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Effects of Firing and Chemical Treatments on Berea Permeability and Wettability

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The alteration of the wettability from liquid-wetting to intermediate gas-wetting has great potential in improving gas well productivity, from mitigating water blocking to condensate banking in gas reservoirs. Even a small quantity of salt ions (such as Na^+) in the initial saturation in rock has a detrimental effect on the alteration of the wettability by chemical treatments. The initial salt ions may cause clay release and permeability reduction. Berea cores are usually used in laboratory flow studies, including wettability alterations. In this work, we present a comprehensive study on the use of Berea, both unfired and fired, in single- and two-phase flows, with a focus on the salt and firing effect on the chemical treatment. Three fluoropolymeric surfactants are used. We find that one of the three, a nonionic surfactant, is effective in the alteration of wettability in the fired Berea (with and without salt in the initial saturation). The treatment efficiency of ionic surfactants is reduced in the presence of the initial salt.

Introduction

Results obtained from displacement experiments on Berea are commonly correlated with those obtained from reservoir cores. Use of Berea rather than reservoir rock for routine core-displacement tests is attractive because it is commercially available, inexpensive, and relatively homogeneous.[1] Some reservoirs have the same range of porosity and permeability as Berea.[2]

There have been reports that the permeability of Berea sandstone decreases significantly when fresh water is injected into brine-saturated Berea.[3] This reduction, which is associated with the colloidal phenomenon known as "water sensitivity", is primarily due to the release of clay particles from the pore walls and subsequent migration to pore constrictions, where blockage occurs.[4] The decline in the permeability is a serious problem in some oil field operations, such as water flooding and acidization, and its control is essential to the effective operation of many fields. Tang and Morrow[5] have found that the salinity of the connate water and invading brines can have a major influence on wettability and oil recovery. The clay particle release mediated by the salinity may play a role in the underlying mechanism of oil recovery.

The primary factor that determines the release and migration of clay particles is the salt composition in the initial saturation in formation, prior to the flow of fresh water.[6] There may be a permeability reduction of more than 95% from a sodium salt pretreatment, and virtually no permeability reduction is observed when the cation in the solution is divalent.[7] Kia et al. have analyzed the electrokinetic and ion-exchange properties of the clay particles and describe the effect of both Na^+ and Ca^{2+} ions on fine particle migration, in terms of the double-layer theory.[8] Similar to the pretreatment with divalent ions, no reduction in permeability occurs from clay blockage when the rock is pretreated with hydroxyl-aluminum and hydroxylable multivalent ions.[9−11] Sydansk reports the clay particle stabilizing effect of potassium hydroxide.[12]

We have treated Berea with chemicals to alter the wettability from water-wetting to intermediate gas-wetting in the past.[13] Water retention in reservoirs is often caused from drilling, completion, and fracturing fluids.[14] Using the wettability alteration, the gas production rate may improve by mitigating the water blocking. Our prior work uncovered the fact that the in-place brine has adverse effects on the chemical treatment of Berea.[15] The initial saturation by NaCl brine before treatment may induce the clay release and permeability reduction. The salt and clay may significantly reduce the efficiency of the chemical adsorption.

To desensitize the indigenous clay minerals that can lead to fine particle migration and permeability reduction, a core is often fired at temperatures over 500 °C. Berea core commonly contains > 4 wt % clay and consists of kaolinite, illite, chlorite, and trace amounts of mixed-layer illite or smectite.[16] The

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transformation of the fine particles minimizes the core's sensitivity to the fresh-water injection.[17] In addition, firing may result in lower residual oil saturation in water flooding and may improve oil recovery.[18] Potts and Kuehne have found that the firing renders Berea strongly water-wet (Amott wettability index of 0.93−0.99) and the siderite is converted to ferric oxides.[1] Firing ensures complete water-wet conditions by the removal of the adsorbed organic matter from the pore surfaces.[19] The residual gas saturation by spontaneous imbibition in fired Berea is lower than that in a natural Berea.[20] Shaw et al. have investigated the changes in the physical and chemical properties of Berea sandstone upon firing and determined the effect of these changes in their interpretation of the core displacement results.[16]

In this work, we have fired the Berea to transform and desensitize the clay. We have studied the effects of firing on the petrophysical properties, including the wettability and its alteration. Nonionic fluorochemicals are used in our treatment of Berea initially saturated with brine. The initial brine does not have adverse effects on the chemical treatment of fired Berea (using nonionic chemicals).

This paper is organized along the following lines. In the "Experimental Section", we describe the rock samples, fluids, and chemicals; then, the experimental methods for the core testing (contact angle, imbibition, and fluid flow), solution analyses (pH, refractive index, and density) and chemical treatment are discussed. We briefly present the expressions used to calculate the flow parameters in the "Expressions for Fluid Flow" section. In the "Results and Discussion" section, the experimental results of the clay release, firing effect, and treatment effect are provided. We also discuss and interpret the interactions between the clay, silica, salt and chemicals. The "Conclusions" section provides our closing comments.

Experimental Section

Materials. There are three basic materials in this research: cores, fluids, and chemicals.

Cores. Berea cores from Cleveland Quarries (Amherst, OH) are used in this work. They have a diameter (D) of ∼2.5 cm, length (L) of ∼15 cm, gas permeability (k_g) of 600−800 md, and porosity (ϕ) of ∼0.21. A core is placed in a temperature-programmable oven and heated at a rate of 5 °C/min until a temperature of 1000 °C (suggested by Sydansk[21] and Shaw et al.[22]) is reached. This temperature is maintained for 5 h and then the samples are allowed to cool slowly to room temperature. The procedure is designed to limit any thermal shock effects that may cause differential contraction and grain shattering.[16] We fire the cores for three main reasons: (1) to create strong water-wet mineral surfaces by burning off organic contaminants; (2) to transform clay minerals, to reduce clay swelling and fine particle migration; and (3) to minimize problems arising from ion exchange. The objective of firing is to improve the reproducibility and reduce the number of variables that may affect the displacement tests and chemical treatment.

Fluids. Air is the gas phase in the contact angle measurements and imbibition testing. Nitrogen is used in the single-phase gas flow and liquid displacement of gas. Fresh water is used in the contact angle, imbibition, and flow tests. The 3-wt% NaCl and $CaCl_2$ brines are used in the study of the clay release and treatment with the initial saturation. Normal decane (nC_{10}) is used in imbibition tests to study the effects of firing on the oleic phase. At 20 °C, nC_{10} has a specific gravity of 0.73 and a viscosity of 0.929 cP.[23]

Chemicals. Three fluoro-polymeric surfactants "Z8", "Z21", and "Z22", produced by DuPont, are used in the alteration of the wettability. Z8 is ionic, whereas Z21 and Z22 are nonionic. In the past, we have mainly used ionic chemicals to alter the wettability from liquid-wetting to intermediate gas-wetting.[24,25] In the literature, treatment is often conducted using ionic chemicals that are dissolved in water/alcohol.[26,27] The chemical molecules used in this work and in the previous work are composed of various functional groups that have the ability to adsorb onto the core surface, and repel the water and oil phases. The water and oil repellency is provided by the fluoro and/or silane groups. The ionic and/or silanol groups chemically bond onto the core surfaces, providing a durable treatment. The ionic/nonionic groups make the polymer soluble in the polar/nonpolar solvent.[28]

