Effective wettability of minerals exposed to crude oil

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Abstract

This review focuses on the macroscopic phenomena that can be used to assess effective wetting, especially the use of contact angles to quantify wetting conditions in the presence of brine and crude oil or on surfaces that have previously been exposed to brine and crude oil. Reservoir wettability has long been a puzzle. Wetting is almost certainly changed during all but the most careful core recovery processes and there is no guarantee that it can be preserved or recreated in the lab. Thus a great deal of effort has been directed at trying to understand reservoir wetting at a more fundamental level. The most important recent advances have demonstrated that there are multiple ways that crude oil components can adsorb to alter effective wetting, especially when an aqueous phase is also present. © 2001 Elsevier Science Ltd. All rights reserved.

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1. Introduction

When Anderson published his six-part review of the wettability literature in 1986 and 1987 [1–6], his combined lists of references amounted to hundreds of citations. One section of Anderson's review was devoted to wettability measurement [2]; even the apparently simple question of how to measure wettability had no straightforward answer. It was understood in general that adsorption of crude oil components could alter the apparent wettability of rocks exposed to crude oil from their original strongly water-wet condition to some other wettability state. What wettability condition should be expected for a particular combination of oil, brine and rock, however, was less well understood.

In a well-defined system, the contact angle at which two fluid phases meet a smooth solid surface is the macroscopic indication of wetting preference that de-pends upon solid–fluid and fluid–fluid interfacial energies. It is the boundary condition for interfaces between those two fluids in a porous medium composed of that solid. Wetting thus controls fluid distribution and the capillary pressure between immiscible phases in a porous medium.

A system comprised of brine, crude oil and rock, however, is not well defined. Each of the three phases is a complex mixture. Although contact angles are often measured in such non-ideal systems, both the measurements themselves and their interpretation can be problematic, as discussed by Morrow [7] in his 1990 review of reservoir wettability.

Consider a smooth mica surface and a drop of crude oil formed at a microburette tip, both submerged in an aqueous salt solution. When the captive oil drop first contacts the surface, it adopts a shape that reflects the original wetting preference of the solid for water. Water in this case is receding and the water-receding contact angle θ_R, measured through the water phase, is low and does not change with time. If, however, the drop volume is decreased, several phenomena can be observed. The extreme cases

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are: (1) the water re-advances at nearly the same contact angle ($\theta_A \approx \theta_R$), or (2) the three-phase contact line is pinned at its greatest extent and the contact angle increases continuously ($\theta_A \gg \theta_R$). This extreme hysteresis is evidence that the surface under the drop has changed because of its contact with the crude oil. Many different approaches to measuring the extent to which the effective wetting of mineral surfaces is altered by contact with crude oil have been pursued. Techniques aimed at quantifying the extent of wetting alteration on smooth surfaces and what those techniques have taught us about the nature of crude oil/brine/rock interactions that control reservoir wettability are the main subjects of this review.

2. Review of surface studies of effective wetting

2.1. Surface measurements

2.1.1. Contact angles

2.1.1.1. Crude oil, brine, and initially water-wet surfaces. Despite the difficulties outlined above, measurements of contact angles between crude oils (and oil derivatives or related fluids such as coal tar and creosote) and brines on initially water-wet surfaces are made by the captive or sessile drop [8–13] and dynamic Wilhelmy plate [14–17] techniques. Captive or sessile drops sample a small area of the surface and angles are the measured quantity, whereas the Wilhelmy plate produces an average adhesion tension ($\gamma\cos\theta$) for the circumference of the test plate from which an average contact angle can be calculated if interfacial tension γ is known.

Tests of adhesion that distinguish between the two extreme cases of an oil drop not adhering ($\theta_A \approx \theta_R$) or adhering ($\theta_A \gg \theta_R$) to a clean mineral surface as a function of brine composition are also common [10,18–20]. Adhesion tests typically show a pH dependence — evidence of the importance of DLVO interactions between a charged solid surface and charged oil/water interface — that is best defined at ionic strengths of 1 M or less in solutions of monovalent salt species. For negatively charged silicate minerals, adhesion tends to occur at more acidic values of pH (pH 4–6) where oil drops can have a net positive charge and non-adhesion occurs at more basic conditions (pH 8–10) where both oil drop and surface are negatively charged and the intervening water film is stable [18,21,22]. Outside a pH range of 4–10, surfactant extraction and consequent low interfacial tensions complicate the wetting picture. High salinity and even low concentrations of divalent or multivalent ions can also lead to results that cannot be readily explained simply by DLVO forces. Only one report of

a direct measurement of surface forces in the presence of crude oil has ever appeared [23].

Most often these tests are conducted using 'dead' oil samples (from which the components that are gases at 1 atm have been removed) at ambient conditions of temperature and pressure.

