SPE 62934

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 Institute (RERI)

This paper was prepared for presentation at the 2000 SPE Annual Technical Conference and Exhibition held in Dallas, Texas, 1–4 October 2000.

Abstract

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 some 20 times less expensive than 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, due to liquid dropout around the wellbore, the well deliverability drops severely[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 using the Young-Laplace equation:

$$P_c = \frac{2\sigma \cos\theta}{r} \qquad (1)$$

The capillary pressure, P_c, is proportional to interfacial tension, σ, and the cosine of the contact angle, $\cos\theta$, and is inversely proportional to pore size, r. For a gas-liquid system, strongly liquid-wet porous media can hold high liquid saturation due to the low mobility of 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) [5-6]; (2) a decrease in interfacial tension[7]; (3) gas injection[8]; or (4) decrease in liquid wetness[9]. In 1995, Cowney et al.[10] studied the feasibility of improving gas and brine relative permeabilities in Blue Greek 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 easily be removed from either gas or oil wells when the rock was neither oil-wetting nor water-wetting. After wettability alteration, the productivity following cleanup increased 2 to 3 times. Penny et al. and Cowney et al. did not study the wettability alteration for a gas-oil-rock system.

Recently, Li and Firoozabadi[6,9] 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 Firoozabadi[9] 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 phase (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 due to wettability alteration. Li and Firoozabadi[9] used the polymer FC-722 in their wettability alteration. This polymer does not dissolve in water and the solvent is expensive. In this work, in addition to FC-722, we used the polymer FC-759 which is soluble in water and is 20 times 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) effect of wettability on oil injectivity.

Experimental

Fluids and Rocks. Normal-decane (n-C_{10}) with a specific gravity of 0.73 and a viscosity of 0.92 cp at T=24^{o}C was used as the oil phase. Distilled water was used to prepare 0.2% (wt.) NaCl brine and was used as the water phase. The specific gravity and viscosity of 0.2% NaCl brine at 24^{o}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-C_{10} and about 70 dynes/cm for air/water. Berea sandstone and Kansas chalk were the rock samples. For the 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 21-22%. 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 1.3-1.5 md and the porosity was about 30-32%. **Table 1** provides permeability, porosity, dimensions, chemical treatment, and other relevant data for the Berea and chalk samples used in our work. In this table, B represents Berea sample and C represents chalk sample.

Chemicals. FC-722 and FC-759, manufactured by the 3M corporation, were used to alter the wettability of Berea sandstone and Kansas chalk from strongly liquid-wet to intermediately gas-wet. These two chemicals are the fluoropolymer-type with some specific functional groups. **Fig.1** shows the chemical structure of FC-759. The flurochemical group provides the water and oil repellency; the silanol and anionic groups chemically bond onto rock surfaces providing a durable treatment; the anionic and nonionic groups make the polymer hydrophilically soluble[12]. **Table 2** lists some properties of these two chemicals. FC-722 is colorless, only soluble in a specific fluoro-solvent, 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.

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 two hours. The core was then aged at room temperature for about 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^{o}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^{o}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, 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 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 give 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 FTP heat-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 interface from 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-tubing mixer before entering the core with two-phase injection. The pressure-drop across the core was measured by the pressure transducer. The average oil (or water) saturation in the core was measured vs. time by the electronic balance. Two types of coreflooding tests (1) relative permeability, and (2) 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_{wi}=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 oil spontaneous 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). In order 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 all the recoverable gas was produced in less than 60 minutes; the final gas recovery was about 63% (*OGIP*). The imbibition curve for the untreated core 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 about 9% (*OGIP*) even after the test was carried out for more than 7,000 minutes (5.5 days).

Gas-Water-Berea. The 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, water imbibition rate for the untreated core was very high and the final gas recovery was about 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). C-2 sample was treated with 2% FC-722 and 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 about 65% (*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 on tests the untreated and treated cores. C-1 sample was the same core previously used for oil imbibition test; C-3 sample was treated with 2% FC-722 and C-13 sample was treated with 8% FC-759. Water imbibition in the treated cores was very slow and the final gas recovery for C-3 sample was about 3% (*OGIP*) and for C-12 sample was about 8.5% (*OGIP*). The final recovery for the untreated core (C-1) was about 62% (*OGIP*).

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

Wettability Alteration with S_{wi}. For these sets of tests, the treatment was made using 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 into a beaker filled with 8% FC-759 solutions immediately to avoid water evaporation and were saturated with the chemical solution by applying vacuum in a dessicator 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 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 oil imbibition rate and the final gas recovery show a decline in imbibition with increase in initial water saturation from zero to 16.2%. **Fig.7b** depicts the results of spontaneous water imbibition for 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 about 15% (*OIGP*). Increase in initial water saturation did not affect the water imbibition behavior. Similar results were also 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 about 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. The interaction between gas, water, and oil phases may cause such a performance.

Stability Testing. Establishment of stable intermediate gas-wetting is the major goal of our work. We examined the stability of intermediate gas-wetting on treated cores. **Fig.9a** presents the results for the repeated tests for spontaneous oil imbibition. B-5 sample treated with 2% FC-722 was repeatedly used. After each test, the core was dried at 105°C to remove all the oil from the core and weighed to check change in chemical adsorption. 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 above reveal that wettability of Berea and Kansas chalk can be altered significantly by chemical treatment. In order to assess wettability alteration, we used the following equation to estimate a pseudo-contact angle for the treated cores (see the derivation in the **Appendix**).

$$V^2 = \sqrt{\frac{8k}{\phi}} \frac{\sigma A_e^3 \cos\theta_p}{2\mu} t \qquad (2)$$

In the above equation, V is imbibed phase volume, k permeability, ϕ porosity, σ interfacial tension, A_e effective section area, μ viscosity, θ_p pseudo-contact angle, and t imbibition time.

If we assume the permeability, porosity, interfacial tension, and viscosity are constant, Eq.2 can be expressed as

$$V^2 = K\cos\theta_p\, t \qquad (2a)$$

where K is a constant. 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 pseudo-contact angle from the slope of the straight line. Using imbibition data of untreated core as a reference, we could estimate the pseudo-contact angle for treated core using

$$\cos\theta_{p_1} = \frac{K_1}{K_2} \cos\theta_{p_2} \qquad (3)$$

In Eq.3, subscripts 1 and 2 refer to treated and untreated core, respectively. Here we assume the pseudo-contact angle for untreated core to be zero. The pseudo-contact angle estimated from Eq.3 for treated Berea and chalk samples are about 90 degrees (see **Table-1**), giving further indication that the rock surfaces were altered to intermediate gas-wetting.

