Cation Exchange in the Presence of Oil in Porous Media

R. Farajzadeh, H. Guo, J. van Winden, J. Bruining

†Shell Global Solutions International, 2288 GS Rijswijk, The Netherlands
‡Delft University of Technology, 2628 CD Delft, The Netherlands

ABSTRACT: Cation exchange is an interfacial process during which cations on a clay surface are replaced by other cations. This study investigates the effect of oil type and composition on cation exchange on rock surfaces, relevant for a variety of oil-recovery processes. We perform experiments in which brine with a different composition than that of the in situ brine is injected into cores with and without remaining oil saturation. The cation-exchange capacity (CEC) of the rocks was calculated using PHREEQC software (coupled to a multipurpose transport simulator) with the ionic composition of the effluent histories as input parameters. We observe that in the presence of crude oil, ion exchange is a kinetically controlled process and its rate depends on residence time of the oil in the pore, the temperature, and kinetic rate of adsorption of the polar groups on the rock surface. The cation-exchange process occurs in two stages during two phase flow in porous media. Initially, the charged sites of the internal surface of the clays establish a new equilibrium by exchanging cations with the aqueous phase. At later stages, the components of the aqueous and oleic phases compete for the charged sites on the external surface or edges of the clays. When there is sufficient time for crude oil to interact with the rock (i.e., when the core is aged with crude oil), a fraction of the charged sites are neutralized by the charged components stemming from crude oil. Moreover, the positively charged calcite and dolomite surfaces (at the prevailing pH environment of our experiments) are covered with the negatively charged components of the crude oil and therefore less mineral dissolution takes place when oil is present in porous media.

KEYWORDS: Cation exchange, Wettability, Rock-fluid interaction, Wetting film, Heterogeneous charge, Clays, Geochemistry

1. INTRODUCTION

The efficiency of improved or enhanced oil recovery (IOR/EOR) processes is often influenced by the composition of the flowing aqueous phase and is thus affected by the mass exchange between fluid and solid phases. For example, the rheology of polymers or the magnitude of the interfacial tension reduction by surfactants strongly depends on the ionic strength and hardness (concentration of divalent cations) of the aqueous phase. In recent years, the additional oil extracted by improved oil recovery (IOR) processes is often in thin layers of brine residing in the rock pores.1–10 The stability of the water film in between held together by molecular forces on the surface 23–30 On other surfaces, such as quartz, the oil is separated from the rock by a “thicker” non-uniform water film.31 The stability of the water films depends on the equilibrium between interaction of double layer forces and van der Waals forces. 25,29 A double layer occurs when a charged surface is in contact with an aqueous phase. The ions with an opposite charge will have a higher concentration than the bulk concentration near the surface, whereas ions with a charge of the same sign will have a concentration less than the bulk concentration near the surface. When the oil–water surface and the rock–water surface have the same sign, it can be shown that the double layers repel each other, which is conducive to a stable water layer. The presence of high salt concentrations shields the surface charges leading to a reduced double-layer repulsion. 29–31 The Debye length, $k^{-1} [m]$ is the characteristic distance over which a charge is shielded by the ions in a solution and is given by

$$k^{-1} = \sqrt{\frac{e^2 e_0 k_B T}{2 N_A e^2 I}} = 9.63 \times 10^{-9} \sqrt{\frac{1}{I}}$$

where $I$ = $\Sigma 1/2 e z^2$ is the ionic strength [mol/m$^3$], $e_0$ (20 °C) = 80.1 [ ] is the relative permittivity, $\varepsilon_0 = 8.854 \times 10^{-12} [F/m = C^2/J/m]$ is the permittivity of free space, $k_b = 1.38 \times 10^{-23} [J/K]$ is the Boltzmann constant, $N_A = 6.0225 \times 10^{23}$ is Avogadro’s number, and $e = 1.602 \times 10^{-19}$ C is the charge of an electron. In the case of the presence of a water film, van der Waals forces are generally attractive because the dielectric coefficient of water exceeds that for rock and oil and

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because the refractive index of water is generally less than for rock and oil (see Figure 1). These two forces suffice if the thickness of the water film considerably exceeds the molecular size or surface roughness; otherwise structural forces have to be considered. The force per unit surface area is called the disjoining pressure. If the capillary pressure is less than the local maximum disjoining pressure at large film thickness, the water film is stable. The surface charge can be calculated by considering the relevant chemical surface complexation reactions, and can be found using PHREEQC. 

