Available online at www.sciencedirect.com

SCIENCE DIRECT®

Journal of Petroleum Science and Engineering 52 (2006) 187 – 197

JOURNAL OF PETROLEUM SCIENCE & ENGINEERING

www.elsevier.com/locate/petrol

New wettability test for chalk based on chromatographic separation of SCN^- and SO_4^{2-}

S. Strand [a,*], D.C. Standnes [b], T. Austad [a]

[a] Stavanger University College, Postbox 8002, 4068 Stavanger, Norway
[b] Centre for Integrated Petroleum Research (CIPR), University of Bergen, Allégaten 41, N-5007 Bergen, Norway

Received 15 March 2004; accepted 3 July 2006

Abstract

Wettability, water-wetness or oil-wetness, is usually defined in terms of the method used to determine the wetting state of a porous medium. In the Amott test, which is most frequently used for porous media, the wetting indices of water and oil are determined by the extent of spontaneous imbibition of water and oil from the state of the corresponding residual fluid saturations of the core. Thus, the Amott fluid wetting index reflects the potential capillary energy associated with the spontaneous imbibition process, which results in a very insensitive way to detect wetting alterations close to neutral conditions. Unfortunately, the natural wetting state of many carbonate reservoirs is close to neutral conditions or preferential oil-wet. In this paper, the wetting state of porous chalk is characterized by the fraction of surface area covered by one of the two fluids, i.e. water or oil. As the new wettability test is based on the chromatographic separation of two water-soluble components, i.e. a tracer, SCN^-, and a potential determining ion towards chalk, SO_4^{2-}, the fraction of the surface area covered by water was decided to represent the new wetting index. Using a chalk core at residual oil saturation, the area between the effluent curves for SCN^- and SO_4^{2-} is proportional to the area contacted by water during the flooding process. The ratio between this area and the corresponding area obtained from a completely water-wet core will give a water index between 0 and 1, representing completely oil-wet and completely water-wet conditions, respectively. The method is excellent to be used close to neutral condition, which will give a wetting index of 0.5. Experimental results are presented for two different chalks at different wetting conditions. Furthermore, the change in the Zeta-potential of the chalk surface over the dispersion zone of SO_4^{2-} is visualised by a gradient in the Ca^{2+} concentration in the same region.

Keywords: Wetting index; Chalk; Oil recovery; Chromatography

---

1. Introduction

Wettability is defined as “the tendency of one fluid to spread on or adhere to a solid surface in the presence of other immiscible fluids” (Anderson, 1986). In a rock/brine/oil system, water will displace oil if the surface is water-wet and vice versa if the surface is oil-wet. The wettability of the formation is of outermost importance when producing oil from subterranean formations, because all the important parameters for flow of oil and water in porous media like: capillary pressure, relative permeabilities, fluid distribution, and flow directions are dictated by wettability. Reliable data for the wettability state of reservoir core samples is therefore extremely important and the subject of this paper.

The wetting state of a reservoir is the result of adsorption of polar components from the crude oil onto

---

[*] Corresponding author.
E-mail address: skule.strand@uis.no (S. Strand).

0920-4105/$ - see front matter © 2006 Elsevier B.V. All rights reserved.
doi:10.1016/j.petrol.2006.03.021

the originally strongly water-wet mineral surface (some minerals are oil-wet by nature, but they occur very rarely in connection with oil reservoirs). The adsorption of polar components will most likely take place where the rock surface is directly exposed to the oil-phase. In such a way, a non-uniform wettability will appear where certain areas become covered by an organic layer and becomes oil-wet and others remain water-wet according to the initial distribution of fluids. Evaluating wettability by the Amott–Harvey or USBM indices (see below) may be sensitive to the location of water-wet and oil-wet areas, i.e. at pore bodies or pore throats.

Unfortunately, no universal method exists for quantifying wettability of porous samples. The most frequently methods used to quantify wettability of core samples are the Amott–Harvey and the United States Bureau of Mines (USBM) (Donaldson et al., 1969). Both methods are measuring the average wettability of the core sample. The Amott–Harvey index (I_{AH}) is based on the difference between the Amott index of water and oil where $I_{AH}=-1$ represents strongly oil-wet, $I_{AH}=-0.3$ to $+0.3$ intermediate wet, and $I_{AH}=+1.0$ strongly water-wet (Cuiec, 1991). The main drawbacks with this method are its insensitivity close to neutral wettability, to differ significantly between wetting states close to unity (Morrow, 1990), and the fact that there is no standard time allowing spontaneous imbibition to occur (imbibition may proceed for several months in some cases). The USBM index test is based on the work required for the wetting phase to displace the non-wetting phase. This work has been shown to correlate with the area under the capillary pressure curves, and the wettability index $\mathrm{WI_{USBM}}$ can be calculated as:

$$\mathrm{WI_{USBM}} = \log\frac{A_1}{A_2}$$

A_1	Area under the curve resulting from oil displaces water
A_2	Area under the curve resulting from water displaces oil

The range of $\mathrm{WI_{USBM}}$ is therefore from $-\infty$ to $+\infty$, although values between -2 and $+2$ occur most commonly. In addition to these two standard methods, several others have been proposed in the literature. Longeron et al. (1995) determined wettability indices by using the total area under the capillary pressure curve, and Kowalewski et al. (2003) used Cryo-ESEM analysis of Berea cores to detect water-wet and oil-wet areas on the surface.

Two methods based on dynamic adsorption related to the technique used in this paper have been previously described in the literature. Holbrook and Bernard (1958) were able to successfully determine fractional wettability in sandpacks by adsorption of Methylene blue. However, serious problems rose when testing core samples containing large amount of montmorillonite due to irreversible changes in the clay structure of the water-wet reference core. Furthermore, Torske and Skauge (1992) reported a wettability tests based on dynamic adsorption of Methylene blue and *n*-heptanol. They found that Methylene blue adsorbed on both oil-wet and water-wet surfaces in static batch tests, whereas *n*-heptanol only adsorbed on hydrophobic sites. However, the correlation between the suggested dynamic adsorption method and the standard wettability test methods (Amott and USBM) was poor for reservoir cores with varying mineralogy, physical properties, etc. They concluded that determination of wettability by dynamic adsorption should be performed with only one liquid present in the core, which is not a realistic situation.