There are many differences between reservoir and ambient conditions including pressure, temperature, composition of the oil, and state of the oil's asphaltene components. There have been a few attempts to assess crude oil wetting properties at conditions that approach reservoir conditions using variations of the captive drop arrangement [24,25], but problems of pinning and rigid film formation can occur at elevated temperatures and pressures as well and the results to date are contradictory. Hjelmeland and Larrando [24] found for one oil that conditions become more water-wet. Rao [25] suggests that, in general, calcite becomes more water-wet and quartz more oil-wet as temperature is increased, but the evidence is limited. Some intermediate conditions of temperature have also been examined [17,26–28] with contradictory results so that questions regarding the influence of pressure and especially temperature on wetting properties of crude oils must be regarded as unresolved.

Only in cases where selected crude oil components are dissolved in a solvent can adsorption isotherms be measured, since some measure of concentration in the equilibrated fluid is required and contact angles can be measured only if the surrounding fluid is transparent. Nearly all such studies have explored oil/solid interactions in the absence of water [29–31].

2.1.1.2. Crude oil-treated surfaces. Some of the problems of measurements with crude oils can be circumvented if exposure to crude oil is separated from the evaluation process. Surfaces can be exposed to brine and oil under a wide range of conditions. The resulting wetting conditions can then be stabilized for subsequent evaluation by removal of the crude oil.

To evaluate the effective wetting in an oil reservoir, it is not sufficient to observe the interactions between crude oil and rock under dry conditions. Brine is always present in oil reservoirs and the influence of brine must also be considered. Liu and Buckley [32] showed how that could be done by pre-equilibrating a surface with brine, then contacting with oil while still wet. After exposure to oil for some period of time ranging from minutes to months, the crude oil can be removed by gentle rinsing with a solvent such as toluene that does not cause destabilization of asphaltenes. Probe fluids or surface analytical techniques can then be used to explore the effect of adsorbed material. Unlike the dry surfaces treated with oil, the resulting wetting conditions produced can

vary from strongly water-wet to strongly oil-wet and almost anything in between, a surprise to many who assumed that the presence of water would always shield solid from oil. Results depend on the nature of the solid, components in the oil, and on the composition of the intervening brine [10,17,20,32,33]. Recently, this technique has been used to measure surface forces between oil-exposed and clean mica in an aqueous environment [34]. The results showed long-range, polymer-like interactions that did not affect approaching surfaces, but appeared when the surfaces were moved apart after contact.

2.1.2. Other surface techniques

A variety of other surface techniques have been tested for their ability to measure properties that relate to empirical tests of wetting in porous media. X-Ray photoelectron spectrometry (XPS) can quantify the amount of specific elements as a function of position on the surface [35−37]. Funk et al. [38] used Fourier transform infra-red (FTIR) to follow adsorption of polar functional groups on a carbonate surface. Pyrolysis techniques, adapted from source rock evaluation procedures, quantify the amount of material adsorbed, but do not necessary correlate well with wetting changes [39].

2.2. Alteration of wetting by crude oils

There are many components in any crude oil; detailed chemical evaluations tend to produce unmanageable amounts of information. Tests such as those reviewed above have helped to identify the most relevant information with respect to wetting alteration tendencies.

2.2.1. Adsorption of crude oil components

2.2.1.1. Acid / base oil chemistry. Cuiec [40] pointed out that some mineral surfaces (such as silicates) are acidic whereas others (e.g., carbonates) are basic so that different materials should be expected to adsorb from a crude oil to these different mineral types. Contact angles have been used to characterize interactions with known compounds including adsorption of organic acids on calcite [41,42] and an organic base on quartz [43].

Depending on brine composition, crude oil/water interfaces can be either negatively or positively charged, reflecting the presence of both acidic and basic ionizable functional groups [18]. The methods available for quantifying acidic and basic components in oil are not very precise, but improvements in the standard non-aqueous potentiometric titration to obtain base number [44] and recognition that acid and base numbers should be considered together have improved oil characterization. Oils with either a high

ratio of bases to acids or the converse, a high ratio of acids to bases, have recognizable tendencies to alter wetting [45].

2.2.1.2. Asphaltenes and other crude oil fractions. It is often assumed that the material that absorbs most strongly from a crude oil is that in its asphaltene fraction. The asphaltenes — any material in the oil that is not soluble in a designated alkane (usually *n*-pentane or *n*-heptane) that is soluble in toluene — include the highest molecular weight, most polar components in a crude oil. González and Moreira [30,31] compared dry surfaces exposed to solutions of asphaltenes and resins (polar species that are soluble in *n*-pentane) and found greater changes in wetting on the asphaltene-treated surfaces. However, comparisons of glass surfaces treated either with crude oils or with their asphaltenes in toluene solution, in which brine effects were considered, showed that significantly more oil-wet conditions could be produced by the whole oil than by treatment with just the asphaltene fraction [46].

