

Review of Wettability Characterization For Reservoir Rocks



Thesis for the degree of Masters (MS) in Petroleum Engineering

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Abstract

Wettability is a key parameter of a reservoir rock system. The understanding of wettability plays a very important role in reservoir behavior and multiphase flow because it has a huge influence on the different petrophysical characteristics of the reservoir such as relative permeability and capillary pressure. Wettability is perhaps among one of the most important and crucial factors that affects the rate of oil recovery and residual oil saturation, and this is very important in the field of enhanced oil recovery.

Wettability can be measured qualitatively and quantitatively. Qualitative methods include microscopic visualization of fluid distribution, relative permeability curves and imbibition methods and all these qualitative methods are indirectly inferred from other measurements while on the other hand quantitative methods are the direct measurements and wettability is measured on actual reservoir rock samples using reservoir fluids. The most important of these methods are Contact Angle Method, Amott Method and USBM (US Bureau of Mines) Method.

I also discussed a few techniques to alter the wettability like Silanization by treatment with the chemicals of organosilanes compounds and treatment with Chrome complexes.

In this study, my focus was on studying the wettability analysis of different naturally occurring reservoir rocks and minerals as well as the wettability analysis for different artificial produced materials like Glass Chips, PDMS (Polydimethylsiloxane) and NOA81(Norland Optical Adhesive 81). And then to compare the wettability of both of the above mentioned materials in order to study the coherence between them and to select the best artificial material which represents the reservoir for further wettability studies.

Dedicaton

I dedicate my dissertation to

my beautiful parents, professors, siblings and friends for their endless love, support
and encouragement

and to the people who THINK.

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First and foremost, I would like to acknowledge my heartiest gratitude to Almighty Allah, for providing me with this opportunity, to learn from it and to become a better person and a professional. Then I would like to thank my supervisors and my mentors who gave me an opportunity to explore the world of wettability analysis.

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1. Introduction

The description and characterization of the reservoir parameters is fundamental for understanding the reservoir dynamic behavior and for the characterization of the reservoir exploitation strategy. The most important parameters to describe the dynamic behavior of reservoir are porosity, permeability and saturation. Also, the interaction between rock and fluid properties is important and it plays a key role in the oil recovery. These parameters include capillary pressure and relative permeability.

Anderson [11] defined wettability as “the tendency of one fluid to spread on or adhere to a solid surface in the presence of other immiscible fluids”. Fluid has a preferential attraction to itself, and the relative strengths of such cohesive forces result in surface tension that develops on a fluid-fluid interface. The understanding of wettability plays a very important role in reservoir dynamic behavior because it has a huge influence on the different basic properties of the reservoir such as the distribution of reservoir fluids within the pore space of reservoir rock, relative permeability of different fluids, capillary pressure and hence the recovery of hydrocarbons. Therefore, it is also pertinent to say that the proper knowledge of wettability of a reservoir is compulsory for selecting an effective hydrocarbons recovery mechanism. {Czarnota, 2016 #6}

Another important parameter in fluid – rock interaction is the Capillary Pressure which is due to the Capillary forces. Capillary forces result from the interaction of forces acting within and between the rock surface and the fluids. Capillarity is because of adhesive forces of water molecules with the surface of reservoir rocks and due to the cohesive forces within water molecules. Capillary forces play a vital role in the dynamic behavior of the reservoir. It helps us in understanding the amount of water retained by the rocks in the hydrocarbon zones. Capillary forces are also important in

determining the distribution of water saturation in the reservoir, hence helpful in finding the total in-situ volumes of all fluids. Anderson [11].

The purpose of this work is to study wettability of different reservoir rock systems and compare them with the wettability of different artificial materials and to be able to come up with an artificial material which best represents the reservoir rock system for further study of wettability to enhance oil recovery.

2. Theoretical Background

2.1. Young - Laplace Equation

Young - Laplace equation is fundamentally important in the study of capillary surfaces. When two immiscible fluids are in contact with each other, they act to minimize their surface tension (the intermolecular attractive forces) by deforming the contact area and their own shape. The bulk of the fluids exhibits cohesion energy, which stems from the Van der Waals- and other interactions (such as hydrogen bonding) between the constituent molecules. (Li, Bui et al. 2017). Young – Laplace equation describes the capillary pressure difference sustained across the interface between two immiscible fluids. This capillary pressure is the result of the curvature of the fluid interfaces, and the interfacial tension, according to Young - Laplace equation.

We can better understand the physical meaning of Laplace – Young Equation by deducing it by considering the equilibrium condition of a single component liquid drop surrounded by another.

As we know liquids tends to minimize their surface area and as the sphere is the geometrical form with the smallest surface/volume ratio, hence the drops are spherical in the absence of gravity. Consider a single component liquid spherical drop of radius R and have internal pressure P_α in equilibrium with external pressure P_β outside the liquid drop.

We also know that surface tension tends to reduce the surface area and hence the volume of the drop, while the pressure difference between inside and outside of the drop acts to increase the volume of the drop. When these two tendencies i.e. pressure

difference and surface tension counterbalance each other, the equilibrium condition is achieved.

Now if only a hemisphere is considered as shown in the Figure 2.1, the forces due to the surface tension is equal to $2\pi R\sigma$, whereas $2\pi R$ is the length of the hemisphere. The force due to pressure difference is $(P_\alpha - P_\beta)$ times the projected area of the hemisphere. i.e., $(P_\alpha - P_\beta) \pi R^2$.

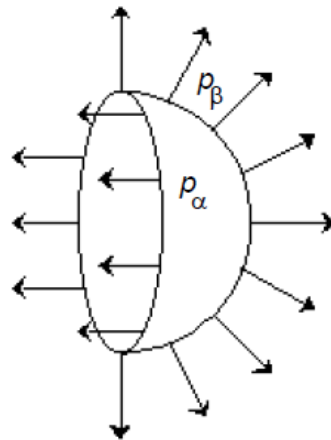


Figure 2.1 Imaginary hemispherical section of a spherical liquid drop. The arrows pointing radially outwards represent forces due to pressure difference and the arrows pointing to the left represent forces due to surface tension. {Pellicer, 2000 #4}

Therefore, the equilibrium condition is;

$$(P_\alpha - P_\beta)\pi R^2 = 2\pi R\sigma \quad (2-1)$$

Which leads to

$$(P_\alpha - P_\beta) = \frac{2\sigma}{R} \quad (2-2)$$

$$P_c = \frac{2\sigma}{R} \quad (2-3)$$

This pressure difference is called Capillary pressure, P_c and σ is the interfacial (or surface) tension between the two fluid phases. Now if we consider the principal radii of curvature i.e., R_1 and R_2 .

The above equation becomes as follows:

$$P_c = \sigma \left(\frac{1}{R_1} + \frac{1}{R_2} \right) \quad (2-4)$$

When the interface is within the cylindrical capillary tube, the radius of the capillary is equal to the product of the radius of the sphere and the cosine of the contact angle θ between capillary surface and the interface (Dake, 1978). In rock system, the shape of a porous medium can be described as a cylindrical capillary tube, so the above-mentioned equation becomes as:

$$P_c = \frac{2\sigma \cos \theta}{R} \quad (2-5)$$

Where R is the radius of the capillary tube and θ is the contact angle, i.e. the angle between the surface of the fluid and rock and this angle quantifies the wettability of rock surface by the fluid.

2.2. Interfacial Tension (IFT)

Interfacial tension exists when we have two fluids and is defined as: the force which acts at the interface when two immiscible fluids are in contact with each other. It is the force acting in the plane of a surface per unit length of the surface. Mathematically it is written as:

$$\sigma = \frac{F}{L} \left[\frac{N}{m} \right] \quad (2-6)$$

Surface tension is related to the work required to create new surface area

$$W = FdX$$

From Equation (2-6)

$$W = \sigma dA$$

This force between liquids and gas is called surface tension and between two liquids like oil and water is termed as interfacial tension. We have a thin film at the surface of liquids. Although this film has little strength, but it resists to get broken and acts like a membrane due to the attraction between the molecules.

