OIL RECOVERY FROM BENTHEIM SANDSTONE BY SEQUENTIAL WATERFLOODING AND SPONTANEOUS IMBIBITION

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ABSTRACT

Sequential waterflooding refers to cycles of flooding for which initial water saturation is re-established after a waterflood by flow of crude oil followed by further waterflooding (Loahardjo et al. 2012). Numerous tests have shown that sequential waterfloods can result in significant reduction in residual oil from one flood to the next. As part of an investigation of the mechanism of sequential flooding, an extensive study of sequential waterflooding and spontaneous imbibition has been performed on Bentheim Sandstone, an outcrop sandstone which has, typically, high permeability and low clay content. The waterfloods showed systematic decrease in residual oil saturation from one flood to the next. After firing and acidizing, reduction in residual oil was no longer observed.

Extended aging of cores at residual oil saturation during the course of sequential waterflooding usually resulted in increased recovery for the next waterflood whereas aging at initial water saturation resulted in decreased recovery. The inference that variation in recovery by sequential flooding is related to wetting phenomena was tested through imbibition tests on companion Bentheim core samples with and without a previous history of waterflooding. No additional oil recovery was obtained by forced displacement after spontaneous imbibition. The Amott index to water of unity indicated that, for the tested crude oil, all of the cores were very strongly water wet. However, the rate of imbibition, a more direct test of wettability because it is closely related to the capillary driving force, increased for cores that had been previously waterflooded. These observations imply that the strong response in recovery behavior observed for sequential flooding of Bentheim sandstone is linked to transition in wetting behavior between conditions that would, traditionally, all be classed as very strongly water wet.

INTRODUCTION

Previous studies indicated that Sequential WaterFlooding, SWF, can significantly reduce residual oil saturation from one waterflood to the next (Loahardjo et al. 2010a; 2010b; 2012). There was no cleaning or re-aging between floods. In initial studies, each SWF was completed within 24 hours. It was later shown if, during the course of sequential flooding, the core was allowed to age at the residual oil saturation, there could be further significant benefit to recovery. Conversely, if the core were allowed to age at high initial water saturation prior to waterflooding, the trend of increased recovery for each cycle was reversed (Loahardjo et al. 2012). This pattern of behavior implies that the observed variations in waterflood behavior were tied to changes in wettability. In this study, tests of SWF have been extended to Bentheim sandstone, a high permeability sandstone of very low clay content, and are complemented by measurements of wettability based on rate and extent of spontaneous imbibition.

EXPERIMENTAL

Oil

An asphaltic crude oil, designated as WP was filtered to remove particulate matter and then vacuumed for 2 hours at room temperature to minimize the possibility of gas production during the course of displacement at elevated temperature. Crude oil properties are listed in Table 1. Soltrol 220 of 3.9 cP viscosity with density of 0.728g/cc was used in tests with mineral oil. Polar contaminants were removed by flow through a packed column of aluminum and silica gel.

Brine

Brine was based on the composition of synthetic sea water given in Table 2. The brine was degassed by vacuum. The viscosities of the brines were all close to 0.6 cP at 60^{o}C. The density of the seawater was 1.0233 g/cc at 22^o C.

Cores

The cores were outcrop Bentheim sandstone. Gas permeabilities, K_g, were usually about 2 D. Porosity, φ, ranged from 21 to 28 % (see Table 3). Tests on each core with respect to number of SWFs, Spontaneous Imbibition (SI) tests, and firing and acidizing, are included in Table 3.

Establishment of Initial Water Saturation

The cores were saturated with synthetic seawater and held for 14 days at room temperature to establish ionic equilibrium. For Cores Bh 1, 2 and 3, initial water saturation was established by oil flooding at 2 cc/min horizontally, for about 5 Pore Volumes (PV). The core was then flooded with 1 PV of oil in the reverse direction to mitigate possible end effects. For Bh 1 and Bh 2, oil flooding was performed at ambient temperature, and at 60^{o}C for Bh 3.

For the recovery tests that included spontaneous imbibition, initial water saturation was established by displacement of brine with nitrogen using a porous plate. The core was saturated with crude oil and then placed in a stainless steel cell and pressurized to 1000 psi to ensure complete saturation with liquid.

Initial Aging

After establishing initial water saturation, S_{wi}, the core was submerged in crude oil in a pressure vessel, and aged at elevated temperature. For Cores Bh 1, 2 and 3, the aging temperature was 75^{o}C, with aging times of 4 months for Bh 1 and 4 weeks for both Bh 2 and 3. For tests that included imbibition measurements, the aging time was 4 weeks. Aging, displacement, and spontaneous imbibition were performed at 60°C.

Additional Aging between Sequential Floods

Tests, for Core Bh 3, were also made on the effect of extended aging at either residual oil or initial water saturation at 60°C. For extended aging at residual oil saturation, S_{or}, the core was placed in an imbibition cell so that any additional oil production could be recorded.