Chemical Adsorption and Effect on Permeability. Permeability reduction due to polymer adsorption onto rock surfaces has been reported in the literatures[13]. In the following, we examined 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 about 2.2-2.4 mg per g-sand, and on chalk was about 2.5-2.8 mg per g-chalk; the adsorption of FC-759 on Berea was 5.0-6.1 mg of g-sand and on chalk was about 0.8-1.6 mg of g-chalk (see **Table-1**). Adsorption of FC-759 on chalk was less than that on Berea. This may be due to 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 using the Cozeny correlation[14]; the estimated surface area of Berea was about 0.03 m^2 per g-sandstone and of chalk was about 2.73 m^2 per g-chalk. The average thickness of FC-722 onto Berea surface was about 0.08 μm and onto chalk surface was about 0.002 μm; the average thickness of FC-759 onto Berea surface was 0.09 μm and was about 0.0004 μm onto 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. B-9 and C-6 samples were untreated; B-10 and C-7 samples were treated with 2% FC-722 twice; and 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. In order to reduce the end effect, core samples with a length of about 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 using an ISCO pump. Gas and oil (water) were mixed before entering the core. We assumed that 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 due to high flow rate and the use of long core in the tests.

Effect of Wettability on k_{rg} and k_{ro} (k_{rw}). **Fig.10** shows measured gas and oil relative permeabilities for untreated core (B-9) and treated cores (B-10 and B-11). B-10 sample was treated with 2% FC-722 twice and B-11 sample was also treated with 5% FC-759 twice. Treatment for these two cores was for S_{wi}=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 $k_{rg}=k_{ro}$ 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 about 0.15 PV. These results are in agreement with relative permeabilities in oil-water systems when one alters wettability[15].

Gas and water relative permeabilities were also 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). C-7 sample was treated with 2% FC-722. Due to low permeability, the gas injection pressure was about 50 psi. It is interesting to note that both gas and oil relative permeabilities increased for S_o> 0.2 after wettability alteration to intermediate gas-wetting. Increase in oil relative permeability was greater than that for gas relative permeability. Also, the oil saturation at the cross-point $k_{ro}=k_{rg}$ 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, $k_{rg}=k_{ro}$, for treated cores was less than 0.5 PV for treated Berea and treated chalk, implying a preferential 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_{rg} and k_{ro}. 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 cores (B-10) are presented in **Figs.13a** and **13b**, respectively. For untreated core, gas relative permeability increased systematically with increase in pressure gradient while oil relative permeability did not change much. This result is in agreement with the experimental results by Henderson et al.[16] and Chen et al.[17] and the modeling results by Li and

Firoozabadi[6]. For treated core, both gas and oil relative permeabilities increased with pressure gradient systematically; the increase in k_{rg} at S_o< 0.5 PV seems to be small. Similar results were obtained in an intermediate wettability rock for an oil/water system by Heaviside et al.[18] 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 work on the effect of wettability alteration on water injection on oil recovery from low permeable chalks[19].

Effect of Initial Water Saturation on k_{rg} and k_{ro}. We assumed the initial water saturation is immobile due to low saturation. **Fig.14a** shows the effect of initial water saturation on gas and oil relative permeabilities for untreated Berea (B-9). Increase in initial water saturation from zero to 0.11 PV did not affect oil relative permeability; it reduced gas relative permeability significantly. Note that oil saturation at k_{ro}=k_{rg} and relative permeability at the cross-point did not change with 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**). Increase in initial water saturation from zero to 0.075 PV did not change gas relative permeability, but reduced oil relative permeability significantly. Oil saturation at k_{ro}=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.[20]. In their work with water-wet and mixed-wet Berea (water-wetting and mixed-wetting in the content of oil and water phases), they did not find any 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 using 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. 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 due to 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 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 oil saturation of around 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. Increase in pressure gradient from 0.1 to 0.3 psi/cm resulted in a decrease in average oil saturation from 0.65 PV to 0.53 PV in untreated core.

With treated core (B-10), we did not observe an interface between invaded-oil phase and 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 psi/cm. Thereafter, oil saturation increased to 0.3 PV. Oil accumulation was more sensitive to pressure gradient for treated core. It decreased from 0.3 to 0.12 PV as pressure gradient increased from 0.1 to 0.3 psi/cm (see **Fig.15b**), indicating substantial increase in oil mobility with altered wettability.

As oil saturation decreased from about 0.55 to 0.15 PV due to wettability alteration from strong liquid-wetting to intermediate gas-wetting (see Fig.15), gas relative permeability increased from 0.05 to 0.5 due to 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 cm^3/min and for chalk it was 0.33 cm^3/min). 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 was calculated from gas production rates using material balance. The test was initiated with 100% gas saturated cores.

Figs. 17 shows the results for oil injectivity in Berea. The pressure drop quickly increased to about 7 psi, then decreased gradually to about 6 psi. Oil injection rate at the inlet of the untreated core varied from 0.5 to 0.9 cm^3/min, but at the inlet of the treated core varied from 3.0 to 3.5 cm^3/min. The ratio of oil injectivity in treated Berea and in untreated Berea was about 4 to 6. Oil injectivity data for chalk are shown in **Fig.18**. The pressure drop after breakthrough was about 43 psi. Oil injection rate in the treated core increased quickly and then gradually stabilized at about 0.28 cm^3/min; oil injection rate in untreated core was initially higher due to strong effect of capillary pressure, but it decreased quickly and then gradually stabilized at about 0.05 cm^3/min. The ratio of oil injectivity in treated core to untreated core was about 6.

This simple test firmly establishes 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 the work in Refs. 6 and 9 have 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 experienced sharp drop in deliverability due to condensate dropout around the wellbore. In order to proceed with field application, the research work should advance along two main directions. In one direction, the effect of high temperature on wettability alteration to intermediate gas-wetting should be studied. In another direction, the search of other suitable polymers should continue. We have embarked upon the work on both directions; in future publications the results will be made available.

Nomenclature

A_e = effective sectional area, cm^2
C_{ad} = chemical adsorption, mg/g-rock
L = length, cm
K = coefficient, dimensionless
k = permeability, md
k_r = relative permeability, fraction
$OGIP$ = original gas in place, %
Δp = pressure drop, psi
P_c = capillary pressure, psi
PV = pore volume, cm^3
q_o = oil injection rate, cm^3/min
SLW = strong liquid-wetting
S_{wi} = initial water saturation, fraction of PV
t = time, min or day

Greek Letter

ϕ = porosity, fraction
μ = viscosity, cp
θ = contact angle, degree
σ = interfacial tension, dyne/cm

Subscripts

g = gas
o = oil
w = water

Acknowledgements

This work was supported by the US DOE grant DE-FG22-96BC14850 and the members of the Reservoir Engineering Research Institute (RERI). Their support is appreciated. We thank Mr. R. Jahanian for his assistance in the experimental work.

