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Presented by :

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-TOPIC-

# EFFECT OF WETTABILITY ON THE OIL RECOVERY MECHANISMS

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Secondly I would like to express my special thanks to my teacher Djebbas Faycal and Bazzine Zineb who gave me the golden opportunity to do this wonderful project on the topic ’’Effect of wettability on the oil recovery mechanisms’’, which also helped me in doing a lot of research and i came to know about so many new things, i am really thankful to them.

ZENNANI WALID

## ***I dedicate this modest work :***

To my dear parents to my grandmother and all my family and my friends to whom i owe what i all am what I realize thank you for supporting and loving me during all these years of being so proud of me.

ZENNANI WALID

# Acknowledgment

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I address my sincere thanks to all the professors, speakers and all the people who by their words, their writings, their advice and their criticisms guided my reflections and agreed to meet me and answer my questions during my research, I thank my dear parents, my friends.

Moncef Rachid

# Dedication

**Finally, I thank my friends djamal issam hamza who have always been there for me. Their unconditional support and encouragement has been a great help.**

**To all of these speakers, I present my thanks, respect and gratitude.**

Moncef Rachid

# Abstract:

In hydrocarbon reservoirs the ultimate oil recovery is the main goal for all petroleum companies, the recovery mechanism are different from reservoir to another and it depends of several criteria, either in microscopic or macroscopic level.

The wettability of the rock to a fluid is a fundamental factor as it impacts on the capillary phenomena in particular while the two main flowing process, the imbibition (the re-saturation) process can be happen spontaneous or forced it depends of the value of the capillary pressure (Pc).

A spontaneous or forced imbibition process impacts directly to oil recovery factor for a water-wet system, the important amount of the oil is recovery by applying the spontaneous imbibition process, and no further increase in water saturation in the forced imbibition process.

Otherwise, for an oil-wet the process there will be a significant recovery by forced water injection and for a mixed wet system layers can lead to medium oil recovery by spontaneous imbibition, followed by significant further recovery by forced water injection as a greater force is applied to displace the oil. Through this project a bibliographic research work will be done to check the impact of the wettability on the oil recovery mechanism and the different factors altering the rock wettability.

Reservoir wettability plays an important role in various oil recovery processes. It is a significant issue in multiphase flow problems ranging from oil migration from source rocks to such enhanced recovery processes as alternate injection of CO2 and water.

**Key words:** enhanced oil recovery, wettability, alteration, recovery, injection.

# Résumé :

Dans les réservoirs d'hydrocarbures, la récupération ultime du pétrole est l'objectif principal de toutes les sociétés pétrolières, les mécanismes de récupération sont différents d'un réservoir à l'autre et dépendent de plusieurs critères, que ce soit au niveau microscopique ou macroscopique.

La mouillabilité de la roche à un fluide est un facteur fondamental car elle a un impact sur les phénomènes capillaires en particulier alors que les deux principaux processus d'écoulement, le processus d'imbibition (la resaturation) peut être spontané ou forcé cela dépend de la valeur de la pression capillaire. Un processus d'imbibition spontanée ou forcée a un impact direct sur le facteur de récupération d'huile pour un système humide, la quantité importante d'huile est la récupération en appliquant le processus d'imbibition spontanée et aucune augmentation supplémentaire de la saturation en eau dans le processus d'imbibition forcée.Sinon, pour un processus humide, il y aura une récupération significative par injection d'eau forcée et pour un système humide mixte, les couches peuvent conduire à une récupération d'huile moyenne par imbibition spontanée, suivie d'une récupération supplémentaire significative par injection d'eau forcée car une force plus grande est appliqué pour déplacer l'huile.

A travers ce projet un travail de recherche bibliographique sera effectué pour vérifier l'impact de la mouillabilité sur le mécanisme de récupération du pétrole et les différents facteurs altérant la mouillabilité de la roche.La mouillabilité des réservoirs joue un rôle important dans divers processus de récupération du pétrole. Il s'agit d'un problème important dans les problèmes d'écoulement multiphasique allant de la migration du pétrole des roches mères à des processus de récupération améliorés comme l'injection alternée de CO2 et d'eau.

**Les mots clés :** récupération améliorée d’huile, mouillabilité, altération, récupération, injection.

## الملخص :

في مكامن الهيدروكربون، يعتبر الاستخراج النهائي للنفط هو الهدف الرئيسي لجميع شركات البترول، وتختلف آلية الاستخراج من خزان إلى آخر وتعتمد على عدة معايير، إما على المستوى المجهري أو العياني.

إن قابلية البلل في الصخور إلى سائل هو عامل أساسي لأنه يؤثر على الظواهر الشعرية، ولا سيما عملية التشبع (إعادة التشبع) التي يمكن أن تحدث تلقائيًا أو قسريًا يعتمد على قيمة الضغط الشعري.

تؤثر عملية التشرب العفوي أو القسري بشكل مباشر على عامل استخلاص الزيت لنظام ماء-رطب، والكمية المهمة للزيت هي الاستعادة من خلال تطبيق عملية التشرب العفوي، ولا زيادة أخرى في تشبع الماء في عملية التشرب القسري.

خلاف ذلك، بالنسبة لنظام زيت-رطب، سيكون هناك استرجاع كبير عن طريق الحقن القسري للمياه، ويمكن أن تؤدي طبقات النظام رطب-مختلط إلى استخلاص الزيت المتوسط عن طريق التشريب التلقائي، متبوعًا باستعادة إضافية كبيرة عن طريق الحقن القسري للماء كقوة أكبر يتم تطبيقها لتحل محل الزيت. من خلال هذا المشروع، سيتم عمل بحث ببليوغرافي للتحقق من تأثير القابلية للبلل على آلية استعادة النفط والعوامل المختلفة التي تغير قابلية ترطيب الصخور.

تلعب قابلية البلل في الخزان دورًا مهمًا في عمليات استرداد النفط المختلفة إنها قضية مهمة في مشاكل التدفق متعدد المراحل التي تتراوح من هجرة النفط من صخور المصدر إلى عمليات الاستعادة المحسنة مثل الحقن البديل لثاني أكسيد الكربون والماء.

**الكلمات الدالة:** تعزيز إستعادة النفط, الرطوبة, تغيير, إستعادة, حقن

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# List of abbreviations:

| | |
|---|---|
| USBM: | United State Bureau of Mines |
| S: | Saturation |
| P: | Pressure |
| WAG: | Water Alternating Gas |
| PV: | Pore Volume |
| EOR: | Enhanced Oil Recovery |
| IFT: | Interfacial tension |

# List of symbols:

| | |
|---|---|
| $\sigma$ : | Interfacial tension |
| $R_c$: | Interface radius of curvature |

# Introduction:

Recovery efficiency of oil is dependent upon the wettability of the rock matrix. In a water-wet system, the oil (which is the nonwetting phase) resides predominantly in the larger pores of the rock matrix and is relatively more mobile than if it resided in the smaller pores. Therefore, in a primary recovery with a pressure drop at the wellbore, the oil phase moves towards the production well with relative ease compared to oil in the oil-wet system that is trapped in smaller pores of the rock matrix. The efficiency of drive mechanisms (solution gas, gas cap, or natural water drive) in primary recovery is also dependent on the wettability of the rock under most circumstances, the recovery efficiency is higher in a water-wet reservoir because of higher relative permeability.

Secondary recovery involves the injection of water (sometimes with dissolved additives) to displace reservoir oil to nearby production wells. In a water-wet reservoir water imbibes into the matrix pores, including the small pores, and displaces the resident fluids. The water resides in the smaller pores and is displaced by the injected water, which in turn displaces the oil from the larger pores towards the production well. With the continued injection of water, the water phase saturation increases and the capillary pressure decreases. Water saturation continues to increase until the differential pressure between water (wetting) and oil (nonwetting) becomes zero. To increase the water saturation beyond this point (meaning to produce more oil) the pressure of the water phase has to be greater than the oil phase or in other words, there has to be negative capillary pressure. This is observed in mature waterflood cases in a water-wet reservoir. It is also observed in the initial phases of a waterflood in an oil- wet reservoir.

In an oil-wet reservoir, the pressure in the nonwetting phase (water phase) is increased with the injection of water. It displaces the oil phase from pore spaces (oil resides in the smaller pores) that are increasingly more difficult for the water (nonwetting) phase to enter because of pore throat restrictions or adhesion force of the oil phase to the matrix. Subsequently, a point is reached when the water phase cannot enter the remaining pore spaces where the oil phase resides (even at very high injection pressure), resulting in a relatively smaller recovery efficiency compared to a water-wet system.

Recovery efficiencies can be enhanced by wettability reversal and some tertiary recovery processes can achieve these reversals. Research has shown that, in general, the recovery efficiency is higher in a water-wet system however, reservoirs are seldom completely water-wet. In general, reservoirs have a combination of water- and oil-wet regions with overall preferential wettabilities that are either water- or oil-wet. Therefore injection of water (even in a water-wet reservoir) may not be as efficient as expected in order to make the recovery process more efficient, application of wettability modifiers (chemicals or heat) are used. These modifiers can reverse the wettability of the portions of the reservoir that are not water-wet. Although heat applications generally change reservoir wettability towards more water-wet conditions heat has also been shown to change the wettability toward more oil-wetting conditions in some cases.

Tertiary recovery processes such as surfactant flooding and nanoparticals and polymers injection can alter the wettability of the reservoirs in some cases which can improve oil recovery. Though the primary additional recovery mechanism in the surfactant flooding process is attributed to the lowering of the interfacial tension between the injected fluid and the oil, wettability alteration can also improve recovery significantly. Selection of the type of surfactant is essential in ensuring improved recovery because of wettability alteration. Some surfactants could even adversely affect the wettability and lower ultimate recovery. Surfactants also are used extensively in drilling mud and completion fluids that can change the wettability at the wellbore and affect ultimate recovery.

# *CHAPTER I :*

## *Mainly about wettability*

## I-1 Understanding Wettability :

Wettability is the relative adhesion of two fluids to a solid surface. With respect to two immiscible fluids in a porous media, wettability is the measure of the preferential tendency of one of the fluids to wet (spread or adhere to) the interstitial surfaces of the porous medium in the presence of the other fluid. The surfaces of the pores in rocks contain a wide variety of exposed minerals that have preferential affinities for water, hydrocarbons, or constituents suspended and dissolved in the fluids.Thus for a water/oil/rock system, the term wettability refers to the average, overall, relative wetting preference of the interstitial surfaces of the rock. [1]

Four general states of wettability have been recognized: water-wet, fractional-wettability, mixed-wettability, and oil-wet.

