Experimental Study of Wettability Alteration to Preferential Gas-Wetting in Porous Media and its Effects

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Abstract
In a recent theoretical study, Li and Firoozabadi showed that if the wettability of porous media can be altered from preferential liquid-wetting to preferential gas-wetting, then gas well deliverability in gas condensate reservoirs can be increased. In this paper, we present the results that the wettability of porous media may indeed be altered from preferential liquid-wetting to preferential gas-wetting. In the petroleum literature, it is often assumed that the contact angle through liquid phase $\theta$ is equal to $0^\circ$ for gas-liquid systems in rocks. As this work will show, while $\theta$ is always small, it may not always be zero. In laboratory experiments, we altered the wettability of porous media to preferential gas-wetting by using two chemicals, FC754 and FC722. Results show that in the glass capillary tube $\theta$ can be altered from about $50^\circ$ to $90^\circ$ and from $0^\circ$ to $60^\circ$ by FC754 for water-air and normal decane-air systems, respectively. While untreated Berea saturated with air has a 60% imbibition of water, its imbibition of water after chemical treatment is almost zero and its imbibition of normal decane is substantially reduced. FC722 has a more pronounced effect on the wettability alteration to preferential gas-wetting. In a glass capillary tube $\theta$ is altered from $50^\circ$ to $120^\circ$ and from $0^\circ$ to $60^\circ$ for water-air and normal decane-air systems, respectively. Similarly, because of wettability alteration with FC722, there is no imbibition of either oil or water in both Berea and chalk samples with or without initial brine saturation. Entry capillary pressure measurements in Berea and chalk give a clear demonstration that the wettability of porous media can be permanently altered to preferential gas-wetting.

Introduction
In a theoretical work, we have modeled gas and liquid relative permeabilities for gas condensate systems in a simple network. The results imply that when one alters the wettability of porous media from strongly nongas-wetting to preferential gas-wetting or intermediate gas-wetting, there may be a substantial increase in gas well deliverability. The increase in gas well deliverability of gas condensate reservoirs is our main motivation for altering the wettability of porous media to preferential gas-wetting.

Certain gas condensate reservoirs experience a sharp drop in gas well deliverability when the reservoir pressure drops below the dewpoint. Examples include many rich gas condensate reservoirs that have a permeability of less than 100md. In these reservoirs, it seems that the viscous forces alone cannot enhance gas well deliverability. One may suggest removing liquid around the wellbore via phase behavior effects through CO2 and propane injection. Both have been tried in the field with limited success; the effect of fluid injection around the wellbore for the removal of the condensate liquid is temporary. Wettability alteration can be a very important method for the enhancement of gas well
deliverability. If one can alter the wettability of the wellbore region to intermediate gas-wetting, gas may flow efficiently in porous media.

As early as 1941, Buckley and Leverett\textsuperscript{5} recognized the importance of wettability on water flooding performance. Later, many authors studied the effect of wettability on capillary pressure, relative permeability, initial water saturation, residual oil saturation, oil recovery, electrical properties of reservoir rocks, reserves, and well stimulation\textsuperscript{6-16}. In 1959, Wagner and Leach\textsuperscript{7} reported that it might be possible to improve oil displacement efficiency by wettability adjustment during water flooding. In 1967, Froning and Leach\textsuperscript{8} reported a field test in Clearfork and Gallup reservoirs for improving oil recovery by wettability alteration. Kamath\textsuperscript{9} then reviewed wettability detergent flooding. He noted that it was difficult to draw a definite conclusion regarding the success of detergent floods from the data available in the literature. Penny et al.\textsuperscript{12} presented a technique to improve well stimulation by changing the wettability for gas-water-rock systems. They added a surfactant in the fracturing fluid. This yielded impressive results; the production following cleanup after fracturing in gas wells generally was 2 to 3 times greater than field averages or offset wells treated with conventional techniques. Penny et al.\textsuperscript{12} believed that increased production was due to wettability alteration. However, they did not demonstrate that wettability had been altered.

Recently, Wardlaw and McKellar\textsuperscript{17} reported that only 11\% pore volume (PV) water imbibed into the Devonian dolomite samples with bitumen. The water imbibition test was conducted vertically in a dry core (saturated with air). Based on the imbibition experiments, they pointed out that many gas reservoirs in the western Alberta foothills of the Rocky Mountains were partially dehydrated and their wettability altered to a weakly water-wet or strongly oil-wet condition due to bitumen deposits on the pores. The water imbibition results of Wardlaw and McKellar\textsuperscript{17} demonstrated that the inappropriate hypothesis for wetting properties of gas reservoirs might lead to underestimate hydrocarbon reserves.

