White Paper

AUTHOR

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Wettability Measurements for Enhanced Oil Recovery Optimization

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[Progress Together]

Wettability Measurements for Enhanced Oil Recovery Optimization

Wettability of the rock has been identified as one of the key factors affecting oil recovery. To study the wettability of the core as well as the wettability alteration caused by enhanced oil recovery (EOR) methods, different wettability measurement techniques have been utilized. The first part of the white paper discusses the wettability and its relation to the enhanced oil recovery techniques. The main emphasize is in the most used wettability measurement methods; contact angle, Amott-Harvey and USBM. In the last part, the methods are compared to each other.

Introduction to Wettability

Wettability describes the preference of a solid to be in contact with one fluid rather than the other [1]. Interfacial interactions determine whether a fluid, surrounded by another fluid, will spread or bead up at the solid surface. In enhanced oil recovery (EOR) wettability plays an important role as it determines the interactions between the solid (rock) and the liquids in the reservoirs (crude oil, brine). Wettability has been recognized as one of the key parameters controlling the remaining oil-in-place.

Reservoirs are Characterized by their Wettability

Rocks can be classified as water-wet, intermediate-wet or oil-wet. When the rock is water-wet, water is preferentially in contact with the mineral when oil is the surrounding phase. The rock is said to be oil-wet when oil is the liquid in contact. The state in between is called intermediate wet. Contact angles are used as a measure of wettability. The balance of forces in the oil/water/solid system will result in a contact angle. Thus contact angle ranges for different wetting states can be defined as in Fig 1.

There are also other terms used to describe the wettability of the reservoirs, namely neutrally-wet, fractionally-wet and mixed-wet.

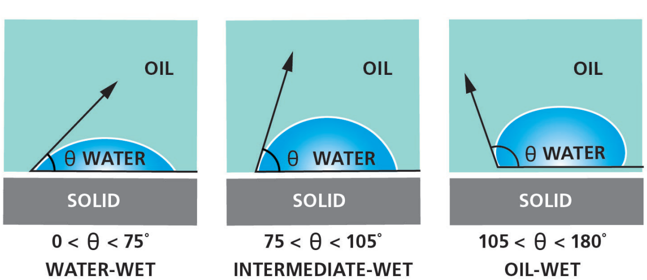

Figure 1 Contact angle ranges of different wetting states of the reservoir

The term neutrally-wet is sometimes used to refer to a situation where the contact angle is close to 90 degrees. The terms fractionally – or mixed-wet can be used almost interchangeably and refer to a situation where parts of the reservoir are oil-wet while others are water-wet. The term mixed-wet is more commonly used. [2]

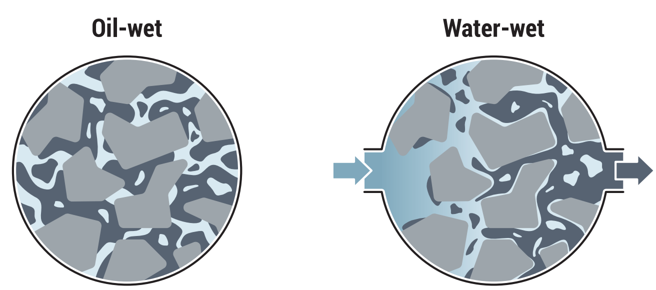

Figure 2 From oil-wet to water-wet

From Oil-wet to Water-wet by Wettability Alteration

Wettability alteration is an effective approach to enhanced oil recovery. Problems with oil-wet reservoirs are related to early break-through of water which causes low sweeping efficiencies and poor oil recovery [3]. The purpose of the wettability alteration is thus to change the wetting state of the rock to be more water-wet. Several factors, including crude oil, brine, and rock composition as well as pressure and temperature affect the wettability.

Several chemical and thermal approaches have been taken to alter the wettability of the reservoir to be more water-wet [4]. Wettability alteration methods currently gaining attention for both carbonate and sandstone reservoirs include nanofluids [5] and low-salinity or smart water flooding [6]. Below are four examples of some of the currently studied enhanced oil recovery methods.

We present four examples of currently studied enhanced oil recovery methods.