## I-2- Wettability mesurement:

### I-2-1 Contact Angle:

Consider a drop of water resting on a horizontal surface immersed in oil **FIG I-1**. The drop of water will adopt a position between completely spreading on the surface (infinitely water-wet with a contact angle equal to $0^0$) or a round drop resting lightly on the surface because its density is greater than the oil's density (infinitely oil-wet surface, contact angle = $180^0$), Between these two extremes, the general shape of the drop will exhibit a measurable contract angle (measured through the denser phase). The force exerted by the oil-water interfacial tension acts tangent to the surface of the drop with its horizontal component **$\sigma wc$ Cos$\theta$**, pulling the circumference of the drop toward its center, **FIG I-1**. The water-solid IFT pulls the circumference of the water drop area of contact with the solid toward the center. At equilibrium these two forces are balanced by the oil-solid IFT of an adsorbed layer of oil on the solid surface acting to pull the circumference of the drop's area of contact away from its center.

The contact angle and interfacial tensions of a sessile drop are related according to Young's equation (1855) : $\sigma_{os} - \sigma_{ws} = \sigma_{ow} \cos\theta$

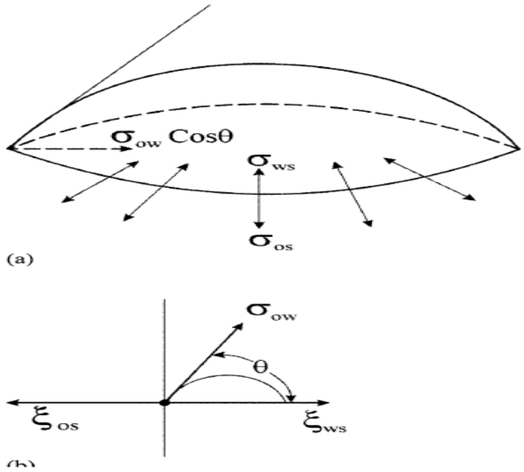


**FIG I-1** : Drop of liquid resting on a solid surface. (a) The tensile interfacial forces pull the drop into a spherical shape. (b) Two dimensional view of the forces acting on the drop and the contact angle.[2]

**FIG I-2** a-c show the configuration of sessile drops and the water/oil interface for different conditions of wettability. The surface is water-wet (hydrophilic) when the contact angle is less than $90^0$ and the pressure difference across the interface (capillary pressure, PJ is positive; neutral-wet at contact angles close to $90^0$ (Pc=0); and oil-wet (hydrophobic) for angles greater than $90^0$ ($P_c$ is negative).[2]

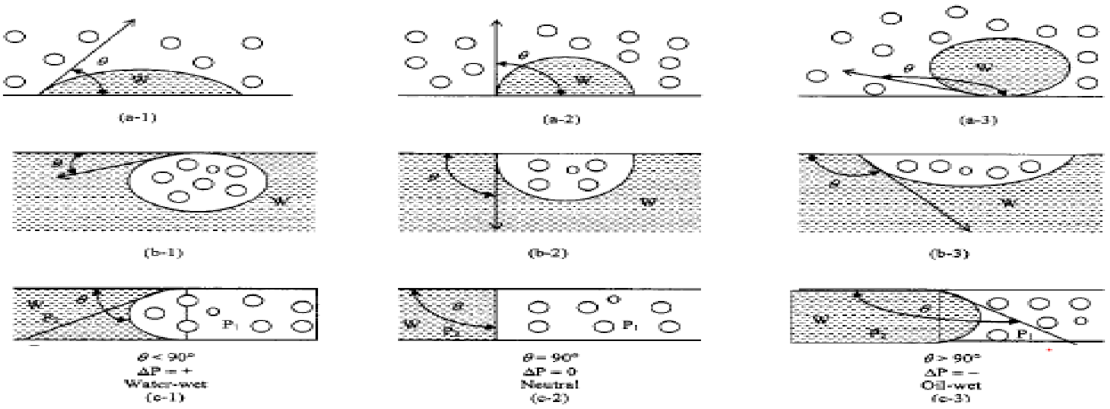


**FIG I-2**: contact angles for various wetting conditions of water and oil: (a) drops of water in oil on a plane surface, (b) drops of oil on a plane surface, and (c) water and oil in a capillary tube.

## I-2-2 Amott test :

Wettability measurements by the Amott method give a guide to the relative oil or brine wetting tendencies of reservoir rocks. This can be crucial in the selection of relative permeability test methods to generate data relevant to the reservoir situation. It is not always possible to reproduce reservoir wettabilities in room condition relative permeability tests. However, an appreciation of the difference between reservoir and laboratory wettabilities can assist in interpretation of laboratory waterfloods.[3]

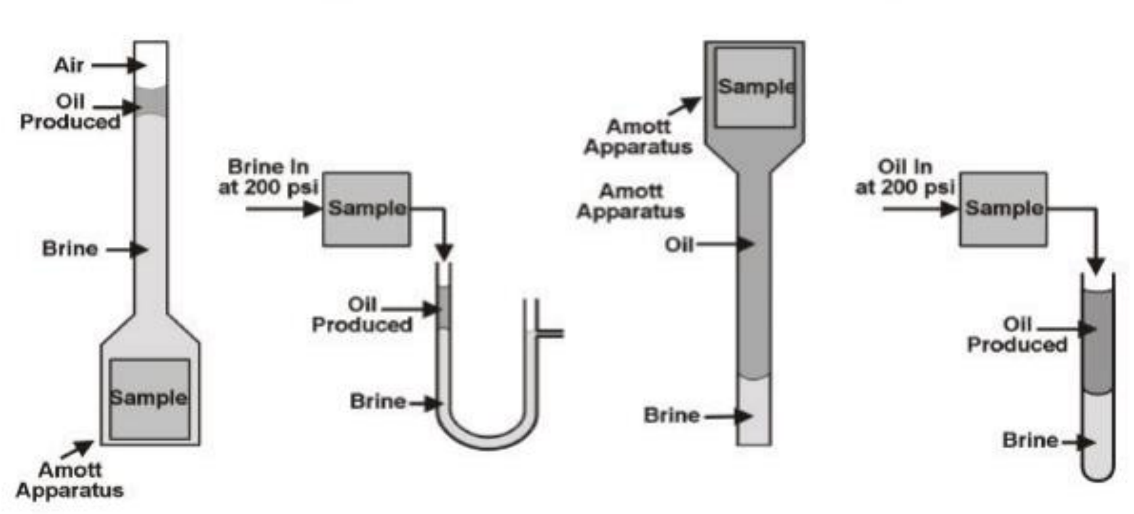


**FIG I-3 :** Amott wetting technique

In general use the samples to be measured are centrifuged or flooded with brine, and then flooding or centrifuging in oil to obtain $S_{wi}$. The standard Amott method is then followed. At the end of the experiment the so called Amott-Harvey wettability index is calculated :

$$\text{Index} = \frac{\text{SpontaneousWaterImbibition}}{\text{TotalWaterImbibition}} - \frac{\text{SpontaneousOilImbibition}}{\text{TotalOilImbibition}} \quad [3]$$

Wettability indices are usually quoted to the nearest 0.1 and are often further reduced to weakly, moderately or strongly wetting. The closer to unity the stronger the tendency.

### I-2-2-1 Spontaneous imbibition:

In very strongly water-wet systems, spontaneous imbibition of water from $S_{wi}$ may increase the water saturation all the way to $S_{or}$, (the imbibition capillary pressure curve (**FIG I-4**) curve 2, is greater than zero until it reaches $S_{or}$). When this occurs, the USBM wettability index I cannot be determined, and only the displacement-by-water ratio of the Amott wettability index can be determined. Thus both indices only indicate that the system is very strongly water-wet however, the rate of imbibition and the capillary pressure curve versus water saturation (measured at incremental increases of capillary pressure as the saturation changes from $S_{wi}$ to $S_{or}$) can be used to examine the wettability of very strongly water-wet systems.

When water is displaced to $S_{Wi}$ the capillary pressure begins a rapid increase toward an infinite value. If the fluid pressure is relaxed at this point in a water-wet or intermediate-wet system, the core will imbibe water as the capillary pressure declines to zero because of a decrease of the surface free energy. As imbibition takes place, the wetting phase saturation increases from $S_{Wi}$ to Sz (the point at which the imbibition pressure is equal to zero).[3]

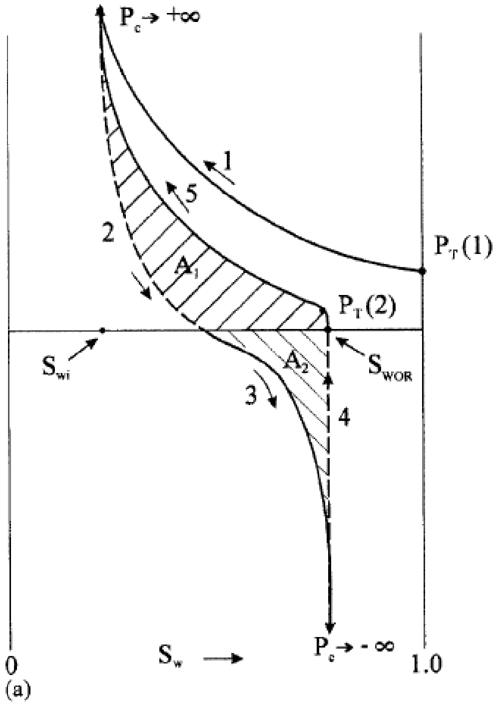


**FIG I-4** : water-wet capilary pressure curves :

1: oil displacing water Sw=1 to 0.

2: spotaneous imbibition of water.

3: forced displacement of oi for Swor .

4: threshold pressure PT(2) must be exceeded before oil can enter.

5: forced displacement of water by oil.

