Petroleum Science and Technology

Wettability Restoration of Limestone Cores Using Core Material From the Aqueous Zone

S. F. Shariatpanahi [a] , S. Strand [a] , T. Austad [a] & H. Aksulu [a]

[a] Department of Petroleum Engineering, Faculty of Science and Technology , University of Stavanger , Stavanger , Norway
Published online: 24 Apr 2012.

PLEASE SCROLL DOWN FOR ARTICLE

Taylor & Francis
Taylor & Francis Group

Wettability Restoration of Limestone Cores Using Core Material From the Aqueous Zone

S. F. SHARIATPANAHI,[1] S. STRAND,[1] T. AUSTAD,[1] AND
H. AKSULU[1]

[1]Department of Petroleum Engineering, Faculty of Science and Technology
University of Stavanger, Stavanger, Norway

Abstract   *In the struggle to mimic the wetting state of a limestone reservoir, strongly water wet preserved cores from the aqueous zone have been used. By exposing the cores to the reservoir crude oil and formation water, the authors tried to mimic core properties from the oil leg. Wettability and oil recovery of restored cores were compared, confirming that both wettability and oil recovery depended on the fluids used in the cleaning process. When the preserved cores from the water zone was cleaned mildly and restored with formation brine and crude oil, they behaved in strongly water-wet way (reference core), while restored oil contaminated cores cleaned by organic solvents acted less water-wet. The water wetness was improved when the oil-contaminated cores were cleaned with hot seawater or hot seawater containing cationic surfactant. The oil recovery by spontaneous imbibition for the reference cores was significantly higher than the restored cores previously exposed to crude oil. In the case of forced displacement, the oil recovery from the water-wet reference core was lower than the same restored core.*

Keywords   core cleaning, limestone, special core analysis, wettability restoration

Introduction

Prior to special core analysis, the wetting condition of the cores should be restored as close as possible to the actual reservoir conditions. Normally, the core is cleaned to a completely water-wet state (i.e., the state of the reservoir before oil migrated into it) and then formation brine and crude oil are used to regenerate the initial wetting condition by aging the core at reservoir temperature. The most commonly used cleaning solvents are toluene and methanol (Grist et al., 1975). Toluene effectively removes the hydrocarbons including asphaltenes and some of the weakly adsorbed polar components, while methanol removes water and the strongly adsorbed polar components (Anderson, 1986). Thomas et al. (1993) examined the adsorption and desorption of organic components from the carbonate surface. Water-saturated toluene appeared to be the most efficient solvent for desorbing carboxylic material from the carbonate surface.

Later studies have shown that seawater and seawater containing cationic surfactant can improve the water wetness of carbonates (Standnes et al., 2003; Zhang et al., 2007). The questions asked in this paper are the following: Will carbonate cores sampled in the

Address correspondence to S. Shariatpanahi, Department of Petroleum Engineering, Faculty of Science and Technology, University of Stavanger, 4036 Stavanger, Norway. E-mail: seyed.f. shariatpanahi@uis.no

aqueous zone behave as a representative completely water-wet in special core analysis? Do restored cores, previously exposed to crude oil, show similar behavior as the initial water-wet cores? This was tested in the following way:

- The wettability of mildly cleaned preserved core from the aqueous zone was determined. The oil recovery by spontaneous imbibition (SI) was also determined after saturating and aging the core with formation water and crude oil (reference core).
- After being exposed to crude oil, the core was cleaned and restored to mimic core sampled from the oil zone. The wettability and oil recovery by SI were then determined, and the results were compared with the reference core.