All the studies described above, except those in Refs 12 and 17, were conducted on oil-water-rock systems instead of gas-liquid-rock systems (gas-oil- or gas-water-rock systems). Refs 12 and 17 do not provide a direct measurement of wettability. For gas-liquid systems in reservoir rocks, it is often assumed that the contact angle, $\theta$, equals 0° (contact angle is measured through the liquid phase later). While the contact angle for gas-liquid systems may be small, it may not be zero. When a small amount of liquid is put inside a capillary tube and it is held in the vertical position, the liquid does not flow. Analysis of this simple experiment using the following equation

$$h_l = \frac{2\sigma}{\Delta \rho gr}(\cos \theta_R - \cos \theta_A), \quad (1)$$

reveals that the contact angle is not zero. Eq.1 is derived from the balance between the gravity and capillary forces. The symbols are: $h_l$ the liquid height in a circular capillary tube of radius $r$, $\theta_R$ the receding contact angle and $\theta_A$ the advancing contact angle, $\Delta \rho$ the density difference between the gas and liquid phase, and $\sigma$ the surface tension. There are also indications that in porous media the contact angle may not be zero in gas-liquid systems; it is of the order of several degrees or more but not intermediately gas-wetting.
Al-Siyabi et al.\textsuperscript{18} measured the gas-oil contact angles of four binary mixtures ($C_1/nC_4$, $C_1/nC_8$, $C_1/nC_{10}$, and $C_1/nC_{14}$) at reservoir conditions. Their results showed that the gas-oil contact angles were about 20° for surface tension values greater than about 0.2 dynes/cm. Morrow and McCaffery\textsuperscript{19} reported a summary of gas liquid displacement behavior in a low energy porous polytetrafluoroethylene (PTFE) solid. The intrinsic contact angle of water against air on smooth PTFE (Teflon) measured by Morrow and McCaffery\textsuperscript{19} was 108°. They also studied the effect of wettability on spontaneous imbibition, capillary pressure, and relative permeability properties in artificial PTFE cores for different wetting conditions varied by using different fluids and different extent of roughness. Morrow and McCaffery\textsuperscript{19} found that the retained liquid saturation by drainage decreased with increase in intrinsic contact angle from 22° to 108°.

Zisman\textsuperscript{20} reviewed the relation of the equilibrium contact angle to liquid and solid constitution on low and high energy surfaces, both bare and covered with a condensed monomolecular adsorbed film. He pointed out that even a single, close-packed, adsorbed monolayer of wetting agent was sufficient to convert the wetting properties of a high energy surface into those of a low energy surface. This remark demonstrated the possibility of varying the wettability of a high energy rock surface from preferential liquid-wetting to gas-wetting by adsorption of a monolayer of an organic polar compound. In spite of the work of Zisman\textsuperscript{20}, it is often understood that the contact angle for a gas-liquid system may not be altered substantially in rocks. In this paper, we present the results for the wettability alteration to preferential gas-wetting with or without initial water saturation and study its effect on the characteristics of liquid (oil and water) imbibition, oil drainage, permeability, and relative permeability in different porous media, including Berea and chalk. We also study the thermal stability and effectiveness of the rock in which wettability was altered.

Theory

To the best of our knowledge, wettability alteration to preferential gas-wetting in rocks has not been suggested in the petroleum literature. Consider the sketches in Fig. 1. When the contact angle $\theta < 90^\circ$ the liquid will rise in the circular capillary tube inserted vertically in the liquid, as shown in Fig. 1a. If $\theta = 90^\circ$, there will not be liquid rise, and the gas-oil interface will be flat (that is, $P_c=0$, see Fig. 1b). When $\theta > 90^\circ$, the liquid level will go down in the circular capillary tube as sketched in Fig. 1c. The rise and fall of the liquid level are given by

$$h_l = \frac{2\sigma \cos \theta}{\Delta \rho g r},$$

(Eq. 2)

Eq. 2 can be used to estimate $\theta$ in a capillary tube, once $h_l$, $\sigma$, $\Delta \rho$, and $r$ are known.

According to Eq. 2, for a gas-liquid system, one may define preferential liquid-wetting when $\theta < 90^\circ$, and preferential gas-wetting when $\theta > 90^\circ$. However, this definition is related to the geometry of the substrate. Let us consider a capillary tube with an equilateral triangle cross section. The gas-liquid interface will be flat when $\theta = 60^\circ$ for this geometry (Fang et al.\textsuperscript{21}). Therefore, one may define preferential liquid-wetting when $\theta <$
60° and preferential gas-wetting when \( \theta > 60° \). For a capillary tube of square cross section, the gas-liquid interface will be flat when \( \theta = 45° \), which implies preferential liquid-wetting for \( \theta < 45° \) and preferential gas-wetting for \( \theta > 45° \). When the capillary tube assumes triangular-curved interfaces and rough wall surfaces, other complications arise so that the contact angle looses some of its significance. The contact angle for the gas-liquid-rock system due to complex geometry and surface roughness may have a qualitative definition. A simple definition is adopted here from the expression for capillary pressure

\[
P_c = \frac{\sigma \cos \theta_p}{\sqrt{k \phi}},
\]

where \( k \) and \( \phi \) are permeability and fractional porosity, respectively; \( \theta_p \) is pseudo contact angle. One can measure entry capillary pressure (that is, threshold capillary pressure), and then infer \( \theta_p \) from Eq. 3, when \( \sigma, k \) and \( \phi \) are available. The contact angle calculated from Eq. 3 may not have the same physical meaning as the contact angle in Eq. 2. In order to emphasize the difference, we represent the contact angle in Eq. 3 by \( \theta_p \), and call it the pseudo contact angle.

