Relative Permeability Modification in Gas/Liquid Systems Through Wettability Alteration to Intermediate Gas Wetting

Guo-Qing Tang, SPE, and Abbas Firoozabadi, SPE, Reservoir Engineering Research Inst.

Summary

The wettability of Berea and chalk samples for gas/oil and gas/water fluids were altered from strong liquid wetting to intermediate gas wetting. Two polymers, FC-722 and FC-759, were used to alter the wettability. FC-759 is soluble in water and 1/3 as expensive as FC-722. Gas and liquid relative permeabilities were measured before and after wettability alteration. The results demonstrated a significant increase in liquid phase relative permeability. Gas-phase relative permeability for a fixed saturation may increase or decrease; however, because of the very high liquid mobility and reduced liquid saturation, the gas mobility also increased for a fixed pressure drop.

A number of liquid injectivity tests were also carried out. The results revealed that the liquid-phase mobility could increase significantly when the wettability of rocks was altered from strong liquid wetting to intermediate gas wetting. All the results show clearly that the application of wettability alteration to intermediate gas wetting may significantly increase deliverability in gas condensate reservoirs.

Introduction

In some gas condensate reservoirs, the well deliverability drops severely owing to liquid dropout around the wellbore.1-4 Wettability plays an important role in condensate accumulation around the wellbore. The effect of wettability on condensate accumulation in porous media can be explained with the Young-Laplace equation.

\[
P_s = \frac{2 \sigma \cos \theta}{r}
\]  

(1)

The capillary pressure, \(P_s\), is proportional to interfacial tension, \(\sigma\), and the cosine of the pseucontact angle, \(\cos \theta\), and is inversely proportional to pore size, \(r\). For a gas liquid system, strong liquid-wet porous media can hold high liquid saturation because of the low mobility of the wetting phase. Experimental and numerical studies show that the condensate saturation around the wellbore could be reduced by (1) an increase in viscous forces (also gravity forces), (2) a decrease in interfacial tension, (3) gas injection, or (4) a decrease in liquid wetting.7 In 1995, Cowney et al.10 studied the feasibility of improving gas and brine relative permeabilities in Blue Creek coal and Ohio sandstone for a gas/brine/rock system by adding surface-tension-reducing agents. They found that it might not be possible to increase gas relative permeability through a lowering of the interfacial tension. Penny et al.11 studied removal of the load water from gas and oil wells through wettability alteration from strong water wetting to intermediate wetting. They showed that the load water could be removed easily from either gas or oil wells when the rock was neither oil wetting nor water wetting. After wettability alteration, the productivity following cleanup increased two to three times. Penny et al.11 and Cowney et al.10 did not study the wettability alteration for a gas/oil/rock system.

Recently, Li and Firoozabadi8,9 have proposed the enhancement of gas-well deliverability by wettability alteration from strong liquid wetting to preferential gas wetting in gas condensate reservoirs. The laboratory study by Li and Firoozabadi8 showed that a permanent intermediate gas wetting could be established in Berea and chalk through chemical treatment.

The major goal of this work is to study the mobility of the gas and liquid phases (both water and hydrocarbon liquids) before and after wettability alteration from strong liquid wetting to intermediate gas wetting. For this purpose, in addition to relative permeability measurements, we also conducted various other tests to demonstrate that liquid mobility can be improved significantly because of wettability alteration. Li and Firoozabadi8 used the polymer FC-722 in their wettability alteration. This polymer does not dissolve in water, and the solvent is expensive (20 times the cost of FC-759). In this work, in addition to FC-722, we used the polymer FC-759, which is soluble in water and less expensive than FC-722. This chemical has a specific application in porous media.12

In this paper, we first present the experimental procedures and the apparatus. Then we discuss the results of (1) the spontaneous imbibition tests without and with initial water saturation; (2) the effect of chemical adsorption on permeability; (3) the gas/oil and gas/water relative permeabilities, (4) the effect of wettability alteration on oil accumulation; and (5) the effect of wettability on oil injectivity.

Experimental

Fluids and Rocks. Normal-decane (n-C10) with a specific gravity of 0.73 and a viscosity of 0.92 cp at T = 24°C was used as the oil phase. Distilled water was used to prepare 0.2% (wt) NaCl brine as the water phase. The specific gravity and viscosity of 0.2% NaCl brine at 24°C were 1.012 and 1.0 cp, respectively. Air was used as the gas phase. The surface tension is 23.4 dynes/cm for air/n-C10 and approximately 70 dynes/cm for air/water. Berea sandstone and Kansas chalk were the rock samples. For Berea sandstone, the samples were divided into two groups. The first group of Berea samples had an air permeability of 500 md and a porosity of 21 to 22%. The second group of Berea samples had an air permeability of 340 md and a porosity of 20%. For Kansas chalk, the air permeability was 1.3 to 1.5 md, and the porosity was approximately 30 to 32%. Table 1 provides permeability, porosity, dimensions, chemical treatment, and other relevant data for Berea and chalk samples used in our work. In this table, B represents Berea and C represents chalk.

