12. W. G. Anderson, J. Pet. Technol. October:1125–1144 (1986).
13. G. J. Hirasaki, Wettability: Fundamentals and Surface Forces, SPE/DOE Paper 17367 presented at the SPE/DOE Enhanced Oil Recovery Symposium, Tulsa, Okla., April 17–20, 1988.
14. N. E. Burke, R. D. Hobbs, and S. F. Kashou, Measurement and Modeling of Asphaltene Precipitation from Live Reservoir Fluid Systems, SPE Paper 18273 presented at the 63rd Annual Technical Conference and Exhibition, Houston, Tex., October 2–5, 1988.
15. J. H. Hansen, A. Fredenslund, K. S. Pedersen and H. P. Ronningsen, AICHE J. 34:1937–1942 (1988).
16. S. W. Yeh, Chevron Oil Field Research Company, personal communication. La Habra, CA 1989.
17. J. B. Auman, A Laboratory Evaluation of Core Preservation Materials, SPE Formation Evaluation 4, March 1989, pp. 53–55.
18. P. K. Hunt and S. L. Cobb, Core Preservation with a Laminated Heat-Sealed Package, SPE Formation Evaluation 3, December 1988, pp. 691–695.
19. D. B. Lerner, Chevron Oil Field Research Company, personal communication. La Habra, CA 1988.
20. P. L. Gant and W. G. Anderson, Core Cleaning for the Restoration of Native Wettability, SPE Paper 14875 presented at the Rocky Mountain Regional Meeting of the Society of Petroleum Engineers, Billings, Mont., May 19–21, 1986.
21. B. F. Swanson, J. Pet. Technol. August:1459–1464 (1980).
22. F. G. McCaffery, J. Can. Pet. Technol. July–September:26–32 (1972).
23. F. Gm McCaffery, R. W. Wunderlich, and R. P. Cartwright, Laboratory and Simulation Studies of Oil Displacement Behavior Due to Bottomwater Drive, SPE Paper 17959 presented at the Middle East Oil Technical Conference and Exhibition, Manama, Bahrain, March 11–14, 1989.
24. D. J. Wendel, W. G. Anderson, and J. D. Meyers, Restored State Core Analysis for the Hutton Reservoir, SPE Formation Evaluation, December 1987, pp. 509–517.
25. F. H. L. Wang, Effect of Wettability Alteration on Water/Oil Relative Permeability, Dispersion, and Flowable Saturation in Porous Media, SPE Paper 15019 presented at the Permian Basin Oil And Gas Recovery Conference of the Society of Petroleum Engineers, Midland, Tex., March 13–14, 1986.

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Evaluation of Reservoir Wettability and Its Effect on Oil Recovery

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I. INTRODUCTION

To recover oil contained in petroleum reservoirs, waterflooding, sometimes with "improved" water, is widely used. Understanding the phenomena occurring during waterflooding of a porous medium containing reservoir fluids (brine and crude oil) is thus extremely important. Research has long since shown that oil recovery during waterflooding depends on numerous parameters, among which are pore geometry, fluid distribution, saturation, saturation history, and oil/water viscosity ratio [1]. This is why it is always strongly recommended that laboratory experiments of oil displacement by water be performed using the reservoir rock and reservoir fluids, while respecting the initial saturation and the temperature and pressure conditions of the reservoir.

The wettability of the rock is related to the affinity of its surface for water and/or oil. Surface properties affect oil displacement by water (quantity displaced and how displacement proceeds) because they determine fluid distribution in the pores. Consequently, it is important not only to respect pore geometry by using a sample of the reservoir rock in question, but also to see that this sample has surface properties that are representative of those existing in the reservoir. The quality of production forecasts determined by numerical simulation models depends to a large extent on the representativeness of the measurements made in the laboratory.

The first part of this chapter reviews methods of evaluating wettability. Then the influence of this parameter on the behavior of rock/oil/brine systems during oil displacement by water is examined in greater detail. A review is then made of the problems that arise in obtaining reservoir-rock samples that are as representative as possible with regard to their surface properties. This is done either by preserving the original surface state or by restoration. The last part of the chapter deals with results concerning the evaluation of reservoir-rock wettability.

II. WETTABILITY EVALUATION METHODS

A. Definition

The wettability of a solid surface can be defined in several ways. It can first be defined quantitatively on the basis of thermodynamic considerations. In this case, the wettability of a solid by a liquid is the "variation in free Gibbs energy caused by the contact between a surface unit of a solid and a liquid, assuming that the contact with air has not varied" [2]. A comparison of the wettability values obtained for different liquids with regard to a given solid is then a way of predicting whether the displacement of one liquid by another is possible for the solid considered. This definition can be used for making a quantitative evaluation of ideal systems, that is, pure and immiscible liquids and a homogeneous solid. For actual and often complex systems (solid/fluid 1/fluid 2), another definition is generally used. It is "the relative preference of that surface to be covered by one of the fluids under consideration" [3].

B. Evaluation Methods

Numerous methods have been proposed for evaluating the wettability of a solid surface with regard to a fluid or a fluid system (see reviews in refs. 4–6).

1. Methods Based on the Thermodynamic Definition of Wetting

The thermodynamic definition of wetting relates to physicochemical reaction caused by intermolecular forces of attraction [2]. Wettability, designated by γ_m, thus represents the energy lost by the system during the wetting of a solid by a liquid, with

$$\gamma_m = -\left(\frac{\partial G}{\partial s}\right)_{T,P}$$

in which G is the free Gibbs energy, T the temperature, P the pressure, and s the surface of the solid.

If $(\partial G/\partial s)_{T,P} < 0$, the reaction is spontaneous, and wettability γ_m is positive.

This quantity can also be written

$$\gamma_m = \gamma_{SV} - \gamma_{SL}$$

in which γ_{SL} is the free surface energy of the solid/liquid interface and γ_{SV} is the free surface energy of the solid/vapor interface.

When there is a contact angle θ, we have Young's equation (Fig. 1):

$$\gamma_{SV} - \gamma_{SL} = \gamma_{LV} \cos\theta$$

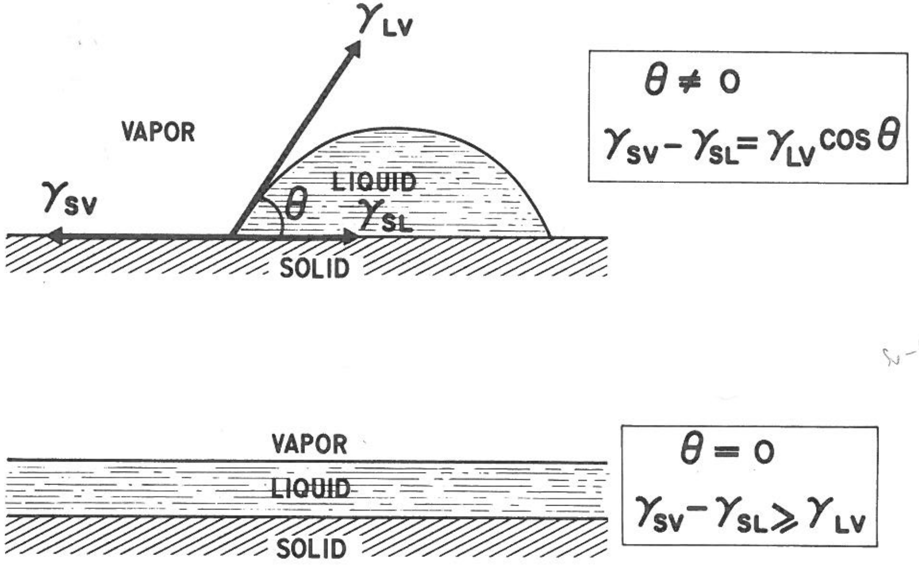
in which γ_{LV} is the surface tension of the liquid.

It then suffices to separately evaluate γ_{LV} (by a tensiometer) and $\cos\theta$ (see below) or the product $\gamma_{LV} \times \cos\theta$ directly to obtain γ_m. Methods have been proposed for the direct measurement of $\gamma_{LV} \times \cos\theta$ (strip method [7], capillarimetric method [8], dynamic Wilhelmy plate wettability technique [9]).

When the contact angle is zero (Fig. 1), the evolution of γ_m is more delicate because the liquid is spread out on the solid, but this does not mean that the wettability is the same for all the liquids thus spread out. It can simply be affirmed from the spreading out that we have the following equation:

$$\gamma_m = \gamma_{SV} - \gamma_{SL} \geq \gamma_{LV}$$

Nonetheless, it is important to know the value of γ_m. Indeed, when two liquids are in contact with a rock, it is the respective wettability values that cause one liquid to be displaced by the other one. Different methods have been proposed for evaluating γ_m in such cases (for example from adsorption isotherms, Briant and Cuiec [2]).



Sv-SL: LV

FIG. 1 Examples of behavior of solid/liquid systems. (After Ref. 4. Reproduced by permission of the Norwegian Institute of Technology, Trondheim, Norway.)

Such treatments for ideal systems (pure liquids, clean and well-defined solids) cannot usually be translated to actual reservoir systems because of problems of surface properties, highly complex geometries, complex fluids, adsorption phenomena, transfer of components from one phase to another, etc.

Other methods have therefore been proposed for evaluating the wettability of natural rocks with respect to a fluid pair. The great diversity of these methods stems from the fact that the concept of wettability is not easy to quantify strictly for such systems, and therefore it is not surprising that no single method has received unanimous acceptance.

Different effects of wettability on the behavior of the rock/water/oil system have been studied in several types of experiments. As we will see, some methods are limited to a qualitative evaluation. Others result in quantifying wettability by using an index. Some methods require an assumption to be made concerning the homogeneous or heterogeneous nature of the wettability. Others do not. Sometimes the entire surface of a porous medium has the same wettability, which may be more or less preferential to one of the fluids. More often wettability should be considered as heterogeneous, with some parts of the surface being preferentially water-wet and others

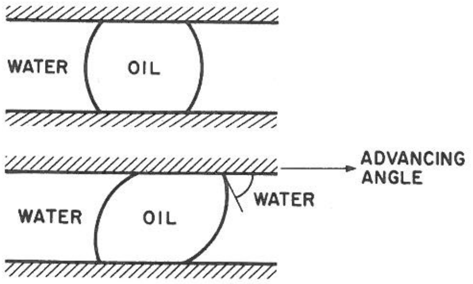


FIG. 2 Measurements of contact angle, static and dynamic conditions. (After Ref. 4. Reproduced by permission of the Norwegian Institute of Technology, Trondheim, Norway.)

preferentially oil-wet. The overall wettability of the sample will then depend on the type and extent of heterogeneity. We will return to such assumptions later on. Let us now examine the different methods proposed.

2. Method Based on Contact-Angle Measurement

Many laboratories have used this technique [2, 10–19]. It consists of placing a drop of oil or water on a flat surface of a solid having the same mineralogical nature as the reservoir considered, and of submerging this solid in water or oil (Fig. 2). Some devices may even operate at reservoir temperature and pressure. The angle can be measured under static or dynamic conditions (water-advancing contact angle measurements have been reported for a large number of crude oils [15]).

When the contact angle θ measured in water is small, the solid is said to be water-wet. When it is large, the solid is said to be oil-wet. For angles of about 90°, the solid is said to have neutral or intermediate wettability. Some authors have chosen exact boundaries to separate the three types of wettability. For example, Treiber et al. [15] have chosen cut-off values of 75° and 105°. Morrow [18] has adopted 62° and 133° on the basis of spontaneous imbibition behavior of uniformly wetted systems. Chilingar and Yen [19] use 80° and 100°. However, this technique for evaluating the wettability of a reservoir is often criticized on the grounds of selecting pure minerals as the solid substrate, polishing the solid (which creates new surfaces), the problem of heterogeneous rocks from the mineralogical standpoint, the influence of roughness, and the influence of pore geometry on the contact angle.

3. Method Based on Interfacial-Tension and Displacement-Pressure Measurements

Slobod and Blum [20] consider that wettability can be measured quantitatively by the contact angle but that this angle is difficult to measure in a porous medium. Therefore, they define an apparent contact angle using interfacial-tension and displacement-pressure measurements. They propose that two displacements be performed, with the displacement pressure being obtained by a centrifuge. First they displace the water saturating the sample by oil, and then the oil saturating the sample by air. In this way, two displacement pressures are obtained (pressure at which the displacement of the wetting phase is initiated). Assuming that the displacement pressure of any wetting phase corresponds to the invasion of the same pores and that the oil perfectly wets the rock in the presence of air, then an equation giving the cosine of the apparent contact angle as a function of the displacement pressures and the interfacial tensions measured is obtained.

Compared to the previous method for measuring θ, this method has the advantage of being applicable to a natural sample. But the wettability index is obtained solely when the pores with large thresholds are filled, thus corresponding to one point on the capillary-pressure curve. Moreover, the measurement is made under static conditions. This method has been criticized (see discussions in refs. 6 and 20) and has not, to our knowledge, been used in other laboratories.

4. Method Based on the Shape of Relative-Permeability Curves

Many laboratories have investigated the influence of wettability on the shape of relative-permeability curves. Their observations are summed up in Fig. 3. Raza et al. [21] point out that the ratio of permeability to water in the presence of residual oil and of permeability to oil in the presence of connate water is approximately 0.3 from strongly water-wet porous media. This ratio is in the vicinity of 1 for strongly oil-wet porous media. The logarithm of the k_w/k_o ratio can also be plotted as a function of water saturation. For water-wet samples, the slope obtained is very steep. For oil-wet samples this slope is much smaller. If available, the k_g/k_o and k_w/k_o ratios can be plotted as a function of oil saturation. For strongly water-wet samples the slopes of both curves are the same, as are the saturation ranges. According to Raza et al., what has been said above is valid when the relative permeabilities are determined by the steady-state method (Penn State method). In this case, physicochemical equilibria that may influence the wettability are attained during measurement.

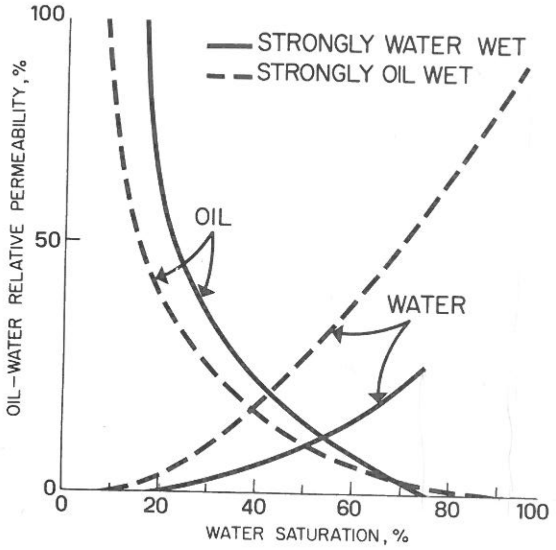


FIG. 3 Oil–water relative permeability/saturation characteristics. Note that in this case residual oil saturation is lower for oil-wet case than for water-wet one. (After Ref. 21.)