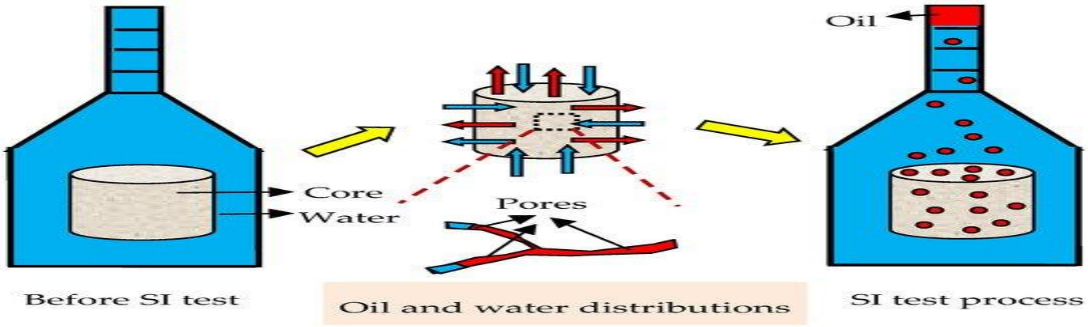


**FIG I-5 :** Spontaneous imbibition test [3]

## I-2-2-2 Forced imbibiton :

forced imbibition are recognized as important recovery mechanisms in naturally fractured reservoirs because the capillary force controls the movement of the fluid between the matrix and the fracture. For unconventional reservoirs, imbibition is also important because the capillary pressure is more dominant in these tighter formations, and a theoretical understanding of the flow mechanism for the imbibition process will benefit the understanding of important multiphase-flow phenomena such as waterblocking.[3]

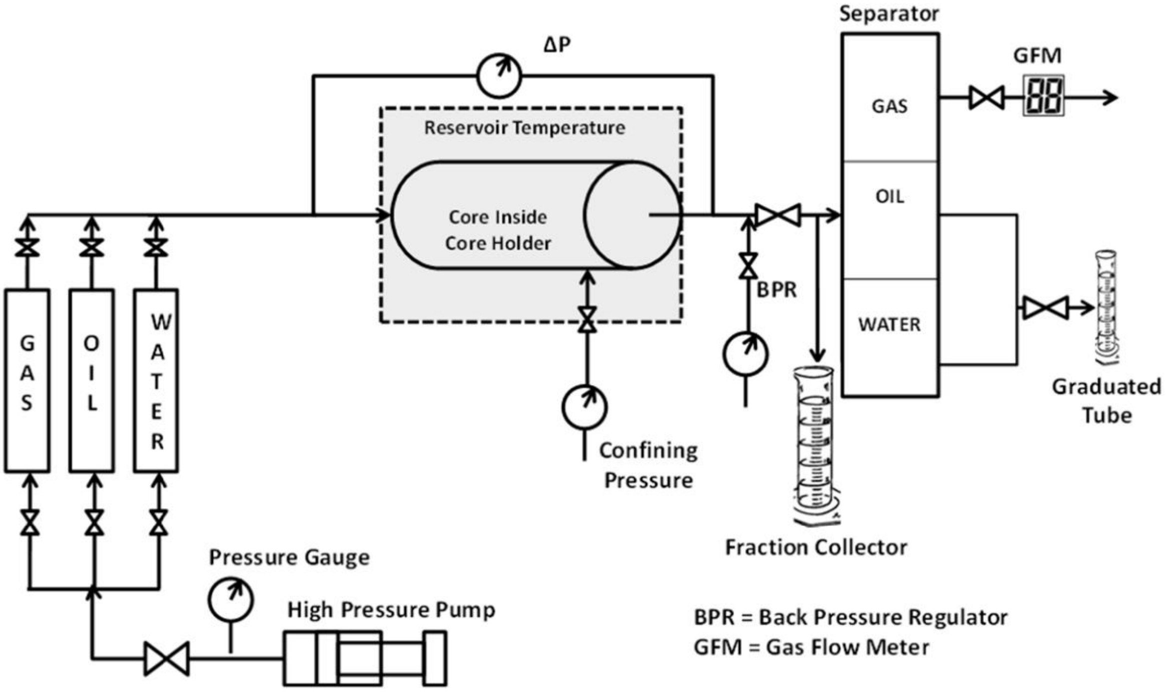


**FIG I-6:** Forced imbibiton [3]

## I-2-3 USBM Wettability Measurements:

This method is very similar to the Amott method, but measures the work required to do the imbibitions. It is usually done by centrifuge, and the wettability index W is calculated from the areas under the capillary pressure curves A1 and A2: $W=\log\frac{A1}{A2}$ [2]

where, A1 and A2 are defined in Figure Note that in this case the initial conditions of the rock are Sw=100%, and an initial flood down to Swi is required, although either case may be necessary for either the Amott or USBM methods.[2]

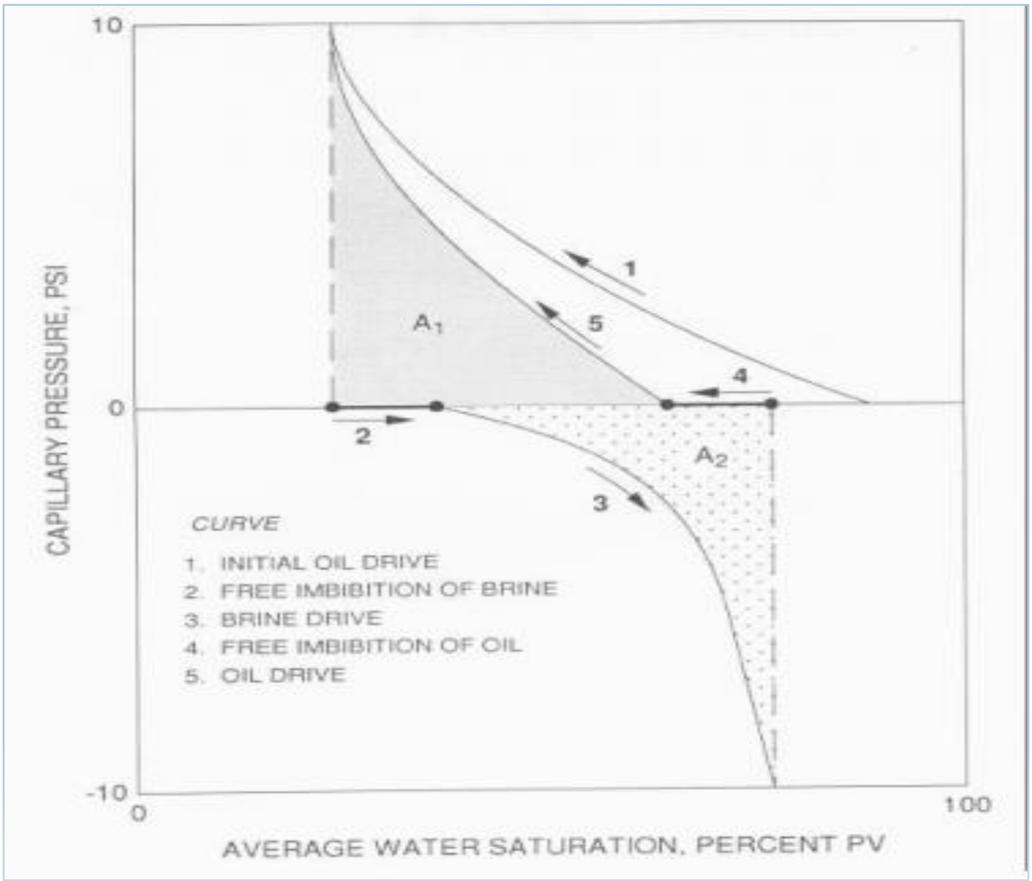


**FIG I-7** : USBM wettbility test capillary pressure curve [2]

# CHAPTER ll :

# Impact of the wettability in the different petrophysical properties

## II-1-1 Impact of the wettability on capillary pressure :

The interfacial tension induces a pressure difference between the two sides of the interface, the pressure in the non-wetting fluid (index nm) is greater than that in the wetting fluid (index m), This condition results in Laplace's law. [4]

Displacement processes in capillary systems are described as drainage and imbibition. Drainage means that the wetting fluid is displaced by the nonwetting fluid, and imbibition is the opposite (the displacement of the nonwetting fluid by the wetting fluid). Spontaneous imbibition of the wetting phase occurs as the capillary pressure declines to zero.

The terms drainage and imbibition can be confusing because they apply to the specific wettability condition: for a water-wet rock the terms refer to water, but for an oil-wet rock they apply to oil. For an intermediate-wet system the terms apply to both phases because they are both equally wetting the rock surfaces. Therefore, instead of using drainage and imbibition, the fluid leaving the core will be referred to as the displaced fluid and the fluid entering the core will be referred to as the injected fluid regardless of the wettability condition of the porous medium.[4]

$P_c = (P_{nm}-P_m) = \frac{\sigma}{Rc}$ [4]

σ :Interfacial tension

Rc :Interface radius of curvature

The difference between the respective pressures Pc = (Pnm-Pm)is called the capillary pressure.

Capillary pressure is an important reservoir property because it directly or indirectly affects other properties such as residual saturations and relative permeability curves. The relationship between capillary pressure and phase saturation is a function of wettability, pore structure, interfacial tension, rock properties, and saturation history, When two immiscible fluids are in contactin the interstics of pourous medium.

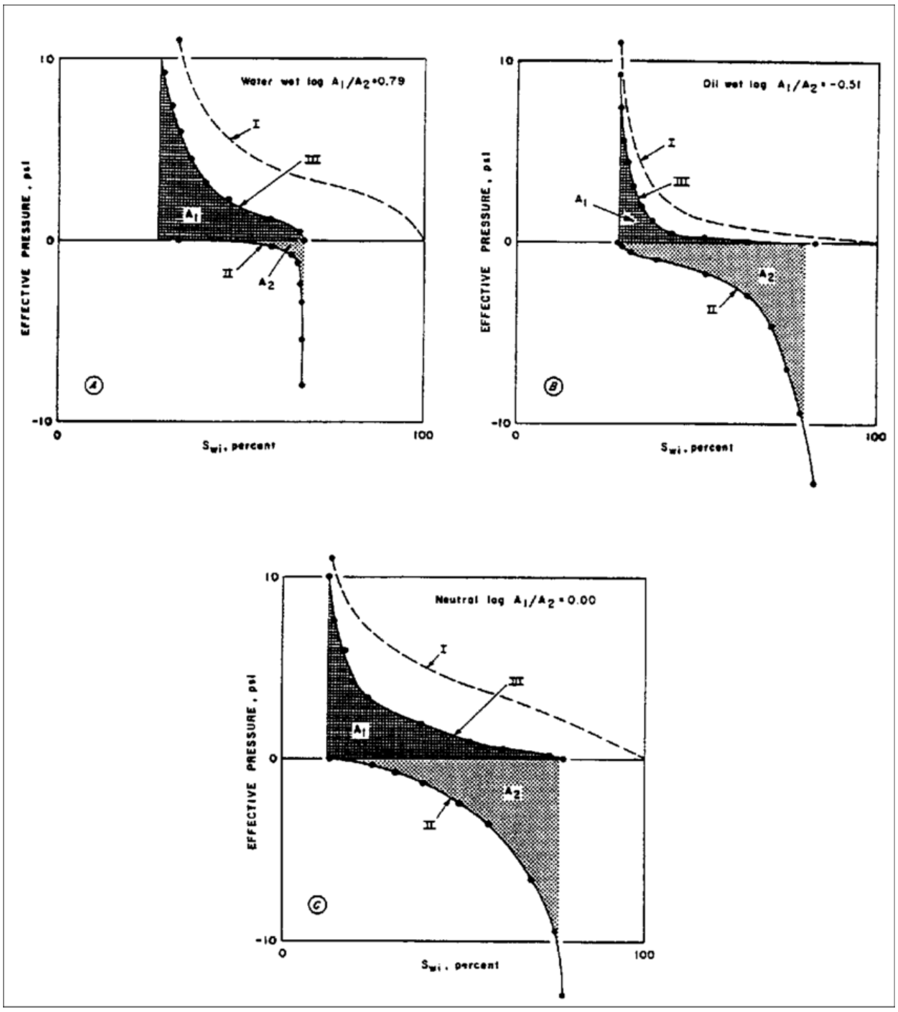


**FIG II-1** : capillary pressure saturation curve [4]

As we see in capillary pressure saturation curve shows that in the same water saturation Sw we observe that Pc1> Pc2> Pc3 note that :

Pc1 : water wet.