The charge of the oil–water surface is determined by the presence (or more strictly ionization) of functional groups such as carboxylic acids (negative charge) and basic compounds such as pyridines and quinolones (positive charge) at a given pH. A larger part of the rock surface is covered with a water film of variable thickness, depending on the ionic strength and pH of the flowing solution; however, some “asperities” will stick out of the water layer into the crude oil. The diffusion of polar components of the crude oil into the water film may lead to direct contact of oil with the rock and alteration of the wetting state of the surface similar to “spot-welding”. Depending on the nature of the charges on the rock surface (mineral type) and components of the crude oil and water, oil can be attached to the rock surface through several mechanisms such as ligand exchange, cation bridging, anion and cation exchanges, hydrogen bonding, van der Waals interaction, and so forth. These mechanisms require polar groups in the crude oil and their relative contribution depends on the composition of the phases; in particular, the composition of the aqueous phase is strongly affected by the geochemical reactions.

Cation exchange is an interfacial process during which a cation on, for instance, a clay surface is replaced by another cation. The capacity of the rocks to retain cations is measured by the cation-exchange capacity (CEC), which is the sum of the quantity of positive charges (cations) neutralizing permanent and variable pH-dependent charges. The CEC strongly depends on the rock mineralogy, the surface area, and charge and size of the ion. Under steady-state chemical conditions, the composition of a cation exchanger is in equilibrium with the formation brine. When the composition of the brine is altered, the cation exchanger readjusts its composition to a new equilibrium with the injected brine. The exchanger acts as a temporary buffer and may alter the brine composition through a process known as ion chromatography. If the resulting salinity is too high or the capillary pressure is high, the water film covering the rock surface becomes unstable resulting in a direct contact of oil with the rock surface (albeit often in presence on a thin hydration layer). On the other hand, if the salinity is low dominance of repulsive forces results in expansion of the double layer and eventually stabilizes the water films on the rock surface. If salinity becomes too low, simultaneous effects of (viscous) drag and electrostatic forces mobilize some fines and/or deflocculate clays (interlayer forces between clay layers that control the swelling state and integrity are mainly electrostatic interactions), which might be entrapped and block the rock pores. The charge density and distribution on the alumina-like surfaces of the clay also varies because of the cation-exchange reactions.

The effect of cation exchange on oil recovery was first applied to surfactant flooding and has been since considered as an important component of the chemical enhanced-oil-recovery processes. All the experiments on this topic have been exclusively conducted without crude oil. However, as we will show in this study, the presence of oil and the dynamics of the interactions between the crude oil, brine, and the rock can lead to different results than those inferred from the single-phase experiments. This can in return pose questions to the direct translation of the coreflood experiments to field-scale water- or chemical-flooding projects. We hypothesize that (1) adsorption of basic components of the crude oil on the cation exchange sites reduces the cation exchange capacity of the rock, and (2) adsorption of acidic components of the crude oil on the calcite and dolomite inhibits the dissolution of these minerals at elevated temperatures. It is therefore our objective to investigate the effect of the oil type and composition on the extent and nature rock-fluid interactions in porous media. We perform experiments in which brine with a different composition than that of brine initially in the cores is injected into these cores with and without the remaining oil saturation. The CEC of the rocks was calculated using the ionic composition of the effluent histories. Single-phase experiments were conducted to obtain the cation-exchange capacity of the cores, denoted by $Q_c$ (mequiv/mL pore volume), in the absence of the oil. The two-phase experiments were conducted with and without ageing the cores with crude oil. When the cores were not aged at room temperature, the effect of oil on the CEC was insignificant; however, at a higher temperature the polar components of the oil started to interact with the oil. A kinetic behavior was observed for this process. This was confirmed by the reduced CEC of the core that was aged with the crude oil. In this case, because the oil was in contact with the rock for a longer period, the positively charged components of the oil exchanged with the cations adsorbed on the rock. The structure of the paper is
as follows. In Section 2, we briefly present the reactions considered in this study. Next, we describe the experimental material, setup, and procedure in Section 3. In Section 4, the results of the experiments and their interpretations are discussed. We end the paper with the main conclusions of this study.

2. CALCULATION OF CATION EXCHANGE CAPACITY

In the simulations, we consider two main geochemical reactions, namely, cation exchange and dissolution of dolomite and calcite. The simulations were performed using Shell’s in-house transport simulator, MoReS, which is coupled to the chemistry package PHREEQC. PHREEQC is a software program with an extensive and editable database (with chemical reactions and their equilibrium constants) and can simulate chemical reactions to provide the composition of the aqueous phase in contact with minerals, gases, exchangers, and sorption surfaces. The default phreeqc.dat database file was included in our calculations, which uses Davies or Debye–Hückel equations for charged species.