Waterfloods

After aging, cores were set in a core holder and waterflooded at 0.25 cc/min at 60°C. Initial water saturation was re-established by flow of crude oil. For the tests on Bh 3, a back pressure of 20 psi was applied during the course of waterflooding. Oil recovery and residual oil saturation were compared at 5 PV injection.

Spontaneous Imbibition

In imbibition measurements, a core was set in a glass imbibition cell filled with brine and placed in an oven set at 60°C. Produced oil versus time was recorded.

RESULTS and DISCUSSION

Sequential Waterflooding

Core Bh 1. Recovery for Bh 1 (aged for 4 months) for the initial seawater flood was 35% Original Oil In Place, OOIP, at breakthrough and final recovery was 45% (see Fig. 1). The subsequent increases in oil recovery (Fig. 1a) and associated reductions in residual oil were the largest yet seen for sequential waterflooding (from 50% down to 12% after the fourth SWF). Core Bh 1 gave the lowest breakthrough, 35% OOIP. The low recovery for SWF 1 probably contributed to the large subsequent increases in recovery by SWF.

The pressure drop, ΔP, toward the end of oil production for Core Bh 1 showed very little change from one SWF to the next, even though the residual oil saturation decreased by over a factor of four (Fig. 1b). The permeabilities to brine at residual oil saturation, K_w^*, were close to 4.5 mD for all four floods (see Fig. 1b).

Core Bh 3. SWF 1 through SWF 4 for Bh 3 showed systematic reduction in residual oil saturation: 46%, 44%, 38%, and 29% for initial water saturations of 21%, 13%, 18% and 28% (Fig. 3a). K_w^* for Bh 3 decreased by a factor of 6 from 182 mD to about 40 mD for SWF 1 vs. SWF 2 (Fig. 4a) even though the residual oil saturation was decreased by 2% (Fig. 3a). K_w^* increased only slightly for SWF 3 and 4, despite the large decrease in the residual oil from 38% to 29% (Fig. 3a). After completion of the 4th SWF, the core was aged for 14 days at 29 % residual oil saturation (Fig. 3b). After injection of crude oil, the initial water saturation increased from 28% (start of 4th SWF) to 37% (start of 5th SWF). The residual oil saturation, an absolute measure with respect to pore volume, fell from 29% (4th SWF) to 20% (5th SWF, see Fig. 3b). K_w^*, was halved (47 mD for SWF 4 to 23 mD for SWF 5, see Fig. 4b) even though the residual oil had decreased by 9%. The increase in % OOIP recovery for flood SWF 5 was consistent with previous observations that aging at residual oil saturation was favorable to the mechanism of oil recovery by SWF (Loahardjo et al. 2012).

Initial water saturation was re-established at 12% and the core was aged for 8 days. For SWF 6, the trend of increase in recovery was reversed. Oil recovery fell from 69% OOIP for SWF 5 to 53 % OOIP for SWF 6 (see Fig. 3b); decrease in oil recovery was accompanied by slight increase in K_w^*. Aging at initial water saturation had also been previously reported to decrease recovery for both low (84 mD) and medium (615 mD) permeability Berea sandstone (Loahardjo et al. 2012).

The first example of departure from increase in recovery after aging at residual oil for 3 months occurred for SWF 7. The oil recovery decreased from 53% OOIP at SWF 6 to 49% OOIP for SWF 7 (Fig. 3b); the residual oil saturation, rose from 42% to 46%. This decrease was inconsistent with respect to previous observations and may be related to changes that occurred after many SWFs. Even though residual oil saturation rose from 42% to 46%, marked change in the oil distribution is indicated by 50% decrease in K_w^* (Fig. 4b).

Core Bh F. As a test of change in rock properties, SWF was tested after firing and acidizing a Bentheim sandstone core designated as Bh F (see Table 3). Core Bh F was fired at 800^{o}C for 6 hours. The core was then acidized with HCl 1 [M] and flushed with distilled water until the effluent pH was close to neutral (6.5). After aging in brine, initial water saturation was established by injection of crude oil. Results for recovery of WP crude oil for 4 SWFs are presented in Fig. 5a.

Initial water saturation increased after the first flood and then residual oil and subsequent initial water saturations showed little variation from one flood to the next. The results are the closest to reproducibility of initial water saturation and recovery of crude oil yet observed for SWFs. However, it can be seen that there were substantial differences in the pressure response during the early two phase flow period (commonly used to derive unsteady state relative permeabilities) for all four floods. Furthermore, above about 1 PV injection, the pressure drop decreased substantially between floods (see Fig. 5b). The corresponding increase in K_w^* was opposite to the trends observed for the three unfired Bentheim cores, Bh 1, 2, and 3.

Comparison between Cores

Although the flow rate and PV injected for establishing initial water saturation were the same for each flood, there was significant variation in initial water saturation for the SWFs. For all three unfired cores, the initial water saturation decreased for the second SWF and increased for subsequent SWFs. Initial water saturations, normalized with respect to values for SWF 1 are shown in Figure 6. This trend in values of initial water saturation for SWFs was qualitatively consistent with previously reported behavior for Berea sandstones (Loahardjo et al., 2010a and b).