Pc1 : neurtal.

Pc1 : oil wet.

Thats mean that the changing of wettability of reservoir rock change capillary pressure.

In other experment require to study how the different wettability core can change the capillary pressure that we can see in the next curve of capillary pressure saturation curve shows that in the same water saturation Sw we Note that in the mixed wettability give a lower capillary pressuer that shoes also the effect of reservoir rock wettabillity oncappillary pressure.

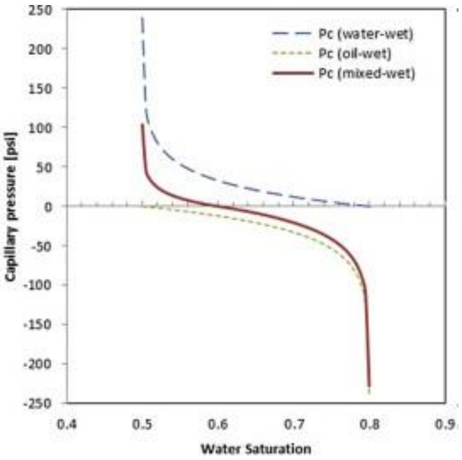


**FIG II-2** : capillary pressure saturation curve [5]

## II-1-2 Impact of the wettability on Saturation:

Fluid saturation is how much each fluid is present in pore spaces of a rock, this will affect the abillity of each fluid flow through porous media. this is one of critical values for reservoir engineering since many engineering calculations need fluid saturation values.[6]

The saturation is an important reservoir property because it directly or indirectly affects other properties such as water saturations and relative permeability curves. The relationship between saturation and phase saturation is a function of wettability, pore structure, interfacial tension, rock properties, and saturation history, When two immiscible fluids are in contactin the interstics of pourous medium. The next curve of relative permiability and water saturaton with different wettability caractirstics (oil wet, water wet, neutal wet).

Shows that the changing of wettability in reservoir rock will affect the final water saturation, whish also give an idea to how residual oil saturation can be.

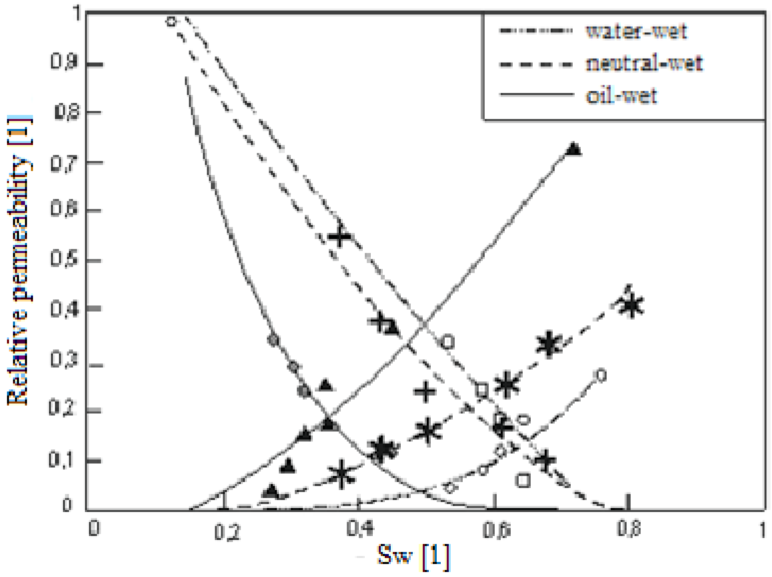


**FIG II-3** : Relative permeability water saturation curve [6]

## II-1-3 Impact of wettability on Relative permeability:

The ability or measurement of a rock's ability, to transmit fluids, typically measured in darcies or millidarcies. The term was basically defined by Henry Darcy, who showed that the common mathematics of heat transfer could be modified to adequately describe fluid flow in porous media. Formations that transmit fluids readily, such as sandstones, are described as permeable and tend to have many large, wellconnected pores. Impermeable formations, such as shales and siltstones, tend to be finer grained or of a mixed grain size, with smaller, fewer, or less interconnected pores. Absolute permeability is the measurement of the permeability conducted when a single fluid, or phase, is present in the rock. Effective permeability is the ability to preferentially flow or transmit a particular fluid through a rock when other immiscible fluids are present in the reservoir (for example, effective permeability of gas in a gaswater reservoir). The relative saturations of the fluids as well as the nature of the reservoir affect the effective permeability. Relative permeability is the ratio of effective permeability of a particular fluid at a particular saturation to absolute permeability of that fluid at total saturation. If a single fluid is present in a rock, its relative permeability is 1.0. Calculation of relative permeability allows for comparison of the different abilities of fluids to flow in the presence of each other, since the presence of more than one fluid generally inhibits flow.[4]

The relative permiability is an important reservoir property because it directly or indirectly affects other properties such as water saturations and capillary pressure curves. The relationship between relative permiability and wettability is When two immiscible fluids are in contactin the interstics of pourous medium. The next curve of relative permiability and water saturaton with different wettability caractirstics.

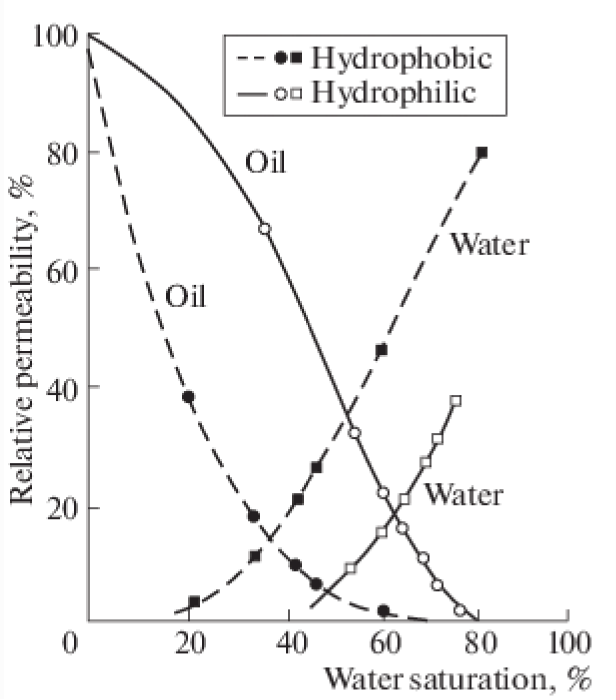


**FIG II-4** : Relative permiability water saturation curve [7]

## II-1-4 Impact of wettability on Viscosity :

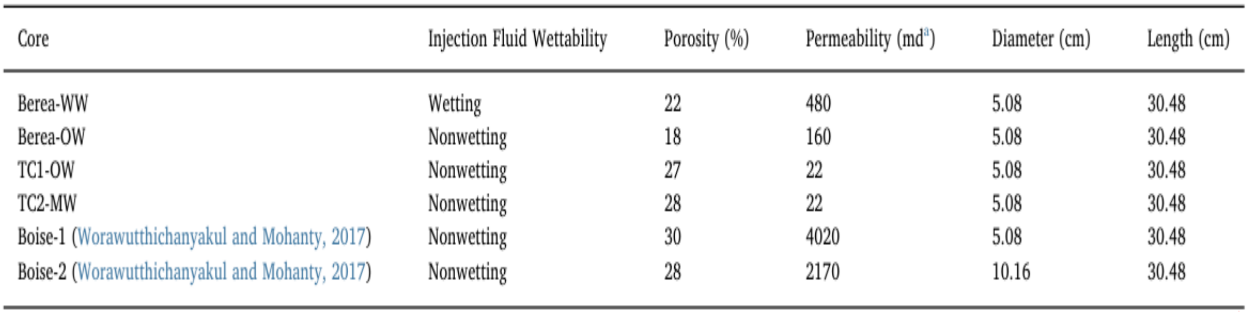
Many natural and industrial processes involve unstable displacements in porous materials. Instability can be caused by unfavorable viscosity ratio (the displacement of a high viscosity fluid with a low viscosity fluid), these displacement processes can be classified into immiscible and miscible processes.

## Experement :

A Berea sandstone (Berea-OW) and a Texas cream limestone (TC1 OW) were used to study fingering in strongly oil-wet (drainage mode) systems. The cores were used in their original water-wet state, but the water and oil were switched (as the displacing/displaced fluid pair) so that a light hydrocarbon (heptane or decane) was used to displace a viscosified water phase. Since the cores were still strongly water-wet, the displacements will be unstable drainage processes and will be analogous to water displacing oil in a strongly oil-wet reservoir. The water recovery in these experiments is therefore analogous to the oil recovery in strongly oil-wet systems.[8]

The Texas Cream limestone core (TC2-MW) was saturated with a crude oil and aged at 80 °C for 30 days. After aging, wettability was tested by putting hexane and water droplets on the surface of the dry core. Only hexane droplet imbibed spontaneously; water droplet stayed on the surface. This test indicated that the core is relatively oil-wet. However, treatments with crude oil often yield an intermediate/mixed degree of oil-wetness (Kovscek et al., 1993). This is because crude oil may only contact parts of the rock surface with certain minerals and make that part oil-wet. Other areas may remain water-wet after aging in a crude oil. This core is labeled “mixed-wet”.

**Table II-1** : Properties of the cores used in unstable corefloods [8]



| Core | Injection Fluid Wettability | Porosity (%) | Permeability (md[a]) | Diameter (cm) | Length (cm) |
|---|---|---|---|---|---|
| Berea-WW | Wetting | 22 | 480 | 5.08 | 30.48 |
| Berea-OW | Nonwetting | 18 | 160 | 5.08 | 30.48 |
| TC1-OW | Nonwetting | 27 | 22 | 5.08 | 30.48 |
| TC2-MW | Nonwetting | 28 | 22 | 5.08 | 30.48 |
| Boise-1 (Worawutthichanyakul and Mohanty, 2017) | Nonwetting | 30 | 4020 | 5.08 | 30.48 |
| Boise-2 (Worawutthichanyakul and Mohanty, 2017) | Nonwetting | 28 | 2170 | 10.16 | 30.48 |

To better quantify the wettability condition in experiments, contact angles between the displacing/displaced fluid pair on each core were measured using the sessile drop method with a contact angle goniometer.