Consider two immiscible fluids, oil and gas, shown in the Figure 2.2. Let us take a liquid molecule inside the oil, which is far away from the interface and is surrounded by other liquid molecules. The force acting on that molecule is equal from all the direction, hence the resulting net attractive force on the molecule is zero. Meanwhile a molecule at the interface has a force acting on it from the gas molecules lying above the interface and from liquid molecules lying below the interface. As the forces are not equal, so the resulting forces are unbalanced and give rise to surface tension.

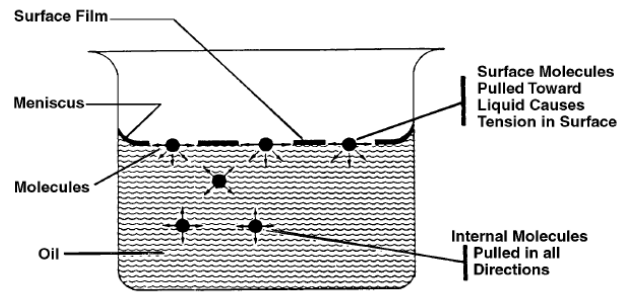


Figure 2.2 Illustration of Surface Tension. (Ahmed 2018)

2.3. Wettability

Anderson [11] defined wettability as “the tendency of one fluid to spread on or adhere to a solid surface in the presence of other immiscible fluids”. Fluid has a preferential attraction to itself, and the relative strengths of such cohesive forces result in surface tension that develops on a fluid-fluid interface. However, the molecules of a fluid may also have a preferential attraction to solid interfaces. If two fluids are in contact with a solid surface, the fluid whose molecules display the greatest attraction for the atoms that compose the solid will be the fluid that occupies most of the surface, hence displacing the other fluid.

Figure 2.3 [Ahmed 2018] help us in the understanding of wettability. We have three different liquids namely mercury, oil and water and are placed over a clean glass plate. As from the figure we can observe that all these three droplets have different ways of spreading on the plate – mercury tends to form a spherical shape, oil tends to have approximately hemispherical shape and water tends to spread on the glass plate. This explains the tendency of likeness or dis-likeness of these liquids for the glass plates. Hence this explains the tendency of the liquid to spread over the surface of any solid surface which indicates the wetting characteristics of the liquid over the solid. These

characteristics can be measured by measuring the angle of contact between solid-liquid interface and this is called contact angle.

This is a very basic and important way of measuring wettability. Further explaining the Figure 2.3 we can say that decrease in the contact angle increases the wetting characteristics of the liquid. We have two extreme situations i.e. a complete wetting condition has 0° contact angle while a non-wetting condition has a contact angle of 180° . As Sometimes we also have intermediate wettability value with having an angle between 60° - 120° . Hence, the contact angle is used as the measure of wettability.

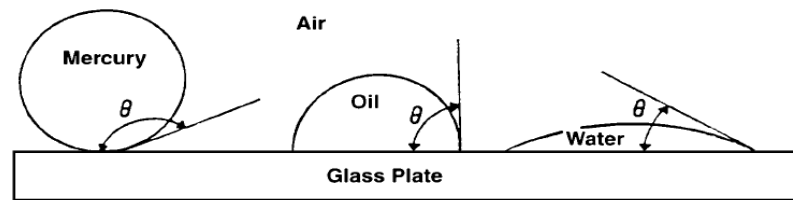


Figure 2.3 Demonstration of Wettability (Ahmed 2018)

Table 2.1 below shows different possible scenarios of wettability in oil – water system.

Table 2.1 Contact angles for different wettabilities. (Ahmed 2018)

| Contact Angle (θ in degrees) | Description |
|---|-------------|
| $0^{\circ} - 60^{\circ}$ | Water wet |
| $60^{\circ} - 120^{\circ}$ | Neutral |
| $102^{\circ} - 180^{\circ}$ | Oil wet |

Wettability of reservoir rocks is a very important and fundamental parameter to understand because distribution of fluids in the porous medium is a function of wettability. Wettability affects the saturation of fluids and relative permeability of fluid rock system; this can be demonstrated in the figure 2.4 depicting residual oil saturations in a strongly water-wet and strongly oil-wet rock. In water-wet system, water has the tendency to adhere to the majority of the surface of the rock and occupying the small pores of the rock, whereas in the oil-wet system, oil adhere to the most part of the rock surface.

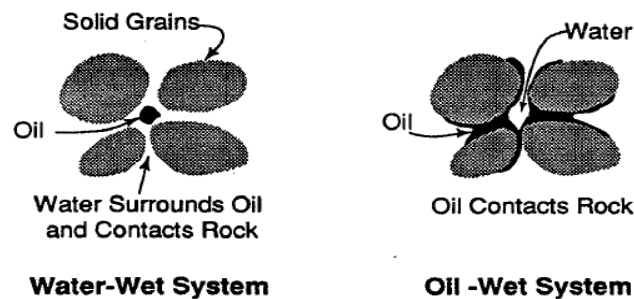


Figure 2.4 Effect of Wettability on Saturation (SPE Series - EOR)

Depending on the interaction between rock and fluid in the reservoir, the system can be classified as a strongly water-wet or oil-wet. However, in some cases, both water and oil tend to adhere to the surface of the rock which is termed as 'intermediate' or neutral wettability. Also, there is another type of wettability called as 'fractional' wettability in which different parts of the rock have different wetting preferences for the fluid present. This happens in the systems where rock has variable composition of minerals and chemistry of the rock surface.

Here are the values of wettability of different lithologies as well as the contact angle value as per their wetness behavior depicted in the following Tables 2.2 and 2.3.

Table 2.2 Wettability Values for Different Lithologies

| Descriptions | | Rocks/Lithology | | |
|--------------------------|---------------|---------------------------------------|--|--|
| | | Clastic Formations (Sandstones) | Limestone Formations (Carbonates) | Dolomites |
| Wettability | Water-Wet | 30% | 10% | Mostly Oil wet but can be altered with surfactants |
| | Neutrally-Wet | 55% | 50% | |
| | Oil-Wet | 15% | 40% | |
| Contact Angles (Degrees) | Water-Wet | 0° – 70° | 0° – 70° | 120° – 180° |
| | Neutrally-Wet | 70° – 110° | 70° – 110° | |
| | Oil-Wet | 120° – 180° | 120° – 180° | |
| Techniques Used | | Sessile Drop Method | Contact angle cell Method | Imbibition Method |
| References | | {Wang, 2013 #8} {Treiber, 1972 #9} | {Treiber, 1972 #9} {Leach, 1962 #1} | {Shariatpanahi, 2016 #2} |

| Minerals | Wettability | Contact angle (Degrees) | References |
|---------------|-----------------------------|--|---------------------|
| Quartz | Water-Wet | Differs but normally it is in the range of Water-Wet 0° – 75° | {Treiber, 1972 #9} |
| Calcite | Oil-Wet | Differs but normally it is in the range of Oil-Wet 120° – 180° | {Brady, 2016 #3} |
| Chalk | Naturally Oil-Wet Mostly | Range of 120° – 180° | {Brady, 2016 #3} |
| Clay Minerals | Naturally Oil-Wet Mostly | Above 90° if Oil-Wet Below 90° if Water-Wet | {Schrader, 1990 #4} |

| Minerals | Wettability | Contact angle (Degrees) | References |
|-----------|--------------------------------------|-------------------------|-----------------------|
| Kaolinite | Prefer to adsorb Oil, Hydrophobic | In the Oil-Wet Range | {Bantignies, 1997 #5} |
| Illite | Preference for Brine | In the Water-Wet Range | {Bantignies, 1997 #5} |

Table 2.3 Wettability Values for Different Minerals

Similarly, there is a special type of fractional wettability introduced by (Salathiel 1973), known as 'mixed-wettability' in which smaller pores of the rock are water-wet and are filled with water whereas the larger pores of the rock are oil-wet and are filled with oil. Author explains this phenomenon as: Initially when oil invades a reservoir which is a water-wet reservoir, it displaces water from the bigger pores while the water remains in the smaller pores due to the capillary forces.