Chemicals. Polymer FC-722 and FC-759, manufactured by the 3M corporation, were used to alter the wettability of Berea sandstone and Kansas chalk from strong liquid wet to intermediate gas wet. These two chemicals are the fluoropolymer type with some specific functional groups. Fig. 1 shows the chemical structure of FC-759. The fluoroochemical group provides the water and oil repellency; the silanol and anionic groups chemically bond onto rock surfaces, providing a durable treatment; and the anionic and non-ionic groups make the polymer soluble in the aqueous solution. Table 2 lists some properties of these two chemicals. FC-722 is colorless, only soluble in a specific fluorosolvent, and expensive; FC-759 is of a light-yellow color, water-soluble, and less expensive than FC-722. The volatile organic content (VOC) for FC-759 is less than 0.1% and will not cause an environmental problem when applied in the field.
<table>
<thead>
<tr>
<th>Core</th>
<th>$k$ (md)</th>
<th>$\phi$ (%)</th>
<th>$L$ (cm)</th>
<th>$S_w$ (% PV)</th>
<th>Chemical Treatment</th>
<th>$C_{or}$ (mg/g-rock)</th>
<th>$\theta_s$ (degrees)</th>
</tr>
</thead>
<tbody>
<tr>
<td>B-1</td>
<td>507</td>
<td>21.5</td>
<td>6.05</td>
<td>0</td>
<td>no</td>
<td>0</td>
<td>0</td>
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<tr>
<td>B-2</td>
<td>522</td>
<td>21.9</td>
<td>6.1</td>
<td>0</td>
<td>2% FC-722</td>
<td>4.6</td>
<td>90</td>
</tr>
<tr>
<td>B-3</td>
<td>511</td>
<td>22.1</td>
<td>6.2</td>
<td>0</td>
<td>no</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>B-4</td>
<td>503</td>
<td>22.2</td>
<td>6.0</td>
<td>0</td>
<td>2% FC-722</td>
<td>2.4</td>
<td>90</td>
</tr>
<tr>
<td>B-5</td>
<td>495</td>
<td>21.7</td>
<td>6.3</td>
<td>0</td>
<td>2% FC-722</td>
<td>2.2</td>
<td>90</td>
</tr>
<tr>
<td>B-6</td>
<td>552</td>
<td>21.7</td>
<td>5.5</td>
<td>0</td>
<td>8% FC-759</td>
<td>6.0</td>
<td>90</td>
</tr>
<tr>
<td>B-9</td>
<td>341</td>
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<td>B-10</td>
<td>343</td>
<td>20.0</td>
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<td>4.5</td>
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<tr>
<td>B-11</td>
<td>339</td>
<td>20.1</td>
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<td>0</td>
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<td>10.3</td>
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<tr>
<td>B-12</td>
<td>501</td>
<td>22.1</td>
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<td>8% FC-759</td>
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<tr>
<td>B-13</td>
<td>489</td>
<td>22.0</td>
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<td>6.0</td>
<td>90</td>
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<tr>
<td>B-14</td>
<td>513</td>
<td>21.9</td>
<td>6.2</td>
<td>0</td>
<td>8% FC-759</td>
<td>5.9</td>
<td>90</td>
</tr>
<tr>
<td>B-15</td>
<td>487</td>
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<td>6.1</td>
<td>9.8</td>
<td>8% FC-759</td>
<td>5.7</td>
<td>—</td>
</tr>
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<td>B-16</td>
<td>495</td>
<td>21.3</td>
<td>5.9</td>
<td>16.2</td>
<td>8% FC-759</td>
<td>5.0</td>
<td>—</td>
</tr>
<tr>
<td>B-17</td>
<td>503</td>
<td>21.5</td>
<td>6.3</td>
<td>8.5</td>
<td>8% FC-759</td>
<td>6.3</td>
<td>—</td>
</tr>
<tr>
<td>B-18</td>
<td>483</td>
<td>20.5</td>
<td>6.8</td>
<td>16.5</td>
<td>8% FC-759</td>
<td>5.2</td>
<td>—</td>
</tr>
<tr>
<td>C-1</td>
<td>1.34</td>
<td>31.1</td>
<td>5.6</td>
<td>0</td>
<td>no</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>C-2</td>
<td>1.32</td>
<td>32.0</td>
<td>5.9</td>
<td>0</td>
<td>2% FC-722</td>
<td>2.5</td>
<td>90</td>
</tr>
<tr>
<td>C-3</td>
<td>1.30</td>
<td>31.7</td>
<td>5.7</td>
<td>0</td>
<td>2% FC-722</td>
<td>2.8</td>
<td>90</td>
</tr>
<tr>
<td>C-4</td>
<td>1.34</td>
<td>32.0</td>
<td>5.5</td>
<td>0</td>
<td>8% FC-759</td>
<td>0.9</td>
<td>90</td>
</tr>
<tr>
<td>C-6</td>
<td>1.33</td>
<td>31.8</td>
<td>18.1</td>
<td>0</td>
<td>no</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>C-7</td>
<td>1.31</td>
<td>32.2</td>
<td>18.0</td>
<td>0</td>
<td>2% FC-722</td>
<td>2.7</td>
<td>90</td>
</tr>
<tr>
<td>C-8</td>
<td>1.28</td>
<td>32.0</td>
<td>17.9</td>
<td>0</td>
<td>8% FC-759</td>
<td>1.0</td>
<td>—</td>
</tr>
<tr>
<td>C-11&quot;</td>
<td>1.33</td>
<td>32.0</td>
<td>5.9</td>
<td>0</td>
<td>5% FC-759</td>
<td>1.6</td>
<td>—</td>
</tr>
<tr>
<td>C-12&quot;</td>
<td>1.33</td>
<td>32.1</td>
<td>6.1</td>
<td>0</td>
<td>5% FC-759</td>
<td>1.4</td>
<td>—</td>
</tr>
<tr>
<td>C-14</td>
<td>1.28</td>
<td>31.6</td>
<td>5.8</td>
<td>0</td>
<td>8% FC-759</td>
<td>0.8</td>
<td>90</td>
</tr>
<tr>
<td>C-15</td>
<td>1.30</td>
<td>31.9</td>
<td>5.5</td>
<td>11.7</td>
<td>8% FC-759</td>
<td>0.9</td>
<td>—</td>
</tr>
</tbody>
</table>

