

Microfluidic Investigation of Low-Salinity Effects During Oil Recovery: A No-Clay and Time-Dependent Mechanism

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Summary

We present a study of the low-salinity effect during oil recovery using microfluidics experiments in an attempt to narrow the gap between pore-scale observations and porous-media-flow mechanisms, and to explain one type of low-salinity effect with delayed oil recovery and without the presence of clay. A microfluidic toolbox is used, including single-pore-scale microchannels, a pore-network-scale (approximately 10^2 pores) micromodel, and a reservoir-on-a-chip model (approximately 10^4 pores with heterogeneity), all with 2D connectivity. Experiments at the single-pore scale reveal a time-dependent oil dewetting and swelling behavior when a crude-oil droplet is in contact with low-salinity water. An interplay between water chemical potential and oil-phase polar compounds explains this pore-scale observation well. Experiments at the pore-network scale illustrate that the dewetting and swelling of residual oil in the swept region increase the water-flow resistance, modifying the flow field and thus redirecting the flooding liquid into unswept regions. This pore-network-scale effect is re-expressed into a macroscale model as a sweep-efficiency improvement derived from the change of relative permeabilities, which requires time to develop. Finally, experiments on our “reservoir-on-a-chip” model show significant incremental oil recovery during tertiary low-salinity waterflooding and confirm that late-time sweep-efficiency improvement contributes to most of the incremental oil recovery. On the basis of this microfluidic framework, we emphasize the following three findings:

- Low-salinity tertiary waterflooding can improve oil recovery by an improvement of sweep efficiency, which is a consequence of residual-oil dewetting and swelling.
- The low-salinity effect can occur without the existence of clay.
- The wettability alteration and oil swelling are time-dependent processes and should be expressed as a function of oil/water contact time rather than dimensionless time [pore volume (PV)], which explains some observations from previous coreflood experiments.

Introduction

Low-salinity waterflooding is considered a promising, cost-efficient, and environmentally friendly method for improved oil recovery (Morrow and Buckley 2011) and has attracted much attention over the past 2 decades. Tang and Morrow (1997) first reported that the oil recovery of a sandstone core increases by waterflooding with decreased salinity. Meanwhile, they found the decrease in salinity resulted in a transition toward a more-water-wet state. Studies, including field tests (Webb et al. 2003; McGuire et al. 2005; Robertson 2007; Lager et al. 2011) and laboratory corefloods (Tang and Morrow 1997; Webb et al. 2005; Zhang and Morrow 2006; Zhang et al. 2007; Rivet et al. 2010; Nasralla et al. 2010; Aghaeifar et al. 2018), reported up to 22% incremental oil recovery by injecting a decreased-salinity brine.

A wettability alteration toward a more-water-wet state and the essential role of polar compounds in the crude-oil phase (Lager et al. 2008a; Austad et al. 2010; RezaeiDoust et al. 2011; Emadi and Sohrabi 2013; Collins et al. 2018) are generally observed and believed to be direct causes of low-salinity-waterflooding effects. Some numerical-modeling work has accounted for the wettability alteration by interpolating the relative permeabilities between the water-wet and oil-wet state, and relative permeabilities are always assumed to be functions of saturations and salinity (Jerauld et al. 2006; Gupta et al. 2011; Masalmeh et al. 2014; Suijkerbuijk et al. 2014; Khorsandi et al. 2017a, 2017b).

However, the underlying mechanisms and dynamics of such wettability alteration and the role of clays and other polar compounds are still not well-understood. Multiple mechanisms have been proposed from different perspectives. Fines migration (Tang and Morrow 1999), pH elevation (McGuire et al. 2005; Austad et al. 2010), multicomponent ion exchange (Lager et al. 2008b, 2011), expansion of electrical-double-layer effects (Ligthelm et al. 2009; Myint and Firoozabadi 2015), water osmosis (Sandengen and Arntzen 2013; Sandengen et al. 2016; Fredriksen et al. 2017), and water microdispersion and coalescence of connate water (Emadi and Sohrabi 2013) are examples of popular hypotheses. Although it is believed that more than one mechanism might simultaneously contribute to the improved recovery (Suijkerbuijk et al. 2012; Sandengen and Arntzen 2013; Sheng 2014), none of the proposed mechanisms has received a general acceptance (Jackson et al. 2016). Furthermore, there are other questions related to the low-salinity effect. The significance of clays for the low-salinity effect is still under debate: Some suggest that the existence of clay in sandstones has an important influence on the low-salinity effect (Tang and Morrow 1999; Lager et al. 2008a; RezaeiDoust et al. 2011; Song and Kovscek 2015), while some more-recent studies have shown that the low-salinity effect can occur without the existence of clay (Emadi and Sohrabi 2013; Sohrabi et al. 2017; Bartels et al. 2017). In addition, some studies reported a time delay of tens of hours for the low-salinity effect, but few studies have discussed it (RezaeiDoust et al. 2011; Emadi and Sohrabi 2013; Masalmeh et al. 2014; Suijkerbuijk et al. 2014). One explanation is that such a delay is caused by the mixing of the injected low-salinity brine and the high-salinity formation brine (Masalmeh et al. 2014; Suijkerbuijk et al. 2014), but it has not been well-supported by direct experimental evidence.

One way to prove or disprove existing hypotheses and improve understanding of the process is to directly visualize oil/water/rock interactions at the pore scale (Song and Kovscek 2015). In recent years, microfluidics has become a powerful tool in the investigation of flow in porous media because of the ability to directly visualize fluid behavior at the pore scale (Karadimitriou and Hassanizadeh 2012; Ma et al. 2012; Yun and Kovscek 2015; Lifton 2016; Li et al. 2017; Xu et al. 2017a, 2017b; Yun et al. 2017; Anbari et al. 2018). Pore-scale studies of the low-salinity effect in microfluidics have been performed by many researchers. Emadi and Sohrabi (2013)

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performed micromodel experiments in 2D rock-like-pattern glass micromodels with different brines at pressure and temperature of 2,300 psig and 38°C, respectively. They attributed the increased oil recovery to the coalescence and swelling of connate water. They also observed the formation of water microdispersion in crude oil and wettability alteration while low-salinity brine is present; they hypothesized that the water-in-oil dispersion and the wettability alteration are both attributed to the release of surface-active components from the oil/water interface to the bulk oil. Song and Kovscek (2015) coated 2D silicon micromodels with clay and performed high- and low-salinity waterfloods in sequence. They showed that clay migration during a low-salinity waterflood can contribute to more oil recovery (up to 8%). Fredriksen et al. (2016, 2017) observed water-in-oil emulsions in 2D micromodels and attributed the low-salinity effect to water osmosis and water-in-oil swelling. Bartels et al. (2017) performed a series of high- and low-salinity waterfloods in single-channel 2D dead-end micromodels and observed contact-angle change in single pores during low-salinity waterflood, regardless of the presence of clay or the initial wettability state. These previous fundamental studies provide important pore-scale details, which can be valuable for developing core- or reservoir-scale models.

In this work, we first investigated the low-salinity effect in a dead-end micromodel as shown in the subsection Single-Pore-Scale Observation: Oil Dewetting and Swelling, where we observed a time-dependent oil dewetting and swelling caused by the water diffusion and spontaneous emulsification when the crude-oil droplets were in contact with the low-salinity water. Second, the subsection Pore-Network Visualization: Pore/Pore Interactions and Upscaling shows experiments performed in an intermediate pore network (containing approximately 10^2 interconnected pores), and we observed oil mobilization and oil recovery with improved sweep caused by a wettability change. Finally, as shown in the subsection Reservoir-on-a-Chip Validation: Delayed Increase in Oil Recovery, from the experiments performed in the reservoir-on-a-chip model (containing approximately 10^4 interconnected pores), we confirmed that the late-time sweep-efficiency improvement contributes to most of the incremental oil recovery. The low-salinity effect at all three scales shows similar time dependency with the response time of 10^1 to 10^2 hours, although the spatial scales are very different.

Experimental Method

Materials. A heavy crude oil was used in this study. The oil viscosity is 220 cp. The oil properties are listed in **Table 1**. This oil is active, characterized by an acid number of 3.01 mg/g. The interfacial tension (IFT) between the crude oil and deionized (DI) water is 9.5 mN/m. The relatively low IFT resulted from the high content of active compounds within the crude oil. An additional discussion of the oil properties is included in the supplementary information. Two crude-oil dilutions were also used in this study. We diluted the crude oil three times and 10 times by adding 2 and 9 volumes of dodecane for every volume of crude oil, respectively. Dodecane and crude oil are completely miscible under these two mixing ratios. The viscosity of the two diluted-oil samples are 4.4 and 2.2 cp, respectively. The viscosity of dodecane used in the dilution is 1.3 cp.