The subject in this paper is to describe a new wettability test for chalk samples based on chromatographic separation of two water-soluble components, i.e. a tracer, SCN^-, and a potential determining ion towards chalk, SO_4^{2-}. Chromatographic separation will only take place at the water-wet sites at the pore surface, and the fraction of the surface area covered by water is assumed to represent the new wetting index parameter. Using a chalk core at residual oil saturation, the area between the effluent curves for SCN^- and SO_4^{2-} is proportional to the area contacted by water during the flooding process. The ratio between this area and the corresponding area obtained when flooding a completely water-wet core will give a water index between 0 and 1, representing completely oil-wet and water-wet conditions, respectively. The new method should be an excellent way to evaluate the wettability of chalk material independent of initial fluid saturations and the location of oil-wet and water-wet areas.

2. Experimental

2.1. Materials

2.1.1. Oils

Three different oils were used in the experiments. The first oil referred to as Crude 1 AN 1.8 was prepared by diluting a crude oil in the ratio 40/60 heptane/crude by volume and filtered through a 5 μm Millipore filter. No precipitation of asphaltenes was observed after diluting with heptane. The properties of Crude 1 AN 1.8: Acid number (AN) of 1.84 mg KOH/g; Density at 20 °C 0.806 g/cm^3; Viscosity at 20 °C 2.5 cP; Asphaltenes 0.23 wt.%.

The second oil referred to as Crude 1 AN 0.1 was prepared by adding 10 wt.% Silica Gel to Crude 1 AN

Table 1
Composition of seawater with and without SO_4^{2-} present (molar compositions of individual components and total salinity)

	Brine A (mol/l)	Brine B (mole/l)	Brine C (mole/l)
Na^+	0.500	0.475	0.450
K^+	0.010	0.022	0.034
Mg^{2+}	0.045	0.045	0.045
Ca^{2+}	0.013	0.013	0.013
Cl^-	0.623	0.574	0.525
HCO_3^-	0.002	0.002	0.002
SO_4^{2-}	0.000	0.012	0.024
SCN^-	0.000	0.012	0.024
TDS, g/l	35.72	35.72	35.72

1.8. The mixture was stirred on a magnetic stirrer at room temperature for 3 days before an equal amount of Silica Gel was added and stirred for two more days. The oil was then centrifuged and filtered through a 5 μm Millipore filter. The properties of Crude 1 AN 0.1 are: AN of 0.13 mg KOH/g; Density at 20 °C 0.799 g/cm^3; Viscosity at 20 °C 2.5 cP. The third oil referred to as Crude 1 AN 1.0 was prepared by mixing 50/50 of Crude 1 AN 1.8 and Crude 1 AN 0.1 by weight.

2.1.2. Brines

The brines used are termed A, B, and C and the compositions are listed in Table 1. All brines have a constant total dissolved solid (TDS) of 35.72 g/L. Brine C is synthetic seawater with sulfate content of 0.024 mol/l and with the same amount of thiocyanate used as tracer. Brine B has a reduced sulfate and thiocyanate content with both ion concentrations equal to 0.012 mol/l. The TDS was held constant by increasing the amount of NaCl. Brine A contains no sulfate and thiocyanate. The equilibrium water (Eq. Water) used is tap water, which has been exposed to Liège chalk material at room temperature for a long period. The water was filtered through 0.65 μm Millipore filter prior to use.

2.2. Porous media

The porous media used are outcrop chalk form Stevns Klint (SK) nearby Copenhagen, Denmark, and from Liège (LI) in Belgium. Pure chalks are mainly built up of fragmentary skeletons produced by planktonic algae known as coccolitho-phorids. The building blocks of the skeletons are calcite tablets or platelets of typical dimension 1 μm. The calcite grains are arranged in rings or rosettes known as coccoliths, typically 10 μm in diameter. Pure high porosity chalks consist of a mixture of intact coccoliths rings and greater and smaller fragments. This gives the chalk material a rather open structure, where the dimensions of the pore space may be considerably greater than the dimensions of the individual grains. On the other hand, the smallness of the grains makes the pore throats rather narrow, and the permeability of even high porosity chalk is typically only a few mD. Cylindrical samples were drilled from blocks with an oversized core bit (water was used for cooling). After drying, the samples were machined to the right diameter in a lathe and then cut to the desired length of 73–81 mm with a diamond saw.

The *Stevns Klint chalk* is a soft and highly porous material of Maastrichtian age. It is mainly composed (96%) of fine-graded coccolithic matrix (Milter, 1996) The chalk has a high porosity from 45% to 50%. The matrix permeability is in the range between 1 and 3 mD. The Stevns Klint chalk has a specific area about 2 m^2/g as determined by the Braunauer–Emmett–Teller (BET) adsorption isotherm (Heimenz and Rajagopalan, 1997).

The *Liège chalk* is from the Upper Campanian age. The chalk has porosity approximately around 40% and with a permeability of 1–2 mD. The silica content is less than 2%. The Liège chalk has a higher strength than the Stevns Klint chalk.

2.3. Chemicals

Silica Gel used for crude oil treatment has the grade 60, with a particle size of 0.035–0.070 mm. and was supplied by Fluka Chemica. Heptane used in the experiments has a purity of 98% and was supplied by Merck. All other chemicals used for brines and chemical reagents were PA-graded and delivered by either Riedel de Haën or Merck.

2.4. Core handling

After machining the cores to the right diameter of 36.0–38.1 mm, the cylindrical cores were dried at 90 °C to constant weight. In the case without initial water, the cores were placed in a container, evacuated, and surrounded with the specified oil. The cores rested in the oil for 2 h and the porosity could then be calculated from the weight difference, bulk volume and oil density. The cores were then placed in Hassler core holders, flooded with 1.5 pore volume (PV) of oil in each direction with a confining pressure not exceeding 25 bar, and finally aged for 5 days at 50 °C in closed containers surrounded with oil.