Experimental

Materials

The properties of the preserved low-permeable reservoir limestone cores from the aqueous zone are summarized in Table 1. Prior to delivery, all the cores were preflooded with kerosene. The composition of the brines used is listed in Table 2. The terminology is as

Table 1
Properties of limestone cores used

Core	L, cm	D, cm	Φ, %	k, mD
C1-3	8.26	3.80	18	1.3
C2-4	8.08	3.80	14	0.4
C4-11	8.22	3.79	15	0.3
C4-14	8.08	3.80	16	0.4
C5-15	8.25	3.79	17	1.0
C5-16	7.11	3.80	17	1.0
C5-18	3.82	3.77	17	—

Table 2
Brine composition

Ions	FW, mol/L	SW, mol/L	SW0S, mol/L	SW1/2T, mol/L
HCO^{3-}	0.003	0.002	0.002	0.002
Cl^-	3.643	0.525	0.583	0.583
SO_4^{2-}	0.000	0.024	0.000	0.012
SCN^-	0.000	0.000	0.000	0.012
Mg^{2+}	0.076	0.045	0.045	0.045
Ca^{2+}	0.437	0.013	0.013	0.013
Na^+	2.620	0.450	0.460	0.427
K^+	0.000	0.010	0.000	0.022
TDS, g/L	208.94	33.39	33.39	33.39
IS, mol/L	4.158	0.657	0.643	0.645

follows: FW is limestone formation water, SW is seawater, SW0S is SW without sulfate, and SW1/2T is SW containing 0.012M SO_4^{2-} and tracer SCN^-.

The reservoir crude oil was centrifuged at room temperature to remove water and solid particles. The acid and base numbers of the filtrated oil were determined by a modified version of ASTM D664 and ASTM D2896, AN = 0.08 and BN = 0.35 mgKOH/g oil, respectively (Fan and Buckley, 2006). The oil density and viscosity were measured at 20°C as 0.838 g/cm^3 and 5.8 cP, respectively.

Methods

Mild Cleaning of Preserved Cores From the Aqueous Zone. All the cores were first flooded with heptane to remove the kerosene. DI water was then injected to remove FW. All the cores were dried at 90°C to constant weight.

Core Cleaning After Exposure to Crude Oil. After exposing the core to crude oil, the cores were cleaned by the fluids as shown in Table 3. After the injection of DI water, the cores were dried at 90°C until constant weight.

Core Saturation. Initial water saturation, $S_{wi} \approx 10\%$, was established using the desiccator (Springer et al., 2003). Then, the cores were evacuated, saturated, and flooded with 2 PVs of oil in each direction. Finally, the cores were aged in the oil for two weeks at 90°C.

Table 3
Fluids used in the different restoration process

| Core | Fluids used for core cleaning | | |
	First restoration, reference case	Second restoration	Third restoration
C1-3	Kerosene, heptane DI water	Toluene/methanol DI water	—
C2-4	Kerosene, heptane DI water	Toluene/methanol DI water	—
C4-11	Kerosene, heptane DI water	Heptane DI water	—
C4-14	Kerosene, heptane DI water	Hot SW (@130°C) toluene/methanol DIW	—
C5-15	Kerosene, heptane DI water	Hot SW (@130°C) Toluene/methanol DI water	—
C5-16	Kerosene, heptane DI water	Hot SW Toluene/methanol DI water	Water-saturated toluene heptane C_{12}TAB+SW (@ 130°C) DI water
C5-18	Kerosene, heptane DI water	Toluene/methanol DIW	—

Wettability Test. The chromatographic wettability test, by Strand et al. (2006) was used. The test is based on the chromatographic separation of two water-soluble components: the nonadsorbing tracer, thiocyanate, SCN^-, and the adsorbing ion, SO_4^{2-}. The area between the effluent curves for SCN^- and SO_4^{2-} is directly proportional to the water-wet surface area of the core. This test was used to quantify changes in the wetting state of preserved and restored cores after exposure to cleaning fluids. The ionic concentrations of SO_4^{2-}, and SCN^- were analyzed by an ion-exchange chromatograph, ICS-3000 Reagent-free produced by Dionex Corporation (Sunnyvale, CA).

