

TWO-PHASE FLOW IN POROUS MEDIA: INFLUENCE OF PH ON WETTABILITY

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Abstract Wettability is an important factor in petroleum engineering due to its effect on fluid flow and distribution in reservoir rocks. The preferential wetting of the rock surfaces by either oil or water was demonstrated to mainly depend on the short range forces applied on the liquid films (essentially electrostatic, Van der Waals and structural interactions). As a consequence, it has been shown that both brine pH and salinity could control crude oil adhesion on given mineral surfaces.

Laboratory experimental studies performed at different scales of observation are reported on the wetting behaviour of oil-brine-glass systems.

Surface-scale experiments: Adhesion tests of a crude oil were performed on a glass surface as a function of pH. For this system, adhesion was found to occur only for pH values below 5.8.

Pore-scale experiments: Experiments were performed on a single column of glass spheres packed in a square-cross-section glass tube. This model was aimed at the observation of oil trapping and two-phase flow behaviour within the pore volume. Experiments were performed for different values of brine pH.

Porous medium model experiments: Two-phase flow experiments (crude oil displaced by water) were performed in a

porous medium consisting of calibrated glass beads packed in a square-cross section glass tube. This was aimed at studying the influence of brine pH on the oil recovery processes.

At high values of the brine pH, most of the oil is displaced before water breakthrough, and this behaviour is attributed to a water wettability of the system. Under the same conditions, no adhesion of the oil on the glass was observed during the surface-scale experiments.

At low values of the brine pH, an early brine breakthrough was observed followed by a slow increase in oil production. This behaviour, typical of an oil-wet system was found to be coherent to the crude oil adhesion observed at the surface-scale under the same conditions.

INTRODUCTION

The role of wettability in petroleum engineering is essential, by its effects on the displacement efficiency of oil by water and on the distribution of the fluids in the reservoir (Anderson, 1986a to f). It was usually thought that reservoir rocks were water-wet because of the presence of brine in the reservoir prior the hydrocarbons migration.

In the last thirty years, it was found that reservoir wettability could vary from oil-wet to water-wet depending strongly on the oil and brine compositions, and on the nature of the reservoir rock. As wettability has a strong effect on relative permeabilities, capillary pressure and recovery curves, many researchers have investigated the different means to evaluate it. Basically, wettability is evaluated by the measure of contact angle in a three phase system (solid/fluid 1/fluid 2), but most of the wettability tests are based on the influence of wettability on the capillary pressure curves. This means that this evaluation gives an average property of the medium, which cannot be used to investigate pore-scale wettability heterogeneities. Finally, difficulties to preserve cores in their original state, and the qualitative aspect of wettability studies led several authors to take into account the microscopic sources of this phenomenon. Surface forces such as Van der Waals forces and electrostatic interactions control " the relative preference of a surface to be covered by one of the fluids under consideration" (Amott, 1959). Contact between crude oil and rock is strongly

dependent on the stability of water films between rock surface and the crude oil. The existence of stable water film which prevent the adhesion of heavy strongly polar molecules on the solid surface has been proved to be dependent on electrical double-layers forces (Buckley et al., 1987). Starting from the assumption that the reservoir is initially water-wet (before the migration of oil), an interpretation of existence of mixed wettability may be the following: when oil drains the porous medium, it invades only the largest pores because of the capillary forces action, and adsorption of crude oil components at the rock surface can only occur in these regions of the medium. This yields a medium of mixed wettability in which the largest pores have become oil-wet while the smallest ones remained water-wet. In a Water/Oil/Glass system it has been shown (Buckley et al., 1987) that oil adhesion on a mineral surface depends mainly on brine pH and salinity. A theoretical model, based on DLVO theory and Ionizable Surface Group Model (Thomas et al., 1978), allows to predict the oil behaviour on the surface and to compare with experimental measurements of electrophoretic mobilities. The analysis is given in terms of disjoining pressure, which conveys the interactions between the Glass/Water and Oil/ Water surfaces and, therefore, the stability of the thin water film spread between oil and glass.

In this study we investigate experimentally the influence of adhesion phenomena on the waterflooding process at two different scales :

(i) at the pore-scale, i.e., in a model porous medium made of a column of glass spheres packed in a square-cross-section glass tube,

(ii) at the core-scale, i.e., in a porous medium made of calibrated glass beads packed in a square-cross-section glass tube.