In the case of initial water saturation present, the dry cores were placed in a container, evacuated, and surrounded with brine. The material rested in the brine for 2 h, and the porosity was calculated from the weight differences, bulk volume, and brine density. The cores were then placed in Hassler core holders, and flooded with 1.5 PV of oil in each direction with a confining pressure not exceeding 25 bar. The total displaced brine volume was measured, and the S_{wi}-value calculated. Then, the cores were aged for 43 days at 90 °C in a closed container surrounded with the specified crude oil.

2.5. New wetting test

2.5.1. Establishing Sor

The aged cores were shaved about 1–2 mm at each end to avoid "skin" effects and then placed in Hassler core holders with a confining pressure not exceeding 25 bar. The cores were then flooded with 1 PV Brine A (no sulfate and tracer) with a rate of 0.2 ml/min, followed by 1 PV of the same brine at 0.4 ml/min. The total displaced oil volume was measured, and the S_{or}-value calculated.

2.5.2. Flooding

The cores were flooded with at least 2 PV with brine containing sulfate and tracer (Brine B or Brine C) with a rate of 0.2 ml/min. Small fractions (1–3 ml) of the effluent were collected using a fraction collector. The exact volume and PV of each fraction could then be calculated using the weight and the density of the fluid.

2.5.3. New wettability index calculation

Each fraction was analysed for relative concentrations of sulfate and thiocyanate, and plotted against pore volume injected. The delay in the sulfate concentration compared to the thiocyanate concentration in the effluent is proportionate to the pore surface accessible to "adsorption". The area ratio between the thiocyanate and sulfate curves of the sample, A_{Wett}, and a reference core containing heptane, A_{Heptane}, which is assumed to be completely water-wet system, is then defined as the new wettability index ($\mathrm{WI}_{\mathrm{New}}$):

$$\mathrm{WI}_{\mathrm{New}} = \frac{A_{\mathrm{Wett}}}{A_{\mathrm{Heptane}}}$$

where:

A_{Wett}	The area between the thiocyanate and sulfate curves generated by flooding a core aged in crude oil
A_{Heptane}	The reference area between the thiocyanate and sulfate curves generated by flooding a core assumed to be strongly water-wet (saturated with heptane)

The area between the two curves is calculated by subtraction of the area under each of the curves which were determined by the trapeze method.

2.6. Amott–Harvey index

In two cases (Test 4/1 and 5/1), the Amott–Havey indices for Stevns Klint cores exposed to Crude 1 AN 0.1 and Crude 1 AN 1.8 were determined in order to compare the result with the present new wettability test. The initial 100% oil saturated aged cores were flooded with Brine A without SCN^- and SO_4^{2-} present, and then resaturated with oil to establish residual water saturation, S_{wr}, prior to spontaneous imbibition. The Amott indices were calculated allowing a spontaneous imbibition time of 21 h with no recorded imbibition for the last 12 h. Forced flow rate was set to a maximum of 1.0 ml/min for both water and oil.

$$\text{Crude 1 AN 0.1}: \quad I_{\mathrm{AH}} = I_w - I_o = 1.00 - 0.00 = 0.99$$
$$\text{Crude 1 AN 1.8}: \quad I_{\mathrm{AH}} = I_w - I_o = 0.04 - 0.06 = -0.01$$

Where:

$$I_w = \frac{\Delta S_{ws}}{1 - S_{wr} - S_{or}} = \frac{\Delta S_{ws}}{\Delta S_{wt}}$$

$$I_o = \frac{\Delta S_{os}}{1 - S_{wr} - S_{or}} = \frac{\Delta S_{os}}{\Delta S_{ot}}$$

ΔS_{ws}	Increase in water saturation during spontaneous imbibition of water
ΔS_{os}	Increase in oil saturation during spontaneous imbibition of oil
ΔS_{wt}	Total increase in water saturation during spontaneous and forced displacement of oil
ΔS_{ot}	Total increase in oil saturation during spontaneous and forced displacement of water

The results are also presented in Table 2.

2.7. Chemical analysis

The content of sulfate and thiocyanate in each fraction from the wettability flooding tests was analysed. The thiocyanate concentration was analysed by diluting an exact sample volume with 0.2 M solution of $Fe(NO_3)_3$ dissolved in 1.0 M aqueous HNO_3 solution:

$$Fe^{3+}_{(aq)} + SCN^-_{(aq)} \rightarrow FeSCN^{2+}_{(aq)} \qquad (1)$$

When $[Fe^{3+}] \gg [SCN^-]$, all thiocyanate ions will be converted to the thiocyanato complex ion ($FeSCN^{2+}$), according to reaction (1). Since the $FeSCN^{2+}$ solution is deep blood red, the absorbance can be measured with a spectrophotometer at 447 nm and compared with a

Table 2
Data from the different wettability tests

Core/ test	Chalk type	Core preparation			Wettability data			Wett results		
		Core saturation	S_{wi}	Aging cond.	AN	S_{or}	Flooding brine	A_{Wett}	WI_{New}	I_{AH}
1/1	SK	Brine A	1.00				Brine B	0.251		
1/2	SK	Brine A	1.00				Brine B	0.231		
1/3	SK	Brine A	1.00				Brine C	0.168		
1/4	SK	Brine A	1.00				Brine C	0.171		
2/1	SK	Brine A	1.00				Brine C	0.173		
3/1	SK	Heptane	0	–	0	0.22	Brine C	0.159	1	–
4/1	SK	Crude 1 AN 0.1	0	5 days 50 °C	0.13	0.27	Brine C	0.123	0.71	0.99
5/1	SK	Crude 1 AN 1.8	0	5 days 50 °C	1.84	0.36	Brine C	0.059	0.34	−0.01
6/1	LI	Eq. Water/Heptane	0.39	–	0	0.26	Brine C	0.172	1	–
7/1	LI	Eq. Water/Crude 1 AN 0.1	0.33	43 days 90 °C	0.13	0.25	Brine C	0.153	0.89	–
8/1	LI	Eq. Water/Crude 1 AN 1.0	0.32	43 days 90 °C	0.99	0.23	Brine C	0.086	0.50	–
9/1	LI	Eq. Water/Crude 1 AN 1.8	0.25	43 days 90 °C	1.84	0.29	Brine C	0.085	0.49	–

calibration curve to find the thiocyanate concentration (Lahti et al., 1999).