References

1. Fussell, D.D., “Single-Well Performance Predications for Gas Condesnate Reservoirs,” JPT, (July, 1973), pp. 860-870.
2. Bamum, R.S., Brinkman, F.P., Richardson, T.W., and Spillete, A.G., “Gas Condensate Reservoir Behavior: Productivity and Recovery Reduction Due to Condensation," paper SPE 30767, presented at the 1995 Annual Technical Conference and Exhibition, Dallas, TX, Oct. 22-25.
3. Hinchman, S.B. and Barree, R.D., “Productivity Loss in Gas Condensate Reservoirs,” paper SPE 14204 presented at the 60th Annual Technical Conference and Exhibition of SPE, Las Vegas, NV, Sept 22-25, 1985.
4. El-Banbi, A., McCain W.D., Semmelbeck, M.E., “Investigation of Well Productivity in Gas-Condensate Reservoirs,” paper SPE 59773 presented at the 2000 SPE/CERI Gas Technology Symposium, Calgary, Canada, 3-5 April 2000.
5. Boom, W., Wit, K., Zeelenberg, J.P.W., Weeda, H.C., and Maas, J.G., “On the Use of Model Experiments for Assessing Improved Gas-Condensate Mobility Under Near-Wellbore Flow Condition,” paper SPE 36714 presented at 1996 SPE Annual Technical Conference and Exhibition, Denver, CO., 6-9, Oct., 1996.
6. Li, K. and Firoozabadi, A., “Phenonenological Modeling of Critical Condensate Saturation and Relative Permeabilities in Gas Condensate Systems,” SPEJ (June, 2000),
7. Ali, J.K Butler, S., Allen, L., and Wardle, P., “The Influence of Interfacial Tension on Liquid Mobility in Gas Condensate Systems,” paper SPE 26783 presented at the Offshore European Conference, Aberdeen, 7-10, Sept., 1993.
8. Ahmed, T., Evans, J., Kwan, R., and Vivian, T., “Wellbore Liquid Blockage in Gas-Condensate Reservoirs,” paper SPE 51050 presented at the1998 SPE Eastern Regional Meeting, Pittsburgh, PA., 9-11 Nov., 1998.
9. Li, K. and Firoozabadi, A. “Experimental Study of Wettability Alteration to Preferential Gas-Wetting in Porous Media and Its Effects,” SPE Reservoir Evaluation and Engineering, (April, 2000), pp.139-149.
10. Conway, M.W., Smith, K. and Thomas, T., “The Effect of Surface Active Agents on the Relative Permeability of Brine and Gas in Porous Media,” paper SPE 28982 presented at International Symposium on Oilfield Chemistry, San Antonio, TX. Feb. 14017, 1995.
11. Penny, G.S. Soliman M.Y.,Conway, M.W., and Briscore, J.E., “Enhanced Load Water-Recovery Technique Improves Stimulation Results,” paper SPE 12149 presented at the 58th Annual Technical Conference and Exhibition of SPE, San Francisco, CA., Oct. 5-8, 1983.
12. Linert, J.G., “A New Water-Soluble Fluoropolymer Silanol and Its Application in Stone and Concrete Protection,” paper presented at the 1997 Waterborne, High-Solids, and Powder Coating Symposium, Feb. 5-7, 1997.
13. Hirasaki, G.J. and Pope, G.A.. “Analysis of Factors Influencing Mobility and Adsorption in the Flow of Polymer Solution through Porous Media,” *SPEJ*. (April, 1974) pp. 337.
14. Tiab, D. and Donaldson, E.C., “Petrophysiscs: Reservoir Rock Properties”, Gulf Publishing Co., Houston, TX, 1996, pp.98-99

15. Anderson, W.G., "Wettability Literature Survey-Part 5: The Effects of Wettability on Relative Permeability," JPT (Nov., 1987), pp.1453-1468.
16. Chen, H.L., Wilson, S.D., and Monger-McClure, T.G., "Determination of Gas Condensate Relative Permeability on Whole Cores under Reservoir Conditions," SPEFE, (Feb., 1986), pp.
17. Henderson, G.D., Danesh, A., Tehrani, D.H., and Peden, J.M., "An Investigation into the Process Governing Flow and Recovery in Different Flow Regimes Present in Gas Condensate Reservoirs," paper SPE 26661 presented at the 1993 Annual Technical Conference and Exhibition, Houston, Texas, 3-6 Oct, 1993.
18. Heaviside, J. Brown, C.E., and Gamble, I.J.A., "Relative Permeability for Intermediate Wettability Reservoirs," paper SPE 16968 presented at the 62th Annual Technical Conference and Exhibition of SPE, Dallas, TX, Sep. 27-30, 1987.
19. Tang, G. and Firoozabadi, A. "Effect of Viscous Forces and Initial Water Saturation on Water Injection in Water-Wet and Mixed-Wet Fractured Porous Media," paper SPE 59291 presented at the DOE/SPE Improved Oil Recovery Symposium, Tulsa, OK. 2-5 April, 2000.
20. Narahara, G.M., Pozzl Jr., A.L. and Blackshear Jr., T.H., "Effect of Connate Water on Gas/Oil Relative Permeabilities for Water-Wet and Mixed-Wet Berea Rock," paper SPE 20503 presented at 65th Annual Technical Conference and Exhibition of SPE, New Orleans, L.A., Sept., 23-26, 1990.

Table-1 Core Properties and Chemical Treatment Data

Core	k md	ϕ %	L cm	S_{wi} PV	Chem. Treatment	C_{ad} mg/g -rock	θ_p deg.
B-1	507	21.5	6.05	0	no	0	0
B-2[b]	522	21.9	6.1	0	2% FC-722	4.6	90
B-3	511	22.1	6.2	0	no	0	0
B-4	503	22.2	6.0	0	2% FC-722	2.4	90
B-5	495	21.7	6.3	0	2% FC-722	2.2	90
B-6	552	21.7	5.5	0	8% FC-759	6.0	90
B-9	341	20.1	18	0	no	0	0
B-10[b]	343	20.0	17.9	0	2% FC-722	4.5	-
B-11[b]	339	20.1	18.0	0	5% FC-759	10.3	-
B-12	501	22.1	6.3	0	8% FC-759	6.1	90
B-13	489	22.0	6.5	0	8% FC-759	6.0	90
B-14	513	21.9	6.2	0	8% FC-759	5.9	90
B-15[a]	487	20.9	6.1	9.8	8% FC-759	5.7	-
B-16[a]	495	21.3	5.9	16.2	8% FC-759	5.0	-
B-17[a]	503	21.5	6.3	8.5	8% FC-759	6.3	-
B-18[a]	483	20.5	6.8	16.5	8% FC-759	5.2	-
C-1	1.34	31.1	5.6	0	no	0	0
C-2	1.32	32.0	5.9	0	2% FC-722	2.5	90
C-3	1.30	31.7	5.7	0	2% FC-722	2.8	90
C-5	1.34	32.0	5.5	0	8% FC-759	0.9	90
C-6	1.33	31.8	18.1	0	no	0	0
C-7	1.31	32.2	18.0	0	2% FC-722	2.7	90
C-8	1.28	32.0	17.9	0	8% FC-759	1.0	-
C-11[b]	1.33	32.0	5.9	0	5% FC-759	1.6	-
C-12[b]	1.33	32.1	6.1	0	5% FC-759	1.4	-
C-14	1.28	31.6	5.8	0	8% FC-759	0.8	90
C-15	1.30	31.9	5.5	11.7	8% FC-759	0.9	-

