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In situ wettability distribution and wetting stability in outcrop chalk aged in crude oil

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Abstract

This paper reports an investigation of in situ wettability distribution and wetting stability of moderately water-wet and nearly neutral-wet outcrop chalk cores, aged in crude oil at elevated temperature.

In this paper, in situ wettability measurements by magnetic resonance imaging (MRI) tomography are shown to give Amott indices that agree well with the standard wettability indices based on average saturations. The in situ method provides information concerning Amott index distribution radially and along the length of the core plugs.

Applying multidirectional crude oil flooding during aging, uniform wettability distributions, both radially and axially, were obtained.

Tests of wetting stability confirmed that stable wettability alterations for repeated waterfloods and Amott tests were established. The results showed that the core plugs should not be dried or cleaned because this will render the core plugs strongly water-wet. Stable wettability conditions were measured for cores subjected to storage in brine at 90 °C.

Keywords: Wettability; Wettability alteration; Wettability distribution; Chalk; Aging

1. Introduction

Due to insufficient amounts of reservoir core material for laboratory studies aimed at improved oil recovery from North Sea chalk reservoirs, outcrop rocks must be used. As for many other reservoirs, to simulate the in situ wettability conditions, the outcrop cores are aged in crude oil at elevated temperature. The stability of the altered wettability is important for carrying out reliable experiments, where an essential part is to reproduce the results in repeated or duplicated experiments.

Submerging core plugs in crude oil at elevated temperature may be a satisfactory method to alter the wettability if shorter aging time (about 5 days) is sufficient (Graue et al., 1999b). However, at certain conditions, especially for longer aging times, it has been shown that a nonuniform radial wettability distribution may be established (Spinler et al., 1999, 2002). An aging technique using low-rate flushing

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of crude oil while aging introduced an axial nonuniformity (Graue et al., 2002). In this paper, these effects have been further investigated. The aged core plugs exhibit reduced water wetness; no oil-wet conditions were established.

Axial wettability distributions have been measured in two long cores aged by multidirectional flooding of crude oil. Radial wettability distribution has been measured in two core plugs using magnetic resonance imaging (MRI).

Seven core plugs were saturated with decane and brine and aged using multidirectional flooding to obtain wettabilities corresponding to Amott indices ranging from 0.3 to 0.8 (Amott, 1959; Anderson, 1986). The cores were then tested for potential change in wettability by conducting Amott tests before and after: 1) 6 months storage in decane at room temperature, 2) storage in brine at 90 °C at S_{or}, 3) the core plugs had been dried and resaturated, and 4) the core plugs had been cleaned by methanol and toluene, dried and resaturated.

2. Experimental

2.1. Rock and fluids

The core plugs were all cut with the same orientation from large chunks of Rørdal chalk from the Portland Cement Factory (Ålborg, Denmark). Porosity was determined from weight measurements and the absolute fluid permeability was measured. Core data are listed in Table 1. Further information on this chalk is found in Graue and Bognø (1999). The core plugs were vacuum-evacuated and saturated with brine containing 5 wt.% NaCl + 3.8 wt.% $CaCl_2$. $CaCl_2$ was added to the brine to minimize dissolution of the chalk. Sodium azide, 0.01 wt.%, was added to prevent bacterial growth. The density and viscosity of the brine were 1.05 g/cm^3 and 1.09 centipoise (cP) at 20 °C, respectively. The brine was filtered through a 0.45 μm paper filter membrane. The physical properties of the fluids are summarized in Table 2.

Table 2
Fluid properties

Fluid	Density [g/cm^3]	Viscosity [cP] @ 20 °C	Composition	Purity [%]
Brine	1.05	1.09	5 wt.% N_aC_l 3.8 wt.% C_aCl_2 0.01 wt.% NaN_3	– – –
n-Decane	0.73	0.92	–	>95
Decahydronapthalene	–	–	–	>95
Crude oil type-1	0.85	14.3	–	–
Deuterium	–	–	D_2O	>99.9
Toluene	0.87	–	C_7H_8	>99.5
Methanol	0.79	–	CH_3OH	>99.8

Table 1
Core data

Core	Length [cm]	Diameter [cm]	Treatment	Porosity [%]	Permeability [mDa]	Iw (1)	Iw (2)	Iw (3)
CPA-7.1	15.9	5.0	–	48.0	3.8	–	–	–
CPA-7.2	15.9	5.0	–	47.0	3.9	–	–	–
CPA-7.1.1	5.3	5.0	Drying	47.5	5.0	0.31	0.32	0.92
CPA-7.1.2	5.3	5.0	Drying	46.9	3.7	0.52	0.56	1.0
CPA-7.1.3	5.2	5.0	Cleaning	46.7	3.6	0.45	0.44	1.0
CPA-7.2.1	1.9	5.0	Hot brine	–	–	0.57	0.50	0.61
CPA-7.2.2	4.9	5.0	Drying	46.0	4.9	0.75	0.73	1.0
CPA-7.2.3	4.7	5.0	Hot brine	–	–	0.82	0.89	0.90
CPA-7.2.4	4.2	5.0	Cleaning	46.2	3.6	0.76	0.85	1.0
CPA-6.2	6.0	3.8	–	45.7	3.3	0.49[a]/0.51[b]	–	–
CPA-6.5	6.0	3.8	–	46.1	4.0	0.19[a]/0.18[b]	–	–

[a] Amott test using material balance.

[b] Amott test using MRI.

2.2. Axial wettability distribution in long cores

Two 16-cm-long, 5-cm-diameter cores, denoted CPA-7.1 and CPA-7.2, were used in a study of wettability alteration using constant flow of crude oil through the core during aging. Emphasis was on determining the axial distribution of the induced wettability alteration.