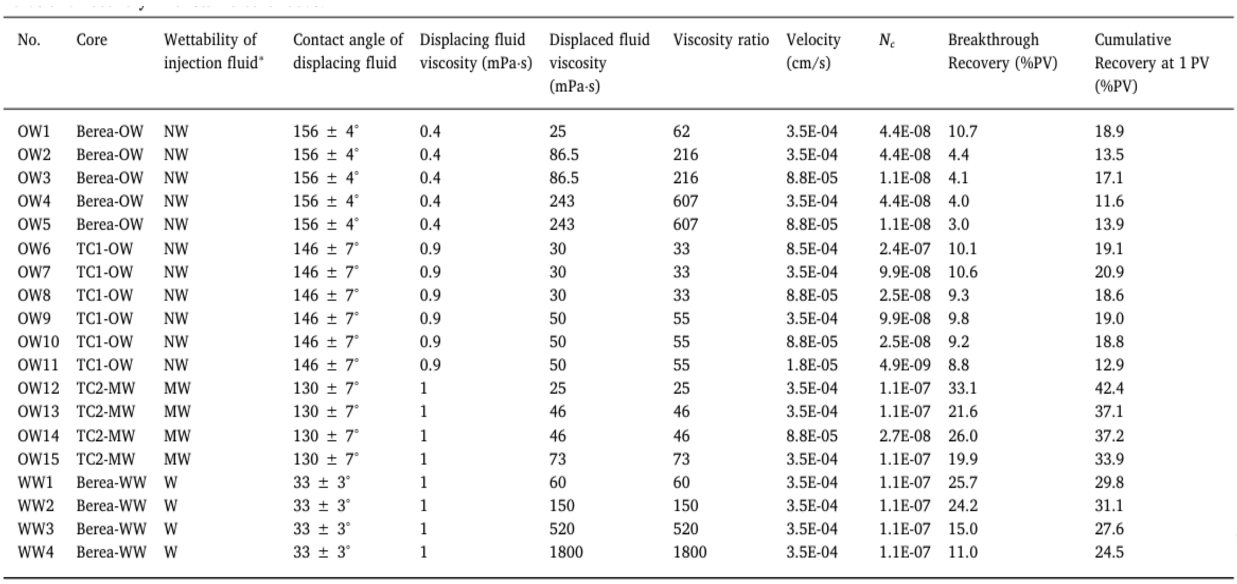
A stainless-steel Hassler Type core holder was used for the coreflood experiments. An overburden pressure of 1000 psi was maintained for all experiments. The core holder was mounted vertically and kept at the room temperature. Flow direction during the coreflood is selected so that no instability is caused by the gravity effect. In all experiments, the capillary number Nc were kept below the normal critical capillary number for water-wet sandstone, so that capillary desaturation effect is minimal in the experiments.

For WW1-4, the core was first vacuum saturated with 1% NaCl brine. Then mineral oils of different viscosities were injected from the top until no brine was produced and the core reached residual water saturation ($S_{wr}$). Then the coreflood was started by injecting brine from the bottom of the core holder at a constant flow rate. After each experiment, the core was cleaned by injecting toluene - acetone and then oven dried before the next experiment.

For OW1-OW11, the core was first vacummed saturated with 1% NaCl brine. Then glycerol solutions of different viscosities were injected from the bottom until the effluent had the same viscosity as the injected glycerol solution. Then the coreflood was started by injecting heptane or decane from the top of the core holder at a constant flow rate. This is analogous to water displacing oil in an oil-wet medium with an initial oil saturation of 100%. After each experiment, the core was cleaned by injecting toluene - acetone and then oven dried before the next experiment.

For OW12-15, the core was first vacuum saturated with 1% NaCl brine. Then mineral oils of different viscosity were injected from the top until no brine was produced and the core reached the residual water saturation ($S_{wr}$). Then the coreflood was started by injecting brine from the bottom of the core holder at a constant flow rate. After each experiment, the core was cleaned by injecting heptane and then oven dried before the next experiment. [8]

**Table II-2** : Fuids and recovery in unstable corefloods



| No. | Core | Wettability of injection fluid* | Contact angle of displacing fluid | Displacing fluid viscosity (mPa·s) | Displaced fluid viscosity (mPa·s) | Viscosity ratio | Velocity (cm/s) | $N_c$ | Breakthrough Recovery (%PV) | Cumulative Recovery at 1 PV (%PV) |
|---|---|---|---|---|---|---|---|---|---|---|
| OW1 | Berea-OW | NW | 156 ± 4° | 0.4 | 25 | 62 | 3.5E-04 | 4.4E-08 | 10.7 | 18.9 |
| OW2 | Berea-OW | NW | 156 ± 4° | 0.4 | 86.5 | 216 | 3.5E-04 | 4.4E-08 | 4.4 | 13.5 |
| OW3 | Berea-OW | NW | 156 ± 4° | 0.4 | 86.5 | 216 | 8.8E-05 | 1.1E-08 | 4.1 | 17.1 |
| OW4 | Berea-OW | NW | 156 ± 4° | 0.4 | 243 | 607 | 3.5E-04 | 4.4E-08 | 4.0 | 11.6 |
| OW5 | Berea-OW | NW | 156 ± 4° | 0.4 | 243 | 607 | 8.8E-05 | 1.1E-08 | 3.0 | 13.9 |
| OW6 | TC1-OW | NW | 146 ± 7° | 0.9 | 30 | 33 | 8.5E-04 | 2.4E-07 | 10.1 | 19.1 |
| OW7 | TC1-OW | NW | 146 ± 7° | 0.9 | 30 | 33 | 3.5E-04 | 9.9E-08 | 10.6 | 20.9 |
| OW8 | TC1-OW | NW | 146 ± 7° | 0.9 | 30 | 33 | 8.8E-05 | 2.5E-08 | 9.3 | 18.6 |
| OW9 | TC1-OW | NW | 146 ± 7° | 0.9 | 50 | 55 | 3.5E-04 | 9.9E-08 | 9.8 | 19.0 |
| OW10 | TC1-OW | NW | 146 ± 7° | 0.9 | 50 | 55 | 8.8E-05 | 2.5E-08 | 9.2 | 18.8 |
| OW11 | TC1-OW | NW | 146 ± 7° | 0.9 | 50 | 55 | 1.8E-05 | 4.9E-09 | 8.8 | 12.9 |
| OW12 | TC2-MW | MW | 130 ± 7° | 1 | 25 | 25 | 3.5E-04 | 1.1E-07 | 33.1 | 42.4 |
| OW13 | TC2-MW | MW | 130 ± 7° | 1 | 46 | 46 | 3.5E-04 | 1.1E-07 | 21.6 | 37.1 |
| OW14 | TC2-MW | MW | 130 ± 7° | 1 | 46 | 46 | 8.8E-05 | 2.7E-08 | 26.0 | 37.2 |
| OW15 | TC2-MW | MW | 130 ± 7° | 1 | 73 | 73 | 3.5E-04 | 1.1E-07 | 19.9 | 33.9 |
| WW1 | Berea-WW | W | 33 ± 3° | 1 | 60 | 60 | 3.5E-04 | 1.1E-07 | 25.7 | 29.8 |
| WW2 | Berea-WW | W | 33 ± 3° | 1 | 150 | 150 | 3.5E-04 | 1.1E-07 | 24.2 | 31.1 |
| WW3 | Berea-WW | W | 33 ± 3° | 1 | 520 | 520 | 3.5E-04 | 1.1E-07 | 15.0 | 27.6 |
| WW4 | Berea-WW | W | 33 ± 3° | 1 | 1800 | 1800 | 3.5E-04 | 1.1E-07 | 11.0 | 24.5 |

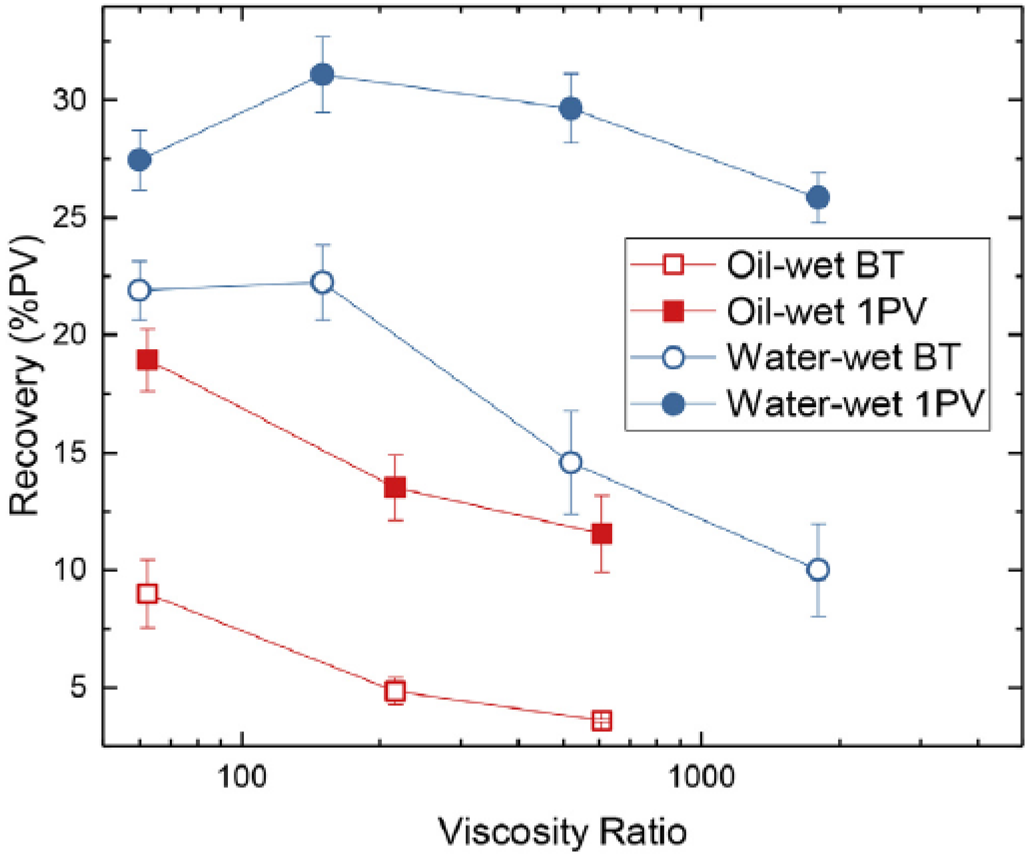


**FIG II-5** : Breakthrough (hollow) and cumulative recovery (solid) comparison between water-wet and strongly oil-wet systems over a wide range of viscosity ratio. All experiments were conducted with 5.08 cm diameter Berea sandstone at flow rate of 3.53 × 10−4 cm/s. [8]

Viscous fingering is more severe in strongly oil-wet media than in weakly oil-wet media or water-wet media. For strongly oil-wet system, permeability does not affect fingering and recovery significantly, unlike that in water-wet media where viscous fingering is stronger at lower permeabilities. Opposite to water-wet systems, increasing flow rate leads to increasing recovery by overcoming the capillary pressure to displace oil-wet pores.