**Experimental**

In the experimental work, brine, distilled water, and normal decane were used as the liquid phase, air as the gas phase, and glass capillary tube, Berea, and chalk (from Kansas outcrop and from a North Sea reservoir) as the substrate. Two types of chemicals were employed to alter the wettability of the substrates. The experiments were conducted at a room temperature of around 20°C.

**Fluids:** Normal decane was used as the oil phase; its specific gravity and viscosity are 0.73, 0.95cp at 20°C, respectively. The surface tension of air-normal decane is 23.4 dynes/cm at 20°C. Brine of 1.0 percent (wt) NaCl was used as the water phase in the Berea and chalk experiments; its specific gravity and viscosity are 1.01 and 1.0cp at 20°C. Distilled water was used as the water phase for the experiments in the capillary tube; the surface tension of air-distilled water is 72.7 dynes/cm at 20°C.

**Core and Capillary Tube:** In order to study the alteration of wettability to preferential gas-wetting, we used two different substrates: (1) capillary tube, and (2) rock (Berea and chalk). The glass capillary tube from Fisher Scientific used in our work has an internal diameter of 0.23 mm; the diameter was measured by dividing the total volume by the length of the tube. Glass tubes were cleaned by alcohol. After cleaning, they were rinsed using distilled water and then dried by blowing high pressure air. The relevant data for Berea and chalk samples are summarized in Table 1.

**Chemicals:** In our work, two chemicals with brand names, FC754 and FC722, were used to alter the wettability: 1) FC754 (inexpensive) and 2) FC722 (more expensive). FC754 is a cationic surfactant and is water-soluble. Its specific gravity (at 25°C) is 1.15. FC722 is a
polymer with molecular weight of about 100,000; it is neither water nor oil soluble. FC722 can be dissolved in a fluorocarbon-type solvent in a wide temperature range; the specific gravity of the solvent is around 1.7 at 25°C.

Procedure: The chemicals FC754 and FC722 were dissolved in water, and the solvent in various concentrations, respectively, and the glass capillary tube, Berea, and chalk were aged in them. The aging period depends on temperature and can vary from several minutes to several hours. After saturation with the chemical solution, the capillary tube, the Berea, or the chalk was evacuated for about half an hour and then dried in order to remove the extra liquid chemicals. A very small amount (unmeasurable) lingers in the substrate as an adsorbed layer; as a result of adsorption the surface energy decreases and the solid surface is rendered preferential gas-wetting.

Prior to wettability alteration, we measured the capillary rise of liquid (both oil and water) in the tube and the imbibition of water and oil into the air-saturated Berea and chalk samples. We repeated the same measurements after wettability alteration, and performed gas-oil gravity drainage tests on the Berea cores with and without wettability alteration. After wettability alteration, we also measured the entry capillary pressure of oil and water in the air-saturated Berea and chalk samples in order to demonstrate the preferential gas-wetting.

The following describes the procedure for establishing initial water saturation. First, Berea was saturated with water (1.0%wt NaCl brine) and initial water saturation was established by humidified air displacement. We used humidified air instead of dry air because it was found that the distribution of initial water saturation established by dry air may not be uniform. Humidified air was prepared by forcing air through a 1.0%wt brine before entering the core sample. The initial water saturation was determined by direct weighing. Since it is difficult to establish low initial water saturation (say 10%) in Berea by only humidified air displacement, we used dry air displacement following humidified air displacement in order to establish a low initial water saturation. Then, humidified air displacement was implemented again and the water saturation in the core increased slowly. The displacement direction was changed from time to time in order to make the distribution of initial water saturation more uniform. We stopped air displacement only after the desired initial water saturation had been established. Following that, the core was saturated with FC722 solution in the presence of initial water saturation. After a certain aging period, the chemical solution was removed by humidified air displacement at a velocity less than that for establishing the initial water saturation. Care was taken to avoid water production. The imbibition tests were then performed using the apparatus shown in Fig. 2.

For measuring gas phase relative permeability before and after wettability alteration, the core was first saturated with oil (normal decane). The absolute permeability of the core was measured. The air displacement in the core without the chemical treatment was then carried out in the vertical direction at room temperature with a confining pressure of 500psi. The air was passed through the oil before entering the core sample and its pressure at the inlet was kept at 3.0psi while the outlet was open to the atmosphere. Oil recovery, residual oil saturation, and end-point value of gas phase relative permeability were measured. The oil relative permeability was also calculated at low oil saturations. After the
air displacement without chemical treatment, the core was cleaned, dried, and treated by 2.0%wt FC722 solution. Following that, the chemical solution was removed from the core and the core was saturated with oil. Air displacement was performed again. Oil recovery, residual oil saturation, and gas phase relative permeability were then measured.

**Imbibition and Drainage:** Traditionally, spontaneous imbibition tests are conducted by immersing the core samples saturated with one liquid in another one. This type of imbibition is countercurrent imbibition. For water imbibition in oil-water systems, the traditional method for performing imbibition has an unavoidable disadvantage; one may have to remove the produced fluid on the rock surface from time to time. Berea and chalk without chemical treatment are strongly liquid-wet in gas-liquid systems. The early spontaneous imbibition may also be too rapid to record the data accurately. This classic method is difficult to implement in gas-liquid systems due to the limitation described above. The schematic of the apparatus used in our study for the measurement of liquid spontaneous imbibition into an air-saturated rock (Berea or chalk) is shown in Fig. 2. The core sample was kept vertical. When the bottom of the rock touched the liquid (oil or water), the liquid was spontaneously imbibed into the rock. The scale then recorded the change in weight of liquid with imbibition time. The average liquid saturation in the rock was calculated using the data from the scale. After the imbibition test, the core sample is weighed and the final average liquid saturation in the core can be obtained from the weight of the core. The experimental imbibition data recorded by the scale was in agreement with the final liquid saturation determined by weighing. The readability of the scale was 0.01g. When the wettability of the rock is altered to neutral-wetting or preferential gas-wetting, there should be no imbibition of liquid into the rock.