Note: Diameter of the core was 2.54 cm for Berea and 2.7 cm for chalk.

*Core was aged with $S_w$ at $T=90^\circ$C without drying; **core was treated twice;*** permeability to brine.

**Rock Treatment.** A core sample was treated with the chemicals in two different processes: Process 1 and Process 2. For Process 1, the dry core was saturated with either FC-722 or FC-759 solution after being evacuated for 2 hours. The core was then aged at room temperature for approximately 3 days to allow the chemical to adsorb onto the solid surface. After aging, the core was dried by evacuation and then aged at $T=105^\circ$C for 12 to 24 hours. For Process 2, the wet core (containing initial water saturation) was saturated with FC-759 solution and then aged at 90°C for 3 days. After aging, the core was displaced with air to remove liquids. Thereafter, initial water saturation was re-established in the core before it was used for imbibition or coreflooding tests. Process 2 was intended to simulate the application procedure under reservoir conditions.

**Spontaneous Imbibition.** The core, saturated with air and chemically treated or untreated, was placed in either oil or water to perform spontaneous imbibition tests using the setup shown in Fig. 2a. The core sample was hung under an electronic balance and submerged in a liquid (either oil or brine). Change in the weight of the core vs. time was recorded. The decrease in the rate and recovery by spontaneous imbibition of water or oil after chemical treatment indicated the extent of wettability alteration.

**Coreflooding.** Fig. 2b shows a schematic of the apparatus for coreflooding tests, which consisted of a visual coreholder, a pressure transducer, an ISCO pump, an air compressor, a gas pressure regulator, a gas flow meter, and an electronic balance. The core sample was wrapped in a polytetrafluoroethylene (PTFE) heat-
Table 2—Properties of Chemicals

<table>
<thead>
<tr>
<th>Chemical</th>
<th>FC-722</th>
<th>FC-759</th>
</tr>
</thead>
<tbody>
<tr>
<td>MW</td>
<td>10^5</td>
<td>10^5</td>
</tr>
<tr>
<td>Concentration, %</td>
<td>2</td>
<td>5-8</td>
</tr>
<tr>
<td>Viscosity, cp at 25°C</td>
<td>1</td>
<td>3.3</td>
</tr>
<tr>
<td>Specific gravity</td>
<td>1.8</td>
<td>1.1</td>
</tr>
<tr>
<td>Boiling point, °C</td>
<td>59</td>
<td>100</td>
</tr>
<tr>
<td>Color</td>
<td>clear</td>
<td>Light yellow</td>
</tr>
<tr>
<td>VOC, %</td>
<td>—</td>
<td>&lt;0.1</td>
</tr>
</tbody>
</table>

*Volatile organic content.

The chemical structure of FC-759 is given as:

\[ R_f'N(Si(OH))_3 \]

Rf—Fluorochemical

A—Anionic group

N—Nonionic group

W\#X\#Y\#Z

Fig. 1—Chemical structure of FC-759.\(^{12}\)

shrinking tubing and placed in a visual coreholder. A confining pressure of 300 psia was used for all tests. The visual coreholder allowed for observation of the movement of liquid/gas interfaces at the surface of the core. The gas was injected at a constant injection pressure using the gas-pressure regulator, the oil (or water) was injected at a constant rate using the ISCO pump. The gas and oil (or water) were mixed in a capillary-tube mixer before entering the core with two-phase injection. The pressure drop across the core was measured by the pressure transducer. Average oil (or water) saturation in the core was measured vs. time by the electronic balance. Two types of coreflooding tests, relative permeability and oil injectivity, were performed.

Both spontaneous imbibition and coreflooding tests were carried out at room temperature. We are currently conducting tests at reservoir temperature. The results will be published later.

**Results**

**Wettability Alteration at S_w=0.** In these sets of tests, all the core samples were treated with the chemicals at zero initial water saturation and then used for spontaneous imbibition tests.