2.3.1. Wettability Measurements of Artificial Materials

Here we will discuss the wettability measurements values for different artificial materials like Glass Chips, Polydimethylsiloxane (PDMS) and Norland Optical Adhesive(NO A81). First of all, we will talk about some properties of these materials.

Glass Chips have high transparency, chemical stability, excellent flatness, good biocompatibility and most importantly they are relatively low-cost. {Wang, 2018 #6}

Polydimethylsiloxane(PDMS) have good chemical and thermal stability and can obtain complicates 2D and 3D microstructures but the downside of fragility, poor mechanical strength, relatively high-cost, opacity, poor electrical insulation and complex surface chemical properties impede its applications.

On the other hand, Norland Optical Adhesive (NOA81) shows good chemical resistance to organic solvents, adjustable surface properties, relatively good transparency, impermeability to oxygen and water vapor, persistence against swelling upon contact with fluids and stability under surface treatments e.g. by oxygen plasma, also a further advantage of NOA81 is its high Young's Modulus that allows for channels with large aspect ratios while still maintaining straight rigid walls. {Rezvani, 2018 #7}

Moreover, the wettability trends of these artificial materials are as following in Table 2.4.

Table 2.4 Wettability Values for Different Artificial Materials

| Descriptions | | Material | | |
|--------------------------|-------------|---|--|--|
| | | Glass Chips | PDMS | NOA81 |
| Contact Angles (Degrees) | Hydrophilic | 25° - 30° (Pre-Modification) | PMDS is inherently Hydrophobic. 115° (No Treatment) 160° (With fluorinated nanoparticle) | 45° – 51° (Without any Modification) |
| | Hydrophobic | 101° – 111° Post-Modification (With O ₂ Plasma With UV Exposure) | | 85° – 90° (With Additive Treatment) |
| References | | {Thirumalai, 2017 #8} {Arayanarakool, 2011 #9} | {Kanungo, 2014 #2} {Martin, 2017 #3} | {Kirichenko, 2017 #10} {Wägli, 2011 #1} |

2.3.2. Comparison between Wettability of Naturally Occurring Reservoir Rocks and Artificial Materials

As previously we have discussed the wettability of naturally occurring reservoir rocks in details as well as the wettability of artificially produced synthetic materials.

Henceforth, we would like to draw a comparison between the wettability of these above-mentioned systems. This may enable us in understanding the properties of the artificial materials to be best suited to characterize the reservoir rock system.

Comparison between Wettability of Naturally Occurring Reservoir Rocks and Artificial Material is listed in the below mentioned Table 2.5.

| Description | | Natural Reservoir Rock System | | | Artificial Materials | | | |
|------------------------------------|-------------|---------------------------------|-------------------------------------|------------------|----------------------|-------------|------------------------|-----------|
| Rocks/Materials | | Clastic Formations (Sandstones) | Limestone's Formations (Carbonates) | Dolomites | Type | Glass Chips | PDMS | NOA81 |
| Wettability and Contact Angles (o) | Water-wet | 30% rocks (0° - 70°) | 10% 0° - 70° | Mostly Oil - Wet | Hydrophilic | 25° - 30° | Inherently hydrophobic | 45° - 51° |
| | Neutral-Wet | 55% rocks (70° - 110°) | 50% 70° - 110° | | | | | |
| | Oil-Wet | 15% rocks (120° - 180°) | 40% 120° - 180° | (120° - 180°) | Hydrophobic | 101°-111° | 115°-160° | 85° - 90° |

Table 2.5 Comparison between Wettability of Naturally Occurring Reservoir Rocks and Artificial Materials

Hence, by comparing these two systems, we are able to employ to use a desired artificial material to study our original reservoir rock system for the analysis of wettability measurement and characterization, e.g. from the Table: 2.5 we can say that we can select Polydimethylsiloxane (PDMS) material (as it is inherently hydrophobic and tends to be oil wet) to study the Dolomite reservoir system.

2.4. Capillary Pressure

Capillary pressure exists due to the interaction between a wetting and a non-wetting fluid and the solid surface represented by the rock matrix. Capillary pressure critically influences the initial reservoir distribution and dynamic processes of oil recovery. Capillary pressure is the most fundamental rock fluid property in multi-phase flows, just as porosity and permeability are the most fundamental properties in single-phase flow in oil and gas reservoirs [Falode 2014][Q Chen 2006]. Two immiscible fluids (non-wetting phase and wetting phase) produce a discontinuity in the pressure across the interface in a capillary tube.

$$P_c = P_{non-wetting} - P_{wetting} \quad (2-7)$$

In evaluating Hydrocarbon reservoirs, laboratory P_c curve measurements on reservoir cores are directly applied to measure many basic petrophysical properties, for example: pore size distribution, irreducible water saturation and wettability of reservoir rocks. In addition, they are used to determine the initial water and oil saturation as a function of height above the free water level, approximate oil recovery efficiency, and to calculate relative permeability. Capillary Pressure can also have a significant impact on water flood performance.

2.4.1. Capillary Pressure Measurements

Capillary pressure can be measured experimentally. Figure 2.5 shows the process of the measurement of P_c w.r.t the saturation of water in the below mentioned order.[7]

1. Primary drainage,
2. Spontaneous imbibition,
3. Primary imbibition,
4. Spontaneous drainage,
5. Secondary drainage.

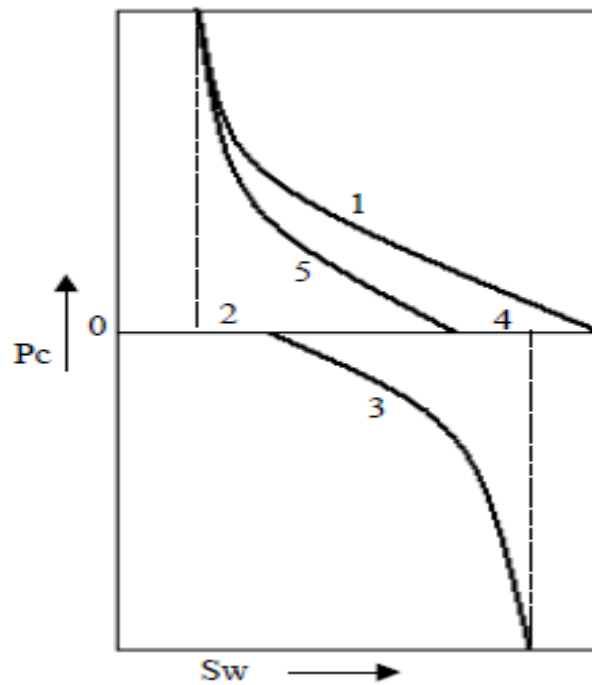


Figure 2.5 Sequence of steps (Falode and Manuel 2014)

The capillary pressure curves can be constructed by these three given methods:

1. Porous Plate Method.
2. Mercury Injection Method.
3. Centrifugal Method.

Here we will discuss these methods.