The ionic chemical Z8 is dissolved at a concentration of 30 wt % in water; the nonionic chemicals Z21 and Z22 are dissolved in a concentration of 25 wt % in naphtha and in *n*-butyl acetate, respectively. We dissolve the chemical solutions in iso-propanol (IPA) to dilutions of 1 wt % and 5 wt % for treatment, which respectively correspond to polymer concentrations of 0.25−0.30 wt % and 1.25−1.5 wt %. IPA has a low vapor pressure and is safe in practical applications. It also reduces the surface tension more effectively than methanol when dissolved in water. Water buildup has been reduced through evaporation by adding volatile solvents.[29]

Experimental Methods. The wettability of the cores is evaluated by measuring the gas−liquid−rock three-phase contact angle, spontaneous imbibition, and the mobility of gas and liquid in flow tests. The wettability is altered by injecting a chemical solution into the cores and aging them overnight at high temperature and pressure. These experimental methods are described in our recent work.[25]

Contact Angle Measurements. We use a pipet to place a liquid drop on the surface of the air-saturated core at an ambient temperature of ∼20 °C. The configuration of a sessile liquid drop on the core surface in the ambient air is magnified on a monitor screen. We take snapshots of the drop image with a digital camera under a light source. The contact angle is measured through the liquid phase using the imaging software's goniometry tool.

Spontaneous Imbibition Test. The spontaneous liquid imbibition into the air-saturated cores is monitored at a fixed temperature of 20 °C, maintained by a thermocirculator and a tempering beaker. We immerse the air-saturated core in the liquid while hanging it under an electronic balance. The dynamic process of liquid imbibition into the core is studied by recording the core weight with time. We evaluate the effect of the wettability alteration by comparing the liquid saturation (S_l) versus

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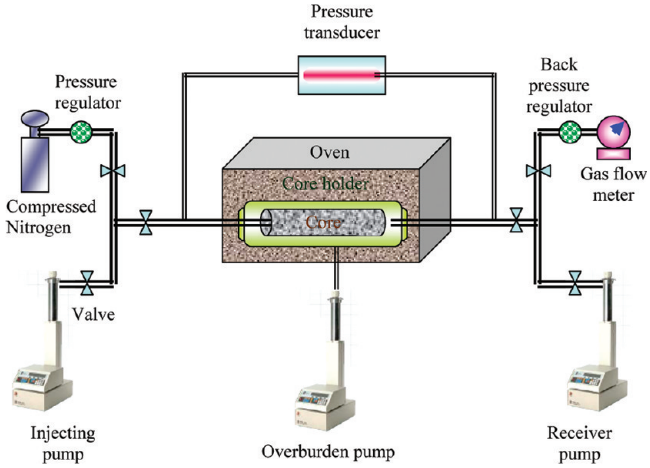

Figure 1. Experimental setup for fluid flow test and chemical treatment.

time before and after chemical treatment. The imbibition decreases as the wettability is altered from liquid-wetting to intermediate gas-wetting. The final saturation in the liquid imbibition test is called the "final imbibition", to avoid confusion with the "initial saturation".

Fluid Flow Test. We conduct a test of the gas and liquid flow using the setup shown in Figure 1. An overburden pressure of 1000 psig (7.0 × 10^3 kPa) is applied with a syringe pump on the core placed inside the biaxial-type core holder. The temperature of the system is maintained by a universal oven. Compressed nitrogen from a cylinder flows through the pressure regulator, and the liquid is injected from the inlet pump. The inlet pressure and pressure drop are measured by pressure transducers and demodulators, with an accuracy of 0.2 psi (1.4 kPa) after calibration by a dead-weight tester. We use a back-pressure regulator to adjust the outlet pressure while measuring the gas flow rate, using a flow meter in the range of 1−80 cm^3/s (with an accuracy of ∼0.5%). The liquid flow rate is fixed by the inlet pump while the outlet pressure is maintained with the receiver pump. In a single-phase gas flow, the inlet and outlet pressures at various gas flow rates are recorded at steady state. When the liquid displaces gas in the two-phase flow, the liquid is injected at a fixed flow rate into the gas-saturated core. The transient pressure drop is recorded until steady state is reached.

Chemical Treatment. The wettability of the core is altered by chemical treatment at 140 °C and 200 psig (1.5 × 10^3 kPa). The experimental setup for treatment is similar to that used in the fluid flow test. Five pore volumes (PV) of the chemical solution is injected into the core under various treatment conditions, followed by aging (∼15 h). About 20 PV of fresh water is then injected to displace the chemical solution and wash the core. The injection of the chemical solution and washing with water are performed at a rate of 4 cm^3/min. We then inject nitrogen (∼30 PV) to drain the water from the core at $Q \approx 10$ cm^3/min. The purpose of water washing is to test the durability of the chemical treatment at a high temperature through the examination of the contact angle. The term "treatment condition" refers to the condition of the cores before the chemical injection. Table 1 shows the variation in the treatment conditions from a combination of the core state, initial saturation, treatment chemicals, and concentration.

Analysis of Solution Mixture. We analyze untreated and treated solution mixtures. The pH is measured by the pH meter; the reproducibility of the pH measurements for the aqueous solution is ∼0.02 units. Because of the low dissociation of chemicals to form the H^+ ion in the IPA solution, the pH readings for the chemicals in the IPA solutions have fluctuations of ∼0.5. The refractive index and density are measured by a refractometer (to an accuracy of 0.0003) and pycnometer (a specific-gravity bottle with a volume of 25 cm^3), respectively. All the measurements are conducted at a fixed temperature of 20 °C.

Expressions for Fluid Flow

We evaluate the fluid mobility in single-phase gas flow and a liquid injection test. We measure the absolute permeability and high-velocity coefficient by applying the Forchheimer equation to the steady-state high-velocity gas flow. Using Darcy's law, the effective liquid permeability is calculated when the liquid flow reaches the steady state. The effect of the chemical treatment is evaluated from the change of these fluid mobility parameters.

Forchheimer Equation. The Forchheimer equation is usually used to quantify the gas flow in high-velocity regime:[30]

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

where p_1 and p_2 are the inlet and outlet pressure; M_g, μ_g, and j_g are the molecular weight, viscosity, and mass flux of the gas, respectively. R and Z are the gas constant and the gas deviation factor, respectively; T is temperature, and L is the core length. The gas absolute permeability (k_g) and the high velocity-coefficient (β) are determined from the intercept and slope in the plot of $M_g({p_1}^2 - {p_2}^2)/(2\mu_g ZRTLj_g)$ vs j_g/μ_g. The Klinkenberg effect is negligible in our pressure range for the high-permeability Berea. We quantify the effect of the chemical treatment in a high-velocity gas flow from the change in the absolute permeability and high-velocity coefficient after treatment:

$$\frac{\Delta k_{\mathrm{g}}}{k_{\mathrm{g}}} = \frac{k_{\mathrm{g}}(\text{treated core}) - k_{\mathrm{g}}(\text{untreated core})}{k_{\mathrm{g}}(\text{untreated core})} \qquad (2a)$$

$$\frac{\Delta \beta}{\beta} = \frac{\beta(\text{treated core}) - \beta(\text{untreated core})}{\beta(\text{untreated core})} \qquad (2b)$$

