Fluid distribution in kaolinite- or illite-bearing cores. Cryo-SEM observations versus bulk measurements.

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Abstract: Cryo-SEM has become a powerful tool to show the distribution of oil and brine in cores, which may be highly influenced by wettability properties. Previous studies have shown special affinity between kaolinite and oil after aging. The present work clarifies the behavior of illite or kaolinite-bearing cores, and compares with the measurements made at the plug scale ("bulk" measurements). After aging, fibrous illite has still no affinity for oil, kaolinite has an affinity for oil, but platy illite behaves more like kaolinite. However, a minimal quantity of kaolinite-like surfaces is needed to change the wettability of the bulk sample towards oil-wetness. The "bulk" wettability depends thus, although not linearly, on the nature, morphology, amount and distribution of clay, but cannot ignore phenomena occurring at larger scales such as trapping. A qualitative agreement is found between the amount of oil and brine, depending on the state of saturation, and the bulk measurements (wettability index, Swi, Sor).

Introduction

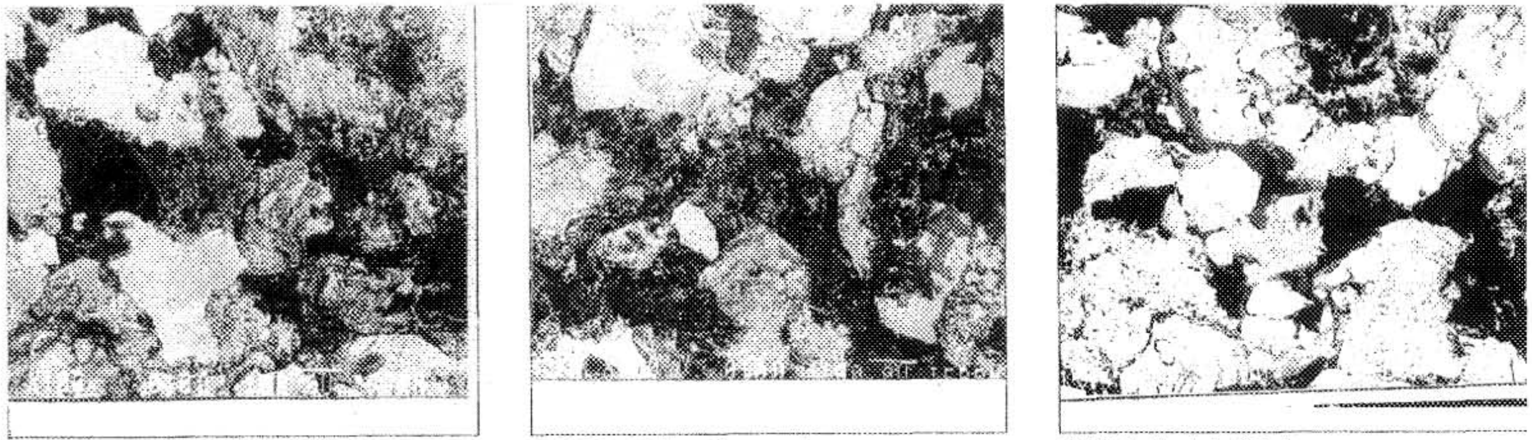
Cryo-Scanning Electron Microscopy has become, in the last few years, a powerful tool to visualise the distribution of fluids, namely oil and brine, in cores, related to the geometry and composition of the pore walls, i. e. of the framework grains and of the clays within the porous space (Fassi-Fihri et al, 1992). Qualitative information on this distribution is likely to support interpretation of the chemical affinities, and of their evolution as a function of experimental processes, and thus to provide insight on the behaviour of fluids in reservoirs. Comparison with wettability indexes measured at the plug scale ("bulk" measurements) allows the influence of microscopic versus macroscopic scales to the overall process of oil recovery to be checked.

