Article

Straightforward Assessment of Wettability Changes by Washburn Capillary Rise: Toward a Screening Tool for Selecting Water Compositions for Improved Oil Recovery

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ABSTRACT: Evaluating the wettability state of reservoir rocks is key for understanding and optimizing waterflooding and improved oil recovery techniques that imply the use of low-salinity water. Aside from established petrophysical techniques, such as Amott imbibition tests, we evaluated the Washburn capillary rise method as a low-cost, easy-to-implement, and rapid screening tool for probing the wettability state of rock samples. The well-known limitations of this method are discussed and circumvented. We show that measuring the capillary rise of two liquids —brine and *n*-octane—is required to assess the evolution of the wettability state of a material induced by various treatments. The wettability state is quantified by the adhesion tension of brine to the solid. The higher the adhesion tension of brine, the more water-wet the sample. An increase in oil-wetness is observed when the sample is contacted with a crude oil or its released waters; an increase in water-wetness is obtained by postcontacting the oil-wet sample with low-salinity brine or surfactant solutions. The Washburn capillary rise is revealed to be a robust method for screening wettability alteration. With a typical duration of 1−10 min, it allows reproducibility check and screening of a wide range of brine compositions in a reasonable time frame. Therefore, it is a relevant tool to identify the most favorable brine compositions to be tested afterward with more time-consuming techniques, such as Amott tests and corefloods.

Washburn Capillary Rise

Wettability assessment

Brine adhesion tension (mN/m)
$\Delta\gamma(brine) = \gamma(brine) \times cos\Theta(brine)$
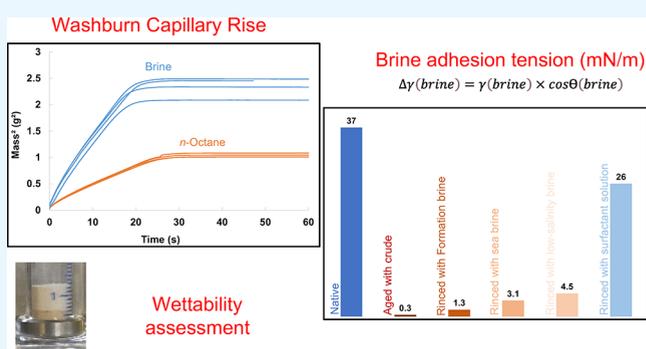
1. INTRODUCTION

After a period of production through natural or artificial rise of hydrocarbons, most fields undergo a so-called "secondary" oil recovery period during which gas or water is injected into the reservoir to displace the oil. Usually, the produced water is reinjected, which is also a way to dispose of it, but seawater may be injected instead for practical reasons, especially in offshore fields. In several cases, lab and field studies have shown that the injection of seawater resulted in an increased oil recovery compared to the reinjection of produced water. These kinds of evidence have led to investigate the impact of the injected water salinity on oil production and opened the way to a new enhanced oil recovery method known as "low-salinity waterflooding"[1] or more generally "chemically tuned waterflooding",[2,3] also known as "smart water injection methods" (SWIM).

Even if the underlying mechanisms are not fully understood yet, the increase in oil production when low-salinity water is injected is usually associated with a change of the rock wettability, from oil- or mixed-wet to a more water-wet state. The preferred rock wettability toward oil is due to the adsorption of organic compounds from the oil onto the rock surface.[4,5] The change of rock wettability toward more water-wet is likely due to the partial desorption of these compounds through low-salinity water flooding. The injection of surfactants

at low concentration can also induce a change in wettability of the rock to a more water-wet state due to the desorption of the adsorbed crude oil components by formation of ion-pairs or to the adsorption of the surfactant molecules on the rock surface.[6−8] These low-concentration surfactant injections have been successfully implemented on the field.[9] In all cases, the change in rock wettability can therefore be a marker of the efficiency of the chemically tuned injection brine to increase the oil recovery.

Petrophysicists assess the wettability of rock samples through established petrophysical techniques.[10] These are based on the measurement of the relative amounts of oil and water displaced from the sample by one or the other fluid. The volumes of fluids displaced are measured under spontaneous or forced processes (either under centrifugation or via the flow of the imbibing fluid through the rock sample). These experiments lead to the definition of the Amott−Harvey wettability index, which takes

positive values for water-wet samples, negative values for oil-wet samples, and near-zero values for neutrally wet samples. These experiments usually require long and tedious procedures and the use of large amounts of oil. In the end, the efficiency of a water composition is definitely established from the volume of oil produced during corefloods.

For physicists, the most rigorous way to quantify wettability is to measure contact angles and oil/water interfacial tensions to determine the adhesion tension.[5] However, a correct contact angle measurement requires working with perfectly plane surfaces, and usually, polished analogous surfaces are taken (polished marble to simulate a carbonate rock and glass slides or polished quartz for sandstones for example). Questions on the representativity of these model surfaces with regard to the real rock can indeed arise.

Alternatively, Washburn capillary rise[11] is a common tool to measure the wettability of packed powders.[12] Recently, it has been applied to measure the wettability of different solvents on quartz and oil sands, allowing the calculation of their surface-free energies.[13] A capillary rise experiment consists in measuring the weight of liquid spontaneously imbibing the sample with time. If the characteristics of the powder arrangement or porous media are known, then the value of the advancing contact angle of the liquid on the solid sample can be determined. Nevertheless, the knowledge of these characteristics (distribution of pore radii and tortuosity) for such morphologically poorly defined bodies is an issue to overcome. In the treatment of capillary rise data, these characteristics are embedded in a "capillary constant" c.

We propose to evaluate the Washburn capillary rise technique to quickly determine the change in wettability of crushed minerals promoted by the adsorption of organic species extracted from the crude oil and then to quantify the efficiency of brines for further wettability modification. Wettability is assessed from the adhesion tension of the fluids to the rock, which appears more relevant than the contact angle.[5] However, strictly speaking, Washburn capillary rise experiments provide results where the adhesion tension is convoluted with the capillary constant c embedding the morphological characteristics of the powder bed. One way to accede to this constant is to measure the capillary rise of a liquid probe, often n-hexane, completely wetting the mineral surface.[12] We evaluated whether the modifications of this capillary constant for a given powder could provide indirect information on the occurrence of adsorption of organic species. The extent of wettability alteration by treatment with different chemically tuned brines (different concentrations and nature of salts and introduction of low-concentration surfactants) was evaluated, and special care was taken to assess the reproducibility of these experiments.

In the first section, preliminary experiments were performed on Sikaisol sand treated with a cationic surfactant—tetradecyl trimethylammonium bromide (TTAB)—which is known to adsorb on this mineral and to change its wettability.[14] Then, the wettability of two carbonates (Tacon and Edwards White) was evaluated after aging by contact with crude oil-released waters or by direct contact with the crude oil. The oil-wet samples were then postcontacted with various brines, and the wettability was assessed again by the Washburn procedure.

2. THEORETICAL APPROACH

During Washburn capillary rise experiments, the mass m of the liquid spontaneously imbibing the solid is measured accurately as a function of time with a high precision balance. The observed capillary rise generally shows three stages: the first one is dominated by the inertial forces, and m is proportional to the time; the second one is governed by the capillarity, and m^2 is proportional to the time (so-called Washburn regime). In the last regime, gravity dominates and the mass increase with time is nearly null.[12]

The information extracted from the curves is in the Washburn regime. In that case, capillary forces are greater than gravitational forces, and the latter can be neglected. This regime was described by Washburn for a continuous and incompressible Newtonian fluid, in a stable laminar flow, without external pressure and by neglecting the gravitational forces.[11] These conditions are fulfilled for the experiments carried out in this work. In this regime, writing the flow equations leads to eq 1:

$$m^2 = \frac{c \times \rho^2 \times \gamma \times \cos\theta}{\eta} \times t \tag{1}$$

with m being the weight of liquid rising in the powder bed (kg), c the capillary constant (m^5), ρ the liquid density (kg/m^3), γ the liquid surface tension (mN/m), θ the contact angle of the liquid on the solid ($°$), η the liquid viscosity (mPa·s), and t the time (s). The product $\Delta\gamma = \gamma\cdot\cos\theta$ is the liquid adhesion tension to the solid (noted liquid adhesion tension for the sake of simplicity in the rest of the paper). At equilibrium, according to Young-Dupré (1805), $\Delta\gamma = \gamma_{SA} - \gamma_{SL}$ where γ_{SA} and γ_{SL} are the surface tension of the solid and the solid−liquid interfacial tension, respectively.[15] When the adhesion tension increases, wetting of the solid by the liquid is favored and vice versa.