Crude-Oil Property	Value
Density	0.937 g/cm ³
Viscosity	220 cp
Total acid number	3.01 mg/g
IFT with DI water	9.53 mN/m*
IFT with 500 ppm brine	8.97 mN/m*
IFT with 3,000 ppm brine	8.06 mN/m*
IFT with 20,000 ppm brine	7.24 mN/m*
IFT with 120,000 ppm brine	5.32 mN/m*

*Crude-oil/water IFT vs. brine salinity is plotted in Fig. 7.

Table 1—Crude-oil properties.

A synthetic high-salinity brine with a salinity of 120,000 ppm total dissolved solids (TDS) was used. Other brines with lower salinities (20,000, 3,000, and 500 ppm) used in this study were diluted from this synthetic brine. The diluted brines with salinities of 20,000 and 500 ppm were used for characterization purposes, and the brine with a salinity of 3,000 ppm was used for both flow experiments and characterization. DI water was also used as a model low-salinity water (approximately 0 ppm, ideally). The formula and properties of the five brine/water samples are listed in **Table 2**. We measured the pH values of the five brine/water samples (pH values from 5 to 7) and ensured that alkali/crude-oil interactions did not exist in our experiments (Guo et al. 2006; Samanta et al. 2011). The pH values of the low-salinity-brine samples (DI water and 500 and 3,000 ppm brine) are between 5 and 6 because of the dissolving and dissociation of carbon dioxide when the salt contents are low.

We fabricated 2.5D glass micromodels using the method developed in Xu et al. (2017a). Detailed fabrication procedure can be found in their work. Compared with the 2D micromodels, the 2.5D micromodels have pore-scale 3D features in addition to the 2D array of pores, which has continuity of both the pore space and the grain phase. Therefore, capillary snap-off of the nonwetting phase and the continuity of the wetting phase are both allowed, making the system more realistic in studying multiphase-flow behavior. In addition, glass is used as the material because it has surface properties similar to those of quartz, which is the main component of sandstones, and has been widely applied by other researchers (Bowden et al. 2009; de Haas et al. 2013; Emadi and Sohrabi 2013; Song and Kovscek 2015; Bartels et al. 2017).

Microfluidic Platform Designs. Three types of micromodels (A, B, and C) were used in our experiments. Actual images of these three micromodels and their microscopic details are shown in **Fig. 1**. Micromodel A has a pair of dead-end pores connecting to a single main channel by pore necks. The pores are 200 μ m in diameter and the channel is 200 μ m in width. The pore throats are narrower and shallower than the pore bodies and the channel. Micromodel B has a 0.2×2.4 -cm homogeneous pore-network matrix; the matrix contains 1.4×10^3 identical interconnected pores. Micromodel C has a 1.6×3.2 -cm fractured geometry, containing a pore-network matrix of more than 10^4 identical pores and a fracture in the center of the geometry. **Table 3** summarizes the pore and throat sizes and depth of each micromodel.

Brine	Composition	Density	pH
High-salinity brine (120,000 ppm)	8.6% NaCl, 1.2% KCl, 2.0% CaCl ₂	1.070 g/cm ³	6.80
High-salinity brine (20,000 ppm)	Six times diluted from 120,000 ppm brine	1.013 g/cm ³	6.32
Low-salinity brine (3,000 ppm)	40 times diluted from 120,000 ppm brine	0.999 g/cm ³	5.46
Low-salinity brine (500 ppm)	240 times diluted from 120,000 ppm brine	0.997 g/cm ³	5.78
DI water (0 ppm)	—	0.997 g/cm ³	5.25

Table 2—Brine properties. NaCl = sodium chloride; KCl = potassium chloride; CaCl₂ = calcium chloride.

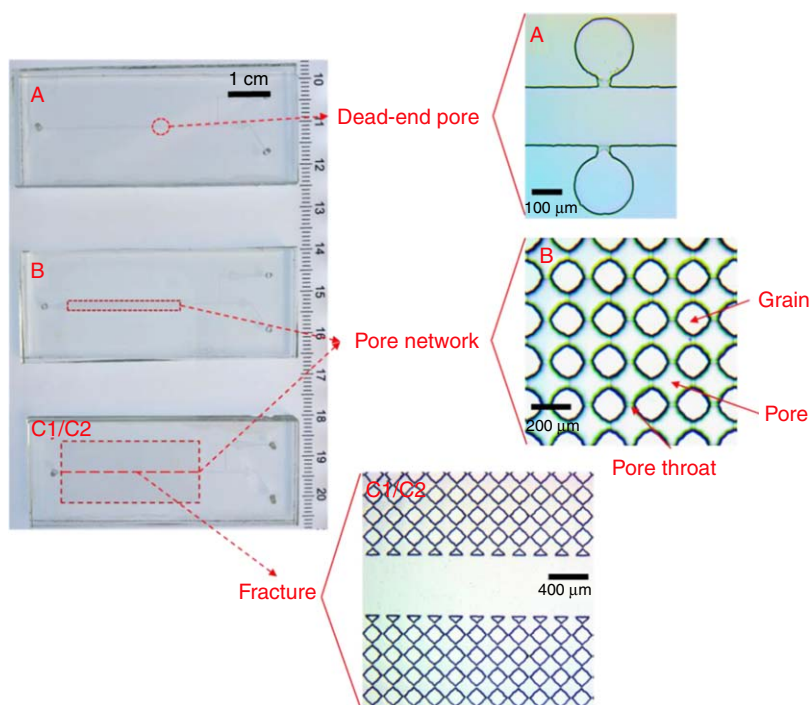


Fig. 1—Images of micromodels at the macroscale (left) and pore scale (right). Micromodel A is a dead-end pore micromodel, Micromodel B is a narrow homogeneous micromodel, and Micromodel C (C1 and C2) is a homogeneous micromodel with a fracture. The scale on the left is in centimeters.

Micromodel		Pore-Body Width (μm)	Pore-Throat Width (μm)	Pore-Body Depth (μm)	Pore-Throat Depth (μm)	Aspect Ratio (length/width)
Micromodel A		200	37	21±1 μm	≈5	5.4
Micromodel B		200	40	21±1 μm	≈5	5
Micromodel C	C1	200	37	22±1 μm	≈10	5.4
	C2	200	32	21±1 μm	≈5	6.3

Table 3—Micromodel properties.

Two Micromodel C chips labeled as C1 and C2 were used. C1 and C2 have a similar pattern, except that C1 has slightly deeper etching depths (approximately 1 μm deeper for pore bodies and approximately 5 μm deeper for pore throats) compared with C2. Therefore, the pore-throat/pore-body ratio in C1 is larger than that in C2, which implies a higher pore/pore mass-transfer efficiency. The pores and grains in Micromodels B and C have an average size of 200 μm in diameter, leading to a porosity of 0.55 and a permeability of approximately 1 darcy in the porous medium. **Table 4** shows the experiments performed in Micromodels A and B and Micromodels C1 and C2 and the observation scales in different micromodels. Micromodel C (the “reservoir-on-a-chip” model) contains approximately 10⁴ 2D connected pores and is considered above the representative-elementary-volume (REV) scale according to literature (Zhang et al. 2000; Hilpert and Miller 2001; Joekar-Niasar and Hassanizadeh 2011). With 3D pore connectivity, a minimum of approximately 10⁴ pores is required to be considered above the REV scale, and with 2D pore connectivity, a minimum of approximately 10³ pores is required to be considered above the REV scale.

Experimental Design. 10 experiments were performed in this study. As shown in Table 4, Experiments 1 through 4 were performed in a dead-end micromodel, Micromodel A; Experiments 5 and 6 were performed in a homogeneous porous matrix, Micromodel B; and Experiments 7 through 10 were performed in a “reservoir-on-a-chip” model, Micromodel C (Micromodels C1 and C2). All experiments were performed at room temperature (20°C) and pressure (1 atm). In all 10 experiments, we first saturated the clean and dry micromodels with crude oil, aged the micromodels for 10 hours, and then performed water injection. Discussions regarding the aging time and the micromodel-cleaning procedure are in the supplemental information. To ensure that air was completely expelled, we saturated the micromodels by injecting the oil with a syringe pump at a high injection rate (approximately 500 μL/h) for a long time

(> 0.5 hours), which equals more than 50 PV in Micromodel C. Under this condition, the high-pressure gradient and the dissolution of air in oil synergistically remove the air from the pore systems. We also viewed the micromodel under the high-resolution microscope to ensure that no air bubbles were present. Using these procedures, we effectively removed the air bubbles in all four micromodels (Micromodels A, B, C1, and C2).

Micromodel	Experiment	Dimension Under Observation	Number of Pores Under Observation	Fracture/Channel Width–Etching Depth
Micromodel A	1, 2, 3, 4	400×800 μm	2	200–21±1 μm
Micromodel B	5, 6	2×3 mm	1.65×10 ²	No fracture/channel–21±1 μm
Micromodel C	C1	7	1.6×3.2 cm	≈10 ⁴
	C2	8, 9, 10	1.6×3.2 cm	≈10 ⁴

Table 4—Experiments on micromodels.

