

1-2.2 WETTABILITY OF RESERVOIR ROCKS

1-2.2.1 Definition and measurement of intermediate wettability

A) Introduction: specificity of the situation in porous environment

In Section 1-1.2 we described capillary pressures in the case of “perfect wettability”, i.e. where one of the fluids displays a clearly marked affinity for the solid, homogeneously across the entire wall of the porous space. The simplicity of this case lies in the fact that only the geometry of the porous space needs to be considered to understand capillary phenomena

(the only important parameters of the fluids are their surface tensions τ_s and, possibly, the wettability angles θ). By using the “normalisation” parameter $\tau_s \cos \theta$, we were able, for a given rock, to process equally well the cases water/oil, water/gas or mercury/vapour.

In nature, this favourable situation is only found in very specific cases, such as that of a rock which has never been in contact with anything but water (or brine) and which is invaded by liquid or gaseous hydrocarbons (secondary migration § 1-1.2.6, p. 102). This is also true near the surface, in vadose zone, where the porous space contains both water and air. But even in this case, it is not uncommon to observe states (at least transient) of non-water wettability (see Fig. 1-1.27, p. 53), under the effect of biological phenomena such as microorganisms covering the porous walls.

Petroleum is a mixture of a large number of chemical compounds, including molecules exhibiting a special affinity for solids. This affinity may be more or less marked for certain minerals. We can therefore see that when a porous rock is invaded by oil, deposition of these molecules may have a significant impact on the nature of the relations between the solid and the fluids, in other words, by definition, the wettability. The example we give for the oil reservoirs may be almost identical to the situation in surface geology (hydrogeology, pedology), for example in the event of deliberate or accidental injection of chemical products.

Consequently, the capillary behaviour described in Section 1-1.2 must be reconsidered. If these phenomena led to a clear wettability reversal, i.e. if the rock became as oil-wet as it was previously water-wet, then we could simply apply the principles of Section 1-1.2, exchanging the fluids. This type of wettability reversal can be carried out in the laboratory by depositing silane molecules, for example, on the entire porous wall. In nature, however, this is very rarely the case. The modification undergone by the solid/fluid interface is heterogeneous and, together with the fact that the porous wall is sometimes very rough, it induces phenomena which are extremely difficult to quantify accurately at microscopic scale. This explains why the definition of wettability when studying geological materials can only be based on a “phenomenological” approach.

To make it easy for non-specialists to understand the wettability phenomena observed in rocks, a few elementary but useful remarks must be made. The first, and most important, is that *the diagnosis (and quantification) of petrophysical wettability is not the result of a “rigorous physical analysis”* based, for example, on the interactions of electrostatic forces, *but the result of a particular experiment*. Several types of experiment (see below) giving different results can be performed. It is therefore not surprising that the wettability state of a rock varies depending on the test conducted.

The second remark is that, unlike porosity or single-phase permeability, *wettability is not an intrinsic characteristic of the rock, but a variable state of the interface between the mineral solid and the fluids* contained in the porosity. When defining this state, the fluids and the history of their relation with the solid are as important as the solid itself.

Lastly, it should be added that, in everyday language, oil wettability may not be the reciprocal of water wettability. “Oil wettability” is often the observation deduced from a particular experiment discussed below. Although the same may be true of “water wettability”, the result is often actually more conclusive, being based on a number of observations. It would often be more appropriate to speak of a trend towards oil wettability.

The debate between “innate” and “acquired” is a recurrent feature in some fields of biology. The same applies in petrophysics with the problem of wettability since it is never easy to distinguish clearly between the causes intrinsically related to the nature of the porous space: geometry, mineralogy (innate) and those related to the nature of the fluids and the particular history of their coexistence (acquired). The debate is of much more practical importance than it seems, since only the “innate” parameters can be practically extrapolated by using geology methods.

For detailed information on wettability, readers can refer to the bibliographic work of Anderson [1986-87].

