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AN EXPERIMENTAL STUDY OF THE RELATIONSHIP BETWEEN ROCK SURFACE PROPERTIES, WETTABILITY AND OIL PRODUCTION CHARACTERISTICS

by

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Abstract

The present work is the first part of an interdisciplinary activity to establish a reservoir rock/fluid properties/oil production characteristics data base. The main application of this data base will be to develop an alternative method to predict wettability and production characteristics of oil during water flooding, based on knowledge of rock geometry, surface mineralogy and fluid/rock interactions.

This paper describes the first of a series of experiments with different rocks and fluid systems. A Berea sandstone is characterised by geometric parameters and surface mineralogy by use of scanning electron microscopy. The surface charge of the rock was negative at the conditions of all experiments described in this paper.

Combined Amott/USBM- wettability tests were performed on six Berea core plugs, using a NaCl-brine and three different oils. Negatively or positively charged oil/water interfaces were achieved by adding an organic acid or base to n-decane, respectively. The wettability indexes show that Berea sandstone is water wet in the presence of n-decane and NaCl brine. The wettability remained water wet when the oil with the acid was used, but changed to neutral for the oil with the base. These wettability indexes are consistent with contact angles measured for the three oils on quartz, the main surface mineral in Berea sandstone.

Two displacement experiments were performed, one with pure n-decane and one with base in the oil. Striking differences in oil production were observed. By changing from water wet to neutral conditions the residual oil saturation was reduced by 14% PV. The oil production after water break through was negligible in both cases.

The change in oil production characteristics was obtained by using an additive to the oil. The results are, however, consistent with similar observations with Berea where the rock surface was treated in order to alter wettability.

Introduction

Wettability is usually determined by analyses of core material from the reservoir zones in question. One problem with this approach is that the properties of the core material may have changed from its initial state in the untouched reservoir to its state in the laboratory. Contamination by the drilling fluids with surface active components, oxidation of possible adsorbed hydrocarbons and of the mineral surface during storage and preparation, effects of core cleaning and possible treatments for restoration of the original wettability, are some of the factors that may affect the final result obtained in a wettability test. The representativity of the determined wettability and other properties of the core can thus be questioned. The need for improved methods to characterise wettability seems to be present.

The wettability of a reservoir rock is the result of interactions between the surface of the rock and the fluids present in the pore space. Regarding the solid components, the composition and morphology of surface minerals are believed to be important, as well as pore size distribution and pore surface area. These rock properties will together with the composition of the reservoir brine, pH and temperature, and perhaps most important, the composition of the oil, affect the wetting conditions of the system. There exists indications that the acid/base character of the oil, which controls the surface charge, will determine whether surface active components of the oil will adsorb on the mineral surfaces in the rock. Places where oil components adsorb are likely to become oil wet.

In the approach used in the ongoing project on wettability, there will be made an attempt to predict wettability based on a description of the mineral surface and the properties of the fluids in the pores. The quantification of the surface mineralogy combined with knowledge of the properties of the individual minerals, can be applied to determine the surface charge distribution at relevant conditions. Combined with a description of the reservoir fluids, including the acid/base equilibrium involved, the location of sites with strong interactions between oil and mineral surface can be identified. These sites are likely to be oil wet. The distribution of oil wet sites on the surface of the rock will control the overall observed wettability and will also have strong implications for the flow properties and the residual oil saturation of the porous medium in question.

The outlined approach for determination of wettability can be a supplement to other methods. Some of the uncertainty regarding how well a sample is restored, may be eliminated. Moreover, a detailed description of fluid distribution inside the porous medium may give increased insight into the flow mechanisms taking place.

Rock material

The porous medium used throughout this work was taken from a 60 cm long core with a diameter of 3.8 cm. Six core plugs with an average porosity of 21.5% were cut and used in the wettability tests. The remaining core was used in thin section analyses and displacement experiments (36cm long core, 92.9 ml pore volume). Thin sections were analysed by combined scanning electron microscopy and image analyses. Bulk and surface mineralogy of Berea sandstone are shown in Figure 1.

The wettability has been determined by Amott-tests and from capillary pressure data. The Amott-method (Amott 1959) combines imbibition and forced displacement to measure the average wettability of the core. The capillary pressure curves are applied to determine wettability through the USBM-test by Donaldson et al. (1969). The test compares the work necessary for one fluid to displace the other. The work required for the wetting fluid to displace the non-wetting fluid from the core is less than the work required for the opposite displacement. The required work is proportional to the area under the capillary pressure curve. In this work, the USBM test was run in combination with the Amott-test as described by Sharma and Wunderlich (1985).