The capillary constant c is a characteristic of the morphology of the porous solid or the powder bed and of its arrangement in the measuring chamber in the case of powders. For example, if the sample is considered as an assembly of parallel capillary tubes (capillary bundle model, Kozeny−Carman model), then the capillary constant c is defined as

$$c = \frac{r_{eff} \times A^2 \times \varepsilon^2}{2\tau} \tag{2}$$

with r_{eff} the equivalent radius of the capillary tubes, A the section of the measuring chamber, τ the tortuosity of the sample, and ε its porosity. Developments of eqs 1 and 2 can be found in the Supporting Information (Appendix 1). A decrease in the capillary constant can be produced by a surface modification of a given powder resulting from a more compact arrangement of the powder grains, leading to different tortuosities, lower porosities, permeabilities, and/or pore throats.

The capillary constant c can be determined experimentally by measuring the capillary rise of a liquid considered as completely wetting, i.e., for which the contact angle is assumed to be 0. Usually, a low surface tension liquid, such as n-hexane, is used.[12] The capillary constant c is calculated by extracting the slope of the straight part of the $m^2 = f(t)$ capillary rise curves (eq 3):

$$c = [\text{slope(completely wetting probe liquid)}$$
$$\times\ \eta(\text{completely wetting probe liquid})]$$
$$/[\rho^2(\text{completely wetting probe liquid})$$
$$\times\ \gamma(\text{completely wetting probe liquid})] \tag{3}$$

As c characterizes the morphology of the porous media, it is very important to keep the powder arrangement from one experiment to the other as identical as possible so that the different liquids can be compared. In all experiments, the same

amount of powder was used and its packing in the measuring chamber was reproduced as identical as possible.

In the present work, capillary rise experiments were performed to assess the change in relative wettability toward water and oil for rock samples subjected to various treatments. n-Octane (surface tension = 21.8 mN/m), less volatile than n-hexane, has been used to determine the c constant for all samples. For two native powders, both n-hexane and n-octane were used as probes to evaluate the impact of the nature of the completely wetting reference liquid. It is recognized that different values of c can be obtained with different probes that all completely wet the solid as it will be seen later, thus showing the limitation of this approach.[12] However, it can be considered valid for comparative purposes, which is the goal of this work.

The slope of the straight part of the $m^2 = f(t)$ capillary curve gives access to the product $c \cdot \Delta\gamma$; therefore, knowing c, the variations of the adhesion of water to the solid after various treatments of the sample can be determined. Using n-octane as the completely wetting probe, the adhesion tension of water is determined with eq 4:

$$\Delta\gamma(\text{brine}) = \gamma(\text{brine}) \times \cos\theta(\text{brine}) = \frac{\eta(\text{brine}) \times \text{slope}(\text{brine})}{c \times \rho^2(\text{brine})}$$

$$= \frac{\eta(\text{brine}) \times \text{slope}(\text{brine}) \times \rho^2(\text{octane}) \times \gamma(\text{octane})}{\rho^2(\text{brine}) \times \text{slope}(\text{octane}) \times \eta(\text{octane})} \quad (4)$$

Using eq 4 implies implicitly that the capillary constant c of the powder bed is the same for the capillary rise of the completely wetting probe (n-octane) and brine. The situations where this assumption is reasonable will be discussed later on.

As stated above, the evolution of the adhesion tension of brine for a sample subjected to various treatments indicates how its wettability toward water has been changed: if the adhesion tension of brine decreases, then the treatment has made the sample more oil-wet; on the contrary, if it increases, then the treatment has increased the wettability of the sample toward water.

In the proposed methodology, the adhesion tensions of the probe liquids are defined relative to air, and one may question the pertinence of these values to predict the powder wettability change in an oil—water system. In an oil—water system, the adhesion tension of oil to the rock is defined as $\gamma_{SO} - \gamma_{SW} = \gamma_{OW} \cdot \cos\theta$, with θ being the contact angle taken in the denser phase,
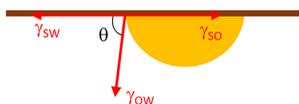
Figure 1. Definition of the contact angle in a water—oil—solid system. γ_{SW} is the solid/water interfacial tension, γ_{SO} is the solid/oil interfacial tension, and γ_{OW} is the oil/water interfacial tension.

i.e., water (Figure 1). The surface state, i.e., the solid wettability, impacts γ_{SO} and γ_{SW}, which results in two possible situations:

If $\gamma_{SO} > \gamma_{SW}$, then $\gamma_{SO} - \gamma_{SW} > 0$ and $\theta < 90°$, which corresponds to a water-wet case.
If $\gamma_{SO} < \gamma_{SW}$, then $\gamma_{SW} - \gamma_{SO} > 0$ and $\theta > 90°$, which corresponds to an oil-wet case.

The Washburn approach gives access to $\gamma_{SA} - \gamma_{SL}$, with L being water or oil. If the treatment applied to the sample increases its wettability toward water, then the adhesion tension of water $\Delta\gamma(\text{brine})$ increases; therefore, $\gamma_{SA} - \gamma_{SW}$ increases. In the methodology applied in this work, the adhesion tension of oil (n-octane) is supposed to be constant (n-octane used as the probe for completely wetting liquid); therefore, $\gamma_{SA} - \gamma_{SO}$ is a constant equaling $\gamma(\text{octane})$. In the water—oil—rock system, the adhesion tension of oil to the rock can be written as in eq 5:

$$\gamma_{SO} - \gamma_{SW} = (\gamma_{SA} - \gamma_{SW}) - (\gamma_{SA} - \gamma_{SO}) \quad (5)$$

A sample treatment that increases $\gamma_{SA} - \gamma_{SW}$ also increases $\gamma_{SO} - \gamma_{SW}$, which therefore evidences an increased wettability toward water in the water—oil—rock system.

Therefore, both approaches (surface vs one fluid and air or surface vs both fluids) provide similar conclusions about the surface wettability modification induced by a specific treatment.

An important point to stress is that the Washburn capillary rise approach implies that the sample can be wet, even slightly, by water. It cannot be applied to completely hydrophobized samples.

3. EXPERIMENTAL SECTION

3.1. Materials. *3.1.1. Rock Samples.* Two crushed carbonate outcrops were investigated: Tacon limestone (Alpes, France) and Edwards White carbonate (Texas, USA). Tacon limestone was obtained from Samin and was used as received. The supplier indicates a mean particle size of 250 μm; however, laser granulometry (Mastersizer 2000, Malvern) shows that the sample is highly polydisperse (see the Supporting Information, Appendix 2). The specific area was measured by the Brunauer—Emmett—Teller (BET) method using N_2 adsorption. It was found at (0.74 ± 0.01) m²/g.

Cores of Edwards White carbonate were obtained from Kocurek Industries. The supplier indicates a porosity of 16—19% and a permeability of 1.5—3 mD. The cores were crushed using a BB50 crusher from Retsch and further ground with a vibrating ball mill (CryoMill Retsch). Finally, the powder obtained was sieved, and the 40—100 μm size range was kept for the experiments. The grain size distribution is shown in the Supporting Information. The specific area of this sample was measured as (0.49 ± 0.03) m²/g by the BET method using N_2 adsorption. It was found that better reproducibility was obtained during the Washburn capillary rise experiments when sieved samples were used.

As preliminary experiments, the reproducibility of the Washburn capillary rises was assessed on Sikaisol silica sand, supplied by Sifraco S.A.S. It was first contacted with sulfuric acid 17 vol % for 24 h at room temperature to remove any metallic contaminant, then rinsed several times with distilled water until reaching pH 6—7, then dried in an oven at 50 °C for 2 days, and

Table 1. Characteristics of Crude Oil A Used in This Work[a]

API	viscosity (mPa·s)/25 °C	density/25 °C	TAN (mg KOH/g)	TBN (mg eq KOH/g)	ASCI index	saturates (wt %)	aromatics (wt %)	resins (wt %)	asphaltenes (wt %)
31	15.31	0.8645	0.54	1.73	17	59.7	28.5	9.1	2.7

[a]ρ = 0.847 g/cm³ at 50 °C, η = 6.3 mPa·s at 50 °C.

then sieved. The 32−50 μm fraction was used for the experiments (see granulometric distribution in the Supporting Information). The specific area of this sample was measured by the BET method using Krypton adsorption at 77 K. It was found at (0.40 ± 0.01) m^2/g.