**Gas/Oil/Berea.** Fig. 3 shows spontaneous oil imbibition results for the untreated Berea sample (B-1) and the treated Berea samples (B-2 treated with FC-722 and B-12 treated with FC-759). To have a stable intermediate gas wetting, B-2 was treated with 2% FC-722 twice, but B-12 was treated with 8% FC-759 only once. For the untreated core (B-1), oil imbibed into the core very quickly, and the recoverable gas was produced in less than 60 minutes; the final gas recovery was approximately 63% original gas in place (OGIP). The imbibition curve for the untreated core (strong oil wetting against air) shows a strong oil wetting and was used as a reference to assess the wettability alteration for the treated cores. For the treated cores (B 2 and B 12), the oil-imbibition rate was low, and final gas recovery was approximately 9% OGIP even after more than 7,000 minutes (5.5 days).

**Gas/Water/Berea.** Gas recovery by spontaneous water imbibition for the untreated core (B-3) and the treated cores (B-4 and B-13) is presented in Fig. 4. B-4 and B-13 samples were treated with 2% FC-722 and 8% FC-759, respectively. Similar to the oil-imbibition test, the water-imbibition rate for the untreated core was very high, and the final gas recovery was approximately 58% OGIP. For the treated cores (B-4 and B-13), water imbibition was negligible, and the final gas recovery was less than 5% OGIP.

**Gas/Oil/Chalk.** Fig. 5 presents the data of spontaneous oil imbibition for the untreated core (C-1) and the treated cores (C-2 and C-11). The C-2 sample was treated with 2% FC-722, and the C-11 sample was treated with 5% FC 759 twice. A high rate of oil imbibition was observed for the untreated core (C-1); the final gas recovery was approximately 90% OGIP. For the treated cores (C-2 and C-11), the oil-imbibition rate decreased significantly; the final gas recovery was less than 6% OGIP.

**Gas/Water/Chalk.** Fig. 6 shows the data for the spontaneous water imbibition tests using the untreated and treated cores. The C-1 sample was the same core used previously for the oil-imbibition test, the C-3 sample was treated with 2% FC-722, and the C-13 sample was treated with 8% FC-759. Water imbibition in the treated cores was very slow, and the final gas recovery was about 3% OGIP for the C-3 sample and approximately 8.5% OGIP for the C-12 sample. The final recovery for the untreated core (C-1) was approximately 83% OGIP.

The results presented in Figs. 3 through 6 demonstrate that wettability of Berea sandstone and Kansas chalk can be altered...
from strong liquid wetting (SLW) to intermediate gas wetting by treatment with either FC-722 or FC-759.

**Wettability Alteration With $S_w$.** For these sets of tests, the treatment was made with Process 2. The cores saturated with 100% water were displaced with air to remove water to a designated initial water saturation ($< 20\%$). They were then placed immediately into a beaker filled with 8% FC-759 solutions to avoid water evaporation and were saturated with the chemical solution by applying a vacuum in a desiccator containing the beaker. The cores were then aged at 90°C for 3 days without drying. After aging, air was injected into them at room temperature to remove the solution. The initial water saturation was re-established by saturating the treated cores with water followed by air displacement. The re-established initial water saturation was close to that established initially.

**Fig. 7a** shows the results of spontaneous oil imbibition for the B-14, B-16, and B-17 samples. The initial water saturation was zero for B-14, 9.5% for B-16, and 16.2% for B-17. **Fig. 7a** reveals that the initial water saturation did not affect the effectiveness of wettability alteration by FC-759; the chemical is water soluble and can reach the rock surfaces through diffusion in the water film covering the rock surfaces. The oil-imbibition rate and the final gas recovery show a decline in imbibition with an increase in initial water saturation from zero to 16.5%. **Fig. 7b** depicts the results of spontaneous water imbibition for the B-18 and B-19 samples. The initial water saturation was 8.5% for B-18 and 16.5% for B-19. Compared to the spontaneous oil imbibition shown in **Fig. 7a**, the water-imbibition rate and the final gas recovery are higher; the final gas recovery was approximately 15% OGIP. The increase in initial water saturation did not affect the water-imbibition behavior. Similar results also were obtained for chalk samples (see **Fig. 8**). The C-14 sample was treated with 8% FC-759 at zero initial water saturation. The C-15 sample was treated with 8% FC-759 at an initial water saturation of approximately 12%. The results shown in **Fig. 8** demonstrate that initial water saturation reduced final gas recovery from 10% to 3% OGIP, which is in agreement with the results obtained for Berea.

**Durability Testing.** Establishment of durable intermediate gas wetting is the major goal of our work. We examined the durability of intermediate gas wetting on treated cores. **Fig. 9a** presents the results for the repeated tests for spontaneous oil imbibition. The B-5 sample treated with 2% FC-722 was used repeatedly. After each test, the core was dried at 105°C to remove all the oil from the core and was weighed to detect how much oil was adsorbed. The results for the repeated imbibition tests were nearly the same. No chemical desorption was observed; the weight of the dry core after each test remained the same. The results in **Fig. 9b** indicate that even after the treated cores (B-6 and C-5) were submerged in oil for more than 90 days, the final gas recovery did not change after 15 days, which indicates a stable altered wettability by the chemicals. Therefore, one may assume that the adsorption of FC-722 and FC-759 onto the surfaces of the selected rocks is stable and permanent.