2.4.1.1. Porous Plate Method

In this method of measuring P_c , firstly we take a core plug sample and saturate it totally with wetting fluid like water and measure its effective porosity is measured. It is then placed on a porous plate in a pressure vessel [4]. Fluids like gas or oil is inserted into the vessel around the sample at a low pressure as shown in Figure 2.6. The porous plate is designed in such a way that it only let the water to pass through. The inserted oil or gas displaces some of the water from the sample and the displaced water passes through the porous plate where it is collected, and its volume is measured.

We leave the vessel at the set pressure until no more water advances, which may take several days. The pressure of the gas or oil is then increased, and more water evolves and is measured. The procedure is repeated usually about 7 times at increasing pressures. A capillary curve can then be constructed with pressure versus the water saturation in the sample. The maximum pressure is limited by the pressure at which the porous plate begins to let the gas or oil pass through with the water (Figure 2.6).

Advantages: It's accurate and can use actual reservoir fluids for the measurements.

Disadvantages: Slow and only provides a few data points on the capillary pressure curve.

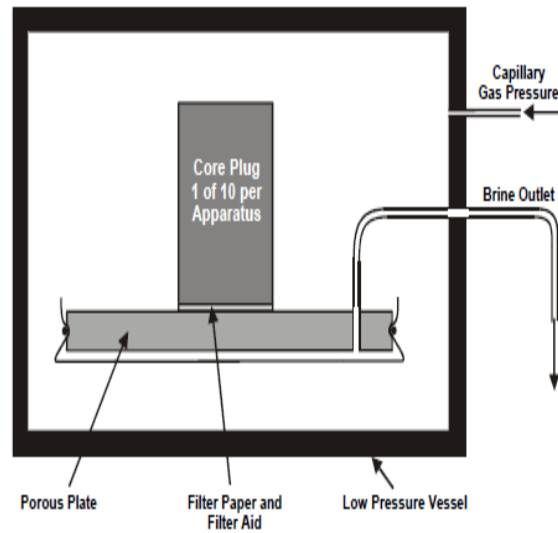


Figure 2.6 Porous plate capillary pressure measurement. (Glover 2000)

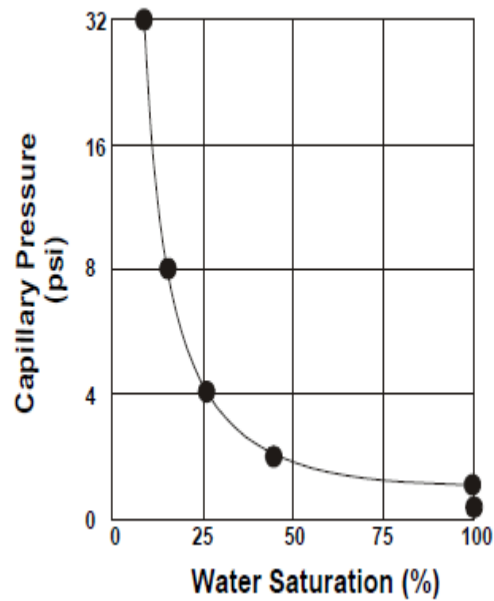


Figure 2.7 Capillary press curve from porous plate measurements. (Glover 2000)

2.5. Impact of wettability on Macroscopic Parameters

Here we will discuss about the impact of wettability on different parameters.

2.5.1. Relative Permeability, k_{rel}

Relative permeability is related to the saturation of reservoir fluids in the formation. Relative permeability takes into account the portion of reservoir saturated with a specific fluid in the porous medium i.e. oil, gas or water. As 'k' is the absolute permeability, and k_{ro} , k_{rg} and k_{rw} is used to symbolize relative permeabilities respectively. Saturations of these mentioned fluids play an important role in defining k_{rel} because of k_o , k_g and k_w so that must be specified accordingly. Effective Permeability represents the conductivity of each phase at a specific saturation.

When we have multiphase fluids are flowing at the same time, the k_{rel} of each fluid is the ratio of the effective permeability to the absolute permeability.

$$k_{ro} = \frac{k_o}{k} \quad (2.8)$$

$$k_{rg} = \frac{k_g}{k} \quad (2.9)$$

$$k_{rw} = \frac{k_w}{k} \quad (2.10)$$

The reservoir fluids interact with each other and hence effective permeabilities of each fluid and the summation of the effective permeabilities of all fluids is lower than the absolute permeability.

$$0 < S \leq 1 \quad (2.11)$$

$$0 \leq k_{eff} \leq k_{abs}$$

$$k_o, k_g, k_w < k \quad (2.12)$$

$$k_o + k_o + k_o < k \quad (2.13)$$

Whereas,

S = saturation

k_{ro} = relative permeability to oil

k_{rg} = relative permeability to gas

k_{rw} = relative permeability to water

k = absolute permeability

k_o = effective permeability to oil for a given oil saturation

k_g = effective permeability to gas for a given gas saturation

k_w = effective permeability to water at some given water saturation

To further understand the concept of relative permeability, we can take an example of oil water system in the Figure 2.8

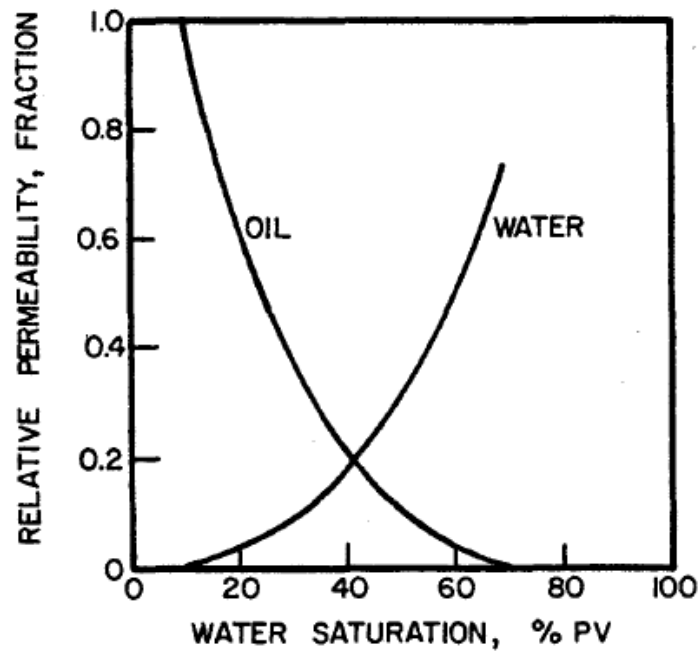


Figure 2.8 Relative Permeability - Oil Water System {Anderson, 1986 #6}

2.5.2. Saturation

The saturation is defined as, it is the fraction or percent of the volume of the pores occupied by any particular fluid (oil, gas, brine). This property can be expressed mathematically by the following relationship:

$$\emptyset = \frac{\text{total volume of the fluid}}{\text{pore volume}} \quad (2.14)$$

We can relate this relationship of saturation for reservoir fluids.

$$S_o = \frac{\text{Volume of Oil}}{\text{Pore Volume}}$$

$$S_g = \frac{\text{Volume of Gas}}{\text{Pore Volume}}$$

$$S_w = \frac{\text{Volume of Water}}{\text{Pore Volume}}$$

Whereas:

S_o = Oil Saturation

S_g = Gas Saturation

S_w = Water Saturation

All of these saturation values are based on pore volume and saturation of each fluid ranges from zero to 100%. Hence by definition of saturation, the sum of all the saturation is 100%, therefore:

$$S_o + S_g + S_w = 1$$

2.5.2.1. Irreducible Water Saturation, S_{wi}

Irreducible water saturation or critical water saturation is the maximum saturation of water at which water phase is not mobile.