Darcy's Law. The liquid injection in a gas-saturated core is a transient two-phase gas−liquid flow in which the gas in the core is displaced by the liquid. When the pressure drop reaches steady state, there is residual gas left in the core. We apply Darcy's law to calculate the effective liquid permeability (k_{el}) in the steady state:

$$\Delta p = Q_{\mathrm{l}}\left(\frac{\mu_{\mathrm{l}}}{k_{\mathrm{el}}}\right)\left(\frac{L}{A}\right) \qquad (3)$$

in which the pressure drop (Δp) is a function of the liquid volumetric flow rate (Q_l), along with the parameters of the liquid viscosity, μ_l, core length, L, and cross-sectional area (A). The effective liquid permeability is dependent on the wetting state, the residual gas saturation, and the liquid absolute permeability. We quantify the effectiveness of the chemical treatment in the liquid flow by the change in the effective liquid permeability:

$$\frac{\Delta k_{\mathrm{el}}}{k_{\mathrm{el}}} \equiv \frac{k_{\mathrm{el}}(\text{treated core}) - k_{\mathrm{el}}(\text{untreated core})}{k_{\mathrm{el}}(\text{untreated core})} \qquad (4)$$

We calculate the liquid relative permeability (k_{rl}) from the ratio of the effective liquid permeability to the gas absolute permeability:

$$k_{\mathrm{rl}} = \frac{k_{\mathrm{el}}}{k_{\mathrm{g}}} \qquad (5)$$

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Table 1. Treatment Conditions

core ID	core state	initial saturation	treatment chemical	chemical concentration (wt %)
B46	fired	nitrogen	Z8	1
B49	fired	nitrogen	Z21	1
B50	fired	nitrogen	Z22	1
B57	fired	3 wt % NaCl(aq)	Z8	1
B51	fired	3 wt % NaCl(aq)	Z21	1
B52	fired	3 wt % NaCl(aq)	Z22	1
B56	fired	3 wt % NaCl(aq)	Z8	5
B58	fired	3 wt % NaCl(aq)	Z21	5
B54	fired	3 wt % NaCl(aq)	Z22	5
B55	fired (neutral)	3 wt % NaCl(aq)	Z22	5
B53	unfired	3 wt % NaCl(aq)	Z22	5

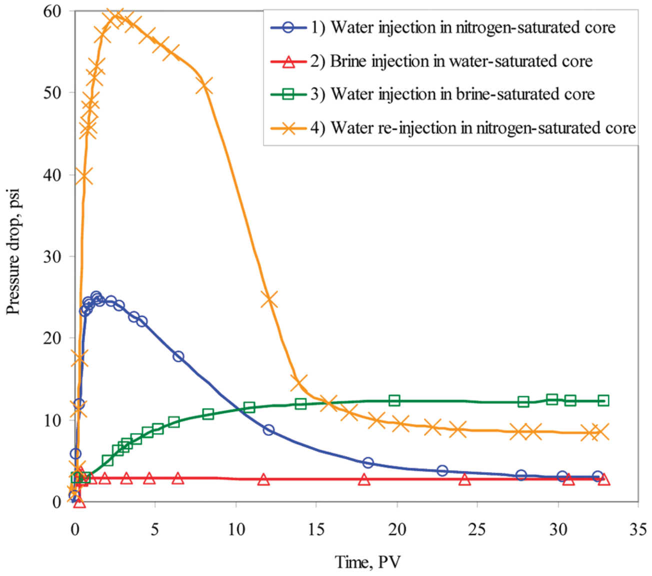

Figure 2. Water and brine injection tests in Berea core B42 (unfired); brine with 3 wt % NaCl(aq).

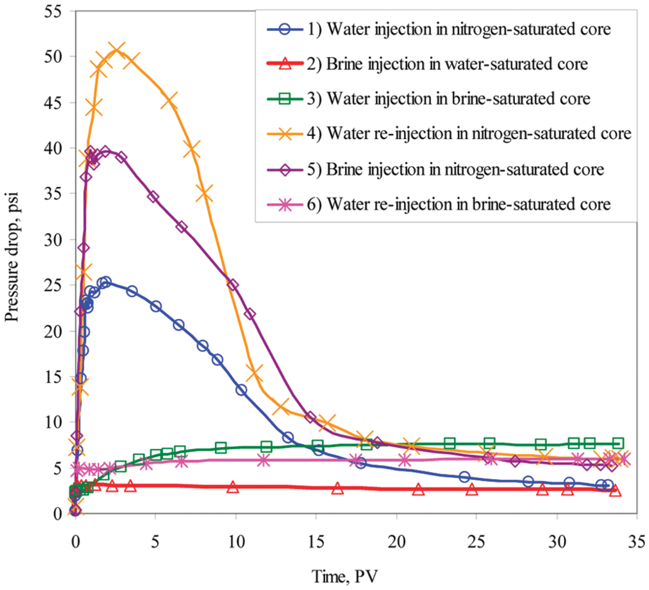

Figure 3. Water and brine injection tests in Berea core B44 (unfired); brine with 3 wt % NaCl(aq).

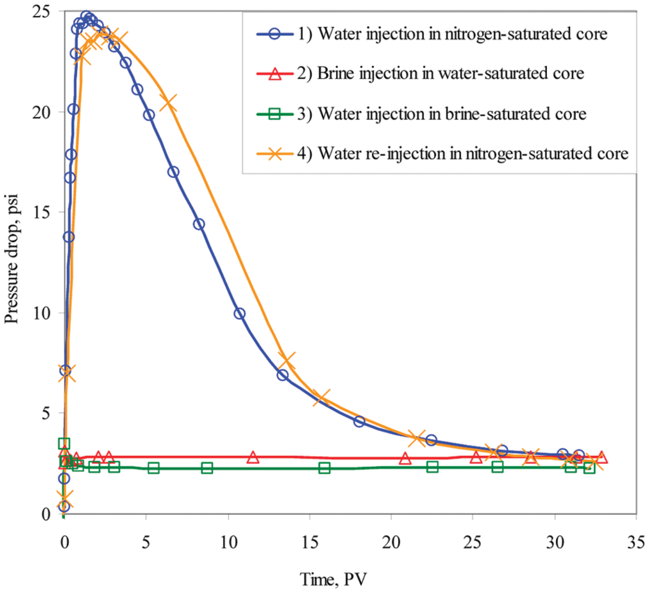

Figure 4. Water and brine injection tests in Berea core B43 (unfired); brine with 3 wt % $CaCl_2$(aq).

Note that, in defining k_{rl}, we can also use the absolute liquid permeability (k_l) instead of the absolute gas permeability (k_g). We use a dimensionless pressure drop to compare the pressure drop versus time in different cores:[31]

$$\Delta p_D = \frac{k_g \Delta p A}{L \mu_l Q} \tag{6}$$

Combining eqs 3, 5, and 6, we obtain the following expression for Δp_D at steady state:

$$\Delta p_D = \frac{k_g}{k_{el}} = \frac{1}{k_{rl}} \tag{7}$$

Results and Discussion

Permeability Reduction from Clay Release. To understand the role of clay in sandstone rocks, we perform liquid injection tests (T = 140 °C, p_2 = 200 psig, Q = 6 cm^3/min) in the following order (each for 33 PV). First, water is injected into a nitrogen-saturated core. Second, brine is injected to displace the water. Third, water is injected to displace the brine. Fourth, after nitrogen drains the water, water is injected into the nitrogen-saturated core again. The pressure drop versus time for the four water and brine injections in core B42 are compared in Figure 2. The brine has a NaCl(aq) concentration of 3 wt %. In the first liquid injection test, the pressure drop increases initially; it reaches a maximum at ~1 PV, then decreases to a steady-state value at the end, reflecting the

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relative permeability effect of the liquid displacing gas. In the second liquid injection, the pressure drop is constant throughout and results in the same final value as that in the first flow. No damage is caused by the brine. In the third liquid injection, the pressure drop increases initially and plateaus at the steady state at a higher value than the previous two flow tests; this may reflect the release of fine clay particles that could plug pore throats. The fourth water injection has a pressure drop performance similar to the first water injection, but the pressure drop is greater. The steady-state pressure drop of the fourth liquid injection is between the first (and second) and third tests (this decrease will be discussed later).