In order to avoid errors due to evaporation, especially for water imbibition measurements, in the setup shown in Fig. 2, we developed a different approach to perform liquid imbibition into the air-saturated core samples; the schematic is depicted in Fig. 3. The core samples pressed strongly by the heat shrink tubing were kept vertical. The liquid level in the container is about 2 mm higher than the bottom of the core. The tubing from the valve to the container is filled with liquid while the section from the valve to the bottom of the core is empty. The liquid (oil or water) will rise and touch the bottom of the rock and imbibe into the rock spontaneously after the valve is opened. The time when liquid touches the rock bottom can be identified from the plot of the weight change of the container vs. time; an abrupt change in the reduction rate of liquid weight occurs when liquid touches the rock bottom due to liquid imbibition into the rock. The average liquid saturation and the amount of liquid imbibed into the core is readily calculated through the data recorded by the scale.

The equipment used to measure air permeability, liquid permeability, end-point gas phase relative permeability, and gravity drainage performance is shown in Fig. 4. A confining pressure of up to 3000psi may be applied in the Hassler type core holder. For air permeability measurement in Berea, the differential pressure between top and bottom ends is measured using a U-shape tube. A Validyne differential pressure transducer was used for the chalk with an accuracy of ±0.25% FS. Both drainage and imbibition tests may be performed in the same setup. A pump is used to apply a confining pressure to the core holder.
**Entry Capillary Pressure**: The schematic of the setup for measuring entry capillary pressure is shown in Fig. 5. When entry capillary pressure is small, it is measured by adjusting the height of the liquid level referenced to the bottom of the core sample; in this case compressed air is not required to pressurize the liquid. Otherwise, the entry capillary pressure is measured by applying air pressure to the liquid (see Fig. 5); the pressure is determined using a Validyne differential pressure transducer with an accuracy of ±0.25% FS. Other components in Fig. 5 are similar to those in Fig. 4.

**Results**

We have conducted different tests in a capillary tube as well as in Berea and chalk samples. Following text discusses our experimental results.

**Capillary Tube Tests**: Fig. 6a shows liquid rise vs. the concentration of FC754 (from the treatment process) for both the gas-oil and gas-water systems; the liquid rise in the capillary tube decreases with an increase of the concentration and then stays constant when the concentration reaches around 0.2%wt. The reduction in the water rise due to wettability alteration is much more pronounced than that of the oil. The contact angle can be calculated using Eq. 2. Fig. 6b plots the computed contact angle vs. the concentration of FC754 for the gas-oil and gas-water systems. Note that the contact angle prior to treatment is about 50° for the gas-water system and about 0° for the normal decane-air system. This figure shows that the contact angle increases with the increase of the concentration; the contact angle of the gas-water systems increases to about 90° at a concentration of about 0.1 percent. This implies that wettability of the gas-water-glass system has been altered to intermediate gas-wetting by FC754. The contact angle of gas-oil increases to about 60° at a concentration of 0.1 percent. The wettability alteration in the gas-water system by FC754 is more pronounced than that in the gas-oil system.

The effect of the concentration of FC722 on the liquid level is shown in Fig. 7a for both the gas-oil and gas-water systems; liquid level in the capillary tube decreases with an increase of the concentration. The effect of the chemical concentration on the liquid level is reduced when the concentration is higher than about 0.1 percent. The interesting observation in this figure is the fall of the water level to negative values in the capillary tube, which confirms the wettability alteration instead of the decrease of the surface tension. It is definitely determined from Eq. 2 that the liquid height in a circular capillary tube shown in Fig. 1 cannot be negative by reducing the surface tension. Because FC722 is neither soluble in water nor in oil, the surface tension is not likely affected in the experiment. The only means to have a fall of the liquid level is to alter wettability from preferential liquid-wetting \((\theta < 90^\circ)\) to preferential gas-wetting \((\theta > 90^\circ)\). Fig. 7b depicts the computed contact angle vs. the concentration of FC722 for both gas-oil and gas-water systems; the contact angle is calculated using Eq. 2. This figure shows that the contact angles of both gas-oil and gas-water in the capillary tube increases with the increase of the concentration. The contact angles of gas-water and gas-oil increase to about 118° and 60° at 1.0 percent concentration, respectively. The wettability alteration in the gas-water system by FC722 is much more pronounced than that in the gas-oil system.
**Berea Imbibition Tests:** We measured both imbibition of oil and imbibition of water into a Berea core saturated with air. The measurements included before and after chemical treatment with FC754 and FC722 solutions, and with or without initial water saturation. We conducted the tests in the setup shown in **Fig. 2.**