After the initial core preparation, the cores were subjected to a miscible brine–brine displacement where more than five pore volumes (PV) of nonradioactive brine were flushed through the cores to saturate adsorption sites with nonradioactive salt. Details of the flood procedures have been published previously (Graue and Bognø, 1999; Graue et al., 1999a). Fluid saturations were monitored by the nuclear tracer imaging (NTI) technique. Detailed description of the NTI can be found in the literature (Bailey et al., 1981; Lien et al., 1988). The cores, saturated with radioactive brine, were then slowly heated to 90 °C and oil from a heated pressure vessel was alternately injected, at each end, in order to obtain uniform initial water saturation, S_{wi}. Analysis of the North Sea stock tank crude oil used can be found in previous publications (Graue and Bognø, 1999; Graue et al., 1999a). To alter the wettability, the cores were oil flooded alternately from both ends at S_{wi} at 90 °C using a low filtration velocity (1.3 cm/h). Different lengths of time were used for the aging of the two cores. This produced different wettabilities. The in situ imaging was essential to determine if uniform initial water saturation was established and to detect any redistribution of the fluid saturations or water production during the aging process. The crude oil was flushed out with 5 PV decahydronaphthalene (decalin), which in turn was flushed out by 5 PV *n*-decane, all at 90 °C. Decalin was used as a buffer between the mineral oil and the crude oil to avoid asphaltene precipitation. Decane and brine were used throughout the rest of the experiments. Decane and brine at room temperature reflect the reservoir condition fluid viscosities and densities relevant for the actual reservoir under study.

The long cores, CPA-7.1 and CPA-7.2, were cut at S_{wi} with a band saw into three and four shorter core plugs, respectively. Initial water saturation distribution for each core was obtained by NTI. Amott tests based on material balance calculations were then performed on each plug to determine the wettability distribution in the long cores.

2.3. Radial wettability distribution

Two 6-cm-long, 3.8-cm core plugs, denoted CPA6-2 and CPA6-5, received the same preparation and aging procedures as the long cores. To investigate the extent of radial nonuniformity of the induced wettability alteration, high spatial resolution MRI was used. Axial porosity distributions were obtained for both core plugs utilizing the MRI. After aging, the brine was exchanged at S_{or} with 2 PV of D_2O with the same salt concentration during a low-rate miscible flood to create an aqueous phase that was invisible to the MRI. Nuclear magnetic resonance (NMR) spectroscopy produced information on the efficiency of the miscible floods (Coates et al., 1999). Finally, the cores were oil flooded by decane in order to obtain S_{wi}.

To improve the Amott test, high-resolution two-dimensional MRI images of 4-mm-thick slices along the central axis of the cores were taken at each step of the test, i.e. at S_{wi}, after spontaneous imbibition and, finally, at S_{or}. An Amott index was then calculated for each pixel of the 2-D images, and average axial and radial wettability profiles on a millimetre scale were calculated.

2.4. Wetting stability

To test the wetting stability, each of the seven core plugs obtained from the long cores was then scheduled for a series of Amott tests. Four set of tests were performed:

1) All seven core plugs were stored in decane for 6 months at ambient temperature, then a second set of Amott tests were performed to evaluate any changes in wettability.

2) In order to investigate if extended exposure to hot water changed the established wettability, two core plugs, CPA-7.2.1 and CPA-7.2.3, were stored at residual oil saturation in brine at 90° C for 3 weeks. After being cooled to room temperature, the cores were oil flooded to S_{wi} by decane, and Amott tests were performed.

3) To investigate if the altered wettability was stable after drying and resaturation and flooding with freshwater, three of the core plugs, CPA-7.1.1, CPA-7.1.2 and CPA-7.2.2, were flooded with 2 PV of freshwater at low filtration velocity to remove salts and then dried at 90 °C for 5 days. Weight measurements during drying ensured complete water evaporation. After the cores were resaturated with brine, new porosity and permeability measurements were carried out before the cores were oil flooded to S_{wi} by decane, followed by Amott tests.

4) To determine if the established wettability by aging was stable after core cleaning, two of the core plugs, CPA-7.1.3 and CPA-7.2.4, were flooded with 10 PV of toluene and 4 PV of methanol at low filtration velocity, dried at 90° C for 4 days and resaturated with brine. Porosity and permeability were measured, then the core plugs were oil flooded to S_{wi} using decane before the Amott tests were performed.

3. Results and discussion

3.1. Axial wettability distribution in long cores

Measurements of the variation in porosity and flow characteristics were obtained for the long cores by imaging a miscible brine–brine displacement after the cores had been 100% saturated with nonradioactive water. Fig. 1 shows the one-dimensional brine saturation distributions in the two chalk cores, CPA-7.1 and CPA-7.2, while radioactive brine displaced nonradioactive brine. The injected brine showed a slightly dispersed waterfront with insignificant amounts of fingering. The brine saturation profile when 100% saturated with radioactive brine exhibited a uniform porosity distribution. Thus, no significant porosity or permeability heterogeneities were found in the cores. The corresponding effluent production profiles are shown in Fig. 2. The profiles were analysed according to (Lake, 1989). No significant adsorption was identified in the effluent profile for the injected ^{22}Na-labelled brine. No evidence of dead-end pores was reflected in the production profile of the injected water (Coats and Smith, 1964).