The influence of the viscosity ratio of fluids on the shape of k_r curves (Lefebvre du Prey [22]) must also be taken into account especially if formation fluids are not used (see also refs. 1 and 21).

In the author's experience, the shape of the k_r curves is consistent with what has just been discussed when the rock is strongly wetted by one fluid or the other. However, it is risky to evaluate the wettability of a reservoir solely from such data, because many reservoirs appear to have a heterogeneous wettability. Recent results (Heaviside et al. [23]) also show that, when the rock has intermediate wettability, it is more difficult to deduce the wettability from the shape of the k_r curves.

5. Method Based on the Shape of Recovery Curves

Figure 4 (Raza et al. [21]) shows the shape of recovery curves as a function of the volume of water injected in the waterflooding of a natural sample, using low viscosity fluids. For strongly water-wet samples, almost all if not all of the oil is displaced (curve A) before breakthrough, and the water/oil ratio (curve A') increases very quickly after breakthrough. For strongly oil-wet samples the volume of oil recovered before breakthrough is relatively small in relation to the total amount recovered (curve B), and the water/oil ratio (curve B') increases slowly after breakthrough.

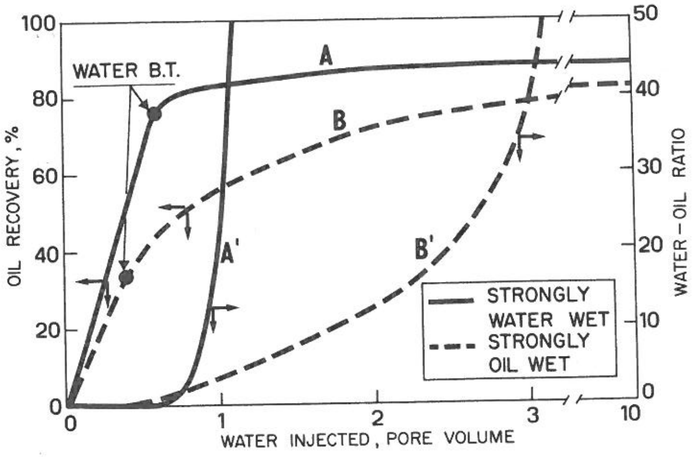


FIG. 4 Idealized waterflood performance of a sandstone type core (linear). Case of low-viscosity fluids. (After Ref. 21.)

Before interpreting such curves to deduce wettability, the possible influence of the viscosity ratio of the fluids used and of the rate of displacement should be known. This method is not reliable for quantifying the wettability with respect to one or the other of the fluids or for recognizing cases of intermediate wettability (Heaviside et al. [23]). In addition, the influence of wettability is not always considered to be that shown in Fig. 4. This point will be discussed in the next part of this chapter.

6. Method Based on Permeability and Saturation Measurements

According to Frehse [24], this method can be used to determine whether a reservoir is water-wet, oil-wet, or has neutral wettability. It is based on saturation frequency distributions of samples as a function of their permeabilities. The principle of the method is described below.

All reservoirs are known to be heterogeneous with regard to their pore structure. Yet the permeability of a sample depends on the diameter of its pores. It is all the lower as average pore radii are smaller. Insofar as the wetting fluid is in contact with the surface of the solid, the saturation of the smallest pores by the wetting fluid will be relatively greater than in the larger pores.

The method consists in classifying samples from all parts of a reservoir according to permeability groups and in plotting the frequency of different saturation classes as a function of each saturation class for the two extreme permeability groups. Depending on whether the solid is oil-wet, has neutral wettability, or is water-wet, diagrams such as the ones in Fig. 5 will be obtained.

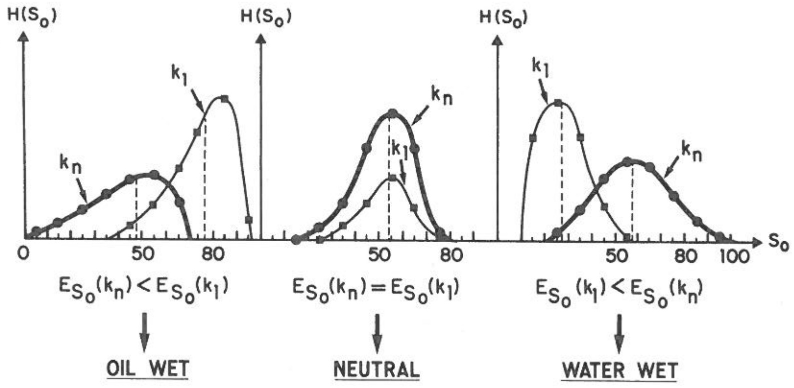


FIG. 5 Examples for frequency versus S_o diagrams. (After Ref. 24.)

Let k_1 be the lowest permeability range, k_n the highest permeability range, $H(S_o)$ the frequency of saturation class, S_o the oil saturation, E_{so} the mean value of oil saturation in a permeability group, N_e the number of samples in permeability class e, and n_i the number of samples in saturation class i. Then

$$E_{so}(k_e) = \frac{\sum_{i=1}^{N_e} S_{oi}\, n_i}{\sum_{i=1}^{N_e} n_i}$$

If $E_{so}(k_1) < E_{so}(k_n)$, the reservoir is preferably hydrophilic.
If $E_{so}(k_1) > E_{so}(k_n)$, the reservoir is preferably hydrophobic.
If $E_{so}(k_1) = E_{so}(k_n)$, wettability is neutral.

This method is an original one and uses data that are often available. However, in extreme permeability ranges, samples must be available from each part of the reservoir, and the number of samples must be great enough. It is obvious that the interest of this method is linked to the reliability that can be attributed to the k and S values used.

Frehse considered that permeability depends on pore size. In reality, permeability depends on the size of the thresholds separating the pores. In addition, Frehse assumed implicitly that pore volumes are linked to the size of the thresholds that limit the pores. However, this is probably not always the case. Finally, the possibility of having heterogeneous wettability in the pores is not considered.

7. Method Based on Spontaneous Imbibition Experiments

The spontaneous imbibition phenomenon is largely controlled by the capillary pressure, which is proportional to the interfacial tension between the two fluids and to the cosine of the contact angle. Consequently, imbibition which may be characterized by its rate (particularly its initial rate) and by the total amount of fluid displaced, depends on the wettability.

Gatenby and Marsden [25] performed imbibition experiments in oil, using water-saturated sintered Pyrex samples, and found that the rate of imbibition and the total amount imbibed increased when the solid was more oil-wet. Using various assumptions, they determined a proportionality relationship between the rate of imbibition and the cosine of the contact angle. However, for the cases normally investigated, this relationship cannot be used. Other attempts have been made to work out an equation for the imbibition phenomenon, but no formulation is yet able to take into consideration the influence of all the acting forces present (capillary as well as gravitational, viscous, and inertial). Nevertheless,a useful evaluation of wettability can be made from the rate of imbibition or from the total amount imbibed.

Bobek et al. [26] have used such a method. Using simple equipment similar to the one shown in Fig. 6, they obtained curves giving the amount of fluid imbibed versus time. They either plunged consolidated oil-saturated porous media into water, or water-saturated porous media into oil. They compared the behavior (i.e., the slope of the imbibition curve and the total amount imbibed) of a porous solid with that of the same solid made entirely water-wet by a suitable treatment. This comparison to a reference state can be made without need to consider the effect of the permeability of the rock and the viscosities of the fluids. For unconsolidated media, Bobek et al. used a microscope to observe the movement of fluids in sand either by placing a drop of water on oil-saturated sand or a drop of oil on water-saturated sand. This visualization also showed the position of the fluids in the sand.

Denekas et al. [27] used a similar test. From the curve of the volume of oil or water spontaneously displaced by water or oil versus time, they deduced the initial rates of imbibition. As a reference, they used the rate of imbibition of water in a porous medium made strongly water-wet by a suitable treatment. The ratio of the rate of imbibition of water with any wettability to the reference rate gives the relative rate of imbibition. This ratio is used for a preferentially water-wet solid. If the solid is oil-wet, the rate of imbibition of oil is measured in relation to the same reference rate as before, but a negative sign is assigned to the relative rate.

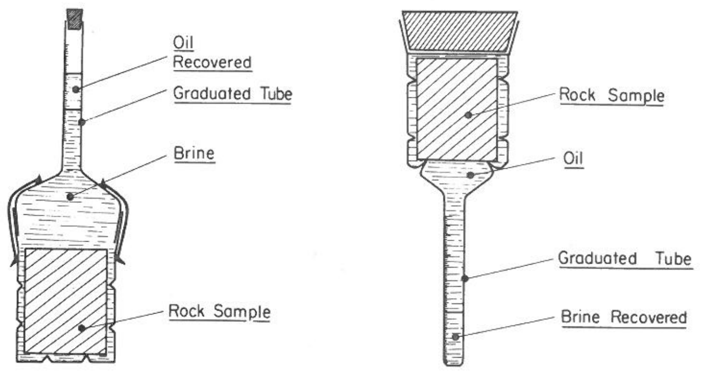


FIG. 6 Apparatus for imbibition experiments in brine and in oil. (After Ref. 4. Reproduced by permission of the Norwegian Institute of Technology, Trondheim, Norway.)

Several other laboratories have used this kind of test (Mungan [28], Duyvis and Smits [29]). Some have adopted short durations for imbibition experiments, for example, 24 hours. According to our experience, such durations are insufficient in some cases, especially when the samples have low permeability.

The following two methods are based on the assumption of heterogeneous or fractional wettability.

8. Method Based on Nuclear Magnetic Relaxation Measurements

This method was developed by Brown and Fatt [30], who mixed varying proportions of two sands treated so that one was strongly water-wet and the other strongly oil-wet. They observed that the surfaces of porous media contribute greatly to the relaxation rate of fluids in the pores. For water-saturated sand packs, it has been noticed that the contribution of the surface to the relaxation rate of water in the pores is much less pronounced if the sand is made oil-wet. Different mechanisms can explain this effect. When water is the wetting fluid, an increase in the viscosity of water in the vicinity of the surface is accompanied by an increase in the relaxation rate. The presence of paramagnetic ions or molecules on the surface can have the same influence on the relaxation rate if water wets the solid. Therefore, if a sample is saturated with water, the relaxation rate will be all the greater as the water wets the solid more intensively.

Brown and Fatt determined a decreasing linear relationship between the nuclear magnetic relaxation rate of water saturating a sample and the percentage of oleophilic sand. Therefore, to determine the fractional wettability of any natural solid, they propose:

1. To saturate it with water and measure the relaxation rate.
2. To make it entirely water-wet by a suitable treatment, to saturate it with water, and to measure the relaxation rate.
3. To make it entirely oil-wet by a suitable treatment, to saturate it with water, and to measure the relaxation rate.
4. To place the first measurement on the straight line obtained with the other two. In this way the percentage of the solid surface wet by oil is determined.

Anderson [6] has rightly pointed out that there is no way of checking to see that the rock has been made strongly hydrophilic or strongly oleophilic during the procedure recommended by the authors.

9. Method Based on Dye Adsorption

This technique (Holbrook and Bernard [31]) had the advantage of not requiring any complicated equipment and of not altering the samples prior to the test.

In a porous medium containing two immiscible liquids, a dye is dissolved in one of these liquids. Their distribution in the pores occurs according to the preferential wettability of the surface. If all solid surface is wet by the fluid not containing the dye, there will then be a film preventing dye adsorption. If, however, the solid is wet by the fluid containing the dye, a maximum amount of this dye will be adsorbed on the solid. Between these two extreme cases, it can easily be conceived that adsorption may be proportional to the fraction of the surface covered by the fluid containing the dye.

Holbrook and Bernard tested this method using methylene blue, a dye that is soluble in water. A porous solid sample containing natural fluids was stirred in a given amount of methylene blue solution, and then it was centrifuged. Then the amount of dye adsorbed was determined. A sample identical to the preceding one was treated to be entirely water-wet, and the amount of dye adsorbed was measured. The ratio of these two amounts gives the surface fraction wet by the water in the natural sample. This evaluation of the wettability was qualitatively in agreement with imbibition rate tests. The presence of minerals with a high adsorption capacity (e.g., clays) make it difficult to interpret the results.

These last two methods do not seem to have been used by other laboratories.

10. Method Based on Flotation Experiments

Methods based on flotation experiments have also been proposed. They can be used for unconsolidated rocks but are not very sensitive and are affected by parameters other than wettability (particle size, particle density, etc.) (see review in Anderson [6]).

11. Method Based on X-ray Photoelectron Spectroscopy Analysis

Recently, Huang and Holm [32] proposed using this technique for the qualitative determination of the wettability of rocks from an evaluation of the amounts of organic carbon and sulfur present on the solid surface. A comparison is made of the contents obtained for a given sample and those of reputedly water-wet and oil-wet samples. This technique is still recent and has not been used very often. However, it does require (1) using crushed samples, (2) cleaning the samples with naphtha and toluene, and (3) drying them at 200°F (93°C) for 16 h. It is not at all certain that the surface state of samples in equilibrium with reservoir fluids is not modified by this preparatory treatment.

12. Method Based on the Use of Well Logs

The electrical resistivity index of an oil-wet rock is known to be greater than that of a water-wet rock. Some authors have suggested that this property can be used to evaluate the wettability in situ. This idea of performing in situ measurements is very interesting, a priori, but it has not been convincingly demonstrated in any practical situation [6, 33–35].

Recently, Desbrandes [36] proposed evaluating in situ rock wettability from formation pressure data.

The advantages and disadvantages of the previous methods have been succinctly reviewed in this paper. Let us finish the review with the two most widely used quantitative methods.

