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Permanent Alteration of Porous Media Wettability from Liquid-Wetting to Intermediate Gas-Wetting

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Abstract Wettability of Berea and low permeability reservoir rocks are permanently altered from liquid-wetting to intermediate gas-wetting. We use water and decane as model liquid, and air and nitrogen as model gas in the experiments. New chemicals with various functional groups are used in the wettability alteration. We perform compositional analyses of the treated chemical solutions extracted from rock treatment by gas chromatography–mass spectrometry (GCMS) and by inductively coupled plasma-mass spectrometry (ICPMS). The analyses demonstrate reaction between the chemicals and the rock substrate. There is no measurable change in permeability from the chemical reaction for the low molecular weight chemicals. The results reveal the permanent alteration of wettability. Tests are conducted to measure contact angle, spontaneous imbibition, and flow to assess the effect of wettability alteration on flow performance as a function of chemical concentration and functionality. For Berea, the contact angle for the water–air–rock is altered from 0° to $\sim$150° depending on the chemical concentration. For the reservoir rock, the contact angle is altered from $\sim$70° to $\sim$130°. As a result of the treatment, the water flow rate may increase two and a half times for a given pressure drop in the Berea. The permanent alteration of wettability with the new chemicals is intended for prevention of water blocking in gas production from tight reservoirs. Instead of hydraulic fracturing when water is introduced in formations with most of the water retained by the water-wet rocks, one may use the new chemical surfactants in fracturing to avoid water retention for high gas well productivity.

Keywords Wettability · Porous media · Rock · Chemical treatment · Contact angle · Imbibition

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1 Introduction

A large amount of natural gas, the premium fuel of the twenty-first century is found in tight formations. Hydraulic fracturing is applied in these formations to increase permeability. Injection of water, however, may result in its retention in the permeable media around the wellbore due to water-wetting (Engineer 1985; Cimolai et al. 1993) leading to water blocking and lowering of gas permeability in the rock matrix. The clean-up of water accumulation from the formation after fracturing will increase gas well productivity. Water is removed in two stages, immiscible displacement by gas, followed by slow vaporization (Mahadevan and Sharma 2003).

A reduction in gas well deliverability is also encountered in many gas-condensate reservoirs due to condensate accumulation (Hinchman and Barree 1985; Afidick et al. 1994). As the pressure drops below the dew-point pressure, condensate accumulates at the wellbore in high saturations and reduces gas relative permeability (Barnum et al. 1995; El-Banbi et al. 2000). The injection of a volatile solvent such as an alcohol has been implemented to remove the accumulated liquid (Ahmed et al. 1998; Du et al. 2000; Walker et al. 2000; Al-Anazi et al. 2005b) at the wellbore to increase gas well deliverability. In a methanol stimulation treatment in Hatter's Pond field in Alabama (Al-Anazi 2005a) where there was an initial decline in well deliverability by a factor of three to five due to condensate blocking, gas deliverability increased by a factor of two after dissolving water and condensate liquids in methanol in the wellbore region. The increased rate was, however, only sustained for a period of four months. There may be also a short term effect from temporary wettability alteration. A permanent solution is a much more attractive approach.

A major factor in liquid accumulation is the liquid's low mobility due to strong liquid-wetting (Anderson 1987). By altering the wettability of the rock from liquid-wetting to intermediate gas-wetting, an increase in liquid mobility can be achieved, preventing the accumulation of liquid in high saturations, and resulting in a high rate of gas production. In 2000, we suggested the alteration of wettability by the chemical treatment from liquid-wetting to intermediate gas-wetting (Li and Firoozabadi 2000). The idea was demonstrated by contact angle measurement, and imbibition testing on cores treated with fluorochemicals at room temperature. Later it was shown that at higher temperatures the effectiveness of chemical treatment may diminish (Fahes and Firoozabadi 2007; Panga et al. 2007; Al-Anazi et al. 2007), and the treatment and flow testing were carried out at high temperature and high pressure. Tang and Firoozabadi (2002, 2003) performed the wettability alteration and showed the increase in liquid mobility at a temperature of 90°C. At 140°C and 1.5×10^6 Pa (200 psig), Fahes and Firoozabadi (2007) established the permanency of wettability alteration by testing reproducibility; Noh and Firoozabadi (2008b) examined the effect of wettability alteration in two-phase nitrogen-water flow.

Following the study of our group, there have been a number of experimental studies by others on wettability alteration to intermediate gas-wetting (Kumar et al. 2006; Liu et al. 2006; Panga et al. 2006) at various treatment conditions (Al-Anazi et al. 2007). Liu et al. (2006) showed that the relative permeability of both gas and the water increases with the altered wettability in a core of low permeability (0.1 md). Panga et al. (2007) reported that the chemical-treated cores give higher clean-up of trapped water when gas is used to displace the brine. Kumar et al. (2006) also reported improvement in gas and condensate relative permeability when reservoir cores were treated with fluorochemicals. To improve the effectiveness of wettability alteration, a key is understanding of the interactions between chemicals and rocks. The treatment efficiency can be optimized by varying treatment procedure (chemical injection volume, aging time, pre- or post-treatment process) and treatment solutions (chemical species, concentration, solvent) to have maximum liquid mobility. Al-Anazi et al. (2007) performed the analysis of the treated cores using an environmental scanning electron microscope (ESEM) and gave an evidence of wettability alteration at the pore scale. Paktinat et al. (2006) demonstrated that the use of microemulsion fluids in hydraulic fracturing gives higher water recovery when compared with conventional surfactant treatments. The oil-in-water microemulsion, composed of oil inside swollen micelles in aqueous solutions, are characterized by drop sizes of 10–20 nm and ultra low oil-water interfacial tensions of 10^{-3} to 10^{-6} mN/m. Adibhatla et al. (2006) found that the rocks become less water-wet as the number of fluoro groups in fluorosilanes increases. Alcohols are often used as the solvent for chemical solutions, in addition to water (Panga et al. 2006, 2007). Fahes and Firoozabadi (2007) and Al-Anazi et al. (2007) used ethanol solvent; Kumar et al. (2006) used methanol-water solvent. The treatment with pure alcohol is not permanent (Al-Anazi et al. 2005b; Du et al. 2000) and the treatment is less effective than the chemical surfactants (Noh and Firooaabadi 2008a).

With the above introduction and review we are now set to define the goal of this study. One of our objectives is definite establishment of treatment permanency. The other objectives are the examination of the effect of chemical concentration, and to evaluate/quantify the treatment efficiency through a series of systematic experiments. In this study, we use iso-propanol as the solvent. Iso-propanol has a low vapor pressure and can be safe in practical applications. It also reduces the surface tension more effectively than methanol when dissolved in water. We analyze the chemical solutions to establish the reaction between the chemicals and the rock.

This article is organized along the following lines. In Sect. 2, we describe the rocks, fluids, and chemicals used in the experiments. The experimental methods of treatment process and core evaluation testing (contact angle, imbibitions, and fluid flow) are then discussed. We briefly discuss the calculation of flow parameters in Sect. 3. In Sect. 4, we provide the experimental results and compare the analysis of chemical solutions before and after treatment to establish the permanency of wettability alteration. We discuss the results from flow testing, chemical treatment and the measurements from contact angle and liquid imbibition in Sect. 5. Our results are also compared with those in the literature. In the end, we draw conclusions.

2 Experimental

Experiments are carried out using Berea and low permeability reservoir cores. The treatment is carried out by injecting chemical solution into the cores and aging at high temperature and high pressure. The wettability alteration of cores is evaluated by measurement of contact angle and imbibition testing. The gas mobility is obtained from single-phase gas flow; while the liquid mobility is examined by flow in two-phase-gas–liquid state. The experiments include: (1) tests in the untreated cores, (2) chemical treatment and analysis, and (3) tests in the treated cores. The cores are oven dried before all the tests (contact angle, imbibition, gas and liquid flow).