Previous studies have shown special affinity between kaolinite and oil after aging (Fassi-Fihri et al, 1992, Rueslåtten et al, 1994, Jerauld et al, 1994). The present work describes the behavior of cores containing diagenetic clays of various composition and morphologies, either illite or kaolinite, and compares the observations with bulk measurements. Besides the evident effects of geometry on capillary effects, and of aging on evolution of fluid distribution, we show that the nature, shape and relative spatial distribution of the clays influence the local distribution of fluids. Comparison with bulk data (wettability index, Sor, Swi) show the need to take into account phenomena occurring at higher scale, as trapping.

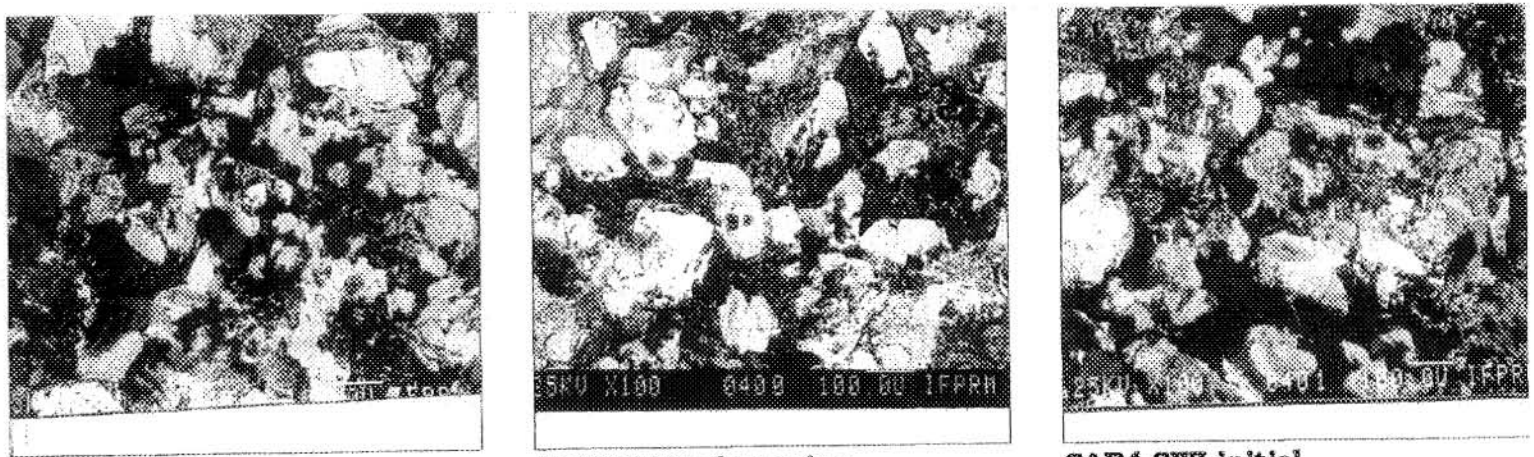
Experimental

The samples were chosen in order to be rich in one particular authigenic clay, within the Brent formation of a North Sea field; all come from the oil zone. Two of them come from the same well, at about 3000 m depth, the upper one, CAR4, in the Tarbert, the second one CAR3 in the Ness, about 50 m below. The other two come from wells in the same area, at a depth about 3600 m, one in the Tarbert, CAR1, the other in the Etive, CAR2. The samples were analysed for quantitative mineralogical and chemical composition (X-ray diffraction, Scanning Electron Microscopy, microprobe analysis, elemental analysis). After cleaning, Amott-IFP wettability tests were performed according

Plate I. Backscattered electron images of the samples, CAR1 and CAR4,
Scale bar is 100 µm.
from left to right, Sor "immediate", Sor after aging, Swi "immediate"
oil is colored in red in Sor images, brine is colored in blue in Swi images.