To model the ion exchange the amount of exchanger, denoted by X (= Qx, mequiv/mL of pore volume) and defined as master exchange species in the PHREEQC database, should be provided. The ion exchange reactions occur in two steps in PHREEQC, which uses mass-action expressions based on half-reactions between the aqueous species and a fictive unoccupied exchange site41 for each exchanger. The following exchange reactions were modeled in this study

\[ \text{Na}^{+} + X = \text{Na}X \quad K_{\text{Na}} = \frac{[\text{NaX}]}{[\text{Na}^{+}][X]} \]  
(2)

\[ \text{Ca}^{2+} + 2X = \text{Ca}X_{2} \quad K_{\text{Ca}} = \frac{[\text{CaX}_{2}]}{[\text{Ca}^{2+}][X]^{2}} \]  
(3)

\[ \text{Mg}^{2+} + 2X = \text{MgX}_{2} \quad K_{\text{Mg}} = \frac{[\text{MgX}_{2}]}{[\text{Mg}^{2+}][X]^{2}} \]  
(4)

The combination of eq 2 with eq 3 and eq 4 provides the reactions that are more commonly used for modeling the exchange of sodium, calcium and magnesium ions

\[ 2\text{NaX} + \text{Ca}^{2+} = \text{CaX}_{2} + 2\text{Na}^{+} \quad K_{\text{Ca}/\text{Na}} = \frac{[\text{CaX}_{2}][\text{Na}^{+}]^{2}}{[\text{Ca}^{2+}][\text{NaX}]^{2}} \]  
(5)

\[ 2\text{NaX} + \text{Mg}^{2+} = \text{MgX}_{2} + 2\text{Na}^{+} \quad K_{\text{Mg}/\text{Na}} = \frac{[\text{MgX}_{2}][\text{Na}^{+}]^{2}}{[\text{Mg}^{2+}][\text{NaX}]^{2}} \]  
(6)

where \( K_{\text{Ca}/\text{Na}} = K_{\text{Ca}}/K_{\text{Na}}^{2} \) and \( K_{\text{Mg}/\text{Na}} = K_{\text{Mg}}/K_{\text{Na}}^{2} \). In the simulations, we used \( \log_{10} K_{\text{Ca}} = 0.0, \log_{10} K_{\text{Ca}} = 0.77^{44} \) and \( \log_{10} K_{\text{Mg}} = 0.60^{45} \). Another important equation is the charge-balance equation, which sets the sum of the equivalent anions and cations, including those on the rock surface, to zero.

We use the measured concentrations of the ions in the first effluent as the initial concentrations of the respective ions in the simulations. The measured concentrations of the injected low-salinity brine were used as boundary condition, which were slightly different from the reported concentrations in Table 1 due to small variations in preparing the various solutions. We neglected the role of proton exchange in competition for exchange sites, which is justified because the pH variations were not large, as can be observed in the experimental results.

3. EXPERIMENTS

3.1. Chemicals. The brine used in the experiments was prepared by dissolving NaCl, MgCl2·6H2O, and CaCl2·2H2O (Fisher Scientific) in deionized water. The compositions of the high-salinity and low-salinity brines are shown in Table 1. The properties of the crude oils are listed in Table 2.

3.2. Core Samples. Berea sandstone cores were used to perform the experiments. The bulk mineral composition of Berea sandstone56,57 was characterized by XRD, the results of which are shown in Table 3. The geochemical reactions occur at the surface of the rock (and in particular clays because of their large surface area)36–39 and therefore bulk mineralogy is only a partial indicator of the presence of minerals that might influence the direction of the reactions.

The cores had a diameter of 3.8 cm and length of 17.0 cm. The permeability and porosity of the cores were about 80–120mD and 0.20 ± 0.1, respectively. The cores were cast in Araldite self-hardening glue to avoid production from the axial core sides. After hardening, the glue was machined so that the core fitted precisely in the core holder. One hole was drilled through the glue layer to the core surface to allow pressure measurements. The core-holder is made of poly(ethylene ether ketone) (PEEK).58–60

In our discussions, we will interchangeably use the terms “external” and “edge” surfaces whose charges are pH dependent. These charges occur on the clay edges because of the protonation/deprotonation of the surface hydroxyl groups and therefore may vary with the pH.61 Moreover, we use the terms “internal surface”, “basal surface”, and “faces” to refer to the sites with the permanent charges on the clay surfaces. These charges occur because of the isomorphous substitution of the cations with a larger valency by the cations with a smaller valency resulting in a net negative charge. Table 4 provides a summary of the main attributes of the clay surfaces.