Oil Displacements. SI tests were performed both at room and reservoir temperature, 110°C, in standard Amott glass and sealed steel cells, respectively. The steel imbibition cell was connected to a supporting pressure cell of ∼10 bar. Forced displacements were performed at reservoir temperature with a back pressure of 10 bar.

Results and Discussion

Wetting Properties

After mild cleaning of the preserved cores from the aqueous zone, the chromatographic wettability tests shown in Figures 1a–d indicated strongly water-wet conditions. The area
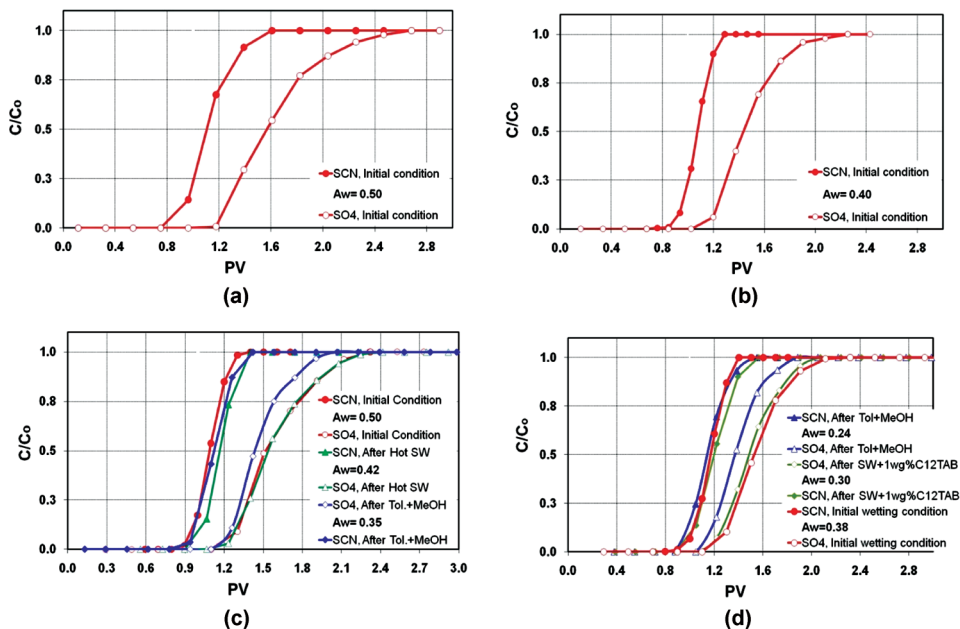

Figure 1. Chromatographic separation between SCN^- and SO_4^{2-} at room temperature. (a) Core C4-11, initial wetting condition after mild cleaning. (b) Core C4-15, initial wetting condition after mild cleaning. (c) Core C4-14, in first restoration: (1) Initial wetting condition after mild cleaning; in second restoration (2) cleaned with hot SW; (3) cleaned with toluene/methanol. (d) Core C5-16, in first restoration: (1) initial wetting condition after mild cleaning; (2) second restoration by water-saturated toluene; (3) third restoration after flooding with SW+1.0 wt% C_{12}TAB. (color figure available online)

between the SCN$^-$ and SO$_4^{2-}$ curves at the initial wetting state varied between 0.38 and 0.50. In all the cases, the SCN- curves were quite symmetric, suggesting homogenous cores with good pore connectivity. The typical asymmetric shape in the last part of SO$_4^{2-}$ curve may indicate the presence of micropores with a significant surface area. After being exposed to crude oil and oil recovery tests, the cores C4-14 and C5-16 were restored using different cleaning fluids.

Core C4-14 was first flooding with hot SW (130°C at low rate, 3 PV/day). The area between the effluent curves decreased from 0.50 for the preserved core to 0.42 for the cleaned restored core with hot SW, see Figure 1c. The asymmetric shape of the SO$_4^{2-}$ curve was the same as for the preserved core. In an attempt to increase the water wetness of the core to the initial condition, it was cleaned by successive toluene/methanol flooding, and surprisingly, the area decreased to 0.35, which is significantly lower than the initial state. Thus, the core C4-14 appeared to become less water-wet when toluene/methanol was used as cleaning solvent. It is also noticed that the SO$_4^{2-}$ curve became less asymmetric after being exposed to toluene/methanol, indicating a decrease in water-wetness of the smaller pores.