B) Phenomenological approach: wettability as the result of an experiment

a) Terminology remark on “capillary pressure, drainage and imbibition”

Before describing the two main methods used to measure wettability, some of the terminology must be clarified:

In Section 1-1.2, in line with convention, capillary pressure has been defined as being the difference in pressure across the interface between the non-wetting fluid and the wetting fluid, in other words the excess pressure required to “force the capillary barrier”. This definition is meaningless if we want to define which is the wetting fluid. Nevertheless, this term is always used in the experiments. Capillary pressure (sometimes called effective or differential pressure) is equal to the algebraic difference between the pressure in oil (or gas) and in water. This pressure can be positive (basic case of water-wet situation) but it can be negative if the pressure in water is actually higher than in the second fluid.

Similarly, the wettability assumptions concerning drainage and imbibition must be clarified. An objective definition of drainage is as follows: operation leading to a reduction in water saturation, imbibition is the opposite phenomenon (increase in water saturation), the adjective “spontaneous” refers to the return to a minimum value of (effective) capillary pressure and “forced” when the absolute (not algebraic) value of (effective) capillary pressure increases under the effect of external forces (e.g. centrifuge).

b) The USBM method

The USBM (US Bureau of Mines) method [Donaldson *et al.*, 1969] is based on the observation that in order to increase the saturation in non-wetting fluid of a porous space, energy must be put into the system (conversely, an increase in wetting fluid releases energy). This observation is clear in case of strong wettability. On a drainage capillary pressure curve (Fig. 1-1.29, p. 57), the area under the curve corresponds to the integral of the product of a volume (saturation) by a pressure (capillary), in other words to work.

This observation can be generalised by measuring the energy required (area between the curve and the x-axis) to increase the saturation of each fluid successively and estimate that the ratio of these areas is an indication of wettability.

We will consider the following sequence of experiments (Fig.1-2.30) conducted, for example, in a centrifuge:

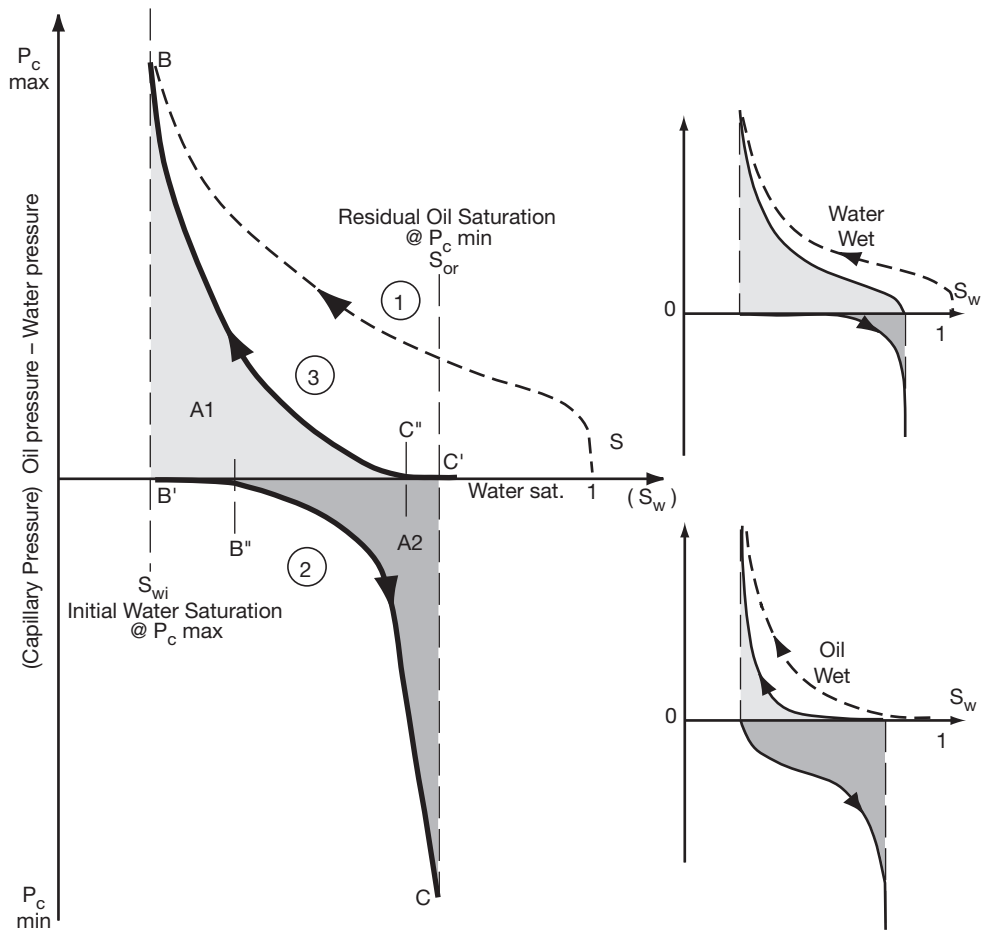


Figure 1-2.30 Schematic diagram of the USBM method for determining wettability

A sample originally totally saturated with water (point S, Fig. 1-2.30) is immersed in oil in a centrifuge cup where it is subjected to increasing accelerations, up to very high values. The sample undergoes a “first drainage” (phase 1 on Figure 1-2.30; see also Figure 1-1.34, p. 65) bringing it into a state of irreducible water saturation (point B on Figure 1-2.30). Stopping the centrifuge does not change this state, even though there is no longer any differential pressure since the sample is completely surrounded by oil (point B' on Figure 1-2.30).

The measurement as such starts at this stage. The sample is transferred into a cup filled with water and centrifuged again. We can apply the same calculation methods as with a “traditional” drainage ($\Delta P = \Delta \rho \gamma h$), but since the water phase is now the continuous phase outside the sample the sign of $\Delta \rho$ must be inverted. The pressure in the water is greater than that in the oil and we are moving along branch No. 2 on Figure 1-2.30 (“forced” imbibition under the effect of “negative” capillary pressures). Note that the “negative” capillary

pressures are only observed from point B” on Figure 1-2.30 since the saturation interval B' – B" corresponds to a spontaneous imbibition phase.

Under very high accelerations, from the saturation corresponding to point C, the oil mobility becomes zero and we reach the residual oil saturation state, a generalisation of the notion of residual saturation discussed in paragraph § 1-2.3.3, p. 188.

Stopping the centrifuge (point C') does not change the saturation (see above). The sample once again placed in a cup filled with oil undergoes a second forced drainage phase (curve 3) which could possibly be preceded by spontaneous drainage (from point C' to point C").

The area (A1) between this second drainage and the x-axis corresponds to the energy required for the oil to penetrate into the system. Equally, the area A2 between curve 2 and the x-axis corresponds to the energy required for the water to penetrate. If the medium is water-wet, this energy will be very low (ideally $A_2 = 0$) and conversely for A1 if it is oil-wet. In the USBM method, wettability is characterised by the logarithm of the area ratio [$W_{\text{USBM}} = \log(A_1/A_2)$]. If $W_{\text{USBM}} > 0$, the medium is preferentially water-wet, if $W_{\text{USBM}} < 0$, the medium is preferentially oil-wet. For example, a medium with USBM index of about 1 is strongly water-wet.

c) Amott's method

Amott's method [Amott, 1959; Cuiec, 1975] is based on estimating the relative importance of the fluid fractions displaceable during spontaneous and forced operations (imbibition/drainage).

After first being totally saturated with water, a sample is brought into a state of “irreducible” water saturation by a long period of oil flooding (or possibly by centrifuging) until no more water is produced.

- In a first step, this sample is placed in water where it undergoes spontaneous imbibition, displacing a volume V_a of oil (Figure 1-2.31a). The sample then undergoes forced imbibition (waterflooding or centrifuging in “water” environment) displacing an additional volume of oil V_b . V_a is the volume of oil displaced spontaneously by the water and $V_a + V_b$ the total volume of displaceable oil (spontaneous and forced). The index I_w is defined: $I_w = V_a / (V_a + V_b)$. If the medium is perfectly water-wet, we obtain the situation of § 1-1.2.2D, p. 59, and after the spontaneous imbibition phase, the residual oil is totally trapped by the capillary forces, forced displacement by water will produce no oil, $V_b = 0$ and $I_w = 1$.
- The second step consists in carrying out the reverse operation with oil: the sample in “irreducible/residual” oil saturation state (note once again the terminology ambiguity as soon as the wettability state is no longer fixed) is immersed in oil (Figure 1-2.31c), drainage spontaneously displaces the volume of water V_c . Forced drainage (flooding or centrifuging) produces an additional volume V_d . We can therefore calculate an index $I_o = V_c / (V_c + V_d)$. We will once again use the example of perfect water wettability from § 1-1.2. Spontaneous drainage will not displace any fluid, so $V_c = 0$ and $I_o = 0$.

