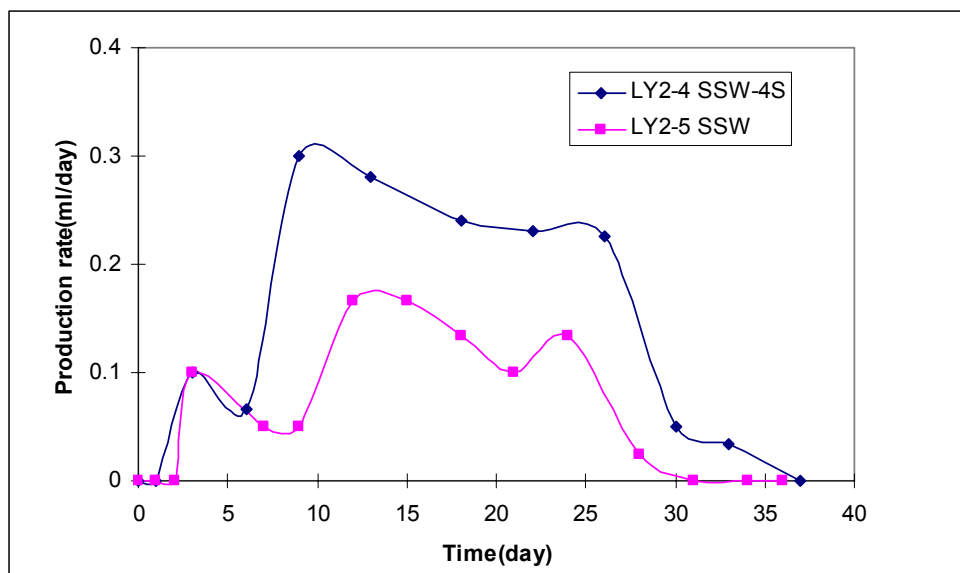


Figure 9. Oil production rate when SSW and SSW-4S imbibed into core plugs LY2-4 and LY2-5 with only top surface open,  $S_{wi}$  about 25%. Tests were performed at 130°C.

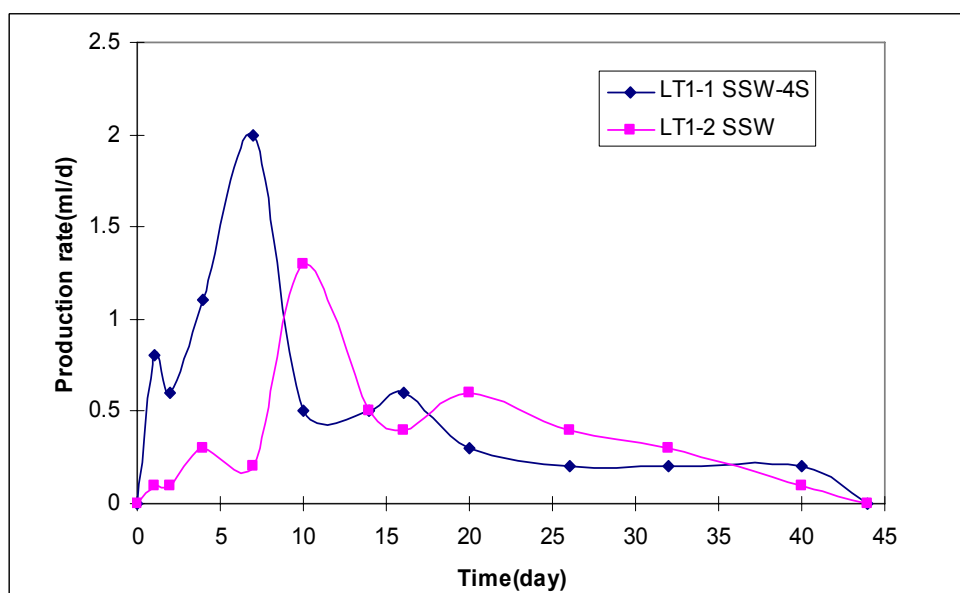


Figure 10. Oil production rate when SSW and SSW-4S imbibes into core plugs LT1-1 and LT1-2 with both top and bottom ends open,  $S_{wi}$  about 25%. Tests were performed at 130°C.