Wettability tests

A step-by-step description of the wettability tests and capillary pressure measurements are presented in the following. All measurements were performed at room temperature (20^{o}C), and the saturations were calculated from weight measurements.

1. The brine saturated core plugs were centrifuged in oil to initial water saturation .
2. The core plugs were submerged in brine, and V_{osp} was produced spontaneously.
3. The core plugs were centrifuged in water. Negative imbibition capillary pressure data were obtained. The final production of oil (V_{od}) was recorded.
4. The core plugs were submerged in oil, and V_{wsp} was produced spontaneously.
5. Finally the core plugs were centrifuged in oil. Complete secondary drainage capillary pressure data were obtained, together with the final production of water, (V_{wd}).

Fluid properties

A brine made of 20 g/l NaCl per litre of solution was used as the aqueous phase throughout the wettability tests and displacement experiments. N-decane was used as the oleic phase, and by use of additives different oil/water interfaces charges were obtained. The compositions of the oils used are summarised in Table 1.

Table 1 Composition of the oils used in the experiments.

Oil no.	charge at o/w interface	Additive	Amount of additive
1	none	none	-
2	positive	dodecylamine	12.9 mg/g n-decane
3	negative	dodecanoic acid	17.9 mg/g n-decane

Pore wall mineralogy

Classification	Area %	Bulk %	Pore Wall %
Porosity	23.9	-	-
Quartz	68.5	90.0	62.1
Plagioclase	0.4	0.5	0.7
K-Feldspar	2.3	3.0	4.3
Kaolinite	2.8	3.7	24.0
Clay	0.6	0.8	3.2
Undef. Clay	0.4	0.6	4.7
Mica	0.3	0.4	0.2
Carbonates	0.7	0.9	0.4
Heavy minerals	0.1	0.2	0.3
Sum	100.0	100.0	100.0