13. Method Based on the Use of Capillary Pressure Curve

Taking the results obtained by Gatenby and Marsden [25] as a point of departure, Donaldson et al. [37] proposed a method that combines the use of the correlation existing between the degree of wetting and the areas under the capillary-pressure curves as well as the speed with which these curves are determined by using centrifuging. Donaldson [38] has also connected these areas to the variation in

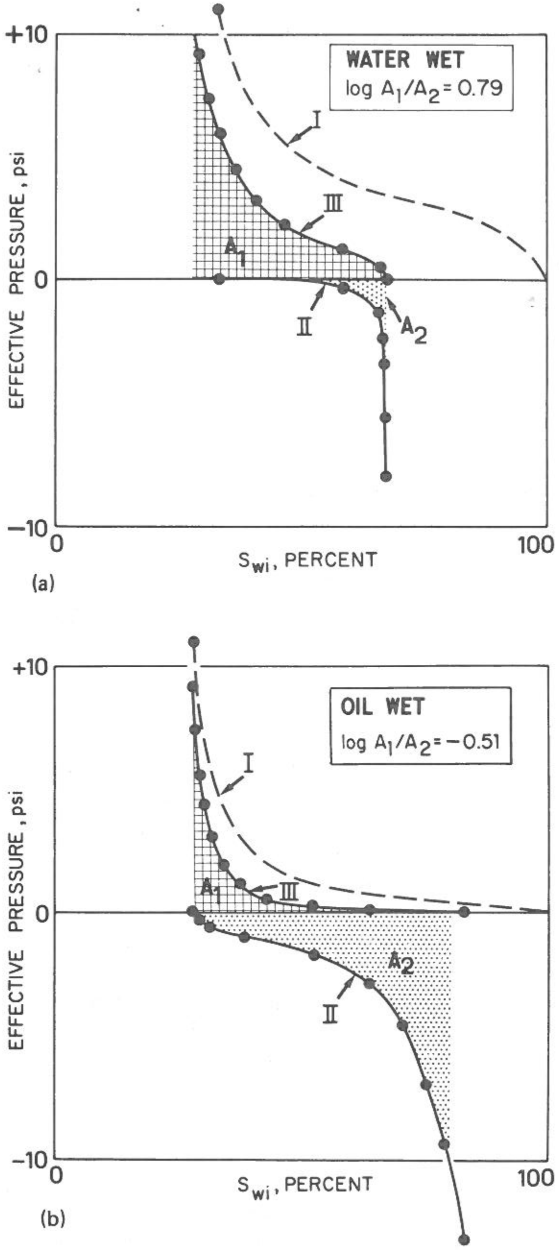


FIG. 7 Effect of wettability on the area of capillary pressure curves: (a) untreated core (water-wet); (b) core treated with 10% Drifilm 99 (oil-wet); (c) core pretreated with oil for 329 h at 140°F (neutral). (After Ref. 37, copyright 1969, SPE-AIME.)

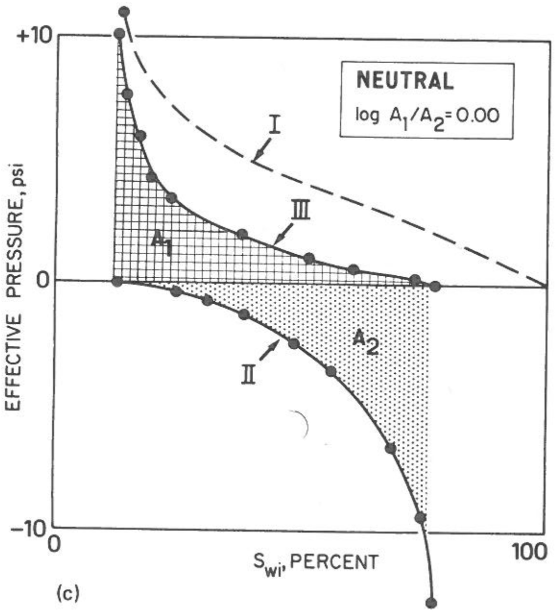


FIG. 7 (Continued)

the free energy of the system. The method generally called the USBM method consists of plotting curves of the type shown in Fig. 7.

The shape of capillary pressure curves depends on the wettability of the solid with regard to water and oil and on the pore-size distribution. In general, for preferentially water-wet solids, $A_1 > A_2$ and $\log(A_1/A_2) > 0$. Conversely, if the solids are oil-wet, $A_2 > A_1$ and $\log(A_1/A_2) < 0$. If the wettability is neutral we have $\log A_1/A_2 \approx 0$. The logarithm of the A_1/A_2 ratio has been proposed to define a wettability scale. As opposed to some tests in which one point on the curve P = f(S) is used, the interest of this method is that it uses all the points on the curve, thus integrating the influence of the pore-radius distribution. If we assume that the influence of pore geometry is similar for both curves, the ratio of the areas is then independent of this geometry. The test performed in this way has proved to have good reproducibility. Donaldson compared this wettability scale to the one adopted by Amott [3] (see next method), and found interesting point of agreement. A more recent comparison reported by Crocker and Marchin [39], showed both tests to give similar results for water-wet systems but not for intermediate wettability systems.

14. Method Based on Imbibition and Displacement Experiments

This method for making a quantitative evaluation of wettability was first proposed by Amott [3]. The method as originally proposed consisted of preparing the samples so as to have water and oil in the pores, with the latter at residual saturation, before making the following four measurements:

1. Volume v_1: Water spontaneously displaced by oil from the sample over a period of 20 h.
2. Volume v_2: Water displaced by oil using centrifugation. A centrifugal force of about 1800 times gravity was used for 1 h.
3. Volume v_3: Oil spontaneously displaced by water from the sample over a period of 20 h.
4. Volume v_4: Oil displaced by water using centrifugation.

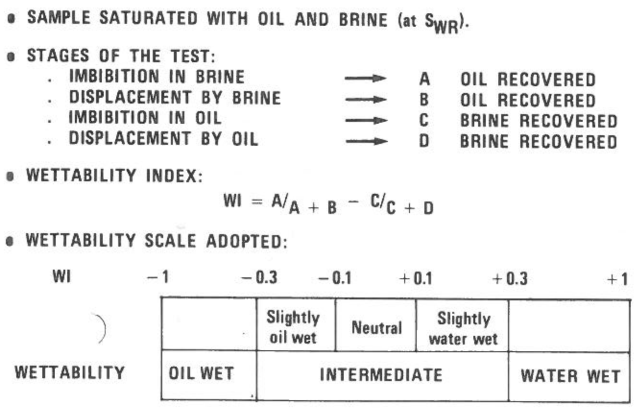
This method thus combines two spontaneous imbibition measurements and two forced displacement measurements. Amott defines the $v_1/(v_1 + v_2)$ and $v_3/(v_3 + v_4)$ ratios as wettability indices. For preferentially oil-wet samples, the first ratio has a positive value and the second a value of zero. The greater the first ratio is, the more the solid is oil-wet, with the maximum value being one. For water wettability, the role of the two ratios is reversed. When both ratios are zero, the samples have an intermediate wettability.

Good reproducibility is obtained with this test. In discussing the method, Amott noted the following points:

1. The required precautions are taken during the test so as not to alter the wettability by impurities.
2. It is a displacement-type test which resembles to some extent the displacement of oil by water in waterflooding.
3. In addition to wettability, permeability and perhaps other properties affect imbibition and displacement. However, the ratios defined above depend mainly on wettability.
4. It is easy to interpret the results of the test because in most cases, one of the ratios is zero. When both ratios are positive, Amott used their difference as the wettability index.
5. The test is fast and easy to perform.

This test or close variants have been adopted by many laboratories and in particular by the author at Institut Français du Pétrole (IFP).

In the procedure used by Cuiec [40, 41] (Fig. 8), centrifuging is replaced by flooding at constant rate or pressure. Flow rates are sufficient to ensure that the quantity $L\mu V$ (L = sample length, μ = viscosity of the displacing fluid, V = rate of filtration) has a sufficient value to minimize the end effects [42]. Times allowed for spontaneous imbibition are adapted to the behavior of individual systems. Indeed, in some cases, it has been found that the imbibition phenomenon does not start up immediately and that the rates can be very slow, particularly when the samples have low permeability. Tests are routinely performed at reservoir temperature or close to this temperature.



- SAMPLE SATURATED WITH OIL AND BRINE (at S_{WR}).
- STAGES OF THE TEST:
  - IMBIBITION IN BRINE → A OIL RECOVERED
  - DISPLACEMENT BY BRINE → B OIL RECOVERED
  - IMBIBITION IN OIL → C BRINE RECOVERED
  - DISPLACEMENT BY OIL → D BRINE RECOVERED
- WETTABILITY INDEX:

$$WI = {}^{A}/_{A+B} - {}^{C}/_{C+D}$$

- WETTABILITY SCALE ADOPTED:

WI	−1	−0.3	−0.1	+0.1	+0.3	+1
		Slightly oil wet	Neutral	Slightly water wet		
WETTABILITY	OIL WET	INTERMEDIATE			WATER WET	

FIG. 8 Description of IFP wettability test. (After Ref. 4. Reproduced by permission of the Norwegian Institute of Technology, Trondheim, Norway.)

Wettability is expressed by a wettability index (WI) defined as follows:

$$WI = \frac{\text{oil displaced by water by spontaneous imbibition}}{\text{oil displaced by water by imbibition and displacement}} - \frac{\text{water displaced by oil by spontaneous imbibition}}{\text{water displaced by oil by imbibition and displacement}}$$

This index can have values ranging from −1 for a strongly oleophilic rock to +1 for a strongly hydrophilic rock. Cut-off values of −0.3, −0.1, +0.1, +0.3, have been chosen to separate various wettability classes.

Results of the test must be interpreted with care and sometimes require comments. For example, two rocks having the following results in the wettability test:

$$WI_1 = 0.65 - 0.25 = +0.4 \qquad WI_2 = 0.4 - 0 = +0.4$$

do not have the same wettability properties. In one case we can speak of heterogeneous wettability with a hydrophilic dominance. In the other we must consider that the sample as a whole has a hydrophilic nature. Sometimes we must also consider the possible role of gravity forces, especially if the permeability is high and/or interfacial tension is low.

In addition to the WI, the above test can be used to obtain recovery curves during imbibition of water and oil versus time, and relative-permeability end points k_{ro} at S_{wr} and k_{rw} at S_{or}.

The USBM and Amott tests are now the most widely used ones by oil companies and service companies. According to the literature, they usually seem to be performed under normal pressure and temperature conditions, using refined oil or stock-tank reservoir oil. When there are reservoir-rock samples for which the wettability is to be assessed, it is nonetheless preferable to operate at reservoir temperature and pressure and using reservoir fluids. We will return to this point below.

III. INFLUENCE OF WETTABILITY ON OIL RECOVERY

As has been pointed out, it is sometimes assumed that the wettability of a reservoir rock is homogeneous (or uniform). This means that the entire surface has the same affinity for water or oil. Alternatively, it may be heterogeneous, which means that some portions of the surface have a preferential affinity for water, while others have a preferential affinity for oil. To describe such systems, the expression fractional wettability is then used [30].

For heterogeneous wettability, there are two possibilities. In the first one, the wettable portions of importance to the displacement mechanism by one or the other fluid have a size approximately equal to pore size, or even to a unit including several pores, but are not continuous throughout the media. Expressions such as spotted, dalmatian, or speckled wettability have also been used by various researchers. They may indicate special types of distribution of oil-wet and water-wet surfaces. For the second one when both surface types are continuous, the expression "mixed wettability" has been proposed.

When the wettability is uniform, it has been shown [43] that, for a strongly hydrophilic sand, the initial water wets the solid surface and saturates the small pores. If the medium is strongly oleophilic, the oil wets the solid surface, and the initial water is found in the middle of the large pores. A simplified illustration of this is given Fig. 9 and 10 [21].

Such a mechanism suggests that a waterflood in a strongly oil-wet medium will be less effective than in a strongly water-wet medium [1].

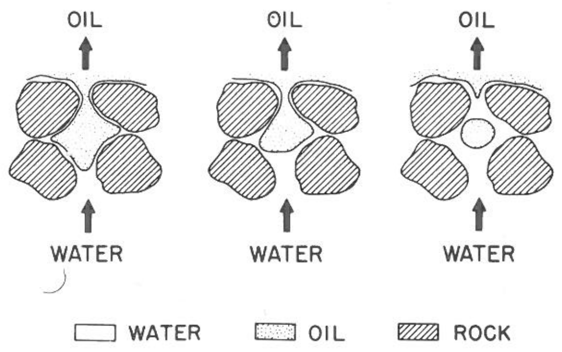


FIG. 9 Schematic diagram of imbibition process, oil displacement by water, water-wet sand. (After Ref. 21.)

Many projects (see ref. 1) involving actual reservoir rocks and outcrop rock samples or unconsolidated sand packs show that the waterflood is more effective when the surface is uniformly water-wet than when it is uniformly oil-wet. In other words, when the porous medium is strongly water-wet, a late breakthrough (end of single-phase oil production and start of two-phase oil + water production) is obtained, and there is little or no production after breakthrough. When the porous medium is strongly oil-wet breakthrough is early, and a relatively long period of two-phase production is seen. But whatever the volume of water injected for the oil-wet case, as long as the conditions are considered to be economically valid, recovery is greater when the porous medium is strongly water-wet [1, 10, 11, 21, 28, 43–59].

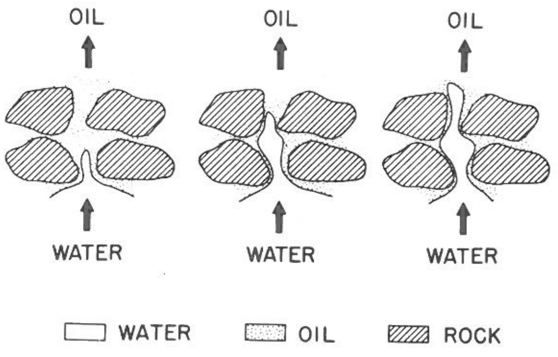


FIG. 10 Schematic diagram of drainage process, oil displacement by water, oil-wet sand. (After Ref. 21.)

Results shown in Figure 4 illustrate this point, even though absolute recovery values do not reflect the values found in the laboratory for natural porous media.

Anderson [1] points out that the μ_{oil}/μ_{water} viscosity ratio is important with respect to when breakthrough occurs and on the length of the two-phase production period considered to be economically cost effective, no matter what the wettability may be. He notes that for the same μ_{oil}/μ_{water} ratio, a waterflood is always less effective for an oil-wet or intermediate system than for a strongly water-wet system. Furthermore, ultimate recovery obtained after a water drive of long duration depends little on the wettability (still assumed to be uniform). Some results indicate the ultimate recovery is higher when there is only slightly preferential wetting for either one fluid or the other [1, 11, 60–62]. This is ascribed to reduction of the interfacial forces that disconnect and trap oil [1, 57, 62–65].

In comparing the effectiveness of a waterflood in porous media, either strongly or moderately water-wet (property again assumed to be uniform), Anderson [1] notes that in both cases there is little production after breakthrough. On the other hand, with regard to the recovery obtained, either at breakthrough or after breakthrough, varied results are found. In some cases, the effectiveness of the waterflood is greater [43, 50], identical [3], or less [3, 57, 66] when the rock is strongly water-wet than when it is moderately so. Anderson attributes these disparities in results to the influence of parameters such as heterogeneity, pore geometry, rate of injection, and inlet and outlet end effects.