Surfactant Assisted Enhanced Oil Recovery

The main function of surfactants in enhanced oil recovery is to reduce the interfacial tension and wettability alteration. Two different mechanisms for wettability alteration with surfactants have been proposed; coating and cleaning mechanisms. In coating mechanism, the surfactant is adsorbed onto the oil-wet solid surface. Cleaning mechanism, on the other hand, refers to a process where surfactant molecules complex with contaminant molecules adsorbed from crude oil to strip them off the rock surfaces. [7]

Surfactants need to be screened for specific reservoir conditions [8]. These include not only the temperature and salinity of the reservoir but also the pressure. Surfactants that perform well at room temperatures may show reduced performance at high temperatures.

Wettability Alteration by Nanoparticles

During the past few years different nanomaterials, especially nanoparticles (NP), have gained a lot of interest as EOR agents [5]. Nanoparticles can alter the wettability of the reservoir as well as reduce the interfacial tension between oil and water. The use of NPs in EOR has several advantages including (1) good stability, (2) possibility to tailor nanoparticle size and shape as well as surface chemical properties, and (3) potential of being environmentally friendly as the majority of the nanoparticles used are based on silicon dioxide.

CO2 as Wettability Alteration Agent

Gas injections are the most widely used EOR method in a carbonate reservoir. CO_2-EOR has been successfully implemented in both mature and waterflooded carbonates. If CO_2 is available, it will be the soundest recovery choice for carbonate unless more viable EOR strategies are developed. An additional benefit of using CO_2-EOR is the possibility to simultaneously capture and storage the used CO_2. [9]

Low-salinity or Smart Water Flooding

Waterflooding has long been used as a secondary recovery method both in carbonate and sandstone reservoirs. However, in the mid-'90s the pioneering work by Yildiz and Morrow [10] showed that changing the brine composition can influence the oil recovery. Since then, the injection of so-called smart water with the correct salt composition and salinity has gained a lot of interest. Several groups have studied the mechanisms by which the improved oil recovery is achieved. At first, the research was mainly concentrated on sandstone reservoirs where extra oil recovered from low salinity flooding varied in the range of 5- 30 % of original oil in place [11]. However, several laboratory studies and field tests have confirmed its potential also in carbonate reservoir enhanced oil recovery. There are two main advantages compared to other enhanced oil recovery methods; (1) low cost and (2) less impact on the environment [12].

Wettability Measurement Methods

As wettability is recognized as one of the most important factors affecting oil recovery, several different methods to study reservoir wettability have been developed. It is commonly accepted that more water-wet reservoirs can produce more oil. The most typical question is how much and to which direction the applied EOR method changes the wettability of the reservoir.

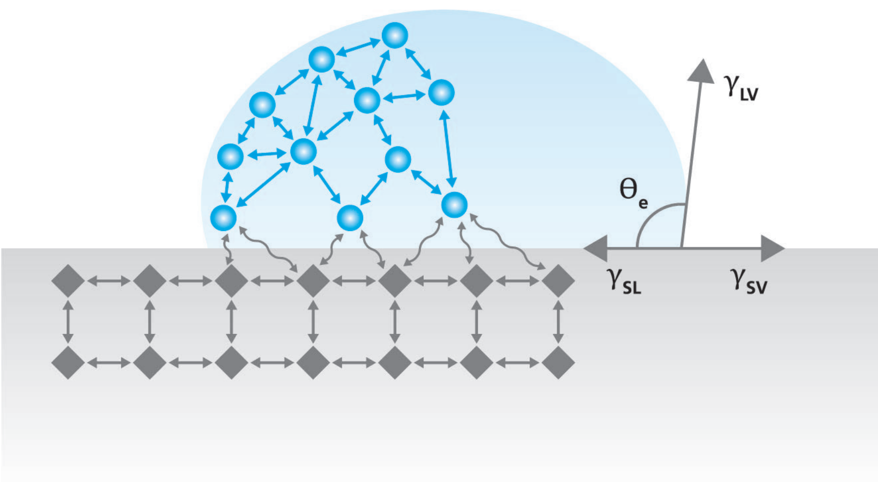

Figure 3 Forces acting on a three-phase contact point between solid-fluid-fluid. γ_{LV} is the surface tension of a liquid, γ_{SL} is the interfacial tension between the solid and liquid and γ_{sv} is the surface free energy of solid.

Contact Angle

Contact angle is geometrically defined as the angle formed by a liquid at the three-phase boundary where a liquid, gas (or another liquid), and solid intersect. There are different forces acting on this three-phase contact point between solid, fluid and fluid as shown in Fig.3. [13]

In practice, a drop of liquid is placed on the solid sample surrounded by another liquid or gas. An image of a drop is taken and analyzed by the software. The measured contact angle value indicates the wetting state of the surface. In EOR studies the solid sample is typically a reservoir rock, the surrounding fluid is either brine, surfactant solution or CO_2 and droplet represents the oil in the reservoir.