CAR1 SOR initial **CAR1 SOR after aging** **CAR1 Swi initial**



CAR4 SOR initial **CAR4 SOR after aging** **CAR4 SWI initial**

to well established procedures. This part of the work has already been described (Durand et al, 1994).

Companion samples (ca 0.5 cm diameter) were saturated in brine, then brought by centrifugation in reservoir stock tank oil (resp. in brine) to the following saturation states:

- "immediate Swi", by centrifuging the brine saturated sample in crude oil without aging: this features the infilling of the reservoir, and is likely to show the effect of sterical hindrance (low permeability)
- "immediate Sor", by centrifuging in brine without aging, immediately after the "immediate Swi": this is a theoretical state, likely to show the effect of spontaneous wettability effects, and also of capillary and trapping effects
- "aged Swi", by aging the samples prepared as above in crude oil during one month, which can be compared to the state of the actual reservoir. The aging time is supposed to be long enough (Cuiec et al., 1991) to allow possible changes in wettability.
- "Sor after aging", by centrifuging in brine the "aged Swi" samples, i.e. after one month aging in crude oil: this features a state after production.

Cryo-SEM was performed on a JEOL 35 CF, fitted with a Hexland/Oxford CT 1000A. The sample is dropped very quickly in a slush of nitrogen at about 80 K, then transferred under a vacuum in a preparation chamber where it is fractured and coated with chromium to ensure electron conductivity. The sample is then observed in the microscope at the same temperature: this procedure allows visualisation of the fluids without further displacement. Images are taken in backscattered electrons mode (BSE), and elemental analysis is performed by Energy Dispersive Spectrometry (EDS). BSE give a chemical contrast: the higher the mean atomic number Z, i.e. the "heavier" the sample in the analysed zone, the "brighter", i.e. the higher level of grey, the image; on the opposite, the "lighter" the sample, the "darker" the image. Combination of BSE and analysis allows identification and location of minerals and fluids.

For interpretation, care must be taken to the scales of resolution:

- backscattered electrons, in the operating conditions used here, have a lateral resolution in the micrometer range.
- X-rays are emitted from a volume of several μm^3.

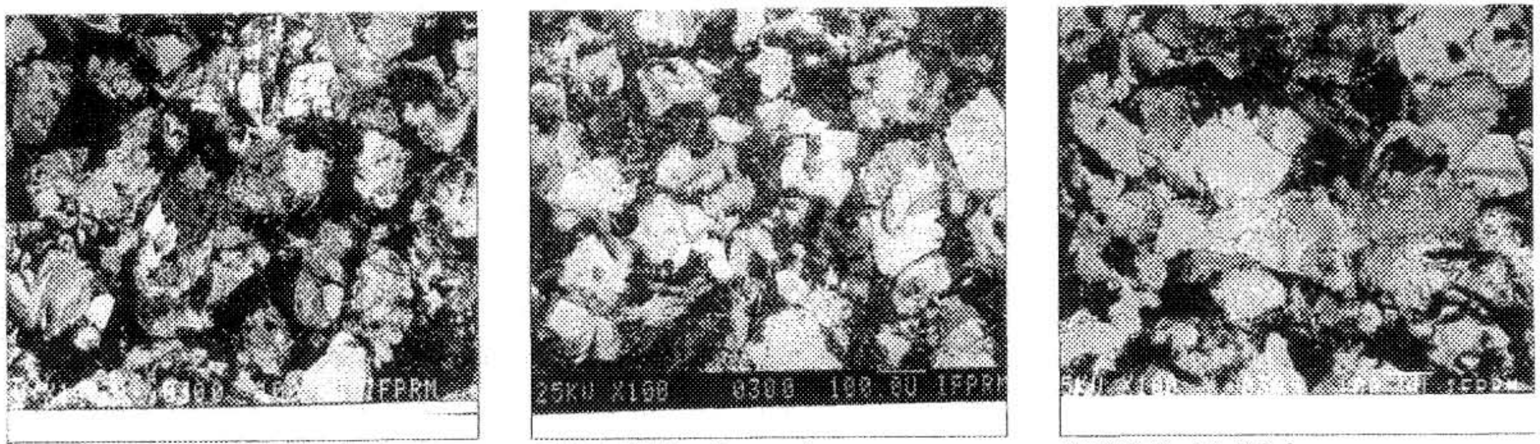
In these conditions, it is difficult to avoid analysis of several particles together when they are themselves micrometric, as clays. It is however impossible to reach the adsorbed layer, which is in the nm range, and is only accessible with specific techniques like X-ray Photoelectron Spectroscopy (Durand and Beccat, 1996).