A similar trend was observed for the core C5-16. In the restoration process after being exposed to crude oil, the core was first cleaned by just water saturated toluene. The chromatographic separation area decreased significantly, from 0.38 for the preserved core to 0.24 for the restored core, see Figure 1d. Also in this case, the SO$_4^{2-}$ curve became less asymmetric compared with the case for the preserved core. In the second restoration, the core was flooded with SW+C$_{12}$TAB at 130°C, and the water wetness of the core was increased as the area increased to 0.30. The asymmetric shape of the SO$_4^{2-}$ curve was similar to the preserved core, which indicated that SW+1 wt% C$_{12}$TAB appeared to remove organic material also in the micropores.

To sum up the results of wettability tests, it can be concluded that the preserved cores appeared to be highly water-wet, and it was also observed that it was difficult to restore the cores, when exposed to the crude oil, to the same initial wetting state. Water-based cleaning fluid, hot SW or hot SW+1.0 wt% C$_{12}$TAB, appeared to be the best fluids to restore the core to the higher water wetness. Introduction of organic cleaning solvents such as toluene/methanol probably decreased the water wetness of the smaller pores, which will affect the capillary forces. Therefore, SI tests were performed on both preserved cores and restored cores using heptane and low acidic crude oil.

Test for Capillary Forces

The presence of capillary forces after core restorations using different cleaning procedures was tested by imbibing water into the cores saturated with heptane, which will not change the wetting properties of the rock. SI test on heptane saturated preserved core C4-11 with $S_{wi} \approx 10\%$ gave 37% of oil initially in place (OIIP) within 0.1 day at room temperature using FW as imbibing brine, see Figure 2a. Core C5-14 was cleaned by toluene and methanol in the second restoration, after being exposed to crude oil, and the core was saturated with heptanes, $S_{wr} = 10\%$, and imbibed by FW at room temperature. An oil recovery plateau of 40% was obtained within 0.2 days, see Figure 2a. The imbibition rate for the preserved core C4-11 was twice the rate for the restored core C5-14, confirming that the preserved core acted more water-wet. Furthermore, the ultimate oil recovery was lowest for the most water-wet core, which is in line with previous observations by Salathiel (1973), who observed that maximum oil recovery was obtained at slightly water-wet conditions.
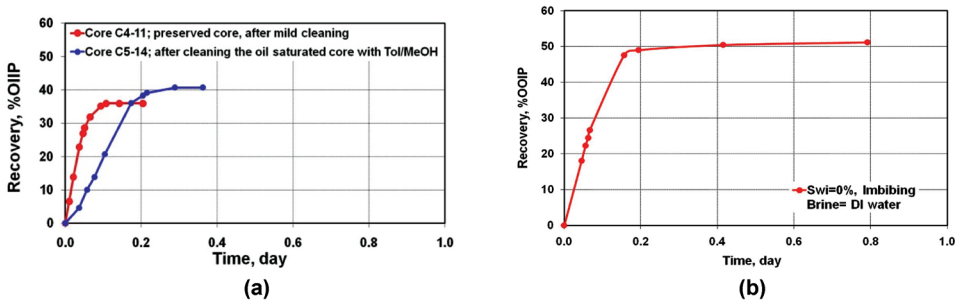
Figure 2. Spontaneous imbibitions tests at room temperature using heptane as a nonwetting reference oil. (a) SI test using FW as imbibing brine on heptane-saturated cores C4-11 and C5-14, $S_{wi} = 10\%$. (b) Core C5-16, Cleaned core using water saturated toluene and SW+C_{12}TAB; $S_{wi} = 0\%$; imbibing fluid DI water. (color figure available online)

Core C5-16, in the third restoration, was again cleaned by water saturated toluene/heptane, and then SW+1.0 wt% C_{12}TAB at 130°C. The core produced about 60% of OIIP after being imbibed with DI water at room temperature. In this case, the core was saturated 100% by heptane, see Figure 2b.