With heterogeneous wettability caused by a mixture of various proportions of grains having the same size, some water-wet and the others oil-wet, recovery of displaced fluid after several pore volumes have been injected can be seen to decrease with the percentage of sand strongly wetted by the displacing fluid [1, 67–71]. This behavior is reminiscent of what is observed in uniformly wetted media.

On the other hand, when porous media are made up of different grain sizes, some water-wet and the others oil-wet, the opposite is found, that is, oil recovery is greater when the medium contains a greater proportion of water-wet grains [72]. Anderson [1] attributes this behavior difference to differences in pore geometry and specific surface area.

Another type of wettability has been suggested by Morrow et al. [73] and consists of a consolidated sandstone in which a crude oil deposits an oil-wet film on some parts of the surface. Elementary water-wet or oil-wet surfaces are probably not continuous and small in size as compared with pore size or particle size of the previously mentioned mixtures, but no direct information is available in this point. Morrow et al. observe that oil recovery by waterflooding is better for speckled wettability, which on the whole has a slight water wettability, than when the same medium is strongly water-wet. Speckled wettability media were shown to have many features similar to those seen for strongly water-wet.

Homogeneous wettability, including both strongly water- and oil-wet continuous surfaces, was first described in relation to the study of the East Texas field. According to Salathiel [74] (see also Alba's discussion [67]), this wettability state is probably due to the following processes: During migration of oil into the initially strongly water-wet rock, the oil invaded the largest pores in the rock. A film of organic matter was deposited and became fixed on the surface of the large pores, making them oil-wet, while the small pores remained water-wet and therefore water-filled. In such a hypothesis, it is assumed that the products that were deposited cannot migrate in the water phase and reach the surface of the finest pores. Salathiel [74] has shown that, in such cases, higher recoveries are obtainable than when the porous medium is strongly water-wet, with production increasing with the number of pore volumes of water injected. Residual oil saturation was reduced to about 10% after 5000 pore volumes of water were injected. The mechanism used to explain this high recovery, linked to the large volume of water injected, is called film drainage by Salathiel. The existence of oil filaments linking the oil situated on both sides of the water front had already been observed during displacements in micromodels [43, 75]. The results previously obtained by Richardson [76] are in good agreement with Salathiel's work. Another feature of heterogeneous media is that they explain the spontaneous displacement sometimes observed for both fluids [77].

Salathiel succeeded in producing a mixed wettability state in some cases by using a mixture of East Texas crude oil and heptane capable of depositing a strongly oil-wet film. It was hypothesized that production of mixed wettability state depended on the mineralogy and on pore geometry [74]. Salathiel proposes the mechanism shown in Fig. 11 to illustrate the role of pore geometry.

Other results can be found in the literature, showing that oil recovery is sometimes greater when some reservoir rocks are weakly water-wet than when these rocks are strongly water-wet [57, 73, 78, 79]. Some authors have attributed this result to the existence of mixed wettability. But without any results concerning the spontaneous displacement of water by oil, it is difficult to say much about the nature of the heterogeneous wettability that is assumed to explain this behavior.

Morrow [80] has compared the effect of wettability on oil recovery reported by various researchers. The comparisons are presented in relative recovery efficiency E_{Dr} versus pore volumes injected:

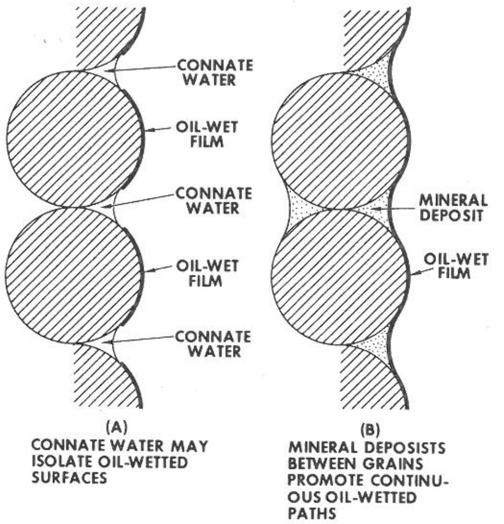


FIG. 11 Relationship of pore geometry to oil recovery. (After Ref. 74, copyright 1973, SPE-AIME.)

$$E_{Dr} = \frac{E_{D\theta}}{E_{Dsw}} \times 100$$

where $E_{D\theta}$ is the recovery at wettability condition θ, and E_{Dsw} is the recovery for the same or similar core sample for strongly water-wet conditions.

It appears (Fig. 12) that the results obtained by Morrow, Wang, Rathmell, and Salathiel for natural porous media show that oil recovery is greater for an overall slightly water-wet sample than when the sample is strongly water-wet. This can be interpreted as follows: a heterogeneous wettability, that overall is slightly more affinitive to water, whether it is mixed or speckled, is more favorable for oil displacement than a uniform wettability condition of similar affinity.

Other research has revealed the importance of the wettability of reservoir rock when recovery methods other than conventional waterflooding are implemented, such as surfactant or polymer flooding [81], CO_2 foam flooding [82], or WAG (water alternating gas) injection [32]. For a preferentially oil-wet reservoir, it has also been shown that it may be more advantageous to inject gas than water [83].

Likewise, numerous finding confirm the major role of wettability in determining how a waterflood proceeds, but show that it is difficult to deduce wettability with certainty from the shapes of recovery curves alone. The influence of wettability on relative permeability curves has also been studied by several researchers. An example is given in Fig. 13, where wettability goes from strong water wetness for core No. 1 to strong oil wetness for core No. 5. Figures 14 [26] and 15 [84] illustrate the mistake that can be made in predicting production when using laboratory results that were obtained with samples that were unrepresentative from the standpoint of wettability. This error in recovery oil volume may be as much as 20% pore volume. The consequences of such a mistake can be considerable when the decision to develop a field is involved.

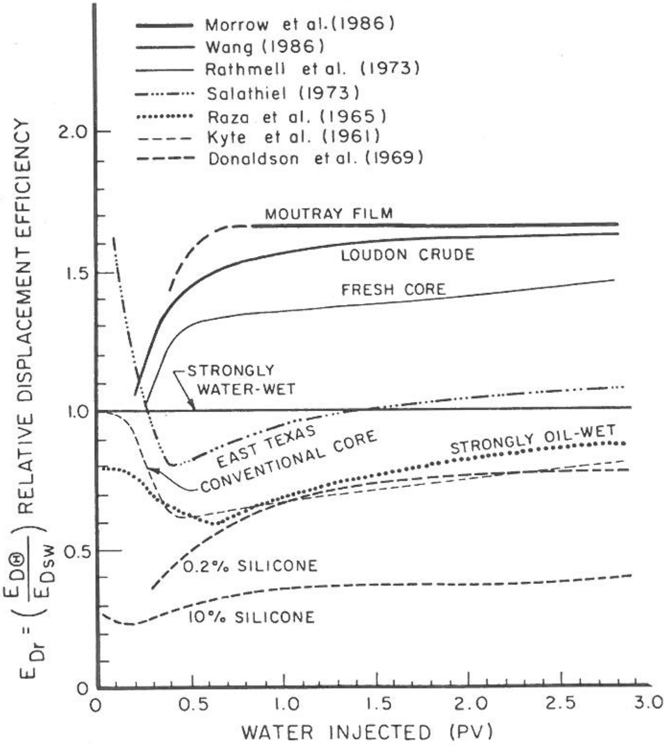


FIG. 12 Effect of wettability on laboratory waterflood relative to recovery at strongly water-wet conditions. (After Ref. 80. Reproduced by permission of the Norwegian Institute of Technology, Trondheim, Norway.)

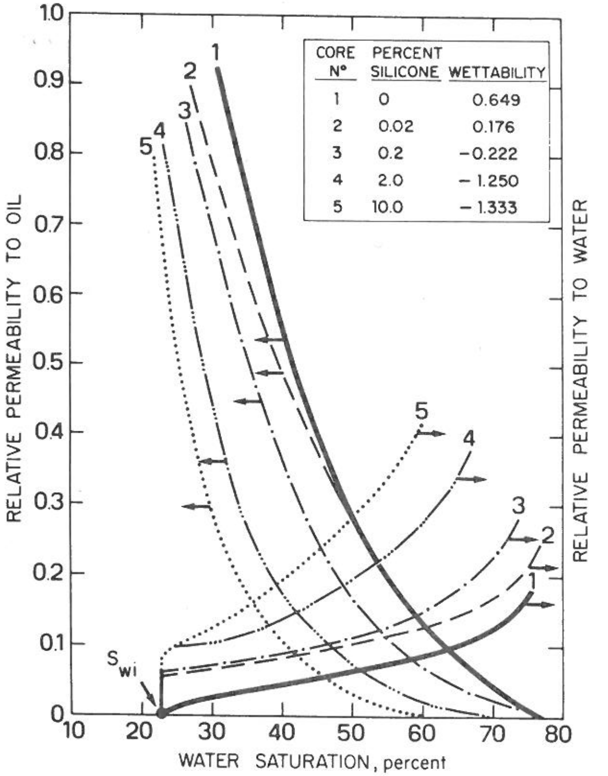


FIG. 13 Oil and water relative permeabilities of sandstone core for water-wet to oil-wet conditions. Note that the k_{ro} and k_{rw} are not completed in the S_{wi} zone. (After Ref. 43, copyright 1971, SPE-AIME.)

IV. OBTAINING REPRESENTATIVE RESERVOIR ROCK SAMPLES

The foregoing discussion of the influence of wettability on oil recovery demonstrated the importance of the surface properties of rock samples with respect to results given by various special core analysis experiments. A consequence is that, to obtain reliable results, reservoir surface properties must be respected. There are two solutions for this, a priori: (1) taking samples without modifying the surface properties of the rock, and (2) using procedures for restoring the original surface properties. It is well known that there are numerous possible and sometimes unavoidable causes of difference in surface properties between the reservoir and the laboratory: (1) the

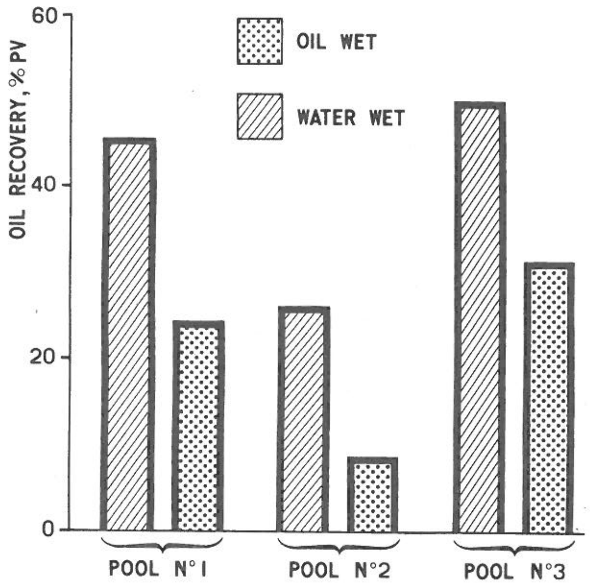


FIG. 14 Effect of wettability on predicted field waterflood behavior, after 1.5 PV water injected, based on core analyses of aged (oil-wet) and cleaned (water-wet) samples. (After Ref. 26, copyright 1958, SPE-AIME.)

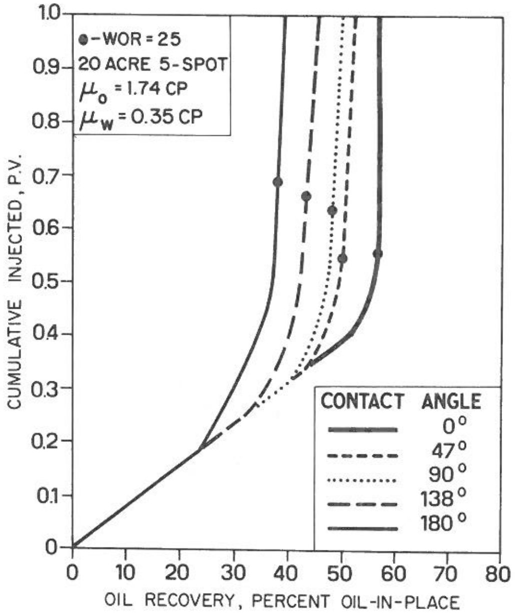


FIG. 15 Effect of wettability on waterflood performance calculations. (After Ref. 84, copyright 1971, SPE-AIME.)

action of mud during sampling, (2) temperature and pressure drop when the sample is being brought to the surface, and (3) contamination, oxidation, and desiccation during handling and storage (Fig. 16).

A. Influence of Drilling Muds

Various studies [3, 26, 77] have shown that some additives for water-base or oil-base drilling muds can change the wettability of reservoir rocks, possibly at the same time as other parameters such as permeability and saturation. Recent results have confirmed this influence for many drilling fluids now in common use. Thomas et al. [85] have evaluated the influence of several oil-base drilling fluids, oil-base coring fluids, and oil-mud additives on the wettability of a clayey sandstone. They have concluded that this parameter is always modified and often strongly modified by these products. Wendel et al. [86] have observed that an invert oil-emulsion mud, used in the Hutton field, changed an originally strongly water-wet rock to strong oil wetness. Moreover, they have shown that cleaning such contaminated samples is possible but difficult and that some damage to the clays can be expected. Sharma and Wunderlich [87] have observed that seven water-base drilling-fluid components, considered to be bland, cannot modify the wettability of initially strongly water wet rocks. On the contrary, all these components but one, bentonite, decrease the oil-wet nature of originally oil-wet rocks. Two other components, excluded from bland muds—amine and lignosulfonate—also modify the wettability of rocks. Ballard and Dawe [88] have also shown that different low-toxicity inverted oil-mud formulations were able to make the surface of glass more oil-wet and to reduce water saturation to below connate water saturation in glass micromodels.