Fluids were injected using a syringe pump. For visualization, in Experiments 1 through 6, a digital camera mounted on a microscope was used to capture time-lapse images from under the micromodel. In Experiments 7 through 10, a digital camera was used to capture time-lapse images from above the micromodel. **Fig. 2** shows a schematic of the microfluidics-experiment setup. In this work, we quantified the oil saturation of the captured images using the open-source image-analysis software ImageJ. We separated the oil phase by binarizing the color of the images and calculated the area percentage occupied by oil to obtain the oil saturation. A spinning-drop tensiometer was used for IFT measurement between the crude oil and different brines.

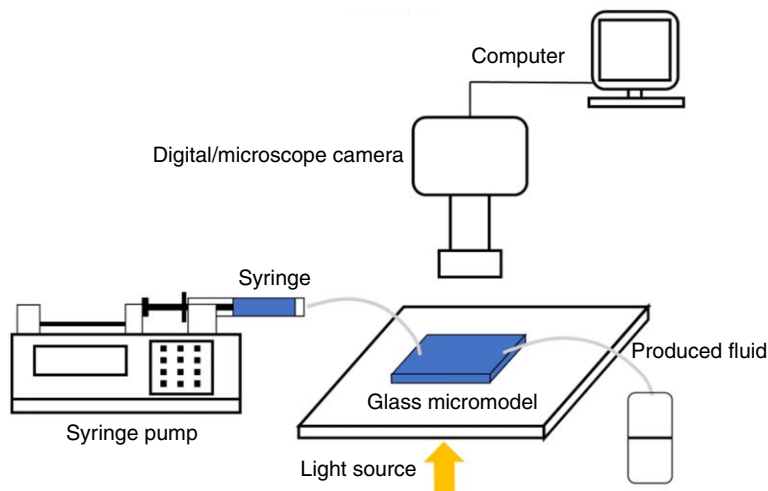


Fig. 2—Schematic of the micromodel experimental setup.

Results and Discussion

Single-Pore-Scale Observation: Oil Dewetting and Swelling. The oil used in Experiments 1 and 2 was the undiluted crude oil, and the oils used in Experiments 3 and 4 were the three-times-diluted crude oil and 10-times-diluted crude oil, respectively. Experiment 1 provided visual observation of the crude oil's behavior with high-salinity brine (120,000 ppm TDS), whereas Experiment 2 provided visual observation of the crude oil's behavior with low-salinity water (DI water). Experiments 3 and 4 provided the dynamics of the two diluted crude oils during their interaction with DI water. It should be noted that Experiments 1 through 4 are typical secondary-flooding processes.

Dead-end pores and the channel in Micromodel A were first saturated with the oil. After 10 hours of aging, water was injected through the channel, removing the crude oil in the main channel and leaving the oil droplets trapped in the pores. In all four experiments, the water-injection rate was kept constant at 1.0 $\mu\text{L}/\text{h}$ and continued for at least 3 days. A microscope camera was used to capture images at different times of a fixed pair of dead-end pores in all four experiments.

Observation From Experiment 1: Undiluted Crude Oil with High-Salinity Water. In Experiment 1, when the crude oil came in contact with high-salinity water, the system remained weakly oil-wet (the contact angle at the interface is greater than 90°) and did not change during the 3 days of high-salinity-water injection, as shown in **Fig. 3a**. The oil droplets in the dead-end pores did not change in shape or in color. Small oil droplets were left on the channel surface and were difficult to remove using brine because of the oil-wetting state of this oil/brine system. The wetting capability of crude oil was also addressed in previous wettability studies of crude oil on different surfaces (Buckley and Liu 1998; Buckley et al. 1998).

Observation From Experiment 2: Undiluted Crude Oil with Low-Salinity Water. In Experiment 2, when the crude oil was placed in contact with DI water, the apparent contact angle gradually decreases, as shown in the microscopic images in **Fig. 3b**. Higher-magnification images at the beginning and after 2 days of DI-water injection are shown in **Fig. 4a**. In the images, the phase boundaries (marked by the thick dark lines) moved inside of the pore, indicating the detachment of the oil from the surface. This confirmed that this apparent contact-angle decrease is caused by wettability change. Wettability change, indicated by a complete detachment of the oil droplet from the surface during the injection of low-salinity water (650 ppm diluted synthetic seawater), was also observed, as shown in **Fig. 4b**. The dead-end pore was only partially filled with crude oil, unlike the pores in **Fig. 3**.

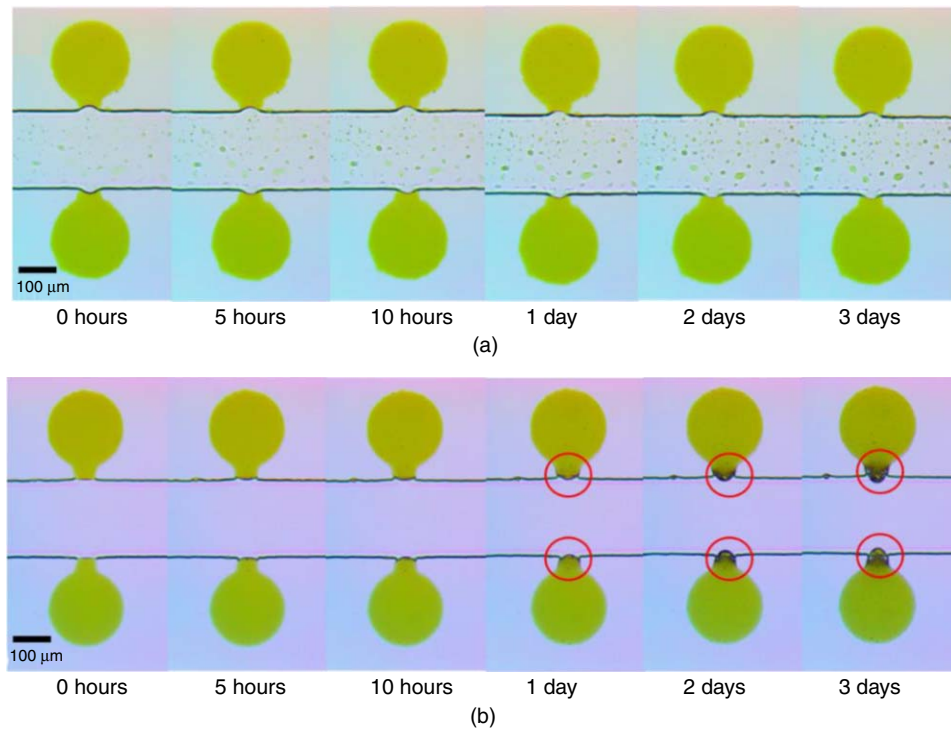


Fig. 3—Crude-oil behavior in the dead-end pores during Experiments 1 and 2. (a) Crude oil in contact with high-salinity water at different times in Experiment 1. (b) Crude oil in contact with DI water at different times in Experiment 2. The yellow phase in each image is the crude oil, and the channel in each image was filled with water. Circled areas with dark color in (b) show oil swelling and the formation of water-in-oil emulsions.

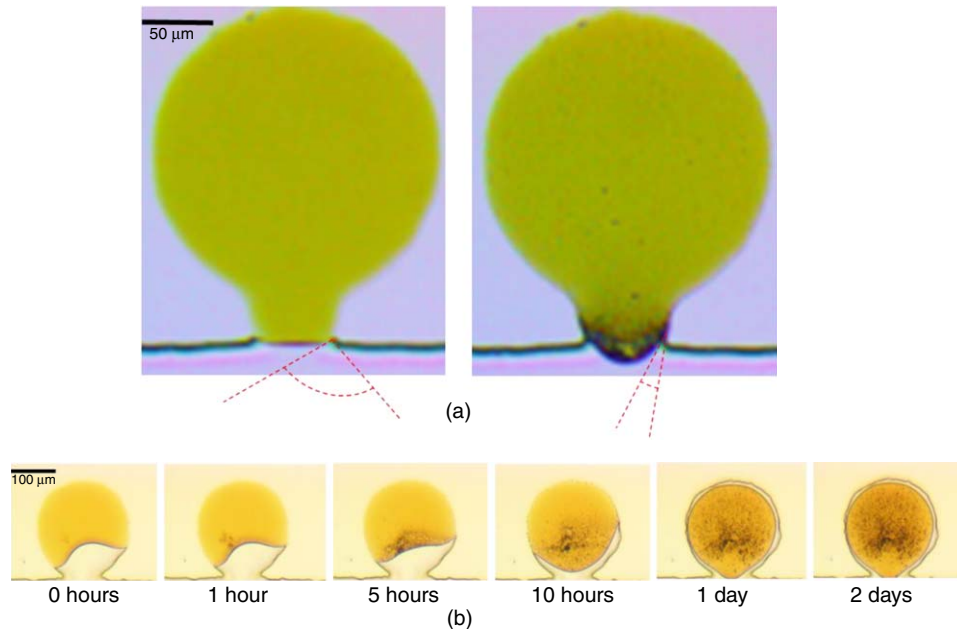


Fig. 4—(a) Higher-magnification images of crude-oil/water/solid contact angle in the dead-end pore captured at the beginning and after 2 days of DI-water injection in Experiment 2. (b) Crude oil in contact with 650 ppm low-salinity water at different times with the pore partially filled with oil. Here, we clearly observe the mobilization of the contact line, which indicates that the low-salinity waterflooding does change the wettability, and contact-line pinning is not the only reason for the apparent contact-angle decrease.