2.5.2.2. Critical Oil Saturation, S_{oc}

Critical oil saturation is the saturation of the oil phase that must exceed a certain value for the oil phase to flow. At this particular value of saturation, oil remains in the pores volume and does not flow.

2.5.2.3. Critical Gas saturation, S_{gc}

As the reservoir pressure declines below the bubble-point pressure, gas evolves from the oil phase and consequently the saturation of the gas increases. The gas phase remains immobile until its saturation exceeds a certain saturation, called critical gas saturation, above which gas begins to move.

2.5.2.4. Residual Oil Saturation, S_{or}

Residual oil saturation is the saturation at the end of the displacing process of oil from the porous media , there is always remains some oil in the pore volumes that can be quantitatively characterized by a saturation value which is called S_{or} .

3. Methods of Wettability Measurements

Different methods have been proposed in the technical literature for the measurement of wettability and they can be classified as; quantitatively and qualitatively methods depending on the procedures use to determine the wettability, time and economics. {Abdallah, 1986 #7} In particular, quantitative methods are the direct measurement methods, where the wettability is measured on actual rock samples using reservoir fluids, including oil and brine. Whereas qualitative methods are indirectly inferred from other measurements, also qualitative methods include microscopic visualization of fluid distribution, relative permeability curves and imbibition methods. {Czarnota, 2016 #6}

The quantitative methods include: [Anderson 1986]

Contact Angle Method

Amott Method (Imbibition and forced displacement)

USBM (United States Bureau of Mines) Wettability Method.

The qualitatively methods include: [Anderson 1986]

Imbibition rates method

glass slide method

relative permeability curves method

permeability/saturations relationships method

capillary pressure curves method

and nuclear magnetic resonance method (NMR)

In the following chapter all the mentioned methods will be described and discussed.

3.1 Quantitative Methods for the measurement of Wettability

The quantitative methods mentioned before for measuring the wettability are discussed below.

3.1.1. Contact Angle Method

This is one of the most important wettability measurement method when fluids or formation fluids are used with the artificial or reservoir rocks samples. Many methods of contact-angle measurement have been developed like Amott and USBM (United States Bureau of Mines), but the most common used in the petroleum industry is Sessile Drop method. At first, it uses a single flat, polished mineral crystal (Figure 3.1), whereas in the second one it uses two flat, polished mineral crystals that are mounted parallel to each other on adjustable posts (Figure 3.2) (Anderson 1986).

The very first step in measuring the contact angle is to clean the apparatus thoroughly because even a very small amount of impurities can change the contact angle. Then the cell containing the mineral crystals is filled with brine to prevent the introduction of foreign metal ions which can alter the wettability. Also, for the second modified Sessile Drop method as shown in Figure 3.2a, an oil drop is placed between the two crystals so that it contacts maximum area of each crystal. After the oil/crystal interface has aged for a few days, the crystals are displaced parallel to each other. This will shift the drop of oil and allows brine to move over the surface which was previously covered by oil. This measure contact angle is called as “water-advancing” contact angle as shown in Figure 3.2b.

During the contact angle measurements, there is also a problem of hysteresis. This is due to surface roughness, surface heterogeneity and surface immobility on a macromolecular scale. [10]

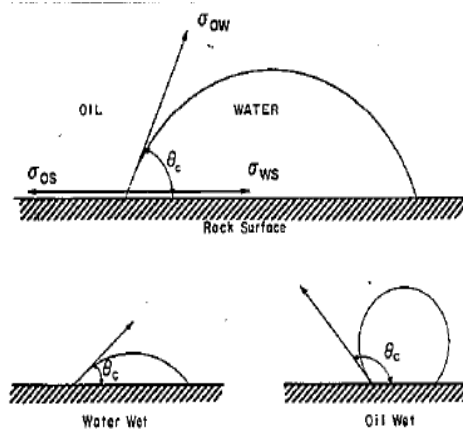


Figure 3.1 Wettability of Oil/Water Rock System (Anderson 1986)

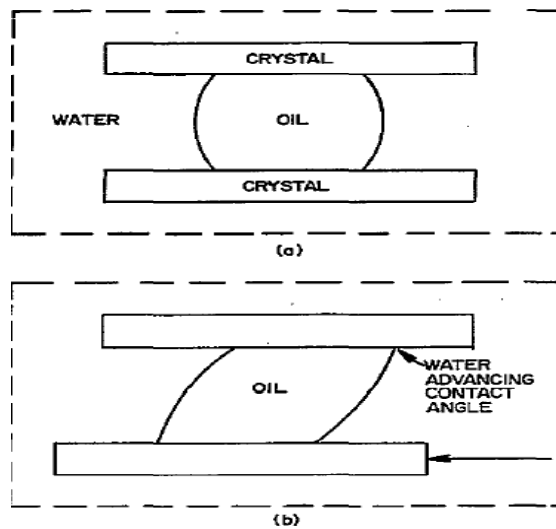


Figure 3.2 Contact Angle Measurements (Anderson 1986)

3.1.2. Amott's Method

This method was described by (Amott 1959). He carried out the experiment to determine the 'average' wettability of the core. This method combines both imbibition and forced displacement of water volume by oil and oil volume by water.

In this method, both reservoir core and fluids can be used. This method considers the fact that the wetting fluid will imbibe spontaneously into the core and will displace the non-wetting fluid. This procedure of core testing consists of the following steps:

1. First of all, flush the core with water and with kerosene to get rid of most of the crude oil and formation water.
2. Remove the gas by evacuating with the kerosene.
3. Centrifuge the core under water to get the residual oil saturation of the core.
4. Immerse the core in kerosene and then record the volume of water spontaneously released (imbibition) after twenty hours.
5. Centrifuge the core under kerosene until we reach the irreducible water saturation and then record again the total volume of water displaced including the volume displaced by spontaneous free imbibition.
6. Immerse the core in brine and then record the volume of oil displaced by spontaneously imbibition of water after twenty hours.
7. Centrifuge the core in brine until residual oil saturation is achieved and record the total volume of oil displaced.

Hence according to Amott test, wettability of the rock can be demonstrated by defining two quantities of ratios:

1. Displacement-by-oil-ratio Index (I_o): It is the ratio between the volume of water displaced by spontaneous oil imbibition alone (V_{wsp}) and the total volume displaced by oil imbibition and forced centrifugal displacement (V_{wt}).

$$I_o = \frac{V_{wsp}}{V_{wt}} \quad (3.1)$$

2. Displacement-by-water-ratio Index (I_w): It is the ratio between the volume of oil displaced by spontaneous water imbibition alone (V_{osp}) and the total volume displaced by water imbibition and forced centrifugal displacement (V_{ot}).

$$I_w = \frac{V_{osp}}{V_{ot}} \quad (3.2)$$

Wettability of the rock is hence given by these indexes. For a strong water-wet core, I_w will be positive whereas I_o will be zero. Similarly, in a strong oil-wet core, I_o will be positive while I_w will be zero. In the case of a neutral wet core, both of these indexes are zero.

There is also a modification of Amott's method called 'Amott-Harvey relative displacement index' and it is being used more frequently. This modified method is similar to the Amott method but there is an additional step in prior to the preparation of the core which is done by centrifuging the core first under brine and then under crude to reduce the plug to irreducible water saturation. The displacement-by-water and displacement-by-oil ratios are then calculated by the Amott method. The Amott-Harvey relative displacement index is the displacement-by-water ratio minus the displacement-by-oil ratio:

$$I = I_w - I_o = \frac{V_{osp}}{V_{ot}} - \frac{V_{wsp}}{V_{wt}} \quad (3.3)$$

This combines the two ratios into a single wettability index that varies from +1 for complete water wetness to -1 for complete oil wetness. Cuiec* stated that the system is water-wet when $+0.3 \leq I \leq 1$, intermediate-wet when $-0.3 < I < 0.3$ and oil-wet when $-1 \leq I \leq -0.3$.