3.3. Experimental Setup. The experimental setup is shown schematically in Figure 2. A P500 pump was used for injection of brine. A transfer vessel connected to another pump was used to inject crude oil into the core. The pressure transducers monitored the pressure-drop over the inlet and outlet. A backpressure regulator was mounted to set the outlet pressure.

### Table 1. Compositions of High-Salinity and Low-Salinity Brines (in mmol/L and mequiv/L)

| Component/Description | High-salinity Brine (HSB) | Low-salinity Brine (LSB) |
|-----------------------|---------------------------|--------------------------|
| Component/Description | mmol/L | mequiv/L | mmol/L | mequiv/L |
| Na⁺ | 217 | 217 | 35.5 | 35.5 |
| Ca²⁺ | 1.8 | 3.6 | 2.55 | 5.1 |
| Mg²⁺ | 1.35 | 2.7 | 0.775 | 1.55 |
| Cl⁻ | 223.2 | 223.2 | 42.15 | 42.15 |
| Solution normality [N] | 223.3 | | 3.325 | 6.65 |
| Fraction of divalents, \( f_{2+} \) | 0.03 | | 0.16 |
| Total divalent concentrations | 3.15 | 6.3 | | |
| Ionic strength | 275 mmol/L | | 136 mmol/L | |
| Debye screening length | 20.4 nm | 26.4 nm |
pressure during the experiment. An in-house data acquisition system was used to record the pressures. The produced fluids were collected using a fractional collector. Water from a thermostated bath was circulated through a sleeve around the core-holder to keep the core at a desired constant temperature. An oven was used to set a constant temperature in experiments.

**3.4. Experimental Procedure.** The leakage-proof setup was flushed with CO$_2$ at atmospheric pressure to remove air from the system and then vacuumed for 12 h to remove the CO$_2$. Next, at least 20 pore volumes of high-salinity brine (HSB) were injected with increasing pressure steps of 5 bar to a maximum pressure of 20 bar to dissolve and remove the remaining traces of CO$_2$ and fully saturate the core with brine. All the fluids were injected with a rate corresponding to an interstitial velocity of 1 ft/d. The permeability of the core was also measured by changing the injection rates. In the single-phase experiments, the low-salinity brine was injected after this step and the effluent was collected at intervals of 5 min to measure its ionic composition using the inductively coupled plasma mass spectroscopy (ICP) technique. In the two-phase experiments, after conducting the single-phase part of the experiment, (1) the core was flushed with the high-salinity brine to reestablish the initial condition similar to the single-phase stage; (2) the core was saturated with the crude oil with an injection rate of 1–4 mL/min until no water production was observed at the outlet and the pressure remained constant; (3) the high-salinity brine was injected to produce the mobile oil; and (4) the low-salinity brine was injected to study the effect of the remaining oil on the cation exchange. In Exp. 6, the

| Table 2. Properties of the Crude Oils Used in the Experiments$^a$
| oil property | IFT with FW | API | density | viscosity | density | viscosity | TBN | TAN |
|---------------|-------------|-----|---------|-----------|---------|-----------|------|------|
|               | [mN/m]      | ['API] | [g/cm$^3$] | (20 °C) | [mPa.s] | (20 °C) | (60 °C) | mPa.s | (60 °C) | [mg KOH/g oil] | [mg KOH/g oil] |
| crude oil A   | 30          | 34.2 | 0.8540  | 4.7765   | 0.8153  | 3.8216   | 0.90  | 0.15 |
| crude oil B   | 27          | 41.6 | 0.8176  | 3.2769   | 0.7911  | 1.6755   | <0.1  | 0.17 |

$^a$IFT, TBN, and TAN stand for interfacial tension, total base number, and total acid number, respectively.

| Table 3. Mineralogical Composition (Mass Fraction, wt %) of the Berea Sandstone Used in the Experiments$^a$
| quartz | dolomite | calcite | illite/mica | kaolinite/chlorite | albite | orthoclase | siderite |
|--------|----------|---------|-------------|--------------------|--------|------------|---------|
| 94.9   | 1.1      | 0.2     | 0.40        | 1.6                | 0.2    | 1.3        | 0.5     |
| clay fraction | 50.6    |         |             | 40.4 (Kao) 9 (Chlor) |        |            |         |
| CEC (cmol/kg) | 10–40 | | 1–15 | | | | |
| surface area (m$^2$/g) | 80–150 | | 5–20 | | | | |

$^a$The numbers in the brackets are the clay fraction of the rock.

| Table 4. Clays Surfaces and Their Main Attributes
| term | charge type |
|------|-------------|
| faces, internal or basal surfaces | Permanent charge due to isomorphous substitution of, for instance, Si$^{4+}$ by Al$^{3+}$. The net charge of the internal surface of the clays is negative. The internal surfaces will not come in contact with oil. |
| edges or external surfaces | Both positive and negative charges may exist at the edges. These charges are pH dependent. The oil will come in contact with the external surface of the clays. |

Figure 2. Schematic of the setup used in the core-flow experiments. It consists of a coreholder in which a core is mounted. The core is kept at a constant temperature using a thermostat bath. The pressure is kept constant using a homemade back-pressure regulator.
setup was shut down after step 3 to age the core at a temperature of 60 °C and 20 bar for 8 weeks.