## II-2 Miscibility:

Miscibility is defined as the ability of two or more substances to form a single homogeneous phase when mixed in all proportions. For petroleum reservoirs, miscibility is defined as that physical condition between two or more fluids that will permit them to mix in all proportions without the existence of an interface. If two fluid phases form after some amount of one fluid is added phases form after some amount of one fluid is added to others, the fluids are considered immiscible. An interfacialtension (IFT) exists between the phases when they are immiscible.

miscible-phase displacement processes that use certain gases as injectants have been developed assuccessful means for increasing oil recovery from many reservoirs.

Miscible displacement implies that with the IFT between the oil and displacing fluid eliminated (IFT=O), the residual oil saturation will be reduced to zero in the swept region. There are basically two types of miscible displacements: first contact and multicontact. The term first contact means that and amount of the solvent can be injected and will exist as a single phase with the oil in the reservoir.

Miscibility of two materials is often determined optically. When the two miscible liquids are combined, the resulting liquid is clear. If the mixture is cloudy the two materials are immiscible. Care must be taken with this determination. [24]

# CHAPTER lll:

# Wettability alteration in laboratory analysis

# Introduction:

Changing the wetting state of materials is a growing field of research in many areas of engineering and science. In the oil industry, the term wettability alteration usually refers to the process of making the reservoir rock more water-wet. This is of particular importance in naturally hydrophobic carbonates, fractured formations, and heavy-oil systems. wettability enhances oil recovery by changing wetting state can make difference in the ultimate oil recovery. for wettability alteration, many methods have been used to predict the recoery: Thermal and chemical and co2 gas injection waterflood. Although many attempts have been made on reviewing the advancement of research in certain aspects of wettability, a comprehensive review of these techniques, especially in terms of the classification of the chemicals used, has been ignored.

# INFLUENCE OF WETTABILITY ON OIL RECOVERY:

## III-1 In the primary oil recovery:

During primary oil recovery the influence of a pressure drop in the wellbore oil has a relatively high mobility and easily moving in its direction. In the case of hydrophobic rock, Wettability is the most important parameter that could change the flowing mechanisme and distribution of reservoir fluids in the reservoir. The quanintity of oil recovery depends on the wettability of reservoir rocks.[9]

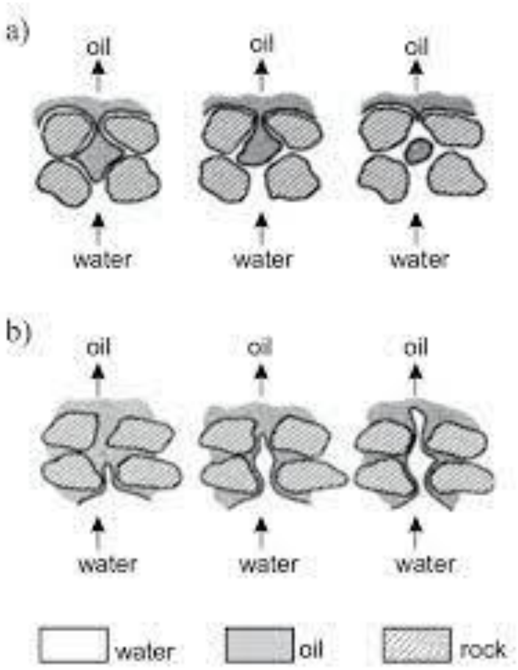


**FIG 3-1** : a) water wet system b) oil wet system

## III-1-1 In the water wet rocks oil:

Located mainly in large pores of the rock formation. under oil is in small pores, of which the harder it is to extract only by the infuence of a pressure difference ,The relative permeability is very important parameter makes the possibility of movement of the individual phases in the pore space of reservoir rocks. This parameter is affected by wettability, pore geometry, distribution of fluids in the rock and the history of saturation. [10]

## III-1-2 In the oil wet rocks oil:

Hydrophobic rocks have a lower water permeability than oil, where rock is hydrophobic is be inverse affect. Extraction of oil from hydrophilic reservoir rocks is greater due to higher relative permeability [10].

When three reservoir fluids are present in the rock, two non-wetting liquids compete with each aiming and fill the larger pores, disrupting the flow of each other. Gas, occurring in hydrophilic rocks lowers the relative permeability to oil. In the hydrophobic rocks the presence of gas reduces the relative permeability to water. In both cases, the relative permeability to the non-wetting fluid does not change. It was observed that the relative permeability of the rock for the wetting fluid is a function of the wetting phase saturation. While the relative permeability of rocks for non-wetting liquids is a function of the fluid saturation distribution of non-wetting phase [11].

At the beginning of oil production by primary methods, relative permeability to oil is high, water permeability is small. The value of permeability for oil decreases, as the decline in oil saturation and increased saturation of rocks with water. Water saturation is increased.

mainly as a result of filling out its smaller pores. During oil exploitation from the reservoir rock, the water gradually occupies pores, which previously were filled with oil. A single pore or a group of pores containing oil may be surrounded by water and isolated from the rest of the pore space occupied by oil [9]. Oil is then immobilized in the form of drops in the middle of the larger pore or in the form of large spots surrounded by water in the pores [11].

## III-2 Secondary oil recovery methods :

During secondary recovery the waterflooding process there are a main changement in pétrophysical réservoir characteristics ,During the injection of water into the oil reservoir (water saturation) being higher because of decreasing of capillary pressure between the two immisible fluids, oil is displaced from the rocks in different ways.[12]

## III-2-1 water wet rock:

In the hydrophilic rocks oil is displaced as the front before the injection of water, and each of the fluid flows through pores of a different size. Small drops of oil remain as a residual oil The efficiency of water displacement is dependent on the amount of injected water and the type of rock wettability.

## III-2-2 Oil wet rock:

In the hydrophobic rocks case oil recovery does not exceed 30% of the geological resources Water flooding of hydrophilic rock allows for a much larger amount of additional oil that can be obtained by flooding hydrophilic and hydrophobic rocks varies. In the case of hydrophobic rock waterflooding, it is less efficient than for hydrophilic rock [11].

Laboratory tests have shown that the amount of oil extracted decreases with decreasing humidity rocks. The conducted tests also showed that higher oil production can be obtained from the rocks weakness and medium moistened with water. Other study maked on reservoir.

Sandstone samples [11] showed that oil production increased as the cores become less wetted with water or the wettability changed in the direction of the intermediate wettability [13].

## III-2-3 Mixed wet rock:

In the mixed wettability rock, with increasing water saturation, it migrates to the largest pores first, remaining inside them, This results in a decrease in the relative permeability to oil, because the most permeable pores are filled with water. For these kinds of rocks, even when the water breaks down into the borehole, oil production lasts a long time, although the water cut increases [9].

As mentioned earlier the oil recovery efficiency from the deposits is dependent on the wettability of reservoir rocks. Reservoir rocks are usually wetted with both water and oil, and therefore water injection is not as effective as would be expected.

## III-3 Tertiary recovery (EOR) :

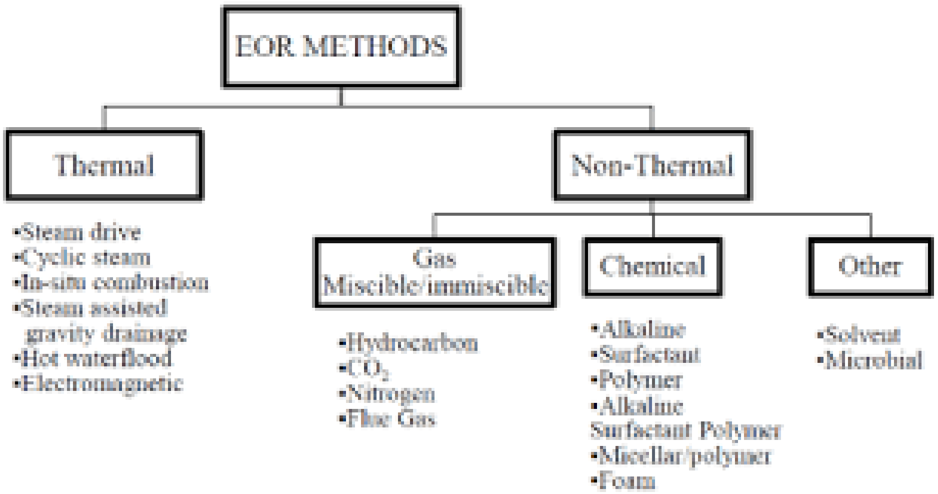


**FIG 3-2 :** EOR methods

Advanced methods (tertiary) allow for oil production, which can not be achieved by primary and secondary methods. Oil is present in the form of isolated droplets trapped in the pores or in the form of the film around the grains of rock. Tertiary effective process methods should start dispersed oil droplets and create a zone saturated with oil which can migrate to the production well [14]. For this purpose are used different methods of modifying wettability chemical and thermal. They allow for changing the wettability of the deposit with the hydrophilic to hydrophobic.

## III-3-1 Thermal recovery:

Thermal methods by the injection of steam or hot water can change the wettability of rocks in the hydrophilic direction [11]. This is confirmed by numerous wettability studies made on different types of geologycal reservoir rocks. Different study showing that with increasing temperature the nature of rock wettability changed towards a more hydrophilic [15]. Changing the character of wettability allows for a greater degree of exhaustion of oil resources the dependence of wettability since the temperature of carbonate and can also desolve the heavy oil viscosity whish can displased freely by temperature effect. At high temperatures, ionic compounds disengage from the surface of the rocks as a result, the wettability of the rock changed again hydrophilic.

The temperature also affects the relative permeability. Relative permeability increases with increasing temperature, whereas decreasing residual oil saturation [11].

## III-3-2 Chemical enhanced tertiary:

### III-3-2- a) Surfactant in waterflood:

Injection of the surfactant can change the wettability of rocks, this taking place by increasing the degree of oil production from the reservoir. Among the various types of surfactants: anionic, nonionic and cationic, the first two are used for EOR methods, because of their good solubility in brine. The surfactants are composed of hydrophilic parts, soluble in water or polar liquids and a hydrophobic portion, soluble in oils and non-polar liquids. Surfactants reduce the viscosity and surface tension between the injection fluid and oil. This results in a change in the wettability and increase in oil production [12]. These changes are due to the adsorption of the hydrophobic portion of the surfactant molecule on the oil droplets, which moves ionic compounds (asphaltenes) of positive and negative charges. The reduced capillary pressure allows for combining the particles into larger oil droplets (coalescence), which are in contact with each other and form a zone of saturated oil (oil bank), that may migrate to the production well [13].

**Notice:** The selection of an appropriate surfactant is The main problem, when using chemical methods is to determine the type of rock wettability, Incorrect determination of rock wettability type may lead to the use of an improper surfactant and do not get a sufficiently large extraction. Surfactants should be selected depending on initial rock wettability.