3.1.3. USBM Method (United States Bureau of Mines)

The third quantitative test that is used to measure the wettability is the USBM test that was developed by (Donaldson, Thomas et al. 1969). This method measures and gives an average wettability of the core based on the two areas under the capillary pressure curves determined with centrifuge. A major advantage of this method as compared to Amott method is that it is more sensitive near neutral wettability. This test consists of the following steps:

1. The core which is saturated with brine is placed in a glass core holder filled with oil. Then it is centrifuged until the residual water saturation is obtained as shown by a dashed line I in Figure 3.3.
2. The core is placed in another core holder filled with brine and centrifuged at different speeds to displace oil. Then this volume is measured to obtain the capillary pressure curve II.
3. After that, the core is placed in a core holder filled with oil and the volume of brine is recorded at each incremental increase in speed to obtain capillary pressure curve III as depicted in Figure 3.3.

The wettability defined by USBM method is demonstrated as:

$$w = \log \left(\frac{A_1}{A_2} \right) \quad (3.4)$$

Whereas,

A_1 = Area under the water-displaced-by-oil curve

A_2 = Area under the oil-displaced-by-water curve

Consequently, a water-wet system has a larger area under the water displaced by oil curve than the area under the oil displaced by water curve which means that the value of the logarithm is positive as demonstrated in the Figure 3.3a.

Similarly, in an oil-wet system, the logarithm of the area is negative as shown in Figure 3.3b. Finally, a neutral-wet system can be observed in Figure 3.3c.

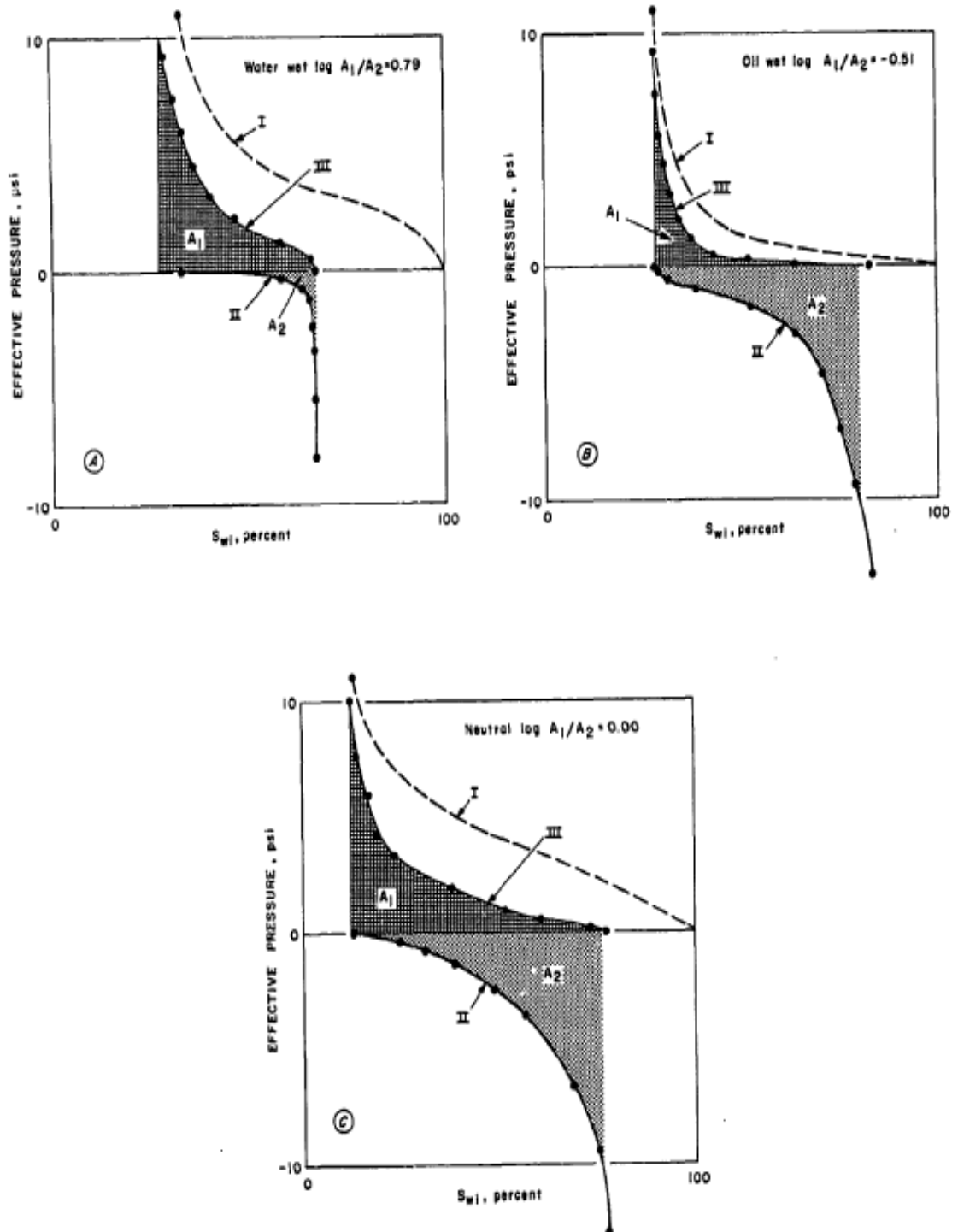


Figure 3.3 Effect of Wettability on the area ratio of Capillary Pressure Curves

a) Untreated Core b) Core treated with 10 percent Dri-film pp c) Core penetrated with Oil for 324 hours at 140 °F. {Donaldson, 1969 #8}

The relationship between wettability, contact angle, and Amott and USBM wettability indexes is shown in the Table 3.1: {Anderson, 1986 #5}

Table 3.1 The relationship between wettability, contact angle, and Amott and USBM wettability indexes

| Description | Water-Wet | Neutrally Wet | Oil-Wet |
|-----------------------------------|------------------|----------------------|----------------|
| Contact Angle(Degrees) | | | |
| Minimum | 0 | 60 to 75 | 105 to 120 |
| Description | Water-Wet | Neutrally Wet | Oil-Wet |
| Maximum | 60 to 75 | 105 to 120 | 180 |
| USBM Wettability Index (W) | | | |
| W Index | W near 1 | W near 0 | W near -1 |
| Amott Wettability Index | | | |
| Displacement-by-Water Ratio | Positive | Zero | Zero |
| Displacement-by-Oil Ratio | Zero | Zero | Positive |

3.1.4. Electrical Resistivity Method

This method is also used to measure wettability. This method was established by (Sondena, Bratteli et al. 1991) by the estimation of saturation of water using Archie's equation.

$$RI = \frac{R_t}{R_0} = S_w^{-n} \quad (3.5)$$

Whereas RI is defined as the resistivity index, R_t and R_o are the electrical resistivities when the rock is partially saturated with water and when the rock is totally saturated with water. The exponent 'n' is defined as the Archie's saturation exponent. Hence, we can write it as:

$$n = - \frac{\log\left(\frac{R_t}{R_o}\right)}{\log(S_w)} \quad (3.6)$$

Sondenaa, Bratteli carried out some of the experiments with different types of oil (crude oil, live crude oil and refined oil) at different conditions (pressure and temperature at reservoir and ambient conditions) to observe the variation of Archie's saturation exponent. Therefore, they concluded that the Archie's saturation exponent is not affected or decreased slightly with an increase in temperature and this exponent should be evaluated using only endpoints values. The saturation exponent increases as the saturation of water decreases. The increase of the saturation exponent can be related to a wettability change.