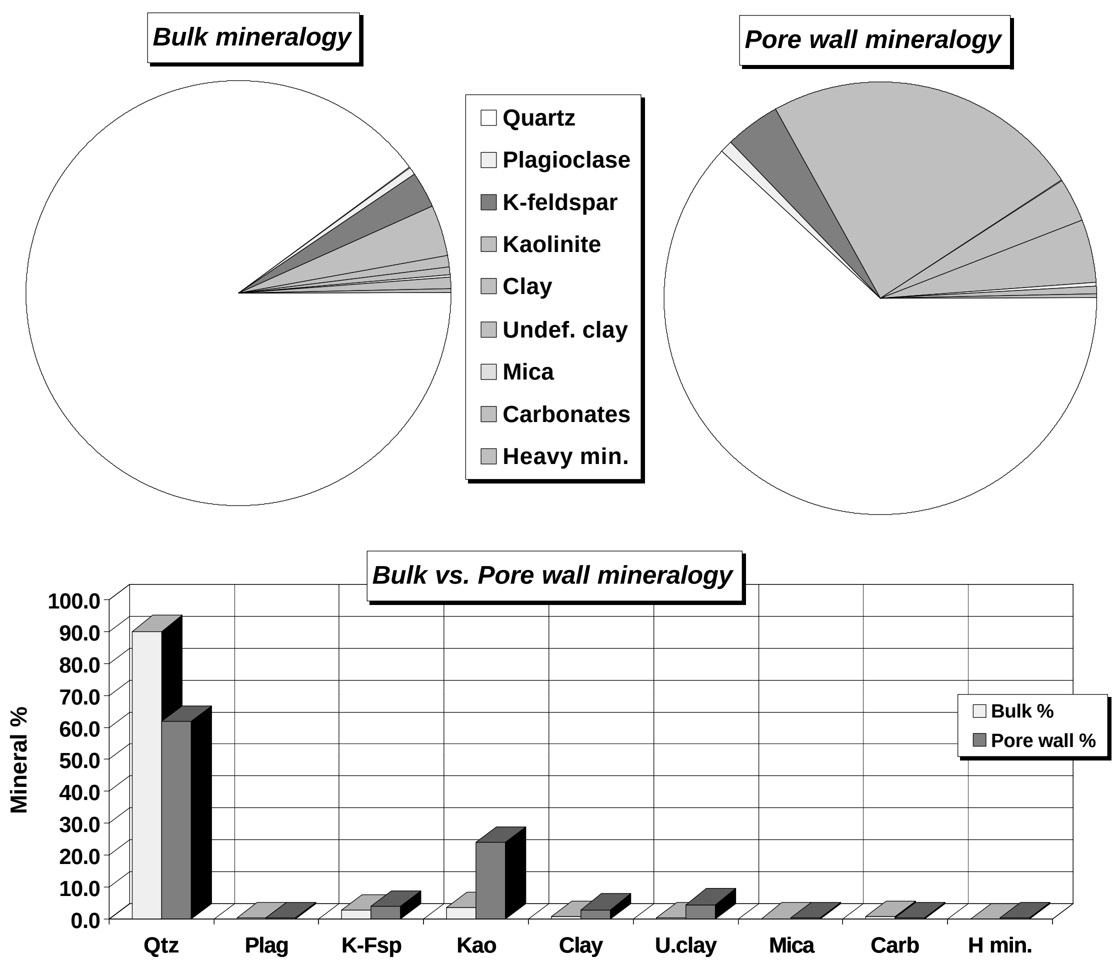

Figure 1 *Bulk and surface mineralogy of Berea sandstone*

Results

Table 2 presents the main results from the Amott wettability tests. Referring to the procedure, the rows V_{osp}, V_{od}, V_{wsp} and V_{wd} state the volumes of imbibed and displaced water and oil, respectively. The wettability index, I, is calculated from the formulae;

$$I = V_{osp}/(V_{osp}+V_{od}) - V_{wsp}/(V_{wsp} + V_{wd}) = r_w - r_o \qquad (1)$$

The relationship between capillary pressure and average saturation of water was calculated with standard centrifuge theory and the capillary pressure data. The USBM wettability index was calculated from the secondary drainage curve and the negative imbibition curve, and the results are given in Table 3 The measured contact angles are given in Table 4.

Table 2 Results from the Amott wettability test.

Core plug no./oil no.	1/1	2/2	3/3	4/1	5/2	6/3
Pore volume (cm^3)	8.20	8.47	8.22	8.39	8.35	8.20
Initial water saturation	0.20	0.13	0.22	0.17	0.15	0.15
V_{osp} (cm^3)	3.85	0.42	4.11	3.69	0.58	3.85
V_{od} (cm^3)	0.08	4.66	0.07	0.33	4.84	0.41
V_{wsp} (cm^3)	0.35	0.22	0.06	0.09	0.27	0.09
V_{wd} (cm^3)	4.06	5.00	4.36	4.17	5.09	4.26
Water index, r_w	0.98	0.08	0.98	0.92	0.11	0.90
Oil index,r_o	0.08	0.04	0.01	0.02	0.05	0.02
$I=r_w-r_o$	0.90	0.04	0.97	0.90	0.06	0.88

Table 3 USBM wettability index.

Core plug no.	Area under the sec. drainage curve, A_1	Area «under» the negative imbibition curve, A_2	WI = log A_1/A_2
1	5.71	0.61	0.97
2	6.55	2.27	0.46
3	5.31	0.58	0.96
4	5.86	2.11	0.44
5	6.28	2.73	0.44
6	4.57	1.89	0.38

Table 4 Contact angles for the different oils on quartz.

Oil no.	pH	Contact angle
1	6.5-11.3	24-10
2	6.5-9.0	144-90
3	6.5-9.1	18-38

Anderson (1987) presents a discussion of the factors influencing the results of experimental determination of rock wettability. He concludes that the Amott and USBM methods are superior to all other core plug tests. But the Amott and USBM methods have some problems both with respect to the main principles and the measurements. The main problem with the Amott test and its modifications is that they are insensitive near neutral wettability. The test measures the ease with which the wetting fluid can spontaneously displace the non-wetting one. However, in most cases unmeasurable volumes of fluid will spontaneously imbibe if the rock is weakly water or oil wet. In addition imbibition behavior is dependent on the initial saturation of the core. The results shown in Table 2 indicate that the rock/fluid system for sample no.1, 3, 4 and 6 is uniformly water wet, while sample no. 2 and 5 are uniformly neutral since neither oil nor water imbibes.

A standard text book statement is that the USBM method is more sensitive near neutral wettability than the Amott method. Theoretically that is true since in the case of neutral wettability the area under the secondary drainage curve, A_1 and the area under the negative imbibition curve, A_2 , are often both large and approximately equal. In this work the areas under the capillary pressure curves for the neutral core plugs (no. 2 and 5) are uncertain due to the difficulties of measuring the produced volumes at low capillary pressures, and the relatively small areas under the capillary pressure curves encountered in this project. The USBM-results for the water wet plugs (no. 1, 3, 4 and 6) are also uncertain due to the small volumes produced during forced imbibition. The end point saturation values obtained during the combined Amott/USBM-test were measured both volumetrically and by weight. The results obtained indicate that the maximum error in produced volumes is $\pm 0.2 cm^3$. This error will affect the Amott wettability indexes less than ± 0.1. The results from the Amott-test will therefore be the basis for the remaining discussions.