Fig. 3 shows the fairly uniform initial water saturation distributions for CPA-7.1 and CPA-7.2 measured by NTI, after the multidirectional oil floods using crude oil followed by decalin and decane flooding at elevated temperature. No water production was detected during aging or during the oil floods with decalin and decane. Only minor changes in the water saturation profiles were observed. After cutting the long cores into shorter core plugs, material balance calculations for each core plug was obtained using NTI. Based on the core sample characterization, the

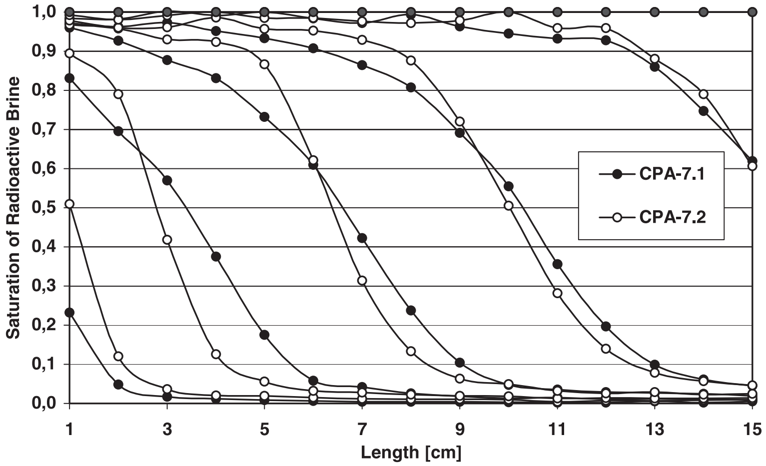


Fig. 1. Saturation profiles of radioactive brine during the miscible brine–brine displacement.

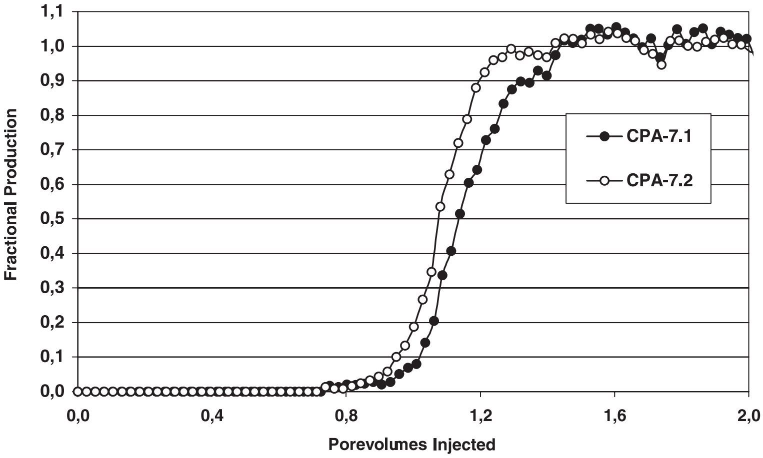


Fig. 2. Effluent production of radioactive brine.

core material was assumed to be homogenous throughout the samples, and the pore volumes were estimated for each core plug. Core plug CPA-7.1 was cut into three approximately equal pieces, denoted CPA-7.1.1, CPA-7.1.2 and CPA-7.1.3. In order to obtain better resolution of the wettability measurements at the inlet end, core plug CPA-7.2 were cut into four pieces: one short inlet piece of 1.9 cm, CPA-7.2.1, and then the remaining part was cut into three core plugs denoted CPA-7.2.2, CPA-7.2.3 and CPA-7.2.4, respectively.

The wettability of each core plug was determined by a series of Amott tests. Spontaneous imbibition curves for the seven core plugs are shown in Fig. 4. The figure shows consistency with respect to induction time, imbibition rate and endpoint water saturation for all of the core plugs according to the measured wettability of the corresponding long cores. For both of the long cores, it is evident that the core plugs cut from the inlet end under primary drainage both exhibit less water-wet conditions. The wettability indices for each core plug are listed in Table 1. In Fig. 5, the axial

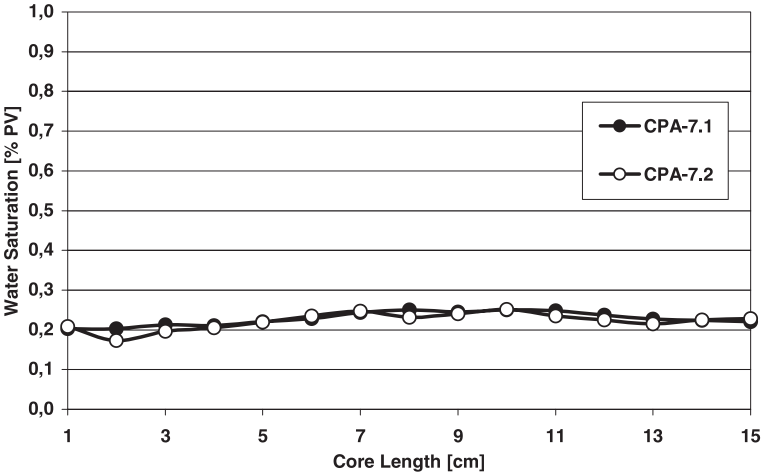


Fig. 3. Water saturation profiles at S_{wi}.

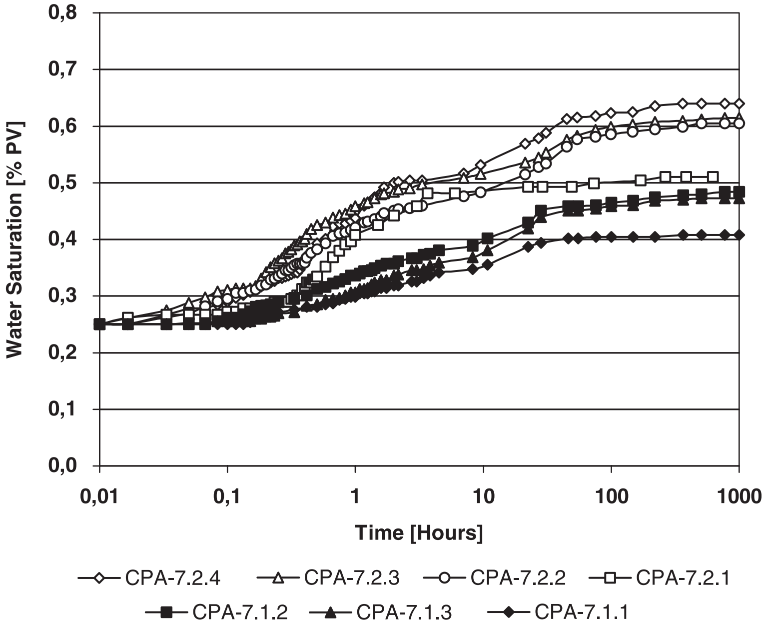


Fig. 4. Spontaneous imbibition characteristics.