3.1.2. Crude Oil. Crude oil A from West Africa was used to prepare oil-wet carbonate powder samples. Its physical chemical characteristics are given in Table 1. TAN (total acid number) and TBN (total base number) were measured using, respectively, the standard method ASTM D664[16] and ASTM D2896,[17] and ASCI index was determined according to a specific method developed internally.[18] API degree was calculated from density extrapolated at 15 °C, and the SARA fraction was determined by TLC-FID.

3.1.3. Chemicals. NaCl (Sigma-Aldrich, 99.5%), KCl (Merck, 99.5%), CaCl$_2$·2H$_2$O (Merck, 99%), MgCl$_2$·6H$_2$O (Acros Organics, 99%), Na$_2$SO$_4$ (VWR, 99.8%), NaHCO$_3$ (VWR, 100.0%), and deionized water were used to prepare the brines. NaOH (1 M) solutions prepared from NaOH (>98%, Fisher) were used to adjust the pH when stated.

Several brines were used to extract the crude oil surface-active species to the water phase, to contact the powder samples, and to perform the Washburn capillary rise experiments. Their compositions are detailed in Table 2. The surface tensions were measured at room temperature $(22 \pm 1$ °C) with a platinum Wilhelmy plate using a Kruss K100 tensiometer.

Table 2. Composition of the Brines Used (g/L)

salt	brine			
	LS	HS	SB	FB
NaCl	2.0	71.1	32.3	60.3
KCl	-	0.71	-	-
CaCl$_2$·2H$_2$O	-	23.8	1.70	16.8
MgCl$_2$·6H$_2$O	-	14.4	12.6	13.6
NaHCO$_3$	-	0	-	-
Na$_2$SO$_4$	-	0.067	-	-
TDS	2.0	110.1	46.6	90.7
salinity	2.0	96.6	39.5	79.4
surface tension (mN/m)	71.6	72.5	73.0	74.0

Toluene (>99%) and *n*-heptane (99%) used to rinse the powder samples aged in crude oil were obtained from Sigma-Aldrich.

In the preliminary experiments, to check the impact of adsorbed species on the wettability of Sikaisol sand, a cationic surfactant, tetradecyl trimethylammonium bromide (TTAB), was used. It was obtained from Fisher (>95%). The surfactant solutions at various concentrations were prepared in deionized water.

An alkylpolyglucoside surfactant (APG) developed and provided by BASF was used in the last section to increase the water-wetness. Its hydrophobic chain is a linear alkyl chain containing 8−16 carbons, and the polymerization degree of the polar head is 1.4−1.5. It was prepared at a concentration of 2000 ppm in SB.

3.2. Methods. *3.2.1. Preparation of Aged Powder Samples. 3.2.1.1. Protocol C1: Contact with Crude Oil-Resolved Waters.* LS (2 g/L NaCl) was first put in contact with crude oil A to extract water-soluble organic species that are suspected to change the rock wettability. Some extractions were performed at a water-to-oil ratio (WOR) of 3:1 in 50 mL flasks, 30 mL of 2 g/L NaCl water was introduced, and 10 mL of crude

oil was added. The flasks were gently agitated by using a carousel rotary mixer (9 rpm) at room temperature for 48 h. After this period of time, the samples were centrifuged (4000 rpm) at 40 °C for 1 h to break the residual emulsions and remove the resolved water phase. In some experiments, the extraction was performed at WOR 1 (20 mL of 2 g/L NaCl was mixed with 20 mL of crude oil). In some experiments, the pH of LS was increased to 10 by the addition of 1 M NaOH before contacting crude A to promote the partitioning of crude oil acid species to the water phase.

In this first protocol, aging of the Tacon carbonate sample was performed by contacting with crude oil-resolved waters (Figure 2). In 50 mL flasks, 3 g of powder was weighed, and 30 mL of the resolved water phase was added. The flasks were agitated using a carousel rotary mixer (9 rpm) at room temperature for 24 h. Then, the powders were recovered by filtration using a Büchner funnel equipped with a Millipore hydrophilic filter (0.45 μm). In some cases, the first filtrated water was recovered to measure its total organic content (TOC). The powder was then slightly rinsed with deionized water to remove interstitial water containing nonadsorbed organic species. The powder samples were then dried in the oven at 50 °C for 48 h. The capillary constant *c* of these treated materials was then determined by the *n*-hexane or *n*-octane capillary rise. The same protocol was used for the preparation of Sikaisol sand treated with TTAB solutions in the preliminary experiments.

The total organic contents (TOCs) of the crude oil-resolved waters before and after contact with the powder were measured with a Shimadzu TOC meter (combustion oven at 720 °C).

3.2.1.2. Protocol C2: Direct Contact with Crude Oil. In another protocol, the rock powder was contacted directly to the crude oil (Figure 3). To reproduce the aging of reservoir rocks, the powder sample was first macerated in formation brine (FB, see Table 2) at 83 °C for 24 h. The powder was then recovered by filtration over a Büchner funnel equipped with a Millipore hydrophilic filter (0.45 μm). It was then macerated in the crude oil at 83 °C for 10 days. After this period of time, the powder was recovered by filtration over a Büchner funnel equipped with a Millipore hydrophobic PTFE filter (0.2 μm). To remove the excess crude oil, the powder was rinsed with toluene/*n*-heptane 50/50 (v/v) over the Büchner funnel. Then, the powder was dried for 24 h at 50 °C in an oven.

3.2.2. Wettability Restoration of Aged Powder Samples. 3.2.2.1. Protocol W1: Contact with Brines. The aged powder was contacted with brines of various compositions (see Table 2) at 50 °C for 24 h using a carousel rotary mixer. The ratio of 10 g of powder for 100 mL of brine was used. The powder was recovered by filtration over a Büchner funnel equipped with a Millipore hydrophilic filter (0.45 μm). It was slightly rinsed with clean brine and then dried for one night at 50 °C in an oven.

3.2.2.2. Protocol W2: Contact with Surfactant Solutions. To evaluate the efficiency of a surfactant compared to brines, the aged powder was contacted with 2000 ppm of surfactant solution (APG) prepared in SB at 50 °C over 24 h using a carousel rotary mixer. The ratio of 10 g of powder for 100 mL of surfactant solution was used. The powder was recovered by filtration over a Büchner funnel equipped with a Millipore hydrophilic filter (0.45 μm). It was slightly rinsed with sea brine SB to remove excess surfactant solution. It was then dried for one night at 50 °C in an oven.

3.2.3. Assessment of Wettability Changes. To assess wettability alterations, capillary rise experiments were performed using a Kruss K100 force tensiometer (Figure 4). In

1) Contact crude oil / LS, room temperature, 48 h

2) Separation of oil and water before (left) and after (right) centrifugation

3) Contact resolved water / powder, room temperature, 24 h

4) Büchner filtration, slight rinsing with deionized water, drying 50°C, 48 h
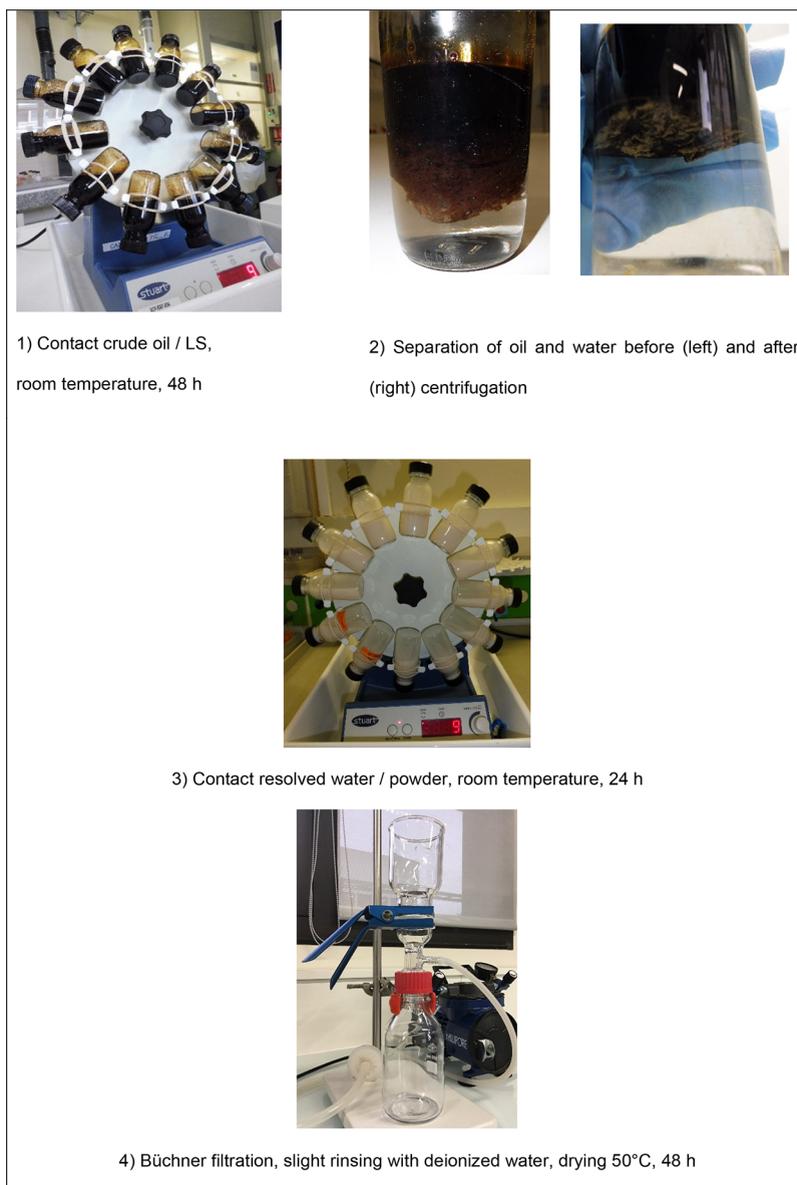
Figure 2. Protocol C1 for the preparation of the Tacon carbonate powder sample aged in crude oil A-resolved waters