We repeat the injection tests in core B44; in addition, we continue with two more tests: after nitrogen drains the water in the fourth injection, we inject 3 wt % NaCl(aq) in the nitrogen-saturated core (fifth test). The sixth test is a water injection in a 3 wt % NaCl(aq)-saturated core. As shown in Figure 3, the trends of the first four pressure drop plots in core B44 are similar to those of core B42. After the fourth injection, the steady-state pressure drops are approximately the same in the fifth and sixth injection tests. Note that in the third test, when water is injected into the brine-saturated core, the pressure drop is highest at the steady state, similar to that in Figure 2.

Figure 4 depicts the plots of the pressure drop across core B43. In this core, we use the 3 wt % $CaCl_2$(aq) brine. The sequence of four liquid injection tests is the same as that in Figure 2. Interestingly, the steady-state pressure drops are approximately the same for all four liquid injection tests. Note that the pressure drop for the two liquid–liquid displacements remains the same during the entire period, indicating no relative permeability effect (as expected).

We calculate the effective permeability of water and brine using eq 3 from the steady-state pressure drop in the above series of liquid injection tests; the results are plotted in Figure 5. The water/brine effective permeability decreases in the third injection when water displaces NaCl(aq) brine (cores B42 and B44), but not when water displaces $CaCl_2$(aq) brine (core B43), or in the second injection when brine displaces water. The decrease in the liquid's effective permeability is mainly due to the reduction in the absolute permeability. In Table 2, we show the absolute gas permeability before and after the third injection. Note that the effective water permeability is often lower than the gas permeability by a factor of 2 in the unfired Berea cores B42, B43, and B44. We make a conjecture that the permeability reduction from the fresh water flooding in a sandstone saturated with sodium salt solutions is primarily due to the release of clay particles.[7] There is no permeability reduction when fresh water floods the sandstones saturated with calcium salt solutions.[6,32] The effect of the fluid composition on the clay

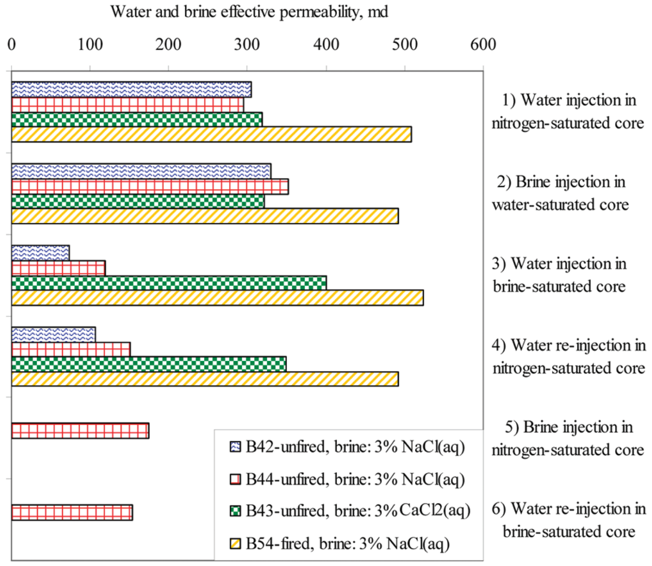

Figure 5. Effective permeability of brine and water in liquid injection tests.

Table 2. Effect of Clay Release on Permeability Reduction, at 140°C

			k_g (md)		k_{ew} (md)	
core ID	core state	injected brine	initial value	after 3rd flow	before 3rd flow	after 3rd flow
B42	unfired	NaCl	670	282	305	107
B44	unfired	NaCl	725	409	295	151
B43	unfired	$CaCl_2$	695	not measured	318	349
B54	fired	NaCl	776	762	509	492

Table 3. Effects of Firing on Berea B46 Properties, at 20°C

property	unfired	fired	percentage change, Δ
bulk volume, V (cm^3)	65.5	66.6	2%
pore volume, V_p (cm^3)	13.9	15.1	9%
porosity, ϕ (fraction)	0.21	0.23	7%
weight W (g)	135.2	132.6	−2%
bulk density, ρ (g/cm^3)	2.06	1.99	−3%
rock density, ρ_s (g/cm^3)	2.62	2.58	−2%
final water imbibition, S_w (%)	61	72	18%
final *n*-decane imbibition, S_o (%)	68	73	8%
absolute gas permeability, k_g (md)	631	692	10%
high-velocity coefficient, β ($\times 10^6$ cm^{-1})	0.29	0.24	−16%
effective water permeability, k_{ew} (md)	181	346	91%
relative water permeability k_{rw} (fraction)	0.29	0.50	74%
effective *n*-decane permeability k_{eo} (md)	590	618	5%
relative *n*-decane permeability, k_{ro} (fraction)	0.94	0.89	−4%
pH of efflux from water injection	7.03	11.46	63%

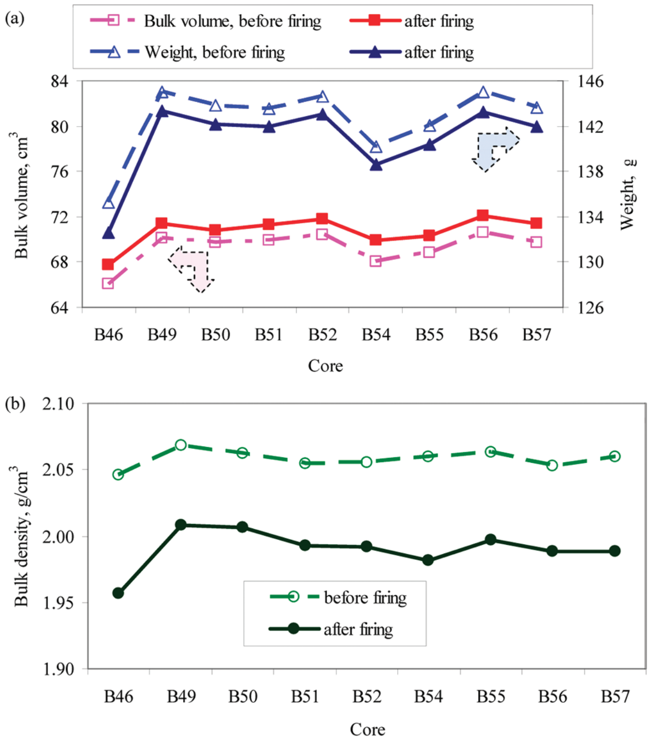

Figure 6. Effect of firing on (a) bulk volume and weight and (b) bulk density of Berea cores.

release can be explained by the double-layer interactions at the surface of the clay particles and the pore walls.[8]