A summary of residual oil saturations given by sequential flooding for the four tested Bentheim sandstone cores is presented in Figure 7 with residual oil saturations normalized by the S_{or} for SWF 1. There is a consistent trend of decreasing S_{or} for the first four sequential floods on Cores Bh 1, Bh 2, and Bh 3. Results for the core Bh F, which did not give decrease in residual oil, are also shown. Inspection of petrographic thin sections of Bentheim sandstone by optical microscopy before and after firing showed mainly open pore space between sand grains and no obvious cause for elimination of the SWF effect.

Relative permeabilities to brine at residual oil saturation as fractions given by normalizing by the brine permeability at 100% saturation, k_{rw}^*, are shown in Fig 8. Except for one data point (Bh 3, SWF 1), all of the k_{rw}^*values for the SWF floods on unfired cores were less than 0.04. As observed previously (Loahardjo et al, 2012) for Berea sandstone, the k_{rw}^* are well below those for reduction in residual mineral oil saturation by increase in capillary number at very strongly water wet conditions. Average values of k_{rw}^* for the fired and acidized core tended to be somewhat higher (between about 0.03 and 0.06) than for unfired cores but still well below those measured after recovery of mineral oil. Traditionally, relative permeabilities are expected to increase as rocks become less water wet (Craig, 1972 and Anderson, 1987). The low k_{rw}^* values indicate that pore throats were partially blocked by the residual crude oil and resistance to flow was maintained even for large reduction in oil saturation. Oil-in-water emulsions may also play a role in the constant resistance to flow of brine. Other examples of low permeability at residual oil and dependence on configurations of remaining oil have been discussed (Morrow et al. 1986 and Wang and Buckley, 1999).

Wettability Assesment

Core Bh 4. Assessment of change in wettability from spontaneous imbibition requires that results be scaled to compensate for other factors which contribute to the observed rates. A basic requirement of scaling spontaneous imbibition data identified by Mattax and Kyte (1962) was that the distribution of initial water saturation be comparable between samples. The most readily reproducible initial water saturation for a range of rock samples is zero. This is the most common starting condition in many studies aimed at understanding the basic scaling laws for imbibition. Proposed scaling groups were reviewed by Mason et al. (2010). Experimental data for a very wide range of viscosity ratio led to modification of the viscosity term in the Ma et al. (1997) scaling group to give a dimensionless time defined by Mason et al. 2010 as:

$$t_D^* = \frac{2}{L_c^2}\sqrt{\frac{K}{\varphi}}\frac{\sigma}{\mu_w\left(1+\sqrt{\mu_{nw}/\mu_w}\right)}t \qquad (1)$$

For studies of recovery of crude oil and wettability by spontaneous imbibition, the use of zero initial water saturation as the initial condition is compromised because brine has been shown to mediate crude oil brine rock interactions (Buckley et al., 1996 and 1998). Nevertheless, the plot of recovery of clean mineral oil vs. t_D^* shown in Fig. 9 for Core Bh

4 provides a reference for Bentheim sandstone under very strongly water wet (VSWW) conditions for assessment of the effect of wettability on recovery of crude oil by spontaneous imbibition.

Core Bh 5. Recovery of crude oil by spontaneous imbibition at 60°C starting at 9% S_{wi} is included in Fig. 9. Scaled rate of recovery for imbibition by Core Bh 5, was over an order of magnitude slower than for recovery of mineral oil (VSWW, S_{wi} = 0%), but the final recovery was almost as high. When the core was set in a core holder and flooded, there was no additional oil recovery. Thus, an Amott index of unity was obtained even though the rate of imbibition was much reduced relative to that for Core Bh 4.

Core Bh 6. Core Bh 6 was first waterflooded and then re-flooded with crude oil to an initial water saturation of 10% before measurement of spontaneous imbibition. The scaled rate of imbibition was distinctly higher than for the Core Bh 5, which had not been subject to waterflooding. The Amott index to water for Bh 6 was also unity. The Amott indices to water of unity indicate that the observed increases in recovery by SWF were not influenced by end effect. Absence of end effect was previously demonstrated for SWF of Berea sandstone by direct imaging of the distribution of oil and water along the whole length of the core including the outflow face (Loahardjo et al. 2010b). The water flood results presented in Figures 1 to 3 clearly show that SWF can give large variations in oil recovery and residual oil. The imbibition data obtained with and without previous waterflooding indicate change in wettability towards water wetness after waterflooding (see Figure 9).

A comparison of dimensionless times for completion of waterflood tests and spontaneous imbibition measurements is included in Fig. 9. Plotting the waterflood data on a log dimensionless time scale demonstrates that oil flow continues, albeit at increasingly slow rates, consistent with behavior identified with mixed wettability by Salathiel (1973). For the waterflood tests to be run for a time equivalent to that needed to reach the stable residual oil saturation by spontaneous imbibition, the volume of injected brine would be almost 50 PV. It is possible that over the longer time taken for spontaneous imbibition, there may have been transition to the measured strongly water wet state, as defined by the Amott index, to give residual oil configurations that are robust with respect to the forced displacement step of the imbibition tests.