SI Test at Reservoir Temperature Using Crude Oil

The wetting of the cores exposed to the low acidic crude oil, 0.08 mg KOH/g, should be only moderately affected. Mildly cleaned preserved cores were restored initially with FW and low acidic crude oil and were spontaneously imbibed with FW at 110°C (reference cases). The oil recovery was about 40% of OIIP, shown in Figures 3a–f, which was very comparable to the SI test using heptane, shown in Figure 2a. The imbibition rate was, however, lower, confirming that the oil was able to modify the wetting properties of the rock. The core C1-4 was restored after being exposed to crude oil by cleaning with toluene/methanol. The oil recovery in the SI test with FW was only ≈4% of OIIP, which is linked to thermal expansion of fluids, shown in Figure 3b. The same core, after mild cleaning in the first restoration produced about 33% of OIIP, when imbibed with the same FW. Obviously, the wetting of the core was changed after cleaning with toluene/methanol.

The mildly cleaned cores C4-15 and C4-16 produced both about 40% of OIIP with FW in the initial restoration. In the second restoration, core C4-15 was cleaned with hot SW, and the core C4-16 was cleaned by toluene/methanol. Otherwise, the cores were prepared for SI test in the same way as for the preserved cores. Also in this case, the oil recovery dropped dramatically from 40% to 18% after 14 days of imbibition for core C4-15 and from 42% to 6% for core C4-16, shown in Figures 3e and f. Obviously, the core cleaned by organic solvents appeared less water-wet compared with the core cleaned by hot SW. The core C4-16, in the third restoration, was flooded with toluene and SW+1.0 wt% C_{12}TAB at 130°C at a rate of 3 PV/day for three days. It was expected that the cationic surfactant would make the core more water-wet. The core was prepared and imbibed by the same procedure as previously. The oil recovery increased from 6% in the second restoration to 20% of OIIP in third restoration, see Figure 3f. Thus, even in this case, we were not able to reproduce the initial wetting, but the capillary forces