wettability distributions of CPA-7.1 and CPA-7.2 are represented by the two sets of core plugs stacked together. Consistent with the results reported by Graue et al. (2002), the wettability distribution was fairly uniform with a slight dome shape, where the central section of the core is more water-wet than near the ends.

3.2. Axial and radial wettability distribution in short core plugs

If the aging process involves adsorption such that the effect of wettability alteration depends on the length from the injection point (Graue et al., 2002), shorter core plugs subjected to aging by alternating

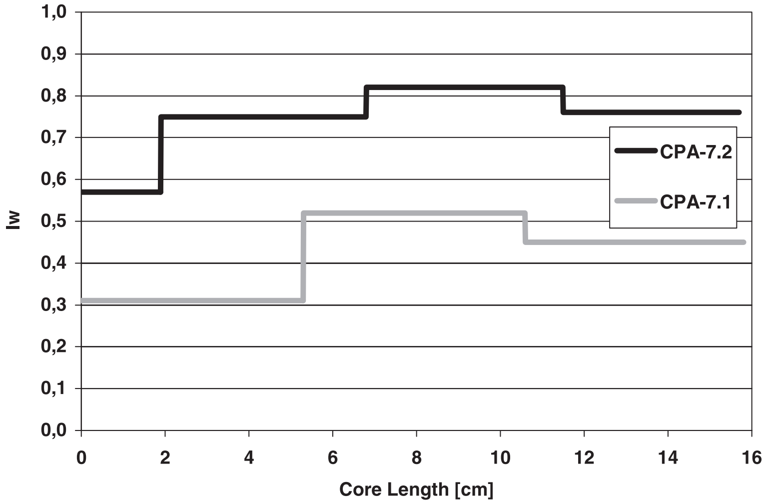


Fig. 5. Axial wettability distributions in the two long cores.

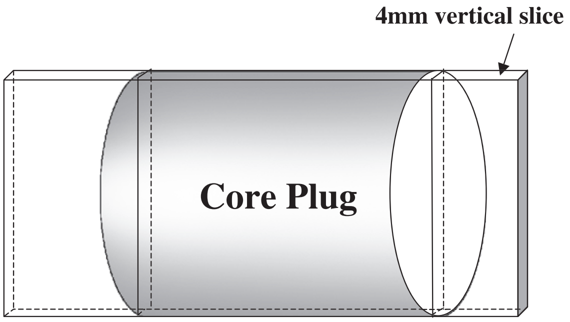


Fig. 6. Schematic drawing of the slice orientation for the axial MRI images.

crude oil injection from both ends should exhibit a more uniform wettability distribution compared to longer cores.

Improving the Amott test by using two-dimensional (2-D) high spatial resolution MRI of the saturation distributions within the core plugs for each step of the Amott test provided 2-D maps of wettability indices on a millimetre scale. Hence, average axial and radial as well as 2-D wettability distributions within the core plugs were obtained. By choosing the 2-D images as axial vertical slices through the horizontally mounted core, the possible effect of gravity segregation during the aging procedure may be studied as well. Fig. 6 shows a schematic drawing of the location of the slice. The axial porosity distributions shown in Fig. 7 show homogeneous rock characteristics on a millimetre scale.

The axial wettability distributions for CPA-6.2 and CPA-6.5, shown in Fig. 8, do not have the dome shape as reported for the longer cores. We conclude that the core plugs are short enough for the adsorption of oil components not to be significant at the chosen flow rate. Nevertheless, the core plugs reflect the reduction in the Amott index near the inlet end in the axial wettability distribution, which seems to be typical for this type of aging procedure.

The aging technique using a constant flow of crude oil injected alternately from both ends at elevated temperature were used mainly because of the results reported in Spinler et al. (1999), showing the significant nonuniform radial wettability distribution for core plugs aged, submerged in crude oil at elevated temperature for extended period of times. However, the radial wettability distributions, shown for the two short core plugs in Fig. 9, are fairly uniform for both moderately water-wet and near-neutral-wet core plugs.

The 2-D wettability index maps in Figs. 10 and 11 show the wettability distributions for thin vertical slices axially through the centres of CPA-6.2 and CPA-6.5. Lighter-grey colours reflect water-wet conditions, and darker shades of grey reflect nearly neutral-wet conditions. During the primary drainage,

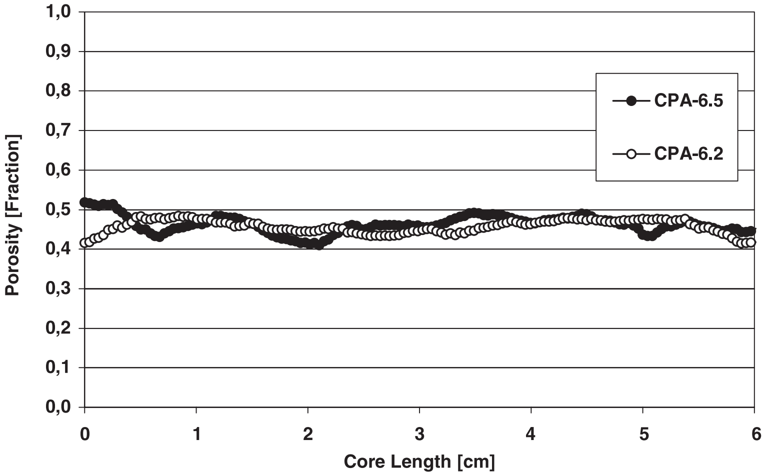


Fig. 7. Average axial porosity profiles obtained by MRI.