4. RESULTS AND DISCUSSION

4.1. Exp. 1: Single Phase Core Flow. Two single-phase experiments were conducted to determine the cation-exchange capacity of the Berea rock samples using PHREEQC as the base case. The results of these two experiments were similar and therefore only one experiment is reported here.

Figure A.1 in Appendix A shows the history of the concentration of Na⁺/Ca²⁺/Mg²⁺/Cl⁻ ions and the measured pH values of the effluents during injection of the HSB into the core. The pH and the concentration of the measured ions slightly decrease and attain values of the injected brine concentration. There is no evidence that significant cation exchange occurs during this process.

Figure 3 shows the effluent concentrations after injection of low-salinity brine (LSB) into a core initially saturated with high-salinity brine. For three cations (Na⁺/Ca²⁺/Mg²⁺), between injection and production points there are three regions separated during this process. Figure 3 shows the effluent concentrations after injection of low-salinity brine (LSB) into a core initially saturated with high-salinity brine. For three cations (Na⁺/Ca²⁺/Mg²⁺), between injection and production points there are three regions separated during this process.

4.2. Exp. 2: Effect of Injection Rate on Cation Exchange. To examine the effect of flow rate on the cation exchange, we performed Exp. 2 at two different flow rates (1 ft/day and 3 ft/day). A single core was used to conduct these experiments. To check the reversibility of the cation exchange process, we carried out an experiment with the sequence of HSB to LSB then again HSB to LSB. Histories of each ion collected in the effluent (Figure 5) and the pH values present in the core) with different rock compositions.

Figure 4. Simulation results of the measured pH during Exp. 1 (no oil present in the core) with different rock compositions.
4.3. Exp. 3: Temperature Effect on the Cation Exchange. To investigate the effect of temperature on cation exchange we carried out Exp. 3, in which the temperature was raised from 20 °C (Exp. 3a) to 60 °C (Exp. 3b). Figures 6 and 7 show the concentrations of the ions determined from the effluent ion concentrations as a function of the injected pore volumes of low-salinity brine at a “remaining” oil saturation of $S_{\text{oil, remaining}} = 0.45 \pm 0.03$ and $T = 20 \degree C$ (Exp. 4a). During the low-salinity water injection, about 2% of the oil initially in place (OIIP) was produced. In view of this small oil production, we assume that the oil saturation remains more or less unchanged and that the PHREEQC solution for a single aqueous phase flow problem can be applied for the interpretation where we assume interaction with a stationary adsorber. With these assumptions, the PHREEQC solution provides a reasonable match with the measured data at 20 °C. We used a $Q_v$ of 0.062 mequiv/mL and dispersivity-length values of 0.055 mequiv/mL and 0.85 cm to optimize agreement between the experiment and PHREEQC results. These values are close to the values obtained from the oil-free experiment shown in Figure 6. However, the small reduction of the $Q_v$ value from 0.062 mequiv/mL to 0.055 mequiv/mL is related to differences in the rock mineralogy and not to the presence of oil, as we will notice in Exp. 6b.

Exp. 4b was conducted after conducting Exp. 4a. In this experiment, HSB was injected to the core at $T = 60 \degree C$. Symbols indicate measured concentration, lines are modeled. The CEC remains constant within the range of temperature investigated in this study.

The attachment of the ions on the rock surface occurs on the pre-existing charged surfaces. The charge distribution of the surface can be determined using streaming potential or zeta potential measurements. In particular, Reppert and Morgan found that the magnitude of the zeta potential for Berea sandstone in contact with brines containing NaCl slightly increases as the temperature increases (0.044 mV/°C). When the dissolution reactions are included, a good match is obtained with a $Q_v$ value of 0.062 mequiv/mL, which indicates that the CEC remains constant when the temperature increases from 20 to 60 °C.

4.4. Exps. 4–6: Cation Exchange in the Presence of Oil. To examine the effect of oil saturation on the cation exchange, we performed three two-phase flow experiments (Exps. 4–6). In Exp. 4, we used crude oil type A (high base/acid ratio) without aging the rock. Using the same core we performed experiment (4a) at 20 °C and (4b) at 60 °C. In Exp. 5 and Exp. 6, we used crude oil type B (low base/acid ratio) and the experiments were both performed at 60 °C. The core was aged in Exp. 6 whereas in Exp. 5 the core was not aged.