Displacement experiments

Experimental

Two displacement experiments were performed at conditions giving either a water wetting or a neutral system, as these were the wetting states that were obtained with the rock material and fluid systems used in the wettability tests. The experimental set-up is illustrated in Figure 2. The liquid level in the reservoir was kept at a predetermined and close to constant height above the level of the outlet tube. The core effluent was collected in 10 ml tubes in the fraction collector that was programmed to change tubes in predetermined intervals.

After iso-propanol (IPA) cleaning, the IPA was displaced with brine. Absolute permeability was measured. Then the core was flooded with a viscous oil until irreducible water saturation. Then the viscous oil was displaced with a light kerosene, that next was exchanged with the oil to be used. Oil permeability was then measured.

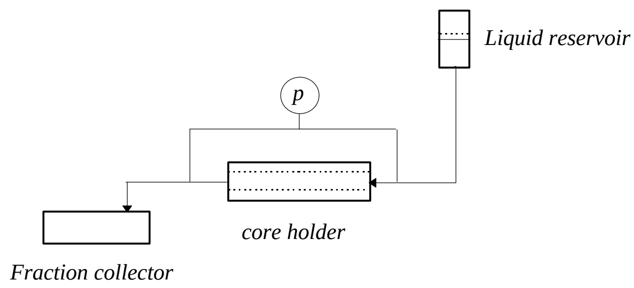

Figure 2 Experimental set-up for displacement experiments.

Results

Production histories of oil and brine for the two experiments are shown in Figure 3. Since the differential pressure across the core, and the measured absolute permeability of the core were different in the two experiments produced volumes are shown as functions of (time·differential pressure·permeability). Some key parameters and results from the two experiments are summarised in Table 5. The difference in oil production, for both rates and total amount, as seen in Figure 3, is striking. By changing from water wet to neutral wetting conditions, the residual oil saturation was reduced by almost 14 %PV.

It is well known that the residual oil saturation often passes through a minimum value, close to neutral wettability, as the wettability of the fluid/rock systems changes from strongly water wet to strongly oil wet. This has been extensively discussed by Anderson (1987). One explanation for the high recovery at neutral wettability is that the capillary forces that retains the displaced fluid is reduced when the contact angle approaches 90°.Residual oil saturation for neutral systems of less than 20 %PV are not uncommon as shown by Anderson. The Berea core used had high residual oil saturations in the water wet state. The high residual oil saturation in the water wet state gives a large potential for further oil production when *e.g.* capillary forces are reduced.

Table 5 Key parameters and results from displacement experiments.

	Experiment 1	Experiment 2
Differential pressure (atm)	0.082	0.145
Absolute permeability (md)	896	714
Irreducible water saturation (%PV)	26.1	25.9
Oil permeability at S_{wi} (md)	914	759
Produced oil volume (ml)	35.8	48.9
Residual oil saturation (%PV)	35.3	21.4
Brine permeability at S_{orw} (md)	41	135

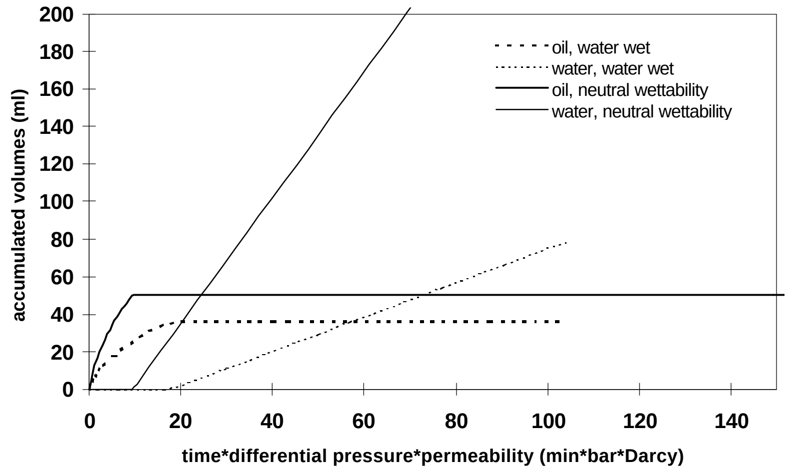

Figure 3 *Produced liquid volumes versus time x differential pressure x permeability for displacement experiments in water wet and neutral wet Berea sandstone.*