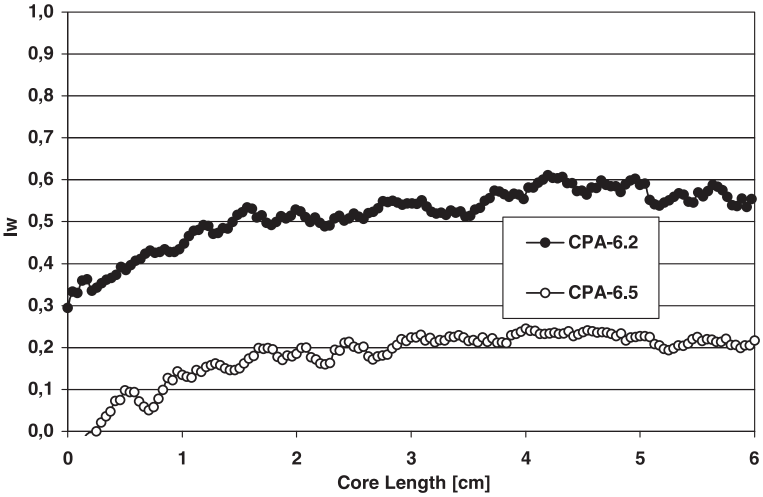


Fig. 8. Axial wettability distributions obtained by MRI for short cores.

the inlet end of the core plugs were located at the left hand side of the figures, and the top of the vertical slices through the cores are located at the top of the figures.

As seen in the 2-D wettability maps, the wettability in each core plug is fairly uniform throughout the sample, except for a less water-wet area at the inlet end. If the inlet ends are not taken into account, there are only a few areas exhibiting a wettability index that vary more than 0.1 from the mean wettability index value of the core plug. The strongly water-wet spot at 4.2-cm length and 0.7-cm height in CPA-6.2 may be due to a small rock heterogeneity. The average wettability obtained by MRI agreed well with the wettability obtained by the standard Amott test. Wettability indices obtained by MRI and the Amott test based on material balance calculations are compared in Table 1.

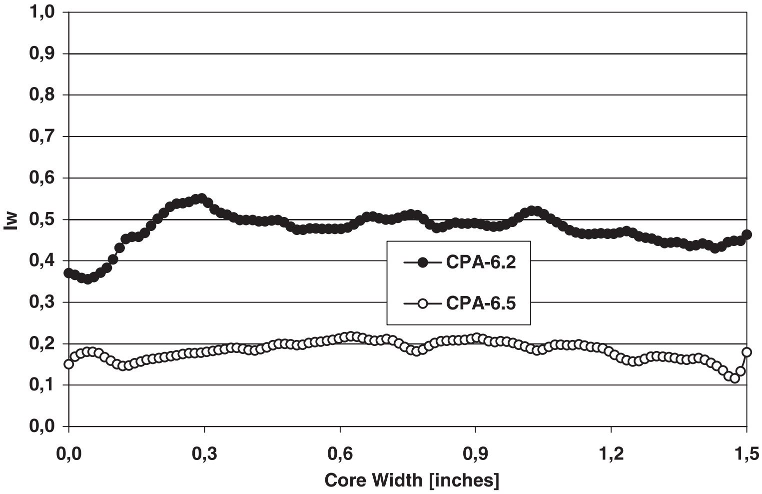


Fig. 9. Average radial wettability distributions for two short core plugs.

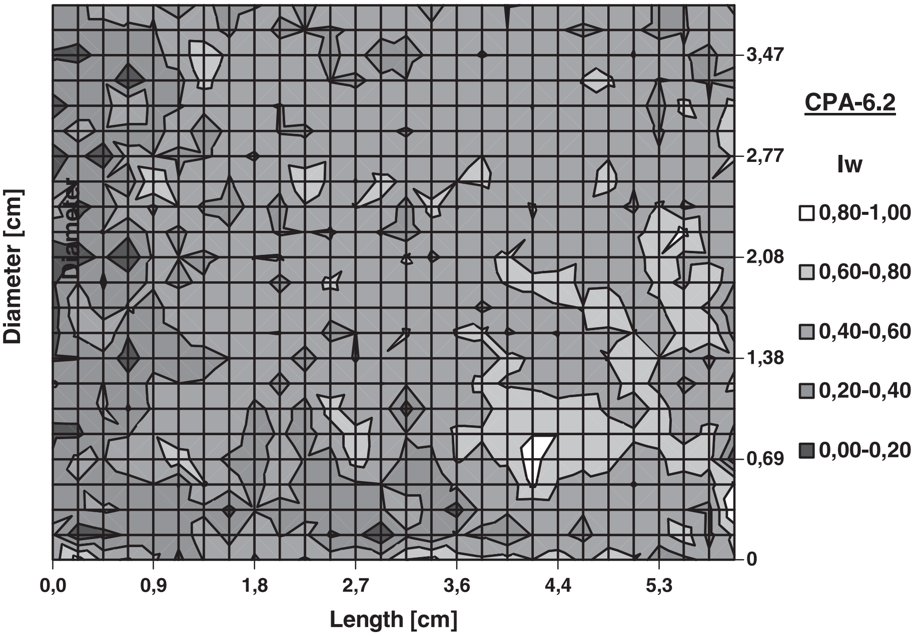


Fig. 10. Distribution of the wettability index in a thin vertical slice along the length axis of CPA-6.2.