The sulfate concentration was determined using a Sulfate Test Kit delivered by Merck. The sulfate ions in an exact sample volume are precipitated with barium ions,

$$Ba^{2+}_{(aq)} + SO^{2-}_{4(aq)} \rightarrow BaSO_{4(s)} \quad (2)$$

and the turbidity of the sample was measured and converted to a sulfate concentration with a photometric instrument. The accuracy of this sulfate test method was compared and verified with ion chromatographic analyses (HPLC) according to ISO 10304-2 Standard Method, performed by West Lab Services.

The acid numbers of Crude 1 AN 1.8 and Crude 1 AN 0.1 were determined by West Lab Services according to ASTM D-664.

2.8. Equipment

Hassler core holders were used for all core-flooding, both in core handling and in the wettability tests. HPLC pump model 305, with a 10SC piston head, delivered by Gilson was used in the flooding experiments. Fraction collector model 222 XL delivered by Gilson was used in the wettability flooding experiments. All samples were collected into 8 ml vials with liners, delivered by Alltech, to avoid evaporation.

Amott cells delivered by J.M. Glassteknikk, Norway were used in all spontaneous imbibition tests. Density measurements were performed on an Anton Parr DMA 4500 Density Meter. Viscosity measurements were performed on a Physica UDS 200 Spectro instrument.

The spectrophotometer used for measuring the absorbance of the thiocyanato complex ion ($FeSCN^{2+}$) was a HITACHI V2000 spectrophotometer. The sulfate analysis was performed using Sulfate Cell Test no. 14548 delivered by Merck, analysed on a Spectroquant NOVA60 photometer, also delivered by Merck.

3. Results and discussion

The present paper is part of an improved oil recovery study linked to chalk formations in the North Sea, with special reference to the Ekofisk field. Seawater is then the natural injection fluid for oil displacement and pressure support. It must be noticed that the initial reservoir brine does not contain any sulfate, while seawater has a sulfate concentration nearly twice the concentration of calcium. Sulfate is a potential determining ion towards the $CaCO_3$ surface, and even at very small concentrations, the surface Zeta-potential will change significantly depending on the pH of the system (Pierre et al., 1990). The effects of sulfate on the Zeta-potential obviously decrease as the pH increases above 7, i.e. as the surface becomes negatively charged. The great catalytic effect of sulfate on the wettability alteration from preferential oil-wet to more water-wet conditions using a cationic surfactant was explained by the influence of sulfate on the surface charge of chalk (Strand et al., 2003). The idea of using sulfate in a dynamic process to quantify the water-wet surface area in low permeable carbonate was then settled using artificial seawater as the mobile phase. Thiocyanate, SCN^-, which is a non-potential determining ion towards the carbonate surface, was used as the non-adsorbing water tracer. The molar concentration of SCN^- and SO_4^{2-} was kept equal in synthetic seawater. The area between the effluent curves for SCN^- and SO_4^{2-} must be directly proportional to the water-wet surface area in the porous medium, because both of the water-soluble components, SCN^- and SO_4^{2-}, must contact the same water-wet area.

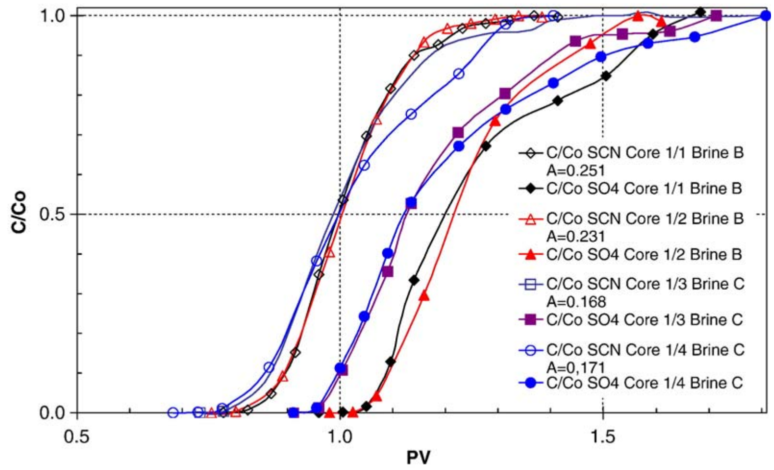

Fig. 1. Effect of concentration on chromatographic separation of SCN^- and SO_4^{2-} in a 100% water saturated chalk core.

The chromatographic separation between SCN^- and SO_4^{2-} was tested at two different concentrations, i.e. 0.012 and 0.024 mol/l, Fig. 1, Table 2 Test 1/1, 1/2 and 1/3, 1/4, respectively. It is noticed that the concentration of sulfate found in seawater is close to 0.024 mol/l. The experiments were performed using the same core. As expected, the area between the effluent curves of the two components increased as the concentration of the two components decreased. At low concentration, the areas were determined to be 0.251 and 0.231, and at high concentration the areas were 0.168 and 0.171, corresponding to an average reproducibility of about 8%. It is noticed that the dispersion front of SCN^- is quite similar for the high and low concentration corresponding to about 0.5 PV. It is also noticed that all the elution curves for SCN^- passed through the point where $(C/C_o)=0.5$ and PV = 1.0, indicating that the injected fluid is contacting the total PV of the core. The dispersion front for sulfate is, due to adsorption, somewhat wider, about 0.7 PV. Thus, the experiments confirm that even for a relative short core the chromatographic separation of SCN^- and SO_4^{2-} is large enough to determine the area between the effluents curves with a reasonable accuracy using a sulfate concentration similar to what is found in seawater.

The reproducibility of the calculated area between the effluents curves was also tested using different cores, Tests 1/3 and 2/1. The cores were from the same chalk block and high concentration of the tracer and sulfate, 0.024 mol/l were applied, at 100% water saturation, Fig. 2. The areas were determined as 0.168 and 0.173, which is a deviation less than 3%.