**Fig. 8** plots the gas recovery by both oil and water spontaneous imbibition in an air-saturated Berea before and after treatment. The gas recovery is represented by the fraction of GOIP (gas originally in-place). Note that the residual gas saturation to oil is not the same as the residual gas saturation to water for the untreated Berea; the residual gas saturation to oil is about 38%, and to water is about 44% (see **Fig. 8**). The residual oil saturation of Berea from water imbibition is about 45 percent\(^{22}\). The properties of the rock samples (Berea) used here are about the same. Therefore, the main factor that influences gas recovery by spontaneous liquid imbibition is wettability. There is no related literature on the effect of wettability on recovery from Berea sandstone in gas-liquid systems. Oil recovery in oil-water-rock systems may increase when the wettability varies from oil-wetting to water-wetting in uniformly-wet porous media as summarized by Anderson\(^{23}\). Other experimental results for rocks with heterogeneous wettability show that oil recovery in weakly water-wet reservoir rocks is sometimes greater than that in strongly water-wet rocks\(^{24,25}\). Compared with oil-water systems, it seems reasonable to assume that the gas recovery by spontaneous liquid imbibition is greater when rocks are more liquid-wet.

Based on the above analysis, one possible explanation for the lower residual gas saturation to oil is that the oil wettability in gas-oil-Berea (GOB) systems is stronger than the water wettability in gas-water-Berea (GWB) systems. This hypothesis seems to be consistent with our contact angle measurements in gas-oil and gas-water systems with capillary tubes presented earlier. Our results showed that the contact angle through liquid phase in gas-oil systems is less than that in gas-water systems.

Gas recovery by water imbibition in Berea treated (sample No.1) by FC754 is much less than that in Berea without the chemical treatment (see **Fig. 8**). The spontaneous imbibition is related to wettability; gas recovery by spontaneous water imbibition decreases from liquid-wetting to preferential gas-wetting. Therefore, **Fig. 8** demonstrates that the wettability of a GWB system has been altered from strong liquid-wetting to somewhat intermediate gas-wetting by FC754 solution. The gas recovery by spontaneous oil imbibition in Berea (sample No.1) when treated with FC754 solution is also less than that without the treatment for a GOB system, demonstrating that the wettability of the gas-oil-rock (Berea) system has been altered to less liquid-wetting after treatment by FC754 solution. Similar to the glass tube, the wettability alteration by FC754 in a GWB system is more pronounced than that in a GOB system.

Neither oil nor water imbibes into Berea (sample No.2) when treated by FC722 solution due to wettability alteration. It can be seen from **Fig. 8** that the wettability in both GOB and GWB systems has been altered from strong liquid-wetting to intermediate wetting or preferential gas-wetting by FC722. We will soon confirm that the wettability was altered to preferential gas-wetting by measuring the entry capillary pressure. It can be seen from the results shown in **Fig. 8** that FC722 is more effective than FC754 for altering the wettability in gas-liquid-Berea systems.

The rate of spontaneous imbibition for both oil and water in gas-oil and gas-water systems is shown in **Fig. 9** in units of GOIP per minute. It can be seen from this figure that
the rate of spontaneous oil imbibition is somewhat higher than that of water imbibition in Berea. The process shown in Fig. 9 may be because of the stronger liquid-wetting in GOB systems than in GWB systems. We will discuss liquid imbibition rates in more detail later.

As described above, the Berea cores were treated without initial water saturation. In order to examine the influence of initial water saturation on wettability alteration, we treated the core after establishing different initial water saturations. The experimental results depicted in Fig. 10a show that there is no water imbibition in Berea (sample No.3) after wettability alteration by FC722 with initial water saturation ranging from 0 to 40.1 percent. The imbibition process was completed after approximately 20 minutes. The same imbibition results were obtained when we extended the test time to about 1000 minutes. Fig. 10a shows that FC722 could alter rock wettability in the presence of initial water saturation in gas-water systems.

Gas recovery by water imbibition decreases with the increase of initial water saturation as shown in Fig. 10a. The effect of initial water saturation on imbibition rates was also studied. Fig. 10b shows that imbibition rate increases with the increase of initial water saturation at an early stage of imbibition. We did not find literature data on the effect of initial water saturation on imbibition recovery and rate in gas-liquid systems. Tang and Firoozabadi\textsuperscript{25}, and Viksund, et al.\textsuperscript{26} report that the initial rate of spontaneous water imbibition in strongly water-wet rocks saturated with oil might increase with an increase in initial water saturation for sandstones and chalks; the trend depends on the range of initial water saturation. Our experimental results, as discussed above, show a consistent increase of initial rate with increasing initial water saturation (see Figs. 10 and 11). Oil and water imbibition tests at the initial water saturation of 50% were also performed without chemical treatment. The same phenomenon as described above was found (results are not shown in Figs. 10 and 11).

Fig. 11a shows that there is no oil imbibition in Berea (sample No.4) after wettability alteration by FC722 when initial water saturation ranges from 0 to 40.5 percent. This implies that FC722 would also alter rock wettability in the presence of initial water saturation in gas-oil systems.