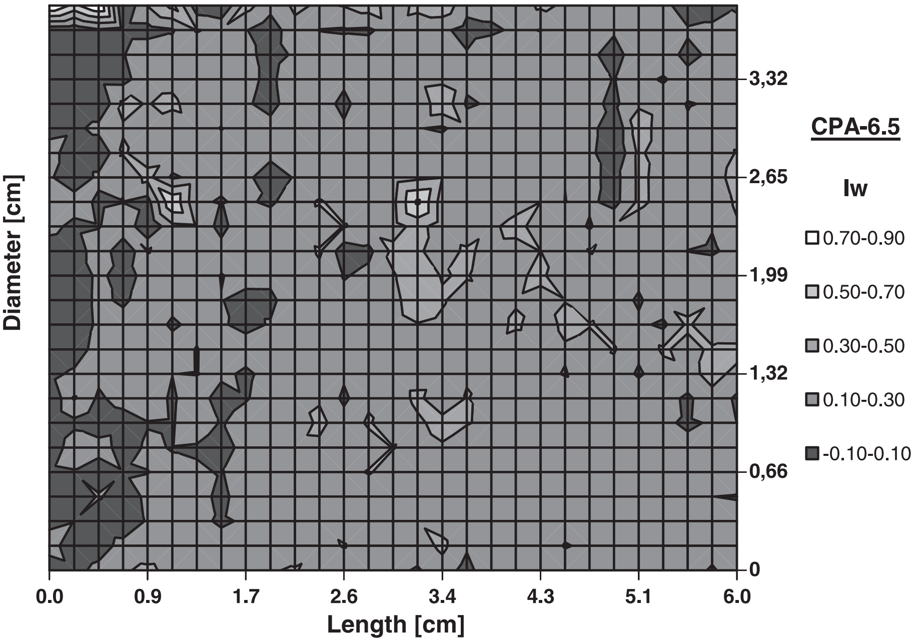


Fig. 11. Distribution of the wettability index in a thin vertical slice along the length axis of CPA-6.5.

3.3. Wetting stability

After the core plugs CPA-7.1.1, CPA-7.1.2, CPA-7.1.3, CPA-7.2.1, CPA-7.2.2, CPA-7.2.3 and CPA-7.2.4 had been stored at S_{wf} for 6 months in decane at ambient temperature and pressure, the core plugs were oil-flooded back to S_{wi} using decane and were then subjected to a second Amott test. The wettability conditions turned out to be stable; the results of the Amott tests are listed in Table 1. In Fig. 12, the wettability index from the Amott tests before and after storage are shown for each core. The wettability is shown to be fairly stable with no core plug showing a change in wettability index of more than 0.1. The average wettability change of the seven core plugs is +0.02, i.e. towards more water-wet conditions, but the value is within the range of the uncertainties.

Spontaneous imbibition characteristics for the core plugs are shown in Fig. 13. By comparing the imbibition characteristics before and after the storage in decane, Figs. 4 and 13, respectively, slight differences in the imbibition rates are observed at early times, but the endpoint saturations are similar. Fig. 15 shows comparisons of imbibition characteristics for each individual core plug. Fig. 14 shows how growing oil droplets produced from a core plug during spontaneous imbibition may adhere to the outer surface of the plug until the buoyancy exceeds the adhesion. This may, to various degrees, delay the measured oil production, and to obtain good accuracy and reproducibility in the production data, the detailed experimental procedures, e.g. whether or not to swirl the imbibition cell before the readings, are crucial.

To test if the established wettability was stable during aging in hot brine, two of the core plugs, CPA-7.2.1 and CPA-7.2.3, were subjected to aging in brine at S_{or} at 90 °C for 3 weeks. After being cooled to room temperature, the cores were subjected to a third Amott test. The test showed that the induced wettability was stable during aging in hot brine. Results from the tests are listed in Table 1 and are included in Figs. 12 and 15.

Three core plugs, CPA-7.1.1, CPA-7.1.2 and CPA-7.2.2, were flooded with freshwater, dried and resaturated. Figs. 16 and 17 show the average of the new porosity and permeability measurements, respectively.

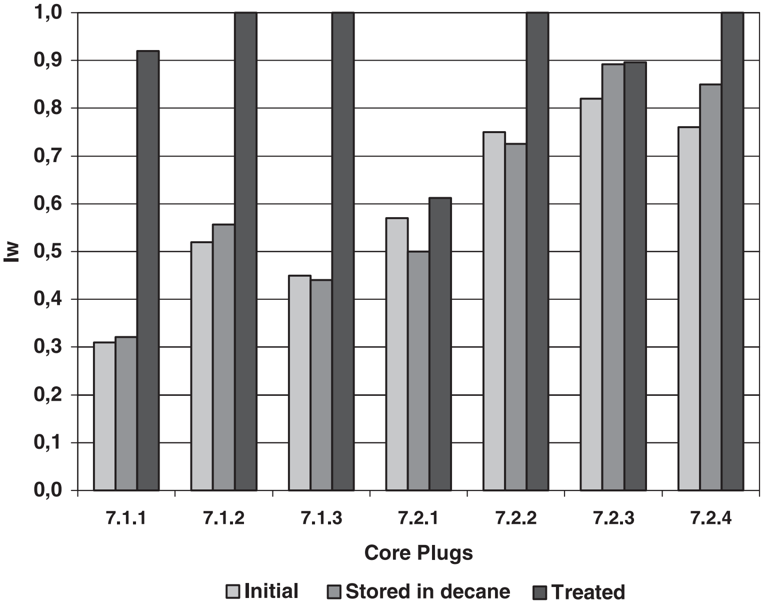


Fig. 12. History of wettability index to water for the different tests.