We can define a unique wettability parameter $W_{\text{IA}} = I_w - I_o$ of value between -1 and 1 . A value of 1 corresponds to the case of perfect water wettability, as mentioned previously.

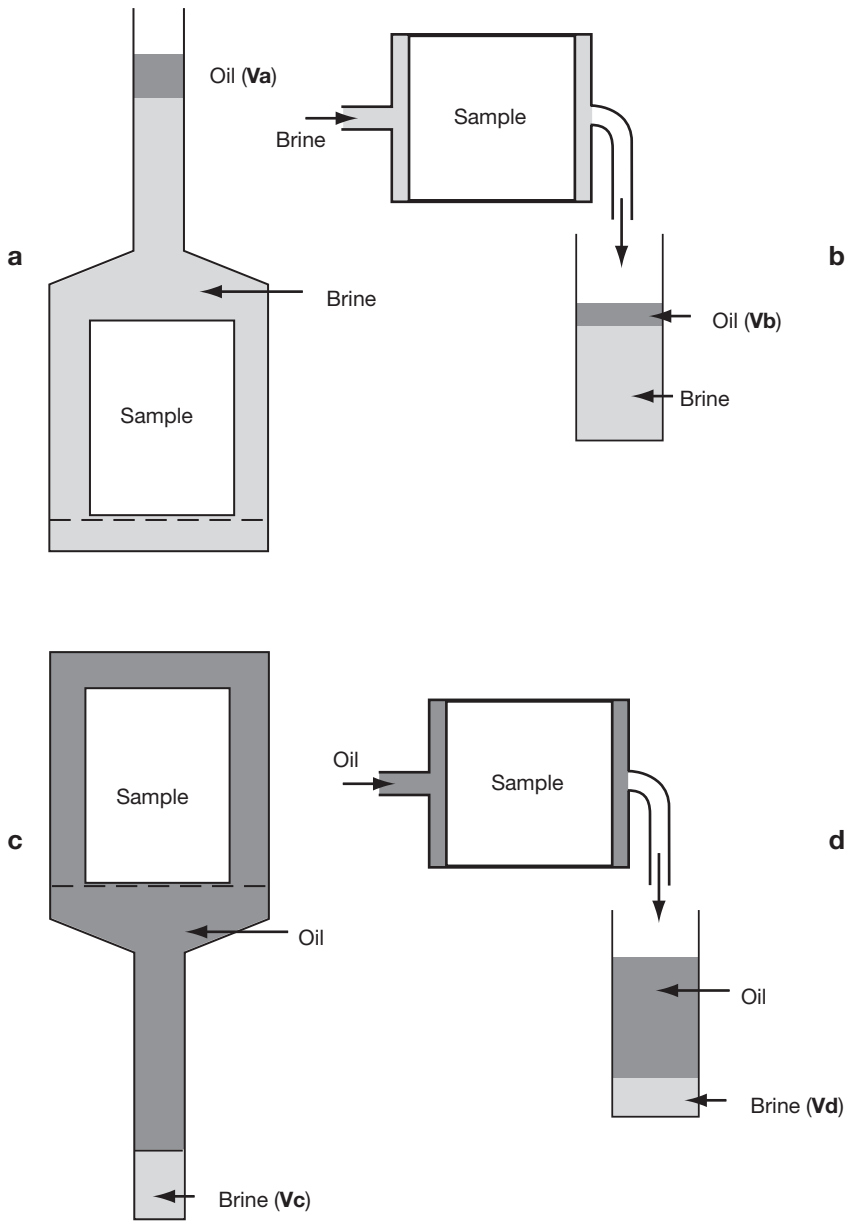


Figure 1-2.31 Schematic diagram of Amott's method for determining wettability

Inversely, a value of -1 corresponds to a case of perfect oil wettability, a situation which is relatively rare in nature. The low values, corresponding to the states for which both fluids are displaced spontaneously in similar proportions, represent the intermediate wettability states.