The goal of this experimental study is to correlate the effects of surface-scale phenomena (adhesion) to pore-scale and core-scale properties such as recovery curves and end-point saturations, and, finally, to provide an interpretation of mixed wettability which seems to be very common in petroleum reservoirs (Cuiec, 1991).

ADHESION TEST

Study of thin liquid films involves surface forces study. Disjoining pressure is a common way to take into account these effects. Three types of forces are usually considered:

(i) long range forces such as Van der Waals and double layers electrostatic interactions,

(ii) short range forces called structural forces.

For a brine/oil/glass system, structural forces effects are often neglected. Let us consider the equilibrium of a thin water film spread between a crude oil and a glass surface. The equilibrium relation for the film is given by the augmented Young-Laplace equation:

$$p_o - p_w = \Pi + 2H_{ow}\gamma_{ow} \quad (1)$$

Where p_o is the pressure in the oil phase, p_w the pressure in the water phase, Π the disjoining pressure, γ_{ow} the interfacial tension of the oil/water interface, and H_{ow} the mean curvature of the film. In this paper, we will consider a flat film, therefore, the last term in equation (1) is equal to zero.

Van der Waals interactions

The Van der Waals interactions are the result of dipole-dipole (Keesom interaction), dipole-non polar (Debye interaction) and non polar-non polar (London interaction) molecular interactions. For two similar molecules Van der Waals forces are always attractive. The pair potential from which Van der Waals forces derive is expressed by :

$$\omega(r) = -\frac{C}{r^6} \quad (2)$$

where C is a constant. Considering two flat surfaces the potential for two interacting surfaces as a function of their distance is:

$$W(h) = \frac{A}{12\pi h^2} \quad (3)$$

where A is the Hamaker constant for the interacting media. The resulting force per unit area (which is the Van der Waals component of the disjoining pressure) is :

$$F_A(h) = -\frac{A}{6\pi h^3} \quad (4)$$

This expression is correct for small distances h . For large values of h one needs to take into account retardation effects and the expression of the interaction between two planar surfaces is given by

$$F_A(h) = \frac{-A(15.96 \frac{h}{\lambda} + 2)}{12\pi h^2 (16 + 5.32 \frac{h}{\lambda})^2} \quad (5)$$

where λ is the London wavelength.

For a water/oil/glass system the value of Hamaker constant is approximately $1.0 \times 10^{-20} \text{ J}$ and the London wavelength about 100 nm (Hirasaki, 1990).

For such a system $F_A(h)$ is always negative (attractive) and the Van der Waals disjoining pressure component tends to thin the water film.

Electrical double layers interaction

In the Brine/Oil/Glass system two charged surfaces are interacting, the glass/brine surface and the oil/brine surface.

The charging of surfaces may be due to the ionization, or dissociation of surface groups or adsorption of ions from solution on a previously uncharged surface.

Whatever the charging mechanism, the final surface charge is balanced by an equal but opposite charged atmosphere of counterions in rapid thermal motion close to the surface, this is known as the diffuse double layer (Israelachvili, 1985).

The charging of the brine/glass surface is due to the amphoteric nature of the mineral oxide/brine interface while the negative charge of the brine/oil interface is assumed to be dependent on the dissociation of carboxylic acids.

The measurements of electrophoretic mobilities for a glass/brine surface show that the isoelectric point is obtained for pH around 2, and for a brine/oil surface, for different crude oils, the isoelectric point is obtained for higher values of pH (Buckley *et al.*, 1987). The results are shown in Figure 1.