The typical value for the saturation exponent is approximately 2 for the majority water wet reservoirs. However, value of n differs significantly from 2 and go beyond 2 to a higher value which is an indication for oil wet reservoirs.

Some authors like (Lewis, Sharma et al. 1988) also determined many different ranges for Archie's saturation exponent depending on the type of the rocks and chemicals used during the experiments (Lewis, Sharma et al. 1988) determined Archie's saturation exponents for Berea sandstones treated with chemical Quilon C from 2.0 (strong water-wet) to 5.2 (strong oil-wet).

3.2. Qualitative Methods for the measurement of Wettability

Qualitative methods discussed by Anderson (10) determined the degree of water or oil wetness based on these two methods: a) the shape of the curves like in relative permeability and recovery curves, or b) behavior of the particles in fluids like in the flotation methods. The methods that will be used here are relative permeability and recovery curves because they are easily obtained in water and surfactant flooding experiments.

3.2.1. Flotation Method

These methods are fast but mostly worked for the strongly wetted systems. Donaldson¹⁴ et al. mentioned that this method is best demonstrated by placing water, oil and sand in a glass bottle and then they are shaken. After this, the behavior of the sand grains is observed to determine the wettability of the system. For a strongly oil-wet system, some of the grains of sand will be suspended at the oil-water interface whereas the grains which are oil-wet in the water, they will cluster together forming tiny globules of oil coated with sand. Similarly, for a strongly water-wet system, the clean grains of the sand will settle at the bottom of the bottle while sand grains which are placed in the oil will make aggregate and form tiny clumps of grains encircled by a thin layer of water.

3.2.2. Glass Slide Method

Another early qualitative wettability measurement technique is the glass slide method. This technique assumed that a glass surface is representative of the reservoir rock. A clean and dry microscope slide is suspended in a layer of crude oil floating on water in a transparent container and aged. The glass slide is then lowered in the water. After observing the results, if the slide is water-wet, the water quickly displaces the

oil on the slide. In the contrast, if the slide is oil-wet, a stable oil-wet film is formed, and the oil is very slowly displaced. (Reisberg and Doscher 1956) aged glass slides in crude oil and found that it took up to thirty days for the final wettability to be reached.

3.2.3. Relative Permeability Method

This is also one of a qualitative method to evaluate the effects of wettability on relative permeability. Nevertheless, this method is best suitable for strongly wetted core systems. (Craig 1971) suggested the rules of thumb to differentiate between strongly water-wet and strongly oil-wet system as shown in Figure 3.4 is as follows:

1. Connate water saturations are typically greater than 20 to 25% of pore volume in a water-wet rock, but less than 10% of pore volume in an oil-wet rock.
2. Water saturation at which water and oil relative permeabilities intersect are equal is generally less than 50% for oil-wet systems and greater than 50% for the water-wet systems.
3. The water relative permeability value is much larger (50 to 100%) in oil-wet systems but have smaller values (less than 30%) in water-wet systems.

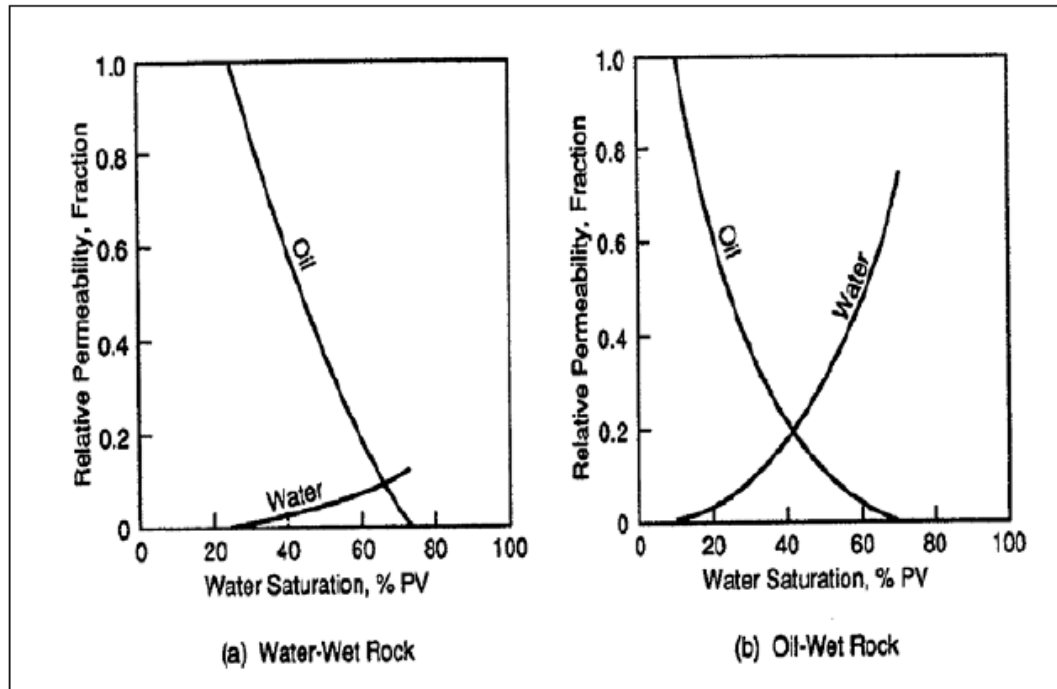


Figure 3.4 Typical Water and Oil Relative Permeability Curves (Anderson, 1986)

3.2.4. Recovery Curves Method

This method is based on the recovery curves of oil recovery factor and it shows recovery curves as a function of pore volumes of formation water injected in the water flooding using low viscosity fluids. As depicted in Figure 3.5, for a strongly water-wet sample (Curve A), oil recovery factor is high before breakthrough, and the water/oil ratio rises sharply (Curve A'), whereas for a strongly oil-wet sample (Curve B), oil recovery is low before the breakthrough, and the water/oil ratio rises slowly after the breakthrough (Curve B')

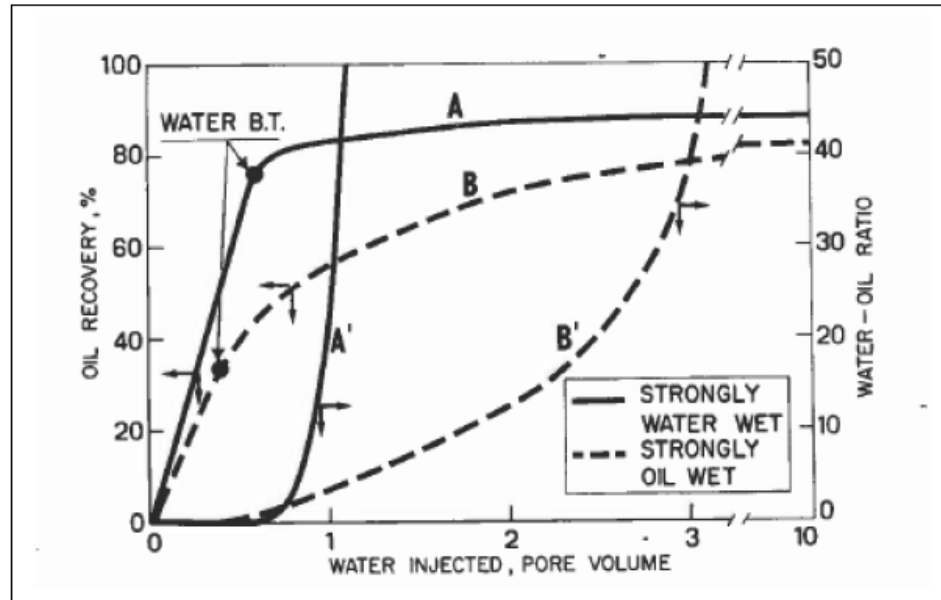


Figure 3.5 Idealized water flood performance of a sandstone type core (linear). Low-viscosity fluid. {Morrow, 1990 #5}