Although contact angle measurements have been widely used to study the wettability in various industrial fields, its utilization to study rock wettability has only started to increase during the last decade or so. In Fig. 4, it can be seen that the number of publications with search terms "contact angle" + "rock wettability" has started to increase drastically since 2010.

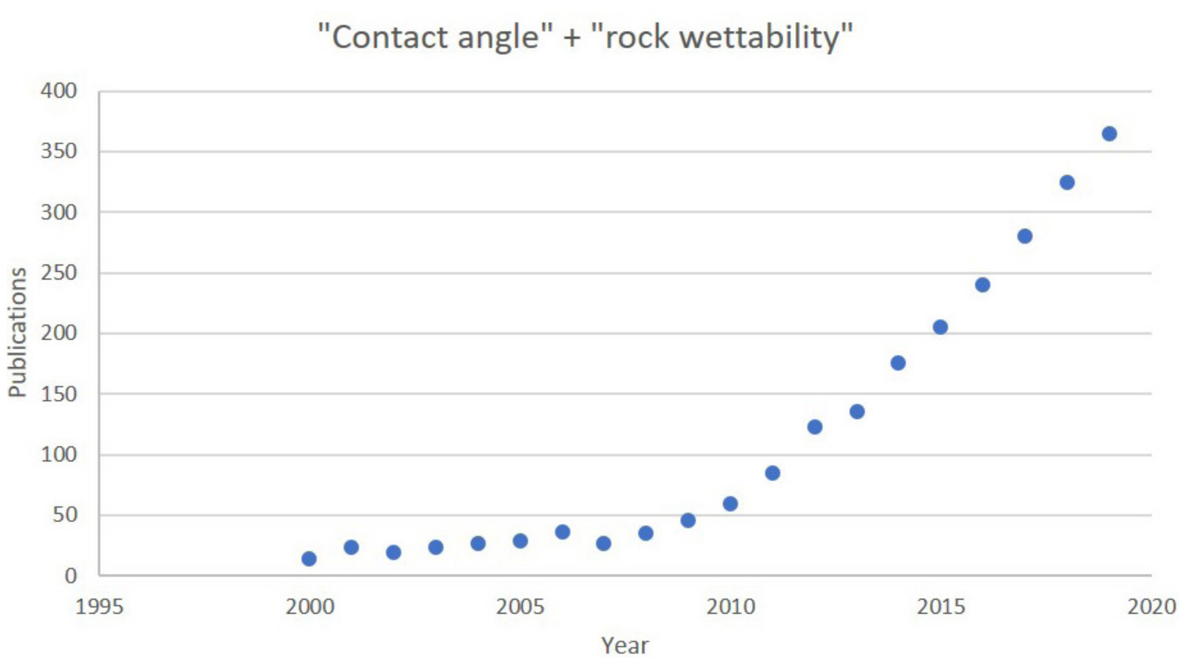

Figure 4 Number of publications per year with search term "contact angle" + "rock wettability"

Amott-Harvey Method

The Amott-Harvey method uses a combination of two spontaneous and two forced imbibition measurements of initially oil-saturated cores [14]. Displacement of both water by oil as well as oil by water is tested. The data is used to calculate the displacement by oil index which is a ratio between water volume displaced by spontaneous oil imbibition alone and the total volume displaced by oil imbibition and forced displacement.

Prior to the measurements, the preparation of the core sample is done so that it is in irreducible water saturation, i.e. at the lowest water saturation possible to achieve. In the first measurement step the core is placed into the water-filled tube and the spontaneous imbibition of water over a period of time, at least 10 days, is measured. Then, the core is placed in a flow cell and water is forced through the sample. The additional oil recovery is recorded. Now the sample is in residual oil saturation point meaning the state where, as much oil is recovered as possible with water. Next, the process is repeated so that the spontaneous imbibition of oil is measured followed by the forced flow.

The result is the Amott-Harvey index which is a difference between the water and oil ratios and varies from + 1 (strongly water-wet) to – 1 (strongly oil-wet).