Oil, mainly composed of carbon and hydrogen, is the "lighter" component, thus the darker in BSE; brine, composed of oxygen and hydrogen, is somewhat "heavier", thus dark grey, and its presence is confirmed by the analysis of chlorine. Quartz and potassium feldspars are easy to distinguish both by their size and shape and their grey level, but albite is easily confused with quartz without chemical analysis. Clays are more difficult to identify, because they are small, and their shape may be difficult to observe when they are in mixture with the "fluids" at the scale of investigation, i.e. some μm^3. Elemental analysis is then necessary to confirm the distribution of phases. New devices allow rapid mapping of elements by EDS: this will improve the soundness of interpretation.

Waiting for such devices, the results have been presented by "coloring" the images, to integrate all the information. On the "Sor" images, water is present everywhere, in the porous space, dark, except in the places where oil has been featured in red, while on the "Swi" images, oil is present everywhere except in the places where the brine has been featured in blue.

Plate II. Backscattered electron images of the samples, CAR2 and CAR3
Scale bar is 100 μm.
from left to right, Sor "immediate", Sor after aging, Swi "immediate"
oil is colored in red in Sor images, brine is colored in blue in Swi images.

CAR2 SOR initial **CAR2 SOR after aging** **CAR2 SWI initial**



CAR3 SOR initial **CAR3 SOR after aging** **CAR3 Swi initial**

Results

The main results are shown on plates I and II, respectively for the states reached for the more and the less "oil-wet" samples.

- CAR1: oil is difficult to identify because of the presence of pyrite, which gives a bright signal disturbing the usual grey values, but the absence of chlorine among illite is interpreted as the presence of oil. At Sor, before aging, water is detected everywhere, near quartz and illite, while oil is more related to zones where the clay induces restrictions. After aging, there seems to be more oil visible, and it is closer to the clay in the porous space; water is well seen near quartz, as "thick films", pores can be filled with water as well as with oil, water globules can be seen within an oil zone. At immediate Swi, water is scarce, seen only near quartz, never in contact with clay, while oil is everywhere, in contact with quartz or with clay. At Swi after aging (not shown), no water can be detected.

- CAR4: at Sor before aging, water is seen in "clean" pores, i.e. without clays, oil is found in the porous space, in the vicinity of kaolinite as well as in large pores, inducing an apparent high oil saturation; at Sor after aging, the distribution of fluids is very similar, with whatever more oil visible, more clearly related to clay, but also to feldspars, with in some place a water globule within oil. Water is found everywhere in large pores. At immediate Swi, water is very scarce, in small globules within oil, or in-between two quartz grains, oil is detected everywhere, in large pores as well as in clays. At Swi after aging (not shown), no water is detected.

- For CAR2, at Sor before aging, water is seen everywhere, nearly no oil is visible, and it appears more clearly after aging, retained in dense clay clusters, while water is in the pores or also in the vicinity of clays. At Swi, water is clearly seen associated to dense clay clusters, with oil in free pores, and the same distribution is found at Swi after aging .

- The last sample, CAR3, is the most "water-wet". At Sor before aging, water is everywhere, in large pores or in clays, oil is scarce, in small globules, near quartz and clays. After aging, there is some more oil, but the distribution is about the same. At immediate Swi, oil can be found everywhere, while water is scarce, related to the clay clusters. Water is no more seen at Swi after aging (not shown).

