CORE SURFACE ANALYSIS FOR WETTABILITY ASSESSMENT

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Abstract Rock wettability is determinant for the behaviour of a reservoir subjected to any oil recovery process. As the surface chemical composition of the mineral is indeed mostly responsible for its wetting behaviour we investigated the relation between wettability and surface chemical composition.
The examination of the surface was achieved mainly through X-ray photoelectron spectroscopy (XPS) whereas wettability determination was established through detailed interpretation of core flooding experiments and wettability index measurements.
In the first part of this paper, the procedure to restore the original wettability of a core in a laboratory is examined. The wetting state of a reservoir is often difficult to assess because it is carried out on reservoir cores which have generally been contaminated by the various chemicals during drilling.
Berea cores have been used to assess the validity of the restoration procedure of polluted cores, by measuring the organic carbon content of the mineral surface layer. Starting from a virgin clean core, wettability was changed by aging with crude oil. The surface was studied before and after cleaning. The results show that the surface organic carbon content is well correlated with the wetting behaviour of the material defined by petrophysical measurements.
In the second part of the paper, we present the use of the surface analysis for the characterization of the intrinsic wettability of a given core. The aim was to establish the correlation between surface composition and the wetting characteristics of the mineral. A variety of cores has been investigated, which include Berea samples as well as reservoir cores.
For very different cases, ranging from totally water to intermediate wet, a relation between surface chemical composition (mainly organic carbon concentration) and wettability has been investigated. Results concerning sandstone and carbonate originating from oil producing reservoirs are presented. We discuss the validity of the correlation for predicting core wettability.

INTRODUCTION

Numerous *in situ* reactions due to water/rock and oil/rock interactions, such as asphaltene precipitation, may induce wettability modifications (Keurentje et al., 1990 ; Ghaicha et al., 1988 ; Crocker and Marchin, 1988). Additionally, successive reservoir flooding often lead to wettability shift towards oil wet systems, due to asphaltene and polar fraction adsorption, and may be considered as a major problem as regards to oil recovery processing (Batycky, 1980 ; Cuiec et al., 1990 ; Mac Clure, 1989). To carry out this last application and also predict the rate of production, rapid determination of a significant quantity related to rock wettability is actually required but remains a task to achieve.

Classical petrophysical methods used for wettability assessment involve core flooding or centrifuge capillary pressure experiments carried out at laboratory scale (Li and Wardlaw, 1986 ; Huang and Holm, 1986). Among them, the Amott test is a well known technique to characterize wettability of core samples. However, the experimental procedure is laborious and its reliability is limited. One reason for this limitation is that the wettability index is directly calculated in accordance with capillary pressure measurements, which have an inherent limitation with respect to the maximum value of the capillary pressure that can be reached. Additionally, it is also recognized that the centrifuge technique often has been used in such a way that the data obtained do not correspond to equilibrium conditions (Melrose, 1990).

Several recent papers address the importance of surface analysis to investigate water/oil wetting phenomena on reservoir rocks (Dekany et al., $1986_{a,b}$, Mitchell et al., 1990). Though applications of the XPS technique in the oil industry are scarce, a successful attempt was made recently to relate rock surface composition and the wettability index (Mitchell et al., 1990). It was shown that the carbon content of core samples can be correlated to the wettability index, hence the resulting relationship can be used as a calibration curve for further studies.

Following this approach, this work investigates the possible correlation between core surface composition and wettability indices, both determined after ageing with crude oil from the same reservoir.

METHODS

Principles of X-RAY Photoelectron Spectroscopy (XPS)

In the processes leading to the acquisition of an XPS spectrum, the sample is irradiated with soft X-rays, sufficiently energetic to cause photoemission of electrons from atoms present in the sample. Photoelectrons generated are collected and passed through an electron energy analyser and detector (see Figure 1). The binding energy of a given core electron is characteristic of the element concerned, thus it is possible to identify the elements present in the sample.

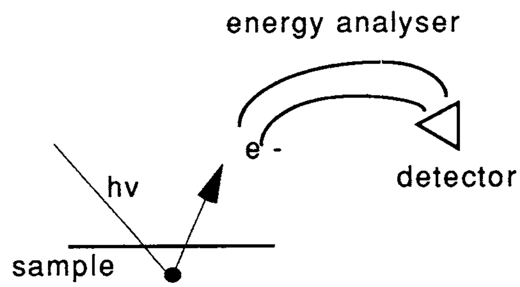

FIGURE 1 Principle of acquisition of an XPS spectrum.