C) Microscopic approach: direct observation of fluid positions

By definition, wettability is the relative affinity of a fluid for a solid surface. For example, the photographs of Figure 1-1.27, p. 53, clearly show that the glass surface is not mercury-wet. Cryomicroscopy techniques (§ 2-2.2.1, p. 334) can be used to make similar observations in porous media, up to the scale of the micrometre. We can therefore consider mapping wettability at pore scale [Robin, 2001]. At least theoretically therefore, we can calculate the percentage of the surface of the porous space wettable to a particular liquid and also observe the relations between wettability and the type of this surface according to mineralogical and/or roughness criteria.

Note, however, that the observation concerns the relative location of the fluids and that wettability is deduced from this location. This observation has major consequences if we consider that the wettability state can be modified by transferring molecules from a liquid to the solid surface without there necessarily being any fluid movement and therefore any variation in the location of the various phases, during the ageing of the “restored” samples (see below) for example.

This direct observation method must therefore be restricted to the cases where fluids in chemical equilibria have been displaced shortly before the observation. For example, assuming that pressurised cores could be sampled in a pristine reservoir, the method would be poorly adapted to drawing conclusions on wettability. In contrast, still taking the same assumption of core protection, the method would be quite suitable for investigating a reservoir which had already produced oil, i.e. where the remobilisation of fluids led to an “update” of the relative phase positions.

D) Remark on drag hysteresis

We mentioned drag hysteresis when describing the capillary pressure curves in case of strong wettability: the phenomenon of “drag hysteresis” which characterises the shift observed between the second drainage curve and the imbibition curve (not to be confused with the phenomenon of “trap hysteresis” between the first and second drainage). Although not specific to intermediate wettability, it is likely that this phenomenon may become even more important in this case. The simplest explanation is that the wettability angle varies with the direction of displacement of the non-wetting fluid. This rather general phenomenon seems to be significantly amplified when the solid surface is very rough [Morrow 1970], which is frequently the case in geological porous media.

1-2.2.2 Wettability of reservoir rocks

Wettability plays a very important role in the oil recovery processes in reservoirs since it has a direct impact on the proportion of oil recovered and on the kinetics of this recovery. We will discuss this point in the “End Points” paragraph (§ 1-2.3.3, p. 186). The obvious practical importance of wettability has led to numerous research studies. Nonetheless, it is still difficult to obtain an accurate picture of wettability in reservoirs since numerous difficulties are encountered when trying to upscale results from laboratory to reservoir. As

we have already pointed out, this is due to the fact that wettability is a state which may turn out to be highly unsteady.

Figure 1-2.32 shows examples of reservoir rock wettability evolution, over the course of geological time and depending on the laboratory sampling and processing conditions.