Diameter of the core was 2.54 cm for Berea and 2.2 cm for chalk.
[a] core was aged with S_{wi} at T=90°C without drying
[b] core was treated twice

Table-2 Properties of Chemicals

Chemical	FC-722	FC-759
MW	10^5	10^5
Concentration, %	2	5-8
Viscosity, cp at 25°C	1	3.3
Specific gravity	1.8	1.1
Boiling point, °C	59	100
Color	clear	light-yellow
VOC, %	-	<0.1

Appendix: Expression for Pseudo-Contact Angle

For a capillary tube with a diameter of r, capillary pressure, P_c, between air and invading liquid can be expressed as:

$$P_c = \frac{2\sigma \cos\theta}{r} \qquad \text{(A-1)}$$

where σ is interfacial tension between air and invading liquid, and θ is the liquid-solid-air contact angle. Using the Poiseuille equation, liquid flow rate in a capillary tubing can be expressed as:

$$q = \frac{\pi r^4 \Delta p}{8\mu l} \qquad \text{(A-2)}$$

where q is liquid flow rate, l length, and Δp 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, liquid advancing rate in the tube can be expressed as:

$$q = \frac{dl}{dt} = \frac{\pi r^3 \sigma \cos\theta}{4\mu l} \qquad \text{(A-3)}$$

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

$$l^2 = \frac{\pi r^3 \sigma \cos\theta}{2\mu} t \qquad \text{(A-4)}$$

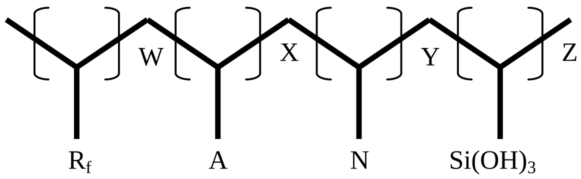
Let A denote the cross-section area of the tube and V the liquid volume at time t, then $l=V/A$, Substituting $l=V/A$ into Eq.A-4, the volume of the advancing liquid into the pore space of the tube is given by:

$$V^2 = \frac{\sigma r A^3 \cos\theta}{2\mu} t \qquad \text{(A-5)}$$

Eq.A-5 shows that a plot of V^2 vs. t would give a straight line provided the interfacial tension between liquid and air, the viscosity of liquid, and 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-section area of the rock, A_e, 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:

$$V^2=\sqrt{\frac{8k}{\phi}}\frac{\sigma A_e^3\cos\theta_p}{2\mu}t \qquad \text{(A-6)}$$

Note that θ_p is the pseudo-contact angle in porous media.



R_f -Flourochemical, A -Anionic group, N -Nonionic group, W≠X≠Y≠Z

Fig.1–Chemical Structure of FC-759 (Ref.12)