The relative permeabilities measured after sequential waterflooding are largely independent of residual oil saturation and imply that the configurations of retained crude oil after waterflooding are very different to those given by mobilization of mineral oil (see Figure 8). Furthermore, the rates of imbibition for recovery of crude oil indicate a different wetting state than for recovery of mineral oil (Fig. 9). A possible explanation of the combination of low values of k_{rw}^{*}, that are essentially independent of residual oil saturation, coupled with Amott indices of unity, is that the crude oil has sufficient adhesion at points of contact on the rock surface to block flow of brine by holding oil drops at, and even occupying, pore throats. Micro CT x-ray imaging provides a possible approach to testing this speculation.

CONCLUSIONS

- Systematic reduction in residual WP crude oil saturation by SWF was observed for three Bentheim cores.
- Relative permeabilities to brine at reduced residual oil saturation were much lower than obtained for reduction of residual oil saturation at VSWW conditions.
- Aging at residual oil saturation usually resulted in increased recovery for a subsequent waterflood, whereas aging at initial water saturation reduced the waterflood recovery.
- Change in recovery by SWF was eliminated after many repeated floods.
- Fired and acidized Bentheim sandstone did not exhibit increased recovery of crude oil by sequential waterflooding.
- Rate of spontaneous imbibition for an aged core was much slower than for cores which had been waterflooded prior to measuring oil recovery by imbibition.
- The low relative permeabilities to brine at residual oil and relatively low rates of imbibition demonstrate that, although the Amott indices for water were unity, the wetting state at completion of a waterflood did not correspond to the very strongly water wet conditions given by recovery of mineral oil.

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REFERENCES

- Anderson, W.G.: "Wettability Literature Survey—Part 5: The Effects of Wettability on Relative Permeability," *JPT* (1987) **39**, No. 11, 1453-1468, November.
- Amott, E., "Observations Relating to the Wettability of Porous Rock," *Trans.*, AIME (1959) **216**, 156-162.
- Buckley, J.S., Bousseau, C., and Liu, Y.: "Wetting Alteration by Brine and Crude Oil: From Contact Angles to Cores," *SPEJ* (Sept. 1996) **1**, No. 3, 341-350
- Buckley, J.S., Liu, Y., and Monsterleet, S., "Mechanisms of Wetting Alteration by Crude Oils," *SPEJ* (Mar. 1998) **3**, 54-61
- Craig, F.F., Jr., "The Reservoir Engineering Aspects of Waterflooding," *SPE of AIME* (1971).
- Loahardjo, N., Xie, X., and Morrow, N.R.," Oil Recovery by Sequential Waterflooding of Mixed-Wet Sandstone and Limestone", *Energy and Fuels*, (2010a) **24** (9): 5073–5080, 2010a. http://dx.doi.org/10.1021/ef100729b
- Loahardjo, N., Morrow, N.R., Stevens, J. and Howard, J., "Nuclear Magnetic Resonance Imaging: Application to Determination of Saturation Changes in a

Sandstone Core by Sequential Waterflooding", paper SCA 2010-16 Proceedings of the 2010 International Society of Core Analysts, Halifax, Canada, 4–7 October

- Loahardjo, N., Xie, X., Winoto, W., Buckley, J., and Morrow, N., "Oil Recovery by Sequential Waterflooding the Effect of Aging at Residual Oil and Initial Water Saturation", SPE 154202 presented at the Eighteenth SPE Improved Oil Recovery Symposium (2012) held in Tulsa, Oklahoma, USA, 14-18 April.
- Ma, S., Morrow, N.R., and Zhang, X., "Generalized Scaling of Spontaneous Imbibition Data for Strongly Water-Wet Systems," *J. Petr. Sci. and Eng.* (1997) **18**, 165-178.
- Mason, G., Fisher, H., Morrow, N.R., Ruth, D.W., "Correlation for the Effect of Fluid Viscosities on Counter-Current Spontaneous Imbibition", *JPSE*., (2010) **72**, 195-205
- Mattax, C.C. and Kyte, J.R.," Imbibition Oil Recovery from Fractured , Water-Drive Reservoirs", *Society of Petroleum Engineers Journal* (1962),177-184, June
- Morrow, N.R., Lim, H.T., and Ward, J.S., "Effect of Crude Oil Induced Wettability Changes on Oil Recovery," *SPE Formation Evaluation,* (1986) **1**, 89-103, April.
- Salathiel, R.A.,"Oil Recovery by Surface Film Drainage in Mixed-Wettability Rocks", *J.Pet.Tech.* (1973) **255**,216-224, October 1973.
- Wang, J.X and Buckley, J., "Wettability and Rate Effects on End-Point Relative permeability to Water," paper SCA – 9937 presented at the 1999 International Symposium of the Society of Core Analysts, Golden, Colorado, August 1-4.