these experiments, the powder sample was placed in a 12 mm diameter glass tube equipped with a hydrophilic filter at the bottom. This tube was suspended to the high precision balance, and the test liquid was slowly moved upward until it reached the sample. The increase in weight due to the capillary rise of the liquid was then measured over time with a precision of 10 μg.

In a series of measurements, the powder arrangement in the tube was kept as identical as possible. For Tacon and Edwards White samples, 1 g of powder was placed in the glass tube and packed consistently by gently tapping the tube on the table 20 times, resulting in powder beds close to 1 cm height. For the Sikaisol samples, 2 g of powder was placed in the glass tube and only five tappings were performed, resulting in powder beds close to 2 cm height. The porosities of the three powders could be calculated from the volume of dry powder, assuming a value of density (Supporting Information, Appendix 3). The porosities of the three materials were close (66, 72, and 67% for Sikaisol, Tacon, and Edwards White, respectively). For one powder sample and one test liquid, four measurements were

generally performed on different packed powder beds to assess the reproducibility.

Figures 5−7 show the capillary rises of *n*-hexane and/or *n*-octane, deionized water, and/or sea brine (SB) on the native samples.

The slopes are taken in the linear parts of the curves and are given in Table 3. The deviations between the slopes determined on the four experiments performed for each liquid are below 10% for Sikaisol and Tacon and below 15% for native Edwards White.

From the slopes obtained with *n*-hexane or *n*-octane and assuming that this liquid is completely wetting ($\cos \theta = 1$), the capillary constant *c* can be calculated for each powder. For Sikaisol and Tacon, both *n*-hexane and *n*-octane can be used to determine *c*. The values are given in Table 4.

It is well known that the nature of the liquid used as reference for the completely wetting condition impacts the value of *c*.[12] Here, *n*-hexane and *n*-octane, even belonging to the same chemical family, have slightly different physical properties,

1) Maceration in formation brine, 83°C, 24 h

2) Recovery of wet powder

3) Maceration in crude oil, 83°C, 10 days

4) Recovery of aged powder

5) Rinsing *n*-heptane/toluene 50/50, drying
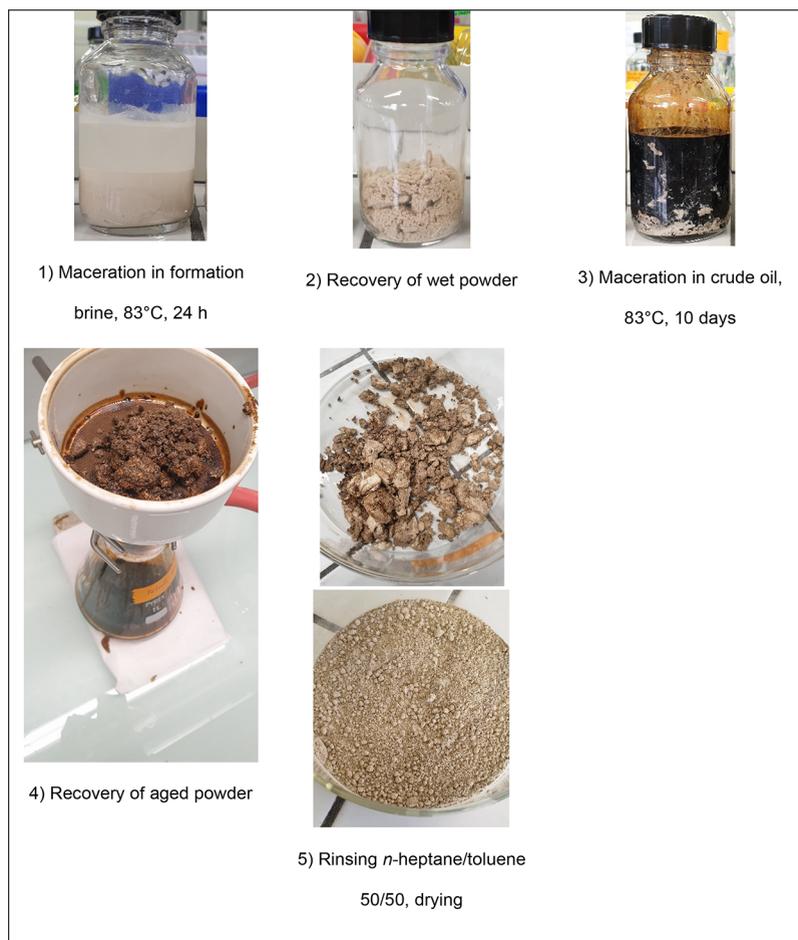
Figure 3. Protocol C2 for the preparation of the Edwards White carbonate powder sample aged by direct contact with crude oil A.

especially surface tensions. Therefore, it is important to always use the same reference liquid when comparing samples.

If we compare the values of capillary constants c obtained with *n*-octane for the three samples, then the two carbonate samples (Tacon and Edwards White) have close c values, which reflects close characteristics in terms of arrangement of the grains, porosity, permeability, and pore sizes. The capillary constant for Sikaisol sand is 1 order of magnitude higher. Since the porosities of the three materials are close (see Appendix 3 in the Supporting Information), this higher c value of Sikaisol reflects probably a higher permeability of the powder.

The amount of liquid imbibed in the sample can also give information about the pore volume. In all experiments, the imbibition of the powders was complete. Table 5 gives the values of the volumes of liquids imbibed in the native powders. They were calculated from the mass at the plateau (Figures 5–7) and the density of the fluid.

For each powder, the volumes are close for all liquids and can give an estimation of the pore volume of the sample. They are close to 0.75 mL/g for Sikaisol and close to 0.3 mL/g for Tacon and Edwards White with the packing protocol used. These pore volumes are lower than that calculated on dry powder (Appendix 3, Supporting Information), which can be due to the additional compaction of the powders during imbibition.

4. RESULTS AND DISCUSSION

4.1. Model System: Sikaisol Sand and Synthetic Cationic Surfactant.
4.1.1. Native Sikaisol. From the capillary rises shown in 3, the contact angles and adhesion tensions of *n*-octane and deionized water have been calculated by using the capillary constant c determined from the ascension of *n*-hexane $[(2.14 \pm 0.15) \times 10^{-15} \text{ m}^5)]$. The values are given in Table 6.

These results show that the surface of native Sikaisol is hydrophilic since the adhesion tension of water is more than twice the value determined for *n*-octane. Considering only the values of contact angles would lead to an erroneous opposite conclusion because the contact angle is the result of three forces, the solid surface tension, the liquid surface tension, and the solid/liquid interfacial tension. The surface tensions of the two probe liquids, DI water and *n*-octane, are very different in this case (72.8 mN/m vs 21.8 mN/m).

If *n*-octane is used to determine the capillary constant c of the native Sikaisol $[(1.97 \pm 0.03).10^{-15} \text{ m}^5)]$, then a mean contact angle of deionized water of $(36 \pm 4°)$ is obtained, which gives an adhesion tension of (59 ± 3) mN/m.

This value will be taken as a reference in the next paragraph to investigate the impact of adsorption of the cationic surfactant on the wettability of the Sikaisol sample.