Discussion

Up to now only one sandstone has been characterised and subjected to wettability tests and flooding experiments, using fluids that exhibit different charges at the oil/water interface. Due to this limited material it is difficult to draw conclusions on how fluid wettability and production characteristics of oil is related to rock geometry and surface mineralogy. The same type of measurements described in this paper will be performed with other types of rock material, both with respect to surface mineralogy and pore size and geometry. Such a database will be necessary in order to investigate if systematic trends can be found.

During the displacement experiments the pH of produced water varied in the range 8.3 to 9.3. At these conditions the charge of the oil/water interface was either negative, positive or neutral, depending on whether an acid, a base or no substance was added to the oil. The pK- values of the acid and base used are approximately 5 and 10.6. In the pH interval of the experiments the surface charge of the Berea rock will be negative. The Berea rock showed a strong water wetness when pure n-decane or n-decane with acid was used as the oil. The brine used in the experiment was made of NaCl, and in the absence of divalent cations the oils and the solid surfaces will have no strong attractions.

When the base was added to the oil the oil interface became positively charged, and attractive forces between the solid and the oil was created. The result was that the wettability changed from water wet to neutral. This indicate that the affinity to oil and water to the solid surface became more alike. As seen in Figure 1 most of the bulk surface of the rock is covered with quartz and kaolinite.

The change in oil production rate and recovery was dramatic when the base was added to the oil as shown in Figure 3. Besides this, the two floods behaved in a similar manner, as little or no oil was produced after breakthrough in both floods. The fluids were produced in tubes that collected the production from given time intervals. For each experiment two defined phases was only observed in the tube collecting effluent at the time of water breakthrough. For Experiment 2 traces of oil was seen in subsequent tubes after water breakthrough, but the amount of oil was so low that it could not be quantified.

The oil production history obtained by water flooding laboratory cores is known to depend on a large number of variables including wettability, viscosity ratio of injected and produced fluids, saturation history, pore geometry and injection rate. Anderson (1987) shows several examples on how wettability may affect the residual oil saturation after water flooding, and the residual oil saturation is often seen to be at a minimum at weakly water wet to intermediate wet conditions when the wettability is altered by treating the surface of the rock. Anderson often uses the terms breakthrough oil saturation , practical oil saturation and true residual saturation. He claims that the break through oil saturation often is lowest in water wet systems, and the reason for lower residual saturations for other states of wetting is due to the after production of oil in non water-wet systems.

Jadhunandan and Morrow (1991) studied oil recovery from Berea cores at different wetting states obtained by changing type of crude oil, brine composition, aging time and temperature. Both oil saturation at water breakthrough, and after continued water injection, was found to be minimum at neutral and weakly water wet conditions. The experiments were performed with unfavourable viscosity ratios between water and oil.

Rathmell *et al*.(1973) performed flooding experiments in long Berea cores at variable wetting conditions, obtained by surface treatment of the core. The wettability was altered from strongly water wet to moderately water wet, and further to a more neutral condition where only small amounts of water imbibed into the core. Breakthrough oil saturation decreased from 40 % PV to 33 % and further to 24 %, respectively, for the three different wettabilities. These results are very consistent with the present data where the oil saturation was found to decrease 14 %-points from 35 % PV to 21 %PV when the wettability was changed by altering the properties of the oil.

Conclusions

This work is the first part of a project that addresses the possibility to determine the wettability and the residual oil saturation in a porous medium, based on a knowledge of pore geometry and surface mineralogy of the rock, and the properties of the fluids present.

A Berea sandstone core has been characterised by geometric parameters and surface mineralogy by use of scanning electron microscopy. The surface charge of the minerals is expected to be negative at the conditions of the present experiments

Amott wettability index and contact angles show that Berea sandstone was water wet in the presence of n-decane and a NaCl based brine. The wettability remained unchanged when an organic acid was added to the oil, which changed the charge of the oil/water interface from neutral (zero charge) to negative. The wettability was changed to neutral wet when an organic base was added to the oil, which changed the charge of the oil/water interface to positive.

During water flooding experiments the oil production increased, and the residual oil saturation decreased, when the oil with added base was used instead of pure n-decane. The behaviour is consistent with similar observations with Berea sandstone at variable wetting conditions obtained, however, by treatment of the rock surface.

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