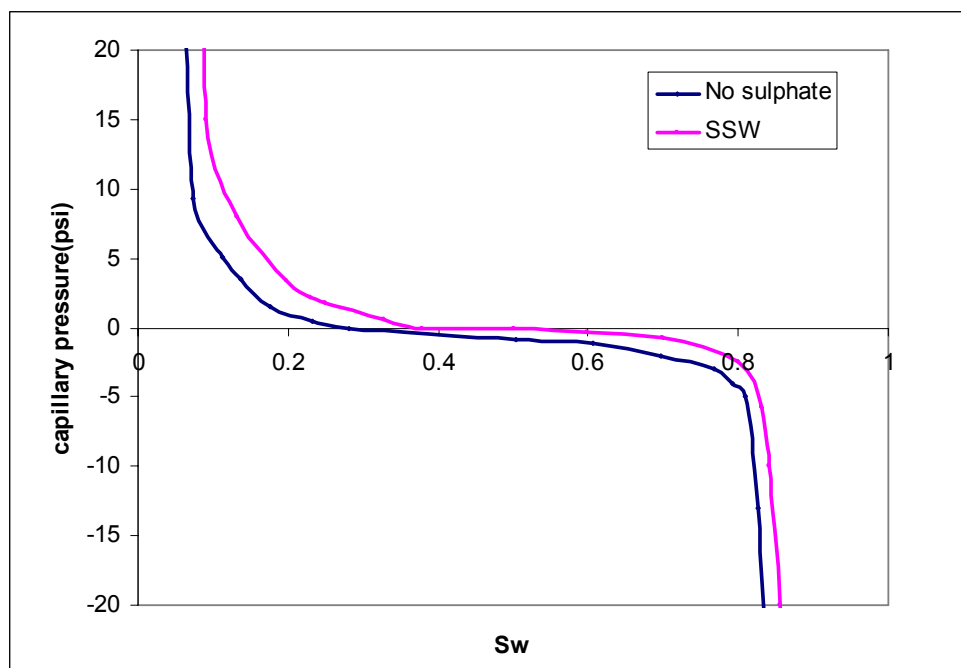


Figure 11. Capillary pressure measured at reservoir condition (Webb et al, 2005). The simulation work in this paper took the curve “No sulphate” as capillary pressure curve for initial wettability condition after aging, and the curve “SSW” as capillary pressure curve for the final wettability after SSW imbibition.

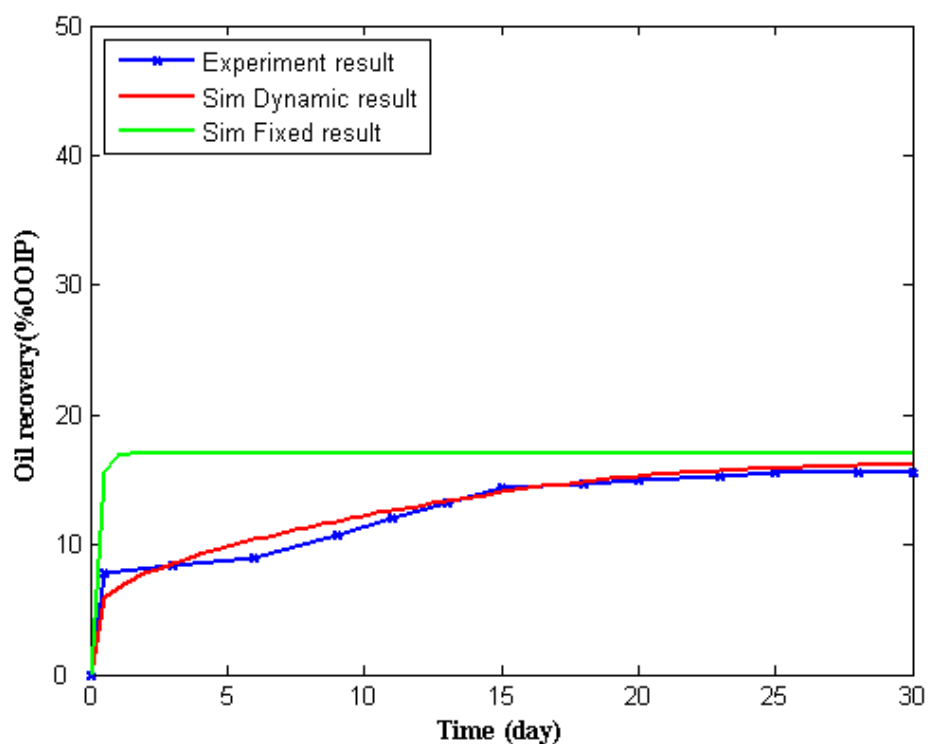


Figure 12. Oil recovery comparison of experimental results with simulation results for core plug LY2-2, dynamic wettability alteration was used in the simulation.