Table 1. Crude Oil Compositions

Crude Oil	**WP**
C_7 asphaltenes, % weight	6.3
Acid #, mg KOH/ g oil	1.46
Base #, mg KOH/ g oil	2.49
Density at 22°C, g/cc	0.91
Viscosity at 22°C, cP	111.2
Viscosity at 60°C, cP	20.1

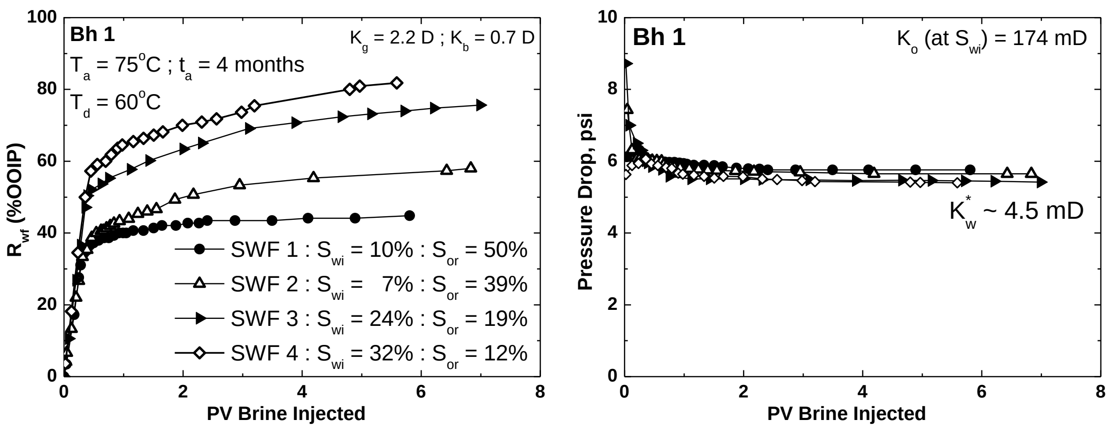
Table 2. Composition of Synthetic Seawater and Its Density

Composition	**g/L**
NaCl	11.0
$CaCl_2.6H_2O$	0.6
$MgCl_2.6H_2O$	3.4
KCl	0.1
NaN_3	0.2
TDS	15.1
Density = 1.024 g/cm^3	

Table 3. Core Properties and tests (number of sequential waterfloods

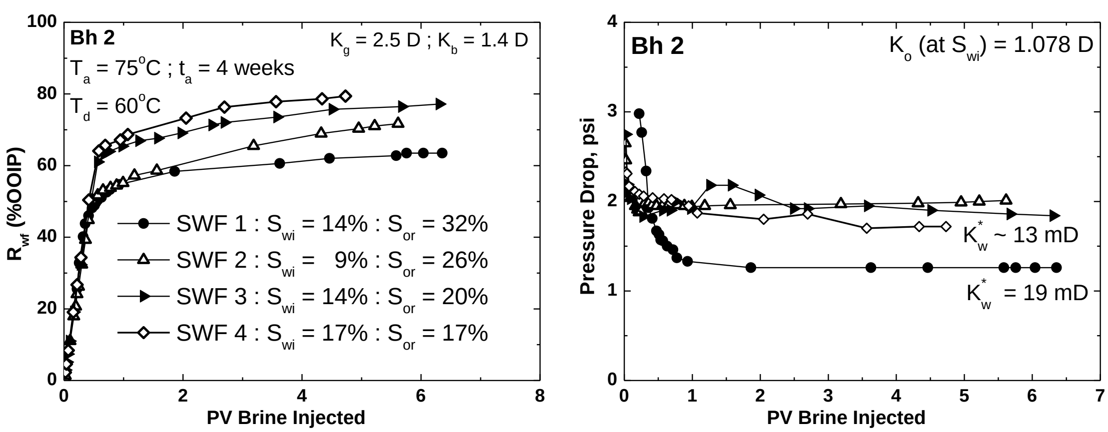
Core ID	Tests	L, cm	d, cm	ϕ, %	k_g, D	S_{wi}, %
Bh 1	SWF(4)*	7.180	3.690	21	2.19	10
Bh 2	SWF(4)	7.100	3.690	21	2.49	14
Bh 3	SWF(7)	7.730	3.770	23	1.56	21
Bh 4	SI** (Mineral Oil)	7.750	3.761	24	0.672	0.0
Bh 5	SI (WP Crude Oil)	6.513	3.756	25	2.330	8.8
Bh 6	SWF(1) SI	7.763	3.755	28	1.900	8.0
Bh F	SWF (4)	7.813	3.760	24	2.025	14.4