Gas recovery by oil imbibition also decreases with the increase of initial water saturation as shown in Fig. 11a. The effect of initial water saturation on oil imbibition rate is shown in Fig. 11b. The relationship between oil imbibition rate and initial water saturation at the early and late stage of oil imbibition in gas-oil systems is the same as in gas-water systems. From a comparison of Figs. 10b and 11b, it seems that in Berea the water imbibition rate is more sensitive to the initial water saturation than the oil imbibition rate.

**Chalk Imbibition Tests:** In order to verify that FC722 can alter the wettability of different rock types, Kansas chalk was used to perform liquid (oil and water) imbibition tests with and without chemical treatment using the setup shown in Fig. 2. The gas recovery by spontaneous oil and water imbibition in Kansas chalk (sample No.5) with and without chemical treatment by FC722 solution is shown in Fig. 12. Neither oil nor water imbibes into Kansas chalk due to the wettability alteration after the treatment with FC722. It can be seen from this figure that the wettability in a gas-water chalk (GWC) or a gas-oil-chalk (GOC) system has been altered from strong water-wetting to intermediate
wetting or preferential gas-wetting by FC722. The state of wettability alteration will be
determined more precisely later.

The imbibition characteristics of oil and water in Kansas chalk is different from that in
Berea as shown in Fig. 13 (see also Fig. 9). Gas production rate by spontaneous water
imbibition in a GWC system is higher than that by spontaneous oil imbibition in a GOC
system at the early stage of imbibition. The process observed in Fig. 13 may be due to the
pore structure of the chalk. The feature of oil and water imbibition is opposite at the late
stage. It can also be seen from Fig. 12 that the ultimate gas recovery by spontaneous oil
imbibition in a GOC system is greater than that by the spontaneous water imbibition in a
GWC system. This may be due to the difference in wettability of liquid phase in GOC and
GWC systems.

The comparison of gas recovery by spontaneous water imbibition in Berea with that in
Kansas chalk is shown in Fig. 14a. This figure demonstrates that the residual gas
saturation by the spontaneous water imbibition in Kansas chalk is about four times less
than that in Berea. Fig. 14b shows that the water imbibition rate in Berea is greater than
that in chalk during the early imbibition process.

The residual gas saturation by spontaneous oil imbibition in Kansas chalk is about three
times less than that in Berea as shown in Fig. 15a, which has a similar characteristics to
those of water imbibition in Berea and chalk (see Fig. 14). Fig. 15b illustrates similar
results for oil imbibition rate as in Fig. 14b. It is noted, however, that the difference in oil
and water imbibition rates is greater in Kansas chalk than in Berea. Our residual gas
saturation data in chalk reveal a unique feature that has not been reported in the literature.

Berea Drainage Tests: The effect of wettability alteration on oil production by gravity
drainage was studied using the apparatus shown in Fig. 4. The core sample was first
saturated with oil (normal decane). The absolute permeability was then measured. A
gravity drainage test was performed without the chemical treatment at a confining
pressure of 500psi. The production outlet was located 23cm below the bottom of the core
because the threshold height is about 35cm. After gravity drainage without chemical
treatment, the core was cleaned, dried, and then treated with FC722 solution. The gravity
drainage test was repeated after the core was saturated with oil following the chemical
treatment. Two sandstone cores were used in the drainage tests. One (sample No.6) was
 treated with a low concentration (0.18%wt) of FC722. The oil production by gravity
 drainage in this core with and without treatment with FC722 solution is presented in Fig.
16a. The incremental oil recovery (OOIP) was around 15 percent in the core treated with
0.18% wt FC722 solution due to wettability alteration.

Another core (sample No.7) was treated by a high concentration (2.0%wt) of FC722
solution. The oil production by gravity drainage in this core with and without treatment
with FC722 solution is shown in Fig. 16b. The incremental oil recovery due to the
wettability alteration in the core with the treatment of 2.0%wt FC722 solution was
around 35 percent.

Oil production can be enhanced by treatment with FC722 solution (see Fig. 16).
Incremental oil recovery by gravity drainage increases with the increase in concentration
of FC722. Not much analysis can be made on the state of gas-wetting from the drainage
tests due to breakthrough of the gas at the core outlet. The results, however, show that drainage and imbibition processes have different features from chemical treatment.

**Preferential Gas-wetting:** The zero imbibition of oil or water in an air-saturated core after wettability alteration shown in Fig. 8 for Berea, and in Fig. 12 for chalk does not establish the extent of wettability alteration. A more precise test is the entry capillary pressure measurement. Any positive pressure on a liquid entering an air-saturated core would establish the degree of preferential gas-wetting of a treated core. Entry capillary pressures for both GOB and GWB systems were measured after the treatment of Berea sample (sample No.9) with 2.0%wt FC722 solution. The porosity and permeability of this core are 19.5% and 616.7md, respectively. The entry capillary pressure after the chemical treatment in the GWB system was measured by using the equipment shown in Fig. 5; it is about 35cm of water column. The pseudo contact angle calculated using Eq. 3 is around 95°. The measured entry capillary pressure in the GOB system is about 12cm oil column; the pseudo contact angle calculated using Eq. 3 is around 93°. The entry capillary pressure in a North Sea chalk (sample No.10) after treatment with 2.0%wt FC722 solution in both GOC and GWC systems was also measured; the porosity and permeability of this North Sea chalk were 29.0% and 1.47md, respectively. The measured entry capillary pressure was about 10.28 psi in the GWC system. The pseudo contact angle calculated using Eq. 3 was around 94°. The water phase used in the measurement was the 1%wt NaCl brine. The measured entry capillary pressure in the GOC system was about 1.49psi; the pseudo contact angle calculated using Eq. 3 was around 92°. Note that these two pseudo contact angles in both gas-oil- and gas-water-rock systems, unlike the more direct measurements established before and the new one that will be discussed next, are less realistic.