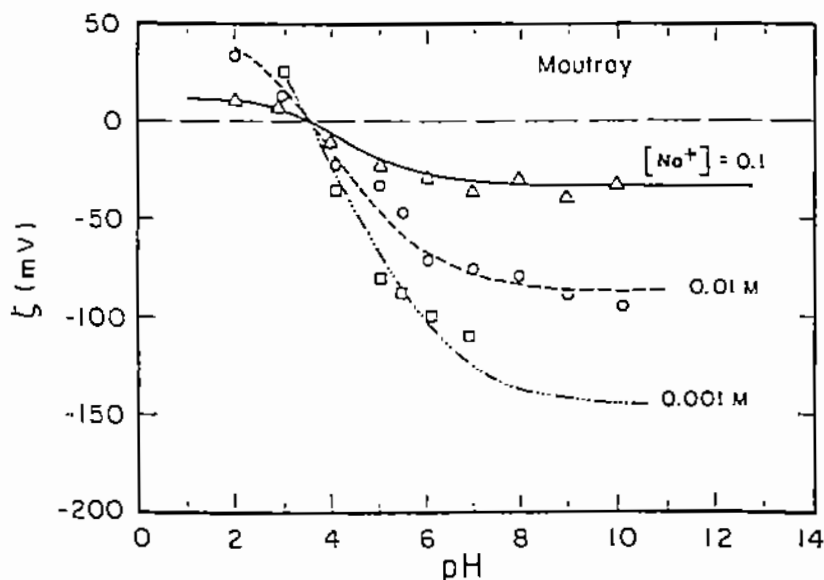


FIGURE 1 zeta potentials versus pH for a crude oil/water interface (from Buckley *et al.*, 1987).

The role of salinity in screening the potentials is to displace the adhesion-non adhesion boundary to higher values of pH. The theory predicts such a relation between pH and surface charge density and surface potentials. An example of calculated disjoining pressure is given in Figure 2.

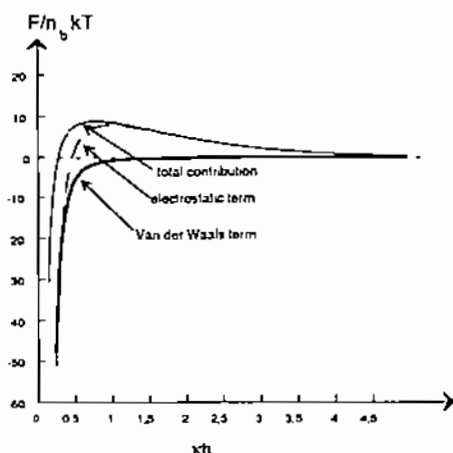


FIGURE 2 dimensionless disjoining pressure for a water/oil/glass system.

The electrical double layer disjoining pressure component for surfaces having different potentials ξ_1 and ξ_2 , is given by two expressions which correspond to two assumptions:

(i) constant potential (Hogg et al., 1965)

$$F_D(h) = n_b kT \frac{(2y_1 y_2 \cosh(\kappa h) - y_1^2 - y_2^2)}{\sinh^2(\kappa h)} \quad (6)$$

where y_i is the reduced potential ($y_i = \frac{e\xi_i}{kT}$) and κ is the reciprocal

Debye-Hückel length ($\kappa^2 = \frac{2e^2 n_b}{\epsilon kT}$)

e : charge on electron
 n_b : ion density in bulk
 ϵ : electrical permittivity
 k : Boltzman constant
 T : temperature °K.

(ii) constant charge (Gregory, 1975)

$$F_D(h) = n_b kT \left\{ 2 \left[1 + \frac{(y_1 + y_2)^2}{4} \operatorname{csch}^2\left(\frac{\kappa h}{2}\right) \right]^{\frac{1}{2}} - \frac{(y_1 - y_2)^2 e^{(-\kappa h)}}{1 + \frac{1}{4}(y_1 + y_2)^2 \operatorname{csch}^2\left(\frac{\kappa h}{2}\right)} \right\}^{-2} \quad (7)$$

Experimental results

The experimental results consist in adhesion maps given for a system oil/brine/glass. The description of the experimental setup is given in Figure 3. The oil droplet is deposited on the glass surface using a capillary tube connected to a pump.

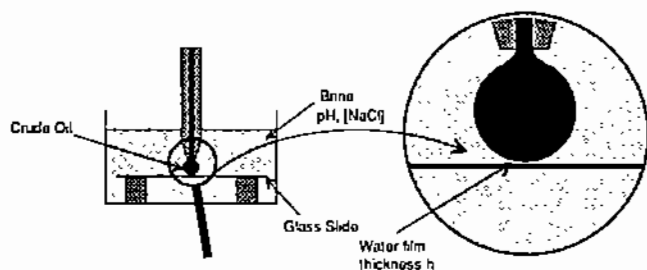


FIGURE 3 adhesion test.

A photo-video system allows us to obtain a picture of the droplet and to calculate, via the treatment of the binary picture, a mathematical expression of its shape. The Figures 4 through 6 show the different possible droplet shapes. Expressions of the corresponding disjoining pressure can be calculated from the zeta potentials measured as a function of pH and concentration of NaCl (Buckley et al., 1987).