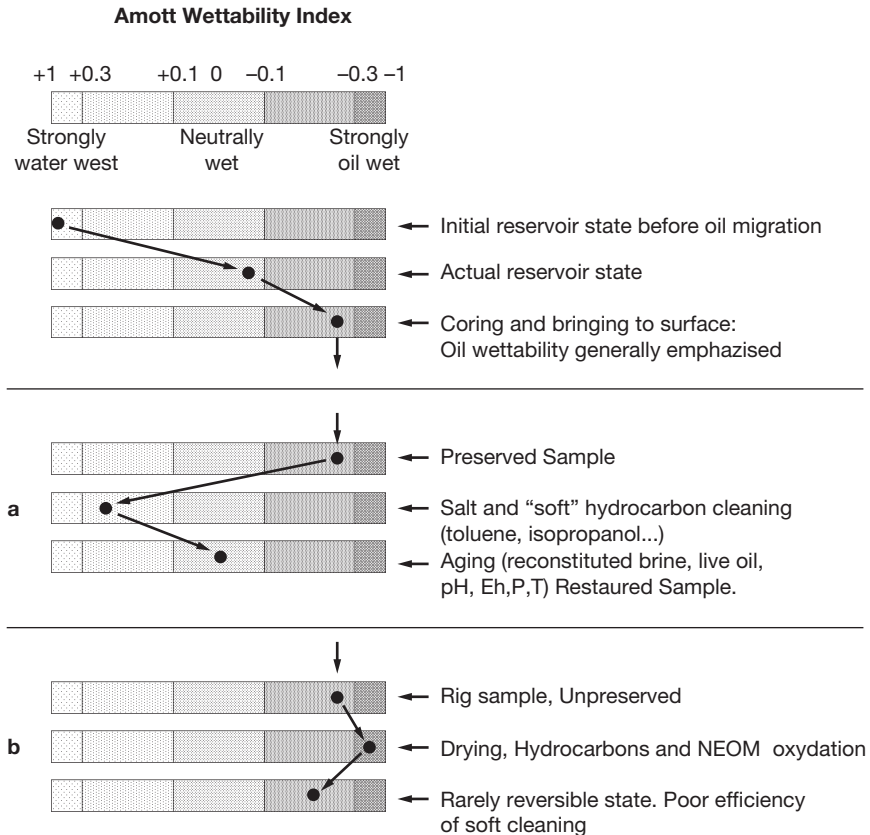


Figure 1-2.32 Diagrammatic example of reservoir rock wettability evolution in case of a preserved sample (a) and an unpreserved sample (b)

A) Difficulty of estimating wettability *in situ*, alteration of core wettability

One major difficulty is that no method is currently available for direct estimation of wettability *in situ*. This data cannot be estimated by any type of log analysis or well test. We might expect that, in the long term, measurements deduced for example from nuclear magnetic resonance (§ 1-3.3.2, p. 258) may provide a means of approximating this notion.

The only “experimental” method to verify the assumption made on wettability lies in the coherence between the production history and the modelling calculation based on wettability data (history matching). This proof which comes *a posteriori* is debatable since numerous other causes may be put forward.

We must therefore rely on the results obtained on cores. Unfortunately, numerous factors may disturb the wettability state of a rock sample between the reservoir and the laboratory. During the coring and storage operations, the rock is subjected to three main types of process which may have a serious impact on wettability.

- *Flushing by drilling mud.* This is one of the most obvious cases of wettability alteration. The muds contain additives (e.g. soda) which may have a drastic effect. Techniques are available, however, to control the degree of invasion, especially by using markers. By adding small quantities of deuterium, tritium or special salt to the mud, the depth of penetration of the filtrate inside the core can be measured on small core samples. It is therefore possible to demonstrate that if coring is carried out with a suitable mud pressure, the core centre is often free from any contamination.
- *Deposition of organic molecules precipitated during depressurisation.* When the core barrel is brought up to the surface, the pressure drops suddenly and the dissolved gas returns to gaseous phase, suddenly “flushing out” the liquids remaining in the core. More importantly, it may also induce the precipitation of high molecular weight molecules (e.g. asphaltene) which have a major impact on wettability. This phenomenon can be limited by carefully controlling the speed at which the core barrel is brought to the surface. The ideal solution would be to have a pressurised core barrel, in order to bring up the core without any pressure variations, or at least without lowering the pressure below the bubble point. Since this aspect represents a major financial stake (more for preservation of saturations than wettabilities) technical solutions have been proposed while still, apparently, remaining outside the scope of routine applications.
- *Drying and alteration during storage and transport.* If left untreated, the core characteristics are soon modified. It is easy to remedy this situation, however. As soon as they are removed from the core barrel, “native” samples are placed in sealed containers, refrigerated or sometimes even frozen. They therefore reach the laboratory under optimum conditions.

B) “Restoring” wettability in the laboratory

The modifications suffered by the cores are such that in order to relate the laboratory results to the conditions prevailing in the reservoir, the state of the samples considered must be clearly specified for the various petrophysical measurements. Three types of sample will be used:

- **Preserved samples.** These samples are carefully protected on leaving the core barrel. Their hydrocarbon content has been significantly modified (degassing) but hopefully, the connate water has been preserved. The qualifier “connate” designates the water always present in hydrocarbon reservoir rocks, at least in very small proportions (§ 1-1.2.2.C, p. 58, § 1-2.3.3, p. 186) (this term may be becoming obsolete). However, it is difficult to machine the core fragments without disturbing them too much and very difficult to remove the residual hydrocarbons without touching the connate water, making the experiments much more complicated. In practice therefore, samples in preserved state are rarely used, except for measuring water saturation in the reservoir (S_{wi}).