We can also study wettability alteration by placing a droplet of water or oil on an air-saturated core. Fig. 17 shows the fate of a droplet of water on the surface of an air-saturated Berea core before and after treatment. Fig. 17a shows that a droplet of water imbibes into the rock instantaneously as soon as it is placed on a Berea core (sample No.1) before chemical treatment. An oil droplet also imbibes. On the other hand, when a droplet of water is placed on an air-saturated Berea (sample No.2) which has undergone wettability alteration with 2.0%wt FC722 solution, the droplet forms a shape that is compatible with its wettability. Fig. 17b shows that a water droplet forms a contact angle of about 125° indicating strong preferential gas-wetting. When a water droplet is placed on a Berea treated with 0.18%wt FC722 solution, the contact angle is around 94° (see Fig. 17c). As expected the treated Berea does not imbibe any water. Fig. 17d shows a droplet of oil on an air-saturated Berea (sample No.2) treated by 2.0%wt FC722 solution; oil does not imbibe into the rock. This figure shows that the contact angle through the oil phase is less than that in gas-water-rock system; the measured contact angle through the oil phase is around 60°.

Fig. 18a shows a droplet of water (or oil) on the top of an air-saturated chalk (sample No.8) without chemical treatment; water (or oil) imbibes into the rock instantaneously when it contacts the rock. After the treatment with 2.0%wt FC722 solution, water does not imbibe into the rock (sample No.8) as shown in Fig. 18b; the contact angle is around 120° through the water phase. Fig. 18c shows a droplet of oil on the chalk (sample No.8).
treated by 2.0%wt FC722 solution; oil does not imbibe into the rock. It can be seen in Fig. 18c that the contact angle in GOC systems is less than that in GWC systems; the measured contact angle through the oil phase is also around 60°.

The results of the simple tests shown in Figs. 17 and 18 also provide a strong evidence of wettability alteration to preferential gas-wetting.

**Thermal Stability of Chemical:** To demonstrate the thermal stability of FC722, a Berea core was saturated with FC722 solution at room temperature. After removing the liquid chemical, the core was dried and then heated to a temperature of 210°F and maintained for around two hours. Neither water nor oil imbibes into this core when saturated with air; the imbibition tests were then performed at room temperature. Therefore, FC722 appears to possess good thermal stability under these conditions.

**Effectiveness of Chemical:** The effectiveness of FC722 was studied by oil displacement and gas displacement in the treated core. One Berea sample was treated by FC722 solution and saturated with oil after it was dried. The core was dried again following 100PV of oil displacement in a single phase state. Then both water and oil imbibition tests were performed. It was found that there was neither water imbibition nor oil imbibition in the core after 100PV of oil displacement. The same procedures were repeated after about 10,000PV of gas displacement. Neither water nor oil imbibed into the air-saturated core. The core was then left in the air for approximately 4 months; there was still no liquid imbibition. The above results show that FC722 might be suitable for permanent wettability alteration.

**Effect of Chemicals on Permeability:** In order to study the effect of chemical treatment on rock property, the permeabilities of both Berea and chalk samples before and after the treatment with FC722 solution were measured using nC10. The setup used to measure the rock permeability is shown in Fig. 4. The permeabilities of two Berea cores (samples No.7 and 9) without chemical treatment were 975 and 616md, respectively; they varied to 938 and 592md after it was treated by 0.18%wt FC722 solution, respectively. The permeability of the North Sea chalk (sample No.10) changed from 1.47md to 1.18md after it was treated by 2.0%wt FC722 solution. The above experimental results show that there is no significant permeability reduction in Berea after treatment with FC722 solution. In chalk, the permeability reduction is greater than that in Berea after treatment with FC722 solution, but it is still acceptable.

All the tests described above confirm that the wettability of porous media can be altered to preferential gas-wetting, and the wettability alteration is permanent. Furthermore, there is no significant reduction in permeability after the wettability of porous media is altered. In the following, we will discuss very limited measurements of gas and liquid relative permeabilities of the treated and untreated Berea to confirm the results from our theoretical work presented in Ref. 1.

**Effect of Wettability Alteration on Relative Permeability:** Gas well deliverability in gas-condensate reservoirs is related to the relative permeabilities. If the gas-phase relative permeability can be increased by wettability alteration, the gas well production may be
enhanced. Berea (sample No.11) with length of 17.85cm and diameter of 2.48cm was used to study the effect of wettability alteration on oil- and gas-phase relative permeabilities; the permeability and porosity of this core sample are 632.3md and 20.5%, respectively. The core was saturated normal decane completely and gravity drainage test was then conducted. After the drainage test, gas was injected from the top of the core until residual oil saturation was reached. Oil and gas relative permeabilities were measured only at the oil saturations close to residual oil saturation. Darcy’s law was applied to calculate oil and gas relative permeabilities only at the end-point and the point close to end-point.