Figure 8 shows the effluent ion concentrations as a function of the injected pore volumes of oil in low-salinity brine at a “remaining” oil saturation of $S_{\text{oil, remaining}} = 0.45 \pm 0.03$ and $T = 20 \degree C$ (Exp. 4a). During the low-salinity water injection, about 2% of the oil initially in place (OIIP) was produced. In view of this small oil production, we assume that the oil saturation remains more or less unchanged and that the PHREEQC solution for a single aqueous phase flow problem can be applied for the interpretation where we assume interaction with a stationary adsorber. With these assumptions, the PHREEQC solution provides a reasonable match with the measured data at 20 °C. We used a $Q_v$ and dispersivity-length values of 0.055 mequiv/mL and 0.85 cm to optimize agreement between the experiment and PHREEQC results. These values are close to the values obtained from the oil-free experiment shown in Figure 6. However, the small reduction of the $Q_v$ value from 0.062 mequiv/mL to 0.055 mequiv/mL is related to differences in the rock mineralogy and not to the presence of oil, as we will notice in Exp. 6b.

Exp. 4b was conducted after conducting Exp. 4a. In this experiment, HSB was injected to the core at $T = 60 \degree C$ to establish the same initial condition as for Exp. 4a. Next, LSB was injected into the core. When the temperature is increased
to 60 °C (Exp. 4b), the behavior was different. Indeed, with the increase of temperature from 20 to 60 °C, more oil was produced due to the reduction of oil viscosity or its expansion, which resulted in a remaining oil saturation of 0.40 ± 0.03. The results of this experiment and the model results for various Qv results are shown in Figures 9 and 10.

Figure 8. History of concentrations of effluent ions in Exp. 4a with crude oil type A (high base/acid ratio) at T = 20 °C and Srw = 0.45 ± 0.03. The core was not aged with the crude oil. Symbols indicate measured concentration, lines are modeled.

Figure 9. History of concentrations of effluent ions in Exp. 4b with crude oil type A (high base/acid ratio) at T = 60 °C and Srw = 0.40 ± 0.03. The core was not aged with the crude oil. The lines present simulations using different assumptions on CEC and the dispersivity length. D denotes the dispersivity length and L is the length of the core.

The conventional concept that determines the wetting effects is as follows: when the charges at the oil−water interface have the same sign as the charges of the rock−water interface it is possible to have a macroscopic water film and typical water-wet behavior. Repulsive forces originate from the double layers at the oil−water and rock−water surfaces. The repulsive forces become less at high ionic strength, which shields the surface charge. van der Waals forces with a layer of high dielectric coefficient and low refractive index (water) between the rock and the oleic phase are always attractive (see ref 29). These forces lead together to the disjoining pressure. If the capillary pressure exceeds the maximum disjoining pressure of the thick water film, then thick water film becomes unstable. When the double layers have opposite signs it is unlikely that a thick water film is stable. In the absence of a macroscopic water film, the rock becomes hydrophobic. At short ranges, the structural forces and the hydrogen bonding must be considered. The Pauli Exclusion Principle leads to repulsion between surfaces at extremely close range. For our interpretation, we refer to Figure 11 in which we extend this conceptual picture in case of highly irregular pore surfaces (more the rule than the exception) and to accommodate the presence of clays, which have both positively- and negatively charged sites. Figures 1 and 11 give a schematic picture of an oil ganglion inside a pore with a highly irregular surface. The conventional division between completely oil-wet or water-wet surfaces is modified as follows. Clay edges and asperities are pinning points for the oil ganglion.20−22 Some parts of the edges can be negatively charged while other parts can be positively charged. The polar components (negatively charged carboxylic, naphthenic acids and positively charged amines, cationic surfactants, pyridines) with opposite charges are adsorbed to the rock and provide surfaces of low interaction energy with the oil ganglion. Also neutral components (e.g., phenols) can be adsorbed by van der Waals forces and ligand bonding and thus create oil-wet spots. Other parts of the rock carry a water film with a thickness of the
order of the Debye length, which will be between the rock and oil surface.