The in-situ contact-angle measurements within the pores in Fig. 3b are shown in **Fig. 5**. Shortly after the DI water contacted the oil droplets (at 0 hours), oil was the wetting phase as the contact angle at the oil/water/solid interface was $110 \pm 10^\circ$. After 3 days, the system became strongly water-wet as the contact angle became $20 \pm 10^\circ$. Quantitative analysis was not performed with partially filled dead-end pores in Fig. 4. Detailed pore-scale observations and the contact-angle measurements are discussed in the supplemental information. Contact-line-pinning results from the presence of surface heterogeneities can affect the macroscopic contact-angle measurement (Joanny and de Gennes 1984; Nadkarni and Garoff 1992; Liu and Zhang 2013; Paxson and Varanasi 2013). Although we

observed the decrease of the contact angle with the movement of the contact lines, as shown in Figs. 4a and 4b, we do not exclude the possibility that the pinning of a three-phase contact line during oil swelling can also contribute to the apparent contact-angle decrease, especially when the contact location is at the convex tip of the grain surfaces (pore throat).

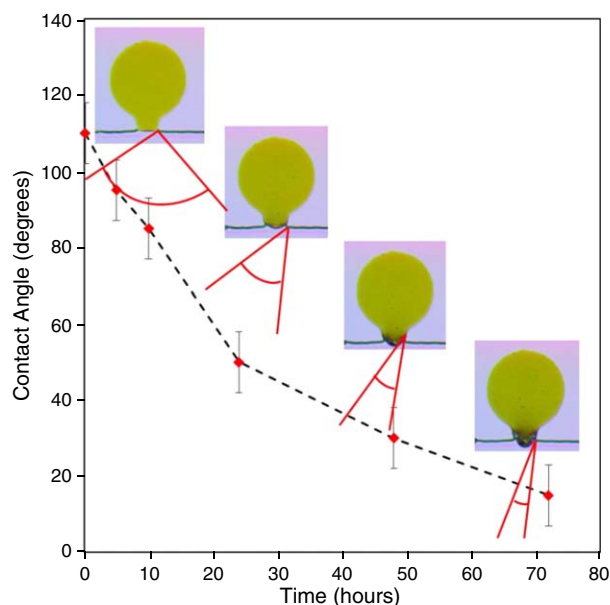


Fig. 5—Contact angles in dead-end pores at different times in Experiment 2. The wettability changed from slightly oil-wet to strongly water-wet during 3 days of DI-water injection.

Oil swelling was observed in Experiment 2 when the oil was placed in contact with low-salinity water. The oil-swelling behavior was also observed in Experiments 3 through 6, as discussed later in this paper. This swelling is confirmed to be caused by the formation of a fine water-in-oil emulsion. During the water-in-oil emulsification process, small water droplets were generated within the crude-oil droplets, especially near the crude-oil/bulk-water interface. These water droplets/emulsions appear to be dark dots under transmitted light, as shown in the circled regions of Fig. 3b. The water emulsions within the oil droplets come from the surrounding water by means of diffusion.

Oil-Swelling Dynamics. Water diffusion and emulsification in the crude oil were observed in Experiment 2, resulting in oil swelling. To further quantify the water-diffusion process, we performed Experiments 3 and 4 with three- and 10-times-diluted crude-oil samples, respectively. Experiments 3 and 4 also show water-in-oil spontaneous emulsion by means of water diffusion. We plotted the oil-swelling ratio in Experiments 2 through 4 vs. time in **Fig. 6a**. The oil-swelling ratio is defined as the ratio of the swelling volume to the initial-oil-droplet volume before swelling. For each experiment, two pores were analyzed, and two sets of plots were obtained. In Fig. 6a, the oil-swelling ratio of the three oils after 70 hours was between 1.5 and 2.5%. It appeared that the oil-swelling rate remained at the same order of magnitude in Experiments 2 through 4.

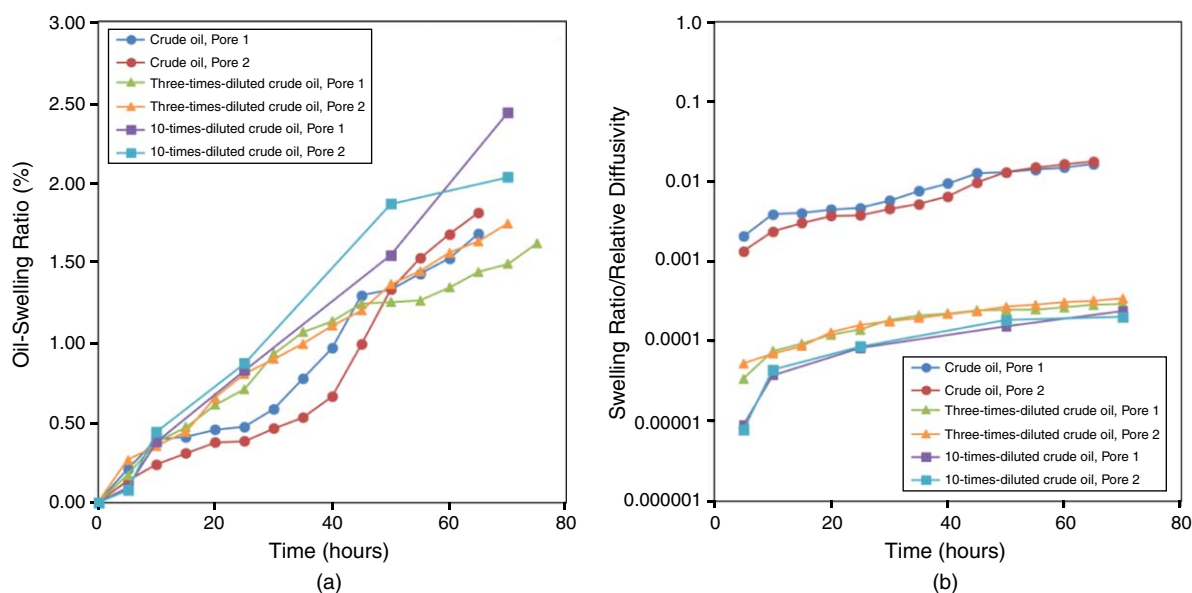


Fig. 6—(a) Oil-swelling ratio vs. time in Experiments 2 through 4 with the original crude oil, the three-times-diluted crude oil, and the 10-times-diluted crude oil. (b) Scaled oil-swelling ratio in Experiments 2 through 4 vs. times after dividing by the relative diffusivity factor because of the viscosity reduction.

In Experiments 3 and 4, the dilution of the crude oil resulted in two consequences: a concentration reduction of the crude-oil components, and a reduction of the oil viscosity. From the Stokes-Einstein equation, the diffusion dynamics in a fluid is affected by atomic diffusion and viscosity (Brillo et al. 2011). Although the crude-oil concentration decreased during the dilution, the viscosity reduction promoted the water-diffusion process and counterbalanced the overall effect. To eliminate the effect of viscosity reduction, we performed a simple scaling. The swelling ratio of the two diluted-oil samples is divided by the relative diffusion factor resulting from the viscosity reduction. The relative diffusion factor is calculated by

$$D_{r1} = \frac{D_1}{D_0} = \frac{\eta_0}{\eta_1}, \dots \dots \dots (1)$$

where D_{r1} is the relative diffusion factor of water in Diluted Oil 1 to the crude oil; D_0 and D_1 are the diffusion coefficient of the crude oil and Diluted Oil 1, respectively; and η_0 and η_1 are the viscosity of the crude oil and Diluted Oil 1, respectively.

Scaled data were plotted in Fig. 5b. In the scaled plots, it can be seen that the swelling ratio decreases by two orders of magnitude when the oil was diluted three times, and further reduced by one-half when the oil was diluted 10 times. The analysis here shows a decreased oil-swelling rate, as well as a decreased water-emulsification rate, when the crude-oil concentration decreased. An essential inference is that both the components in the crude oil and the diffusion of water in crude oil determine the oil-swelling and the wettability-alteration dynamics observed in Experiments 2 through 4.