A recent study was also performed by Cuiec [89] with five oil-base muds supplied by four major makers and various porous outcrop media (one sandstone, one clayey sandstone, and one carbonate, originally strongly water-wet). It has been observed that all such drilling fluids strongly alter the wettability of the three porous media investigated, with a complete reversal of wettability usually being observed. One illustration is given in Fig. 17. Wettability was assessed by the test described in Fig. 8. A check was also made to see that the diesel oil used to prepare different oil-base drilling fluids had little or no influence. It was found that the effect of these muds could be observed, although attenuated, at more than 1.5 cm from the contact surface with the drilling fluid. It was also found that different porous media, after contact with various water-base drilling fluids, exhibited reduced rates of spontaneous displacement of oil by water. However, the original wettability of the rock samples could be recovered by cleaning procedures that included

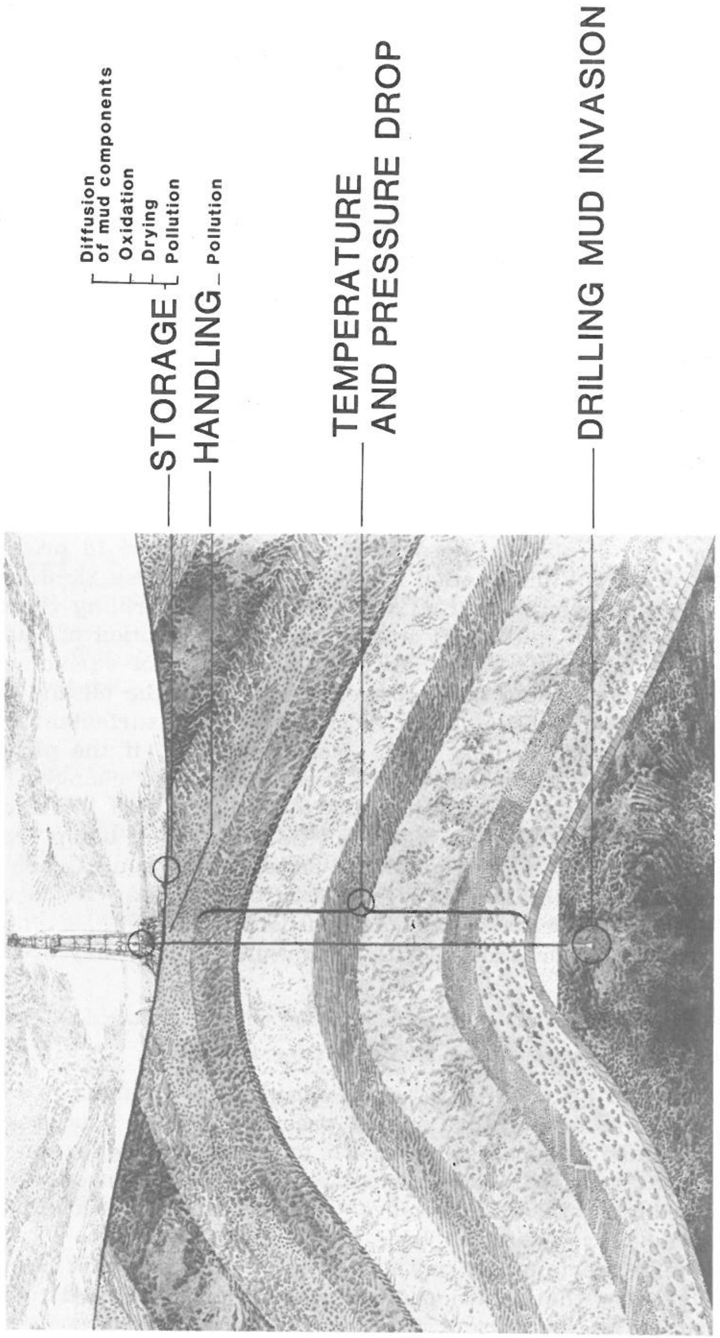


FIG. 16 Causes of wettability modification between the reservoir and the laboratory.

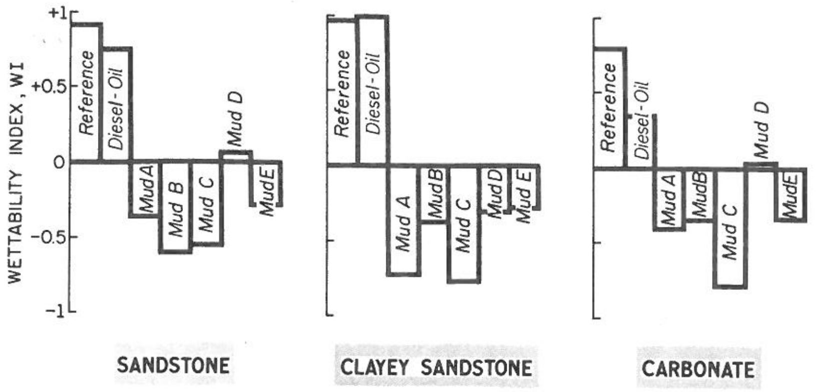


FIG. 17 Wettability evaluation, originally water-wet, and after contamination with diesel oil and various oil-base muds. (After Ref. 89, copyright 1987, SPE-AIME.)

use of isopropyl alcohol, toluene and methanol. Figure 18 provides a summary of all the information contained in references 85–87 and 89 concerning the modification of wettability due to drilling fluids.

Such changes in wettability are caused by adsorption of various components from drilling muds or by the adsorption of surfactants formed by reaction among some components of both the oil and the drilling mud. For example, acids from the oil form surfactant products with a basic drilling mud. More generally, if the pH of the mud is different from that of the formation brine, changes in equilibria may occur at the liquid/solid and liquid/liquid interfaces. However, this change of wettability can be avoided by using fresh or salt water, without any other additives and with neutral pH, or nonoxidized crude oil (Keelan [90]). Such core drilling fluids cannot always be used because of hole conditions. However, even when opportunities for drilling with such fluids exist, they are often not used.

B. Influence of Temperature and Pressure Drop

Under normal coring conditions, when samples are brought to the surface, drops in temperature and in pressure occur. For some reservoir, paraffin deposition is known to occur with reduction in temperature. These paraffins become resolubilized again only at a temperature higher than the reservoir temperature. Three examples of this behavior are given in Table 1.

Asphaltene precipitation may also occur. The pressure drop, particularly below the bubble point, is generally considered to be the determining factor (Briant [91], Bleakley [92]), but temperature may also be involved [92].

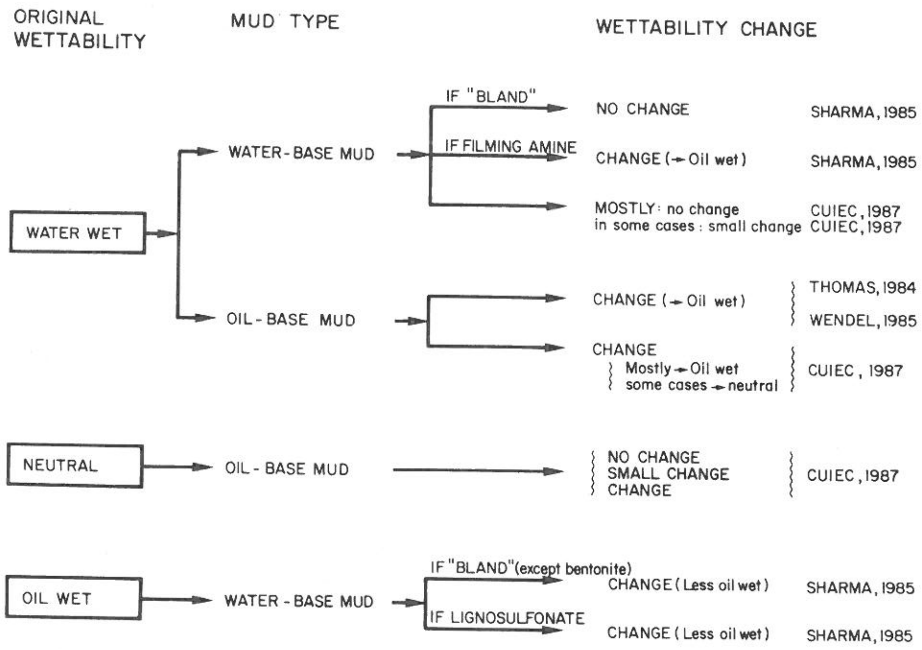


FIG. 18 Wettability modification versus type of mud. Summary of the literature.

As yet there is no means of avoiding a drop in temperature when samples are taken. The pressurized core barrel technique can be used to maintain the pressure in the sample and is recommended for evaluating in situ saturations. However, after the core barrel has been brought up to the surface, the sample must be decompressed after being cooled in ice. There is then a possibility that asphal-

TABLE 1 Examples of Reservoirs Having a Problem with Paraffin Deposits

Reservoir temperature (°C)	Paraffin depositing temperature (°C)	Melting temperature (°C)
43.3	33	52
45	43	70–80
45	40	50–60

tenes are deposited when the gas leaves during this decompression. Therefore, it is not possible to prevent entirely possible modifications of surface properties during the recovery of core samples.

Little research has been done on this subject, and as of now it is not easy to predict, a priori, whether a crude oil will or will not produce deposits with reduction in temperature and pressure. The greater is the amount of paraffins (especially n-paraffins) of high molecular weight. the greater is the risk of deposition. If the examination of a stock-tank oil with a microscope, in polarized light, indicates the presence of a paraffin suspension, the possibility of the existence of a paraffin deposit in the rock sample should be considered likely. A better way to predict such a deposit is to perform a differential thermal analysis on the oil at increasing and then decreasing temperature to obtain the fusion and crystallization temperatures of the paraffins. The variation in viscosity should also be determined under the same conditions of temperature variation.

C. Influence of Oxidation

If the rock sample is stored in air, there is a risk of heavy-product deposits resulting from the evaporation of the light fractions, and of oxidation that creates polar products capable of changing the properties of solid/liquid and liquid/liquid interfaces.

Bartell and Niederhauser [93] have shown that, after contact with air for a fairly long time, crude oils have a tendency to form rigid films at the water/oil interface. A decrease in water/oil interfacial tension by 20–30% of the initial value was also observed.

Treiber et al. [15] measured the contact angle of a drop of crude oil on a calcite plate before and after oxidation (produced by air bubbling). They found (see Fig. 19) that calcite changes from strongly water-wet with the original oil ($\theta = 0^\circ$) to preferentially oil-wet after oxidation of the oil ($\theta = 135^\circ C$).

Cuiec [94] has studied the influence of oxidation for several crude oils. The results have confirmed that the oil/brine interfacial tension decreases after oxidation of all the crude oils investigated (the decrease was between 4 and 15 mN/m depending on the oil investigated). The wettability of crude oil/brine/clayey sandstone systems has also been evaluated for four crude oils before and after oxidation. The wettability test described in Fig. 8 was used. In all cases the wettability after oxidation was changed toward oil wetness (Fig. 20).

As a consequence, the oil to be used for some special core analyses should be protected from oxidation and the rock samples should be protected from exposure to the atmosphere while in storage. However, it is virtually impossible to prevent exposure to oxygen completely during the various operations involved in core recovery storage and testing.

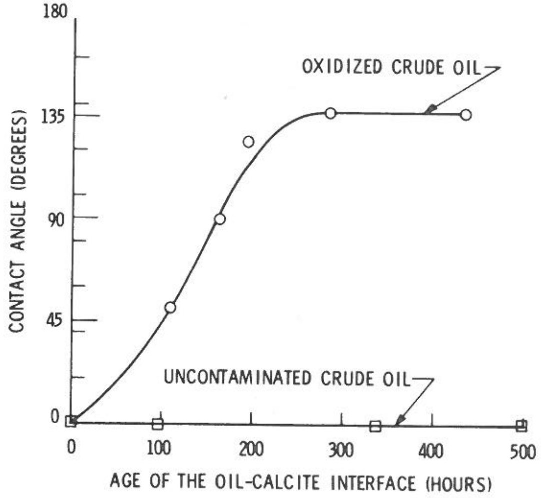


FIG. 19 Influence of aging on contact angle for uncontaminated and oxidized crude oils (Lower Holt). (After Ref. 15, copyright 1971, SPE-AIME.)

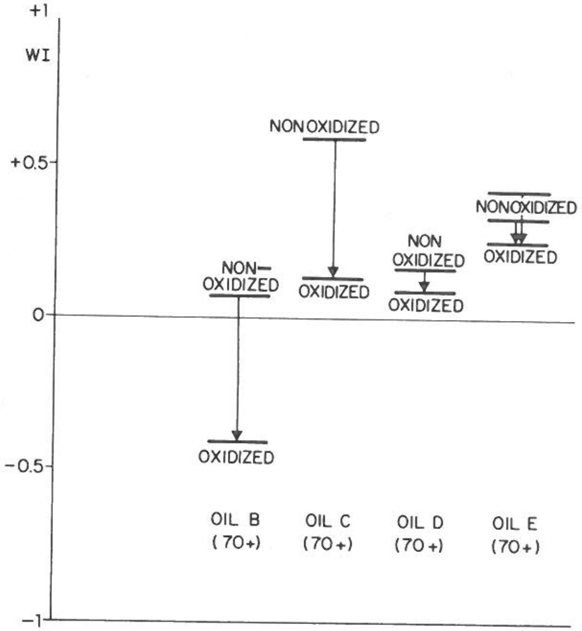


FIG. 20 Influence of oxidation on the wettability of a clayey sandstone and various crude oils.

Thus, even when maximum precautions are taken during and after the sampling, there is no guarantee that the surface properties will be representative of the ones existing in situ.

D. Procedure for Restoring the Original Surface State

In many instances, rock samples available for testing are ones that have been taken and stored without any particular precautions. In addition, the same sample must sometimes be used for a whole series of laboratory experiments involving surfactant products that require the sample to be restored to its original state. When a composite model of a porous medium has to be built by employing a certain number of small samples, it is necessary to clean these samples before assembling them. The wettability of the composite model then needs to be restored.

For all these reasons we have been led to develop a procedure so that the original surface state can be restored. In addition, it allows the degree of representativity of the surface properties of preserved samples (when available) to be evaluated.

This procedure is described in Fig. 21. It consists in evaluating the wettability of the samples at reception, after cleaning, and after restoration, that is, after cleaning, saturation with reservoir fluids, and aging. From the results, recommendations can be formulated so as to respect as closely as possible the rock surface properties parameter.

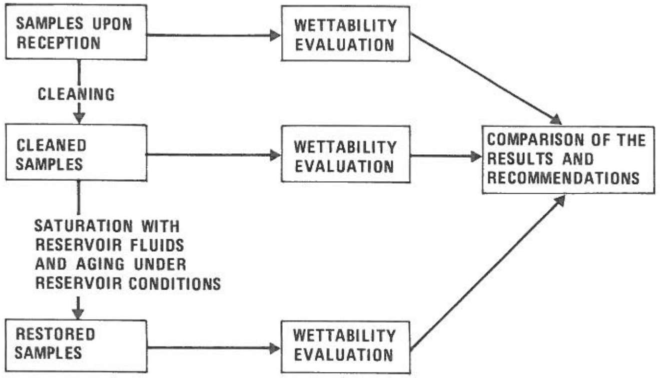


FIG. 21 Method for obtaining reservoir rock samples with surface properties as representative as possible. (After Ref. 4. Reproduced by permission of the Norwegian Institute of Technology, Trondheim, Norway.)

The use of this procedure requires:

Using a sensitive and reproducible wettability test.