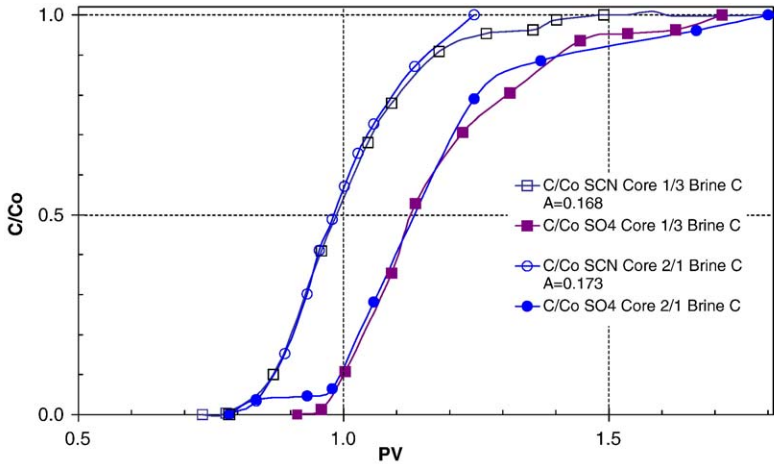

Fig. 2. Test of reproduction of the areas between the effluent curves for SCN^- and SO_4^{2-} for two different chalk cores, 1/3 and 2/1, from the same block.

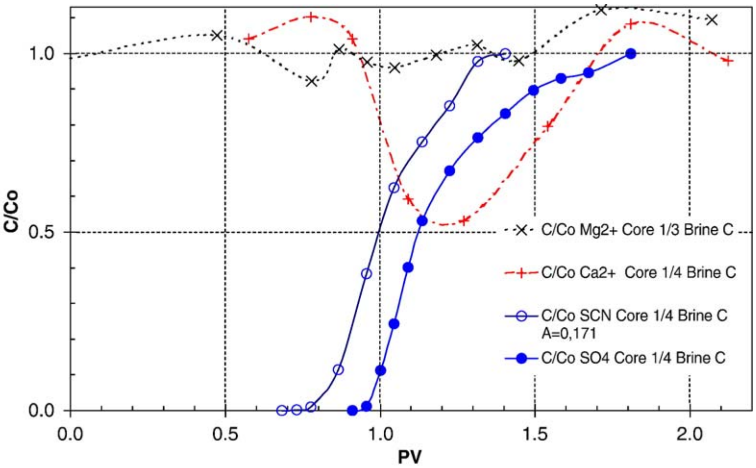

Fig. 3. Relative concentrations of Mg^{2+}, Ca^{2+}, SCN^{-}, and SO_4^{2-} at the core outlet.

The sensitivity of the sulfate ion regarding the surface charge on chalk is clearly demonstrated in Fig. 3. The gradient of the sulfate concentration in the dispersion zone caused a change in the Ca^{2+} concentration. Thus, as the sulfate concentration increases, sulfate adsorbs onto the chalk surface, which will change the Zeta-potential somewhat. The equilibrium condition for the strongly potential-determining Ca^{2+}-ion is then changed, and Ca^{2+} ions will adsorb onto the surface causing a decrease in the equilibrium concentration. The continuous supply of injection fluid will then re-establish equilibrium between ions in solution and adsorbed material. Therefore, it is interesting to note that the minimum in Ca^{2+} concentration is observed close to the inflection point of the sulfate effluent curve. The change in the Ca^{2+} concentration is closely related to the dispersion zone of sulfate. It appears that the Mg^{2+} concentration is much less sensitive to the gradient in the sulfate concentration and no decrease in Mg^{2+} concentration was observed. It must, however, be noticed that the concentration of Mg^{2+} in seawater is 0.045 mol/l, which is nearly twice the concentration of SO_4^{2-} and 3.5 times the concentration of Ca^{2+}. Thus, the concentration of Mg^{2+} may be too high to notice any effect, or Mg^{2+} is a much weaker potential determining ion towards $CaCO_3$ compared to Ca^{2+}.

The new wettability parameter for chalk suggested in this paper is determined by using the area between the effluent curves for a completely water-wet system as a basis. Experimentally, the chromatographic separation between SCN^{-} and SO_4^{2-} is usually performed at residual oil saturations. Even though the system is completely water-wet, the capillary trapped residual oil will block some water-wet areas causing the area

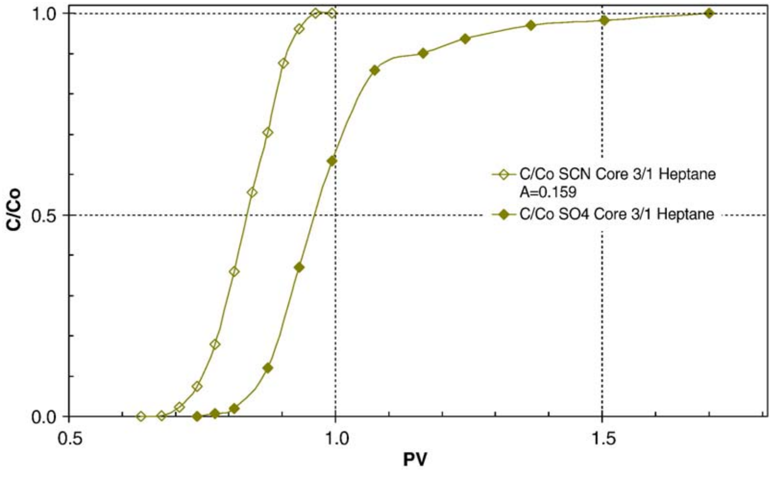

Fig. 4. Effluent profiles of SCN^{-} and SO_4^{2-} for a water-wet system containing heptane at $S_{or}=0.22$, Test 3/1.

between the effluent curves to decrease somewhat compared to a system without residual oil present. This is demonstrated in Fig. 4, where the water-wet chalk core, Test 3/1, contained heptane at a residual saturation of $S_{or}=0.22$. In this case, the area decreased to 0.159 compared to an average value of 0.170 for the 100% water saturated system, Tests 1/3 and 1/4. Thus, an increase in S_{or} from 0 to 0.22 caused a decrease in the area of 6–7% due to a decrease in the access to water-wet surface area. Depending on the wetting state of the porous media, the S_{or}-values will normally change between 0.22 for a completely water-wet system and 0.36 for preferential oil-wet conditions, Table 2. Thus, when calculating wettability indices, it was therefore decided to use the area from the water-wet core containing heptane at residual oil saturation as the reference wetting state. It is also noticed that the SCN$^-$ curve has a (C/C_o)-value of 0.5 close to a PV = 0.8 indicating that the S_{or}-value is about 0.2, Fig. 4.