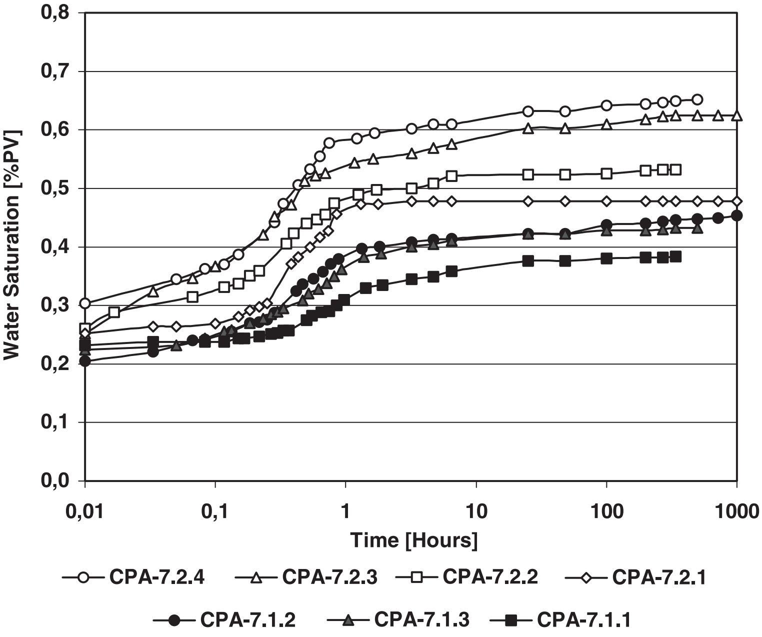
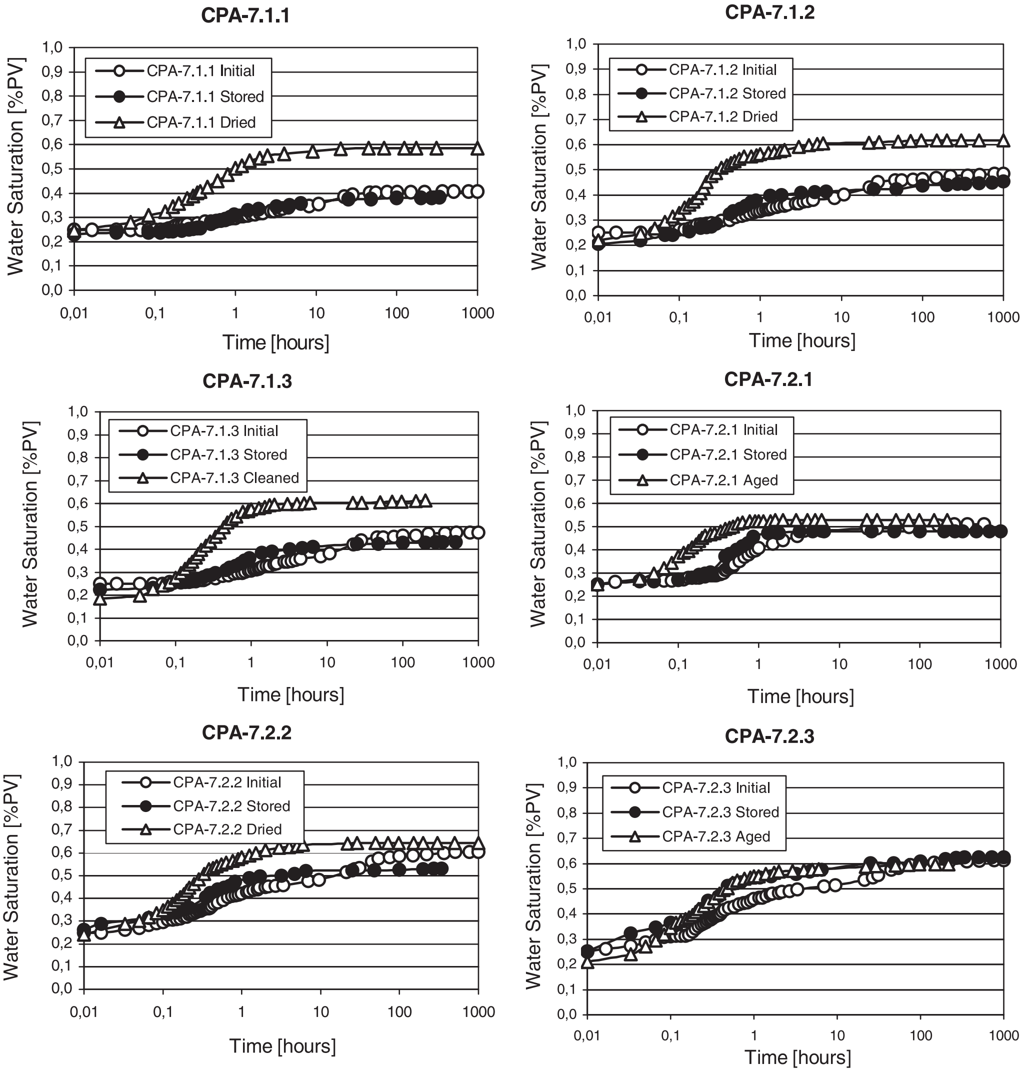


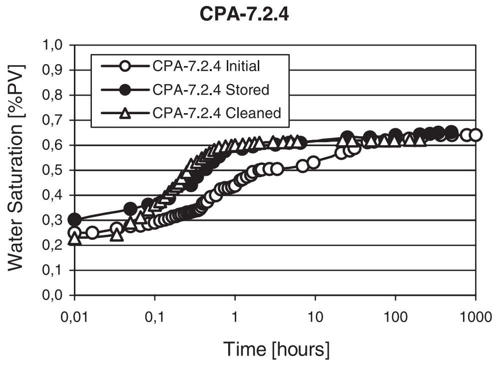
Fig. 13. Spontaneous imbibition characteristics after storage in decane.