**Assessment of Wettability Alteration.** The results presented earlier reveal that the wettability of Berea and Kansas chalk can be altered significantly by chemical treatment. To assess wettability alteration, we used the following equation to estimate a pseudocontact angle for the treated cores (see the derivation in the Appendix).

$$V^2 = \frac{8k\sigma A_\mu \cos \theta_p}{\phi \cdot 2\mu \cdot t}$$

In this equation, $V$ = imbibed phase volume, $k$ = permeability, $\phi$ = porosity, $\sigma$ = interfacial tension, $A_\mu$ = effective section area, $\mu$ = viscosity, $\theta_p$ = pseudocontact angle, and $t$ = imbibition time.
If we assume that the permeability, porosity, interfacial tension, and viscosity are constant, Eq. 2 can be expressed as

\[ V^2 = K \cos \theta_f \]  \hspace{1cm} \text{(3)}

where \( K \) is a constant. A plot of \( V^2 \) vs. \( t \) gives a straight line when the contact angle is constant in the course of imbibition. One could then estimate a pseudocontact angle from the slope of the straight line. Using imbibition data from untreated core as a reference, we could estimate the pseudocontact angle for the treated core with

\[ \cos \theta_{pl} = \frac{K_1}{K_2} \cos \theta_{2c} \]  \hspace{1cm} \text{(4)}

In Eq. 4, subscripts 1 and 2 refer to treated and untreated core, respectively. Here, we assume the pseudocontact angle for untreated core to be zero. The pseudocontact angle estimated from Fig. 4 for treated Berea and chalk samples is approximately 90° (see Table 1), giving further indication that the rock surfaces were altered to intermediate gas wetting.

**Chemical Adsorption and Effect on Permeability.** Permeability reduction caused by polymer adsorption onto rock surfaces has been reported in the literature. In the following, we examine the effect of chemical treatment on permeability.

We determined the chemical adsorption on Berea and chalk samples by weighing dry core before and after chemical treatment. The adsorption of FC-722 on Berea sandstone was approximately 2.2 to 2.4 mg per gram of sand and approximately 2.5 to 2.8 mg per gram of chalk; the adsorption of FC-759 on Berea was 5.0 to 6.1 mg of g-sand and was about 0.8 to 1.6 mg of g-chalk (see Table 1). Adsorption of FC-759 on chalk was less than that on Berea. This may be because of negatively charged chalk surfaces that have some repellency to the anionic groups of FC-759.

Using measured chemical adsorption data, we estimated the thickness of chemical coating on the rock surfaces. The surface areas of the selected rocks were estimated from the permeability and porosity data with the Kozeny correlation. The estimated surface area of Berea was approximately 0.03 m² per gram of sand and about 2.73 m² per gram of chalk. The average thickness of FC-722 onto the Berea surface was approximately 0.018 μm; onto the chalk surface, it was about 0.002 μm; the average thickness of FC-759 was 0.09 μm onto the Berea surface and about 0.0004 μm onto the chalk surface. When a core was treated twice, the chemical film thickness nearly doubled.

The absolute permeability to oil was determined before and after a core was treated with chemicals. The B-9 and C-6 samples were untreated, the B-10 and C-7 samples were treated with 2% FC-722 twice, and the B-11 and C-8 samples were treated with FC-759 twice. Oil permeability was 344 md for untreated Berea and 335 md for treated Berea. Reduction in permeability was negligible for Berea. For the low-permeable chalk, oil permeability was 1.32 md for untreated chalk and 1.20 md for treated chalk. Reduction in permeability was less than 10%. Therefore, there is no appreciable reduction in permeability after chemical treatment.

**Gas and Oil (Water) Relative Permeabilities.** To reduce the end effect, core samples with a length of approximately 18 cm were used. Gas and oil (water) relative permeabilities were measured by the steady-state method. Gas was injected at a constant inlet pressure using a gas pressure regulator. Oil (water) was injected at a constant rate with an ISCO pump. Gas and oil (water) were mixed before entering the core. We assumed that a steady-state was established when the oil (water) saturation in the core, gas- and oil- (water-) production rates, and pressure drop were nearly constant. We mainly studied gas and oil (water) relative permeabilities for imbibition. The effect of capillary pressure was neglected based on high flow rates and the use of long core in the tests.

**Effect of Wettability on \( k_{rg} \) and \( k_{rw} \) (\( k_{rp} \)).** Fig. 10 shows measured gas and oil relative permeabilities for untreated core (B-9) and treated cores (B-10 and B-11). The B-10 sample was treated with 2% FC-722 twice, and the B-11 sample was treated with 5% FC-759 twice. Treatment for these two cores was for \( S_w = 0 \). A duplicate test for each core was made, and the results were nearly the same. We only present the results for one of the duplicate tests for each core. A significant effect of wettability alteration on both gas and oil relative permeabilities was observed. After wettability alteration from strong oil wetting to intermediate gas wetting, (1) the oil saturation at the point for which \( k_{og} = k_{mg} \) was reduced from 0.54 to about 0.45 PV; (2) the cross-point relative permeability increased from 0.03 to 0.15, indicating an improvement of two-phase flow mobility; (3) the gas relative permeability decreased and oil relative permeability increased; and (4) the residual oil saturation decreased from 0.42 to approximately 0.15 PV. These results are in agreement with relative permeabilities in oil/water systems when one alters wettability.