Using effective cleaning methods capable of extracting products adsorbed on the solid surface. Since there is no way of selectively extracting the products adsorbed during and after sampling without touching the ones adsorbed in situ, the aim is to extract all of them and make the rock as water-wet as possible.

Using methods for obtaining oil and water saturations that are as close as possible to the ones existing in the reservoir.

Not having to use inconveniently long aging times to obtain an equilibrium between the cleaned rock and the reservoir fluids.

These four requirements are investigated hereafter.

1. Wettability Test Evaluation

Much work [3, 40, 95–97] has shown that the modified Amott test (see Fig. 8) is a practical approach to evaluation of wettability. In previous research, the maximum deviation of the WI around the average value was evaluated for sample batches having identical or very similar characteristics [40, 96, 97]. The results given in Table 2 [89] were obtained for sample batches that were homogeneous from the mineralogical point of view. We can, however, assume that this maximum deviation increases with the degree of heterogeneity.

For samples at reception or restored, ideally, the four steps required for the wettability test (see Fig. 8) should be made under reservoir conditions without need to handle the core at intermediate stages of the procedure. An apparatus for making measurement in this way has not yet been described in the literature. It will necessarily be intricate and complicated to use. We do, however, find the description of apparatus to make it possible to conduct imbibition in the aqueous phase under reservoir conditions [50, 98, 99].

Until now, the test considered was, therefore, usually performed under laboratory conditions. At IFP, it is now performed, using stock tank oil, at normal pressure. The temperature is that of the reservoir considered if this temperature is equal to or less than 80°C, or equal to 80°C if the reservoir temperature is hotter. Moreover, an apparatus enabling four test steps to be performed without manipulating the sample, under reservoir temperature and pressure conditions ($T_{max} = 180°C$, $P_{max} = 450$ bar), has been built and is now being tested.

Various work has demonstrated that reservoir rock is generally more water-wet under reservoir conditions [T, P) than it is at room temperature and pressure [17, 50, 100, 101]. We might, however, assume that respect for the thermodynamic conditions of

TABLE 2 Reproducibility of Wettability Test

Rock	WI	Maximum deviation
Fontainebleau sandstone ($0.05-0.15\ \mu m^2$)	0.68	0.10
Fontainebleau sandstone ($>0.3\ \mu m^2$)	1.0	0.0
Vosges sandstone (shaly) ($0.5-1.6\ \mu m^2$)	1.0	0.0
Rouffach limestone ($5-20 \times 10^{-3}\ \mu m^2$)	0.85	0.12

Source: Ref. 89.

the reservoir, in particular for the temperature, for evaluating the wettability, becomes even more necessary as we get further from the two extremes of the wettability scale. In this way it has been verified [94] that in the case of a Middle East oil-wet carbonate deposit, and for preserved and restored samples, the wettability index values (WI) depended little on the temperature (see Table 3). Nonetheless, the evolution observed for WI complies with what was stated earlier.

The stock tank oil or recombined oil used must be representative of the reservoir oil, which implies that materials have not been treated with surfactants (demulsifiers for example) nor sampled soon after certain well treatments. Finally, as mentioned previously, they must be protected from oxidation and kept in a closed container to limit the loss of light ends.

When the test is used to check the efficiency of a cleaning procedure, a refined oil should be used.

2. Study of Cleaning

Extensive research has been conducted on determination of effective cleaning methods [95–97, 102, 103]. In an initial study performed with outcrop sandstones and carbonates, whose surface was well defined, it appeared that

1. The solvents currently used, such as chloroform, toluene, ethanol, isopropanol, and methanol (or less currently used, such as pyridine), do not alter the surface properties of the various quarry rocks (one sandstone, one argillaceous sandstone, one carbonate), which were initially strongly water-wet. Drying at 85°C under partial vacuum is able to remove these solvents from the surface.

TABLE 3 Influence of Temperature on WI for Preserved and Restored Samples

Sample	WI	Temperature (°C)
Preserved	−0.76	90
	−0.65 to −0.86	65
	−0.84 to −0.99	20
Restored	−0.68 to −0.75	90
	−0.80	20

2. The "acid" type solvents (acetic acid, benzoic acid, phenol possibly diluted in benzene or toluene, etc.) have the tendency to be effective in the case of sandstones, while the solvents with a basic character (pyridine, dioxane, dimethylformamide, etc.) were more effective in the case of carbonates. This led to making an assumption about acid–base type displacements.

However, this tendency was not verified in an analysis of the cleaning procedures applied to numerous rocks coming from oil reservoirs. It was noted for the case of reservoir rocks that obtaining the best cleaning method resulted from the "trial and error" technique. Similar conclusions were reached by Wendel et al. [86]. Finally, the procedures that gave satisfaction consisted of a series of floods by solvents, or blends of solvents, performed at proper temperature, for example, reservoir temperature [97]. A back pressure must be applied at the outlet face of the samples according to the boiling temperature of the solvent used.

At the beginning of the cleaning it is recommended that a solvent be used that first avoids any deposit of asphaltenes during the solvent/oil contact and second dissolves any deposits of heavy products and/or desorbs any molecules linked to the solid surface, without serious effect on the water film that might be protecting certain parts of the surface. The destruction of such a film might give adsorbable molecules access to the surface. This function is usually performed by an aromatic solvent such as toluene, which has been previously saturated with brine at the temperature selected for the displacement. This solvent can be followed by a succession of nonpolar solvents (cyclohexane, heptane), or "acidics" (chloroform, ethanol, methanol), or "basics" (dioxane, dimethylformamide, pyridine), or solvent blends such as methanol + acetone + toluene or toluene + methanol. It should be noted that the latter two blends have often turned out to be effective (see also reference 104).

Certain argillaceous reservoirs pose problems during cleaning, depending upon the nature and quantity of the clays present. In such cases, we should be particularly careful not to allow a degradation of the clays or an irreversible fixing of a solvent on the surface. However, very few results are available in the literature concerning this problem. We should also note that in the case where deposits of paraffins are to be feared (high content of mainly normal paraffins), it is recommended that first circulation of the solvent be made at a temperature slightly higher than that of the reservoir (cf. Sec. IV.B).

Whenever, high reservoir brine salinity makes salt deposition likely, the core can be flooded with a brine that is less rich in salts. Alternatively, an alcohol such as methanol can be used. However, in cases where the rock is very argillaceous, it is recommended that use of methanol be avoided and that a longer alcohol be used (ethanol, propanol [105]).

After cleaning, the samples are dried at a maximum temperature of 85°C, under vacuum, with a residual water vapor pressure to preserve the clays. In certain cases the drying can be eliminated, the last solvent being miscibly replaced by the brine.

With regard to the effectiveness of the cleaning, in a certain number of cases we observed, in spite of the use of many solvents or solvent blends in series, that it was not possible to make the reservoir rock strongly water-wet after cleaning. A number of different analyses have established that sometimes the rock contained a certain quantity of organic matter that is essentially inextractable [41, 86].

The non-water-wettability observed after cleaning sometimes stems from the "hydrophobic" nature of part of the sites of the rock surface (e.g., coal, graphite, sulfur, sulfides [101] certain silicates like chlorite [101, 106], siderite [107]). In such situations, there is no point in trying to achieve complete water wetness. Also, when the organic matter is very strongly linked to the rock surface, it may be better to avoid using overly effective solvents. This is because the organic products linked to the rock may not come from the crude oil but rather from the material present at the rock surface prior to migration of oil in the reservoir [86, 108]. It would be better not to extract them because they will not be reintroduced during the restored-state procedure.

Consequently, once it is judged difficult to make a reservoir rock sample water-wet by cleaning, we need to examine the rock in detail to determine the cause of the difficulty.

3. Initial Saturations

With regard to the establishment of initial saturations after cleaning, drying and saturation with brine, it is recommended that one allow for equilibrium between the rock and the reservoir brine by circulation of the brine, and choose a method that can establish an S_{oi} as close to the initial S_{oi} as possible. The best method is the capillary desorption method (porous plate method), but it requires considerable time.

Other possible methods are centrifuging in reservoir oil (stock tank oil), flooding with reservoir oil, flooding with a viscous refined oil followed by reservoir oil, and controlled evaporation of the water by circulation of hot gas (the initial brine composition must be chosen based upon expected evaporation) and displacement of gas by reservoir oil.

All flooding can be performed alternately in one direction and then in the other direction so as to obtain a regular saturation profile.

The method should be chosen depending on the actual S_{oi}, the time available, the sample size, etc.

4. Aging of the Rock/Fluid Systems

Finally, after establishing the initial reservoir oil and brine saturations, the rock/oil/brine system has to be aged at reservoir temperature and under pressure during the time necessary to establish adsorption equilibria.

If a recombined reservoir oil has been introduced in the sample, the pressure must be the reservoir pressure. If stock tank oil has been introduced, the pressure can be lower than the reservoir pressure.

A study of the influence of the aging time on the wettability of numerous reservoir rocks, previously cleaned, and then saturated with reservoir fluids, is described in reference 103. It has been demonstrated (Fig. 22) that an asymptotic value is generally quickly obtained for the wettability index. Other work [74, 100, 109, 110] demonstrates that periods of a few days have often been adopted for the aging. But one study (Ehrlich [111]) demonstrates that, in one case, a period longer than 500 hours is necessary. Given this possibility, during a new reservoir case study, the ideal situation is to analyze the influence of the aging time on the system wettability index before deciding on the time to be adopted to restore the original surface state. If such a study cannot be performed, it is recommended that an aging time be chosen of about one week, which, according to our results, is very likely to be sufficient.

We have verified [94] that the restoration procedure, repeated on the same samples, ended up with the same wettability state based on the WI index. Five nonpreserved samples from a Middle East carbonate deposit were cleaned and then "restored", employing different aging periods. Then three of these samples (a, b, and c in Fig. 23)

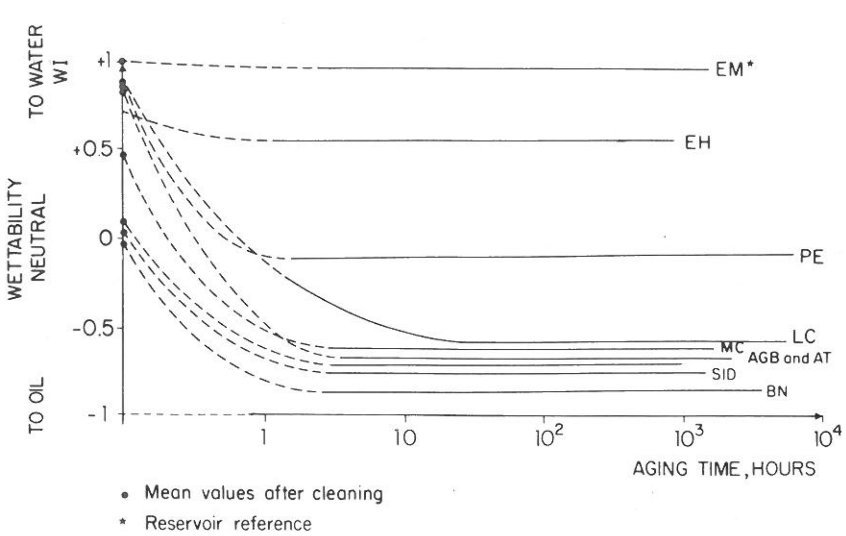


FIG. 22 Evolution of wettability index as a function of time (under reservoir conditions) in the case of nine reservoirs. (After Ref. 103, p. 215.)

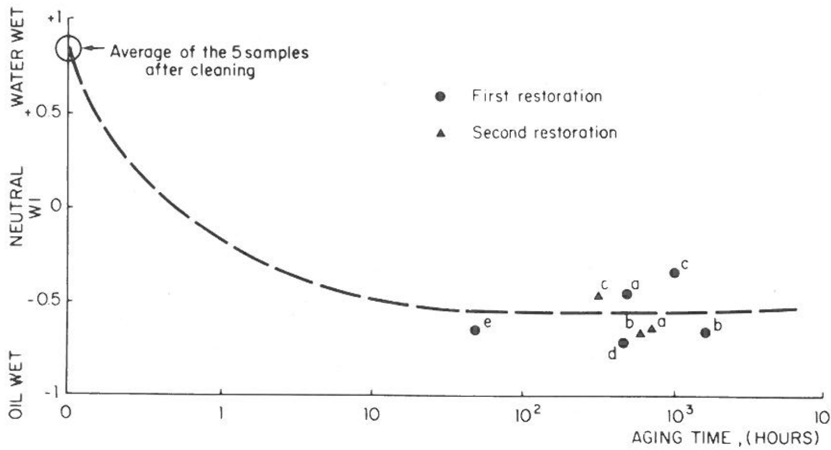


FIG. 23 Evolution of wettability as a function of aging time. Reproducibility or the restoration procedure. Case of a carbonate reservoir from the Middle East.

were once again cleaned (and rendered definitely water-wet) before being subjected to a new restoration. Figure 23 shows that for each of these three samples, the WI index values are close to those obtained after the first restoration.

The phenomena involved in equilibration of the cleaned rock/brine/crude oil system are therefore satisfactorily reproduced. Such a restoration procedure is often used to obtain samples considered as representative from the surface property point of view [28, 86, 100, 109, 112, 113].

This procedure has been used by the author for a large number of reservoirs, whatever the state of the provided rock samples.

V. EVALUATION OF OIL RESERVOIR WETTABILITY

A. Bibliographic Review

Until fairly recently, the "wettability" parameter elicited little interest among petroleum engineers. Some textbooks even considered that all reservoirs were water-wet. But gradually, during production, problems sometimes arose for certain reservoirs, and laboratory research often demonstrated the existence of non-water-wet reservoirs.

Cuiec [41] gave a nonexhaustive list of reservoirs whose non-water-wettability had been proven by various spot analyses. The Chinese Chuanzhong (limestone) and Renquiu (dolomite) fields can be added to this (Wei et al. [114]). The literature also includes several studies on the evaluation of the wettability of more or less large groups of reservoirs. For example, Treiber et al. [15] evaluated the wettability of 55 reservoirs, including 51 situated in North America. This evaluation was made by measuring contact angles at reservoir temperatures, with pre-equilibrated fluids and using a simulation solid. Choosing 75° and 105° as cut-off values for the water-advancing contact angle, they obtained the results shown in Table 4. Out of 30 sandstone reservoirs, 15 have been found to be oil-wet, 2 to have intermediate wettability, and 13 to be water-wet. Out of 25 carbonate reservoirs, 21 have been found to be oil-wet, 2 to have intermediate wettability, and 2 to be water-wet. Treiber et al. also evaluated the wettability of 22 of these 55 reservoirs from the shape of the water/oil and gas/oil relative permeability curves. Good agreement was reported for 18 out of 22 cases with the results deduced from contact-angle measurement.