All elements except H and He are detected. Quantitative analysis is then obtained from measurement of the relative intensities of the photoemission from each of the elements present. The parameters taken into account for quantitative analysis are the cross section for photoionization, the inelastic free path of the characteristic XPS electrons and the analyzer transmission versus kinetic energy of the photoelectrons. In the work reported here, the concentration of the elements is quoted in atomic percentage (at%) derived from the high resolution spectrum (Sutherland, 1989).

The sensitivity of XPS spectroscopy depends on the detected elements. In the case of reservoir rock samples we assumed a sensitivity of 0.3 at% for N and Cl, 0.2 at% for K, Ca and Mg and 0.1 at% for Fe and F. We used a 600x1000 μm^2 X-ray spot, which represents a compromise between high resolution and integration of several rock grains. Nevertheless, because of rock heterogeneity, measurements were repeated on the sample at different locations to provide averaged values.

Core Sample Cleaning

Two cleaning procedures were used on different purposes. In the "modified cleaning procedure", cores were flooded by toluene and isopropanol, to reduce the amount of residual oil present in the sample, prior to adequate XPS measurements. The "standard cleaning procedure" involved a sequence of solvent flooding with brine, isopropanol, isopropanol/toluene and toluene, at room temperature. It was used in an attempt to restore the initial wettability of the samples. Both procedures were followed by nitrogen gas injection to dry the samples.

The respective effect of these cleaning procedures will be discussed in the "conclusion" part of the paper.

Dynamic Displacements

Wettability can be determined by waterflooding experiments since in an oil-wet system breakthrough occurs early and diphasic production is important. Additional oil can be produced when increasing flow-rate, due to end effect. Comparison between experiments with and without wettability restoration gives, by ageing with crude oil, a clear indication of wettability. In some cases wettability was confirmed by measuring Amott's wettability index. After the first drainage, initial water saturation is reached, the sample is set in water for spontaneous imbibition and then in a centrifuge for forced imbibition. Water index is the ratio of oil produced by spontaneous imbibition divided by total produced oil. Then the sample is set in oil for the second drainage. Oil index is the ratio of water produced by spontaneous imbibition divided by total produced water (spontaneous and forced imbibition). The wettability index is the difference between water and oil indices. It varies from +1 (water wet) to -1 (oil wet).

Core Sample Selection

For water flooding experiments we used full size cores of 3 or 4 inches in diameter and 8 inches long. Amott test was performed on 1 in. long and 1 in. in diameter plugs. Three types of reservoir rock samples were available: reservoir 1 is a carbonate, reservoir 2 is a sandstone, also Berea sandstone was used.

Spectra Comparison - Organic Carbon Content Calculation

The XPS technique allows for the determination of the carbon content from organic and mineral origin. For instance, air-polluted calcite samples give two different carbon peaks on the spectrum (see Figure 2).

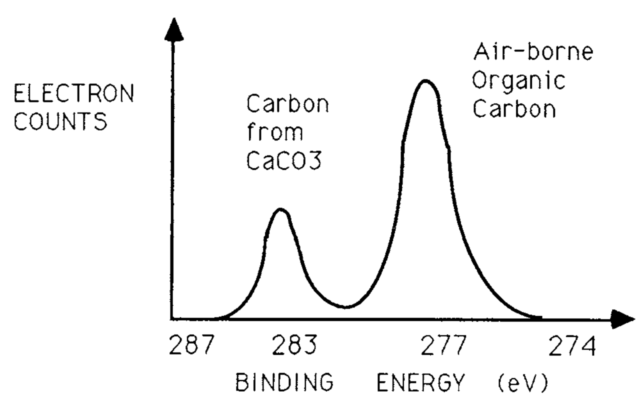

FIGURE 2 XPS spectra of air-polluted calcite sample.

Although the sample had never been brought into contact with oil and was broken and left in the room's atmosphere for few minutes, the air-borne organic carbon level was about 18 at%.

For Berea as well as for reservoir 2 samples, we have checked that mineral carbon level was negligible. However, for both samples, air-borne organic carbon is assumed to be already present at a level between 10 to 20 at%. Since the depth of detection of the XPS technique is about 3 to 5nm, the surface composition is in fact averaged through approximately 10 monolayers. Therefore, the deposited carbon layer hinders somewhat the detection of elements initially present in the mineral matrix.

