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# The adsorption of polar components onto carbonate surfaces and the effect on wetting

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## ABSTRACT

Core material, whether outcrop or reservoir core material, is prepared in the laboratory to mimic reservoir conditions. For carbonate reservoirs, the initial water saturation, S<sub>wi</sub>, is usually established by using either the porous plate technique or the desiccator method. The core is then flooded with crude oil and carboxylic material, R-COO<sup>-</sup>, quantified as acid number, AN, adsorbs onto the carbonate surface and acts as anchor molecules towards the crude oil in the wetting process. The correct reservoir wetting equilibrium is obtained when the AN of the crude oil in the pores is the same as the AN in the original reservoir crude oil. The focus of this paper is to determine the volume of oil a core must be exposed to in order to achieve equilibrium in the wetting process. The volume needed to reach equilibrium in the wetting process was tested by flooding outcrop core material at  $S_{wi}=0.10$  with crude oil, AN=0.35 mgKOH/g, and measuring the change in AN at the core outlet. The tests were performed at three different temperatures, 50, 90, and 130 °C, and the flooding rate was constant, 4 PV/D. The test at 50 °C and 90 °C showed a similar response, where the test at 130 °C clearly required a lower volume of oil to establish equilibrium. A chromatographic wettability test also showed that the water wet fraction of the surface area decreased for the test at 130 °C. A new core was retested at 50 °C and restored by mild cleaning using kerosene and heptane. The restored material required an even lower volume of oil to establish the wetting equilibrium, and the water-wet area was reduced. Thus, outcrop carbonate core material needed longer exposure time to crude oil to achieve wetting equilibrium compared to that of restored core material previously exposed to the same crude oil. Furthermore, the core became even more oil-wet after restoration.

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## 1. Introduction

The initial wettability of an oil reservoir is established over millions of years by a chemical equilibrium between oil, brine and rock. In the laboratory, the aim is to prepare samples, outcrop or reservoir material, that mimic reservoir conditions to get as close to representative reservoir conditions as possible. The wetting properties dictate physical parameters such as capillary pressure, Pc, relative permeabilities  $k_{ro}$  and  $k_{rw}$  and fluid distributions. Polar, acidic and basic components in the crude oil can adsorb onto specific minerals and make the rock mixed-wet. The amount of surface-active components in the crude oil can be quantified by the acid number (AN) and the base number (BN). It can be measured and quantified by titration and has the unit mg KOH/g of oil. The relative affinity of acidic and basic material towards actual reservoir minerals varies. The AN is one of the most important parameters dictating the initial wettability of carbonate reservoirs.

http://dx.doi.org/10.1016/j.petrol.2016.08.028 0920-4105/© 2016 Elsevier B.V. All rights reserved. The oil components containing carboxylic groups, R-COOH, will have the greatest effect on wettability properties in a carbonate reservoir. When outcrop chalk cores were exposed to crude oils of increasing AN, the water wetness was drastically decreased (Standnes and Austad, 2000). Most of the carboxylic acidic material is found in the heavy end fraction of crude oil, in resins and asphaltenes. For high temperature oil reservoirs, the AN is usually much lower than the BN due to decarboxylation of the carboxylic group during geological time (Shimoyama and Johns, 1972). Laboratory experiments have verified a small increase in the water wetness of outcrop chalk samples exposed to crude oils where the BN"AN, probably due to some acid – base complex formation in the crude oil, which partly prevents the acidic material from adsorbing onto the carbonate surface (Puntervold et al., 2007a).

When analysing reservoir material, it is essential that the initial wetting is preserved, so that the core may be investigated in the most representable state. Therefore, steps are taken during core preparation to preserve the initial core wettability. Core material is often cleaned to a completely water-wet state, and the core is aged

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#### 2

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#### P.A. Hopkins et al. / Journal of Petroleum Science and Engineering **I** (**IIII**) **III**-**III**

Nomenclature		OOIP	Original oil in place			
AN BN ASTM D L Φ S <sub>wr</sub> PV S <sub>wi</sub> S <sub>orw</sub> k <sub>ro</sub> k <sub>rw</sub>	Acid Number Base number American Society for testing and materials Core Diameter Core length Core Porosity Residual water saturation Pore volume Initial water saturation Residual oil saturation after water flood Relative permeability of oil Relative permeability of water	A <sub>wet</sub> A <sub>ref</sub> VB0S TDS SW0T SW1/2T C/Co I <sub>CW</sub> AA AA <sub>T</sub>	The area between the thiocyanate and sulphate curve of a sample The area between the thiocyanate and sulphate curve of a water-wet sample Valhall brine with no sulphate Total Dissolved Salt Sea water without thiocyanate tracer Seawater that contains thiocyanate tracer Relative concentration of ion in effluent fractions New wettability index Acid Adsorption Total Acid Adsorption on the surface			

with formation water and reservoir oil to build up initial conditions (Shariatpanahi et al., 2012). It is common to clean reservoir core material with toluene followed by methanol. Toluene should remove hydrocarbons including asphaltenes and adsorbed polar components. Methanol displaces both water and toluene.