The impact of the breakdown shown in Table 4 is moderated by the fact that many reservoirs classified as oil-wet are actually only slightly so (on the basis of the θ value), and the authors point out that in cases where the wettability is not clearly affirmed for either one of the fluids, the original properties can easily be altered. The authors also indicate that the "reservoirs listed should not be considered as a random sampling of petroleum reservoirs in general.

TABLE 4 Contact-Angle-Derived Wettability Information on 55 Reservoirs

Wettability class	Water-wet	Intermediate	Oil-wet
Defining contact angle range (water advancing) contact angle)	0–75°	75–105°	105–180°
No. of silicate reservoirs	13 (43%)	2 (7%)	15 (80%)
No. of carbonate reservoirs	2 (8%)	2 (8%)	21 (84%)
Total reservoirs	15 (27%)	4 (7%)	36 (66%)

Source: Ref. 18.

The sampling is significantly biased: (1) all samples are from Amoco operations areas; (2) almost all of the samples are from reservoirs considered for some type of flooding operation; (3) an unknown number of the reservoirs studied were considered to have demonstrated unusual behavior."

The breakdown given in Table 4 is obviously linked to the choice of cut-off values for the water-advancing contact angle. Using results for spontaneous imbibition in uniformly wetted porous media, Morrow [18] reinterpreted the preceding results by adopting another classification.

The systems were considered to be:

Water-wet if water-advancing contact angle θ_A is less than 62°
Oil-wet if water-receding contact angle θ_R is more than 133°
Intermediate if θ_A more than 62° and θ_R less than 133°

Morrow found a very different breakdown (Table 5), with large-scale transfer from the oil wettability class toward the intermediate wettability class. By using the same cut-off values, but assuming the existence of a hysteresis of 10° ($\theta_R = \theta_A - 10°$), the number of intermediate wettability cases becomes even larger. Eleven additional reservoirs go from the oil wettability class to the intermediate category. This shows the difficulties of the interpretation of measurements. Furthermore, their degree of representativity may be affected by the fact of using a previously polished mineral simulation solid or various simplifications such as taking a pure quartz to simulate an argillaceous sandstone. Nonetheless, the work by Treiber et al. is the first to show that a large percentage of reservoirs must have a wettability other than strongly water-wet, particularly in the case of carbonate rocks.

TABLE 5 Morrow's Interpretation of Treiber's Results

Wettability class	Water-wet	Intermediate	Oil-wet
Defining contact angle range from classification used by Morrow	$\theta_A < 62°$	$\theta_A > 62°$ $\theta_R < 133°$	$\theta_R > 133°$ (with $\theta_R = \theta_A$)
No. of sandstone reservoirs	12 (40%)	10 (33%)	8 (27%)
No. of carbonate reservoirs	2 (8%)	16 (64%)	7 (28%)
Total	14 (26%)	26 (47%)	15 (27%)
Defining contact angle range	As above	As above	$\theta_R > 133°$ $\theta_R = \theta_A - 10°$
Total	14 (26%)	37 (67%)	4 (7%)
Defining contact angle range	As above	As above	$\theta_R > 133°$ $\theta_R = \theta_A - 20°$
Total	14 (26%)	40 (73%)	1 (2%)

Source: Ref. 18.

In another project, Chilingar and Yen [19] evaluated the wettability of 161 carbonate samples coming from reservoirs situated in Iran (90), North or Central America (38), the North Sea (19), India (5), and China (4). The evaluation was based on contact-angle measurements, although without specifying all the experimental conditions for making the measurements: whether the fluids were pre-equilibrated, what angle was measured (static, advancing angle, etc.), or what solid was used and how this solid was prepared. In any case, they found the breakdown given in Table 6, that is, 8% water-wet cases, 12% intermediate wettability cases, and 80% more or less affirmed oil-wet cases. We do not know how many reservoirs are involved, but we do know that the breakdown is greatly influenced by the fact that 90 samples came from the Asmari formation in Iran, which already had the reputation of being oleophilic (Cuiec [41]).

TABLE 6 Results Obtained by Chilingar and Yen

Wettability class	Water-wet	Intermediate	Oil-wet	Strongly oil-wet
Defining contact angle range	0–80	80–100	100–160	160–180
Number of samples (%) (total: 161 samples)	8	12	65	15

Source: Ref. 19.

B. Results of IFP's Investigations

To date, 33 reservoirs have been evaluated using the test based on spontaneous and forced displacement experiments as described in Fig. 8. Twelve sandstone and 21 carbonate reservoirs located in various areas in the world have been investigated [4, 5, 41, 94] (see Table 7). It should be noted that a large proportion of them were subjected to special core analysis because of their unusual behavior. Certain reservoirs have been subjected to several wettability evaluations, for example, when several productive levels show certain differences in the mineralogy, the petrography, or the behavior. For this reason, 43 studies were performed in all.

As to the "quality" of the samples received, Table 8 shows that preserved samples (which means contained in a leak-tight packing, avoiding any contact with the atmosphere) were provided in only 17 cases out of 43, but this does not mean that in every case we know the composition of the core drilling fluid, the sampling date, etc.

In most cases, the wettability has been evaluated at reception, after cleaning, and after restoration. In the other cases, this was done in one or two of the previous three states. In every case, a batch of several samples was used (at least two and usually three to four). An average wettability index has been deduced for each set of samples at each step investigated.

In Table 9–11, all the results obtained are given for the sandstone, chalky, and nonchalky carbonate reservoirs. An examination of these tables elicits the following remarks:

At reception, the wettability of the sandstone reservoirs is distributed over the whole wettability scale, while the nonchalky carbonate reservoirs are most often oil-wet and the chalky reservoirs from neutral to water-wet.

After cleaning, the samples most often have been made water-wet (strongly or weakly). However, a certain number of rocks, in

TABLE 7 Location of the Reservoirs Investigated

	Africa	South America	Europe onshore	Europe offshore	Middle East	Total
Sandstone	Algeria 4	Equator 1	Germany 1	Norway 2		
	Gabon 1		England 1	England 1		
			France 1			12
Carbonate	Tunisia 2		Italy 1	Norway 2	Qatar 1	
	Angola 1		France 5	Denmark 3	Iran 1	
	Lybia 1		Turkey 1		Irak 3	21

TABLE 8 Nature of the Reservoirs Investigated and Quality of the Samples Received

Type	Number of reservoirs	Number of studies	Quality of the samples received		
			Preserved	Not preserved	Previously used and cleaned
Sandstone	12	17	9	7	1
Carbonate	21	26	8	15	3
Total	33	43	17	22	4

TABLE 9 Average Wettability of Sets of Samples from Sandstone Reservoirs

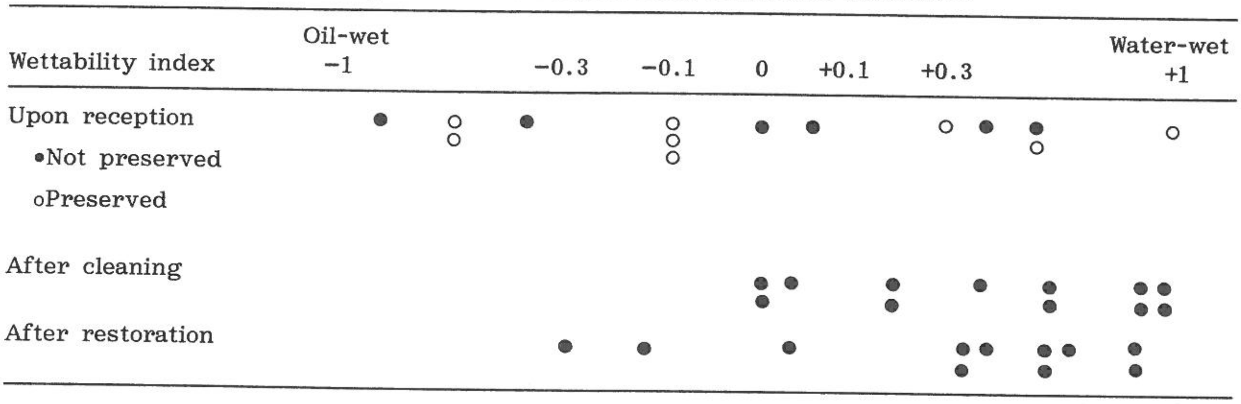


TABLE 10 Average Wettability of Sets of Samples from Carbonate Reservoirs (Chalky Not Included)

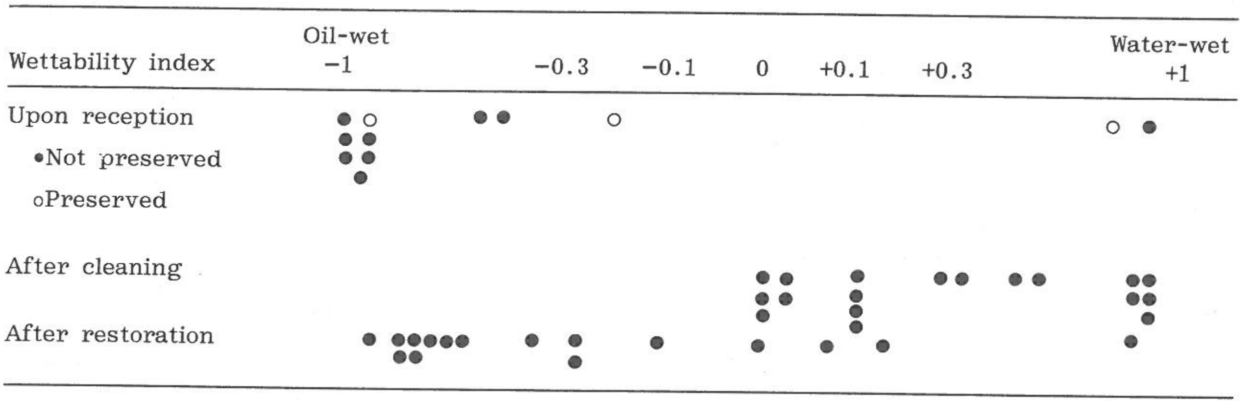
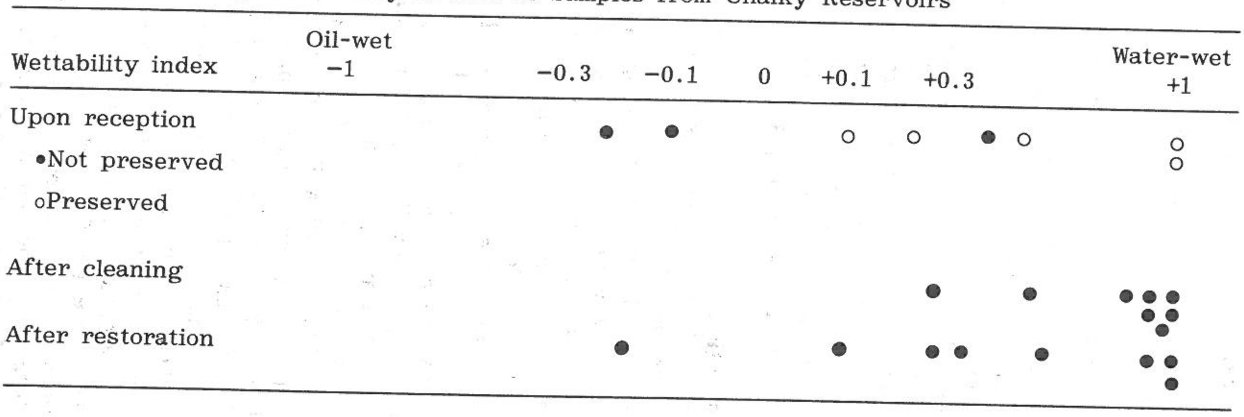


TABLE 11 Average Wettability of Sets of Samples from Chalky Reservoirs



particular carbonate rocks, keep a neutral wettability (cf. Sec. IV.A.4);

After restoration, we obtain a breakdown which is more oriented to water-wettability.

If we consider the wettability after restoration as being the most representative of the wettability in situ, which is fully justified due to the uncertain state of the samples at reception (see Table 8), we obtain the breakdown given in Table 12 for each type of reservoir and for all the reservoirs together.

We see that most of the sandstone reservoirs investigated are preferentially water-wet (8 out of 11). On the other hand, for nonchalky carbonate reservoirs, most are oil-wet (9 strongly and 3 weakly, out of 16). All the chalky reservoirs except one are water-wet. Among all the reservoirs 15 have negative average WI and 20 have a positive WI. If we separate the WI scale into three equal parts, the breakdown is 25.7% oil-wet, 31.4% intermediate, and 42.9% water-wet.

Neither this investigation nor the preceding ones [15, 18, 19] had the pretention of giving any idea of the breakdown of oil reservoirs as a whole by wettability class.

Therefore, care must be taken not to use these results for such purposes. They show, however, that the existence of non-water-wet reservoirs cannot be denied. Likewise, these various evaluations show that wettability problems are more often encountered in carconate formations than in sandstones.

Figures 24 and 25 show the average wettability index obtained for sandstone and carbonate (including chalky) reservoirs, respectively. These figures concern the cases of reservoirs where (1) samples were received "preserved" and (2) the wettability was evaluated at reception, after cleaning and after restoration.

If we consider the sandstone reservoirs (Fig. 24), we note that in two cases out of three the wettability after restoration is fairly close to the wettability at reception in the preserved state. In the third case, the oil wettability is less affirmed after restoration than at reception. This difference might be related to the influence of the drilling fluid, but this was not formally established.

In the case of carbonate reservoirs (Fig. 25), we can consider that often the wettability after restoration is close, even very close, to that evaluated at reception (in the preserved state), considering the semiquantitative character of the WI index. The cause of the slight difference observed in some cases has not been investigated.