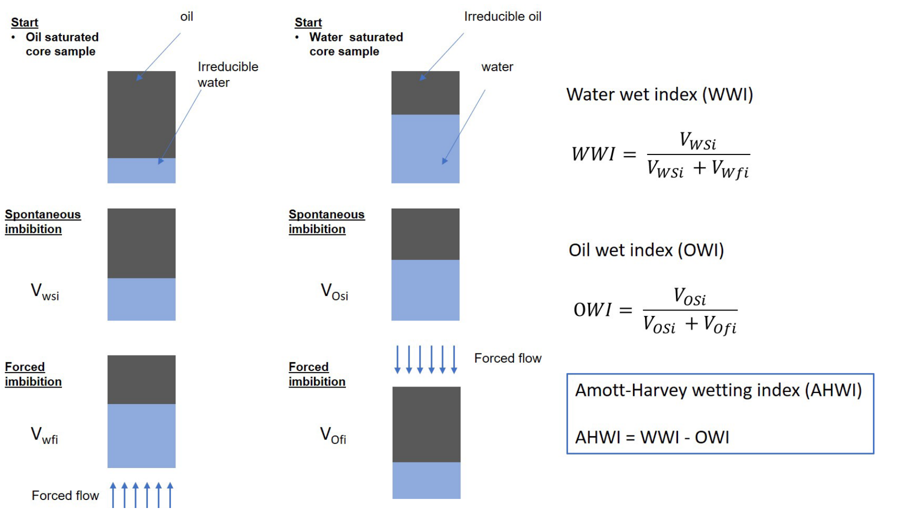

Figure 5 Amott-Harvey measurement with spontaneous and forced imbibition steps for water and oil.

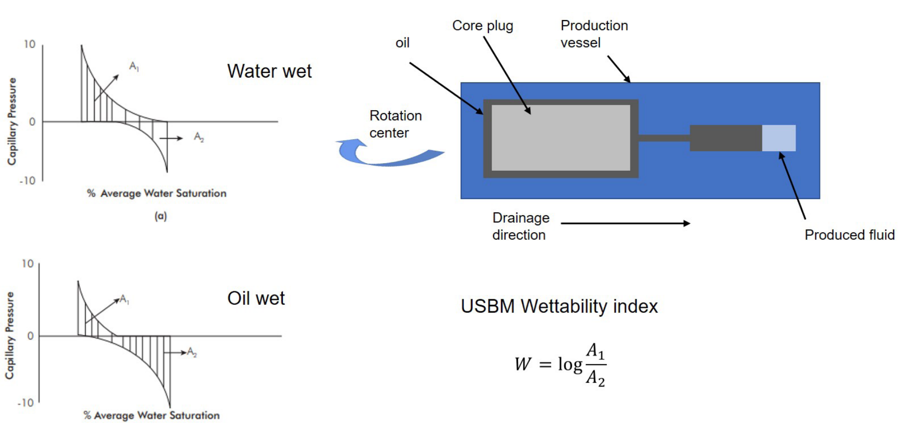

Figure 6 USBM wettability index

USBM

The USBM test was developed by Donaldson in 1969 [14]. As the Amott – Harvey test, it measures the average wettability of the core. The USBM test compares the amount of work required to replace one fluid with the other. The method is based on forced imbibition of fluid inside the core which is achieved by centrifuge spins with stepwise-increasing speed.

As the Amott-Harvey method, the USBM starts with the irreducible water-saturated core inside a water-filled tube. After periods at several spin rates, the sample reaches residual oil saturation, and it is placed in an oil-filled tube for other series of measurements. The produced curve is similar to Amott-Harvey, but now the areas between each of the capillary-pressure curves and the zero capillary-pressure lines are calculated. The logarithm of the ratio of the water-increasing to oil-increasing areas give the USBM wettability index. The practical measurement results are typically in a range of +1 (strongly water-wet) to - 1 (strongly oil-wet). The USBM method is faster than Amott-Harvey since the spontaneous imbibition is not done but must be corrected because the centrifuge induces a nonlinear capillary-pressure gradient in the sample.

Comparison of the methods

The contact angle measures the wettability of the surface whereas the Amott-Harvey and USBM methods measure the average wettability of the core. Anderson has presented a relation between the Amott-Harvey, USBM and contact angle data as shown in table 1 [14].

The main problem of the Amott test is its insensitivity at the intermediately wet region. When contact angle between the core sample and the fluid is in between 60 to 120 degree, neither of the fluids will spontaneously imbibe and displace the other. Also, the initial saturation of the core plays a role [14]. Both contact angle and USBM method work also on the intermediate-wet region.