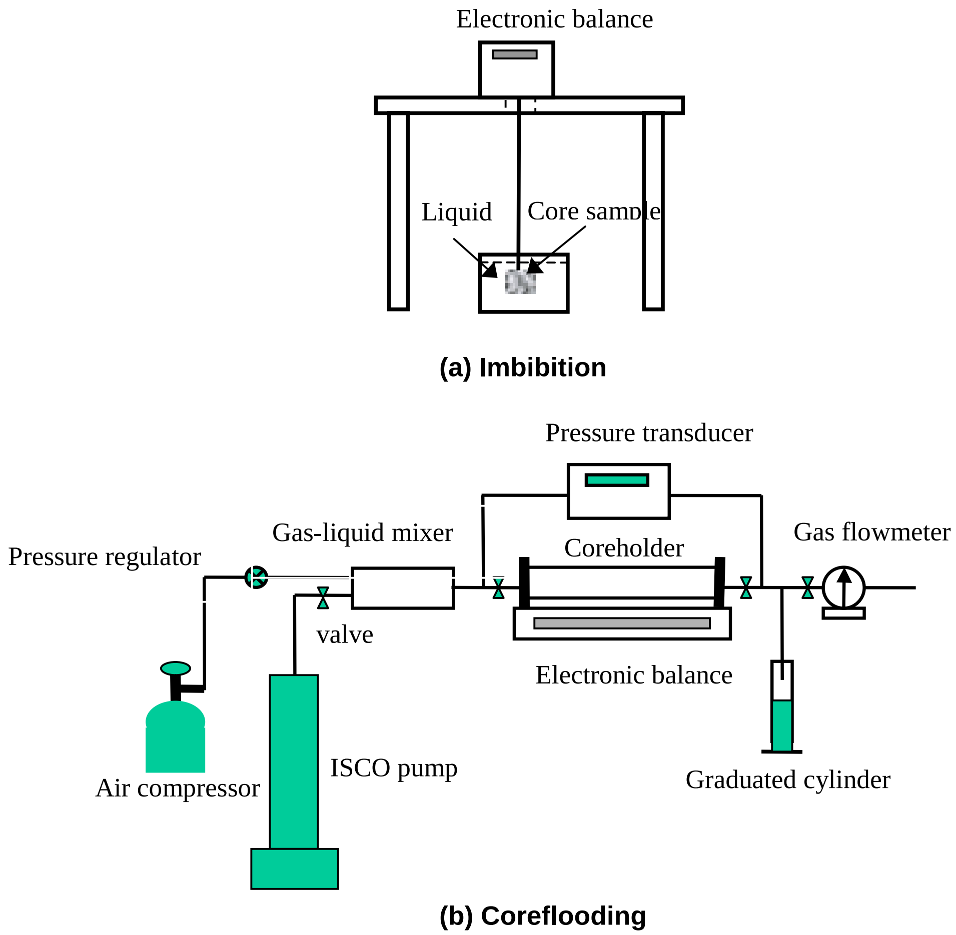


Fig.2–Schematic of the Apparatus for Imbibition and Coreflooding

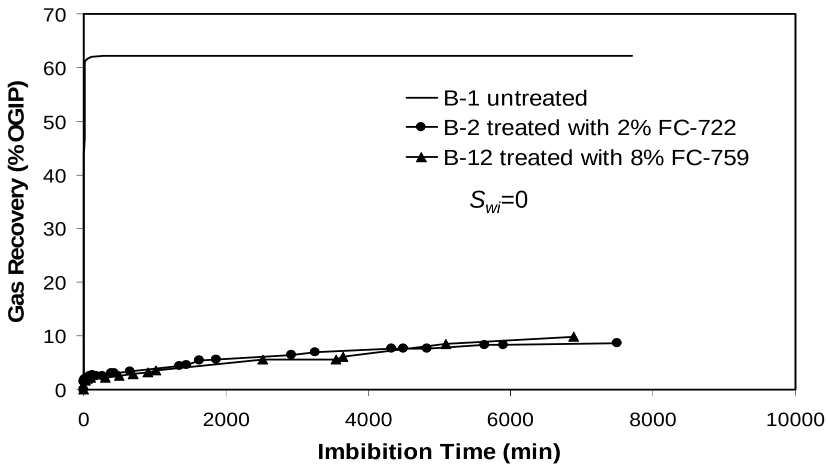


Fig.3–Gas Recovery by Spontaneous Oil Imbibition for Treated and Untreated Berea

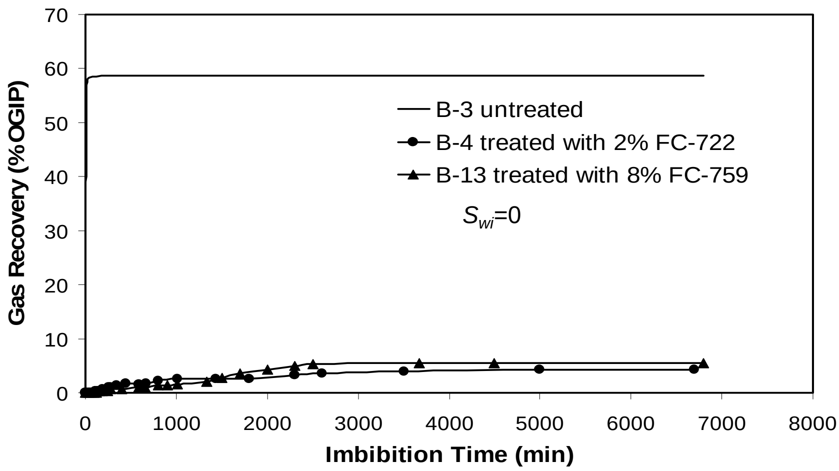


Fig.4–Gas Recovery by Spontaneous Water Imbibition for Treated and Untreated Berea

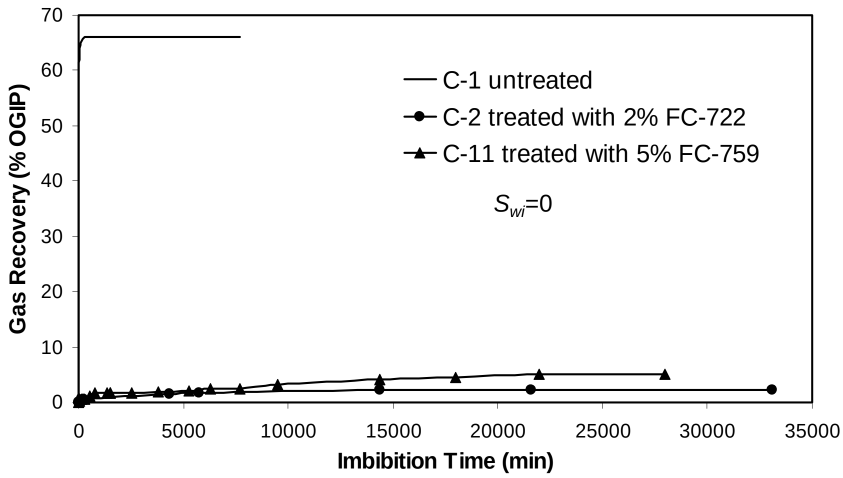


Fig.5–Gas Recovery by Spontaneous Oil Imbibition for Treated and Untreated Chalk

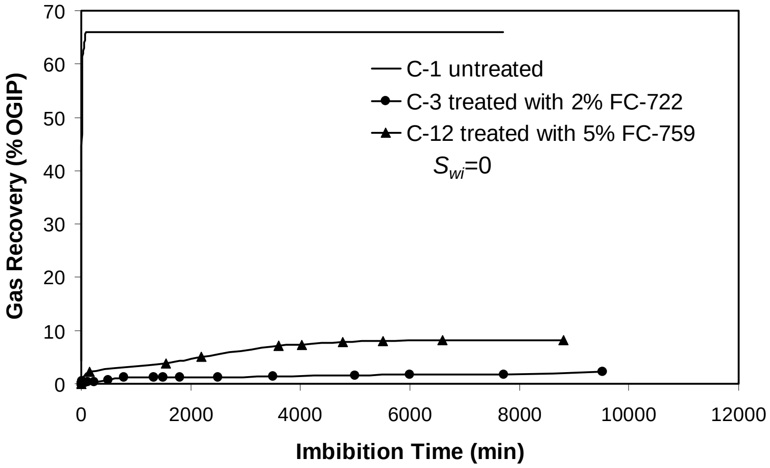


Fig.6–Gas Recovery by Spontaneous Water Imbibition for Treated and Untreated Chalk