4.1.2. Sikaisol Contacted with Cationic Surfactant TTAB. The Sikaisol powder was contacted with a cationic surfactant, tetradecyl trimethylammonium bromide (TTAB). Cationic surfactants are known to adsorb on negatively charged surfaces, such as Sikaisol. Also, it has been shown already that these surfactants are prone to form hemimicelles or bilayers at the solid surface at concentrations close to the critical micellar concentration (cmc).[19] These events taking place at the solid
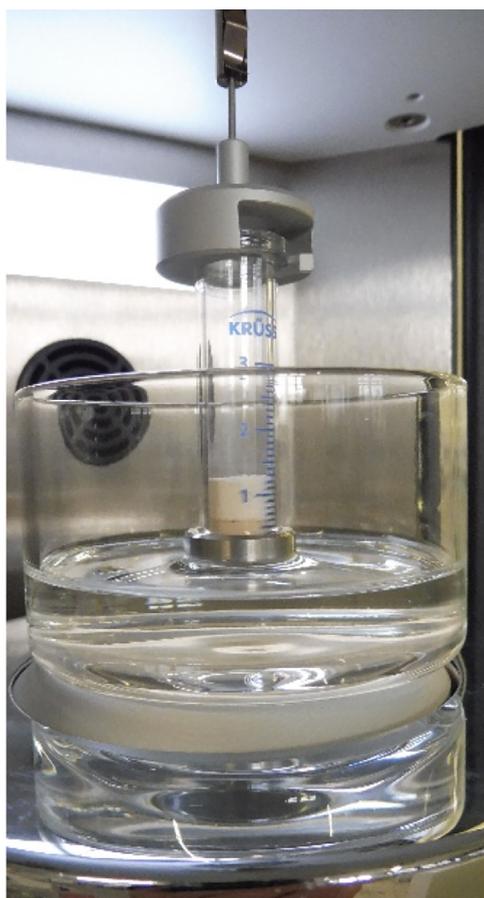
Figure 4. Capillary rise experiments.
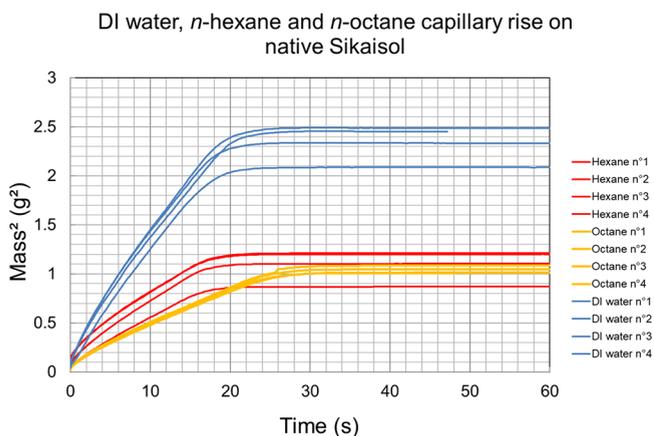
Figure 5. Washburn capillary rise of deionized water, *n*-hexane, and *n*-octane on native Sikaisol. Four rises are performed for each liquid.

surface are known to strongly impact its wettability, which is expected to be detectable by Washburn experiments.

We performed capillary rises of DI water and *n*-octane on Sikaisol powders contacted with TTAB solutions ranging from $7.5.10^{-4}$ to 7.5 g/L (see 3 for details on the powder treatment and recovery). In this series of experiments, only one capillary rise was performed for each liquid. A capillary constant was calculated by using *n*-octane as the completely wetting liquid.

Figure 8 shows the evolution of the adhesion tension of deionized water and the *c* values for Sikaisol powder in contact
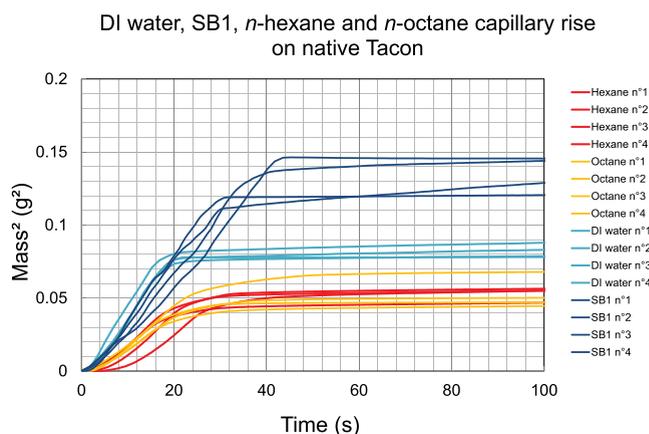
Figure 6. Washburn capillary rise of deionized (DI) water, seawater (SB), *n*-hexane, and *n*-octane on native Tacon powder. Four rises are performed for each liquid.
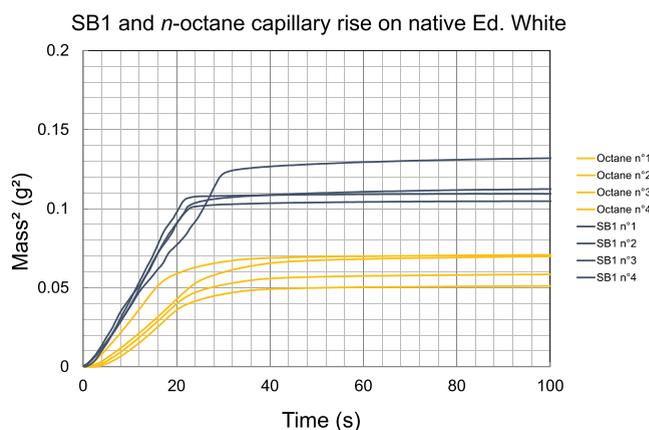
Figure 7. Washburn capillary rise of seawater (SB) and oil *n*-octane on native Edwards White powder. Four rises are performed for each liquid.

with TTAB solutions of increasing concentrations. The cmc of TTAB in deionized water is 1.5 g/L.

The adhesion tension of deionized water decreases steeply for the powders in contact with increasing concentrations of TTAB, which indicates that the hydrophobicity of these samples is increasing. It corresponds to a progressive coverage of the grain surface by a monolayer of individual TTAB molecules. For TTAB concentrations higher than 0.23 g/L (0.15 cmc), the DI adhesion tension starts increasing again, which could be linked to the formation of hemimicelles or bilayers of adsorbed TTAB. The values then stabilize for the highest TTAB concentrations. These results agree with flotation tests and measurements of adsorbed TTAB performed on the same samples (data given in the Supporting Information, Appendix 4), in line with what was already described in the literature.[14]

The evolution of the capillary constant *c* does not show a clear trend, although a tendency to some decrease is observed when the surfactant concentration increases, but the variations are quite low. A mean value of $1.52.10^{-15}$ m[5] is obtained, slightly lower than the value obtained for the native Sikaisol sample with *n*-octane as the reference, which could be an indicator of the adsorption of the surfactant on the grains. The volumes of imbibed liquids are close for all samples, with mean values of 1.2 mL for DI water and 1.3 mL for *n*-octane. They are slightly lower than the values measured on the native sample (Table 5), which

Table 3. Slope (kg^2/s) of the Straight Parts of the Washburn Capillary Rises on the Native Powders[a]

	n-hexane	n-octane	DI water	SB
native Sikaisol	5.54×10^{-8}	3.99×10^{-8}	1.203×10^{-7}	nd
	5.52×10^{-8}	3.96×10^{-8}	1.079×10^{-7}	nd
	5.54×10^{-8}	3.88×10^{-8}	1.203×10^{-7}	nd
	4.54×10^{-8}	3.80×10^{-8}	1.116×10^{-7}	nd
mean slope(kg^2/s)	5.29×10^{-8}	3.91×10^{-8}	1.150×10^{-7}	nd
mean deviation (kg^2/s)	3.73×10^{-9}	6.75×10^{-10}	5.275×10^{-9}	nd
mean deviation (%)	7	2	5	
native Tacon	2.89×10^{-9}	2.71×10^{-9}	5.22×10^{-9}	3.84×10^{-9}
	2.55×10^{-9}	2.33×10^{-9}	4.90×10^{-9}	4.53×10^{-9}
	2.61×10^{-9}	2.30×10^{-9}	5.08×10^{-9}	4.50×10^{-9}
	2.94×10^{-9}	2.67×10^{-9}	4.92×10^{-9}	4.01×10^{-9}
mean slope(kg^2/s)	2.75×10^{-9}	2.50×10^{-9}	5.03×10^{-9}	4.22×10^{-9}
mean deviation(kg^2/s)	1.68×10^{-10}	1.88×10^{-10}	1.20×10^{-10}	2.95×10^{-10}
mean deviation (%)	6	8	2	7
native Edwards White	nd	2.49×10^{-9}	nd	5.73×10^{-9}
	nd	2.46×10^{-9}	nd	4.79×10^{-9}
	nd	2.34×10^{-9}	nd	4.12×10^{-9}
	nd	3.44×10^{-9}	nd	5.17×10^{-9}
mean slope(kg^2/s)	nd	2.68×10^{-9}	nd	4.95×10^{-9}
mean deviation (kg^2/s)	nd	3.79×10^{-10}	nd	4.98×10^{-10}
mean deviation (%)	nd	14	nd	10

[a]nd: not determined.