When the capillary tube is taken off, three cases are predicted theoretically:

(1) adhesion; a drop of oil remains on the glass surface. From a theoretical point of view, this corresponds to a negative disjoining pressure (Figure 4).

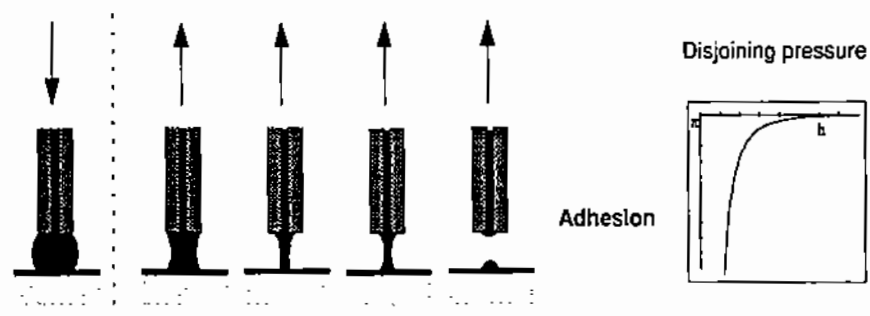


FIGURE 4 adhesion.

(2) limit case; we observe an important deformation of the oil/brine interface but there is no oil deposited on the glass surface. Theoretically, the maximum of the disjoining pressure is positive but below a critical value (Figure 5).

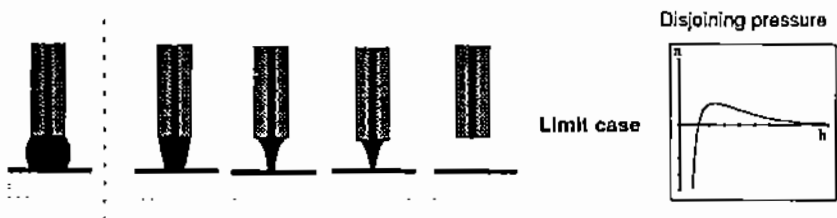


FIGURE 5 limit case.

(3) non adhesion; we do not observe an important deformation of the oil/brine interface and there is no oil deposited on the glass surface. Theoretically, the maximum of the disjoining pressure is positive and above a certain value (Figure 6).



FIGURE 6 non adhesion.

Experimental procedure

- glass is cleaned in a sulfonitric blend during at least 24 hours,
- the brine/glass system is left during at least one week, so as to reach surface potential equilibrium,
- oil/mineral adhesion are performed to see if adhesion occurs or not.

Experimental results obtained for a french crude oil provided by ELF are shown in Figure 7. In our experimental conditions, using the same glass that the one used during the two-phase flow experiments, the NaCl concentration in the brine being close to zero, we obtained that adhesion occurs only for pH below 5.8.

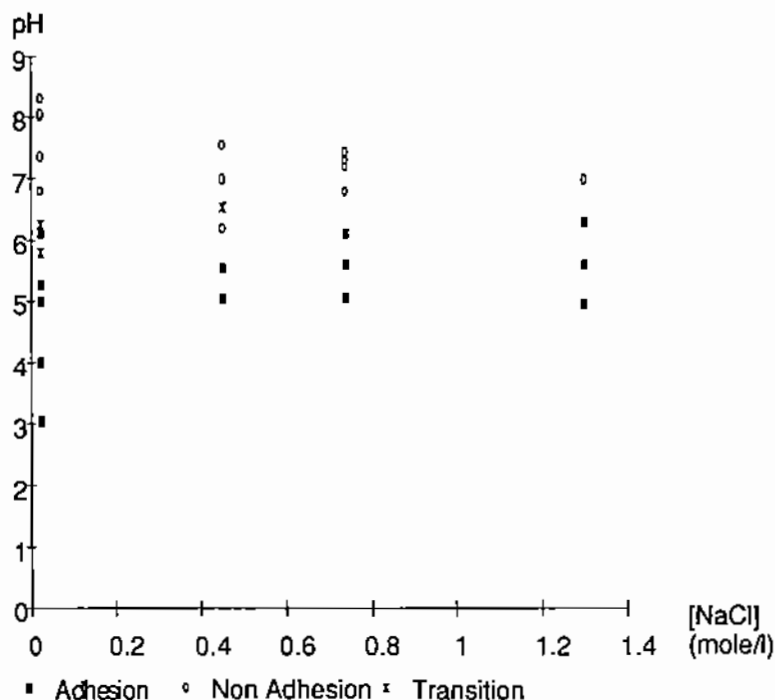


FIGURE 7 adhesion map for a system crude oil/brine/glass.