In a previous paper we have shown that the wetting properties of chalk are sensitive to the acidic compounds present in crude oil (Standnes and Austad, 2000). In this work we have tuned the wetting of the chalk by using oils with different acid number, i.e. an acidic crude oil with AN = 1.84 mg KOH/g was stripped for polar components using silica, resulting in an AN = 0.13 mg KOH/g. Mixtures of these two oils have been prepared to obtain crude oils with different AN. Two different SK-cores saturated with 100% oil with different acid numbers, core 4/1 with AN = 0.13 mg KOH/g and core 4/2 with AN = 1.84 mg KOH/g, were aged for 5 days at 50 °C in the respective oils. The cores were then flooded to residual oil saturation with synthetic seawater where NaCl was substituted for Na_2SO_4, Brine A. The residual oil saturations then became 0.27 and 0.36 for the cores with low and high AN, respectively, Table 2. The wettability tests were performed using seawater with 0.024 mol/l of SCN$^-$ and SO_4^{2-}, Brine C, as described in Fig. 5. The area between the effluent curves for the tracer and SO_4^{2-} was calculated to be 0.059 and 0.123 for the crude with high and low AN. When using the area 0.159 for the water-wet core containing heptane at $S_{or}=0.22$ as the reference wetting state, the new wetting index for the two cores were calculated to be 0.71 and 0.34, Table 2. Thus, as expected, the core containing oil with low AN was preferentially water-wet with a $WI_{New}>0.5$, and the core containing oil of high AN became preferential oil-wet with $WI_{New}<0.5$. The fact that S_{or} increases from 0.22 at completely water-wet conditions to 0.36 at preferential oil-wet conditions will probably have small effects on the chromatographic separation of SCN$^-$ and SO_4^{2-} and also on the calculated wetting index. As discussed above, the inaccuracy of the area will probably be less than 3–4%.

Scaling these new wettability indices in terms of Amott–Havey indices, the values will be 0.42 for the Crude 1 AN 0.1 system and −0.32 for the Crude 1 AN 1.8 system. According to the experimental method used in this paper, the corresponding indices were determined to be 0.99 and −0.01, respectively. It is not surprising that the correlation is poor, knowing that the Amott test does not discriminate adequately between strongly water-wet systems, and it fails close to neutral conditions, as discussed in a later section.

Three different chalk cores from Liège were also prepared using oils of different AN: 0.13, 0.99 and

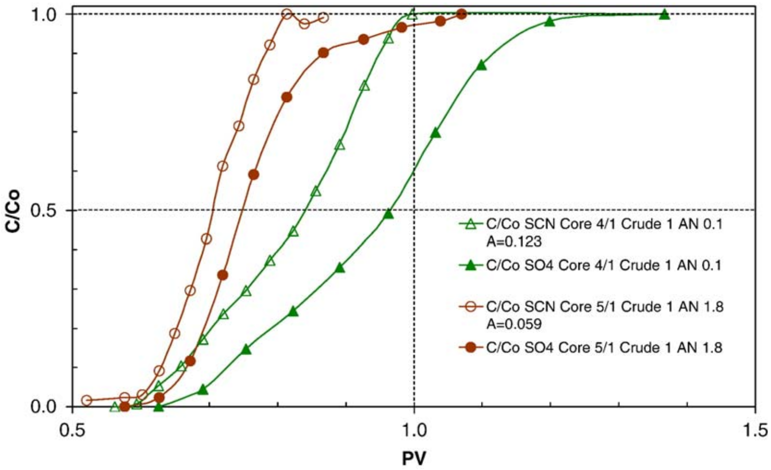

Fig. 5. Effluent profiles of SCN$^-$ and SO_4^{2-} from SK-cores prepared without initial water saturation using oils of different AN, 0.13 and 1.84 for core 4/1 and 5/1, respectively.

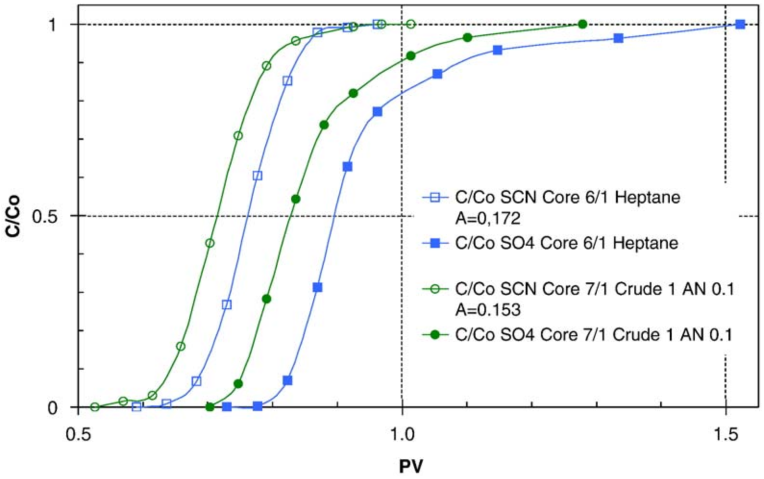

Fig. 6. Effluent profiles of SCN^- and SO_4^{2-} from Liège cores prepared with initial water present. The reference core 6/1 contained heptane as oil, while the core 7/1 contained oil with AN = 0.13 mg KOH/g.