Table 4. Capillary Constants (m^5) Determined for the Native Powders[a]

	from n-hexane	from n-octane
native Sikaisol	2.25×10^{-15}	2.01×10^{-15}
	2.24×10^{-15}	1.99×10^{-15}
	2.25×10^{-15}	1.95×10^{-15}
	1.84×10^{-15}	1.91×10^{-15}
mean c (m^5)	2.14×10^{-15}	1.97×10^{-15}
deviation (m^5)	1.51×10^{-16}	3.40×10^{-17}
deviation (%)	7	2
native Tacon	1.17×10^{-16}	1.36×10^{-16}
	1.03×10^{-16}	1.17×10^{-16}
	1.06×10^{-16}	1.16×10^{-16}
	1.19×10^{-16}	1.34×10^{-16}
mean c (m^5)	1.11×10^{-16}	1.26×10^{-16}
deviation (m^5)	6.79×10^{-18}	9.43×10^{-18}
deviation (%)	6	7
native Edwards White	nd	1.25×10^{-16}
	nd	1.24×10^{-16}
	nd	1.18×10^{-16}
	nd	1.73×10^{-16}
mean c (m^5)	nd	1.35×10^{-16}
deviation (m^5)	nd	1.91×10^{-17}
deviation (%)	nd	14

[a]nd: not determined.

Table 5. Volume of Liquid Imbibed (mL) at the Plateau for the Native Powders[a]

	n-hexane	n-octane	DI water	SB
native Sikaisol	1.67	1.43	1.53	nd
	1.59	1.43	1.57	nd
	1.66	1.46	1.58	nd
	1.41	1.48	1.45	nd
mean volume (mL)	1.58	1.45	1.53	nd
mean deviation (mL)	0.08	0.02	0.04	nd
mean deviation (%)	5	1	3	
native Tacon	0.34	0.30	0.28	0.37
	0.32	0.31	0.29	0.34
	0.33	0.29	0.28	0.34
	0.35	0.35	0.30	0.37
mean volume (mL)	0.33	0.31	0.29	0.36
mean deviation (mL)	0.01	0.02	0.01	0.02
mean deviation (%)	4	6	3	5
native Edwards White	nd	0.38	nd	0.32
	nd	0.35	nd	0.32
	nd	0.33	nd	0.36
	nd	0.38	nd	0.33
mean volume (mL)	nd	0.36	nd	0.33
mean deviation (mL)	nd	0.02	nd	0.01
mean deviation (%)	nd	6	nd	4

[a]nd: not determined.

Table 6. Adhesion Tension (mN/m) and Contact Angle (°) of n-Octane and Deionized Water (DI) on Native Sikaisol[a]

	n-octane	DI water
adhesion tension (mN/m)	20 ± 1	54 ± 2
contact angle (°)	23 ± 2	42 ± 3

[a]c = (2.14 ± 0.15) × 10^{-15} m^5 determined using n-hexane as completely wetting liquid.

may indicate a slight impact of the adsorbed TTAB molecules on the packing, in agreement with the slight decrease in the c value.

These results on a model system show that the proposed methodology is able to evidence changes in the wettability state resulting from the adsorption of organic species on the mineral surface. In the next sections, it is applied to two carbonate samples to study the wettability changes induced by contact with crude oils.

4.2. Tacon Carbonate and Crude Oil-Released Waters.
In this first section, the Washburn technique has been used to

Figure 8. Adhesion tension of deionized water (DI) and capillary constant c for Sikaisol powders in contact with TTAB solutions of increasing concentrations. The dotted line is a guide for the eyes.

track the changes in wettability of Tacon carbonate when it is contacted with water phases that were precontacted with a crude oil. The impact of postwashing the carbonate powder with low-salinity water is then evaluated.

4.2.1. Native Tacon. The contact angles and adhesion tensions of *n*-octane and deionized water on native Tacon are given in Table 7. The capillary constant c was determined from the ascension of *n*-hexane $[(1.11 \pm 0.07) \times 10^{-16} \text{ m}^5]$. The corresponding capillary rises are shown in 3 (Figure 6).

Table 7. Adhesion Tension (mN/m) and Contact Angle (°) of *n*-Octane and Deionized Water (DI) on Native Tacon[a]

	n-octane	DI water
adhesion tension (mN/m)	20 ± 1	37 ± 1
contact angle (°)	22 ± 11	60 ± 1

[a] $c = (1.11 \pm 0.07) \times 10^{-16} \text{ m}^5$ determined using *n*-hexane as completely wetting liquid.

Just as the native Sikaisol, native Tacon has a preferential wettability toward water, as indicated by the difference in the adhesion tensions of DI water and *n*-octane.

If *n*-octane is used to determine the capillary constant c of the native Tacon $[(1.26 \pm 0.09) \times 10^{-16} \text{ m}^5]$, then an adhesion tension of (40 ± 1) mN/m is obtained, which gives a mean contact angle of deionized water of $(57 \pm 1)°$. *n*-Octane has been used as the reference to compare the wettability if different water phases are used as the probe liquid instead of DI water (Table 8).

The adhesion tensions for the various water phases have been calculated from the measured surface tensions given in Table 2 in 3. The adhesion tensions indicate that Tacon's wettability is slightly lower with brines of higher salinity (SB, FB, and HS); however, all values are on the same order of magnitude and

Table 8. Adhesion Tension (mN/m) and Contact Angle (°) of Water Phases of Different Compositions on Native Tacon Using *n*-Octane as Completely Wetting Liquid[a]

	DI water	LS	SB	FB	HS
adhesion tension (mN/m)	40 ± 1	44 ± 5	34 ± 2	32 ± 1	34 ± 5
contact angle (°)	57 ± 1	52 ± 6	63 ± 2	64 ± 1	62 ± 5

[a] $c = (1.26 \pm 0.09) \times 10^{-16} \text{ m}^5$.

indicate that the surface of native Tacon is hydrophilic. The volumes of imbibed liquid are close to 0.3 mL for all experiments as when DI water, *n*-hexane, or *n*-octane is used. Still, if one wants to compare the wettability state of a powder subjected to various treatments, then it is important to always use the same brine as a probe to avoid any discrepancies.

4.2.2. Tacon Contacted with Crude Oil A Released Waters (Protocol C1). To increase its oil-wetness, Tacon was contacted to various water phases precontacted with crude oil A. This procedure has already proved its efficiency to turn carbonate and silica surfaces oil-wet.[5]

Crude oil A was contacted to brine LS with the protocol detailed in 3. Two water-to-oil ratios were used: 1 and 3. In the first set of experiments, the initial pH was not modified, and the resolved waters were separated to treat three batches of Tacon powder. In the second set of experiments, the pH of brine LS was increased to $\text{pH}_i = 10$ with sodium hydroxide before contact with crude A. The resolved water had a final $\text{pH}_f = 6.7$. In this case, only one batch of the powder was prepared. The total organic content (TOC) of the water phases before and after contact with Tacon was measured (values reported in the Supporting Information, Appendix 5). After contact with the resolved waters, the wettability states of the powders were evaluated by performing Washburn capillary rises of *n*-octane and brine HS. Brine HS was used in this set of experiments to limit the potential desorption of organic species during the measurement. Three rises were performed for each liquid. The powder capillary constant c was determined from the capillary rise of *n*-octane, and then, water adhesion tension and contact angle were calculated using eq 4. The results are listed in Table 9.

Within each batch, the reproducibility of the Washburn experiments is slightly poorer than what was obtained on the native sample (previous paragraph). In this series of experiments, only three experiments were performed, and the capillary rise curves, particularly those of brine HS, were more uneven, maybe due to some agglomerates formed during the treatment of the powders. It may also explain the discrepancies in the volume of brine imbibed at the plateau for the last two samples. Nevertheless, within the three batches prepared with the same water phase, the results are consistent and make possible the distinction of different wettability states.