Porosity does not change during drying, but the absolute permeability increased by 18%. The new Amott test indicated that the induced wettability was nullified, leaving the cores strongly water-wet. Results from the tests are listed in Table 1 and shown in Figs. 12 and 15.

Amott tests performed on two core plugs, CPA-7.1.3 and CPA-7.2.4, that had been cleaned using a

Fig. 14. Oil droplets on the core surface during spontaneous brine imbibition.





Stored: 6 months storage in decane.

Aged: 3 weeks aging in brine at 90^0C.

Dried: Dried and resaturated.

Cleaned: Flushed with Toluene and Methanol, dried and resaturated.

Fig. 15. Imbibition characteristics for each core plug in different tests.

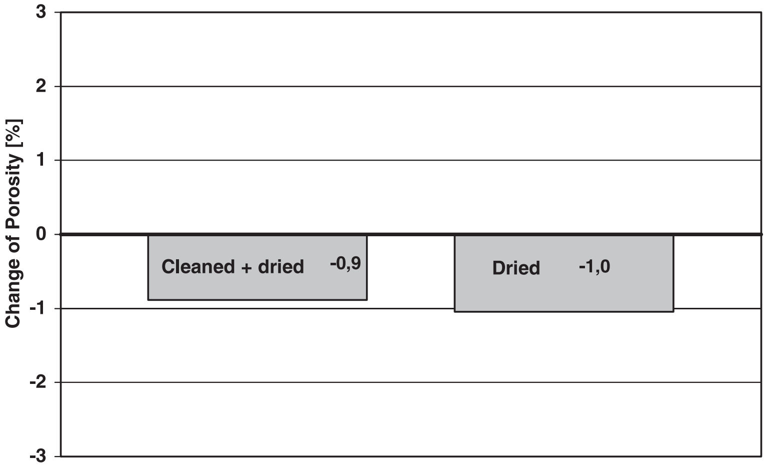


Fig. 16. Average change in porosity after drying and core cleaning.

low-rate flood of 10 PV toluene and followed by 4 PV methanol and then dried and resaturated, showed that cleaning with solvents left the cores strongly water-wet. This may be a result of a removal of components adsorbed on the rock surface during aging. Porosity did not change, but the absolute permeability was reduced by 7% during the treatment. The results are shown in Figs. 16 and 17. The wettability indices and the spontaneous imbibition characteristics shown in Figs. 12 and 15, respectively, both indicated that there were insignificant amounts of active aging components left in the core (Zhou et al., 2000). Hence, the wettability was not resistant to cleaning by the solvents.

4. Conclusion

- Wettability alteration by multidirectional crude oil flooding during aging at elevated temperature produced wettability conditions permanent 1) with respect to long-term storage in decane at ambient

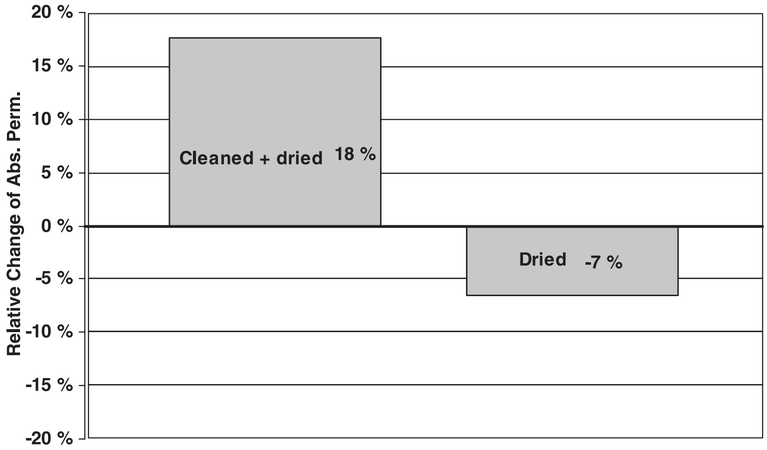


Fig. 17. Average relative change in absolute permeability after drying and core cleaning.

temperature and 2) for exposure to brine at elevated temperature at S_{or}.

- Wettability conditions established by aging at elevated temperature were not resistant to drying and resaturation or cleaning procedures with solvents.
- Aging long cores by multidirectional crude oil flooding produced fairly uniform wettability distributions. A dome-shaped axial wettability distribution, exhibiting more water-wet conditions at the centre of the cores, was observed for long cores, but the variation in I_w was only significant near the inlet end.
- By including information from the in situ saturation distributions in the Amott test, the small-scale wettability distribution, within a core plug, was obtained.
- Aging by the multidirectional crude oil flooding produced short core plugs with uniform axial wettability distributions.
- Aging by crude oil injection alternately from both ends produced uniform radial wettability distributions.

Nomenclature

I	Amott wettability index
MRI	Magnetic resonance imaging
NMR	Nuclear magnetic resonance
NTI	Nuclear tracer imaging
PV	Pore volume
S	Saturation
cm	Centimeter
C	Celsius
wt.%	Present by weight
CP	Centipoise
M	Meter
2-D	Two-dimensional

Greek

μ	10^{-6}

Subscripts

f	Final
i	Initial
im	Imbibition
o	Oil
si	Spontaneous imbibition
w	Amott wettability index to water
w	Water

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