Hypothesis and Evidence of Mechanisms. The oil dewetting and swelling observed in Experiments 2 through 4 agrees with the qualitative observations made in literature (Emadi and Sohrabi 2013). It can be explained by an interplay between water chemical potential and polar compounds (e.g., acids, quaternized nitrogen, heterocyclic ring), as shown in Fig. 7. Before a detailed description, we emphasize several points about the system that have been examined in the literature. The four points are:

1. Reservoir crude oil was in equilibrium with formation high-salinity water before the recovery. Thus, the water chemical potential in high-salinity water is similar to that in the original crude oil.
2. Water chemical potential in low-salinity water is higher than that in high-salinity water (Sandler 2017).
3. Water chemical potential in an oil phase with fewer polar compounds in bulk is higher than that with more polar compounds in bulk (De Gennes and Taupin 1982; Lemaire et al. 1983; Karaborni et al. 1993).
4. The concentration of polar compounds in bulk crude oil, on a solid/oil interface and on a water/oil interface, are in equilibrium and competing. An increase in one of those will lead to a decrease in others (RezaeiDoust et al. 2011; Emadi and Sohrabi 2013).

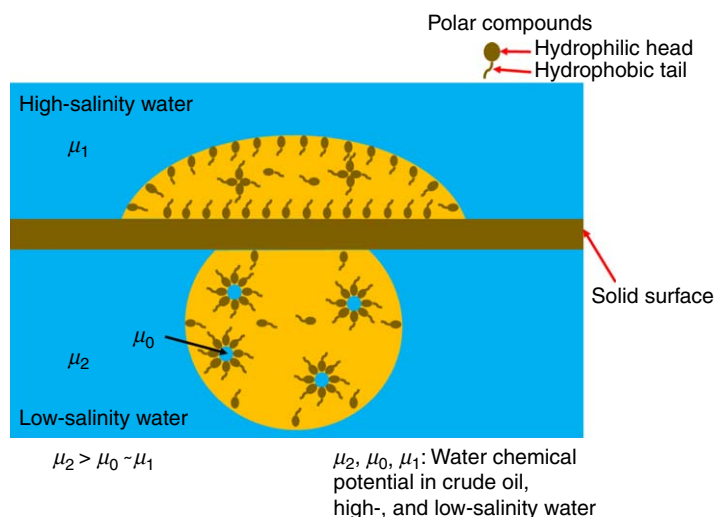


Fig. 7—Illustration of different wettability behaviors in high- and low-salinity environments. The upper half represents the oil droplet immersed in high-salinity water, in which case polar components stay at the oil/water and oil/solid interfaces and thus keep the oil-wetting to the solid surface. The bottom half represents the oil droplet immersed in low-salinity water, in which case the expanding of the internal emulsion droplets' surface provides a large area onto which the polar components adsorb; thus, the amount of polar components on oil/water and oil/solid surfaces decreases, which results in a less-wetting condition. Yellow and blue represent the crude oil and water phase, respectively. The water emulsions in the oil phase come from the surrounding water by diffusion.

From Points 1 and 2, it can be inferred that the water chemical potential in low-salinity water is higher than that in the original crude oil, so there is a tendency to reduce this chemical-potential difference when they are in contact. However, water concentration and salinity cannot significantly change in both phases. Thus, to reduce the water-chemical-potential difference by increasing the water chemical potential in the bulk-oil phase, polar-compound micelles in the oil phase capture the dissolved water and form small water droplets by means of water diffusion through the oil phase, providing more interfaces on which polar compounds can adsorb. As a consequence, polar compounds leave the bulk interface of the oil droplets and oil bulk to adsorb on newly generated droplets' interfaces. Therefore, the reduction of polar-compound concentration, both in the oil bulk and on the oil/solid interface, results in an increase of the water chemical potential in the oil phase and thus reduces the chemical potential difference across the aqueous/bulk-oil interface. During this process, fewer polar compounds on the oil/glass interface make the oil phase less wetting to the solid surface. To summarize, the wettability changes when the water-in-oil spontaneous emulsification occurs with the presence of surfactant-like polar compounds. The spontaneous emulsification in a tertiary system (water, oil, and surfactant) produced by diffusion at a nonequilibrium state has been discussed in the literature (Miller 1988), and our hypothesis provides an explanation for this phenomenon.

It is difficult to measure the dynamic distribution of polar compounds within the crude-oil phase. However, there is an easy-to-examine inference of this hypothesis: The oil/water IFT should increase when the concentration of the polar compounds on the interface

decreases. The oil/solid IFT γ_{os} and the water/oil IFT γ_{wo} should both increase when there are fewer polar compounds on the surface. We measured the IFT between the crude-oil droplets and the water phase at different water salinities, as shown in Fig. 8. The results show that the oil/water IFT increases monotonically as the salinity decreases. The IFT between the crude oil and the 120,000 ppm high-salinity brine is 5.32 mN/m, 44% lower than the crude-oil/DI-water IFT, which is 9.53 mN/m. The IFT data support the hypothesis that the decrease of water salinity reduces the polar compounds absorbed on the surface. In addition, if the initial status is oil-wet, the contact angle θ ($>90^\circ$) decreases when γ_{os} and γ_{wo} increase, according to the Young-Laplace equation ($\gamma_{os} = \gamma_{ws} + \gamma_{wo} \cos\theta$). This contact-angle decrease results in the oil being less wetting for the surface. At a later state, when the contact angle is less than 90° , more-complex analysis is required. However, assuming a constant γ_{os}/γ_{wo} ratio will result in further decreasing of the contact angle θ . This inference of wettability change also agrees with the experimental observation.

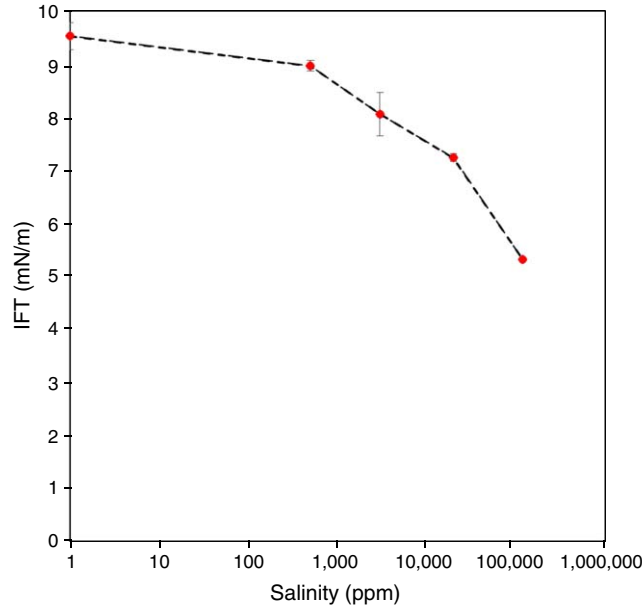


Fig. 8—Crude-oil/water IFT at different brine salinities. The salinity of DI water was plotted at 1 ppm. Error bars were calculated from multiple repeating measurements.

Given that the solubility of water in crude oil is low at the equilibrium state (Pedersen et al. 2014), the wettability alteration and the water-in-oil emulsification are both constrained. Given that the diffusion process is time dependent, wettability change and the spontaneous emulsification also show time dependency, as shown in Experiments 2 through 4. This time-dependent process agrees with previous observations in the literature (González-Ochoa and Arauz-Lara 2007; Santana-Solano et al. 2012).

The observed response time of tens of hours in the dead-end experiments also agrees with the characteristic time of water diffusion into oil in the pore through a narrow throat. We denote the characteristic diffusion time as t_c , the characteristic throat length as L_t , and the characteristic pore length as L_p . We made a zero-order approximation of the characteristic time by linearizing Fick's law of diffusion,

$$VC = \int_0^t D_w A_p \frac{dC}{dL} dt. \quad \dots \dots \dots (2)$$

From Eq. 2, we have the estimation

$$H_p L_p^2 C = D_w (L_t H_t) \frac{C}{L_p} t_c. \quad \dots \dots \dots (3)$$

In Eqs. 2 and 3, V is the total volume of one pore, C is the water concentration in oil, D_w is the water-diffusivity coefficient in oil, A_p is the pore-throat cross area, and H_t and H_p are pore throat and pore-body depth, respectively. Therefore, we have

$$t_c = \frac{L_p^3 H_p}{L_t H_t D_w} = \frac{(100 \mu\text{m})^3 \times 20 \mu\text{m}}{40 \mu\text{m} \times 5 \mu\text{m} \times 0.23 \times 10^{-11} \text{ m}^2 \cdot \text{s}} \approx 12 \text{ hours}. \quad \dots \dots \dots (4)$$

The diffusivity D_w is estimated by scaling the water-in-octane diffusivity (approximately $10^{-9} \text{ m}^2 \cdot \text{s}$) by a factor of the viscosity ratio of 440 (the viscosity of octane is 0.5 cp, and the viscosity of crude oil is 220 cp).