Clay Desensitization by Berea Firing. To desensitize indigenous clays in Berea sandstone, we fire cores at 1000 °C for 5 h.[16] The clay mineral assemblage (consisting of kaolinite, illite, and chlorite) is altered into amorphous, fused aluminosilicates. The conversion of kaolinite ($Al_4Si_4O_{10}(OH)_8$) into its amorphous form occurs between 500 and 550 °C. Chlorite and illite are converted to other mineral phases at ~800 °C.[33] Various iron-rich cements in the unfired Berea (consisting of iron sulfides, siderite, and ferroan dolomite) are converted to iron oxides (hematite) when fired, giving the rock a distinctive red tinge. The cements constitute up to 4% of the rock. Trace amounts of calcite are also converted to calcium oxide. The destruction of the cementing material (carbonate, sulfides, and clays) at elevated temperatures makes Berea more friable. Significant changes in pore geometry occur when Berea is fired at elevated temperatures. These changes can be quantified by examining the petrophysical properties acquired before and after firing (Table 3). An increase in the bulk volume, pore volume, and porosity was noted. The 2% increase in the bulk volume is most likely from irreversible thermal expansion upon firing. However, this small increase in the bulk volume does not fully explain the observed large increase in the pore volume (9%). The additional porosity increase results from the shrinkage of the cementing minerals. As described previously, firing results in the conversion of the carbonates and sulfides to oxides. These oxides are 20% denser than the original minerals.[34] The increased density accompanies a corresponding decrease of the cement volume in pores. The collapse of the layered clay structure and the loss of interlayer water add to the pore volume increase. A decrease in the weight after firing is also noted in Table 3. Most of the observed weight lost is related to the loss of interlayer water associated with the breakdown of the clay structure and the loss of other volatile species such as CO_2 and SO_2 during the oxidation of the carbonates and sulfide minerals. The result is a decrease in bulk and rock density. Figure 6 portrays the change in Berea from firing; the bulk volume increases, the weight decreases (Figure 6a), and the bulk density decreases (Figure 6b).

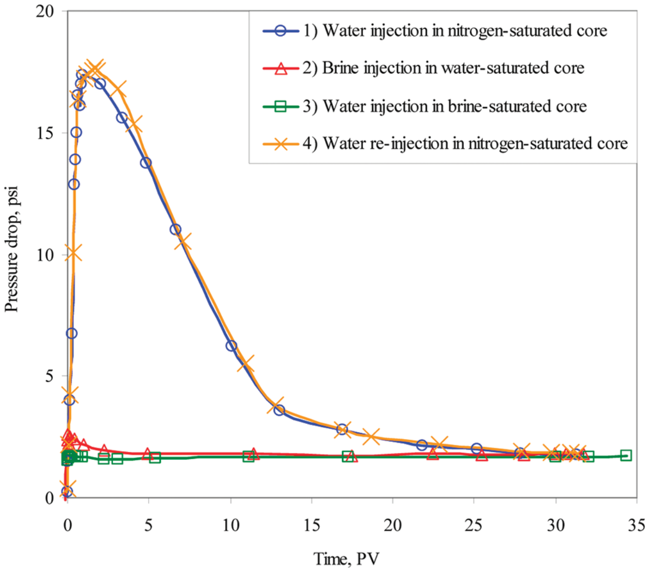

Figure 7. Water and brine injection tests in Berea core B54 (fired); brine with 3 wt % NaCl(aq).

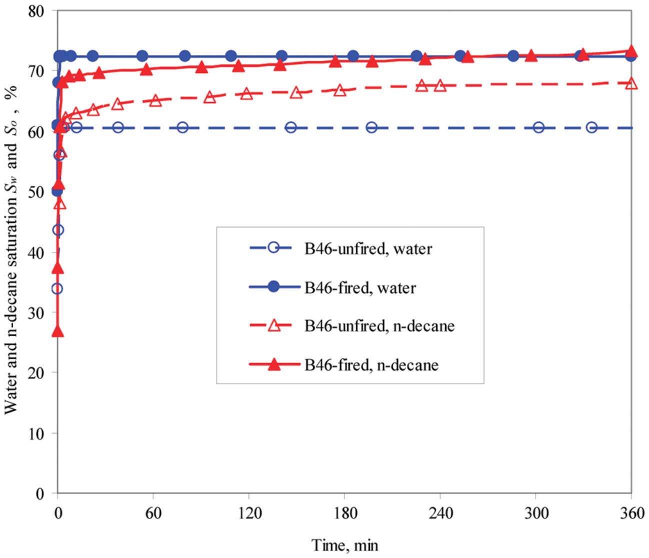

Figure 8. Effect of firing on imbibition of water and *n*-decane (nC_{10}) in Berea core B46 initially saturated with air.

The water/brine injection tests are repeated for the fired core B54, using the 3 wt % NaCl(aq) as brine. As shown in Figure 7, the fired core B54 has the same steady-state pressure drop in the four liquid injection tests. The results may indicate that the clay is transformed and desensitized by

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(33) Brown, G.; Brindley, G. W. *Crystal Structures of Clay Minerals and Their X-ray Identification*; Brindley, G. W., Brown, G., Eds.; Mineralogical Society of London: London, 1980; pp 305–360.

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firing; the fired core is not water-sensitive. The corresponding gas absolute permeabilities and water/brine effective permeabilities of core B54 are shown in Figure 5 and Table 2.

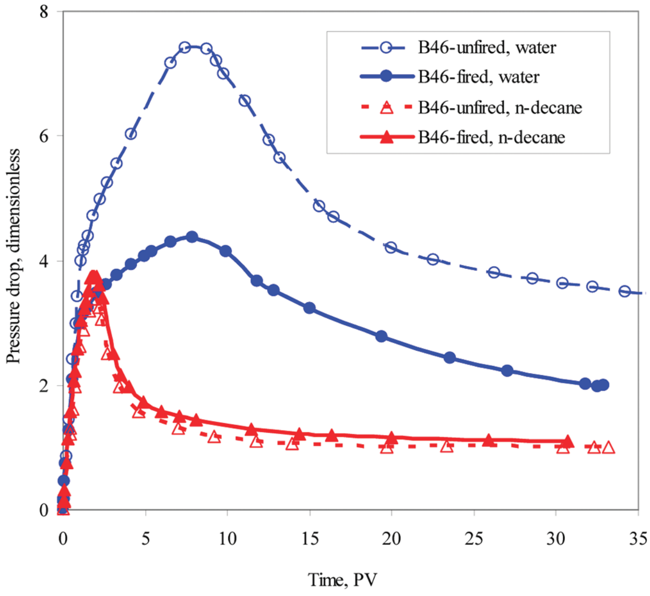

Figure 9. Effect of firing on pressure drop from water and *n*-decane (nC_{10}) injection in Berea core B46 initially saturated with nitrogen.