Consequently, it can also be argued that presence of oil does not impact the total number of exchangeable sites on the rock surface. Recall that in the PHREEQC calculations, the CEC value is calculated from the width of the region with low concentrations of divalent cations. Nevertheless, when oil is present in the core, it is plausible that there is multicomponent adsorption of ions (on the rock surface or oil surface) involving both inorganic species (Na⁺, Ca²⁺, Mg²⁺) and polar compounds in the crude oil, as shown in Figure 11. It appears that these reactions are kinetically controlled and the polar components of the crude oil become more active at higher temperatures. Referring to Figure 11, the geochemical reactions, including cation exchange reactions, occur within the water films. Therefore, the presence of an (inert) oil drop is not expected to influence the final composition of the aqueous phase, although the transport of the ions from (and toward) this film to the bulk brine may be impeded. However, slow mass transfer should affect the whole length of the intermediate stripped region with low divalent-cation concentration (region 2), which is not observed in the results shown in Figures 9 and 10. Instead, it is likely that the polar components such as naphthenic acids, cationic surfactants, and pyridine molecules (base components) are attracted to the surface of the clay minerals with an opposite charge. The positively (negatively) charged compounds such as pyridine (carboxylic or naphthenic acids) can adsorb directly onto the rock surface at negatively (positively) charged pinning points (asperities or edges), albeit in the presence of a very thin water film because the polar functional groups accumulate at the oil(brine) interface. The higher Ca²⁺ and Mg²⁺ concentrations in the shaded area compared to the calculated equilibrium curve from PHREEQC in Figures 9 and 10 are attributed to higher amounts of basic or positively charged species in the crude oil compared to the acidic compounds. In other words, the higher concentrations of the divalent cations are because of the exchange with the positively charged species in the oil. Attachment of acidic or negatively charged components can also occur due to cation bridging or ligand bonding, which strips away exchangeable cations from the bulk aqueous solution.

The total surface of the clay minerals is a sum of external (edge) and internal (basal or faces) surfaces (for the terminologies see Table 4). Both surfaces carry charges; however, the origin of the charge on these surfaces is different. The charges on the external surfaces are pH-dependent and originate from the −OH sites on the (broken) edges of crystal lattices. The charges in the internal surfaces are result of the isomorphic substitution of the ions, that is, a cation with a larger charge (tetra- or trivalent) is substituted by a cation with a smaller charge (tri- or bivalent) resulting in a negative charge. Therefore, in 2:1 clays the interlayer space can accumulate hydrated or dehydrated cations to neutralize the negative charge. In clays like kaolinite, the pH-dependent charges contribute to the major proportion of the total net charge. On the contrary, the charges in internal surface contribute to more than 85% of the total charge of the 2:1 clays like vermiculite, smectite, and chlorite. The first part of the stripped region in Figures 9 and 10 is mainly attributed to cation exchange of the injected brine with the cations residing in the internal surface of the clays (permanent sites). Adsorption of the charged components of the crude oil is therefore expected to occur on the broken edges (with pH-dependent charges) or positively charged minerals such as calcite and dolomite at neutral pH values.

4.5. Exp. 5: Effect of Type of Crude Oil. In order to investigate the effect of the type of crude oil, Exp. 5 was performed at 60 °C and with crude oil type B (low base/acid ratio), which contains less basic compounds compared to crude oil type A (high base/acid ratio) (Table 2). Figures 12 and 13 show the history of the measured ions at the core outlet during single-phase (Exp. 5a) and two-phase (Exp. 5b) of the experiment, respectively. It appears that in both stages the measured values of Ca²⁺ and Mg²⁺ ions are higher than the initial and injected values of the ions, which is attributed to dissolution of Ca- and Mg-containing minerals in the rock. When oil is present after the retardation front, the behavior of Ca²⁺ and Mg²⁺ suggests another exchange between Ca²⁺ and Mg²⁺, where the concentration of Mg²⁺ is lower and Ca²⁺ is higher than the equilibrium concentration. The core we used in Exp. 5 was not from the same block as used in the other experiments. The difference might result from the different mineralogy of the rock. Nevertheless, the CEC value (0.06 mequiv/mL) is the same as in other experiments by fitting two fronts. The history of ions in Exp. 5b exhibits a similar behavior as in Exp. 4b, that is, between the two fronts there exists a region with a low concentration of the divalent ions and a region in which concentration of Ca²⁺ and Mg²⁺ gradually rise to the injected concentrations. Comparing the
shaded areas in Figures 10 and 13 reveals that the length of the transition zone in Exp. 4b is longer than in Exp. 5b. This is because of the difference in net charges of the two oil types. The base/acid ratio of oil type A is higher than that of the oil type B (low base/acid ratio). This again confirms that the base or positively charged components of the oil compete with the divalent ions for the negatively charged sites on clays minerals. Our results are consistent with the finding that polar oil components are adsorbed more on rock for crude oils with a high base/acid ratio,70,71 which is attributed to the adsorption of the base components to the negative sites of the rock.28,29,31

Furthermore, after the second front the concentration of Ca$^{2+}$ in the single-phase stage of the experiment (Figure 12) is higher than that of the two-phase stage (Figure 13). This suggests that when oil is present in the porous medium, less calcite is dissolved because the negatively charged components cover the calcite and dolomite surfaces. In the pH range of our experiments, calcite and dolomite surfaces are positively charged32−34,72 and therefore the negatively charged components of the crude oil can adsorb on the calcite surface and inhibit or delay the dissolution process.