1.84 mg KOH/g and initial water present in the cores. The initial water used had been in equilibrium with the chalk at room temperature for several days. After core preparation, the cores were aged at 90 °C in the respective crude oils for 6 weeks. Thereafter the cores were flooded with seawater without sulfate, Brine A, to obtain residual oil saturations. A reference core was prepared without aging using heptane as the oil-phase. The S_{or}-values varied between 0.23 and 0.29, Table 2. The core-flooding results using seawater with 0.024 mol/l of SCN^- and SO_4^{2-}, Brine C, are presented in Figs. 6 and 7. The area between the effluent curves for the reference core and the core containing the crude oil with lowest acid number, AN = 0.13 mg KOH/g was determined from Fig. 6 as 0.172 and 0.153, respectively. The corresponding areas for the cores with oil of acid number 0.99 and 1.84 mg KOH/g were determined from Fig. 7 as 0.086 and 0.085. Thus, the calculated wetting indices were: 0.89, 0.50 and 0.49 for the cores with crude oil with AN = 0.13, 0.99, and 1.84, respectively. Thus, the cores with AN = 0.99 and 1.84 showed the same wetting index of 0.50, which is described as neutral wetting conditions. It is interesting to note that as the AN of crude oils increases beyond 1.0, its influence on the wetting nature appeared to be unaffected. This may be specific for the way we prepared the crude oil, and not general for all types of crude oil. The relative amount of acid and bases present in crude oil may affect the potential of the crude to wet the chalk surface.

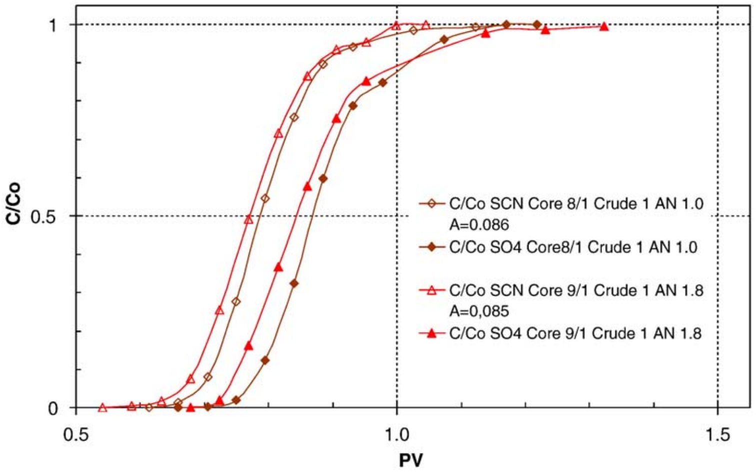

Fig. 7. Effluent profiles of SCN^- and SO_4^{2-} from Liège cores prepared with initial water present. The cores contained oil with different acid number. Core 8/1: AN = 0.99 mg KOH/g and core 9/1: AN = 1.84 mg KOH/g.

3.1. Comments to wettability measurements in porous media

Normally, the wetting state of a porous medium containing two immiscible fluids should be evaluated in terms of the surface area fraction contacted by each of the fluids. Thus, under neutral wetting condition, each of the two fluids should cover 50% of the surface area in the porous medium. In a preferential water-wet system, more that 50% of the surface is covered by water, and in a preferential oil-wet system less that 50% of the surface is covered by water. It is, however, well known that the transport properties of two immiscible fluids in a porous medium do not need to be directly related to the fractional wetting area of the two fluids. Talking about two-phase fluid flow in a porous medium, the fluid distribution in the pore space is a more important key factor to understanding the fluid flow properties. The transport of immiscible fluids in a porous medium is, however, determined by the capillary forces, which are related to the capillary pressure. Therefore, the two most used wetting indices in porous medium, I_{AH} and $\mathrm{WI}_{\mathrm{USBM}}$, are defined in terms of capillary pressure and/or fluid flow, spontaneous imbibition/drainage and forced imbibition/drainage. The Amott–Harvey index is based on both of the flow processes, i.e. spontaneous imbibition/drainage and forced imbibition/drainage, while $\mathrm{WI}_{\mathrm{USBM}}$ is related to the area below the capillary pressure imbibition and drainage curves under forced fluid flow. The indices are determined empirically, and they have been used interchangeably within the petroleum industry. Analytical and numerical network simulation suggested that only for weakly wetted media with randomly distributed water-wet and oil-wet pores should the same value for the two indices be expected (Dixit et al., 1998). Under other wetting conditions the two indices were expected to be different. Besides bad performance at neutral wetting conditions, Ma et al. (1999) pointed out that the Amott test does not discriminate adequately between strongly water-wet systems. In this case, Ma et al. (1999) quantified the wettability from spontaneous imbibition rates by suggesting that the area under the imbibition curve is related to the work of displacement that results from a decrease in surface free energy. However, neither this method nor the Amott test can discriminate between systems close to neutral wetting conditions, i.e. for systems that do not imbibe oil or water in significant quantities. For this type of system, the USBM test is suggested to be useful.

Kowalewski et al. (2003) compared wettability data from Amott tests and Cryo-ESEM analysis for Berea cores. For the latter test, the fraction of water-wet and oil-wet surface was calculated based on tracers dissolved in the two phases. It is interesting to note that the deviation between the Amott and the ESEM index appeared to be greatest close to neutral wetting conditions. Thus, the Amott test may predict neutral wetting conditions even though just a very small fraction of the surface area is coated with organic materials, especially if the oil-wet areas are located at the pore throats.

The new wettability test method for chalk discussed in this paper does not have any limitations regarding significance in certain wetting ranges. Compared to other traditional methods, this new chromatographic method is very fast. No time consuming spontaneous imbibition process is needed. So far, only chalk samples have been tested, but the method should work for other type of carbonate reservoir rock, i.e. limestone and dolomite. Furthermore, the wetting tests have only been conducted at room temperature, but it may also work at actual reservoir temperatures. Further work is in progress in our laboratory to test the method for different types of carbonate rock and temperature effects.