2.1 Materials

2.1.1 Cores and Fluids

Two types of sandstone cores are used: the Berea cores from Cleveland Quarries (Amherst, OH) and the reservoir cores from the subsurface from the Middle East. The Berea and

Table 1 Relevant data of the cores

Core type	Designation	D (cm)	L (cm)	W (g)	ϕ
Berea	BYR	2.58	15.1	163.93	0.224
	B1	2.58	15.1	153.56	0.220
	B2	2.52	14.9	151.69	0.205
	B3	2.52	14.8	149.49	0.205
	B4	2.42	14.5	134.53	0.224
	B5	2.41	14.7	133.90	0.224
	B6	2.39	14.7	131.89	0.224
	B7	2.45	14.6	138.27	0.224
	B8	2.43	14.6	135.35	0.224
	B9	2.43	14.4	133.95	0.224
	B10	2.43	14.3	128.88	0.224
	B11	2.43	14.1	131.14	0.214
	B12	2.42	12.8	118.95	0.217
	B13	2.44	14.2	132.09	0.217
	B14	2.45	14.4	136.94	0.222
	B15	2.45	14.6	138.27	0.225
	B16	2.45	14.1	134.35	0.221
	B17	2.45	14.7	139.87	0.224
	B18	2.45	14.1	134.90	0.222
Reservoir	R1	2.48	9.72	105.50	0.131
	R2	2.48	9.75	106.04	0.134
	R3	2.48	10.48	118.52	0.111
	R4	2.48	10.44	118.56	0.105
	R5	2.48	10.45	117.16	0.109

reservoir cores have the same diameter D of ~2.5 cm, while the length L of Berea (~15 cm) is about 1.5 times that of the reservoir core (~10 cm). The porosity ϕ of Berea (0.21–0.22) is about twice that of the reservoir core (0.11–0.13). The permeability of Berea (600–1000 mD) is two orders of magnitude greater than that of the reservoir core (2–6 mD). The low permeablity of reservoir core may be due to its complex pore structure. The sandstone particle density calculated from porosity and bulk density is ~2.57 and ~2.61 g/cm^3 for Berea and reservoir core, respectively. Table 1 shows the relevant data of the cores used in this study. Prior to the experiments, the cores are cleaned by rinse and injection of water, followed by drying in the oven.

Air is the gas phase in contact angle measurements and imbibition testing at room temperature. Nitrogen is used in the single-phase gas flow and two-phase gas–liquid flow at high-temperature–high-pressure. The model liquid is either water or normal decane (oil). Normal decane (nC_{10}) has 0.73 specific gravity and 0.929 cp viscosity at 20°C (Yaws 1999). We have limited measurements with normal decane which represents the liquid condensate phase. Based on various measurements normal decane and liquid condensate have similar flow behavior from wettability alteration.

Table 2 Properties of the chemicals

Sample designation	Z	A	B	C	D
Polymer concentration [wt%]	30	29	26	17	30
Approximate Molecular weight [g/mol]	10^5	10^4	10^4	10^3	10^3
pH (1 wt% in IPA, 20°C)	6.02	6.12	5.60	4.66	6.24
Refractive index (1 wt% in IPA, 20°C)	1.3775	1.3774	1.3779	1.3774	1.3780
Density [g/cm^3] (1 wt% in IPA, 20°C)	0.780	0.785	0.790	0.774	0.774
Viscosity [cp] (1 wt% in IPA, 20°C)	2.34	2.32	2.35	2.40	2.38

2.1.2 Chemicals

The fluorinated polymeric chemicals produced by DuPont Company (Wilmington, DE) are used in the alteration of wettability of the cores. The wettability is altered from liquid-wetting to gas-wetting. The chemical molecules are composed of various functional groups with the ability to adsorb onto the core surface; repel water and oil phases. The water and oil repellency is provided by the fluoro and/or silane group. The ionic and/or silanol groups chemically bond onto core surfaces, providing a durable treatment (Tang and Firoozabadi 2002). The ionic and/or nonionic functional groups make the polymer soluble in the solution (Linert 1997).

Table 2 lists the pH, refractive index, density, and viscosity of various chemicals (1 wt% in isopropanol (IPA), 20°C). Sample Z (Zonyl® 8740, Lot 201) is commercially available through DuPont and the Sample A, B, C, D (TLF 10198, 10205, 10307, 10308) are in the R&D stage. Samples Z, A, B, and D are the cationic perfluoroalkyl methacrylic copolymer. These compounds contain a small amount of acetic acid added during the manufacturing process. Sample C is a fluorinated siloxane fluid. The chemical liquid before dilution consists of the polymer dispersed in water, with the polymer concentration of 17 to 30 wt%. The molecular weight of chemicals ranges from 10^3 to 10^5 g mol^{-1}. We dissolve the chemical liquid in IPA to a dilution of 1–5 wt%, which corresponds to polymer concentration of 0.17–1.5 wt%. IPA has a flash point of 12°C, close to that of methanol (11°C) and ethanol (13°C).

2.2 Experimental Methods

2.2.1 Contact Angle Measurements

We use a pipette to place a liquid drop of water or nC_{10} of ~50 mm^{3}on the surface of the air-saturated (dry) core at ~20°C. The configuration of a sessile liquid drop on the core surface is magnified on a monitor screen. We take snapshots of the drop image by a digital camera under proper illumination of light source. The air–liquid-rock three-phase-contact angle is measured through the liquid phase using the goniometry tool of the software Image-Pro Express 6.0. The liquid drop of water or nC_{10} imbibes instantly into the liquid-wetting untreated Berea, indicating a contact angle of $\sim 0°$. As the Berea wettability is altered by chemical treatment to liquid-non-wetting (gas-wetting), the water contact angle, θ_w, increases to 130°–150° and nC_{10} contact angle, θ_o, increases to 30°–70° in some test cores.

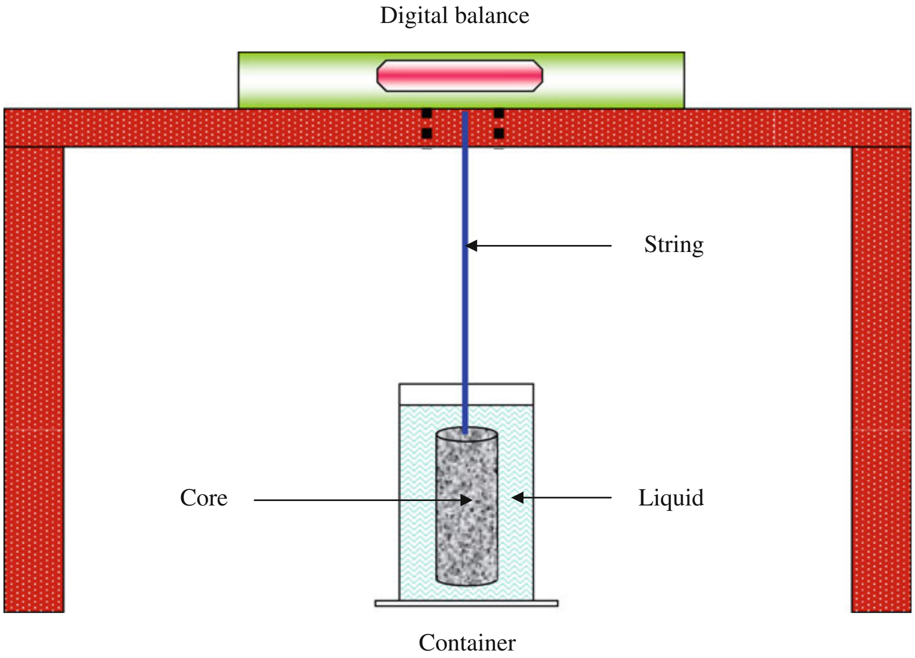

Fig. 1 Experimental setup for spontaneous imbibition testing

2.2.2 Spontaneous Imbibition Test

Spontaneous water imbibition into the air-saturated cores is monitored at ∼20°C. It is performed by immersing the air-saturated (dry) core in water while hanging under an electronic balance as shown in Fig. 1. The dynamic process of water imbibition into the core is studied by recording the core weight gain with time. The water saturation is calculated as the ratio of the amount of water imbibed into the core to the core pore volume (PV). We evaluate the effect of wettability alteration by comparing the water saturation versus time before and after treatment. The imbibition rate decreases as the wettability is altered from water-wetting to non-wetting.