Now after describing different quantitative and qualitative methods of measuring the wettability, here are some advantages and disadvantages of these methods listed in the Table 3.2:

Table 3.2 Advantages and Disadvantages of Quantitative and Qualitative Methods for the evaluation of Wettability

| Methods | Advantage | Disadvantage |
|-------------------------------|--|---|
| Quantitative Methods | | |
| Contact Angle Method | Gives direct measurements. A crystal of quartz or Calcite can be used. Representative of reservoir by using reservoir fluids. Low cost. | Artificial samples are used. Preparation of core sample. Measures a specific surface. |
| Amott's Method | Measure Average Wettability of core sample. | Longer test time. |
| USBM Method | Measure Average Wettability. | Core sample is critical. Sample preparation. |
| Qualitative Methods | | |
| Flotation Method | Only works in strongly wetted systems. | Does not work for neutral wet system. |
| Glass Slide Method | Fast method. | Assumes glass surface as the representative of reservoir. |
| Relative Permeability Methods | Test time is shorter. Only works in strongly wetted systems. | Does not work for neutral wet system. Only works when Krel data is available. |
| Recovery Curves Method | Less time consuming. Gives an overview by oil recovery factor. | Only works when desired data is available. |

4. Techniques for the alteration of wettability

Wettability is perhaps among one of the most important and crucial factors that affects the rate of oil recovery and residual oil saturation, and this is very important in the field of enhanced oil recovery. Wettability of the system controls the rate and spontaneous imbibition of water and the efficiency of the oil displacement as a result of water injection, with or without water additives. (Tiab and Donaldson 2015)

Treatment of the Rock

There are many methods present which has been used widely to alter the wettability of a rock. Few of them are listed as below:

1. Silanization by treatment with the chemicals of organosilanes compounds having general formula of $(\text{CH}_3)_n\text{SiCl}_x$; the silanes chemisorb on the silica surface, producing HCl and exposing the CH_3 groups which produce the oil wetting characteristics;
2. Aging under pressure in crude oil;
3. Treatment with naphthenic acids;
4. Treatment with asphaltenes; and
5. Addition of surfactants to the fluids.

First of all, cores or sand treatment is conducted by cleaning with solvents, acidic chemicals, steam or heating up to 250°C to remove organic materials; but however, heating to such a high temperature dehydrates the clays and changes the surface chemistry of the rock. After cleaning, the core is treated with several concentrations of the additives mentioned in the above methods and then dried once more at 100°C to fix the additive onto the surface of the rock.

The alteration of wettability must be carried out under controlled conditions carefully because the final wettability depends on:

1. The composition of the mineralogy of the rock.
2. The procedure of the cleaning procedures used.
3. The type of the additives used (asphaltenes, silanes, etc.)
4. The concentration of the additive in the solvent used to permeate and infuse the core.
5. The type of the procedure used to evaporate the solvent and dry the core.

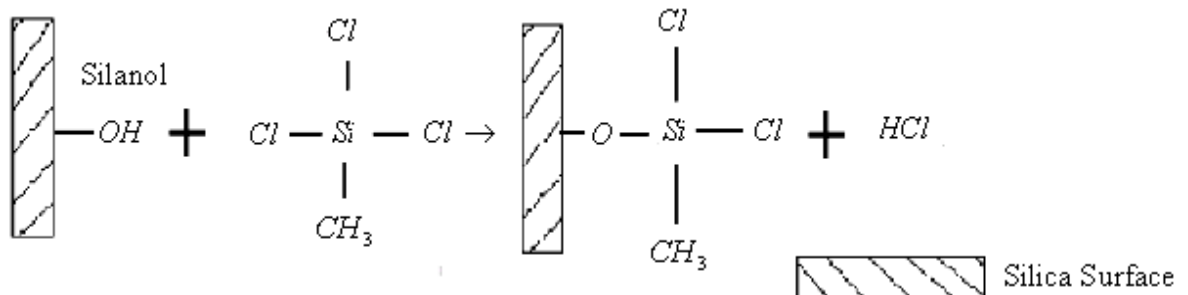
It is highly rare to attain completely uniform wettability throughout the core, nevertheless this method has been used successfully to obtain systems at several states of average wettability for examination of the effects of the wettability on production.

As discussed, there are several methods to modify the wetting properties of the surface of the rock to water or oil. We will discuss two methods to change the wettability of strong water-wet system to less water-wet system.

4.1. Silanization with Organosilanes

The procedure of silanization consists of a chemical reaction in which organosilyl group attacks and displaces the hydroxyl group (OH). In this reaction, organochlorosilane compound (silicon molecules with attached chlorines and non-water organic groups, with the formula R_nSiCl_{4-n}) reacts with the hydroxyl group on silicon dioxide (SiO_2) surface, exposing the organic groups and changing into a hydrophobic system.

In this procedure, trichloro(methyl)silane reacts with water or hydroxyl groups (Silica) to release HCL and form a thin film of methylpolysiloxanes which has low critical surface tension (hydrophobic). The chemical reaction is given below:



Similarly, the procedure used by (Tabrizy, Denoyel et al. 2011) to alter the wettability from a strong water-wet system to strong oil-wet system is as follows:

1. Cleaning procedures are applied to the glass beads with an HCl solution (20%) to get a water-wet system.
2. Rinse the glass beads with distilled water to remove all the residues and then put in an oven for two hours at 100°C.
3. The glass beads are then incubated in a 2% solution of trichloro(methyl)silane and 98% of toluene for almost 15 minutes. A thin film of methylpolysiloxanes covers the grains. It has to be considered the formation of HCl during this reaction before removing the glass beads from the reaction vessel.

4. Finally, rinse the glass beads with methanol and then dried in the oven. This will help to the cross-linking reaction and the formation of monolayer silane film.

4.2. Treatment with Chrome Complexes Quilon

This technique was used alter the wettability in cores of sandstones like Quilon treatments. (Maini, Ionescu et al. 1986) used Quilon-S (the stearic acid complex) whereas (Lewis, Sharma et al. 1988) worked with Quilon-C (modified chrome complex of S-type) to change the hydrophilic surfaces to hydrophobic surfaces (oil-wet).

Quilon-C is a Chromium complex that has a fatty acid group (C₁₄-C₁₈). Chromium is Quilon-C reacts with polar group on charged surfaces (negative) and forms an insoluble layer of polymerized complex which bonds to the rock surface by Chromium. The exposing fatty acids groups repel water; thus, this makes the rock hydrophobic.

The procedure used by (Lewis, Sharma et al. 1988) is discussed as follows:

At first, the cores were dried by vacuum for two hours and then saturated with a 20% solution of Quilon-C and reagent grade isopropyl alcohol. After that, the cores were evacuated out for about four hours. The same procedure was repeated again, and then the core was flushed with ethanol until remaining effluent turned slightly green color. Finally, the core was heated in an oven at 60°C for about whole one night. This whole experiment was repeated again to get a stable treatment.

5. Conclusion

Wettability analysis of a reservoir rock system is a key phenomenon in understanding the dynamic behavior of the reservoir. We discussed about in detail about wettability and many macroscale and microscale parameter affecting it. We also discussed the wettability behavior of different naturally occurring reservoir rocks as well as the wettability analysis of artificially producing materials.

The comparison between naturally occurring and artificially producing materials is very important because this will lead us to better understand the behavior of reservoir by studying and exploiting the artificial materials which are very best suited to represent the reservoir, then this will be very helpful in understanding and learning for the further experimental work regarding wettability analysis for various chemical EOR processes such as surfactant flooding, polymer flooding and gas flooding.

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