TWO-PHASE FLOW EXPERIMENTS

We performed two-phase flow experiments in a model porous medium made of glass spheres packed in a square cross section

glass tube (Figure 8). We used three different sizes for the sides of the tube side-length and the sphere diameters (6, 10, 20 mm).

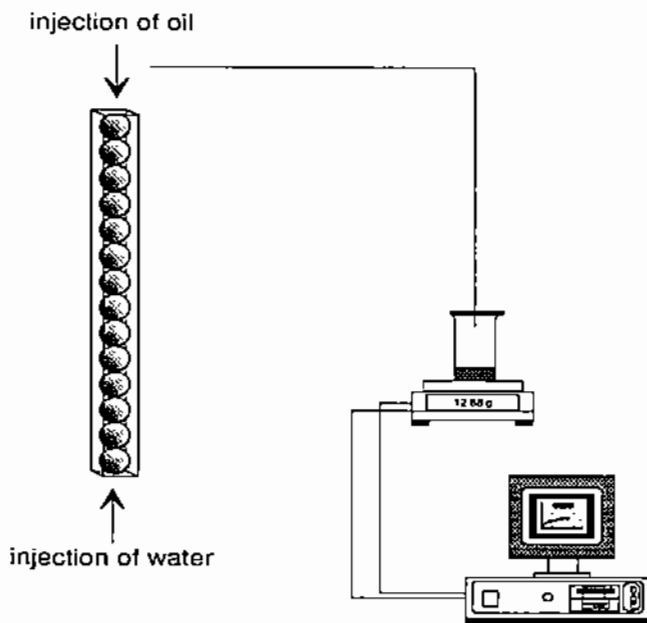


FIGURE 8 pore-scale experiment: experimental setup.

Pore-scale

-Experiments performed with a mineral oil

a) Characterization of the medium

First, a mineral oil and pure water were used to characterize the medium. The experimental procedure consists in:

- saturating the medium with water
- performing an oil/brine displacement (drainage)
- measuring gravimetrically the irreducible water saturation
- injecting water (imbibition) and measurement of the residual oil saturation.

Water is injected from the bottom of the tube and oil from the top to avoid gravity effects.

This preliminary study indicated the location of the trapping zones and the influence of flow rate on the end-point saturations. The fluids are trapped at the sphere-sphere contact and at the sphere-plane contact (Figures 9, 10 and 11).

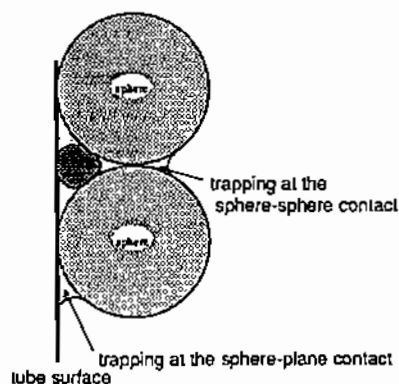


FIGURE 9 description of the trapping zones.

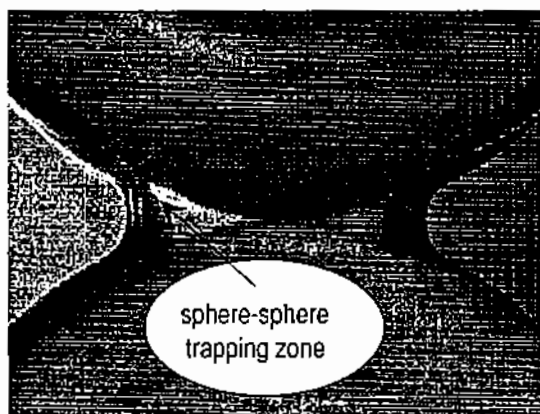


FIGURE 10 picture of trapping zone: sphere-sphere contact.



FIGURE 11 picture of trapping zone: plane-sphere contact.

b) Influence of flow rate

The irreducible wetting phase saturation (S_{wi}) and the residual non wetting phase saturation (S_{nwr}) increase with the Capillary number

($Ca = \frac{\mu_o}{\gamma_{ow}}$, where $U = \frac{Q}{S}$, Q is the injection flow-rate and S the

section area of the tube) (Figure 12).