*SWF ( ): number of sequential waterfloods **SI( ): spontaneous imbibition



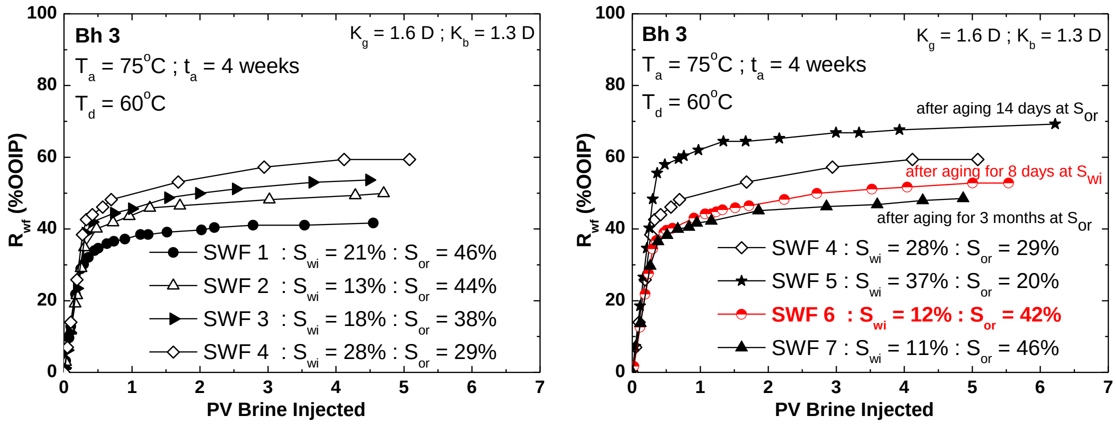
(a) oil recovery (b) pressure drop

Figure 1. Oil recovery and pressure drop vs. PV of seawater injected for Core Bh 1 for four SWFs. (t_a is the aging time and T_a the temperature; T_d is the displacement temperature)



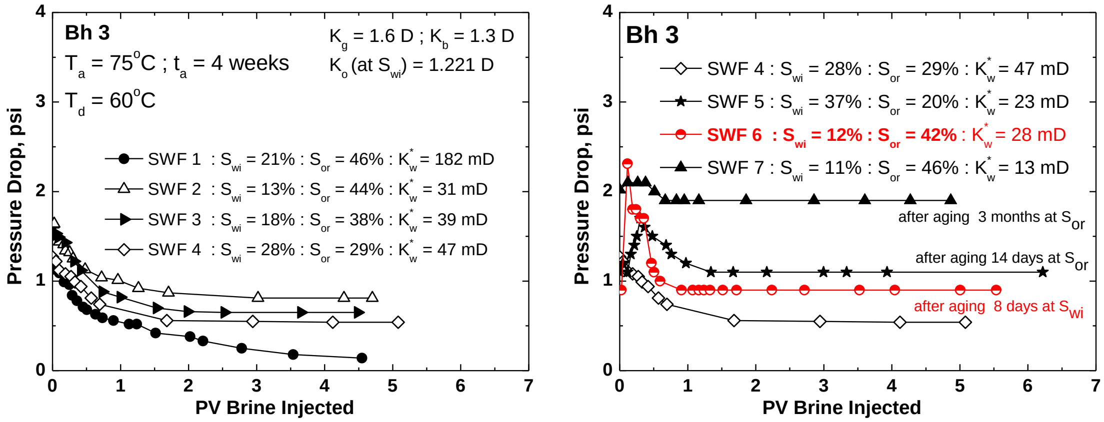
(a) oil recovery (b) pressure drop

Figure 2. Oil recovery and pressure drop vs. PV injected for Core Bh 2 for four SWFs.



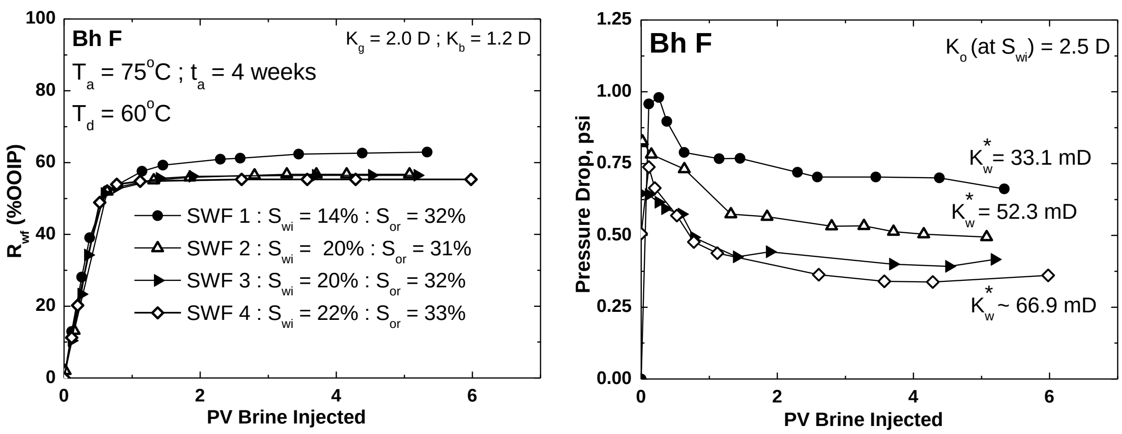
(a) first 4 SWFs (b) with aging at S_{or} and at S_{wi}

Figure 3. Oil recovery by SWF for Core Bh 3 (a) for the first 4 SWFs and (b) SWFs 4-7 for aging periods of 14 days at S_{or} at the end of SWF 4, 8 days at S_{wi} for SWF 6, and 3 months at S_{or} after SWF 6.