![Image](image-url)

**Fig. 7—Effect of \( S_w \) on wettability alteration of Berea by 8% FC-759: (a) spontaneous oil imbibition; (b) spontaneous water imbibition.**
Fig. 8—Effect of $S_w$ on wettability alteration of Berea by 8% FC-759: oil/chalk.

Gas and water relative permeabilities also were measured in untreated core (B-9) and treated core (B-10). The effect of wettability alteration on gas and water relative permeabilities shows a trend similar to that for gas and oil relative permeabilities (see Fig. 11). Water relative permeability increased significantly at $S_w > 0.5$ PV. Residual water saturation decreased from 0.44 to 0.25 PV. Reduction in residual water saturation after chemical treatment was less than residual oil saturation (see Fig. 10).

Fig. 12 presents gas and oil relative permeabilities for the untreated chalk sample (C-6) and the treated chalk sample (C-7). The C-7 sample was treated with 2% FC-722. Because of low permeability, the gas-injection pressure was approximately 50 psi. It is interesting to note that both gas and oil relative permeabilities increased for $S_w > 0.2$ after wettability alteration to intermediate gas wetting. The increase in oil relative permeability was greater than that for gas relative permeability. Also, the oil saturation at the cross-point $k_{ro} = k_{wo}$ decreased from 0.57 to 0.45 PV after the wettability alteration; relative permeability at the cross-point increased from 0.035 to 0.12. Residual oil saturation decreased from 0.45 to 0.15 PV.

Oil (or water) saturation at the cross point, $k_{ro} = k_{wo}$ for treated cores was less than 0.5 PV for treated Berea and treated chalk, implying gas wetting. This result is in line with the spontaneous imbibition measurements. Figs. 10 and 12 imply that the effect of wettability alteration on gas relative permeability may depend on porous media.

**Effect of Viscous Forces on $k_{ro}$ and $k_{wo}$**

Gas and oil relative permeabilities measured at pressure gradients of 0.1, 0.2, and 0.3 psi/cm for both untreated (B-9) and treated (B-10) cores are presented in Figs. 13a and 13b, respectively. For untreated core, gas relative permeability increased systematically with an increase in pressure gradient, while oil relative permeability did not change much. This result is in agreement with the experimental results by Clew et al., and Henderson et al., and the modeling results by Li and Firoozabadi. For treated core, both gas and oil relative permeabilities increased with the pressure gradient systematically; the increase in $k_{ro}$ at $S_w < 0.5$ PV ($S_o < 50\%$) seems to be small. Similar results were obtained in an intermediate wettability rock for an oil/water system by Heaviside et al.. An important observation is that as the pressure gradient increases from 0.1 to 0.3 psi/cm, residual oil saturation decreases from 0.15 PV to 0.04 PV for treated core, but it does not decrease for untreated core (as expected). This result is in agreement with our recent work on the effect of wettability alteration on water injection in oil-saturated, low-permeable chalk.

Fig. 9—Stability testing for treated Berea and chalk. (a) repeated spontaneous oil imbibition; (b) long-term spontaneous oil imbibition.

Fig. 10—Gas and oil relative permeabilities for treated and untreated Berea.

Fig. 11—Gas and water relative permeabilities for treated and untreated Berea.
Fig. 12—Gas and oil relative permeabilities for treated and untreated chalk.

Effect of Initial Water Saturation on $k_{rg}$ and $k_{or}$. We have assumed the initial water saturation to be immobile owing to low saturation based on the observation that there was no water production. Note that the initial water saturation was established with gas injection. Only gas and oil phases were injected for the relative permeability measurement of gas and oil. Fig. 14a shows the effect of initial water saturation on gas and oil relative permeabilities for untreated Berea (B-9). An increase in initial water saturation from zero to 0.11 PV did not affect oil relative permeability; however, it reduced gas relative permeability significantly. Note that oil saturation at $k_{or}=k_{rg}$ and relative permeability at the cross-point did not change with an increase in initial water saturation. The effect of initial water saturation on gas and oil relative permeabilities shows an opposite effect in treated Berea (see Fig. 14b). The increase in initial water saturation from zero to 0.075 PV did not change gas relative permeability, but it reduced oil relative permeability significantly. Oil saturation at $k_{or}=k_{rg}$ increased from 0.41 to 0.45 PV, and relative permeability at the cross-point decreased from 0.18 to 0.12.

In our work, the effect of initial water saturation on gas and oil relative permeabilities for strong liquid wetting and intermediate gas wetting for Berea is different from the work of Narahara et al.\textsuperscript{20} In their work with water wet and mixed wet Berea (water wetting and mixed wetting in the context of oil and water phases), they did not find an effect of initial water saturation on either gas or oil relative permeability. The effect of initial water saturation on gas and oil relative permeability needs further study.