The oil/brine displacement is less stable leading to increased residual and irreducible saturations.

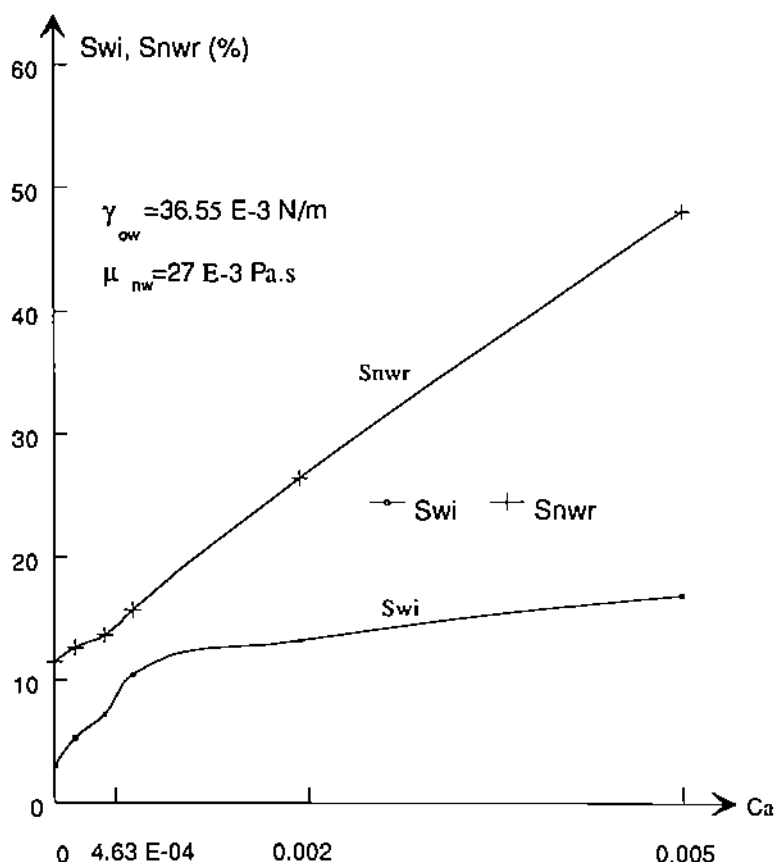


FIGURE 12 influence of capillary number on the end-point saturations

c) Oil-wet medium

Experiments were performed on a medium treated by silanization (the glass is modified in grafting silane molecules on the surface thus providing an oil-wet medium). The medium is first saturated with oil, and then brine is injected, so as to obtain the irreducible oil saturation. Next, we obtain the residual water saturation by displacing water by oil. The results show that the end point saturation are equivalent to the water-wet case (Table 1).

The inversion of the fluids role (wetting/non wetting; Water/Oil) shows that we have a perfect oil wettability with silanized media (Figure 13).

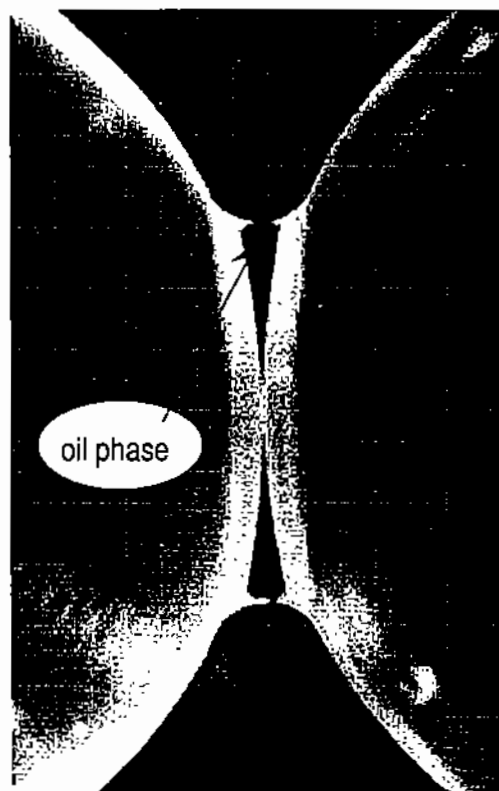


FIGURE 13 oil trapped between two silanized spheres.