Discussion

Presenting the results, we did not indicate the nature of clay. All the images show that there is a geometrical effect, for either fluid: the residual fluid is always better retained in clays, for capillary reasons, if it has been put in.

Effect of aging is also evident. Oil is more clearly related to the clays at Sor after aging than before. Even the water related to clays at initial Swi is no more, or little, seen after aging.

The mineralogical and petrophysical characteristics and the saturation states achieved in displacement experiments are recalled in Tables I and II, giving also the wettability indexes (Durand et al, 1994). Including these data, the following remarks can be made.

- CAR3 sample shows that even a "water-wet" sample, (= before aging) can retain some oil, and this oil is precisely located in the kaolinite clusters, in accordance with the preceding observations (Fassi-Fihri et al., 1992). We have thus a capillary effect, before aging, and this is enhanced by a chemical effect, after aging. But the quantity of kaolinite is not high enough to make the sample "oil-wet"

Table I Mineralogical and petrophysical characteristics of the samples (after Durand et al.,1994)

		CAR1	CAR4	CAR2	CAR3
porosity	% vol	15.9	22.6	21.1	16.6
permeability	mD	50	560	2	340
			kaolinite	dickite	kaol/dick
Kaolinite	wt-%	0	7,8	3,5	3,1
		platy	detrital	fibrous	mixed-layer
Illite	wt-%	13.8	0.8	7.8	<1
Quartz	wt-%	83.7	67.4	85.7	92.5
K-Feldspars	wt-%	0	16.8	0	3.3
surf area	µm-1	0.017	0.028	0.03	0.02
surf clays	µm-1	0.036	0.048	0.046	0.03

- CAR4 contains more kaolinite, and this seems sufficient to overcome a kind of percolation threshold, and to induce an oil-wet, or a mixed-wet behavior for the bulk sample. In this case, one can imagine "continuous" pathways, i.e. allowing percolation, either hydrophilic or hydrophobic, in the sample, has had already been suggested (Fassi-Fihri et al, 1992).

- The behavior of CAR2 is more complex. The sample contains both dickite and fibrous illite, which makes a kind of felt preventing immediate contact between dickite and the invading fluid. The permeability is very low (about 1 mD). Due to this low permeability, the infillings are difficult, either by oil or by water. But it can be seen that, at Sor, aging gives oil a chance to reach dickite, so that oil can be detected after aging, but not before. Meanwhile, water is retained in the illite clusters at immediate Swi, and remains even after aging. There is thus an hydrophilic behavior of the fibrous illite, opposite to the hydrophobic trend of the kaolinite. The quantity of dickite is about the same as in CAR3, and insufficient to make a continuous path.