To provide additional evidence of this hypothesis, we repeated this experiment with model oil (dodecane) with the addition of surfactants (to mimic natural polar components). The wettability alteration and oil swelling were observed when model oil contains oleic surfactants, as shown in the supplemental information.

Pore-Network Visualization: Pore/Pore Interactions and Upscaling. An understanding of the pore-scale oil/water/grain behavior is necessary, but not sufficient, to explain the reservoir-scale oil-recovery performance because the interactions between neighboring pores can be complex and nonlinear (Blunt 2001; Xu et al. 2017b). To capture how pore-scale behavior of wettability alteration and oil swelling contribute to the oil displacement in porous media, we performed intermediate-scale (pore-network-scale) observations in

Micromodel B (Experiment 5 and 6), where 1.65×10^2 interconnected pores are presented in every microscopic image. The pores under observation are a portion of the total 1.4×10^3 pores in Micromodel B. The major difference between Experiments 5 and 6 is whether the pore network was fully swept or only partially swept before DI waterflooding.

Only a portion (2×3 mm) of Micromodel B was visualized and presented in this work. The microscope platform could only provide observation of one fixed area with time. Once the experiment began, the observation location was fixed. The images we provided were taken from the middle section of Micromodel B to minimize entry/end effects.

Observations from Experiment 5: Well-Swept Region During Low-Salinity Waterflood. In Experiment 5, Micromodel B was well-swept, with only discrete residual oil left in pores; no continuous unswept oil remained. This sweep was achieved by flooding the oil-saturated micromodel with high-salinity water at a high flow rate of $100 \mu\text{L/h}$ (with a capillary number of 1.3×10^{-4}) for 5 minutes. Approximately 16 PV of high-salinity water was injected during this procedure. The well-swept pore network is shown in **Fig. 9a** (oil saturation is 67% in Fig. 9a). The injection rate was then slowed down to $1.0 \mu\text{L/h}$. Three days of high-salinity-water injection of 130 PV was first performed and then followed by low-salinity-water injection of 130 PV for another 3 days. The capillary number for the high- and low-salinity injections was 1.3×10^{-6} and 7×10^{-7} , respectively. The capillary number, denoted as Ca , is calculated using

$$Ca = \frac{q_w \eta_w}{W D_p \phi \gamma_{wo}}, \quad \dots \dots \dots (5)$$

where q_w is the injection rate; η_w is the water viscosity; W and D_p are the width and the etching depth of the micromodel, respectively; ϕ is the porosity; and γ_{wo} is the water/oil IFT.

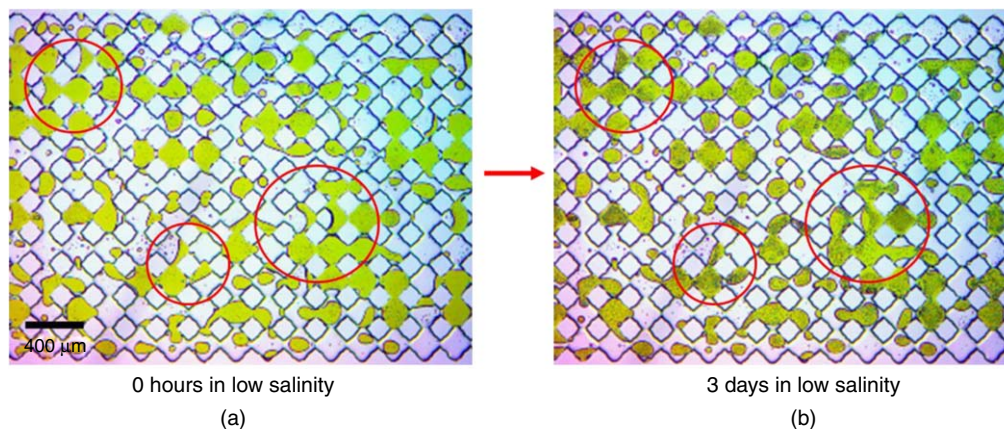


Fig. 9—A well-swept area of Micromodel B at different times in Experiment 5. (a, b) The beginning and the ending of the DI-water injection at $1 \mu\text{L/h}$. Circled areas show oil-droplet swelling and deformation caused by the growth of water-in-oil emulsions. The flow direction in each image was from the left to the right. Water in the amount of 130 PV was injected during the low-salinity injection.

For accurate control of the syringe-pump-injection process, we used injection rate no less than $1 \mu\text{L/h}$. Micromodel B has a relatively small PV of slightly greater than 0.5 μL ; therefore, the total PVs injected were high after several days of injection. The phenomena we observed were time dependent, and so the time duration rather than the injected PV is plotted.

Results show that residual oil saturation in this well-swept region did not significantly change after 3 days of DI-water injection, although wettability alteration did occur and oil swelling (with spontaneous water emulsification) was also observed, as shown in Fig. 9. The oil swelling was determined to be approximately 2% (the oil saturation increased by approximately 2%) by comparing the oil saturation of the two images before and after 3 days of contact with DI water. This result suggests that the low-salinity effect does not help in recovering residual (capillary-trapped) oil. This result is not surprising, because the capillary resistance on a nonwetting oil droplet (10^{-2} to 10^0 psi/droplet) is orders of magnitude larger than a typical pressure gradient (approximately 1 psi/ft) (Stegemeier 1974; Morrow 1979; Blunt et al. 1994), in which case only a slight swelling (2%, as measured from Fig. 9) will not mobilize residual oil droplets.

Observations from Experiment 6: Partially Swept Region During Low-Salinity Waterflood. In Experiment 6, Micromodel B was saturated with crude oil and flooded by 40 PV of high-salinity water at an injection rate of $1.0 \mu\text{L/h}$ until a steady state was reached, and then 130 PV of DI water was injected at constant flow rate of $1.0 \mu\text{L/h}$ for 3 days. The capillary number for the high- and low-salinity injections was 1.3×10^{-6} and 7×10^{-7} , respectively. Because of the fingering effect (Shraiman 1986; Zhao et al. 2016), only approximately 60% of the observed region was swept after high-salinity waterflood, and the other approximately 40% of the observed region was unswept, as shown in **Fig. 10a**.

Considerable further oil recovery was observed after the DI-water injection, as shown in Fig. 10. The oil saturation was plotted against time in **Fig. 11**. Similar to single-pore-scale experiments (Experiments 1 and 2) and Experiment 5, dewetting and swelling of crude oil with spontaneous emulsification are observed. After tens of hours of DI-water injection, although the residual oil droplets in the swept region were not mobilized, invasion of water into the previously unswept oil-saturated region was observed, as shown in Figs. 10d through 10f. This improvement in sweep finally brought 9% incremental oil production in the observation area, as shown in Fig. 10, in this homogeneous micromodel.

Mechanisms from Pore-Scale Perspective. From pore-network-scale experiments, we demonstrated that although the oil dewetting and swelling occur during a low-salinity waterflood, the outcomes can be very different depending on the initial sweep conditions. During the low-salinity DI waterflood in Experiments 5 and 6, we did not see a mobilization of the scattered residual oil droplets in the previously swept region. However, the mobilization of the remaining oil in the initially unswept region in Experiment 6 indicates that improvement of the sweep efficiency is potentially the major source of incremental oil recovery by low-salinity waterflood.