Figure 8 depicts the imbibition of water and nC_{10} in unfired and fired Berea B46. The fired core has a greater water and nC_{10} imbibition. The final imbibition increases 18% for water and 8% for nC_{10} from firing (see Table 3). The firing makes the core more water-wetting and nC_{10}-wetting, perhaps due to the removal of adsorbed organic matter on the pore surfaces. Note that the imbibition of water and nC_{10} are about the same after firing. Table 3 shows the absolute gas permeability increased by 10% and the high-velocity coefficient decreases by 16%, caused by the pore structure change from firing. Figure 9 shows the dimensionless pressure drop in the water and nC_{10} injection in unfired and fired Berea core B46 ($T \approx 20$ °C, $p_2 = 1$ atm). The unfired and fired cores have a maximum pressure drop at ~8 PV water and ~1 PV nC_{10}. The water pressure drop in the fired core is less than that in the unfired core, but the nC_{10} pressure drop is approximately the same for the unfired and fired cores. Firing increases the effective water permeability by 91% and relative water permeability by 74%; firing also increases the effective nC_{10} permeability by 5% and the relative nC_{10} permeability by −4% (see Table 3). Firing increases the porosity, absolute gas permeability, preferential water-wetting, and oil-wetting to gas-wetting. If the porosity and water saturation are fixed, the improved water wetting would

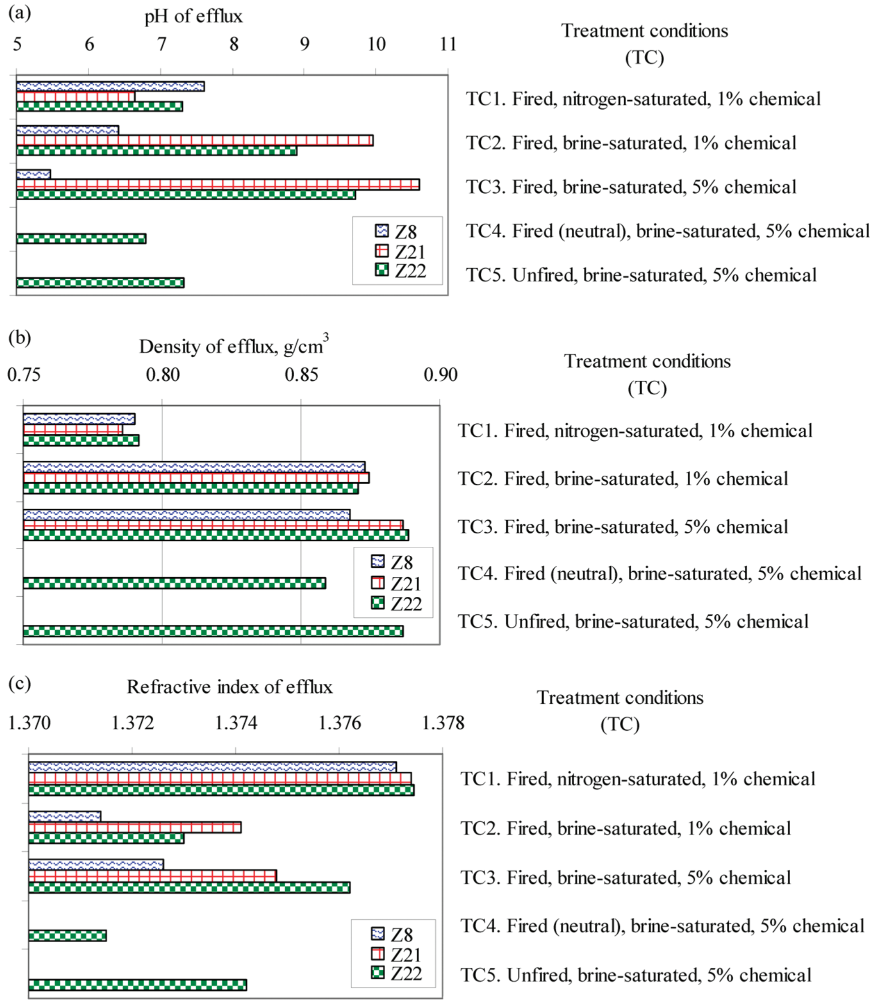

Figure 10. Effect of (a) pH, (b) density, and (c) refractive index of efflux from chemical treatment in Berea under various treatment conditions; brine with 3 wt % NaCl(aq).

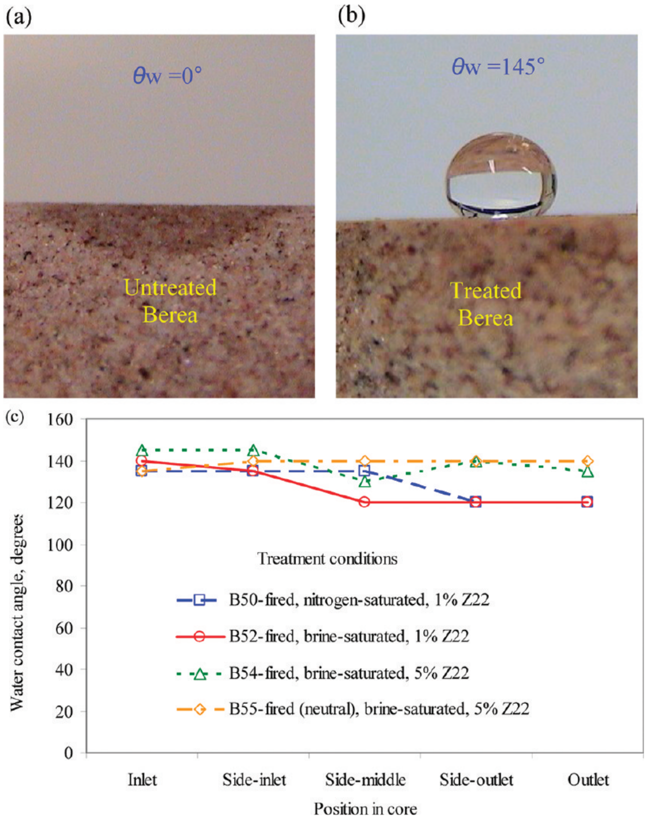

Figure 11. Water contact angle in (a) untreated and (b) treated Berea. (c) Water contact angle distribution in treated Berea under various treatment conditions; brine with 3 wt % NaCl(aq).

decrease the water permeability. The increase in the effective water permeability and relative water permeability may be attributed to the higher water saturation at the end of the water injection test in the fired cores. The compound nC_{10} has a higher imbibition and higher permeability than water. It indicates that Berea is more nC_{10}-wetting and probably has a greater nC_{10} saturation in the nC_{10} injection test than water. Note that there is a lower nC_{10} saturation difference between the unfired and fired cores than the water saturation difference in the imbibition test in Figure 8, which may explain the small difference in the nC_{10} pressure drop in unfired and fired cores.

We measure the pH of the influx and efflux from the water injection ($T \approx 20$ °C) in the unfired and fired core B46. The pH of the influx water is ~6.76. The efflux pH from the unfired core is 7.03 from the unfired core and 11.46 from the fired core (see Table 3). The observed pH increase associated with the fired Berea is attributed to the dissolution of calcium oxide into calcium hydroxide.[16] The pH of the efflux declines slowly with the amount of the water/brine injection. The efflux pH is >10.5, even after the 130 PV water/brine injection ($T = 140$ °C) in the four tests for the fired core B54. Calcium oxide is commonly used as a catalyst in the catalytic degradation of polymers, because of its ability to cleave C−C bonds.[35] To prevent the possible adverse effects of calcium oxide on the treatment by polymeric chemicals, we pretreat one of the fired cores (B55) with an aqueous solution of 20 wt % acetic acid. The efflux of the water injection in the neutralized fired core has a pH of ~7.17.

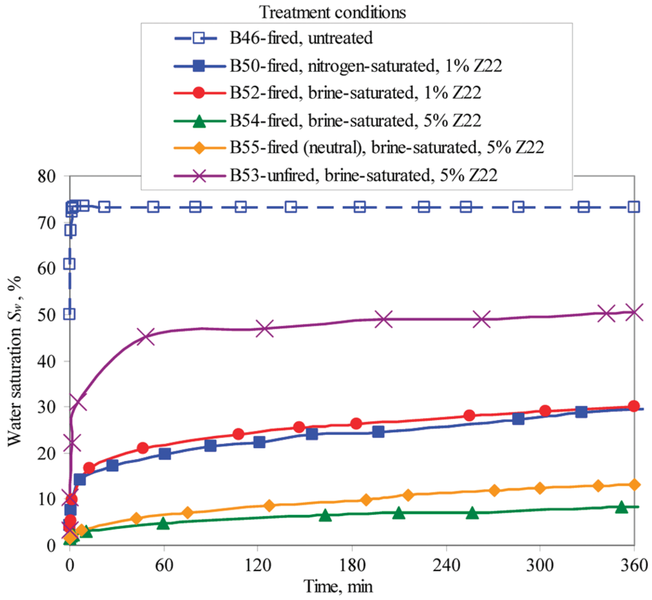

Figure 12. Water imbibition in untreated and treated Berea under various treatment conditions; brine with 3 wt % NaCl(aq).