4.6. Exp. 6: Effect of Aging. In Exp. Four and Exp. Five, the core was directly flushed with the high-salinity brine after saturating the core with oil, that is, there was not ample time for the oil and the rock to interact. In Exp. 6, after the single-phase stage, the core was resaturated with the high-salinity brine. Afterward, the core was saturated with crude oil type B (low base/acid ratio) and the setup was shut down for 8 weeks at constant pressure (50 bars) and temperature of 60 °C to allow time for the minerals and the fluids to interact and alter the rock wettability toward nonwater wet conditions. Under these conditions, the water film covering the surface can be very thin or unstable and therefore the polar components in the crude oil can adsorb onto the rock surface73 (see Figure 11). The low-salinity brine was then injected to study the effect of wetting behavior of the rock surface upon cation exchange.

Figure 14 shows the history of the ion concentrations of the single-phase stage of the experiment. The CEC of this core was calculated to be $Q_v = 0.04$ mequiv/mL, which is about 20% smaller than the CEC of the single-phase stage of the experiment, that is, Exp. 6a (Figure 14). The dashed line in Figure 14, calculated using the CEC value of Exp. 6a ($Q_v = 0.04$ mequiv/mL), deviates from the experimental data. Finally, dissolution of the minerals (calcite or dolomite) can no longer be inferred from the data.

It can be inferred from our experimental data that when there is enough time between the oil and the rock to interact, the positively (negatively) charged components of the crude oil are fully attracted to the rock to neutralize the negatively (positively) charged sites of the rock. In contrast to the water-wet surfaces, the cation bridging of the oil with the rock appears to be less important for the nonwater-wet spots because of their weak nature. Consequently, it is less likely that oil can be desorbed from the rock surface because of multicomponent cation exchange between the aqueous phase and the clays. Furthermore, the acidic
or negatively charged components of the crude oil cover the positively charged calcite and dolomite sites and prevent the rock dissolution. The extent of these multicomponent exchanges depends on the oil, brine, and rock compositions.

5. CONCLUSIONS

Under our experimental conditions (rock type and composition, brine compositions, oil types, and so forth) the following conclusions can be drawn from this study:

• Cation exchange is a reversible process at the salinity range we probed.
• The kinetics effects (nonequilibrium) on the cation exchange in the single-phase flow experiments are insignificant at the range we studied.
• The temperature dependence of the CEC of the Berea sandstone can be disregarded for the temperature range of this study (20−60 °C).
• Inclusion of the dissolution reactions are required to obtain meaningful information on the CEC when experiments at different temperatures are compared.
• In the presence of crude oil, base components of the oil participate in the cation exchange process. In this case, the ion exchange is a kinetically controlled process and its rate depends on residence time of oil in the pore, temperature, and kinetics rate of adsorption of the polar groups on the rock surface.
• At low temperatures (e.g., at room temperature), the exchange of ions between crude oil and the surrounding rock surface can be neglected, that is, all available sites exchange ions exclusively with the aqueous phase.
• The cation-exchange process occurs in two stages during two-phase flow in porous media. Initially, the charged sites of the internal surface of the clays establish a new equilibrium by exchanging cations with the aqueous phase. At later stages, the components of the aqueous and oleic phases compete for the charged sites on the external surface or edges of the clays.
• When there is sufficient time for crude oil to interact with the rock (i.e., when core is aged with crude oil), a fraction of the charged sites are neutralized by the charged components stemming from crude oil. This suggests that the apparent cation exchange capacity of rock decreases in the presence of crude oil.
• The positively charged calcite and dolomite surfaces (at the pH conditions of our experiments) are covered with the negatively charged components of the crude oil and therefore less or no dissolution takes place when oil is present in porous media.

Appendix A

Figures A.1 and A.2 are shown below:

Figure A.1. Production profile of effluents obtained from the ICP measurement and pH value during high-salinity brine injection.

Figure A.2. History of the effluent pH values: (a) Exp. 2, (b) Exp. 3, (c) Exp. 4, (d) Exp. (5), and (e) Exp. 6.
Notes
The authors declare no competing financial interest.

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