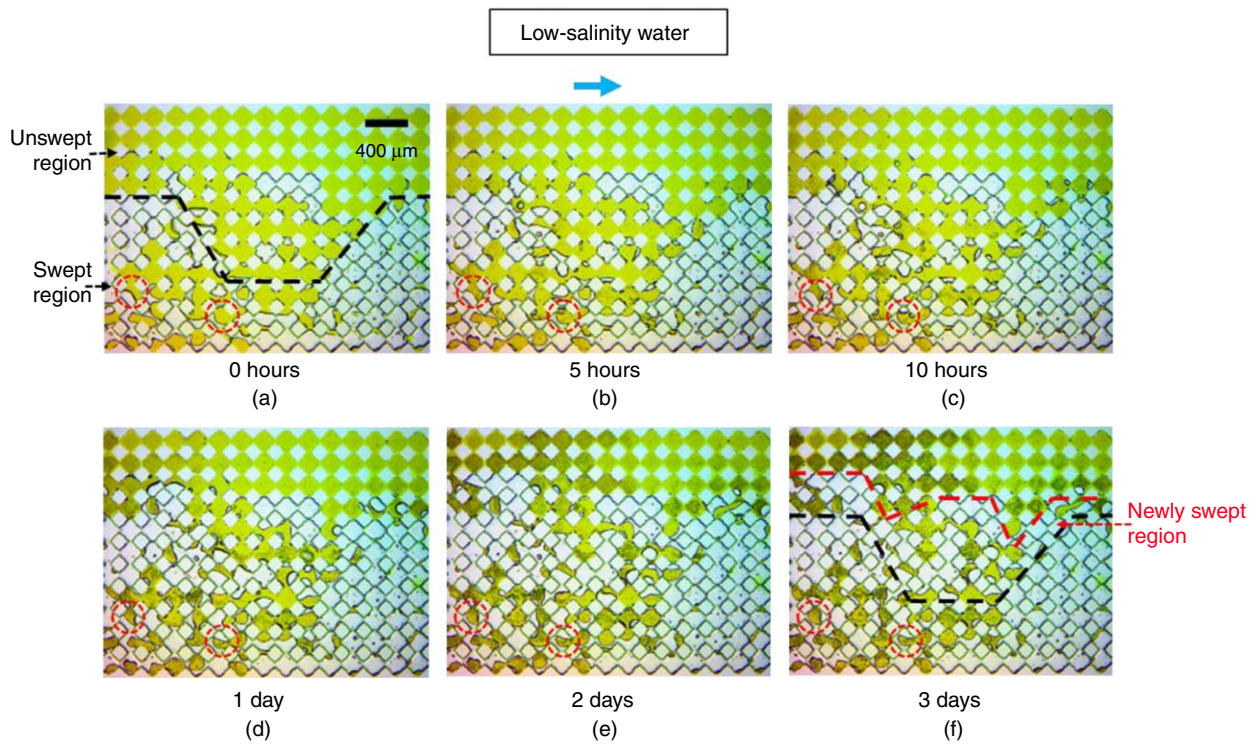


Fig. 10—A not-well-swept area of Micromodel B at different times in Experiment 6. (a) The beginning of the DI-water injection. The flow direction in each image was from the left to the right. The black dashed line indicates the boundary of the swept region after high-salinity-brine flooding, and the red dashed line indicates the boundary of the swept region after tertiary DI waterflooding. (a through f) The oil droplets circled by red dashed lines indicate the oil-droplet dewetting where contact lines also moved. Water in the amount of 130 PV was injected during the low-salinity injection.

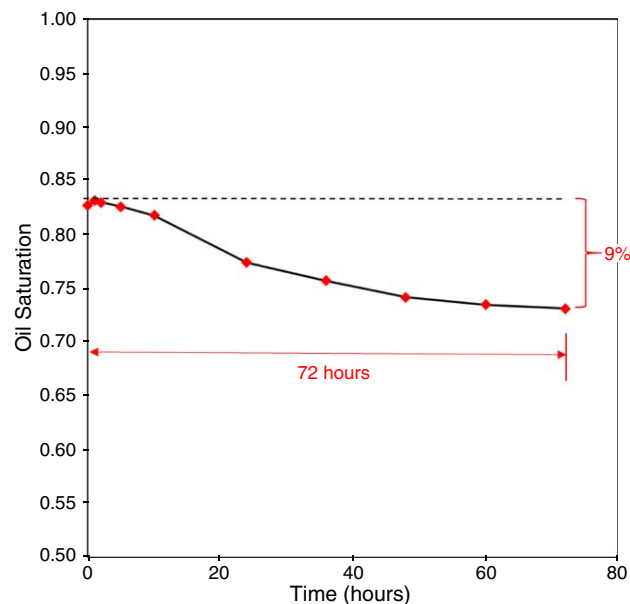


Fig. 11—Oil saturation of the poorly swept cross section of Micromodel B during low-salinity waterflood performed in Experiment 6. The oil recovery has a long tail of 3 days, indicating a continuous change in a time period of tens of hours to several days. Water in the amount of 130 PV was injected during the low-salinity injection.

Quantifications on 80 initially swept pores show that oil- and water-specific areas increased by approximately 18 and approximately 8%, respectively, during the tertiary DI waterflood. The increase in the specific areas indicates the connectivity reduction and the flow-resistance increase of the water in the swept region (Joekar-Niasar et al. 2007; Joekar-Niasar and Hassanizadeh 2011). Thus, we propose that the improvement of sweep efficiency is related to the dewetting and swelling of residual oil droplets in the swept region. From a pore-scale perspective, nonwetting and swelled residual oil droplets can better block the pore throats than wetting and smaller residual oil films (Gardescu 1930). Therefore, the flooding water was redirected toward the previously unswept region. An illustration is given in Fig. 12a.

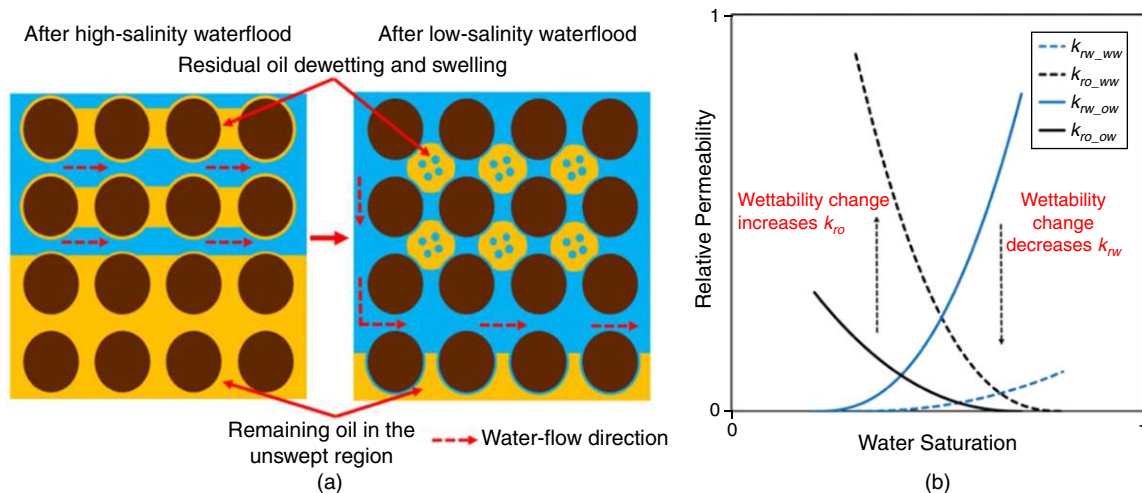


Fig. 12—(a) Illustration of the improvement of sweep efficiency during low-salinity waterflood from pore-scale perspective. Dewetted and swelled residual oil droplets move to the pore body from the grain surfaces and throats, increasing the water-flow resistance and redirecting the water into the previously unswept region. (b) Schematic of relative permeability change during the residual oil dewetting. The blue solid line is water relative permeability in the oil-wet state; the blue dashed line is water relative permeability in the water-wet state; the black solid line is the oil relative permeability in the oil-wet state; the black dashed line is the oil relative permeability in the water-wet state.

This observation differs from previously published statements that low-salinity waterflood can increase the oil recovery by reducing the residual oil saturation (Sharma and Filoco 2000; Masalmeh et al. 2014; Suijkerbuijk et al. 2014). Sweep-efficiency improvement is also a popular hypothesis of the low-salinity-waterflooding mechanism, but many researchers claim that it is related to the content of clay (Abdelmoneim and Nasr-El-Din 2018; Aghaeifar et al. 2018; Alhuraishawy et al. 2018). Here, we confirm the existence of sweep improvement without the existence of clay, but we do not exclude the importance of clay.

Upscaling: From Pore-Scale Model to Reservoir Model. The physical model shown in the subsection Mechanisms From Pore-Scale Perspective clearly illustrates the oil-recovery mechanism at the pore scale. However, similar to most other pore-scale studies, this micrometer-scale physical model cannot be directly used to describe reservoir performance because very different parameter systems are involved (droplet size, droplet number, and micrometer-scale contact angle vs. saturations and relative permeability) (Garboczi 1990; Shabro et al. 2011). To connect the pore-scale physics to a valid reservoir-scale model, mechanisms shown in the subsection Mechanisms From Pore-Scale Perspective and Fig. 12a should be interpreted using traditional reservoir parameters.

The sketch in Fig. 12b demonstrates a typical plotting of relative permeabilities of water and oil at different wetting conditions (water-wet and oil-wet) and different water saturations. When the reservoir changes from oil-wet to water-wet, the relative permeability of oil (k_{ro}) increases, and the relative permeability of water (k_{rw}) decreases. In addition, the oil swelling in the pore scale decreases local bulk-water saturations, leading to the reduction in water relative permeability. Both the wettability change and the oil swelling result in a relative permeability change in the same direction. Those changes will lead to a reduction of mobility ratio M of water to oil (Lake 1989; Sorbie 1991). As the mobility ratio (M) gradually decreases, the sweep efficiency increases over a period of tens of hours to several days. The response time of 10^1 to 10^2 hours agrees with the characteristic diffusion time estimated using Eq. 3. The observations and the explanation agree with studies where the wettability alteration is accounted for by tuning the relative permeability parameters (Delshad et al. 2006; Jerauld et al. 2006; Khorsandi et al. 2017a, 2017b; Jung et al. 2018), and studies that scale up the low-salinity effect from the laboratory scale to the field scale by adjusting the relative permeability model according to experimental measurements (Gupta et al. 2011; Masalmeh et al. 2014; Suijkerbuijk et al. 2014). The assumption in these works is that the relative permeability and the wettability state are static functions of the saturation and the brine composition (salinity, ion types) at a specific timestep and gridblock. This means an equilibrium is achieved instantaneously and the low-salinity effect is triggered instantaneously when the salinity changes.