(a) first 4 SWFs (b) with aging at S_{or} and at S_{wi}

Figure 4. Pressure drop vs. PV injected for 7 SWFs.



(a) oil recovery (b) pressure drop

Figure 5. Recovery of WP crude oil and pressure drop vs. PV of seawater injected for 4 SWFs for fired and acidized Bentheim sandstone.

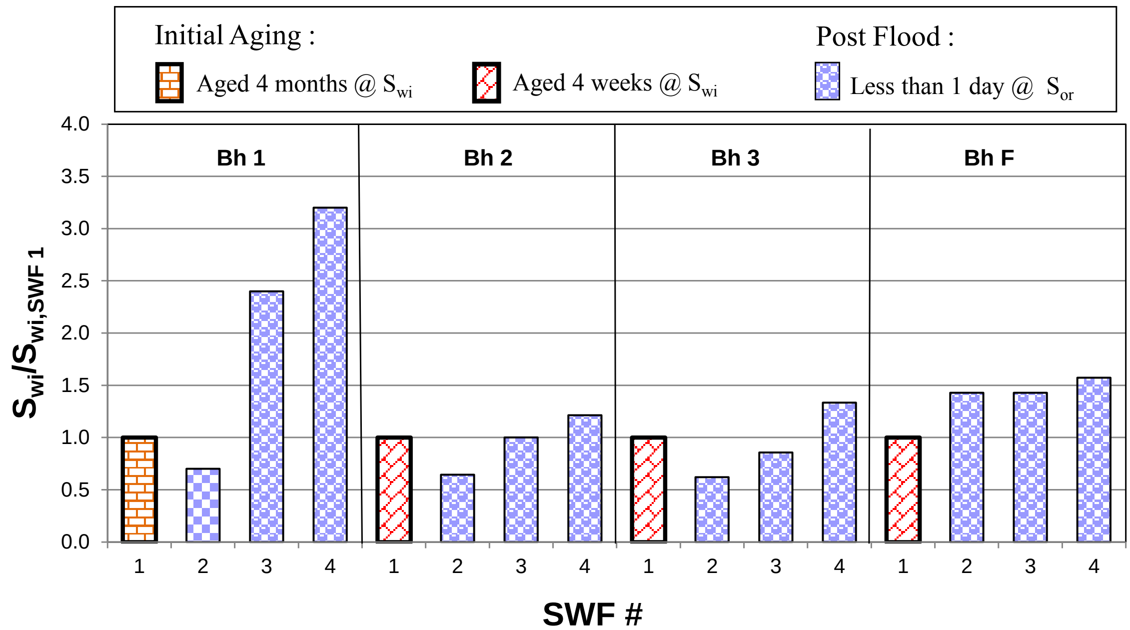


Figure 6. Summary of relative change in initial water saturation for the first four SWFs on each Bentheim core with S_{wi} normalized with respect S_{wi} for SWF 1.