- **Cleaned samples.** There are two quite different types of cleaning:
 - + Soft cleaning. The hydrocarbons and brine are removed from the samples received in the laboratory in true “preserved” state by “soft” cleaning, using mixtures such as alcohol/toluene which do not attack the very long chain organic molecules. We might expect that the samples cleaned in this way retain on the surface of the porous medium a large proportion of the polar organic molecules brought by the oil and deposited over geological times. Studies on the “wettability/geology” relation can be conducted on this type of sample, assuming that some of their “acquired” wettability has been preserved (see below).
 - + Hard cleaning. This type of cleaning seems to be more rarely used. Unlike the previous case, the samples are washed very vigorously using special solvent mixtures. The aim is to remove all the organic molecules to create a perfect water-wet state (assumed initial state).
- **Restored samples.** The sample is then returned to its “initial” water saturation state with oil from the reservoir (preferably “live oil” recombined with its gas content). The saturated sample then undergoes temperature ageing for several weeks. An experimental approach based on wettability measurement (see above) at different times indicates that a stable wettability state is reached after a “certain time” (a few weeks?). The wettability assumed to exist in the reservoir is therefore restored. This method is extremely practical for laboratory experiments since it can be used to obtain samples close to the most “likely” wettability state. However, under no circumstances does it provide an indication of wettability *in situ*. This reserve must be borne in mind to avoid any misunderstanding or confusion.

C) Geological causes of wettability variations

The main difficulty when studying wettability is due to the fact that it is directly related to the surface condition of the wall of the porous space which is itself the result of interaction between the minerals forming the rock and some molecules brought by the hydrocarbons (oil fields) or produced by the microorganisms (soil, rock outcrops). When considering the geological causes of wettability variations, we must therefore consider the distinction between “innate” and “acquired”.

a) Characteristics specific to the porous medium

Amongst the characteristics specific to the porous space, we will mention two which may have a significant impact on wettability:

- The mineralogical nature of the constituents may govern the wettability directly by speeding (or slowing down) the adsorption of polar molecules. Calcite, for example, has been considered as being particularly favourable to these phenomena, which would explain the oil wettability trend of limestone rocks. Similarly, some clay minerals (kaolinite) are considered to be more oil-wet. In actual fact, this point is not as clear as it would appear *a priori*, since in the absence of precise physical measurements, it may be difficult to accurately determine the effect of the mineralogy.

- The roughness may also play an important role. The effect of roughness was mentioned with respect to the capillary pressure hysteresis. It seems likely that it has a direct impact on wettability, for example through its control on the “irreducible” water layer. The roughness of the pore walls may vary considerably. Two contrasting examples of roughness, observed using epoxy pore casts (§ 2-2.1.3, p. 331) are illustrated on Figure 1-2.33. The roughness parameter is difficult to quantify absolutely (numerous microscopic analysis would have to be made on images of the type shown on Figure 1-2.33). However, since the roughness is directly related to the nature of the