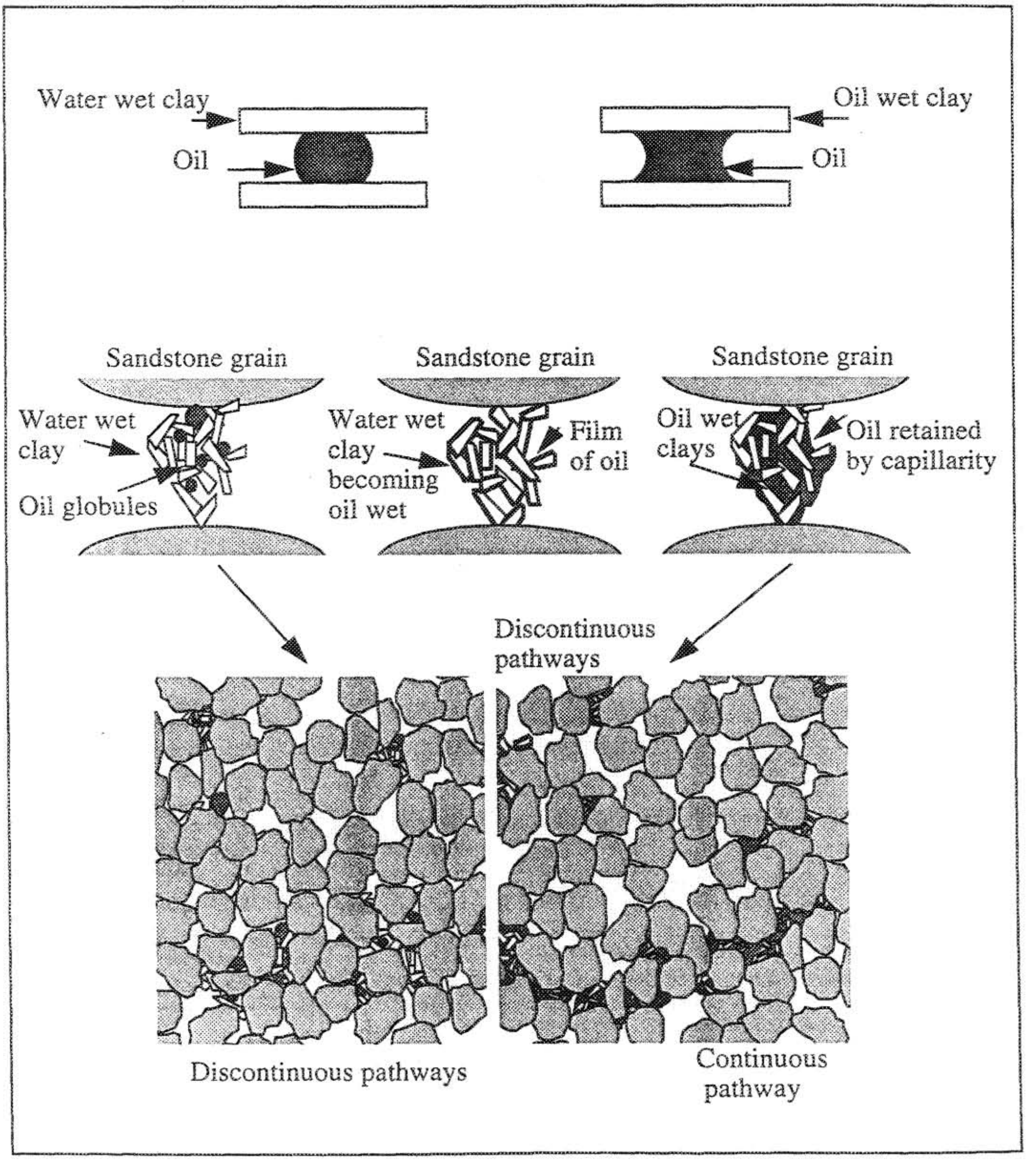
- The most surprising case is that of CAR1, which behaves as the most oil-wet, besides the fact that the clay is pure illite, at the X-ray diffraction scale. This point was already under discussion, for displacement experiments results. The oil-wet behavior is confirmed at the mm scale. If it was due to poor cleaning, or to a pollution, this would be very well spread! The other hypothesis is that the surface of this platy illite is, because of its diagenetic formation conditions, more like kaolinite surfaces, i.e. involves an Al-OH layer. Existence of surface composition different from the bulk has already been suggested by Pevear et al. (1991). The morphology of this illite, appearing as a "negative" of the vermicular kaolinite which is found in many places (e.g.. CAR4) allows to think that the illitization of the kaolinite can keep such layers. In this case, illite is abundant enough to induce an oil-wet behavior for the sample.