In the case of a calcite sample, this masking effect does not change the ratio of elements between them. From our previous results we have shown that the thickness of a hypothetically homogeneous carbon layer is directly proportional to the level of carbon in the range between 20 to 50 at% (100 at% corresponding to an infinite thickness). These calculations were performed using an self-absorption formula and the absolute signal of C1s photoelectrons.

Consequently, XPS is not an absolute quantitative method to estimate rock sample composition and spectra comparison must be performed with caution. In the following section the masking effect has not been taken into account when comparing spectra, due to uncertainty concerning the correction procedure to apply on experimental data.

RESULTS AND DISCUSSION

Preliminary experiments were carried out to verify that surface composition of clean Berea plugs remained unchanged after standard cleaning.

To determine which elements could be then related to wettability changes, we compared spectra obtained before and after ageing of Berea plugs with reservoir 1 crude oil, which is known to induce wettability alteration. Indeed, all core samples showed the presence of oxygen, carbon, silicon, nitrogen, aluminum, potassium and magnesium. Additionally, calcium, baryum and iron were present. These experiments allowed the investigation of the wettability restoration procedure previously described (standard cleaning procedure).

The second part of the study dealt with the determination of surface composition and wettability criteria (core flooding or Amott's wetting index) of selected core samples originating from two different reservoirs.

Preliminary Experiments

To examine possible alteration of the mineral matrix due to standard cleaning, surface composition was determined before and after the cleaning of two Berea plugs. Measurements reported in Table 1 indicated that standard cleaning does not induce any significant change of the mineral matrix composition.

TABLE 1 Spectra comparison between Berea core samples before and after standard cleaning.

Element	Binding energy (eV)	at% "virgin" core	at% cleaned core
Aluminum	74.5	6.5	6.07
Silicon	103.5	26.3	27.7
Carbon	285.1	10.5	10.1
Potasium	293.7	1.8	1.5
Oxygen	532.1	53.8	54.1

Additionally, no remaining trace of cleaning solvents was detected. However, although great care was taken to avoid contaminating the samples, adsorption of air-borne organic carbon was unavoidable to a background level in the range between 10 to 20%, depending on the sample.

Effectiveness of the Restoration Procedure

To examine the effectiveness of the restoration procedure of polluted Berea core samples, we carried out XPS measurements on "clean" and polluted plugs subsequently submitted to standard cleaning.

Starting from a clean plug, wettability was changed by ageing with crude oil from reservoir 1, which is known to induce asphaltenes deposition on the mineral matrix. Plugs were stored for three weeks at constant pressure and temperature (80°C). Initially, wettability index of Berea sandstone was +0.85 and after ageing with crude oil it changed to 0, i.e., from water to intermediate wetting. This change is usually attributed to asphaltene and polar fractions adsorption. Additionally, crude oil from reservoir 1 is known to produce increasing oil wetting with ageing time. Surface composition was determined, by means of XPS measurements, before ageing and after ageing followed by the standard cleaning procedure. The results are listed in Table 2.

TABLE 2 Surface composition (atomic %) determined, by means of XPS measurements, before ageing and after ageing followed by the standard cleaning procedure.

Element	$\overline{at\%}$* Clean plugs	$\overline{at\%}$* Treated plugs	variation
Aluminum	5.9	4.3	⇓
Silicon	19.7	20	–
Carbon	19.4	28.7	⇑
Potassium	1.6	0.9	⇓
Magnesium	0.5	< 0.2	⇓
Calcium	0.4	< 0.2	–
Nitrogen	0.8	< 0.3	⇓
Oxygen	51.4	45.4	⇓
Fluor	0.7	< 0.2	⇓
Iron	< 0.1	< 0.1	–
Baryum	< 0.1	0.6	⇑

* Mean value of the surface concentration obtained for 3 core samples

The $\overline{at\%}$ difference between clean and treated plugs is reported in Figure 3. As expected, the organic carbon content increase due to ageing with oil represents the highest variation measured.