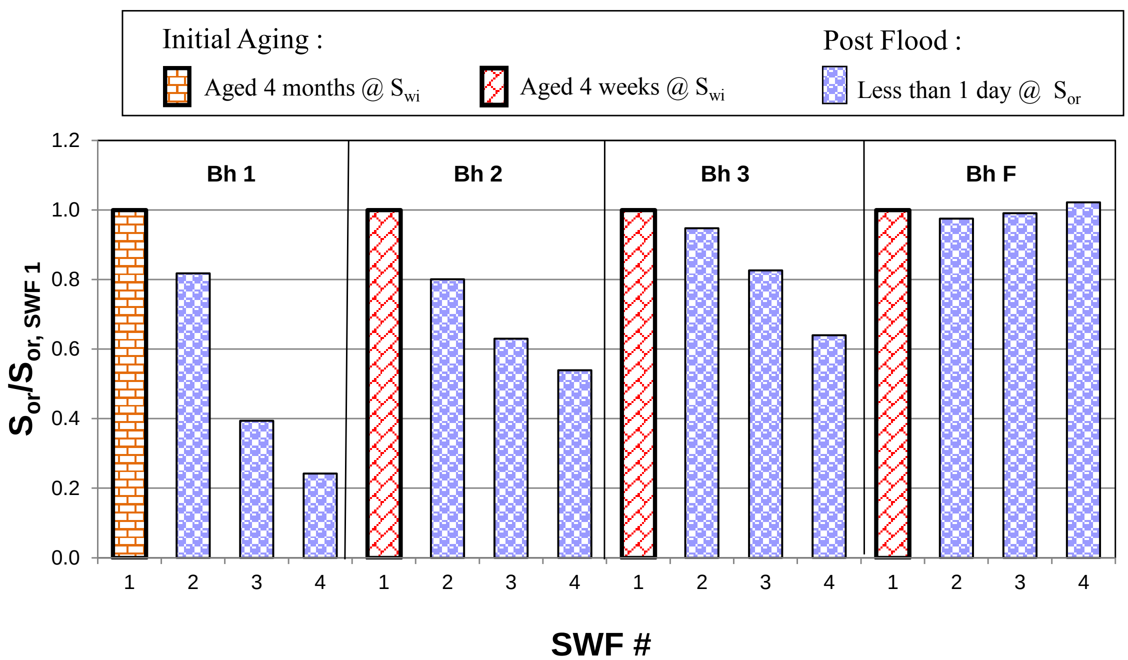


Figure 7. Summary of relative change in residual oil saturation for the first four SWFs on each Bentheim core with S_{or} normalized with respect S_{or} for SWF 1.

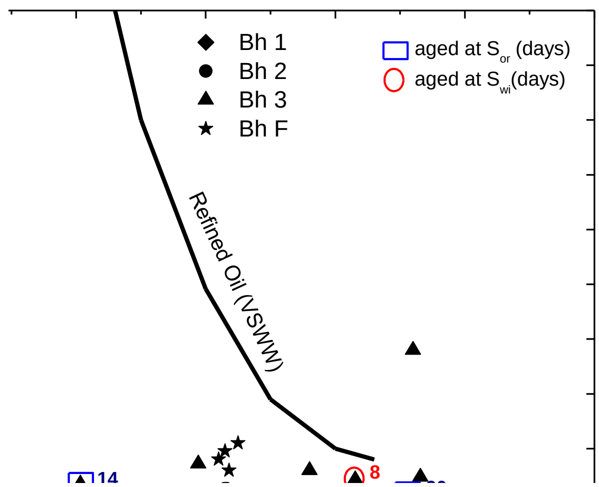


Figure 8: Comparison of relative permeability to brine (normalized to brine permeability at 100% saturation) at residual oil saturation (a) for sequential waterflooding for recovery of crude oil and (b) by increase in capillary number for recovery of refined oil at very strongly water wet conditions (after Morrow et al. 1985).

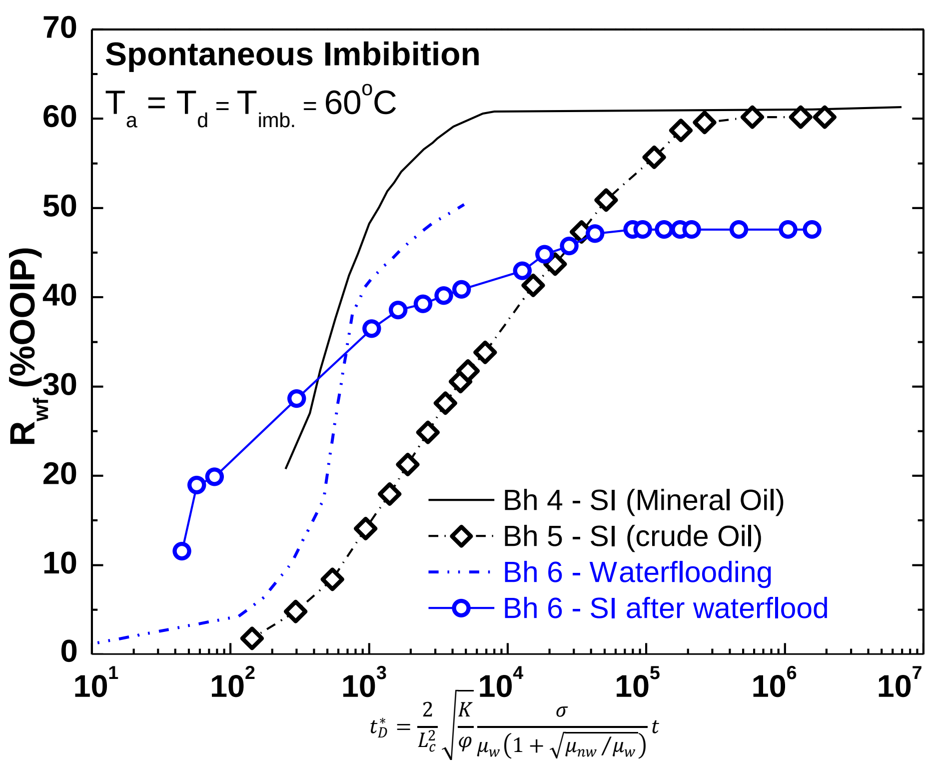


Figure 9: Recovery of WP crude oil by spontaneous imbibition for a core which had not been previously waterflooded (Bh 5) and a core which had been previously waterflooded once (Bh 6) including comparison with time for waterflooding for Bh 6.