Reduction in Oil Saturation. Effect of wettability on oil saturation was also studied with the following tests. Gas and oil were first mixed in a capillary-tubing mixer and then injected simultaneously into an air-saturated core. Gas-injection pressure was changed from 2 to 6 psi, and oil was injected at a rate of 4 cm$^3$/hr. The injected ratio of gas to oil was large, and inlet pressure was close to gas-injection pressure. Outlet pressure was atmospheric. Average oil saturation in the core increased with injection, and no oil was produced from the outlet at early time because of oil accumulation in the core. The oil breakthrough time in untreated core was much greater than that in treated core. In the tests with untreated core (B-9), there was an interface between the invaded oil phase and the displaced-gas phase; the interface moved toward the outlet with time, and the displacement was piston-like. Oil broke through from the core outlet at an oil saturation of approximately 0.63 PV for the test at a pressure gradient of 0.1 psi/cm (see Fig. 15a). Thereafter, oil was produced continuously, and average oil saturation in the core was nearly constant. The increase in pressure gradient from 0.1 to 0.3 psi/cm resulted in a decrease in average oil saturation from 0.65 to 0.53 PV in untreated core.

Fig. 13—Effect of viscous forces on gas and oil relative permeabilities for treated and untreated Berea with 2% FC-722: (a) untreated Berea: B-9; (b) treated Berea: B-10.

Fig. 14—Effect of $S_w$ on gas and oil relative permeabilities for treated and untreated Berea: (a) untreated Berea:B-9; (b) treated Berea: B-10.
With treated core (B-10), we did not observe an interface between the invaded-oil phase and the displaced-gas phase. Oil broke through from the core at an oil saturation of 0.25 PV for the test at a pressure gradient of 0.1 psicm. Thereafter, oil saturation increased to 0.3 PV. Oil accumulation was more sensitive to the pressure gradient for treated core. It decreased from 0.3 to 0.12 PV as the pressure gradient increased from 0.1 to 0.3 psicm (see Fig. 15b), indicating a substantial increase in oil mobility with altered wettability.

As oil saturation decreased from approximately 0.55 to 0.15 PV because of wettability alteration from strong liquid wetting to intermediate gas wetting (see Fig. 15), gas relative permeability increased from 0.05 to 0.5 because of reduced oil saturation (see Fig. 10). These results imply that gas-well deliverability may increase substantially when wettability is altered to intermediate gas wetting.

**Increase in Oil Injectivity**. The setup in Fig. 16 was used to make another comparison of two-phase gas/liquid flow with and without wettability alteration. Untreated and treated cores were assembled in parallel. The difference in oil injectivity from these two cores could be attributed to the sole effect of the wettability.

Oil was injected at a constant rate (for Berea, the rate was 4 cm³/min; for chalk, it was 0.33 cm³/min). The oil-production rate from the outlet of each core was measured separately after breakthrough. Before oil breakthrough, oil rates of the individual cores at the inlet were calculated from gas-production rates using material balance. The test was initiated with 100% gas-saturated cores.

Fig. 17 shows the results for oil injectivity in Berea. The pressure drop quickly increased to approximately 7 psi, then decreased gradually to approximately 6 psi. Oil-injection rate at the inlet of the untreated core varied from 0.5 to 0.9 cm³/min, but at the inlet of the treated core, it varied from 3.0 to 3.5 cm³/min. The ratio of oil injectivity in treated Berea and untreated Berea was about 4 to 6. Oil-injectivity data for chalk are shown in Fig. 18. The pressure drop after breakthrough was approximately 43 psi. Oil-injection rate in the treated core increased quickly and then gradually stabilized at approximately 0.28 cm³/min; the oil-injection rate in untreated core was initially higher owing to the strong effect of capillary pressure, but it decreased quickly and then gradually stabilized at about 0.05 cm³/min. The ratio of oil injectivity in treated core to untreated core was about 6.

These simple tests firmly establish the benefit of wettability alteration for the increase in oil mobility in two-phase gas/liquid flow.

**Discussion and Concluding Remarks**

The work presented in this paper and in Refs. 6 and 9 has established that in gas/oil systems, the wettability of porous rocks can be altered to intermediate gas wetting. In this work, we have demonstrated that as a consequence of intermediate gas wetting, liquid-phase mobility increases significantly. One application of wettability alteration to intermediate gas wetting is enhancement of well deliverability in the gas condensate reservoirs that have experienced a sharp drop in deliverability because of condensate dropout around the wellbore. To proceed with field application, the research work should advance along two main directions. In one direction, the effect of high temperature (>90°C) on wettability alteration to intermediate gas wetting should be studied. In another direction, the search for other suitable polymers should continue. We have embarked upon the work in both directions; the results will be made available in future publications.

**Nomenclature**

- \( A_s \) = effective sectional area, cm²
- \( C_{ad} \) = chemical adsorption, mg/g-rock
- \( k \) = permeability, md
- \( k_r \) = relative permeability, fraction
- \( K \) = coefficient, dimensionless
- \( L \) = length, cm
- \( P_c \) = capillary pressure, psi
- \( q_o \) = oil-injection rate, cm³/min
- \( S_{wi} \) = initial water saturation, fraction of PV
- \( t \) = time, min or day
- \( \Delta \rho \) = pressure drop, psi
- \( \theta \) = contact angle, degree

Fig. 15—Effect of viscous forces on oil accumulation for treated and untreated Berea: (a) untreated Berea: B-9; (b) treated Berea: B-10.

Fig. 16—Schematic of oil-injectivity tests.