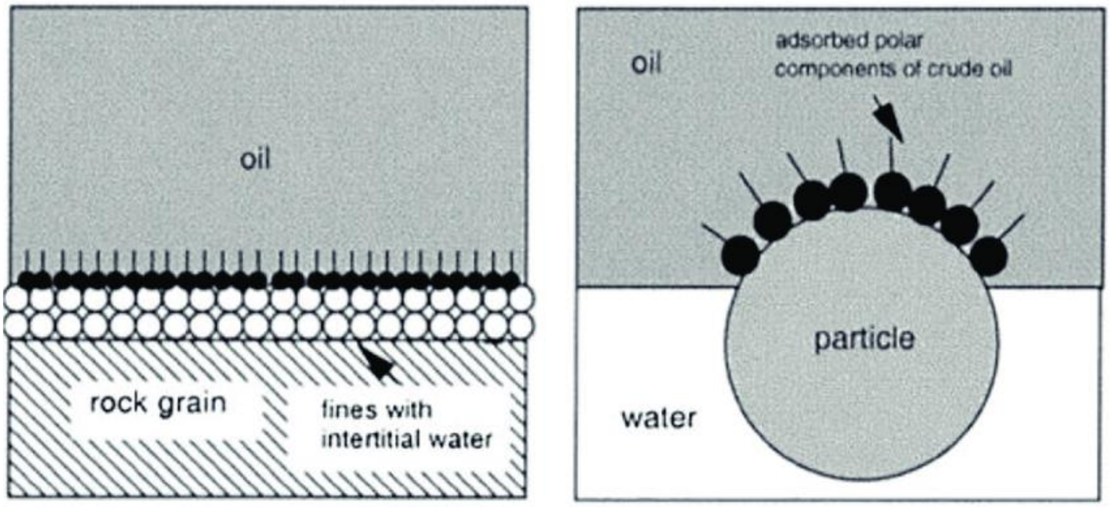


**FIG 3-3 :** Wettability alteration using surfactant [13]

## III-3-2- b) Polymer flooding:

Polymer flooding has been used for more than 40 years to effectively recover the remaining oil from the reservoir wish could, The polymer flooding efficiency ranges from 0.7 to 1.75 lb of polymer per barrel of incremental oil production. Polymers added to water increase its viscosity and reduce water permeability due to mechanical entrapment, thus decreasing its mobility. The process usually starts with pumping water containing surfactants to reduce the interfacial tension between the oil and water phases and to alter the wettability of the reservoir rock to improve the oil recovery. Polymer is then mixed with water and injected continuously for an extended period of time (can take several years). When about 30% to 50% of the reservoir pore volume in the project area has been injected, the addition of polymer stops and the drive water is pumped into the injection well to drive the polymer slug and the oil bank in front of it toward the production wells . [16]

## III-3-3 CO2 miscible flooding:

Wetting characteristic of the reservoir rock appear to be the most controlling factor of the operating strategy for an EOR process and its dependence on is still lacking. There are also indications that core floods and capillary tube visual cell tests can give inconsistent changes in wettability due to CO2 miscible flooding. CO2 reduces the brine pH, and there is some experimental evidence that this reduces the water-wetness in capillary cells. Experience from both laboratory tests and studies of field data supports that wetting characteristic is critical to CO2 floods.

Many study concludes that water-wet conditions suggest continuous gas injection while oil-wet conditions suggest water alternating with gas (WAG) process with an optimum recovery and sweep the residual oil. Other studies also shown that mixed-wet states indicate maximum recovery is a stronger function of slug size in secondary CO2 recovery than in a tertiary flood. In addition, water-wet laboratory models indicate gravity forces dominate while in oil-wet tertiary floods where viscous fingering is a controlling factor.[16]

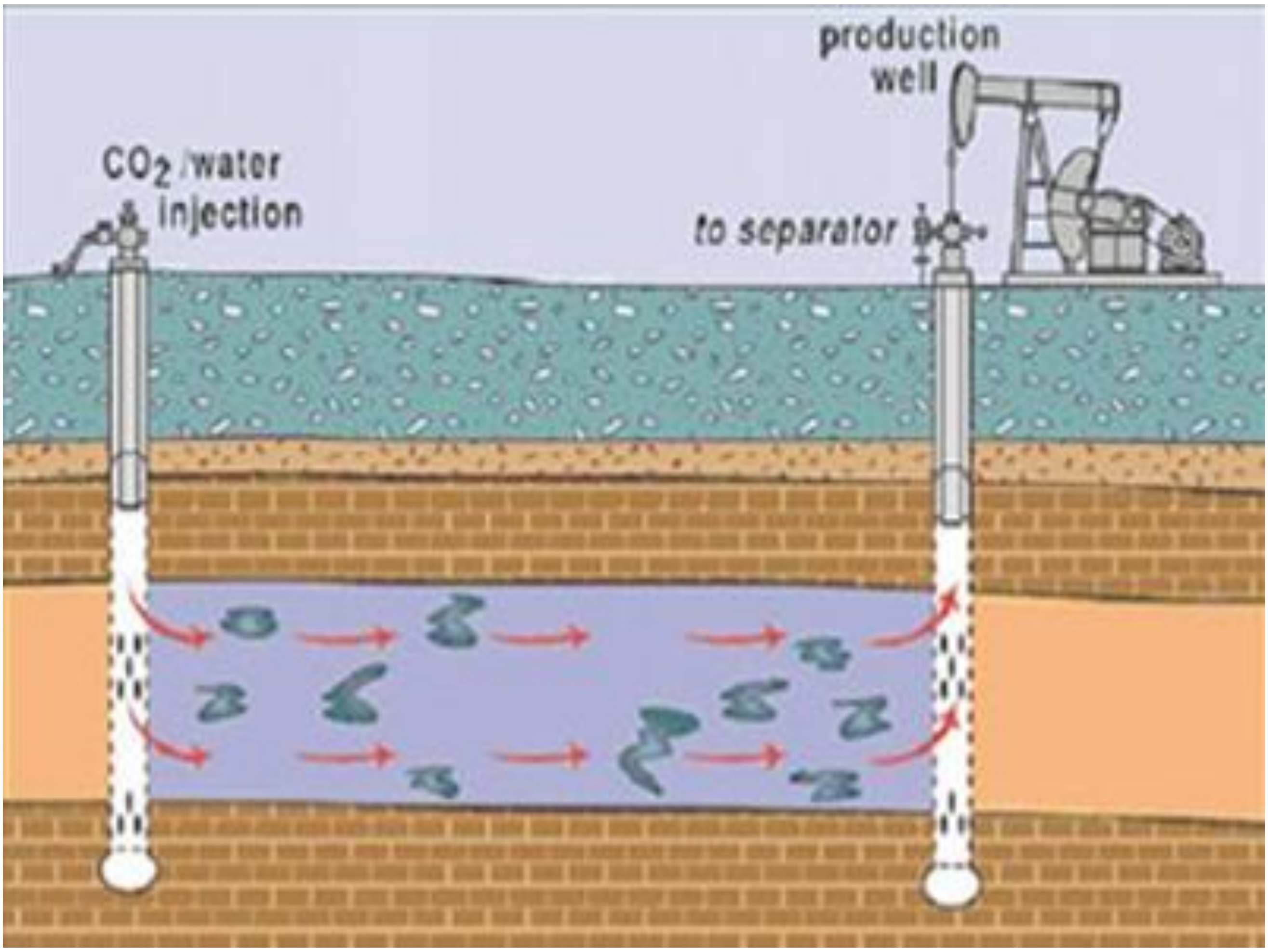


**FIG 3-4** : Enhanced oil recovery using Co2 gas [16]

# *CHAPTER IV:*

# *The reservoir wettability types*

## IV-1 The reservoir wettability types :

The rock wettability can exert a profound influence on the displacement of oil by water from oil producing reservoirs. Core analyses frequently show oil recoveries from preferentially water-wet rock to be significantly greater than those from preferentially oil-wet rock. Thus, an accurate prediction of water-drive or waterflood oil recovery is dependent on the evaluation of reservoir rock wettability.

The measurement of the rate and volume of spontaneous imbibition of the wetting phase by a rock is a reliable and reproducible test for semi-quantitative determination of preferential rock wettability.

The wettability of reservoir rock may depend on both the crude oil composition and the rock type.

Field and laboratory tests have indicated that coring fluids and core handling techniques can cause significant changes in the wettability of rock surfaces, However a few fluids, brine in particular appear not to affect core wettability and may be used when coring to determine reservoir wettability.

Four general states of wettability have been recognized : water-wet, fractional-wettability, mixed-wettability, and oil-wet.

### IV-1-1 Water-wet System :

A water/oil/rock system is considered to be water-wet when more than 50% of its surface is wet by water. Water occupies the smaller pores, and exists as a film covering the surfaces of the preferentially water-wet larger pores of the rock. Oil is lodged in the larger pores as droplets resting on a film of water, oil globules may extend through two or more of the larger pores and coat random areas of the pore surfaces containing minerals that are preferentially oil-wet. Therefore, water exists as a continuous phase throughout the porous system and the nonwetting phase (oil) is a discontinuous phase consisting of globules in the larger pores surrounded by water. If the water saturation is reduced to its irreducible saturation ($S_{wi}$), water remains as a continuous phase in the small pores and crevices through the porous medium. At ($S_{wi}$) the oil saturation is high enough for it to also exist as a continuous phase through the larger pores of the rock. As the water saturation increases, the nonwetting phase quickly becomes discontinuous, with globules and fingers of oil in larger pores completely surrounded by water. The wetting phase saturation exists as a continuous phase at all saturations equal to or greater than $S_{wi}$. If a preferentially water-wet core is saturated with oil then contacted with water, water will spontaneously imbibe into the rock displacing the oil until a state of static equilibrium is attained between the capillary and surface energy forces of the fluids and rock surfaces. If another sample of the same rock is saturated first with water and then contacted with oil, oil will not imbibe into the rock. [17]

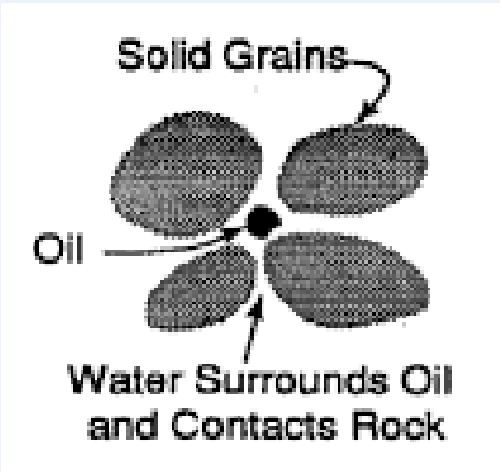


**FIG 4-1** : Water-wet system [18]

## IV-1-2 Fractional-wettability :

The term fractional wettability was proposed to characterize heterogeneous wetting of the pore surfaces where the preferential wetting is randomly distributed throughout the rock. In some cases, the random distribution of minerals (with a variety of chemical properties) exposed to the surfaces in the pores is such that areas which are either preferentially water-wet or oil-wet are scattered through the rock and there are no continuous oil networks through the rock. [17]