The initial water saturation is usually established either by the porous plate technique (Longeron et al., 1989) or by the desiccator method (Springer et al., 2003). Then the core, outcrop or cleaned reservoir core, is flooded with crude oil at T > 50 °C to prevent precipitation of wax. A correct equilibrium between adsorbed carboxylic material and carboxylic material in the crude oil is obtained if the AN of the crude oil in the pores is similar to the AN in the original crude oil. This is usually not obtained by just saturating the core with crude oil at initial water saturation, especially if the initial AN is low and by using outcrop core material. The questions that we ask in this paper are:

- How many pore volumes of crude oil must be flooded through a core, outcrop or cleaned reservoir core, to obtain correct chemical equilibrium between adsorbed and non-adsorbed carboxylic material?
- Is the equilibrium time sensitive to the AN of the crude oil, AN =0.35 and 0.70 mgKOH/g?
- Is the equilibrium time sensitive to the temperature, 50, 90, 130 °C?
- Is the equilibrium wetting conditions different at various temperatures, 50, 90, 130 °C?
- Will a more representative wettability be achieved by using mild cleaning, and can we validate the preservation of polar components by performing wettability tests?

Outcrop chalk cores have been flooded slowly with crude oil at residual water saturation,  $S_{wi}$ =0.10, at different temperatures, and the AN of the effluent oil was measured as a function of pore volume (PV) injected. As expected, outcrop cores not exposed to crude oil needed longer time to achieve equilibrium compared to mildly cleaned outcrop core material previously exposed to crude oil.

# 2. Experimental

## 2.1. Materials

Outcrop chalk samples from Stevns Klint, near Copenhagen, Denmark were used. The cores were drilled in the same direction from the same block and had a permeability and porosity of 1–3 mD and 45–50%, respectively. The chalk samples from Stevns Klint are very homogenous and can be considered representative of many carbonate reservoirs in the North Sea. Therefore, these chalk cores can be used as reference cores to do parametric studies on oil recovery and wettability. The cores had similar dimensions, porosity and permeability, Table 1. Keeping these conditions similar helped the experimental practice become more reproducible.

## 2.2. Brine composition

Synthetic brine, termed VB0S, that mimicked the composition in typical North Sea chalk reservoirs, was used as formation water. The brines termed SW0T and  $SW_{1/2}T$ , were used in the chromatographic wettability tests, as described previously (Strand et al., 2006). The brines were prepared with deionised water (DI) and pure salts. The compositions are given in Table 2.

#### 2.3. Oils properties

A crude oil was diluted with heptane in the volume ratio of 60/ 40, respectively. The oil had a high AN and BN, 1.8 and 0.75 mgKOH/g, and was treated with silica gel to remove polar components and filtered, AN  $\approx$  0 and BN=0.03 mg KOH/g (Zhang and Austad, 2005). By mixing the two samples, crude oils with different AN and BN could be made. **Oil A and B** were prepared by mixing the original crude oil with the modified crude oil. The oils were filtered through a 5  $\mu$ m filter, and no precipitation of asphaltenes was observed during storage. The properties of **Oil A** and **B** are listed in Table 3.

### 2.4. Analysis of acid number and base number in crude oil samples

The acid and base numbers, AN and BN, of the crude oil samples were analysed by potentiometric titration. The methods used

#### Table 1

Physical properties of outcrop chalk cores used where T4b is a subsequent experiment using the T4a core after restoration.

Core reference	T1	T2	T3	T4a	T4b	T5
L (cm) D (cm) Bulk Vol. (cm <sup>3</sup> ) Weight (100% Sat) (g) Dry weight (g) 10% saturated core weight (g) Porosity PV (cm <sup>3</sup> )	6.50 3.90 77.648 136.85 101.14 105.14 0.45 35.27	6.50 3.90 71.9198 137.63 104.63 108.06 0.46 32.9	6.48 3.80 73.49 137.92 103.73 107.28 0.46 34.088	6.21 3.74 68.22 128.56 96.78 100.08 0.46 31.69	6.21 3.74 68.22 119.79 92.28 182.50 0.40 27.43	5.87 3.80 66.57 123.60 91.49 94.82 0.48 32.01

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