Fig. 17—Effect of wettability on oil injectivity in treated and untreated Berea.
Fig. 18—Effect of wettability on oil injectivity in treated and untreated chalk.

\[ \mu = \text{viscosity, cp} \]
\[ \sigma = \text{interfacial tension, dynes/cm} \]
\[ \phi = \text{porosity, fraction} \]

Subscripts
\[ g = \text{gas} \]
\[ o = \text{oil} \]
\[ w = \text{water} \]

Acknowledgments
This work was supported by the U.S. DOE grant DE-FG22-96RC14850 and the members of the Reservoir Engineering Research Inst. (REERI). Their support is appreciated. We thank R. Juhanian for his assistance in the experimental work.

References

Appendix—Expression for Pseudocontact Angle
For a capillary tube with a diameter of \( r \), capillary pressure \( P_c \) between air and invading liquid can be expressed as

\[ P_c = \frac{2\cos\theta}{r} \]  \hspace{1cm} (A-1)

where \( \sigma \) = interfacial tension between air and invading liquid and \( \theta \) = the liquid/solid/air pseudocontact angle. Using the Poiseuille equation, liquid flow rate in capillary tubing can be expressed as

\[ q = \pi r^2 \Delta p \]  \hspace{1cm} (A-2)

where \( q \) = liquid flow rate, \( \Delta p \) = pressure drop across the tube. For spontaneous imbibition, capillary force is the only force driving liquid into the tube when gravity is negligible. Therefore, \( P_c = \Delta p \). Substituting Eq. A-1 into Eq. A-2, advancing liquid rate in the tube can be expressed as

\[ q = \frac{dD}{dt} = \frac{\pi r^2 \sigma \cos\theta}{4\mu} \]  \hspace{1cm} (A-3)

Assuming \( l = 0 \) at \( t = 0 \) and integrating Eq. A-3 with respect to \( t \) gives the expression for calculating the distance of liquid advancing in the capillary tube at time \( t \):

\[ l^2 = \frac{\pi r^2 \sigma \cos\theta}{2\mu} t \]  \hspace{1cm} (A-4)

Let \( A \) denote the cross-sectional area of the tube and \( V \) the liquid volume at time \( t \); then, \( V = A l \). Substituting \( l = A t \) into Eq. A-4, the volume of the advancing liquid into the pore space of the tube is given by

\[ V^2 = \frac{\pi r^2 \sigma \cos\theta}{2\mu} t \]  \hspace{1cm} (A-5)

Eq. A-5 shows that a plot of \( V^2 \) vs. \( t \) would give a straight line provided that the interfacial tension between liquid and air, the viscosity of liquid, and the contact angle do not change with time. The slope of the straight line can provide the contact angle from Eq. A-5. For porous media, we use an effective cross-sectional
area of the rock, \(A_r\), instead of \(A\) and set \(r = \sqrt{8k/\phi}\) in Eq. A-5. Using Eq. A-5, the liquid volume imbibed into the pore space at time \(t\) can be expressed as

\[
V^2 = \frac{\sqrt{8k \sigma A_r \cos \theta}}{\phi} \frac{\sigma A_r \cos \theta}{2\mu} t. \quad \text{........................................} \quad (A-6)
\]

Note that \(\theta_p\) is the pseudocontact angle in porous media.

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**SI Metric Conversion Factors**

- \(1 \text{ cp} \times 1.08\)  
- \(1 \text{ dyne} \times 1.00\)  
- \(1 \text{ °F} = (°F - 32)/1.8\)  
- \(1 \text{ ft}^3 = 9.290 304\)  
- \(1 \text{ in.} = 2.54\)  
- \(1 \text{ in.}^2 = 6.451 6\)  
- \(1 \text{ in.}^3 = 1.638 706\)  
- \(1 \text{ psi} = 6.894 757\)

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*Conversion factor is exact.

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**Guo-Qing Tong** is a research associate in the Dept. of Petroleum Engineering at Stanford U. His current research interests include multiphase flow in porous media, solution gas drive in heavy-oil reservoirs, and thermal oil recovery from low-permeability heavy-oil reservoirs. Previously, Tong was head of the EOR Research Center of Dagang Oilfield (Group) Ltd., CNPC, China, and a research engineer at the Reservoir Engineering Research Inst. (RERI) in Palo Alto, California. He holds a BS degree in physical chemistry from the Inst. of Chemical Engineering, East China, Shanghai, China, an MS degree in petroleum geology from Northwestern U., Xian, China, and MS and PhD degrees in petroleum engineering from the U. of Wyoming.

**Abbas Firoozabadi** is a senior scientist and director at the Reservoir Engineering Research Inst. (RERI) in Palo Alto, California, and a visiting professor at Imperial College in London. His research interests include multiphase flow in porous media and thermodynamics of hydrocarbon reservoirs and production. He is the recipient of the 2000 SPE Reservoir Engineering Award and the 2002 SPE Anthony F. Lucas Gold Medal. Firoozabadi holds a BS degree from the Abadan Inst. of Technology, Abadan, Iran, and MS and PhD degrees from the Illinois Inst. of Technology, all in gas engineering. He is currently serving on the SPE Editorial Review Committee and has formerly served on the Forum Steering and Western Regional Conference Committees.