2.2.3 Fluid Flow Test

We conduct fluid flow tests to evaluate the effect of wettability alteration. Figure 2 shows the setup. The core is placed inside the core holder. We apply an overburden pressure of 7.0×10^3 kPa (1000 psig) by a syringe pump. The temperature of the system is maintained by a universal oven. Nitrogen gas is injected from the compressed nitrogen cylinder or liquid water from the inlet pump. The inlet pressure and pressure drop are measured by pressure transducers, with the accuracy of ∼1.4 kPa (0.2 psia) after calibration by a hydraulic deadweight tester. We use a back pressure regulator to adjust the pressure drop, while measuring the gas flow rate by a flow meter in the range of 1–80 cm^3/s with the accuracy of about 0.5%. The liquid flow rate is fixed using the inlet pump while maintaining the outlet pressure by the receiver pump.

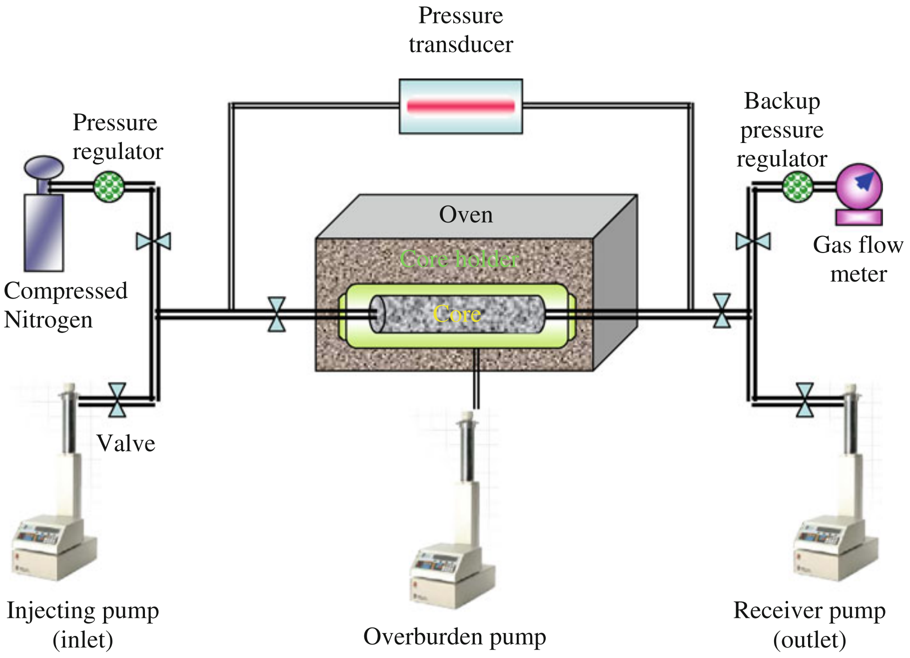

Fig. 2 Experimental setup for fluid flow testing and chemical treatment

In single-phase gas flow, the inlet and outlet pressures at various gas flow rates are recorded at the steady state. In the two-phase flow when liquid displaces gas, the liquid is injected at a fixed flow rate into the gas-saturated core. The transient pressure drop is recorded until the steady state is reached.

2.2.4 Chemical Treatment

After conducting the above evaluation testing in an untreated core, we proceed to the wettability alteration experiments. The wettability of the core is altered by chemical treatment at 140°C and 1.5×10^3 kPa (200 psig). The temperature is high enough for most reservoir applications; the pressure is chosen to avoid vaporization of water and liquid hydrocarbons (Fahes and Firoozabadi 2007). The experimental setup for treatment is similar to that for water injection test in Fig. 2. The chemical solution of 5 PV is injected in the nitrogen-saturated core, followed by aging overnight of ∼15 h. About 20 PV of water is then injected to displace the chemical solution and wash the core. The injection of chemical solution or washing water is carried out at a flow rate of $4\,\text{cm}^3/\text{min}$ in Berea and $0.12\,\text{cm}^3/\text{min}$ in the reservoir core, reflecting the difference of permeability of the two types of rocks. Then, we inject nitrogen (∼30 PV) to drain the water from the core at $\Delta p \sim 6.9 \times 10$ kPa (10 psi) for Berea, and $\Delta p \sim 4.1 \times 10^2$ kPa (60 psi) for reservoir core. The purpose of water injection is to have an indication of durability of chemical treatment at high temperature through the examination of the contact angle. Finally, the core is taken out of the core holder and oven dried to examine the effect of treatment (tests in the treated core).

2.2.5 Permanency of Treatment

The central theme of this study is the study of treatment permanency. We study the reaction between rocks and chemicals by comparing the analysis of chemical streams before they enter the rock (inflow) and after contact with the rock (outflow) in the 5-PV injection process. Qualitative analyses are also made by color change in core and solutions. We also measure the chemical adsorption from the gain in the core weight after treatment. The pH of chemical solutions is measured by a pH meter after calibration by the pH buffer solutions. The reproducibility of the pH measurements for the aqueous solution is ~0.02 units. The refractive index, density, and viscosity of chemical solution are measured by refractometer, pycnometer (specific-gravity bottle, 2 cm^3), and viscometer, respectively. We analyze the composition of chemical solutions using gas chromatography–mass spectrometry (GCMS) and inductively coupled plasma-mass spectrometry (ICPMS). The analysis of the untreated chemical before entering the core is compared to the treated outflow from the core to characterize the rock-chemical reactions during treatment.

3 Flow Parameter Measurements

We examine fluid mobility in a core via single-phase gas flow, and liquid displacing the gas phase. The flow parameters of porous media with respect to gas (nitrogen) and liquid (water) are calculated by two theoretical equations. Applying the Forchheimer equation in the steady-state gas flow, we measure the gas absolute permeability and high-velocity coefficient. In the unsteady-state gas–liquid flow with gas displaced by liquid injection, the effective and relative permeability of liquid is calculated at the final steady state. We quantify the effectiveness of the wettability alteration from the change of fluid flow parameters after chemical treatment.

3.1 Forchheimer Equation in High-Velocity Gas Flow

We calculate the gas absolute permeability and high-velocity coefficient from flow measurements using the Forchheimer equation (Forchheimer 1901):

$$\frac{M_\mathrm{g}\left(p_1^2 - p_2^2\right)}{2\mu_\mathrm{g} ZRTLj_\mathrm{g}} = \frac{1}{k_\mathrm{g}} + \beta\frac{j_\mathrm{g}}{\mu_\mathrm{g}}, \tag{1}$$

where p_1 and p_2 are the inlet and outlet pressure; M_g, μ_g, and j_g are molecular weight, viscosity, and mass flux of the gas, respectively; R and Z are the gas constant and the gas deviation factor; T is temperature and L is the core length. The gas absolute permeability, k_g, and high-velocity coefficient, β, are determined from the intercept and slope in the plot of $M_\mathrm{g}\left(p_1^2 - p_2^2\right)/\left(2\mu_\mathrm{g} ZRTLj_\mathrm{g}\right)$ vs. $j_\mathrm{g}/\mu_\mathrm{g}$.

3.2 Darcy's Law in Liquid Flow

The liquid injection in a gas-saturated core is a transient two-phase gas–liquid flow testing in which the gas in the core is displaced by the liquid. In late stage of liquid injection, we apply Darcy's law at the quasi steady-state,

$$\Delta p = Q_l \frac{\mu_\mathrm{l}}{k_\mathrm{el}}\frac{L}{A}, \tag{2}$$

to describe the pressure drop, Δp, as a function of the volumetric flow rate, Q_l, with the parameters of liquid viscosity, μ_l, core length, L, cross section area, A, and the liquid effective permeability, k_{el}. We use the term 'effective' because the core is not 100% saturated with liquid even the pressure drop has reached steady state. We calculate the liquid relative permeability k_{rl} by the ratio of the liquid effective permeability to the gas absolute permeability obtained from single-phase gas flow:

$$k_{\mathrm{rl}} = \frac{k_{\mathrm{el}}}{k_{\mathrm{g}}}, \tag{3}$$

4 Results

4.1 Analysis of Cores and Chemical Solutions

We observe color change of the cores and chemical solutions due to treatment. The treated cores have some brown spots appearing on the surface. The untreated chemical solutions are transparent in the small vials, but become opalescent in large beakers. The chemical solutions after treatment become an amber color. The untreated and treated chemical solutions at higher concentrations scatter the light more and have more concentrated color. We observe opalescence in untreated chemical solution changes to transparency when adding the acid or using water instead of IPA as the solvent. This is an indication that the solubility of the macromolecules is improved at lower pH and higher water content in the chemical solution.