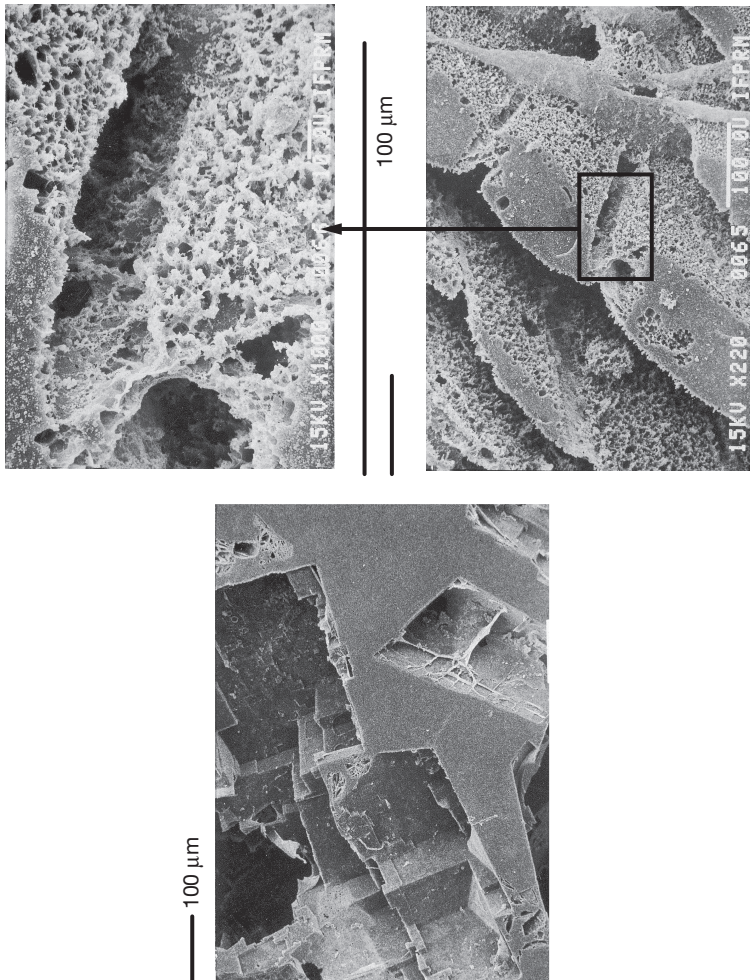


Figure 1-2.33 Examples of roughness on pore walls observed using the epoxy pore cast method (pore cast, see § 2-2.1.3)

- Inner wall of foraminifers, high roughness.
- Dolomite crystal faces, zero roughness.

constituents, it is likely that qualitative conclusions based on a petrological analysis of the roughness could be obtained relatively quickly. In limestone rocks, roughness is probably directly related to the nature of the allochems and especially the bioclasts. In sandstones, it is likely that type of clay covering the pore walls plays the main role. This could possibly represent a better way of accounting for wettability variations depending on the geological context.

b) Geological history: condition and duration of the oil-rock contact

This effect of geological history has been clearly demonstrated by Hamon [2000] who shows the wettability variations of reservoir rocks with respect to their structural positions. The important parameter is the distance to the water level. Since secondary migration (§ 1-1.2.6A, p. 102) takes place mainly under the floor of the caprock, a reservoir level fills from top to bottom and the higher the zone above the water level, the longer it has remained in contact with hydrocarbons. Figure 1-2.34 drawn from data of G. Hamon shows that the oil-wettability (wettability measured according to a method derived from Amott) of the rock increases with the distance from the water level.

We will make a methodological comment which although apparently obvious has serious consequences. Making this type of observation involves the use of samples which have suffered the least perturbation possible (i.e. soft cleaning) and whose “acquired” characteristics have not been erased by extremely thorough cleaning of the porous media walls, after which there should be nothing left to see. What is the situation, however, concerning the true representativeness of core analysis measurements routinely taken on “hard cleaned” samples? This is a typical example of the contradictions which are not always easy to resolve in these wettability studies.

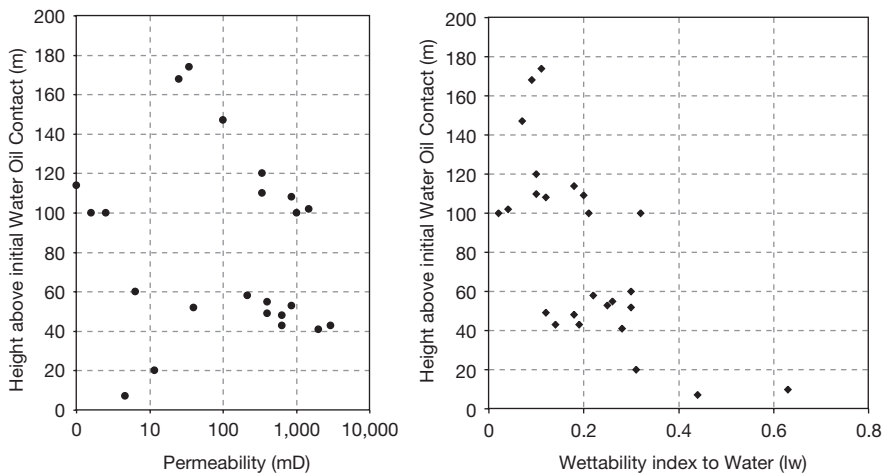


Figure 1-2.34 Evolution of oil wettability against the distance from the oil-water contact. Sandstone reservoir. Wettability index measured using a method derived from Amott, samples subjected to “soft” cleaning then restoring. Experimental values of G. Hamon [2000]. The relation permeability/distance from the water level indicates no special relation between these two parameters.