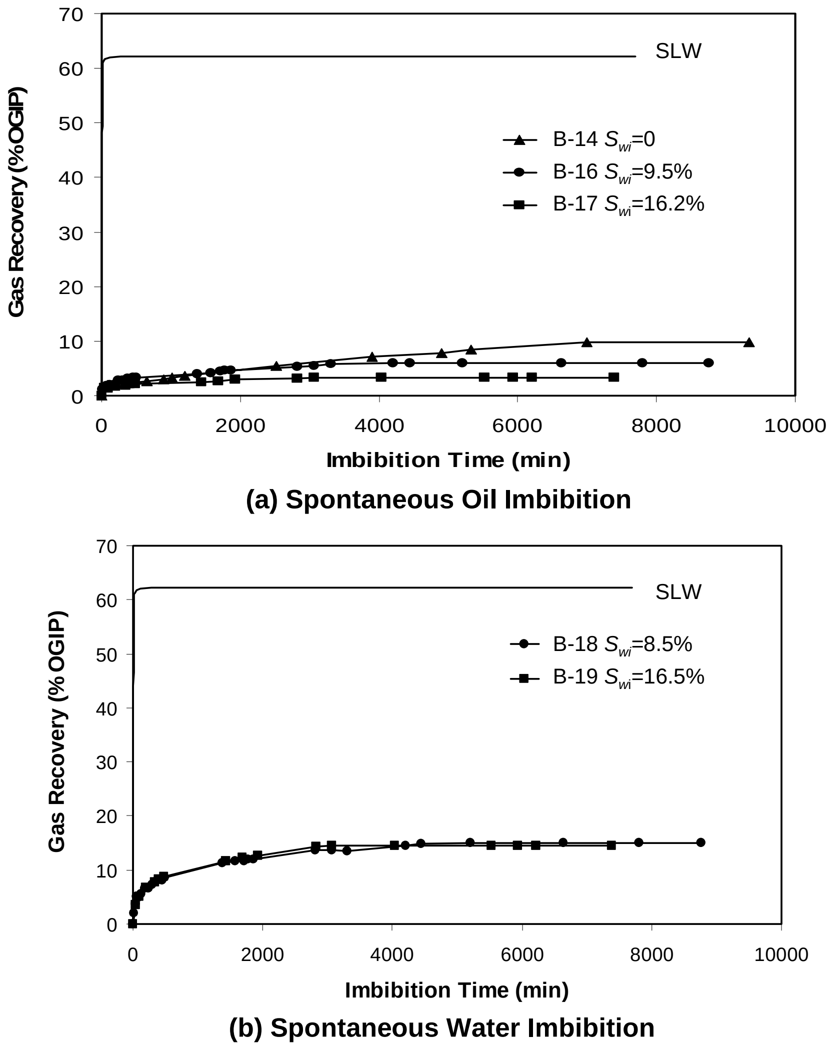


Fig.7–Effect of S_{wi} on Wettability Alteration of Berea by 8% FC-759

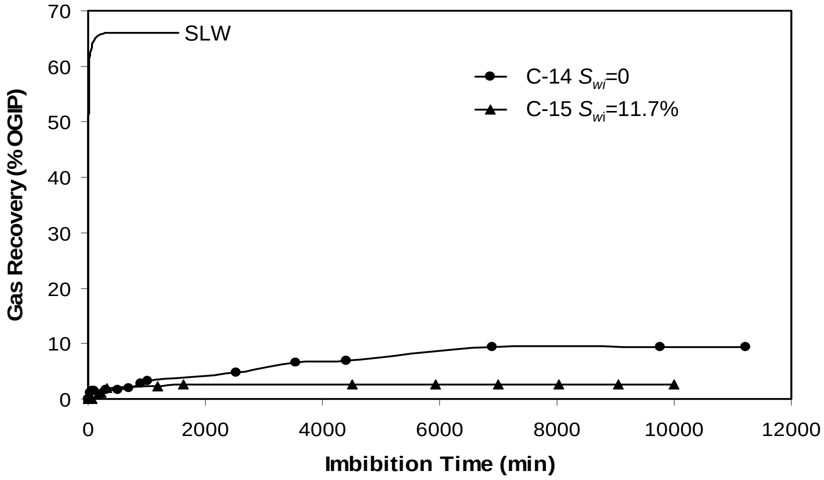
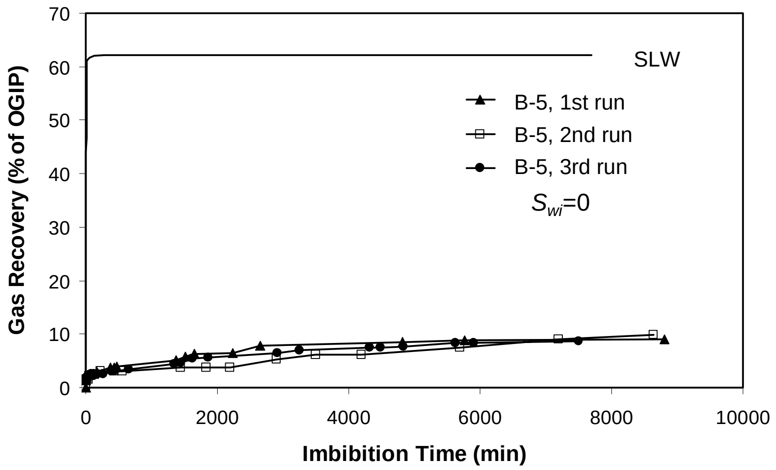
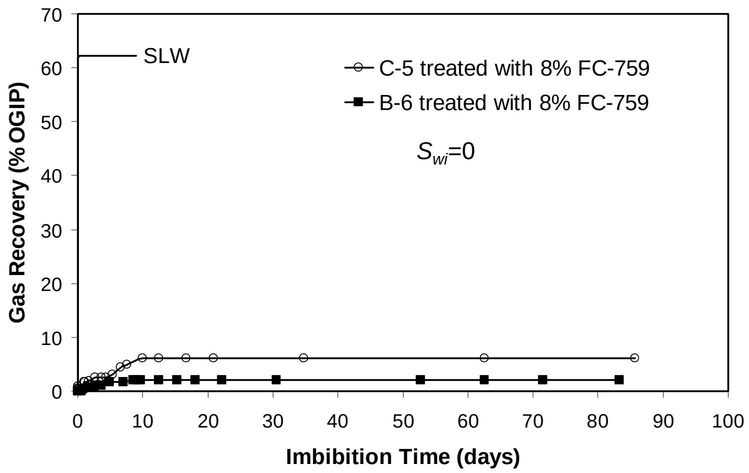


Fig.8–Effect of S_{wi} on Wettability Alteration of Chalk by 8% FC-759: Spontaneous Oil Imbibition