Chemical Treatment of Fired Berea. We have used ionic chemicals to treat unfired Berea cores in the past.[25] The clay in sandstones may cause an absolute permeability reduction from the treatment in cores initially saturated with NaCl brine. Salt and clay may reduce the treatment efficiency significantly. According to the colloidal stability theory,[36,37] ionic chemicals tend to be vulnerable to the brine's electrolytes in the cores. In this work, we fire the cores to desensitize the clay and avoid the clay release. The fired core is used for the treatment with nonionic chemicals to reduce the adverse salt effect. The effects of the treatment conditions on the efficiency of the wettability alteration are described below.

Before we perform the injection tests in the cores, we analyze the efflux from the chemical treatment to elucidate the effect of the treatment conditions. The treatment conditions are varied by different core states, initial saturation, chemical type, and concentration. The influx is 1−5 wt % chemicals in the IPA solution. The efflux is a mixture of the influx and the fluid initially in the core. We measure the efflux's pH, reflective index, and density under various treatment conditions (TC). As shown in Figure 10, the cores are fired in TC1 to TC3, fired and neutralized in TC4, and unfired in TC5. The initial saturation is by nitrogen in TC1, and is by 3% NaCl brine in TC2−TC5. The chemical concentration is 1% in TC1 and TC2, and is 5% in TC3−TC5. Figure 10a shows the pH measurements; the efflux of nonionic chemicals Z21 and Z22 in TC2 and TC3 is basic, because of the calcium oxide dissolved in brine. The efflux of the ionic chemical Z8 is acidic, because of the dissociation of Z8 in brine to form H^+ ions. The other effluxes are approximately neutral. Figure 10b shows the density measurements. The efflux of the chemical-IPA mixed with brine in TC2−TC5 has a higher density than the efflux of chemical-IPA in TC1 because of differences in density: $\rho_{20} = 1.003$ g/cm^3 for 3 wt % NaCl(aq) and $\rho_{20} = 0.788$ g/cm^3

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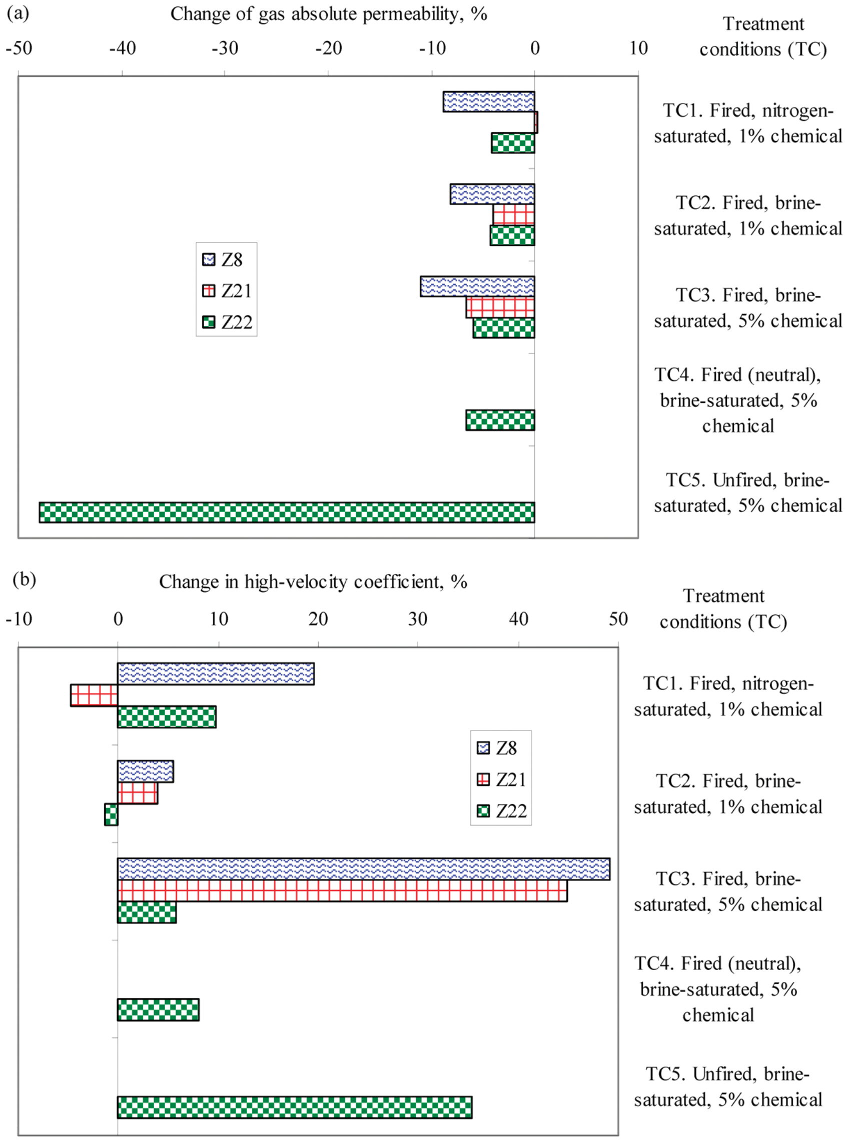

Figure 13. Change in (a) absolute gas permeability and (b) high-velocity coefficient in treated Berea under various treatment conditions; brine with 3 wt % NaCl(aq).

for 1 wt % chemicals in IPA. In Figure 10c, we show the refractive index measurements; the efflux in TC1 has the highest refractive index, because of the differences in the refractive indices ($n_{D_{20}}$ = 1.338 for 3 wt % NaCl(aq) and $n_{D_{20}}$ = 1.378 for 1 wt % chemicals in IPA). The efflux in TC3 has a higher refractive index than TC2, TC4, and TC5, perhaps because of the high chemical concentration (5 wt %) and dissolved ash from firing.