## IV-1-3 Mixed-wet :

The mixed wettability, is a condition where the small pores in the rock are water-wet and saturated with water, but the larger pores are oil-wet and filled with oil in contact with the pore walls that form a continuous path through the length of the rock. this condition could occur during the original accumulation of oil in a reservoir if oil-containing surface active compounds displaced connate water from the larger pores; the surface active compounds would gradually displace the remaining films of water on the pore surfaces. Oil would not enter the smaller pores where the threshold capillary pressure for displacement of water is too large. [17]

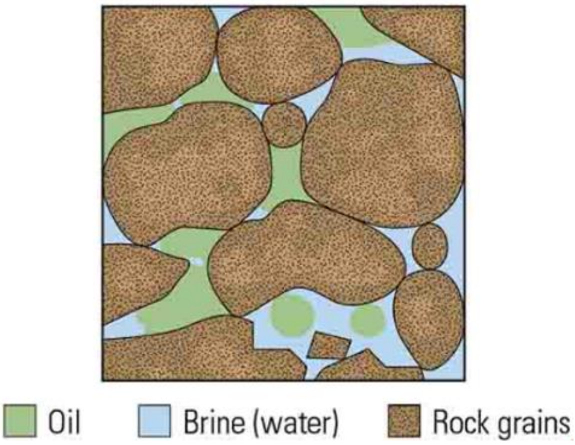


**FIG 4-2** : mixed-wet system [19]

## IV-1-4 Oil-wet :

When the system is preferentially oil-wet, the positions of water and oil in the rock are reversed. Oil occupies the smaller pores to the exclusion of water, and oil is in contact with the rock surfaces of the larger pores. Where water is present in the larger pores, it is generally in the center of the pores resting on a film of oil. Water (the nonwetting phase in an oil-wet system) also exists as a continuous phase distributed through the larger pores when it is present as a high saturation (near the residual oil saturation So). If the water saturation is decreased (by injection of oil), it rapidly loses continuity and becomes isolated in the larger pores as pockets and fingers of water that are surrounded by oil. Thus in an oil-wet system, oil is a continuous phase for all saturations equal to and greater than $S_o$.

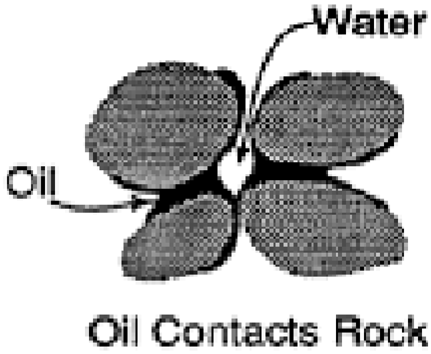


**FIG 4-3** : Oil-wet system [20]

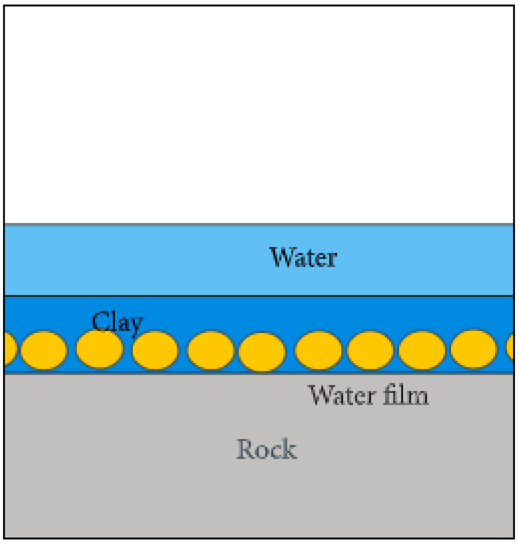
If the preferentially oil-wet rock is saturated with water and contacted with oil, the oil will imbibe into the rock displacing water until a state of equilibrium is attained. Water will not spontaneously imbibe into an oil-wet rock. [17]

## IV-2 Wettability is changing over time:

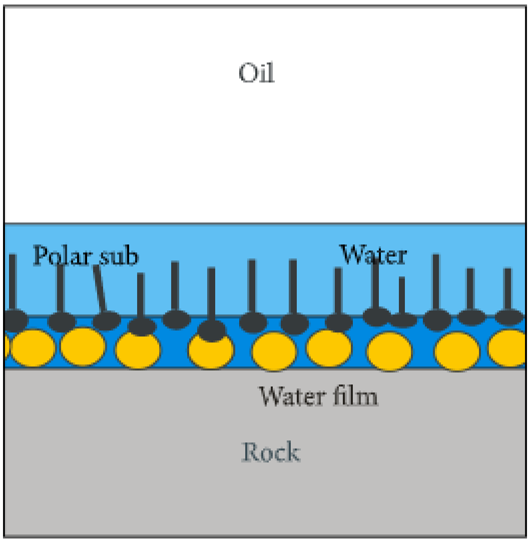
Surface property of rock affects oil recovery during water flooding. Oil wet polar substances adsorbed on the surface of the rock will gradually be desorbed during water flooding, and original reservoir wettability will change towards water-wet, and the change will reduce the residual oil saturation and improve the oil displacement efficiency. However there is a lack of an accurate description of wettability alternation model during long-term water flooding and it will lead to difficulties in history match and unreliable forecasts using reservoir simulators.

In the past, oil reservoirs were commonly interpreted to be strongly water-wet, because water phase is generally the initial fluid contact with the reservoir rock. However, some researchers found that many reservoir rocks were not strongly water-wet. The latter results were obtained without considering the natural surfactant in crude oil, such as asphalt and paraffin substances, which are easily absorbed on the solid-liquid interface and change reservoir rocks to oil-wet . Kusakov found that the rupture of water film could lead to crude oil directly contacting the quartz surface and the surface would become oil-wet instead of water-wet. Schmid claimed that wettability could be changed and strong water-wet rock could become weak water-wet after contact with crude oil.

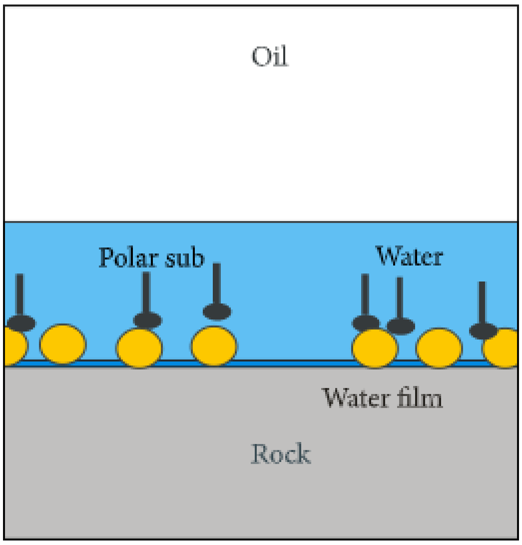
For the sandstone reservoirs, the wettability changes during deposition process, accumulation process, and water flooding process (FIG 4-4). During deposition process, the pores are saturated with water to form a layer of water film during the deposition process, as shown in FIG 4-4 (a). Thus, the reservoir rocks are water-wet. During the accumulation process, the partial polar substances in crude oil penetrate water film to adsorb on rock surface through van der Waals, electrostatic, hydrogen bonding, and acid-base, and the rock with the polar substances changes to oil-wet, as shown in FIG 4-4 (b). Note however, that if the partial polar substances do not penetrate water film, the rock will be water-wet. During long-term water flooding, the polar substances can be washed out and desorbed from the rock surface; the wettability may change to water-wet[21], as shown in FIG 4-4 (c).



**(a)** Deposition process



**(b)** Accumulation process



(c) Water-flooding process

**FIG 4-4** : Wettability variation during reservoir formation process

Wettability may affect almost all the variables in core analysis, including capillary pressure, relative permeability, oil recovery, and EOR. Morrow [22] confirmed that a higher water flooding recovery could be obtained in strongly water-wet core through one-dimensional water flooding experiments. The one-dimensional displacement experiments with high pore volume (PV) of injected water showed that the changes of wettability and pore structure during long-term water flooding reduced the critical capillary number and the residual oil saturation. When the injected water was 5000 PV of rock core, the oil displacement efficiency of cores was about 57%; when the injected water was 1000 PV or even 10000 PV, the oil displacement efficiency was increased (near 80%). Therefore, under different water flooding conditions, oil displacement efficiency of the rock is not a constant.

The wettability changes during long-term water flooding, and this could affect the residual oil saturation and oil recovery. A number of studies showed that, during low-salinity water flooding, the ions could exchange between injecting water and rock, and it could lead to adsorption of divalent ions and minerals dissolution, change the wettability to water-wet, and enhance oil recovery it could also lead to changes of relative permeability.

The main factor affecting wettability is the amount of polar substances adsorbed on the clay surface. In order to model the wettability variation, we should first evaluate the amount of polar substances adsorbed on the surface of clay. Five factors that impact the polar adsorption and desorption should be considered, and these include the concentration of polar substances in crude oil and on rock surface , salinity and pH of injecting water and formation water, clay contents in rock, and flow rate of water through the pore. Yet, an accurate description of wettability alternation model during long-term water flooding from injecting well or aquifer is lacking, which will lead to failure in history matching and unreliable forecasts using numerical simulation. [23]

# Conclusion:

The types of reservoir rocks and its impact on the petrophysical properties are essential in determining the mechanisms of oil recovery and estimating the efficiency of its production

The wettability is a property of reservoir rocks to spread on or adhere to the surface of the rock one fluid in the presence of a second fluid. A drop of preferential wetting fluid displaces the other fluid from the surface of the solid and distributed all over.

Conversely, in the case of non-wetting liquid that hitting the solid surface previously coated with a wetting fluid , creates a drop with a minimum contact area with the solid phase making the distribution of liquide in pore scale and affecting its oil recovery.

The case where the reservoir rock is saturated more fluids, it is important to recognize the type of the rock wettability. Determination of whether we are dealing with the hydrophilic or hydrophobic rock is essential for planning the extraction of crude oil. The quantity of oil production is a function of rock wettability, properties of the pore space and reservoir fluids. Studies of numerous authors have shown that in the case of hydrophobic rock, both the primary method, as well as waterflooding, the oil recovery is less than for hydrophilic rock. Also, weakness and medium water wetted rocks allow for obtaining larger quantities of oil during exploitation than from the hydrophobic rocks.

The determination of Wettability behavior of the type of reservoir rock wettability is crucial for estimating the oil recovery efficiency. The reduction of wettability, which is obtained through EOR methods, is still a complex area of research in secondary and tertiary oil recovery methods.

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