The capillary constants c of the hydrophobized powders are slightly lower than those of the native Tacon $[1.26 \pm 0.09 \times$

Table 9. Exploitation of the Washburn Capillary Rises of *n*-Octane and Brine HS on Tacon Treated with the Resolved Waters Contacted with Crude A[a]

sample	resolved water	Washburn				
		V*n*-octane imbibed (mL)	capillary constant c ($\times 10^{16}$m^5)	V HS imbibed (mL)	adhesion tension brine HS (mN/m)	contact angle brine HS (°)
T aged-Crude A$_{W-3pH7}$	WOR 3/batch 1	0.39 ± 0.01	1.00 ± 0.08	0.34 ± 0.03	18 ± 4	76 ± 3
	WOR 3/batch 2	0.32 ± 0.03	0.93 ± 0.06	0.38 ± 0.02	22 ± 2	72 ± 2
	WOR 3/batch 3	0.37 ± 0.01	1.06 ± 0.03	0.37 ± 0.03	28 ± 5	67 ± 4
T aged-Crude A$_{W-1pH7}$	WOR 1/batch 1	0.33 ± 0.04	1.03 ± 0.23	0.18 ± 0.01	7 ± 3	85 ± 2
	WOR 1/batch 2	0.35 ± 0.02	1.07 ± 0.14	0.33 ± 0.05	10 ± 2	82 ± 2
	WOR 1/batch 3	0.35 ± 0.01	1.04 ± 0.05	0.19 ± 0.01	7 ± 2	85 ± 2
T aged-Crude A$_{W-1pH10}$	WOR 1 - pH$_i$ 10/batch 1	0.36 ± 0.01	1.07 ± 0.09	0.21 ± 0.01	3 ± 1	88 ± 0

[a]Mean values and deviations calculated on three measurements with each liquid. The capillary constants *c* are determined for each sample from the capillary rise of *n*-octane.

Table 10. Exploitation of the Washburn Capillary Rises of *n*-Octane and Brine HS on Tacon Treated with the Resolved Waters Contacted with Crude A and Post-Washed with Low-Salinity Brine[a]

sample	Washburn				
	V*n*-octane imbibed (mL)	capillary constant c ($\times 10^{16}$m^5)	V HS imbibed (mL)	adhesion tension Brine HS (mN/m)	contact angle brine HS (°)
T aged-Crude A$_{W-1pH7}$-rinsed with LS	0.37 ± 0.03	1.15 ± 0.11	0.34 ± 0.03	9 ± 3	83 ± 3
T aged-Crude A$_{W-1pH10}$-rinsed with LS	0.33 ± 0.03	1.13 ± 0.13	0.31 ± 0.02	8 ± 1	84 ± 0

[a]Mean values and deviations calculated from three measurements with each liquid.

10^{-16} m^5], which may indicate that the adsorbed species have an impact on the powder arrangement in the packed powder bed.

The brine adhesion tensions indicate that the Tacon hydrophobation is more pronounced after contact with crude A at pH 10 (last sample). Increasing the pH$_i$ of the contact water to 10 induces the transfer of species, most probably of the naphthenic acid type,[20] that have a buffering effect (pH$_f$ after contact = 6.7) and that increase significantly the hydrophobation of Tacon powder. The contact water obtained at pH 7 at WOR 1 (second samples) is more efficient in hydrophobizing the Tacon powder than the one obtained at pH 7 at WOR 3 (first samples). This could be related to the amount and/or nature of the water-soluble organic compounds transferred in water at WOR 1 compared to those at WOR 3 (see TOC values in Appendix 5, Supporting Information).

The variations of TOC before and after contact with the Tacon powder are not significant and cannot be used to evaluate the level of adsorption of the crude oil surface-active molecules on the Tacon powder (Appendix 5, Supporting Information). The specific area of the Tacon powder is 0.74 m^2/g. If we consider a mean interfacial area of 50−100 Å^2/surfactant molecule having a molar mass of 200 g/mol, then the complete coverage of the powder surface with a monolayer of surfactants would lead to a diminution of TOC from around 30 to 15 ppm. In the frame of these hypotheses, the powder is never completely covered. The amount of species adsorbed onto the carbonate surface is small within the margin of error of the TOC measurement. However, it is sufficient to induce significant hydrophobation of the sample.

These results confirm that the hydrophobation of limestone is possible by organic surface-active species extracted in water from the crude oil.[5] The amount and nature of these extracted species depend on pH and WOR, which impacts the hydrophobation level. The Washburn capillary rise method appears to be able to discriminate the differences in wettability states promoted by various released waters. The reproducibility of the experiments

is fair and confirms that this method is reliable to evaluate the wettability states.

4.2.3. Impact of Rinsing Hydrophobized Tacon with Low-Salinity Water. The hydrophobized carbonate samples were then treated with low-salinity water to assess the possibility of recovering a water-wet state. The Tacon samples hydrophobized by contact with the resolved water of crude A emulsions prepared at WOR 1, pH 7, and pH 10 (samples named T aged-Crude A$_{W-1pH7}$ and T aged-Crude A$_{W-1pH10}$, see Table 9) were used as starting samples. They were contacted with brine LS (2 g/L NaCl), and their wettability state was evaluated by Washburn capillary rise afterward. The results are listed in Table 10.

For both samples, brine adhesion tension increases slightly, which shows that the Tacon powder hydrophilicity has increased slightly after the low-salinity washing. This indicates that some hydrophobic compounds adsorbed on the carbonate surface could be removed by dissolution in low-salinity brine.[5] However, the Tacon powder does not retrieve its initial wettability (values in Table 8). The capillary constant *c* has increased back slightly, but it is still lower than that of the native sample. The volumes of fluids imbibed are close to a standard value of 0.3 mL for Tacon.

4.3. Edwards White Carbonate and Direct Contact with Crude Oil A. *4.3.1. Native Edwards White.* The adhesion tension and contact angle of SB brine on native Edwards White are given in Table 11. For this powder sample, only *n*-octane was used as organic liquid; therefore, the capillary constant *c* was determined from the ascension of *n*-octane. The corresponding capillary increases are shown in 3 (Figure 7).

Just as the native Sikaisol and native Tacon, native Edwards White has a preferential wettability toward water.

4.3.2. Edwards White Contacted with Crude Oil A (Protocol C2). Compared with the Tacon sample, another protocol was used to increase the oil-wetness of the Edwards White carbonate sample. In this case, the powder was directly contacted with

Table 11. Capillary Constant c Determined from the Ascension of n-Octane (m^5), Contact Angle (°), and Adhesion Tension (mN/m) of SB Brine for Native Edwards White

	n-octane	SB
capillary constant c (m^5)	$(1.35 \pm 0.19) \times 10^{-16}$	
adhesion tension (mN/m)	0	37 ± 4
contact angle (°)	0	60 ± 3

crude oil, with an attempt to mimic the natural aging process occurring in the reservoir rocks (see the Protocol C2: Direct Contact with Crude Oil section).

Two batches of aged Edwards White powder were prepared by direct contact with crude A. Because a rinsing step is mandatory at the end of the aging process to remove the excess crude oil (see the protocol and Figure 3 in the Experimental Section), it is impossible to prepare strictly identical samples over two experiments. Consequently, various levels of hydrophobation are obtained starting from the same powder and the same crude, as evidenced on the two batches of aged Edwards White prepared by contact with crude A (see Figure 9 and Table 12).

Both batches A1 and A2 of Edwards White that were aged by direct contact with crude A are significantly hydrophobic. The capillary rise of water (SB) is very slow, nearly null for the second

batch (Figure 9 top). For both samples, no plateau is reached after 15 h.

Table 12 gives the exploitation of the capillary rises of n-octane and SB on these aged Edwards White samples.

The brine contact angle is computed to be nearly 90° for both batches A1 and A2 when a reference contact angle of 0° is chosen for n-octane. The adhesion tensions of brine are close to 0 for both batches, the second one appearing to be even more hydrophobic than the first one. In fact, this level of hydrophobation is considered too high to be properly evaluated by the Washburn procedure used in this work. This indicates that water nearly does not wet the powder; therefore, it is not possible to determine a consistent value of adhesion tension. Interestingly, the volume of n-octane imbibed and the capillary constant c determined for these batches are significantly lower than the values obtained for the native Edwards White sample (see Tables 4 and 5), which expresses that the powder arrangement is strongly affected by the aging procedure. This probably reveals that the inadequate rinsing of the powder left some residual crude oil gluing the grains.

4.3.3. Impact of Rinsing Hydrophobized Edwards White with Water Phases of Various Salinities or Containing a Surfactant. The hydrophobized carbonate samples have been treated with waters of various salinities and also with a low-concentration surfactant solution. For both types of treatments, the hydrophobized carbonate sample was contacted with the aqueous solution, rinsed, and dried before performing capillary rise of the two probe liquids (n-octane and SB brine).