4. Conclusion

The new wettability test for chalk presented in this paper is based on a chromatographic separation of the water-soluble tracer SCN^- and the potential determining ion SO_4^{2-}. The test is conducted at residual oil saturation, and the chromatographic separation of the two components only takes place at the water-wet areas. Thus, the area between the effluent curves, which is a plot of relative concentration vs. pore volume, is directly proportional to the water-wet area inside the chalk core. A completely water-wet core using heptane as oil was used as a reference system, giving an area for a completely water-wet core. The new wetting index, $\mathrm{WI}_{\mathrm{New}}$, will run from: 0 (completely oil-wet), 0.5 (neutral wettability) to 1.0 (completely water-wet). The following improvements compared to traditional Amott tests are obtained:

- Generally, the test has a very good significance in the total wetting range, but it appeared to be very useful close to neutral wetting conditions.
- The test method is fast, and it can be run at residual oil saturations without performing any long-term imbibition test.

So far, the test has only been performed on chalk at room temperature. Experiments are in progress using other carbonates and different temperatures.

Abbreviations

AN	Acid number
ASTM	American Society for Testing and Materials
A_{Heptane}	The reference area between the thiocyanate and sulfate curves generated by flooding a core assumed to be strongly water-wet (saturated with heptane)
A_{Wett}	The area between the thiocyanate and sulfate curves generated by flooding a core aged in crude oil
A_1	Area under the curve resulting from oil displaces water
A_2	Area under the curve resulting from water displaces oil
BET	Braunauer–Emmett–Teller
C	Effluent concentration of sulfate or tracer
C_{o}	Injected concentration of sulfate or tracer
Eq.	Equilibrium
ESEM	Environmental scanning electronic microscope
HPLC	High performance liquid chromatography
I_{w}	Amott water index
I_{o}	Amott oil index
I_{AH}	Amott–Harvey wettability index
LI	Liège
PV	Pore volume
SK	Stevns Klint
S_{wi}	Initial water saturation
S_{or}	Residual oil saturation
S_{wr}	Residual water saturation
TDS	Total dissolved solid
USBM	United States Bureau of Mines
$\mathrm{WI}_{\mathrm{USBM}}$	USBM wettability index
$\mathrm{WI}_{\mathrm{New}}$	New wettability index
ΔS_{ot}	Total increase in oil saturation during spontaneous and forced displacement of water
ΔS_{os}	Increase in oil saturation during spontaneous imbibition of oil
ΔS_{ws}	Increase in water saturation during spontaneous imbibition of water
ΔS_{wt}	Total increase in water saturation during spontaneous and forced displacement of oil.

Acknowledgement

The authors wish to thank Statoil and Reslab for delivering the crude oil and Dr. Peter Frykman at Geological Survey of Denmark and Greenland (GEUS), Copenhagen Denmark, for providing the chalk material from Stevns Klint. Also thanks to P. Delage/V. De Gennaro at Ecole des Ponts et Chaussées, Paris, France, for providing chalk cores from Liège.

References

Anderson, W.G., 1986. Wettability literature survey — part 2: wettability measurement. J. Petrol. 1246–1262 (November).

Cuiec, L.E., 1991. Evaluation of reservoir wettability and its effect on oil recovery. In: Morrow, N.R. (Ed.), Interfacial Phenomena in Petroleum Recovery. Surfactant science series, vol. 36. Marcel Dekker, Inc., New York.

Dixit, A.B., Buckley, J.S., McDougall, S.R., Sorbie, K.S., 1998. Core wettability: should I_{AH} equal I_{USBM}? Paper SCA-9809 Presented at the SCA International Symposium Held in Hague, The Netherlands.

Donaldson, E.C., Thomas, R.D., Lorenz, P.B., 1969. Wettability determination and its effect on recovery efficiency. SPEJ 13–20 (March).

Holbrook, O.C., Bernard, G.C., 1958. Determination of wettability by dye adsorption. Trans. AIME 213, 261–264.

Heimenz, P.C., Rajagopalan, R., 1997. Principles of Colloid and Surface Chemistry, Third edition. Marcel Dekker, New York.

Kowalewski, E., Boassen, T., Torsaeter, O., 2003. Wettability alterations due to aging in crude oil; wettability and Cryo-ESEM analysis. J. Pet. Sci. Eng. 39 (3–4), 377–388.

Lahti, M., Vilpo, J., Hovinen, J., 1999. Spectrophotometric determination of thiocyanate in human saliva. J. Chem. Educ. 76 (9), 1281–1282 (September).

Longeron, D., Hammervold, W., Skjaeveland, S.M., 1995. Water– oil capillary pressure and wettability measurements using micropore membrane technique. Paper SPE 30006 Presented at the International Meeting on Petroleum Engineering held in Bejing, PR China, November 14–17.

Ma, S., Morrow, N.R., Zhou, X., Zhang, X., 1999. Characterization of wettability from spontaneous imbibition measurements. J. Can. Pet. Technol. 38 (13), 56 (Special Edition).

Milter, J., 1996. Improved Oil Recovery in Chalk. Ph. D. Thesis, Department of Chemistry, University of Bergen, Norway.

Morrow, N.R., 1990. Wettability and its effect on oil recovery. J. Pet. Technol. 1476–1484 (December).

Pierre, A., Lamarche, J.M., Mercier, R., Foissy, A., Persello, J., 1990. Calcium as potential determining ion in aqueous calcite suspensions. J. Dispers. Sci. Technol. 11 (6), 611–635.

Standnes, D.C., Austad, T., 2000. Wettability alteration in chalk 1. Preparation of core material and oil properties. J. Pet. Sci. Eng. 28, 111–121.

Strand, S., Standnes, D.C., Austad, T., 2003. Spontaneous imbibition of aqueous surfactant solutions into neutral to oil-wet carbonate cores: effects of brine salinity and composition. Energy Fuels 17 (5), 1133–1144.

Torske, L., Skauge, A., 1992. Core wettability measurement by dynamic adsorption. Paper SPE/DOE 24167 Presented at the 8th Symposium on Enhanced Oil Recovery held in Tulsa, OK, USA, April 22–24.