TABLE 1 example of end-point saturations (tube 20x20)

Treated glass	
Residual Water Saturation (Non wetting phase)	6.5±1.8%
Irreducible Oil Saturation (Wetting phase)	0%
Clean glass	
Irreducible Water Saturation (Wetting phase)	4.1±2.6%
Residual Oil Saturation (Non wetting phase)	0%

-Experiments performed with a crude oil

a) experimental procedure

First, the medium is cleaned with different solvents in order to eliminate pollutants on the glass surface. We use several successions of a solution of Methanol, Acetone, Toluene (M.A.T.) then chloroform and M.A.T., ... After these successive operations the medium is cleaned by a sulfochromic blend, and the medium is finally rinsed with deionized water. The spheres are dried at 200°C in an oven, and the tube is flowed by nitrogen.

Water saturation

We use deionized and degased water with HCl and NaOH to impose an acid or a basic pH. Water is injected into the medium, and we wait one week for the electrochemical equilibrium.

Injection of crude oil

We wait one week for the electrochemical equilibrium.

Injection of brine

Brine is injected at a very low flow-rate to reduce the inertial effects and flow instabilities. We measure continuously the mass effluents to deduce the recovery curves.

b) Results

Only a thin film of oil is deposited on the glass surface in both adhesion and non-adhesion conditions. The trapped volumes of oil

are very small and difficult to measure. Most of the residual oil is located on the surface of irreducible water as films which are not in contact with glass. The recovery curves correspond to a "piston-like-displacement". First, we only recover oil and, after the breakthrough, only water is produced in both cases. We used two different crude oils and obtained the same results. With a silanized medium (oil-wet medium) the behaviour is similar. These results show that viscosity and inertial effects are preponderant in comparison with the capillary effects. This is illustrated by Table 2 where the Capillary numbers are very low compared with usual values found in petroleum recovery. Therefore, we choose to modify the geometry of the medium.

TABLE 2 characteristic numbers of the two-phase flow experiment for different flow-rates.

Q(cm ³ /h)	6	30	60
Re	0.04	0.21	0.42
Ca	$3.1 \cdot 10^{-6}$	$1.5 \cdot 10^{-5}$	$3.1 \cdot 10^{-5}$
Bo	4.40	4.40	4.40

Core scale

The form and dimension of the pores have a great influence on the oil trapping mechanisms due to the capillary effects. Therefore, we performed experiments similar to the previous ones using a porous medium made of calibrated glass beads ($\phi = 0.40 - 0.45$ mm) to decrease the pore size and increase the capillary effects packed in a square cross section glass tube (Figure 13).

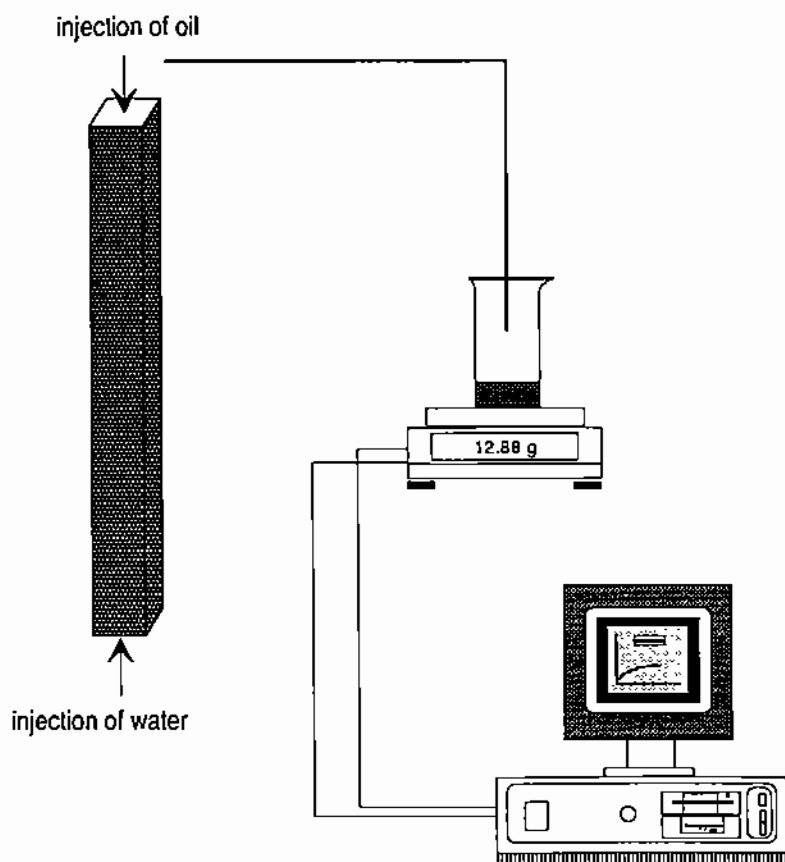


FIGURE 14 core-scale experiments: experimental setup.