Gas relative permeability at an oil saturation of about 16.2% increased from 0.54 to 0.89. Oil relative permeability at an oil saturation of about 27.1% changed very little from 0.025 to 0.030. The lower values belong to the untreated core and the higher values to the treated cores with 2.0%wt FC722 solution. It seems that the effect of wettability alteration on oil and gas relative permeabilities supports the network modeling predictions by Li and Firoozabadi1.

**Conclusions**

In addition to new data on residual gas saturation to oil and water imbibition in strongly liquid-wet chalk, the following conclusion related to wettability alteration can be drawn from our work:

1. The wettability of gas-water-rock systems can be altered from strong water-wetting to intermediate gas-wetting by FC754 and can be altered from strong water-wetting to preferential gas-wetting by FC722.
2. The wettability of gas-oil-rock systems can be altered from strong oil-wetting to less oil-wetting by FC754 and can be altered from strong oil-wetting to preferential gas-wetting by FC722.
3. The oil recovery and gas phase relative permeability in gas-oil systems could be increased by the treatment of FC722 due to the wettability alteration.
4. FC722 is thermally stable and seems to alter wettability permanently.
5. The gas recovery by spontaneous oil imbibition is greater than that by spontaneous water imbibition in both Berea and Kansas chalk.
6. The gas recovery by both spontaneous oil and water imbibition in Kansas chalk is greater than that in Berea.

**Nomenclature**

\[D = \text{diameter of core}\]
\[h_l = \text{height of liquid column}\]
\[k = \text{permeability}\]
\[L = \text{length of core}\]
\[P_c = \text{capillary pressure}\]
\[PV = \text{pore volume of core}\]
\[r = \text{radius of a capillary tube}\]
\[\phi = \text{porosity}\]
\[\theta = \text{contact angle}\]
\[\theta_a = \text{advancing contact angle}\]
\( \theta_p \) = pseudo contact angle
\( \theta_r \) = receding contact angle
\( \sigma \) = surface tension
\( \mu \) = fluid viscosity

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We thank D. E. Ouzzane of Imperial College of Science, Technology and Medicine for his help to study the effect of initial water saturation on imbibition. This work was supported by the Technology Research Center of the Japan National Oil Corporation (JNOC), the US DOE grant DE-FG22-96BC14850 and member companies of the Reservoir Engineering Research Institute (RERI). Their support is greatly appreciated.

References


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*: k = 500md; ★: k = 5md
Fig. 1: Liquid level rise or fall in a capillary tube at various wettability conditions

(a) Strong liquid-wet ($\theta < 90^\circ$)

(b) Intermediate gas-wet ($\theta = 90^\circ$)

(c) Gas-wet ($\theta > 90^\circ$)
Fig. 2: Instant surface contact method for measuring liquid imbibition into an air-saturated rock

Fig. 3: Liquid rise method for measuring liquid imbibition into an air-saturated rock
Fig. 4: Schematic of the apparatus used for measuring drainage and imbibition

Fig. 5: Schematic of the apparatus used for measuring the entry capillary pressure
Fig. 6: Liquid level and contact angle vs. the concentration of FC754 — glass tube.
Fig. 7: Liquid level and contact angle vs. the concentration of FC722 — glass tube
Fig. 8: Gas recovery by oil and water imbibition into the air-saturated Berea with and without chemical treatment

Fig. 9: Oil and water imbibition rates for the air-saturated Berea without chemical treatment
Fig. 10: Effect of initial water saturation on water imbibition into the air-saturated Berea with and without treatment with FC722.
Fig. 11: Effect of initial water saturation on oil imbibition into the air-saturated Berea with and without treatment with FC722.
Fig. 12: Gas recovery by liquid imbibition into the air-saturated chalk with and without treatment with FC722

Fig. 13: Oil and water imbibition rates for the air-saturated chalk without chemical treatment
Fig. 14 Water imbibition and rate of the air-saturated Berea and chalk samples without chemical treatment.
Fig. 15 Oil imbibition and rate of the air-saturated Berea and chalk samples without chemical treatment.
Fig. 16: Oil recovery by gravity drainage with and without treatment of Berea with FC722

(a) 0.18% FC722 ($k=1089\text{md}$)

(b) 2.0% FC722 ($k=975\text{md}$)

Fig. 16: Oil recovery by gravity drainage with and without treatment of Berea with FC722
Fig. 17: Liquid droplets on the surface of the air-saturated Berea before and after treatment with FC722

(a) Water (without chemical treatment)

(b) Water (treatment with 2.0% FC722, $q=125^\circ$)
(c) Water (treatment with 0.18% FC722, $q=120^\circ$)

(d) Oil (treatment with 2.0% FC722, $q=60^\circ$)

Fig. 17: Liquid droplets on the surface of the air-saturated Berea before and after treatment with FC722 (continued)
Fig. 18: Liquid droplets on the surface of the air-saturated chalk before and after treatment with FC722.

(a) Water (without chemical treatment)

(b) Water (treatment with 2.0% FC722, $q=120^\circ$)

(c) Oil (treatment with 2.0% FC722, $\theta=60^\circ$)

Fig. 18: Liquid droplets on the surface of the air-saturated chalk before and after treatment with FC722.