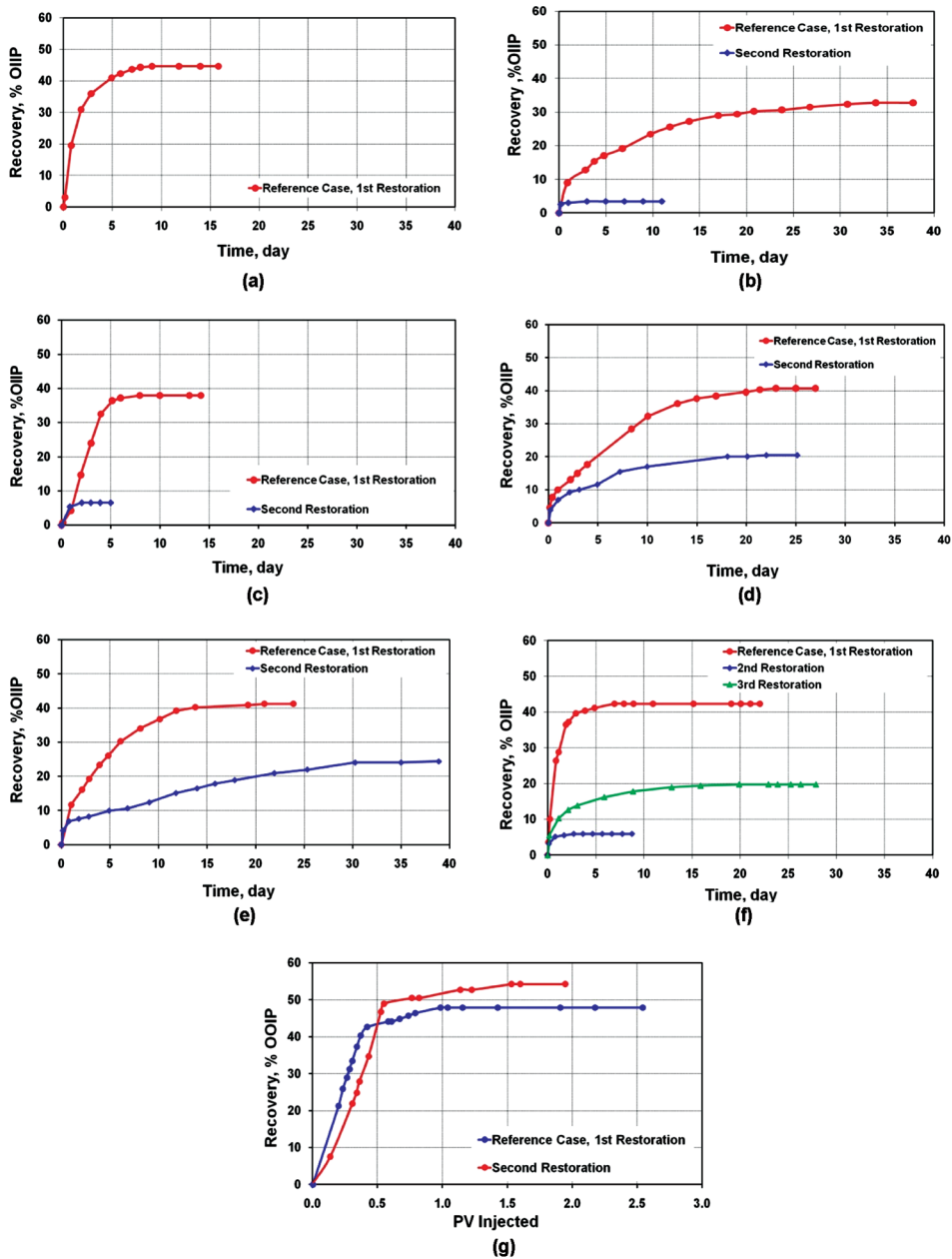
Figure 3. Oil recovery by spontaneous imbibitions using crude oil and FW as imbibing fluid. Viscous flooding on core C5-18, first restoration (reference case) and second restoration (oil-saturated core was cleaned with toluene/methanol); $S_{wi} = 10\%$, Temperature: $110°C$. (a) Core C1-3. (b) Core C1-4. (c) Core C4-11. (d) Core C4-14. (e) Core C5-15. (f) Core C5-16. (g) Core C5-18. (color figure available online)

were increased significantly by flooding the core with $SW+C_{12}TAB$ at high temperature compared to cleaning the core with toluene/methanol.

The core C4-11 in the reference state produced 39% of OIIP with FW, Figure 3c. In the second restoration, after cleaning with heptanes, the core was restored according the same procedure as previously. Without removing the initial water from the core, it was expected to maintain the initial wetting properties. The oil recovery by SI test with FW was low, 7% of OIIP. Heptane probably decreased the solubility of polar components when mixed with crude oil, causing enhanced adsorption of organic components onto the reactive carbonate surface. The SI tests for the water-wet reference cores and the restored cores after being exposed to crude oil were completely in line with the wettability tests (i.e., the restored oil-saturated cores were less water-wet compared with the reference cores, which have never been exposed to oil). The different wetting resulted in a great impact on oil recovery by SI. Normally, core material for lab tests are sampled from the oil leg of a reservoir, and the cores are cleaned by traditional fluids (toluene/methanol), prior to use in wettability and oil recovery tests.