All these observations suggest a schematic drawing of the behavior of the clay-bearing samples (see plate III):

- the "oil-wet prone" clay surface, e.g. kaolinite, either coating the framework grains, or dispersed in the porous space, adsorbs oil components at the surface of the particles, immediately or after some time of contact. This occurs at the nanometric

Plate III

Sketches showing the correlation between the wettability behavior at the microscopic (μm) and the bulk (cm) scales



level, cannot be seen in SEM, but modifies the wettability, so that oil seems to "stick" to the minerals,

- between the particles, oil is trapped by capillary forces that may be huge: the distance between particles may be in the submicrometric range; clusters are thus created, made of clay and oil, which have a repelling effect on water,
- water cannot reach the mineral surface, and behaves as globules.

The reverse happens with water on "water-wet prone" clay surface, e.g. illite

There is thus a co-operating effect of adsorption and capillary forces, from the nm scale to the µm scale, which is made visible by cryo-SEM. At the mm scale and higher, globules may be trapped, depending on the geometry of the porous space. Further studies on flow of oil or brine, e.g. on relative permeabilities, should take into account the modifications of the size and shape of the pores in which the liquids flow, induced by the clustering of clay and associated oil.

Table II: Arnott-IFP test values for wettability index, and saturation values obtained during the tests (after Durand et al, 1994)

	CAR1	CAR4	CAR2	CAR3
Wettability Index, with Soltrol	-0.61	-0.24	+0.07	+1
WI, with reservoir oil, after aging in reservoir oil	-1	-1	-0.32	+0.57
immediate Swi	0.28	0.23	0.58	0.32
immediate Sor	0.52	0.42	n.d.	0.47
Sor after aging	0.41	0.38	0.11	0.36

Comparisons with the saturation values obtained by displacement (see table II) can be only qualitative. Indeed, the latter result from 3D experiments, at the cm scale, while images are 2D, and the number examined is not high enough to reach representativity (Durand, 1994). Another point is that the effect of aging is to spread the oil on specific mineral surfaces, so that the location and "shape" of the oil is modified, and stereology cannot allow extrapolation from 2D to 3D with shapes that can change from spherical globules to plane films. This may explain that the Sor saturation values found by displacement were not higher after aging than before.

The influence of location of samples in the oil field, versus depth, burial, oil infilling time, has not yet been studied: more samples are needed to find trends in that direction.

Conclusions

Cryo-SEM brings information which is at the intermediate scale between the surface techniques, which "see" only a few nm depth below the surface, and the bulk measurements. The technique gives access to the distribution of oil and water, in relation with the mineral interface, from the micrometric to the millimetric scale. Minerals play an evident role in this distribution, due not only to their chemical composition, but also to their shape, size and clustering, either in the porous space, or as coatings. The spatial distribution of the "fluids" versus the minerals show that after aging:

- when there is little dickite, e.g. CAR3 and CAR2, it retains oil, but does not change the bulk wettability: samples remain rather water-wet,
- when there is more kaolinite, e.g. CAR4, the sample can become oil-wet,

So, both quantity and morphology are likely to play a role:

- when there is fibrous illite, e.g. CAR2, it remains hydrophilic; when the illite coats dickite, it prevents or delays the contact between oil and dickite; the sample undergoes both influences, which in this case are insufficient to shift the wettability towards oil-wetness,
- when platy illite is generated from kaolinite, e.g. CAR1, it keeps a kaolinite-like surface, and the sample behaves as oil-wet when the clay quantity is high enough.

So, the "bulk" wettability depends on the nature of clays, which has already been a subject of numerous studies, but also on the morphology, amount and distribution of clays, which are still to investigate more thoroughly, in regard to their influence on fluid flow. Because of the low number of well documented studies, the relationships cannot be expressed more precisely, and additional work is needed to better evaluate the weight of all parameters.

Qualitative agreement is found between the amounts of oil and brine, depending on the state of saturation, and the bulk measurements (wettability index, Swi, Sor). Looking for more quantitative agreement will require information in 3 dimensions, and at centimetric scale at least: other techniques will be necessary.

Up to now, the location of the samples in the oil field, burial, time of oil infilling, cannot be related to the wettability observations on so few samples: more samples are needed to find any trends.

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