One limitation of both, the Amott-Harvey and USBM, methods is that they are relatively slow, expensive and/or labor-intensive. Contact angle measurement, even at high temperatures and pressures, is relatively fast to perform. Amott-Harvey and USBM methods also change the fluid saturation in the sample and are not then suitable for monitoring changes in wettability as a function of time or other experimental parameters [15].

One clear advantage of the contact angle measurement is that it is relatively simple to conduct also under the reservoir temperature and pressure. Commercial instruments are readily available. Amott-Harvey [16] and USBM wettability [17] at high pressures and temperatures have been presented in literature but both have limited availability.

The main criticism to contact angle has been inconsistency in results. However, the current understanding is that this is due to differences in: substrate type and their preparation methods as well as fluid types (purity, saturation stage) and contact angles reported (static vs. dynamic) [18]. It is also clear that the traditional contact angles measured in air are not representative contact angles to study reservoir conditions [2].

	Water-wet	Intermediate-wet	Oil-wet
Contact angle	0 ° to 75 °	75 ° to 105 °	105 ° to 180 °
Amott-Harvey wettability index	0.3 - 1.0	-0.3 - 0.3	- 1.0 - -0.3
USBM wettability index	Near 1	Near 0	Near -1

Table 1 Relation between contact angle, Amott-Harvey and USBM wettability data

	Contact Angle	Amott-Harvey	USBM
Measurement time	1-4 hours	Over 10 days	1-2 days
High temperature	Yes	Limited	Limited
High pressure	Yes	Limited	Limited
Reservoir type	All	Not applicable with shales and other tight reservoirs	Challenging with shales and other tight reservoirs
Other measurement	Interfacial tension	N.A.	N.A.

Table 2 Comparison of contact angle, Amott-Harvey and USBM methods

One additional advantage of contact angle measurement is that the same instrument can also be used to measure interfacial tension values. Interfacial tension between different fluids in the reservoir is, together with reservoir wettability, a key parameter when effectiveness of EOR methods are being evaluated.

Reservoir type makes a difference

Contact angle offers by far the best measurement method when pure liquids and minerals are being studied. To study the fundamentals of enhanced oil recovery mechanisms or to make first evaluations of the new method, contact angle measurements with pure hydrocarbons and polished mineral surface are often conducted. Mica and silica are used to represent sandstone while marble and calcite are used in place of carbonate. [4]

Contact angle measurements are also superior for shales and other tight reservoirs. Shales are difficult for Amott-Harvey method as spontaneous imbibition is very slow, and thus impractical. Also, the centrifugal force in the USBM method is not enough to replace fluids in shale or tight cores. [19]

Right method for your application

The most frequently used surfactant screening test is contact angle measurement [4]. Contact angle provides a fast and efficient tool to screen the ranges of surfactants for their ability to change the surface wettability. In addition to mimicking reservoir conditions, pressure is also needed to perform contact angle measurements in an aqueous environment at above 100 °C as boiling would make the measurements impossible.

Contact angle measurements are superior when pure liquids and minerals are studied. It also provides the best method to study the effect of experimental conditions on wettability.

Contact angle measurements have been utilized to evaluate the effect of different nanoparticle solutions to rock wettability [20]. Contact angle is measured on oil-saturated rock samples. They show oil-wet behavior when oil contact angle is measured on sample immersed in brine. When brine is changed to nanofluid the sample is turned more water-wet.

Water/brine – CO_2 contact angles are measured on mineral surface and effect of temperature and pressure on contact angle values have been studied [21]. Also, the effect of carbonated brine to the contact angle has been evaluated [22].

To study the wettability alteration caused by low salinity water, contact angle measurements have been utilized. In the study of Ding et. al. [12], the contact angles of different brine solutions were measured on the rock surface. To mimic the oil-wet state of the reservoir rock, the surface was aged in mineral oil. The water contact angle after the aging period was measured to range from 121° to 130°. To conduct the measurements with different brine solutions, the rock was immersed into mineral oil and the brine contact angles were measured through the oil phase.

Conclusions

The three most used wettability measurement techniques in oil industry have been discussed. They are all able to provide quantitative information on the wetting state of the reservoir. Contact angle measurements are superior when pure liquids and minerals are studied. It also provides the best method to study the effect of experimental conditions, such as temperature, pressure, and brine chemistry, on wettability. USBM method appears to be superior to the Amott-Harvey which is insensitive at intermediate wet range. The selection of the wettability measurement method should be done based on the application and reservoir type.

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