Figure 11 shows the water contact angles in the untreated and treated Berea using the chemical Z22. The core is fired, and a water drop imbibes in the untreated Berea core B54 immediately after being placed onto the core surface (see Figure 11a). After treatment with 5 wt % Z22 at an initial saturation of 3 wt % NaCl(aq) brine, a water drop forms on the core at the inlet face (see Figure 11b). The contact angle shown is 145°, and it has an error of ~5°. The change in the water contact angle from 0° to 145° implies alteration of the wettability from water-wetting to intermediate gas-wetting. The existence of fluoropolymer films on the rock surface from treatment affects the rock's wettability. To evaluate the homogeneity of chemical treatment throughout the core, we compare the contact angle at different positions on the core surface: at the inlet, the outlet, and the core sides close to the inlet, outlet, and middle. Figure 11c shows that treatment in the fired Berea with chemical Z22 under various conditions yields a homogeneous water contact angle throughout the core, ranging from 120° to 140°. The uniformity of the contact angle is a strong indication of the effective alteration of wettability. The chemical treatment with the unfired Berea in the initial saturation of 3 wt % NaCl(aq) brine results in water imbibition toward the core outlet.[15]

Figure 12 shows water imbibition in untreated and treated Berea with chemical Z22 under various treatment conditions. We only show the imbibition data for the untreated Berea B46 since water imbibition varies by < 3.5% in untreated Berea for a large number of cores. Most imbibition in Berea occurs within the first 10 min. The water imibibition reduction in treated Berea reflects the alteration of the wettability from water-wetting to intermediate gas-wetting. The water imbibition in the treated core varies with the

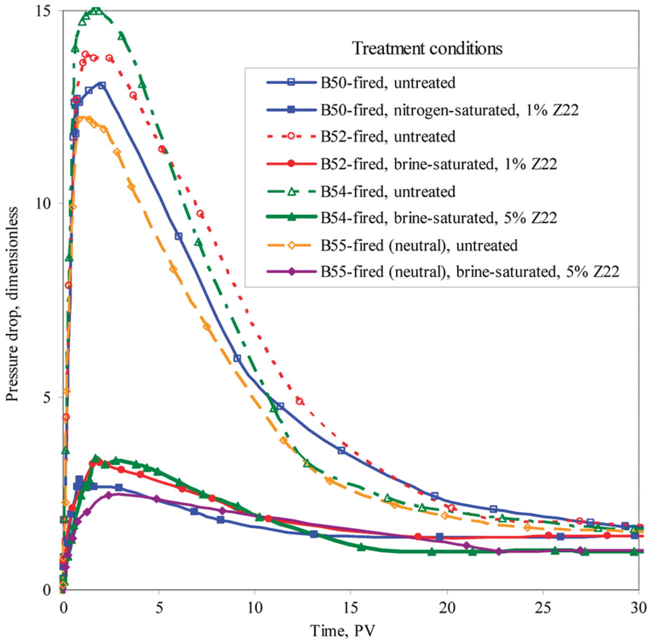

Figure 14. Water injection in untreated and treated Berea (fired) under various treatment conditions; brine with 3 wt % NaCl(aq).

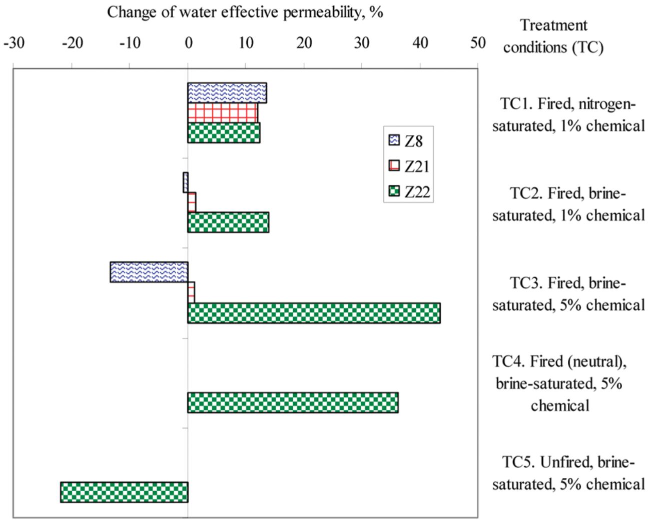

Figure 15. Change of water effective permeability in treated Berea under various treatment conditions; brine with 3 wt % NaCl(aq).

treatment conditions. The cores B50 and B52 treated with 1 wt % Z22 have similar imbibitions, indicating that the initial saturation by 3 wt % NaCl(aq) in a fired core does not decrease the treatment efficiency. The cores B54 and B55 treated with 5 wt % Z22 have similar imbibitions, indicating that the calcium oxide in a fired core does not cause noticeable adverse effects. The increase of the Z22 concentration from 1 wt % (cores B50 and B52) to 5 wt % (cores B54 and B55) reduces the water imbibition from treatment. The treatment of an unfired core (B53) results in a lower water imbibition reduction and lower treatment efficiency than that of a fired core (cores B54 and B55).

We compare the change in absolute gas permeability and high-velocity coefficient in the treated cores under various treatment conditions. The errors of absolute permeability and high-velocity coefficient measurement are estimated to be 5% and 20%, respectively. As shown in Figure 13, the fired cores after treatment with nonionic chemicals (Z21 and Z22) have absolute gas permeability changes of $<10\%$ and high-velocity coefficient changes of $<15\%$ (except for the 5% Z21 treatment by 3% NaCl(aq)-saturated Berea). Treatment with the ionic chemical Z8 gives a greater permeability reduction and a greater high-velocity coefficient increase than treatment with the nonionic chemicals. The treatment in the unfired core initially saturated by 3 wt % NaCl(aq) causes a 50% reduction in permeability and a 35% increase in the high-velocity coefficient, which may be due to the release of clay particles.

The effect of treatment on the pressure drop from water injection in fired Berea is shown in Figure 14. The dimensionless Δp_D value in untreated Berea varies somewhat from core to core in the transient stage, but their values are approximately the same at steady state. There is a decrease in the pressure drop after chemical treatment, indicating an increase in the effective water permeability from the alteration of wettability. The difference between the untreated and treated core is distinct in the two-phase flow region (unsteady state). Similar to the water imbibition, the treated cores with the same chemical concentrations (cores B50 and B52 at 1 wt % Z22; cores B54 and B55 at 5 wt % Z22) have the same steady-state pressure drops. The initial saturation with brine, and the calcium oxide produced from firing, have negligible effects on the Z22 treatment in fired cores. We calculate the water effective permeabilities from the steady-state pressure drop. The changes in the water effective permeabilities by treatment with the three chemicals are shown in Figure 15 (error of ~5%). The three chemicals have approximately the same treatment efficiency in the fired cores initially saturated by nitrogen. The chemical concentration increase from 1 wt % to 5 wt % greatly improves the water effective permeability (~50%) for the Z22 treatment in the fired cores initially saturated by brine, but not for Z8 and Z21. The treatment in the unfired core initially saturated by brine reduces the water effective permeability. The ineffectiveness may be due to the absolute permeability reduction by the clay particle release. It is believed that the effect of brine on reservoir rocks is established in the geological process; if there is no injection of water for hydraulic fracturing, there will be no adverse effects. However, since Berea is often used in laboratory work, firing seems necessary to alter the wettability, as we have clearly demonstrated in this work.

Conclusions

The following conclusions are drawn from this work:

(1) The wettability of fired Berea is altered from water-wetting to intermediate gas-wetting by chemical treatment. In the treated core, the water contact angle increases, imibibition decreases, and the pressure drop in the water injection test is reduced.

(2) The initial saturation by brine in fired Berea does not have an adverse effect on the treatment using the nonionic chemical Z22. The water effective permeability increases by ~50% after treatment in the brine-saturated core. These results have important implications for the proper choice of chemicals in the alteration of wettability to intermediate gas-wetting.

(3) Firing Berea increases its porosity and bulk volume, as well as the wetting by water and oil and permeability for gas and water.

(4) The permeability reduces when water is injected in a unfired Berea core saturated with brine. There is no permeability reduction when brine is injected in a water-saturated core. On the other hand, there is no permeability reduction when water is injected in a core saturated with $CaCl_2$ brine, or when $CaCl_2$ brine is injected in a water-saturated core.

(5) The clay is desensitized by firing the Berea. As a result, there is no permeability reduction when water is injected in a core saturated by NaCl brine.

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