(a) Repeated Spontaneous Oil Imbibition



(b) Long-Term Spontaneous Oil Imbibition

Fig.9–Stability Testing for Treated Berea and Chalk

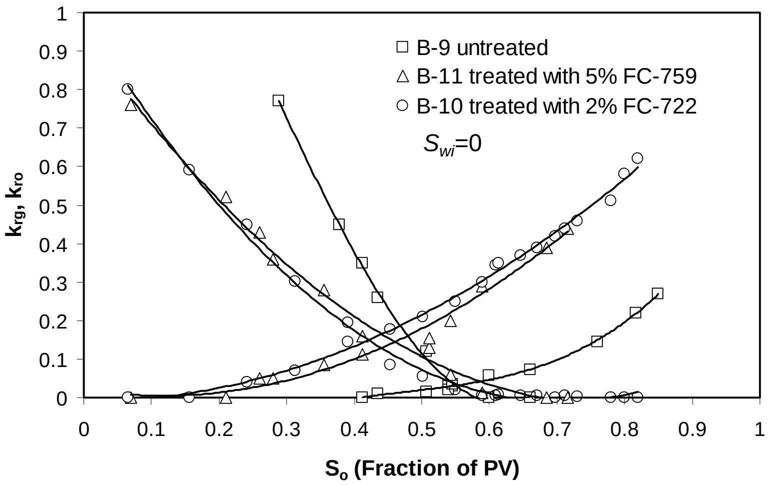


Fig.10–Gas and Oil Relative Permeabilities for Treated and Untreated Berea

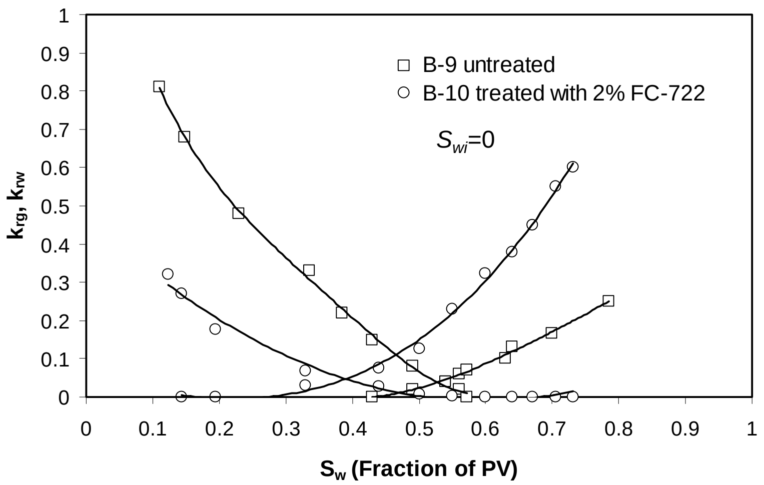


Fig.11–Gas and Water Relative Permeabilities for Treated and Untreated Berea

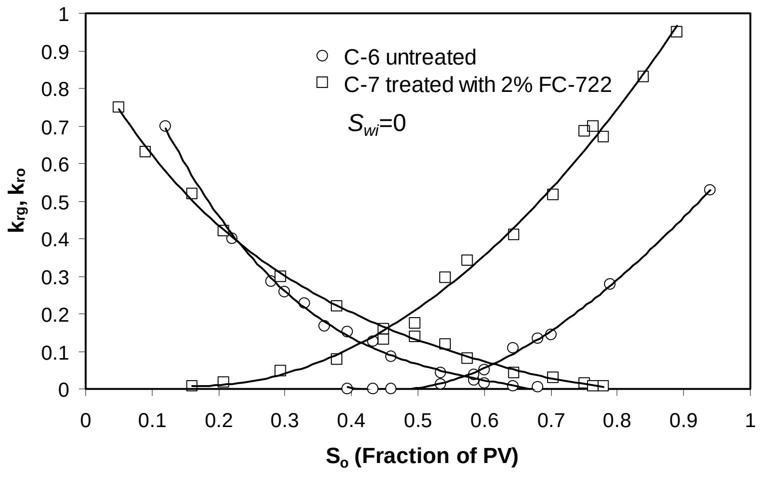
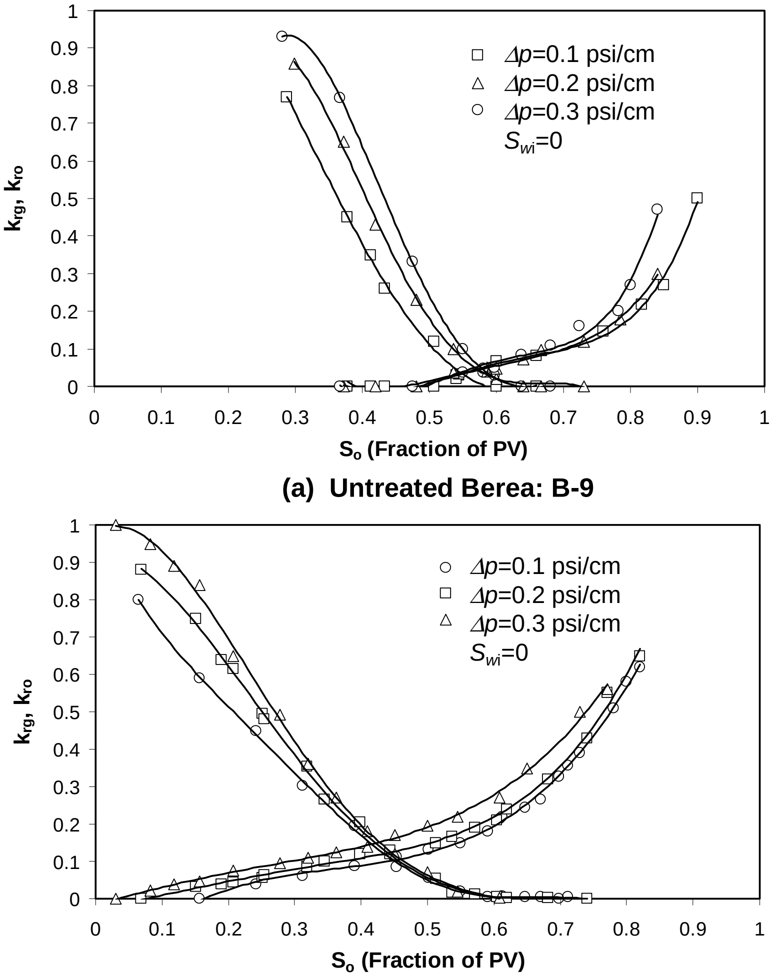
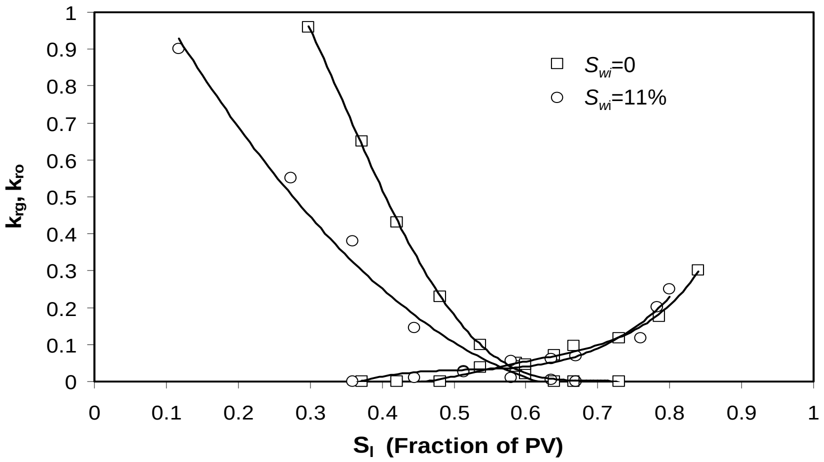


Fig.12–Gas and Oil Relative Permeabilities for Treated and Untreated Chalk

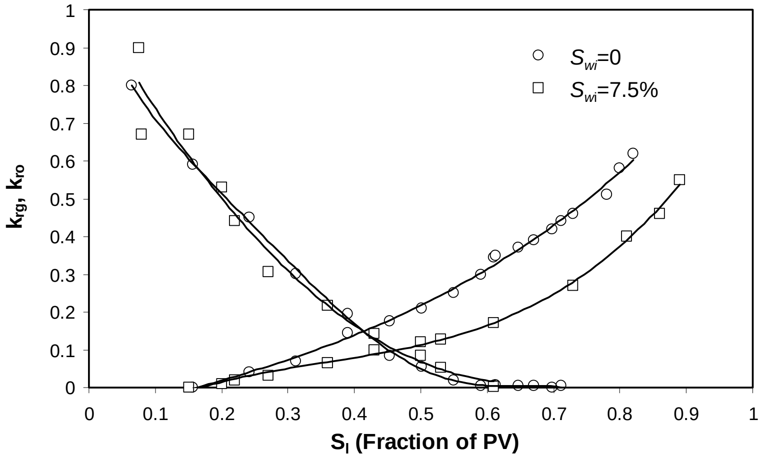


(b) Treated Berea: B-10

Fig.13–Effect of Viscous Forces on Gas and Oil Relative Permeabilities for Treated and Untreated Berea with 2% FC-722