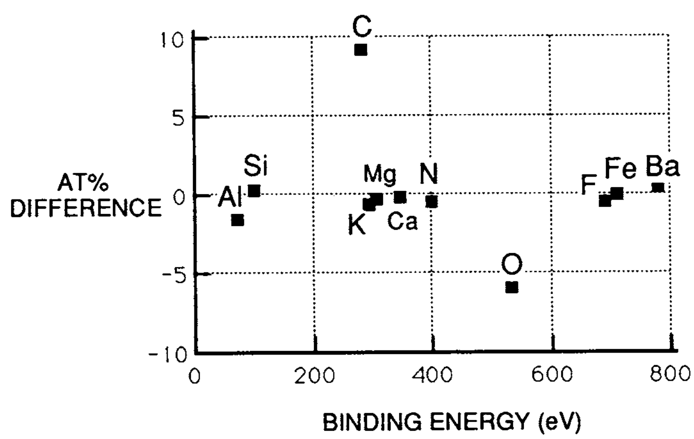

FIGURE 3 Differences between spectra obtained before ageing and after ageing followed by the standard cleaning procedure (Berea cores).

From these results it appears clearly that the standard cleaning procedure did not fully restore the initial core surface composition. It can be conjectured that this modification is representative of a change in wettability although no Amott test was performed to demonstrate it.

Influence of Irreducible Water Saturation (S_{wi}) on Wetting Behaviour of Cores aged with Crude Oil.

The aim was to investigate the influence of S_{wi} on surface composition of reservoir 1 (carbonate) core samples having aged for three weeks with crude oil from the same reservoir. Wettability was restored on two different cores: one with an initial water saturation (S_{wi}) and the other one without S_{wi}. XPS measurements indicated a significant increase in the organic carbon content when ageing without S_{wi}: 37% of organic carbon was initially measured and increased up to 46% after ageing and modified cleaning prior to XPS analysis. In contrast, no significant variation of the organic carbon content was measured when ageing was performed with S_{wi}. However, for much longer ageing time, i.e., at the geological time scale, this result could be totally different.

Determination of Surface Composition and Wettability Index on Reservoir 1 and 2 Core Samples aged with Crude Oil.

Reservoir 2 results: figure 4 is a schematic illustrating of reservoir 2 sampling locations. Three plugs and two crude oil were used for the study. Two plugs were obtained from the well n°1 in two different field layers, US (1-Upper Sleipner) and MS (1-Middle Sleipner), and one from the well n°2 in the US layer (2-US). Oil samples originated from both layers, as represented in Figure 4.

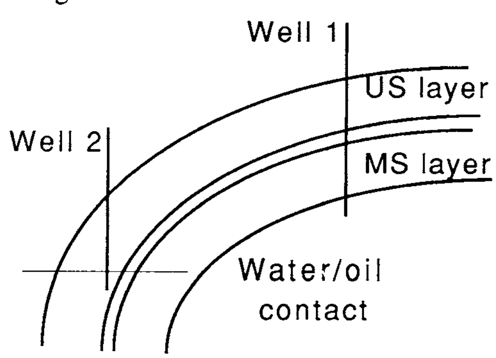

FIGURE 4 Core sampling locations on reservoir 2.

Core flooding experiments and XPS measurements were carried out on the set of plugs either cleaned (standard cleaning), or aged with US or MS oil and subsequently cleaned (modified cleaning). XPS measurements were repeated several times when variability exceeded 5% ; results are reported in Table 3.

TABLE 3 Global analysis on Reservoir 2 (sandstone).

ageing		*Cores* 1-MS	1-US	2-US
None (cleaned cores)	**C at%**[a]	32.3	40.4	28.6
	Data N.[b]	2	14	5
	Sigma[c]	1.5	2.4	1.7
	Sor[d]	35	-	38
	P. Test[e]	O.W.	O.W.	-
ageing with MS oil + Swi		47.2	43.8	52.2
		3	7	3
		0.5	4	2.1
		30	17-22	-
		O.W.	O.W.	-
ageing with US oil + Swi		40.5	48.2	16.9
		6	9	7
		5	2.4	1.4
		-	36	37
		-	O.W.	W.W.

[a]Organic carbon content, [b]Number of measurements, [c]Standard deviation on measurements, [d]Residual oil saturation, [e]Petrophysical test (core flooding), [f]Oil Wet or Water Wet criterion.

The value 16.9 obtained on samples 2-US aged with US oil was surprisingly low and may be due to inappropriate cleaning. From available core flooding experiments, ageing with MS oil rather than with US oil seems to induce a preferential wetting for oil. In addition, comparing the carbon at% of preferentially oil wet and water wet systems, it can be noticed that oil wet systems have also the highest levels of carbon, with no exception. This provides support for the correlation between the high organic carbon content and the preferential wetting for oil.