Adsorption of asphaltenes is influenced by the tendency of those species to aggregate, forming larger, colloidal-sized entities in the oil. Extent of aggregation varies with solvent quality. As the asphaltenes approach phase separation, their tendency to partition to either oil/water or oil/solid interfaces can be expected to increase. Compared to treatment with an oil in which the asphaltenes are in stable dispersion, more oil-wet surfaces have been produced on mica that was exposed first to an aqueous salt solution of known pH and ionic composition, then to oil to which an amount of asphaltene precipitant slightly less than what would be required to initiate phase separation was added [47].

Precise formulae to predict the balance of different types of interactions between suites of crude oil components and solid surfaces are not yet available, but more general assessments about which oils are good or poor solvents and which have an excess of either acidic or basic species provide a framework for understanding the complex interactions by which crude oils alter the wetting of mineral surfaces.

2.2.2. Hysteresis between water-receding and water-advancing conditions

The hysteresis between initial contact of crude oil with a clean, water-wet mineral surface and subsequent re-advance of water over the oil-exposed surface can be accounted for by adsorption that occurs during the measurement. Removing the crude oil eliminates further adsorption, but hysteresis — between advancing and receding probe fluids — can be extensive and repeated through multiple displacement cycles [48].

Although the probe fluids are initially pure, either

phase may extract material from the surface. Even more likely, however, is that the hysteresis is related to the failure of the surface to fit the assumptions that it is smooth, rigid, and chemically homogeneous. Oil-treated surfaces are probably none of these.

Artificially prepared surfaces with areas of high and low contact angles, uniformly or randomly distributed, have been used to test the Cassie equation [49] that relates contact angles to the fractions of area covered by materials with different properties [50–52]. Yang et al. [10] envision such partially covered surfaces with areas to which components from the oil adsorb and other areas of exposed high-energy mineral surface. They hypothesize that, depending on the extent of coverage, bridges of oil may form between rough, oil-wet patches that make the surface appear more oil-wet to an advancing water interface than to a receding one. Average roughness of surfaces treated with two crude oils and their mixtures with *n*-heptane was estimated from atomic force microscopy (AFM) images and a positive log-arithmic correlation between roughness and advancing angle was found for one of the oils [10].

Detailed studies on self-assembled monolayers (SAMs) of hexadecanethiol and mercaptohexade-canoic acid on gold have been prepared to investigate deviations from the Cassie equation [53]. Hysteresis between advancing and receding conditions was greatest not for surfaces with alternating strips of high and low contact-angle material, but for smooth gold surfaces covered with a uniform monolayer that terminated in acid groups, perhaps due to a surface reconstruction process [54]. The extent of hysteresis on some oil-treated surfaces is higher still and may reflect a combination of chemical heterogeneity, roughness, and surface reconstruction. While hysteresis between imbibition (water saturation increasing) and drainage (water saturation decreasing) is well recognized in oil displacement, extreme differences between wetting conditions due to contact angle hysteresis are not included in any current models of recovery processes.

2.2.3. Development of mixed wetting

It is now generally agreed that Salathiel-type mixed-wetting is probably the most common reservoir condition [55]. This is a situation in which wetting is altered — by adsorption of crude oil components — on some surfaces, but the original, more water-wet condition is preserved on others. Mixed wetting might occur if wetting alteration were dictated by the geologic distribution of the rock-forming and pore-lining minerals, but Salathiel's contribution was to suggest that wetting alteration can be dictated by the areas of contact between oil and rock. Kaminsky and Radke [56] demonstrated that strongly adsorbing species

would convert all surfaces to oil-wet conditions over much less than geologic time. Since oil reservoirs do not seem to be universally oil-wet, it appears that the combination of weakly adsorbing crude oil species in contact with rock surfaces where water films are unstable and water-wet surfaces protected from contact with oil by bulk water yields the non-uniform effective wetting situation that is referred to as mixed-wet.

Models of triangular tubes [57,58], star-shaped pores [59], and networks of pores with a distribution of contact angles [60–62] are progressing toward the ability to incorporate a mechanistic understanding of wetting alteration into predictions of displacement of oil.

3. Concluding remarks

During the period covered by this review, progress has been made in understanding the interactions that can occur between crude oil components and mineral surfaces in the presence of an aqueous solution. Contact angle measurements using probe fluids can be used to assess wetting after prolonged exposure of mineral surfaces to brine and oil. More sophisticated techniques have been evaluated, but have not yet been shown to provide evidence specifically about the material that most influences effective wetting and thus displacement properties.

Translating this understanding into a knowledge base that can be used to define wetting for newly discovered reservoirs or to predict changes in wetting during production or in the course of a contamination event remains as a goal for the future. Modeling tools are being developed that can incorporate mixed wetting and a range of contact angles, but questions remain. The effect of temperature on those interactions that govern effective reservoir wettability are complex and must be better understood. Specific interactions involving multivalent ions must also be addressed. The time available for interactions to occur is very long and approach to equilibrium conditions is probably very slow. The possibility that laboratory time scales are insufficient to approach reservoir conditions must also be considered.

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