The chemical adsorption onto the core surface is calculated from the weight gain after treatment. The adsorption is in the order of mg per gram of the core, as shown in Table 3. The error of chemical adsorption is ~0.3 mg/g due to the loss of chips during core packing in the coreholder. Note that due to the chip loss, "N/A" means that we are unable to measure a change in the weight of the core. The pH of the chemical solutions before and after treatment are compared in Table 3 ("N/M" = not measured). Due to the low dissociation of chemical to form H^+ ion in the IPA solution, the pH reading has fluctuations (error) of ~0.5. There is no noticeable trend for the pH change by treatment; the variation may be from the specific chemical-rock interactions. Figure 3 shows the pH dependence on the concentrations of the untreated chemical solution. The pH linearly decreases with concentration of Sample Z in the range from 0.25 to 3 wt% and for Sample D from 1 to 5 wt%. The siloxane-containing Sample C at 1 wt% has the lowest pH among all the chemicals; it may be due to dissociation of silanol:

$$\mathrm{SiOH} \leftrightarrow \mathrm{SiO}^- + \mathrm{H}^+ \tag{4}$$

We use ICPMS and GCMS to measure the composition of elements and compounds in the chemical solutions. Table 4 shows the ICPMS results for the 1 wt% Sample Z solution before and after treatment in the reservoir core R1. The relevant analysis for pure Sample Z liquid and IPA solvent are also available. There is an obvious decrease in calcium (Ca), increase in silicon (Si) and sulfur (S) in the treated chemical solution. Table 5 shows the GCMS results for the 1 wt% Sample Z solution before and after treatment of the reservoir core R1. The compounds of stearyl amine, tetradecane, dibutyl sebacate and siloxane appear in the treated solution. Table 6 shows the GCMS results of 1 wt% Sample A, B, D solutions before and after treatment of Berea. The acetic acid and 1-propanol exist at much higher levels in the untreated solution; and eicosane, dibutyl sebacate, siloxane, and 9-methylnonadecane exist only in the treated solution. The analyses using ICPMS and GCMS show the reactions between the chemicals

Table 3 Adsorption and pH data

Core			Chemical				
Type	Designation	Chemical adsorption (mg/g)	Sample designation	Conc. (wt%)	pH		
					Before treatment	After treatment	Change
Berea	B11	N/A	Z	0.25	6.14	6.89	0.75
	B4	N/A		1	5.97	5.66	−0.31
	B10	1.20			5.85	5.93	0.08
	B12	N/A			6.06	6.18	0.12
	BYR	0.65		2	N/M	N/M	N/M
	B2	0.50			6.07	N/M	N/M
	B6	N/A			5.69	6.00	0.31
	B9	0.52		3	5.73	5.07	−0.66
	B15	0.51	A	1	6.12	6.01	−0.11
	B16	0.60	B	1	5.60	5.81	0.21
	B7	0.43		2	5.64	6.31	0.67
	B13	0.00	C	1	4.66	5.38	0.72
	B14	0.22	D	1	6.13	5.38	−0.75
	B17	1.07		3	6.13	5.87	−0.26
	B18	0.63		5	6.09	5.70	−0.39
Reservoir	R1	0	Z	1	6.06	5.36	−0.70
	R3	0			6.18	5.74	−0.44
	R2	0.18		2	6.01	5.25	−0.79
	R4	0	D	1	6.34	5.68	−0.66
	R5	0		3	6.17	5.57	−0.60

and the cores, in which the chemical bonding between fluoro-polymer and sandstone result in the permanency of the treatment. Since the cores are composed mainly of silica and some of the chemicals contain an amino group, a hypothesized chemical reaction is proposed as follows:

$$\text{Amino (chemical)} + \text{silica (rock)} \rightarrow \text{stearyl amine} + \text{siloxane} \tag{5}$$

4.2 Contact Angle

We evaluate the effect of wettability alteration by measuring the contact angle in the untreated and treated cores. Water and nC_{10} liquid drops imbibe into the untreated Berea core immediately after being placed on the core surface. The snapshots of liquid drops at core inlet on untreated and 3 wt%-Sample Z-treated Berea and on untreated and 2 wt%-Sample Z-treated reservoir core are shown in Fig. 4a–d, respectively. There is an increase of contact angle (measured through the liquid phase) after treatment. We have homogeneous water contact angle distribution throughout the core surface after treatment (Wu and Firoozabadi 2010). The contact angle in nC_{10} is not homogeneous and treatment is judged to be ineffective for

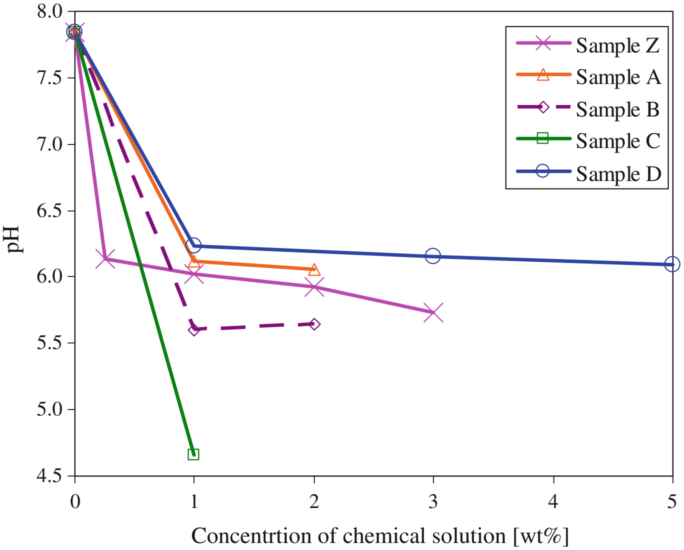

Fig. 3 pH versus concentration of chemical solution before treatment

Table 4 Analysis of 1 wt% Sample Z solution, pure Sample Z liquid and IPA solvent by ICPMS method: reservoir core R1

Element	1% Solution of Sample Z		Sample Z liquid	IPA solvent
	Before treatment	After treatment	Before treatment	
	Concentration (ppm)			
Ca	50	35	16	25
Si	<1	22	6	<1
S	10	47	10	6

Table 5 Analysis of 1 wt% Sample Z solution by GCMS method: reservoir core R1

Compound	Before treatment	After treatment
	MS area (%)	
Stearyl amine	0	36.7
Tetradecane	0	7.3
Dibutyl sebacate	0	6.7
Siloxane	0	1.1

reducing oil-wetting. The homogeneous contact angle in the treated cores is a key evidence of successful wettability alteration. The uniform treatment is believed to be a requirement for successful reservoir applications.

Contact angle data at the core inlet of the untreated and treated cores are listed in Table 7. The error of the measured contact angle is ∼5°. As the table shows there may be an effect of concentration on the increase of the contact angle. The increase of water contact angle is 132°–149° from treatment in Berea; but the increase for the reservoir core is only 23°–61°. The increase of nC_{10} contact angle at core inlet ranges from 0° to 70° for the treated

Table 6 Analysis of 1 wt% Sample A, B and D solutions by GCMS method: Berea core

Compound	Core B15		Core B16		Core B14	
	1 wt% Sample A		1 wt% Sample B		1 wt% Sample D	
	Before treatment	After treatment	Before treatment	After treatment	Before treatment	After treatment
	MS Area (%)					
Acetic acid	28.7	3.6	42.5	1.7	57.3	3.2
1-Propanol	4.7	1.1	7.8	1.4	3.7	0.3
Eicosane	0	39.1	0	48.2	0	63.2
Dibutyl sebacate	0	17.2	0	14.7	0	1.035
Siloxane	0	2.9	0	1.1	0	0.258
9-Methylnonadecane	0	2.9	0	2.9	0	13.1