Only the first batch of contact with crude A (A1) was used because the hydrophobicity of the second batch was considered to be too high. The results are given in Table 13.

Three brine salinities were tested (a simplified formation brine FB, a simplified seawater SB, and a low-salinity brine LS). By soaking the aged carbonate powder in water, it is possible to increase the water-wetness of the samples, as evidenced by the increase in the adhesion tension of brine. The efficiency in increasing the wettability toward water increases when the brine salinity decreases, as expected. Note that for these samples, the volume of n-octane imbibed, and the capillary constant c remains lower than the values of the native Edwards White sample, indicating that the arrangement of the powder bed is still impacted by the aging and rinsing procedures.

The treatments with brines decrease the oil-wetness, but they do not succeed in restoring the wettability state of the native carbonate. Interestingly, for all samples, the volume of brine imbibed at the plateau is higher than the volume of n-octane, whereas a similar volume of the two fluids (0.3 mL) imbibed the native Edwards White sample. This is a quite counterintuitive result since the powders are much more hydrophobic. We could not find a convincing explanation for this. This could be related to the presence or not of the precursor film ahead of the liquid front that affects the capillary rise.[21]

Finally, the efficiency of a low-concentration surfactant solution in increasing the water-wetness of the aged surface was evaluated. An alkylpolyglucoside surfactant was used, prepared at a concentration of 2000 ppm in SB. The Edwards White sample aged with crude A was soaked in this surfactant solution, and its wettability was assessed afterward using the Washburn procedure. After treatment with the surfactant solution, a strong increase in the water-wetness was observed: the adhesion tension of brine is increased to 26 mN/m, which is much more efficient in restoring water-wetness than all of the rinsing brines tested. This wettability state is slightly less water-
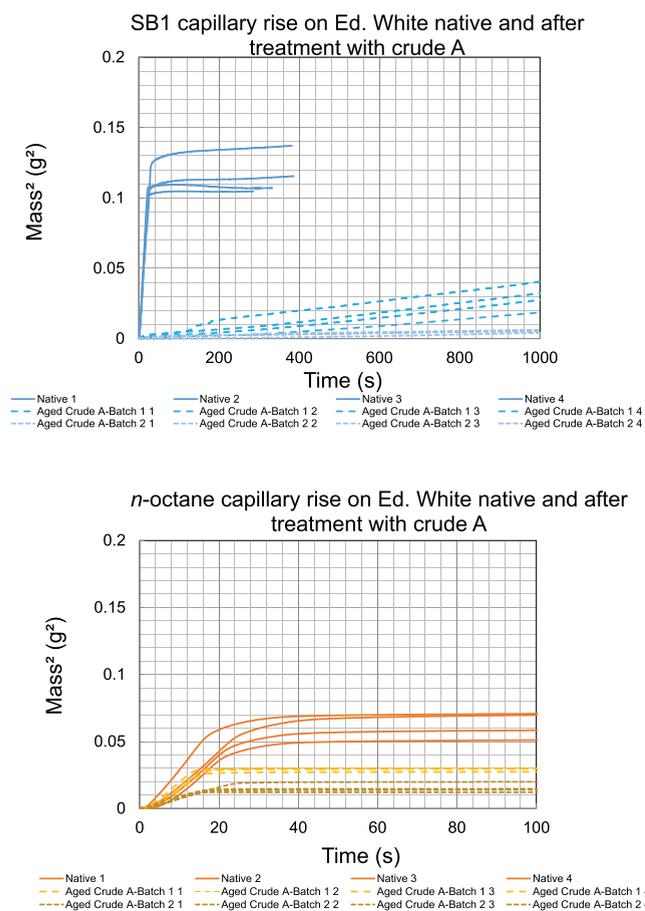
Figure 9. Washburn capillary rise of water (SB, top) and oil (n-octane, bottom) on Edwards White before (native) and after aging with crude A (batch A1 and batch A2). Four rises are performed for each liquid.

Table 12. Exploitation of the Washburn Capillary Rises of *n*-Octane and Brine SB on Edwards White Aged with Crude A[a]

		Washburn				
sample	protocol	V*n*-octane imbibed (mL)	capillary constant *c* ($\times 10^{16}$m^5)	V SB imbibed (mL)	adhesion tension brine SB (mN/m)	contact angle brine SB (°)
EW aged-Crude A-1	direct contact with crude A-/batch A1	0.24 ± 0.01	1.11 ± 0.06	no plateau	0.3 ± 0.0	89.8 ± 0.1
EW aged-Crude A-2	direct contact with crude A-/batch A2	0.17 ± 0.01	0.45 ± 0.05	no plateau	0.1 ± 0.0	89.9 ± 0.0

[a]Mean values and deviations calculated on four measurements with each liquid.

Table 13. Exploitation of the Washburn Capillary Rises of *n*-Octane and Brine SB on Edwards White Aged with Crude A and Post-Washed with Various Water Phases[a]

		Washburn				
sample	rinsing water	V*n*-octane imbibed (mL)	capillary constant c ($\times 10^{16}$m^5)	V SB imbibed (mL)	adhesion tension brine SB (mN/m)	contact angle brine SB (°)
EW aged-Crude A-1	FB	0.29 ± 0.02	0.70 ± 0.18	no plateau	1.3 ± 0.2	89.0 ± 0.1
	SB	0.27 ± 0.02	0.80 ± 0.17	0.55 ± 0.04	3.1 ± 0.6	87.5 ± 0.5
	LS	0.26 ± 0.03	0.78 ± 0.21	0.55 ± 0.01	4.5 ± 0.2	86.4 ± 0.2
	surfactant	0.27 ± 0.03	0.73 ± 0.09	0.31 ± 0.01	26 ± 5	69 ± 4

[a]Mean values and deviations calculated on four measurements with each liquid.

wet than the one of the native sample (brine adhesion tension = 37 mN/m), but it indicates that the carbonate has recovered a preferential wettability toward water (adhesion tension of brine > adhesion tension of *n*-octane). The mechanism for a wettability alteration by this surfactant is probably adsorption on the adsorbed oil layer via hydrophobic interactions.[22] This leads to the exposition of the surfactant polar head toward the surrounding medium, which promotes surface hydrophilicity. The volumes of *n*-octane and brine imbibed come back to the level obtained with the native powder (ca. 0.3 mL); however, the capillary constant *c* does not recover its initial value.

5. CONCLUSIONS

In this work, we evaluated the Washburn capillary rise as a tool for quantifying wettability alterations. Particularly, the objective was to find a rapid laboratory screening tool to select water compositions able to change the wettability of an oil-wet rock sample to a more water-wet state in the framework of enhanced oil recovery.

Our work shows that the repeatability of the technique is acceptable: the deviations between the slopes determined on four experiments performed for each liquid (*n*-hexane, *n*-octane, and water) are below 10% for Sikaisol and Tacon and below 15% for Edwards White. The capillary constants, adhesion tensions, and contact angles calculated from these slopes are obtained within this margin of error. Some treated samples showed higher deviations, but the variabilities remained below the differences observed between samples, and we have been able to discriminate different levels of oil- and water-wetness after the various treatments applied.

One important aspect to consider is that the capillary rise of any liquid in the sample depends not only on the wettability but also on the fluid and on the powder characteristics. The fluid characteristics are well known; however, the powder characteristics (morphology) are not defined and require using a reference liquid to encompass all these unknows into the "capillary constant" *c*. This implies compacting the powder in a reproducible manner and using a reference well-wetting liquid, which has to be kept constant when different samples are compared. *n*-Octane is a good candidate and less volatile than *n*-

hexane, which is commonly used. The treatments of the powders that change its wettability also impact the capillary constant *c*.

Both the direct contact of the powder with crude oil and its contact with water phases precontacted with crude oil induce hydrophobation of the powders. These two protocols can be used to prepare samples representative of oil-wet conditions in reservoirs. In the examples shown, some water-wetness could be recovered by rinsing these oil-wet samples with waters of various compositions and a ranking in efficiencies could be defined from the experimental results. Contacting a low-concentration surfactant solution proved to be the most efficient manner to recover water-wetness.

Linking these wettability data with the fine analysis of the organic compounds on the powder surface[23] could give valuable information to drive the choice of the most efficient water compositions for EOR. At the end, selected core flooding experiments have to be carried out to correlate with the above results.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.3c08630.

Appendix featuring additional equations, tables, and figures (PDF)

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Notes

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