Finally, it appears that the wettability after restoration is often very close to that of the samples that are preserved at reception, which indicates that given maximum care, in a great number of cases, the "preserved" samples are representative. As a precaution, we need to know how to choose the mud, limit the contact with the

TABLE 12 Average Wettability after Restoration: Case of 35 Sets of Samples from 33 Reservoirs

	Wettability class and defining WI range					
	Oil-wet −1 to −0.3	Slightly oil-wet −0.3 to −0.1	Neutral −0.1 to +0.1	Slightly water-wet +0.1 to +0.3	Water-wet +0.3 to +1	Total
Sandstone reservoirs	0	2 (18.2%)	1 (9.1%)	0	8 (72.7%)	11
Carbonate reservoirs (nonchalky)	9 (56.3%)	3 (18.8%)	2 (12.5%)	1 (6.2%)	1 (6.2%)	16
Chalky reservoirs	0	1 (12.5%)	0	1 (12.5%)	6 (75%)	8
All carbonate reservoirs	9 (37.5%)	4 (16.7%)	2 (8.3%)	2 (8.3%)	7 (29.2%)	24
Total (sandstone + carbonate)	9	6	5	2	15	35
	25.7		31.4		42.9	100

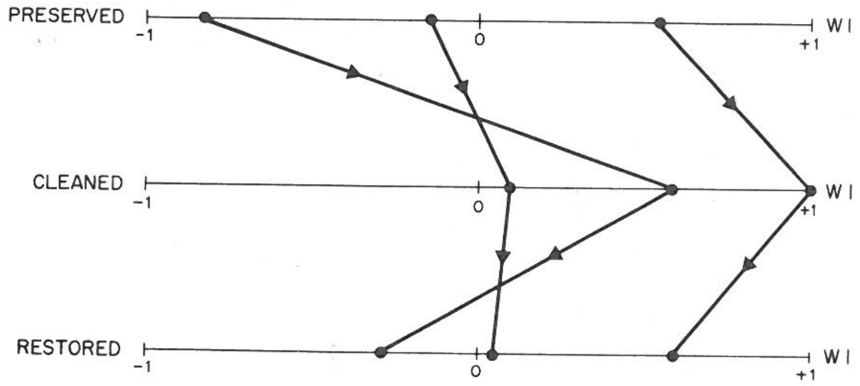


FIG. 24 Comparison of wettability of preserved, cleaned, and restored samples from sandstone reservoirs.

air, use a packing that does not reach with the brine or the oil, avoid substantial temperature changes, use the samples as quickly as possible, take samples in the central part of large diameter core pieces, etc.

If the preserved samples received are strongly water-wet, we can consider that they have a good chance of being representative. In all the other cases, the question of representativeness must be posed (Table 13).

In certain cases, the reason for the non-water-wettability of a reservoir rock in situ can be explained satisfactorily, based on analyses performed on the crude oil and on the rock [106, 108].

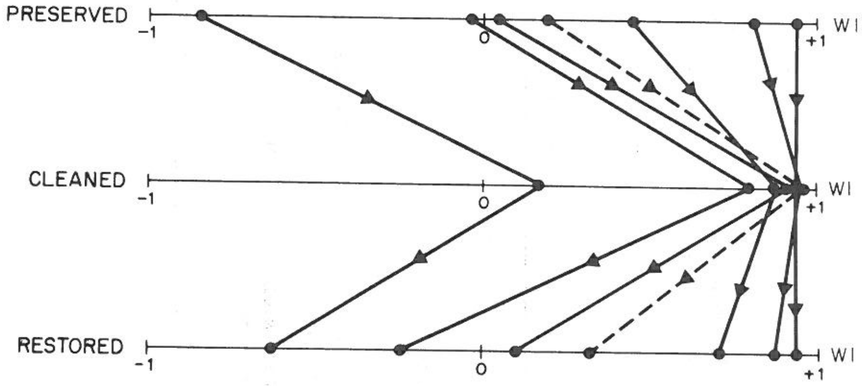


FIG. 25 Comparison of wettability of preserved, cleaned, and restored samples from carbonate reservoirs.

TABLE 13 Recommendations about the Representativity of the Samples

Available samples	Mud used	Wettability at reception	Recommendations
Preserved	Lease crude oil or water base	Water-wet	Samples acceptable
		Neutral Oil-wet	Better to know the origin of the nonwater wetness before considering samples are acceptable
Preserved	Oil base		Do not use samples directly Restore original wettability
Exposed	Water base or oil base		Restore original wettability

Many hypotheses have been made in this field and different results, sometimes contradictory ones, have been obtained (see review in refs. 4, 41, and 101). But because of the complexity of the systems analyzed, much remains to be done to understand the origin of the nonwater wetness observed for a large number of reservoirs.

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REFERENCES

1. W. G. Anderson, J. Pet. Technol. Dec.:1605–1622 (1987).
2. J. Briant and L. Cuiec, in Proceedings of the 4th ARTEP Symposium, Rueil Malmaison, June 7–9, 1971, Editions Technip, Paris, 1971.
3. E. Amott, Pet. Trans. AIME 216:156–162 (1959).
4. L. Cuiec, in Proceedings of the North Sea Oil and Gas Reservoirs Seminar, Trondheim, Norway, December 2–4, 1985, Graham and Trotman Ed, London, 1987, pp. 193–207.
5. L. Cuiec, Rev. Inst. Fr. Pet. 41(4):487–509 (1986).
6. W. G. Anderson, J. Pet. Technol. Nov.:1246–1262 (1986).
7. J. J. Guastalla, J. Chim. Phys. 49:250 (1952).
8. R. T. Johansen and H. D. Dunning, Producers Monthly 20–22 (1959).
9. M. A. Andersen and D. C. Thomas, Paper SPE/DOE 17368, EOR Symposium, Tulsa, Okla., April 17–20, 1988.
10. J. Newcombe, J. Mc Ghee, and M. J. Rzaza, Pet. Trans. AIME 204:227–232 (1955).
11. H. Y. Jennings, Jr., Producers Monthly 21(5):20–24 (1957).
12. D. R. Wagner and R. O. Leach, Pet. Trans. AIME 216:65 (1959).
13. R. O. Leach et al., J. Pet. Technol. 206–212 (1962).
14. N. Mungan, SPE J. 115–123 (1964).
15. L. E. Treiber, D. L. Archer, and W. W. Owens, SPE J. 12: 531–540 (1972).
16. O. S. Hjelmeland and L. E. Larrondo, SPE paper 12124, 58th Annual Technical Conference and Exhibition, San Francisco, Oct. 5–8, 1983.

17. O. Hjelmeland, O. M. Selle, and H. Rueslatten, in Proceedings of the European Symposium on EOR, Hamburg, Oct. 27–29, 1987, pp. 791–801.
18. N. R. Morrow, J. Can. Pet. Technol. 49–69 (1976).
19. G. V. Chilingar and T. F. Yen, Energy Sources 7(1):67–75 (1983).
20. R. L. Slobod and R. A. Blum, Pet Trans. AIME 195:1–4 (1952).
21. S. H. Raza, L. E. Treiber, and D. L. Archer, Producers Monthly 32(4):2–7 (1968).
22. E. J. LeFebvre Du Prey, SPE J. 13:39 (1973).
23. J. C. Heaviside, J. J. Black, and J. F. Berry, Paper SPE 12173, 58th Annual Technical Conference and Exhibition, San Francisco, Oct. 5–8, 1983.
24. W. Frehse, Z. Für Ang. Geol. 19(2) (1973), in German.
25. W. A. Gatenby and S. S. Marsden, Producers Monthly 22(2):5 (1957).
26. J. E. Bobek, C. C. Mattax, and M. O. Denekas, Pet. Trans. AIME 213:155–160 (1958).
27. M. O. Denekas, C. C. Mattax, and G. T. Davis, Pet. Trans. AIME 216:330 (1959).
28. N. Mungan, J. Pet. Technol. 247-252 (1966).
29. E. M. Duyvis and L. J. Smith, SPE J. 3–4 (1970).
30. R. J. Brown and I. Fatt, Pet. Trans. AIME 207:262 (1956).
31. O. C. Holbrook and G. G. Bernard, Pet. Trans. AIME 213: 261–264 (1958).
32. E. T. S. Huang and L. W. Holm, Paper SPE 15491, 61st Annual Technical Conference and Exhibition, New Orleans, Oct. 5–8, 1986.
33. B. F. Swanson, J. Pet. Technol. 32:1459-1464 (1980).
34. E. C. Donaldson and T. K. Siddiqui, Paper SPE 16790, 62nd Annual Technical Conference of the SPE, Dallas, Tex., Sept. 27–30, 1987.
35. E. C. Donaldson and M. J. Bizerra, in Proceedings of the Third UNITAR/UNDP International Conference on Heavy Crude and Tar Sands, Long Beach, Calif., Paper HCTS/CF. 3/8.14, 664–684, July 22–31, 1985.
36. R. Desbrandes, in Proceedings of the 28th Annual Logging Symposium, SPWLA, London, June 29–July 2, 1987.
37. E. C. Donaldson, R. D. Thomas, and P. B. Lorenz, SPE J. Mar.:13–20 (1969).
38. E. C. Donaldson, in Proceedings of the Symposium on Chemistry of EOR, Atlanta, Ga., March 29–April 3, 1981.
39. M. E. Crocker and L. M. Marchin, DOE/NIPER Status Report-183, Aug. 1986.
40. L. Cuiec, et al., Rev. Inst. Fr. Pet. XXXIII(5) (1978).
41. L. Cuiec, Paper SPE 13211, 59th Annual Technical Conference, Houston, Tex., Sept. 1984.

42. L. A. Rapoport and W. J. Leas, Pet. Trans. AIME 198:139–148 (1953).
43. E. C. Donaldson and R. D. Thomas, Paper SPE 3555, 46th Annual Fall Meeting, New Orleans, La., Oct. 3–6, 1971.
44. P. T. Kinney and R. F. Nielsen, Producers Monthly 14(3):29–35 (1950).
45. P. T. Kinney and R. F. Nielsen, World Oil 132(4):145–154 (1951).
46. T. M. Geffen et al., Pet. Trans. AIME 192:99–110 (1951).
47. W. Von Engelhardt and H. Lübben, Erdöl und Kohle 10(11): 747–752 (1957).
48. W. Von Engelhardt and H. Lübben, Erdöl und Kohle 10(12): 826–830 (1957).
49. A. M. Sarem, in Proceedings of the Conference on the Theory of Fluid Flow in Porous Media, University of Oklahoma, Norman, 1959, pp. 191–209.
50. J. R. Kyte, V. O. Naumann, and C. C. Mattax, J. Pet. Technol. June:579–582 (1961).
51. J. E. Bobek and P. T. Bail, J. Pet. Technol. Sept:950–954 (1961).
52. G. P. Colpitts and D. E. Hunter, J. Can. Pet. Technol. 3(2): 66–70 (1964).
53. H. Y. Jennings, J. Pet. Technol. Jan.:116–120 (1966).
54. I. S. K. Kamath and S. S. Marsden, Paper 14D presented at the AIChE National Meeting, Dallas, Tex., Feb. 6–9, 1966.
55. N. Mungan, SPE 247–253, Sept. 1966.
56. L. W. Emergy, N. Mungan, and R. W. Nicholson, J. Pet. Technol. Dec.:1569–1576 (1970).
57. J. J. Rathmell, P. H. Braun, and T. K. Perkins, J. Pet. Technol. Feb.:175–185 (1973).
58. P. K. Shankar, Experimental Investigation of Two-Phase (Oil-Brine) Relative Permeability Characteristics in Mixed Wet Sandstone Systems With Reference to Oil Recovery Efficiency, Ph.D. thesis, University of Waterloo, Waterloo, Ontario, 1979.
59. N. Mungan, World Oil 192(4):77–83 (1981).
60. H. T. Kennedy, E. O. Burja, and R. S. Boykin, J. Phys. Chem. 59:867–869 (1955).
61. P. B. Lorenz, E. C. Donaldson, and R. D. Thomas, Report 7873, U. S. Bureau of Mines, Bartlesville Energy Technology Center, Bartlesville, Okla., 1974.
62. J. J. Taber, in Surface Phenomena in Enhanced Oil Recovery (D. O. Shah, ed.), Plenum Press, New York City, 1981, pp. 13–52.
63. N. R. Morrow, J. Can. Pet. Technol. 18(3):35–46 (1979).
64. N. C. Wardlaw, Paper SPE 8843, presented at the SPE/DOE Enhanced Oil Recovery Symposium, Tulsa, Okla., April 20–23, 1980.

65. N. C. Wardlaw, J. Can. Pet. Technol. 21(3):21–27 (1982).
66. T. F. Moore and R. L. Slobod, Producers Monthly 20(10):20–30 (1956).
67. I. Fatt and W. A. Klikoff, Pet. Trans. AIME 216:426–432 (1959).
68. E. N. Iwankow, Producers Monthly 24(12):18–26 (1960).
69. A. W. Talash and P. B. Crawford, Producers Monthly 25(2): 24–26 (1961).
70. A. W. Talash and P. B. Crawford, Paper SPE 36 presented at the SPE Permian Basin Oil and Gas Recovery Conference, Midland, Mich., May 4–5, 1961.
71. A. W. Talash and P. B. Crawford, Producers Monthly 26(4): 2–5 (1962).
72. A. K. Singhal, D. P. Mukherjee, and W. H. Somerton, J. Can. Pet. Technol. 15(3):63–70 (1976).
73. N. R. Morrow, L. T. Lim, and J. S. Ward, SPEFE J. Feb.: 89–103 (1986).
74. R. A. Salathiel, J. Pet. Technol. Oct.:1216–1224 (1973).
75. C. C. Mattax and J. R. Kyte, Oil Gas J. 59(42):115–128 (1961).
76. J. G. Richardson, F. M. Perkins, and J. S. Osoba, Pet. Trans. AIME 204:86–91 (1955).
77. J. A. Burkhardt, M. B. Ward, and R. H. McLean, Paper SPE 1139-G, presented at the SPE Annual Meeting, Houston, Tex., Oct. 5–8, 1958.
78. F. H. L. Wang, Paper SPE 15019, presented at the SPE Permian Basin Oil and Gas Recovery Conference, Midland, Mich., March 13–14, 1986.
79. P. D. Patel, P. G. Christman, and J. W. Gardner, SPERE J. Nov.:507–513 (1987).
80. N. R. Morrow, in Proceedings of the North Sea Oil and Gas Reservoirs Seminar, NTH, Trondheim, Norway, Dec. 2–4, 1985, Graham and Trotman ed., London, 1987, pp. 179–191.
81. J. Novosad, in Proceedings of the Third European Meeting on Improved Oil Recovery, Agip, s.p.a., vol. 2, Roma, April 16–18, 1985, pp. 145–153.
82. B. M. Lescure and E. L. Claridge, Paper SPE 15445, 61st Annual Technical Conference and Exhibition of the SPE, New Orleans, La., Oct. 5–8, 1986.
83. C. R. K. Murty et al., J. Pet. Technol. Mar.:363–368 (1987).
84. W. W. Owens and D. L. Archer, J. Pet. Technol. July:873–878
85. D. C. Thomas, H. Hsing, and D. E. Menzie, Paper SPE 13097, 59th Annual Technical Conference, Houston, Tex., Sept. 1984.
86. D. J. Wendel, W. G. Anderson, and J. D. Meyers, Paper SPE 14298, 60th Annual Conference and Exhibition, Las Vegas, Nev., Sept. 22–25, 1985.
87. M. M. Sharma and R. W. Wunderlich, J. Pet. Sci. Eng. 1(2): 127–143, 1987.