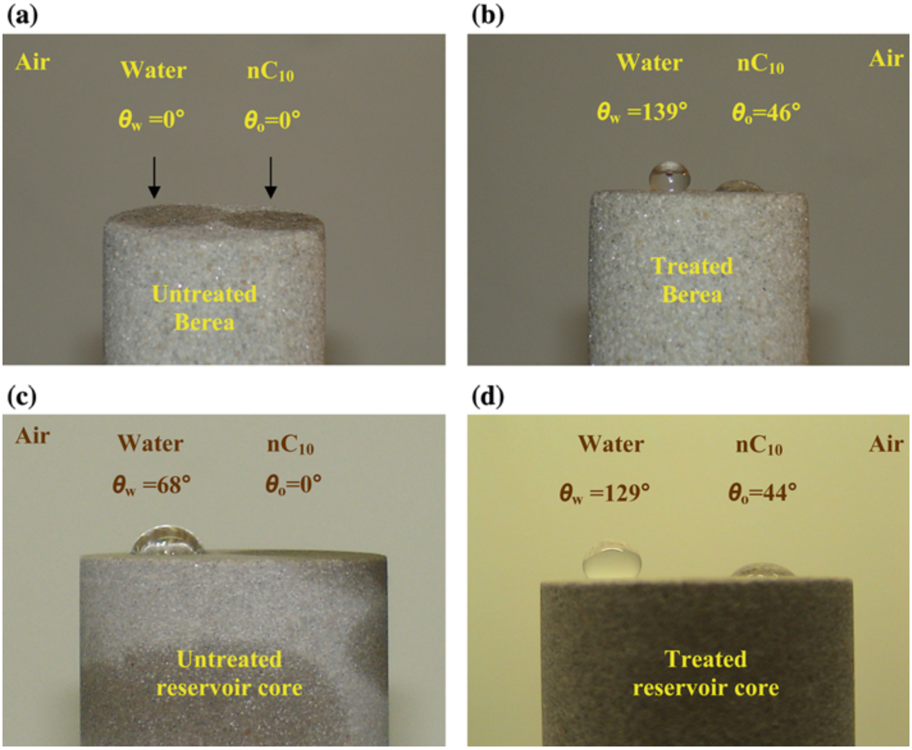

Fig. 4 Contact angle of water and nC_{10} at core inlet in Berea **a** before and **b** after treatment with 3 wt% Sample Z solution, and in reservoir core **c** before and **d** after treatment with 2 wt% Sample Z solution

Berea and from 30° to 44° for the reservoir core. The treatment with Sample D (5 wt%) and Sample Z (2 wt%) increases water contact angle in most of the Berea and reservoir cores. The sandstone surface is altered to preferential gas (air)-wetting by chemical treatment.

Table 7 Contact angle data at ~20°C

Core		Chemical		Contact angle of water and nC_{10} at core inlet					
Type	Designation	Sample designation	Conc. (wt%)	Before treatment		After treatment		Change	
				θ_w[°]	θ_o[°]	θ_w[°]	θ_o[°]	$\Delta\theta_w$[°]	$\Delta\theta_o$[°]
Berea	B11	Z	0.25	0	0	132	0	+132	0
	B4		1	0	0	139	0	+139	0
	B10			0	0	135	0	+135	0
	B12			0	0	141	0	+141	0
	BYR		2	0	0	135	0	+135	0
	B2			0	0	138	32	+138	+32
	B6			0	0	139	0	+139	0
	B9		3	0	0	139	46	+139	+46
	B15	A	1	0	0	134	63	+134	+63
	B16	B	1	0	0	138	53	+138	+53
	B7		2	0	0	139	43	+139	+43
	B13	C	1	0	0	134	0	+134	0
	B14	D	1	0	0	138	65	+138	+65
	B17		3	0	0	141	57	+141	+56
	B18		5	0	0	149	70	+149	+70
Reservoir	R1	Z	1	64	0	92	40	+28	+40
	R3			108	17	131	47	+23	+30
	R2		2	68	0	129	44	+61	+44
	R4	D	1	80	3	125	36	+46	+33
	R5		3	86	3	130	39	+45	+36

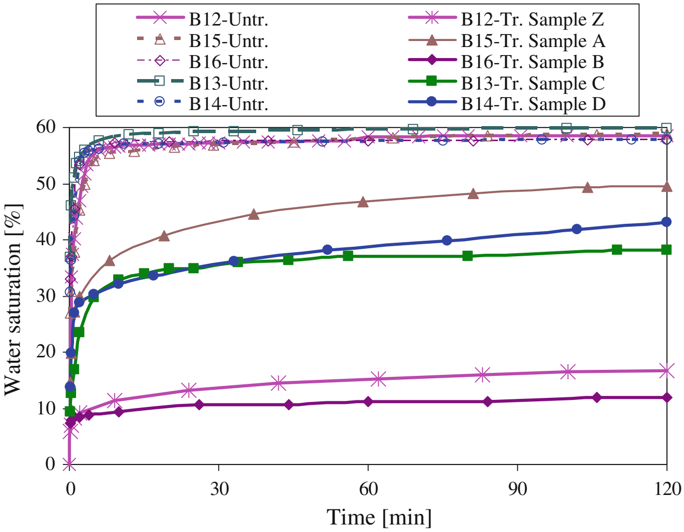

Fig. 5 Water imbibitions versus time before and after treatment with various chemicals at concentration of 1 wt%: Berea, 20°C

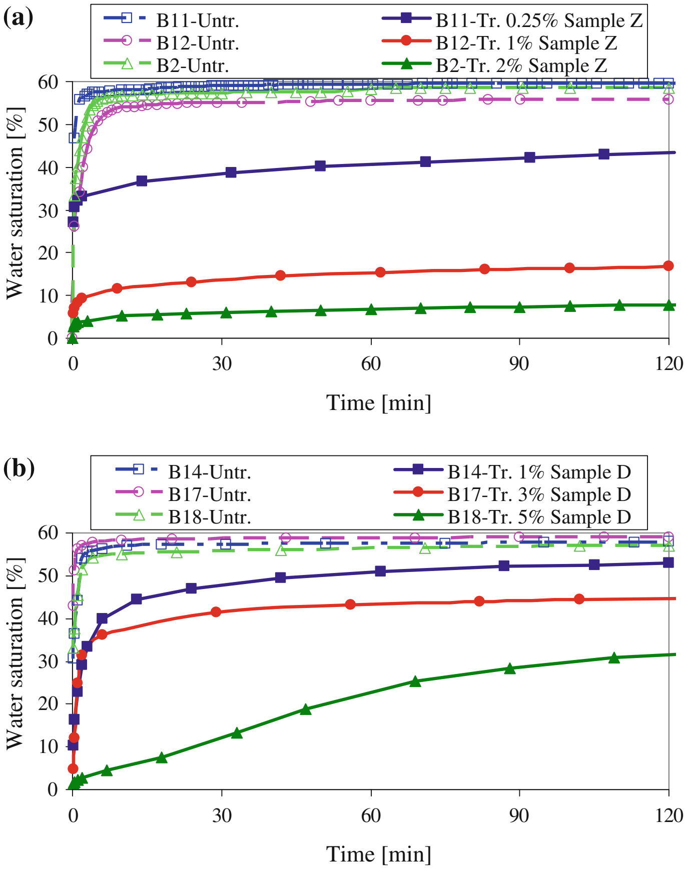

Fig. 6 Water imbibition versus time before and after treatment with **a** Sample Z at 1–3 wt%, **b** Sample D at 1–5 wt%: Berea, 20°C

4.3 Spontaneous Imbibitions

Figures 5, 6, and 7 show the imbibition measurements in the untreated (Untr.) and treated (Tr.) cores. The error is ~3%. Figure 5 depicts water imbibition in untreated and treated Berea with various chemicals at 1 wt% concentration. The plots in Fig. 6a, b show the effect of chemical concentration of Samples Z and D, respectively. The effect of treatment with 1 to 2 wt% Sample Z on the reservoir-core imbibition is shown in Fig. 7. Most of the water imbibition occurs in the first 10 min for Berea, but takes ~2h for the reservoir core. The untreated Berea reaches the steady-state water saturation of ~60%, but the untreated reservoir core has variations in final water saturation for different cores. The chemical treatment reduces water imbibition in both the Berea and reservoir cores; the effect of treatment in the reservoir core is much less pronounced. Higher concentration of chemical is more effective in the reduction of imbibition. Sample Z (2 wt%) is the most effective followed by Sample B (1 wt%) in imbition reduction (Berea) and subsequent alteration of wettability to less water-wetting (that is, to hydrophobicity).