Reservoir 1 (carbonated) results: three couples of core samples located in the water zone of reservoir 1 were used for the study. A first one was analyzed and tested as received, a "modified cleaning" was applied to the second, finally the third was aged with crude oil from reservoir 1 and cleaned (modified cleaning). In an attempt to quantify the correlation previously defined, wettability index (Amott's test) and surface composition were both determined on each plug, which provided a comparison between the two methods. Results are reported in Table 4.

TABLE 4 Water, Oil and overall Wetting Indices, and organic carbon concentration determined on reservoir 1 plugs.

Treatment	Plug N°	Carbon (at%)	$W I_W$	$W I_o$	W I
none	1	46.4-44.7-49.3	0.11	0	0.11
	2	31.3-25.1-34.5	0.17	-0.04	0.13
modified cleaning	3	25.3-31	0.43	0	0.43
	4	46.3-35.9-45.6	0.15	0	0.15
ageing and modified cleaning	5	32.7-31.6	0.20	-0.11	0.09
	6	34.7-42.5	0.11	0	0.11

It can be noticed that most of the wettability indices determined in these experiments, except one, are very close to 0.1. The differences are too small to indicate significant wettability modifications due to the different treatments. Conversely samples' history seems more relevant since they originated from the water zone and hence, were characterized by an intermediate wettability. The carbon composition is plotted against the wettability index (overall) in Figure 5.

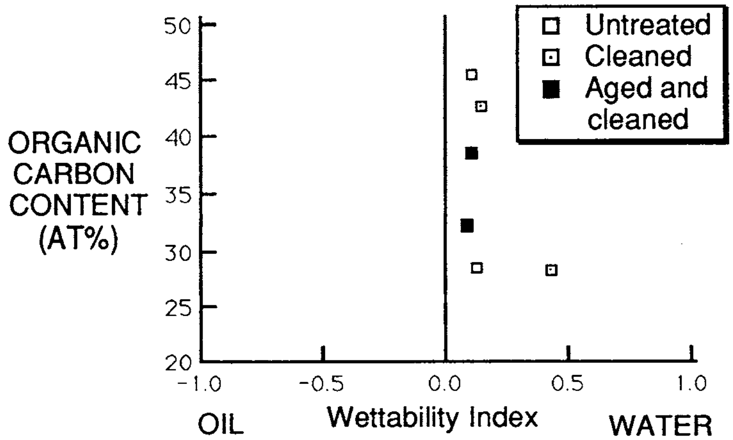

FIGURE 5 Amott wetting indices Vs. organic carbon levels determined on reservoir 1 core samples.

A similar shape for this plot has been found by Mitchell (Mitchell, 1990). It appears that intermediate or mixed wettability, according to Amott test, is observed in a range of surface carbon concentration, typically between 30 to 45 at%. Further experiments are required to provide data especially in the domains of pronounced water wettability and oil wettability. In any case, it seems that these behaviours should correspond to surface carbon concentration respectively lower than 30% and higher than 45%, which is in fair agreement with the results reported in table 3. Besides this, it seems that the "modified cleaning procedure" performed before XPS analysis might be responsible for removal of heavy and polar components adsorbed on mineral surfaces, since toluene is considered as an efficient solvent. If so, the organic carbon content of samples having being aged and subsequently cleaned (modified cleaning) before XPS analysis was reduced, which hindered the comparison with "clean" (standard cleaning) samples. In any cases, for future work, "mild" cleaning should be prefered.

CONCLUSIONS

In the first step of this study the effectiveness of the wettability restoration procedure has been examined. In the second step, the possible correlation between the carbon content of the surface of core samples and the wettability index has been investigated. Our main results are summarized below:

(i) The "standard cleaning procedure", which is actually the usual one performed on "as received" reservoir cores, provides only a partial restoration of polluted cores.

(ii) Despite heterogeneity between core samples, the organic carbon content seems to be a meaningful quantity as regards to rock wettability assessment.

(iii) The correlation between wettability index and the organic carbon content needs to be further investigated. Mixed wettability behaviour is observed for a range of carbon surface concentration.

(iv) As a result of unavoidable "masking effects", caution should be taken when comparing XPS spectra for quantitative purpose.

Further studies are in progress to develop a similar correlation from measurements performed on model systems, i.e., Berea core samples and a simplified oil. In these conditions, masking effects will be taken into account when comparing the organic carbon content of clean and treated plugs.

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