The restored cores, after being exposed to crude oil, should represent core material from the oil zone, and the question is the following: Should we struggle to achieve a completely water-wet core, or should we just clean the core by using traditional fluids? If SI of injected water is an important oil displacement mechanism, the present results have shown, then the oil recovery can be changed dramatically depending on the core preparation method used. In that case, it is also relevant to ask, Will differences in wetting between preserved and restored cores also be reflected in different oil recovery in a forced displacement process?

Forced Imbibition

After mild cleaning, the core C5-18 was restored using the low acidic crude oil, and then flooded with FW at 110°C with a rate of 0.5 PV/day. The oil recovery amounted to 48% of OIIP, see Figure 3g. After cleaning the same core in a second restoration using toluene/methanol, the core was prepared for oil displacement in the same way, and the oil recovery increased to 55% of OIIP. Thus, the trend in oil recovery by forced imbibitions was opposite to what was observed in the SI process. The difference in oil recovery between the preserved and restored state was, however, much smaller in the forced displacement process. This is in agreement with previous studies by Salathiel (1973).

Conclusions

The results from the experimental work are shortly summarized as

1. In all cases, mildly cleaned preserved cores from the water zone appeared to be highly water-wet. The wetting properties were verified by wettability and SI tests.
2. After cleaning the cores, which were previously exposed to crude oil, by using toluene + methanol + DI water, the cores still behaved water-wet as confirmed by wettability test and SI of FW into heptane saturated core.
3. The oil recovery from mildly cleaned cores was in the range of 40% of OIIP, but the recovery dropped below 10% in most cases after cleaning the oil contaminated cores by toluene/methanol. Oil recovery by SI was improved significantly, from 6% to 20%, when hot SW or $SW+C_{12}TAB$ was used as cleaning fluid compared with the organic solvents.

4. In a forced imbibitions process, the impact on oil recovery by different core treatments was much smaller, but significant. In this case, oil recovery from the initially water-wet core was 48% of OIIP, compared with 55% for the core cleaned by successive injection of toluene/methanol (i.e., opposite to what was observed for an imbibitions process).

Acknowledgment

References

Anderson, W. G. (1986). Wettability literature survey. Part 1: Rock/oil/brine interactions and the effects of core handling on wettability. *J. Petrol. Tech.* 38:1125–1144.

Fan, T., and Buckley, J. S. (2007). Acid number measurements revisited. *SPE J.* 12:496–500.

Grist, D. M., Langley, G. O., and Neustadter, E. L. (1975). The dependence of water permeability on core cleaning methods on the case of some sandstone samples. *J. Can. Pet. Technol.* 14:48–52.

Salathiel, R. A. (1973). Oil recovery by surface film drainage in mixed-wettability rocks. *J. Pet. Tech.* 25:1216–1224.

Springer, N., Korsbech, U., and Aage, H. K. (2003). Resistivity index measurement without the porous plate: A desaturation technique based on evaporation produces uniform water saturation profiles and more reliable results for tight North Sea chalk. *International Symposium of the Society of Core Analysts.* Pau, France.

Standnes, D. C., and Austad, T. (2003). Wettability alteration in carbonates: Interaction between cationic surfactant and carboxylates as a key factor in wettability alteration from oil-wet to water-wet conditions. *Colloids Surf., A* 216:243–259.

Strand, S., Standnes, D. C., and Austad, T. (2006). New wettability test for chalk based on chromatographic separation of SCN^- and SO_4^{2-}. *J. Pet. Sci. Eng.* 52:187–197.

Thomas, M. M., Clouse, J. A., and Longo, J. M. (1993). Adsorption of organic compounds on carbonate minerals. 1. Model compounds and their influence on mineral wettability. *Chem. Geol.* 109:201–213.

Zhang, P., Tweheyo, M. T., and Austad, T. (2007). Wettability alteration and improved oil recovery by spontaneous imbibition of seawater into chalk: Impact of the potential determining ions: Ca^{2+}, Mg^{2+} and SO_4^{2-}. *Colloids Surf., A* 301:199–208.