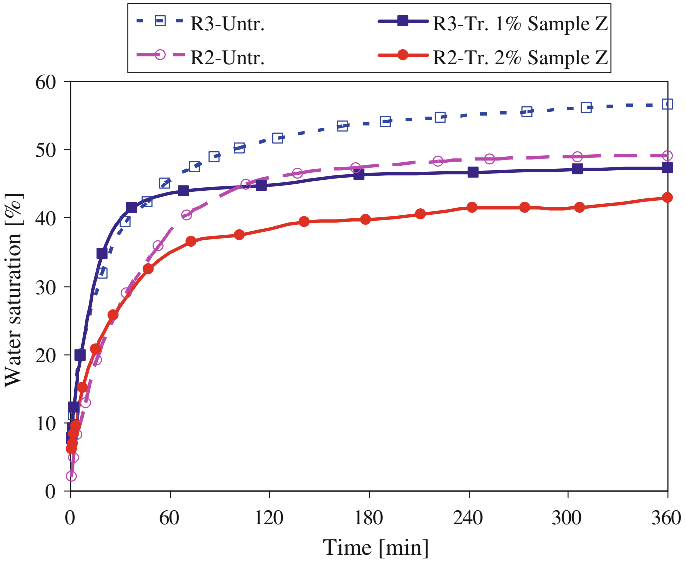

Fig. 7 Water imbibition versus time before and after treatment with Sample Z at various concentrations: Reservoir core, 20°C

4.4 High-Velocity Gas Flow

The dependence of pressure drop on gas flow rate is studied using the Forchheimer expression from Eq. 1 at 140°C. In our measurements the average pressure, $\bar{p} = (p_1 + p_2)/2$ and the pressure drop, $\Delta p = p_1 - p_2$ across the core are $\bar{p} \sim 3.9 \times 10^2$kPa and $\Delta p \sim 1.6 \times 10^2$ kPa for Berea, and $\bar{p} \sim 4.7 \times 10^2$ kPa and $\Delta \mathrm{p} \sim 7.1 \times 10^2$ kPa for the reservoir core. Measured gas absolute permeability and high-velocity coefficient in the untreated and treated cores are presented in Table 8. The errors of absolute permeability and high-velocity coefficient data are estimated to be 5 and 20%, respectively. In most cases, there is a reduction of absolute permeability, and an increase in high-velocity coefficient from treatment. The permeability reduction increases and high-velocity coefficient decrease with increasing concentration of most chemicals. The treatment for Berea with Sample D (1–5 wt%) has a negligible effect on permeability. A permeability reduction of 10% and a high-velocity coefficient increase by factor of two will have a negligible effect in two-phase performance as we will see later. Sample D has the best performance in single-phase gas flow among all the chemicals. Gas mobility parameters obtained from single-phase gas flow are a good measure in the evaluation of the treatment effect other than wettability. It is undesirable to have a large reduction in gas permeability from treatment. Although high-velocity coefficient in single-phase gas flow increases after treatment, there is a substantial decrease of high-velocity coefficient in two-phase flow (Noh and Firoozabadi 2008b).

4.5 Two-Phase Flow by Water Displacement of Gas

Water is injected into the nitrogen-saturated cores at a constant flow rate of 6 cm^3/min for Berea and 0.12 cm^3/min into reservoir rock at 140°C at outlet pressure of 1.5×10^3 kPa (200 psig). The pressure drop across the untreated and treated core is monitored with time.

Table 8 Gas absolute permeability and high-velocity coefficient data at 140°C

Core		Chemical		Absolute permeability and high-velocity coefficient					
Type	Designation	Sample desig-nation	Conc. (wt%)	Before treatment		After treatment		Change	
				k_g (mD)	β (10^6cm^{-1})	k_g (mD)	β (10^6cm^{-1})	$\Delta k_g/k_g$ (%)	$\Delta\beta/\beta$ (%)
Berea	B11	Z	0.25	747	0.10	681	0.42	−9	+319
	B10		1	957	0.33	811	0.78	−15	+136
	B6		2	911	0.26	723	0.49	−21	+86
	B9		3	984	0.27	722	0.57	−27	+111
	B15	A	1	670	0.37	639	0.34	−5	−8
	B16	B	1	843	0.27	765	0.26	−9	−4
	B7		2	875	0.25	681	0.42	−22	+69
	B13	C	1	677	0.29	651	0.31	−4	+7
	B14	D	1	708	0.28	682	0.32	−4	+14
	B17		3	693	0.33	677	0.42	−2	+26
	B18		5	721	0.31	702	0.48	−3	+53
Reservoir	R1	Z	1	4.82	253	4.71	708	−2	+180
	R3			2.36	3605	2.20	8746	−7	+143
	R4	D	1	2.50	2415	2.46	3334	−1	+38
	R5		3	2.23	3440	2.06	2966	−8	−14

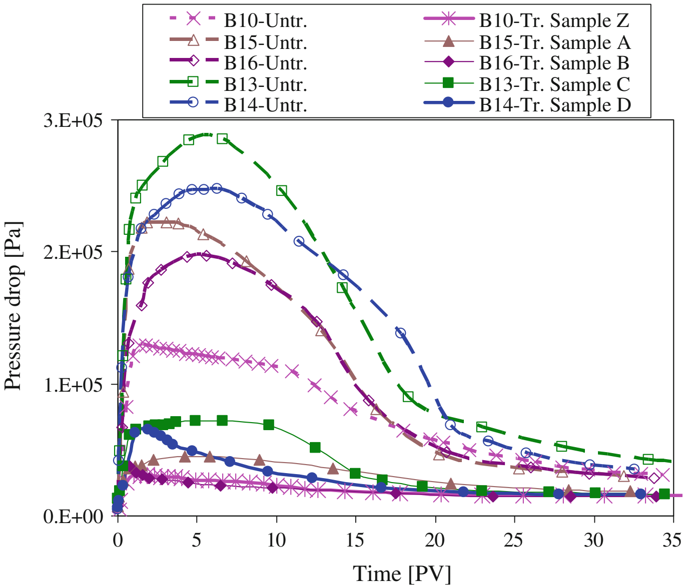

Fig. 8 Pressure drop versus PV injection before and after treatment with various chemicals at 1 wt%: Berea, 140°C

Figure 8 shows the results for untreated Berea cores and treatment with various chemicals at 1 wt% concentration. The plots in Fig. 9a, b present the effect of chemical concentration in Berea with Samples Z and D, respectively. The effect of treatment with 1 wt% Sample Z on the water injection in reservoir core is shown in Fig. 10. The pressure drop increases in early time as expected; a maximum is reached at ~1 PV. Afterward, the pressure drop decreases gradually to a near constant value at the steady state. The trend in the pressure drop plots is distinct in the untreated and treated cores. The treated cores have a significantly lower pressure drop during the early liquid injection period, which is the evidence that wettability alteration has a pronounced effect in two-phase flow region where both phases are flowing. At the steady state the liquid saturation reaches a maximum around 96–99%, estimated from the core weight gain at the test termination. Most of the trapped nitrogen is dissolved in water at high-temperature–high-pressure conditions. The effect of treatment in the two-phase flow in reservoir core is less pronounced than that of Berea.

We have calculated the water effective and relative permeability from steady-state pressure drop using Darcy's law. The results are listed in Table 9. The error is ~5%. The chemical treatment decreases the pressure drop, and increases the effective and relative permeability for both Berea and reservoir cores. We evaluate the treatment effectiveness by calculating the changes in the effective permeability and relative permeability. Samples Z and D have the optimum concentrations at 1 and 3 wt%, respectively. Among all the chemicals, Sample C (1 wt%) has the best performance in increasing the water effective permeability in Berea, followed by Sample D (3 wt%) and Sample Z (1 wt%). Sample C is the only chemical containing siloxane, which is perhaps contributing to its superior performance to repel water. However, for the reservoir core, Sample Z is more effective than Sample D. All the results for water effective and relative permeability in Table 9 provide a strong indication that the chemical treatment changes the core surface from preferential water-wetting (hydrophilic) to preferential gas-wetting (hydrophobic) resulting in an increase in water mobility.