The experimental procedure is similar to the previous one (injection of brine, equilibrium waiting, injection of oil, equilibrium waiting, then a waterflooding at a constant flow-rate). In this case we consider only recovery behaviour (Figure 15).

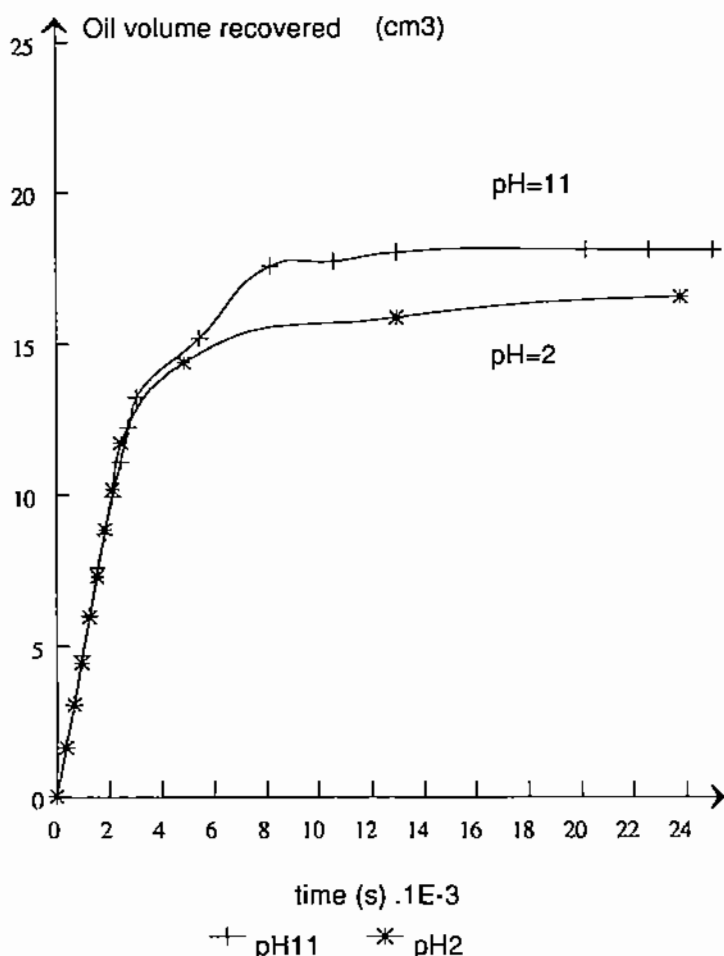


FIGURE 15 influence of pH on recovery curves.

At low values of pH (adhesion condition), the breakthrough appears early and the oil production continues slowly after. Under non adhesion conditions (basic pH), the behaviour is slightly different and we have a "piston-like-displacement" of water. This behaviour is characteristic of a water-wet medium while the previous one was characteristic of an oil-wet medium.

CONCLUSIONS AND PERSPECTIVES

The influence of adhesion phenomena on two-phase flow properties of a porous system was studied in terms of the various wettability conditions found in petroleum reservoirs.

-At the surface-scale: The surface scale experiments give the adhesion behaviour of a crude oil on a mineral substrate as a function of brine pH and salinity.

-At the pore-scale:

The use of a model porous medium allows us to describe the influence of the pore geometry and the trapping phenomena. The residual saturation is not affected by pH conditions. However they can alter wettability when acidic brines are used.

-At the core-scale:

A decrease in the pore size increases capillary forces, therefore, a wettability change occurs which explains the differences in the observed recovery curves.

Experiments with a realistic porous medium made of either sandstone or unconsolidated sand are under way for which differential pressure, recovery curves as well as the local saturations (absorption gamma) will be measured.

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