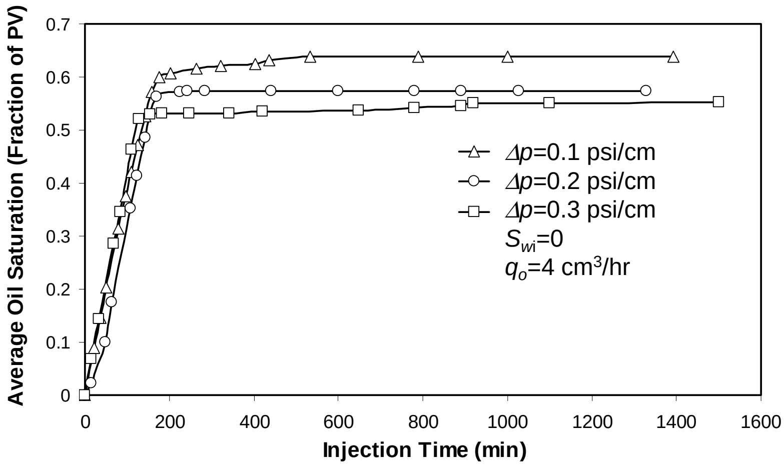


(a) Untreated Berea: B-9

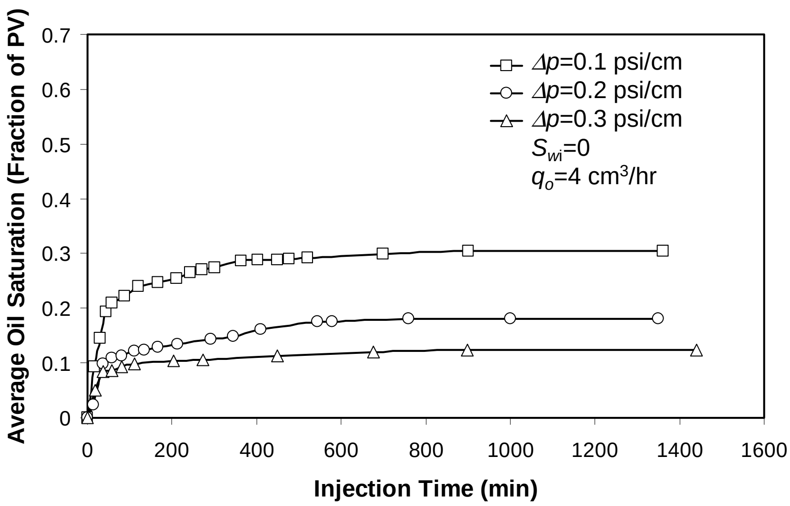


(b) Treated Berea: B-10

Fig.14–Effect of S_{wi} on Gas and Oil Relative Permeabilities for Treated and Untreated Berea



(a) Untreated Berea: B-9



(b) Treated Berea: B-10

Fig.15–Effect of Viscous Forces on Oil Accumulation for Treated and Untreated Berea

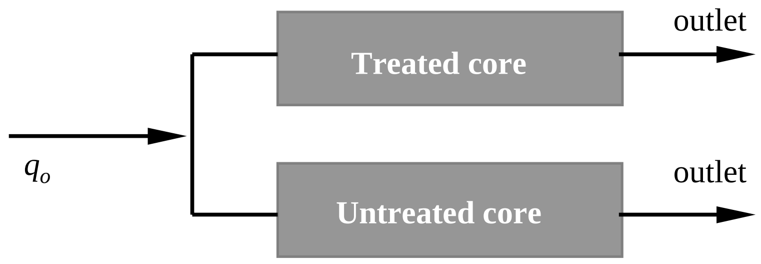


Fig.16–Schematic of Oil Injectivity Tests

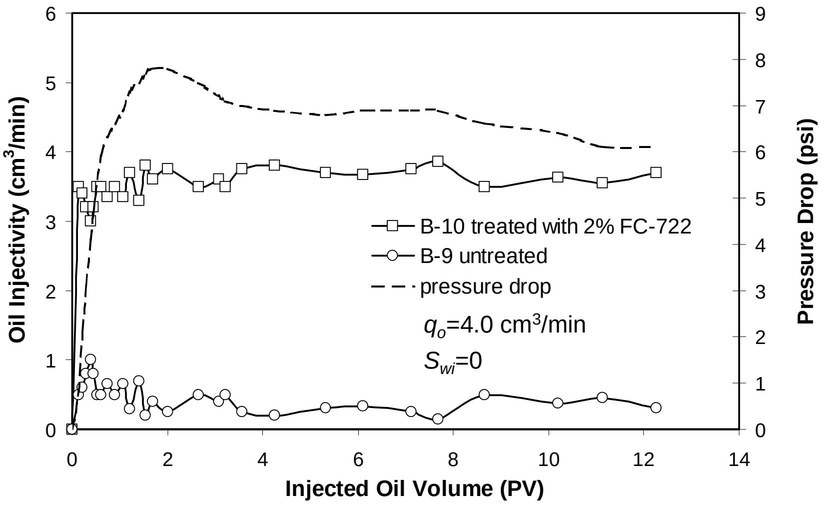


Fig.17–Effect of Wettability on Oil Injectivity in Treated and Untreated Berea

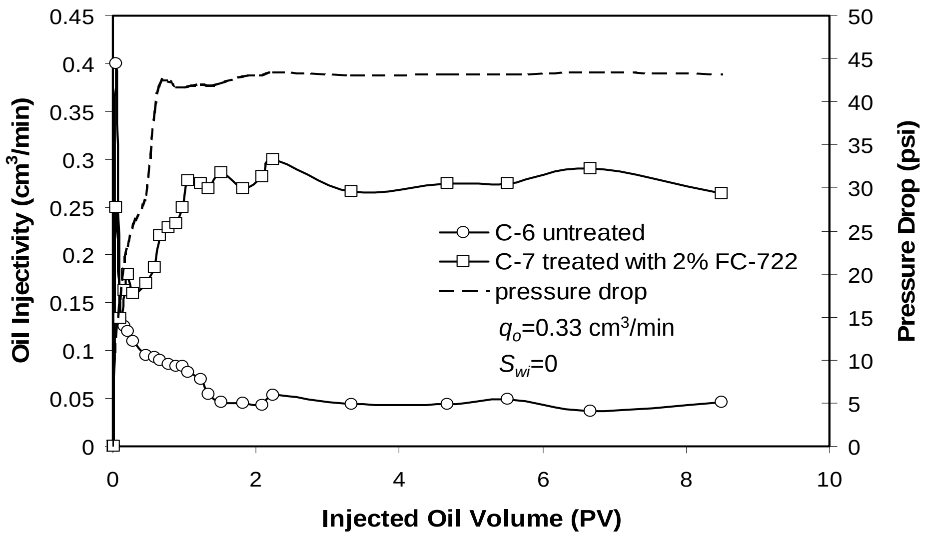


Fig.18–Effect of Wettability on Oil Injectivity in Treated and Untreated Chalk