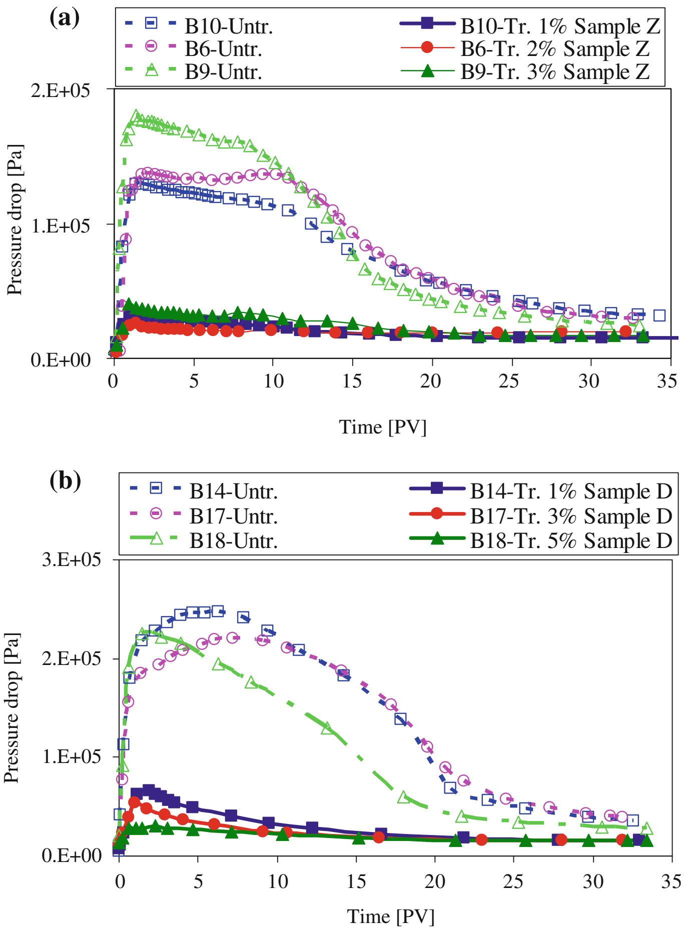

Fig. 9 Pressure drop versus PV injection before and after treatment with **a** Sample Z at 1–3 wt%, **b** Sample D at 1–5 wt%: Berea, 140°C

5 Discussions

5.1 Rock-Chemical Reaction

Sandstone is a sedimentary rock composed of quartz (silica tetrahedra in crystal form) held together by silica (silicon dioxide). Berea sandstone contains ~93% SiO_2, ~4% Al_2O_3 and the other components of Fe_2O_3, FeO, MgO, CaO, etc. (Cleveland Quarries 2009). Figure 11a shows the hydrogen atoms in water bond to the oxygen groups from silica. The hydrogen bonding causes the water-wetting of sandstone. We alter the wettability of sandstone from water-wetting to intermediate gas-wetting by chemical treatment. For the chemicals with a silanol group, the covalent bonding of oxygen in silica in the rock with the silanol group in the chemical (Fig. 11b) can be contrasted to the hydrogen bonding with water (Fig. 11a). The strong bonding of the polymer onto the rock surface may relate to permanency of treatment. When the core weight increases by ΔW_c after the treatment, one may use the following simple expression to compute the number of adsorbed chemical molecules

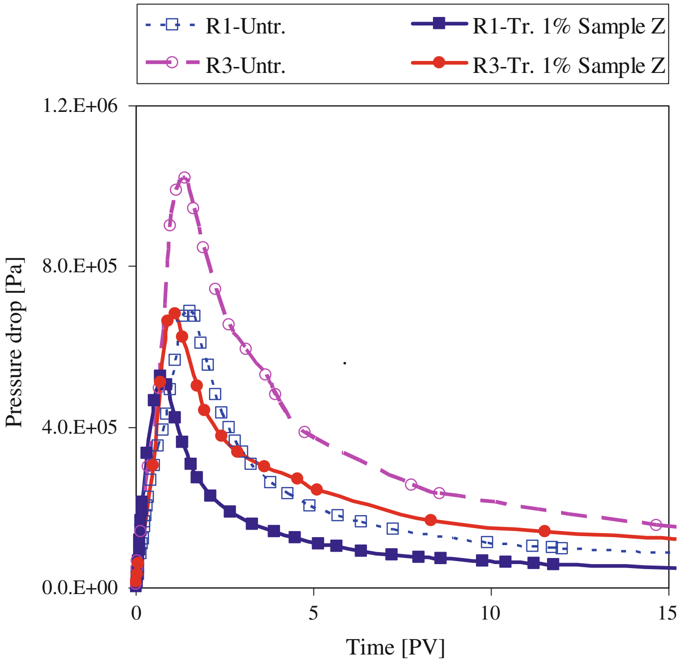

Fig. 10 Pressure drop versus PV injection before and after treatment with Sample Z at 1 wt%: Reservoir core, 140°C

$$\Delta W_c / M_c = W \times S_p \times A_c, \tag{6}$$

where S_p is the pore surface area per unit core weight; W is the core weight; M_c and A_c are the molecular weight and surface concentration (the inverse of surface coverage per molecule) of the chemical. The surface area of Berea estimated from the permeability and porosity data (Tiab and Donaldson 1996) is $S_p \sim 0.03\text{m}^2/\text{g}$. We measure the chemical adsorption of $\Delta W_c / W \sim 1$ mg/g in treatment. The calculated surface coverage per molecule of chemical with M_c of 20,000 g/mol is $\sim 1\text{nm}^2$ from Eq. 6. If we regard the porous media as an assembly of capillary tubes, the pore surface area can be written as

$$S_p W = 2V_p / R_c, \tag{7}$$

where R_c, is the equivalent radius of capillarity. Substitution of definition of porosity $\phi = V_p / V$ and the bulk density $\rho = W / V$ provides

$$R_c = \frac{2}{S_p} \frac{\phi}{\rho}. \tag{8}$$

The bulk density for Berea is $\rho \sim 2.0\,\text{g/cm}^3$, surface area is $S_p \sim 0.03\,\text{m}^2/\text{g}$ and porosity is $\phi \sim 0.22$. The calculated $R_c \sim 7\mu\text{m}$ from Eq. 8 is of the correct order.

The chemical treatment provides water repellency by reducing the surface energy of the treated material. The fluorinated additives are among the most effective chemicals used for wettability alteration. The very high electronegativity of fluorine atom together with its small ionic radius leads to a very stable carbon–fluorine (C–F) bond with very low polarizability. It, therefore, gives a low surface energy from treatment, measured to be ~6 mN/m by DuPont

Table 9 Water effective permeability and relative permeability data at 140°C

Core		Chemical		Water effective and relative permeability					
Type	Designation	Sample designation	Conc. (wt%)	Before treatment		After treatment		Change	
				k_{ew} (mD)	k_{rw}	k_{ew} (mD)	k_{rw}	$\Delta k_{ew}/k_{ew}$ (%)	$\Delta k_{rw}/k_{rw}$ (%)
Berea	B11	Z	0.25	217	0.29	313	0.46	+44	+58
	B10		1	197	0.21	393	0.48	+100	+136
	B6		2	223	0.24	334	0.46	+50	+89
	B9		3	261	0.27	365	0.51	+40	+90
	B15	A	1	208	0.30	331	0.52	+59	+70
	B16	B	1	214	0.25	415	0.54	+94	+114
	B7		2	262	0.30	366	0.54	+40	+80
	B13	C	1	152	0.22	376	0.58	+147	+157
	B14	D	1	176	0.25	379	0.56	+116	+124
	B17		3	153	0.22	415	0.61	+142	+148
	B18		5	219	0.30	390	0.56	+78	+82
Reservoir	R1	Z	1	1.33	0.28	2.00	0.42	+50	+53
	R3			0.77	0.32	0.91	0.41	+19	+28
	R4	D	1	0.96	0.38	1.01	0.41	+5	+6
	R5		3	0.93	0.42	1.09	0.53	+17	+27

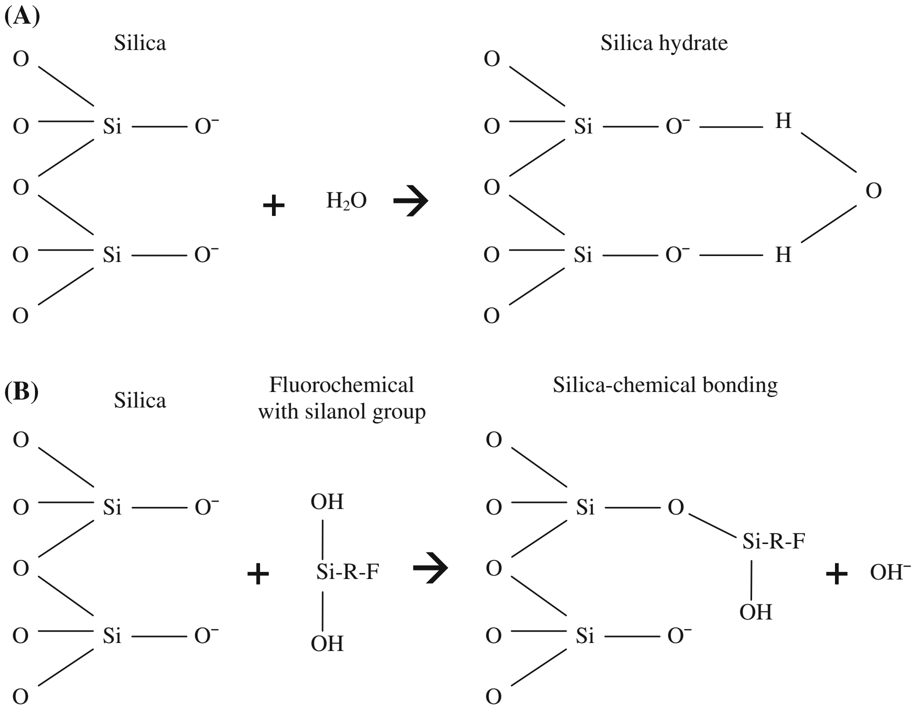

Fig. 11 Suggested reactions of silica in sandstone with water and chemicals: **a** hydrogen atoms in water bond with the oxygen groups from silica forming the hydrogen bonding, **b** silanol group in chemical bonds with the oxygen in silica.

(DuPont Chemical 2003). However, such a low value is probably due to surface roughness and an estimate of ∼15 mN/m would be more realistic (Bonn et al. 2009). Another functional group providing liquid repellency is silane. Fluorinated silanes have been added in the spacecraft coating to enhance the repellence nature of the films (Wolf 2009). Silanization is the process of covering of the solid surface with silane-like molecules. Mica, glass, and metal oxide surfaces can all be silanized, because they contain hydroxyl groups. Berea consists of 93% silica (silicon dioxide), with the surface containing the silanol group (the hydroxyl bonds directly to silicon atoms). A covalent siloxane bond is formed between the silane in polymeric chemical and the hydroxyl group of the rock surface (similar to the bonding between rock and silanol chemical in Fig. 11b).

5.2 Wettability Evaluation

We employ various tests to evaluate the effectiveness of wettability alteration. These tests relate to the interactions between the rock and the fluid phase (liquid or gas). In contact angle measurements, we place a water drop on the core surface in the ambient air. The imbibition test is the process of water penetration into an air-saturated core. Water injection into a nitrogen-saturated core is a two-phase-liquid displacement of gas, as compared to the single-phase gas flow for nitrogen. Measurements of contact angle and gas flow are conducted at equilibrium and at steady state, respectively; imbibition and liquid injection tests are the dynamic processes in transient state. The liquid saturation increases and gas saturation decreases with time in the imbibition and water injection tests. The driving force for liquid movement is capillary pressure in the spontaneous imbibition test, and is the pressure drop in water injection test.

The goal of chemical treatment is to increase contact angle and lower spontaneous imbibition in liquids; decrease pressure drop in liquid injection; and avoid gas absolute permeability reduction and high-velocity coefficient increase. Since the main purpose and application of wettability alteration is to improve the liquid mobility, the fluid flow test is the determining evaluation method for the treatment effectiveness. With the increased relative permeability of both liquid and gas, we therefore reduce the liquid blocking and improve the gas production rate. Among all the chemicals, Sample Z performs the best in water imbibition test, but has the largest reduction in gas permeability. Sample C has the best result in water injection in Berea, but has less colloidal stability and shorter shelf life than the others. As a whole, Sample D performs the best in Berea and Sample Z is most effective in the reservoir core. The test results reveal that the performance of Sample [A/B] is somewhere between Sample Z and Sample [C/D]. The order of molecular weights is: Sample Z > Sample [A/B] > Sample [C/D]. We may conclude that the large molecular weight lowers water imbibition, and the small molecular weight improves the liquid contact angle and fluid mobility.

Different research groups have made chemical treatment by different procedures. For example, when the soaking treatment is employed (Adibhatla et al. 2006; Panga et al. 2007) there is greater contact angle and less imbibition, but higher permeability reduction, as compared to the injection treatment. In our study, we use the injection treatment and additional step of treatment durability examination, by water flushing after treatment at high temperature. Noh and Firooaabadi (2008a) used similar Berea cores and similar treatment process as what we have in this study. Among their treatments, the chemical L-19062 at 12 wt% has the best performance; there is a gas absolute permeability reduction ($\Delta k_g/k_g = -5\%$), an increase in water relative permeability ($\Delta k_{rw}/k_{rw} = +158\%$) and an increase in high-velocity coefficient ($\Delta\beta/\beta = +110\%$). In our study, when Berea cores are treated with Sample C at a concentration of 1 wt%, the change in gas absolute permeability is $\Delta k_g/k_g = -4\%$. The increase in water relative permeability is, $\Delta k_{rw}/k_{rw} = +157\%$, and the increase in high-velocity coefficient is $\Delta\beta/\beta = +7\%$. The performance of the chemicals used in the current study is higher at a lower chemical concentration compared to our past study.

5.3 Contact Angle and Liquid Imbibition

Contact angle measured through the liquid phase, θ, is described by the Neumann–Young equation:

$$\sigma_{gs} = \sigma_{sl} + \sigma_{gl}\cos\theta, \tag{9}$$

where σ_{gl}, σ_{gs} and σ_{sl} are the liquid–gas interfacial tension, gas–solid surface energy, and liquid–solid surface energy, respectively. In our study, the contact angle increases from chemical treatment. The increase in θ is mainly from a reduction in ($\sigma_{gs}-\sigma_{sl}$). A model surface completely covered with –CF_3 groups from fluorochemical treatment has a surface energy σ_{gs} as low as ~6 mN/m (DuPont Chemical 2003).

Imbibition in a collection of capillaries driven by capillary pressure can be determined using the generalized Young-Laplace equation:

$$p_c = \frac{2\sigma_{gl}\cos\theta}{R_c}, \tag{10}$$

where p_c is the capillary pressure. From the chemical treatment the surface energy reduction increases the contact angle, and reduces the capillary pressure. In surfactant flooding, the water retention and blocking is reduced from the decrease in surface tension and the capillary pressure. The process, however, requires continuous injection of surfactants whereas in wettability alteration the process is permanent.

Porous media are an assembly of granular particles. Contact angle for a single macroscopic liquid drop on a porous substrate may be different from that on one granular particle (Shahidzadeh-Bonn et al. 2004). Contact angles in porous media and in a single granular particle have different hysteresis phenomena. Liquid imibition in porous media may be related to both advancing and receding contact angles (Fang et al. 1996), but may not be analogous to capillary rise in a capillary tube. Liquid does not rise in a circular capillary when contact angle is greater than 90°. However, there is imbibition in the treated Berea when the contact angle measured on the porous substrate is greater than 90°. The Young-Laplace equation discussed above only explains factors affecting capillary pressure, imbibition and liquid flow in porous media (i.e, surface tension, contact angle and pore size). We measure the contact angle on the porous substrate of sandstone as an indicator of the wettability alteration and treatment homogeneity. We need to perform fluid flow testing to evaluate treatment efficiency and effectiveness.

6 Conclusions

The main conclusions from this study are:

(1) We demonstrate the permanency of the wettability alteration to intermediate gas-wetting (air and nitrogen) by providing the evidence of a chemical reaction. Repeated fluid injection tests after treatment show permanency of treatment.

(2) The adsorption of the fluorochemicals onto the core surface may have a negligible effect on the gas absolute permeability (nitrogen) for the chemicals with small molecular weight.

(3) The effect of chemical concentration on wettability alteration is clarified as follows. With increased chemical concentration, the water contact angle increases and imbibition decreases. There exists an optimum concentration for the maximum water permeability.

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