However, our work shows that the process is time dependent and the relative permeability should also be a function of the oil/water-contact time. Therefore, future work is required to determine the validity of the assumption of the equilibrium state. Because the wettability alteration and the oil swelling both are functions of time after contacting with low-salinity water, the improvement of sweep efficiency should also be a function of time over a period of 10^1 to 10^2 hours. The time is not negligible compared with the timestep used in reservoir simulations, where the maximum timestep is usually restricted to 1 day (Nolen and Berry 1972; Jensen 1980; Ganis et al. 2017).

Reservoir-on-a-Chip Validation: Delayed Increased in Oil Recovery. To validate the observation of the sweep-efficiency improvement, we performed Experiments 7 through 10 in a “reservoir-on-a-chip” micromodel, Micromodel C (Micromodels C1 or C2). Model B and C are both at the scale of a 1-in.-long pore network. However, the observation scale of Micromodel C was larger than that of Micromodel B. Micromodel C1 used in Experiment 7 has deeper throat depth of $10\ \mu\text{m}$ compared with Micromodel C2 used in Experiments 8 through 10, where the throat depth was $5\ \mu\text{m}$. The pore-throat/pore-body ratio in Micromodel C1 is larger than that in Micromodel C2.

In Experiments 7 through 10, the micromodel was first saturated 100% with the crude oil and was aged for 10 hours. In Experiments 7 and 8, the 120,000 ppm salinity brine was injected into the oil-saturated micromodel, followed by the injection of DI water. The high-salinity-brine injection continued for 23 and 21 hours before switching to DI-water injection, respectively. In Experiment 9, the high-salinity brine was injected for 20 hours, followed by the 3,000 ppm low-salinity-brine injection. Experiment 10 was a control experiment, where the 120,000 ppm high-salinity brine was injected continuously into the micromodel for 8 days. In Experiments 7 through 10, the water-injection rate was kept at $1\ \mu\text{L/h}$ ($0.5\ \text{ft/D}$), corresponding to a capillary number of 1.8×10^{-7} for high-salinity injection and 0.9×10^{-7} for low-salinity injection. Fig. 13 shows a series of visualizations captured during Experiment 7 (Experiments 8 and 9 were qualitatively similar). The oil saturation at different times in Experiments 7 through 10 was calculated using ImageJ and plotted in Fig. 14. Table 5 summarizes the injection procedures during Experiments 7 through 10.

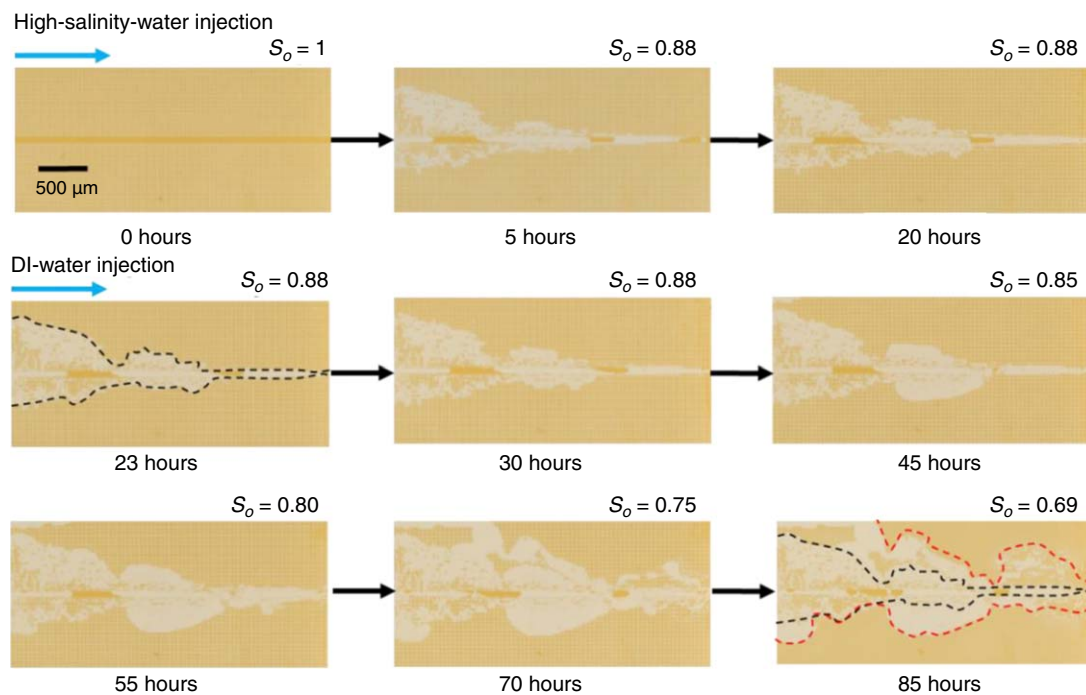


Fig. 13—Images of Micromodel C1 at different times in Experiment 7. High-salinity water was injected from 0 to 23 hours, and DI water (low salinity) was injected from 23 to 85 hours. The yellow and white represent crude oil and water, respectively. The scale bar in the left-top image is 500 μm and applies to all images. The injection direction is from the left to the right for all images. The black dashed line indicates the boundary of the swept region after high-salinity-brine flooding and before DI waterflooding; the red dashed line indicates the boundary of the swept region after tertiary DI waterflooding. Both dotted lines are extrapolations for better understanding, and not the actual experimental results.

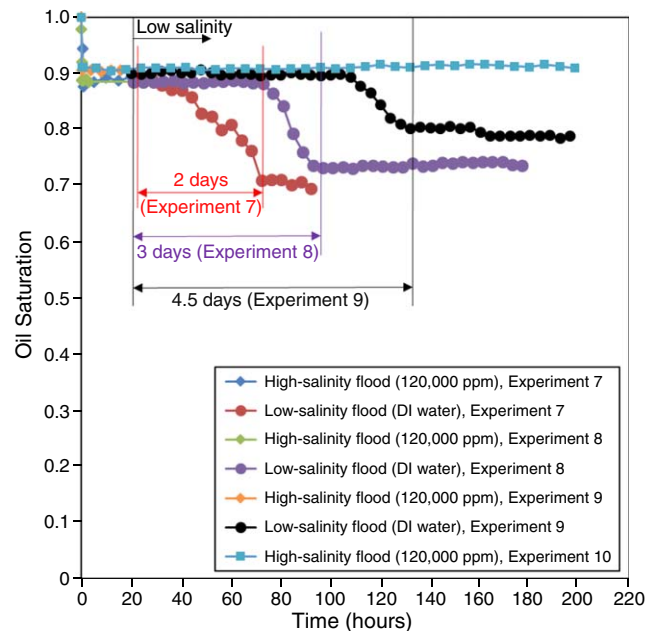


Fig. 14—Oil saturation vs. time in Experiments 7 through 10. The horizontal lines mark the response time for the tertiary low-salinity waterfloods.

Experiment	High-Salinity Brine	High-Salinity-Injection Duration	Low-Salinity Brine	Low-Salinity-Injection Duration
7	120,000 ppm	4.6 PV over 23 hours	DI water	14 PV over 70 hours
8	120,000 ppm	4.2 PV over 21 hours	DI water	31 PV over 156 hours
9	120,000 ppm	4 PV over 20 hours	3,000 ppm brine	35 PV over 176 hours
10	120,000 ppm	39.6 PV over 198 hours	—	—

Table 5—Water injection in Experiments 7 through 10.

Improved Oil Recovery from Tertiary Low-Salinity Flooding. In Experiments 7 through 10, the oil recovery from the secondary high-salinity waterflood was 9 to 12%. The oil saturation in all four experiments reached a steady state after a short time of high-salinity-water injection when the water broke through (less than 0.5 hours). The relative low oil recovery (9 to 12%) from the high-salinity flooding was caused by the existence of the fracture and the high viscosity of the crude oil. The oil recovery is primarily from the fracture and nearby region, leaving a large amount of unswept oil in the porous matrix.

In the tertiary DI waterflood, 18% of incremental oil recovery was obtained after 2 days of DI-water injection in Experiment 7, and 15% of incremental oil was obtained after 3 days of DI-water injection in Experiment 8. In Experiment 9, where the salinity of the tertiary-flooding water was 3,000 ppm, the incremental oil recovery was 10% after 4.5 days of injection. In Experiment 10, where the salinity of the injection water was kept unchanged at 120,000 ppm, no further oil recovery was obtained after water breakthrough. The incremental oil recovery from the tertiary low-salinity waterflood in Experiments 7 through 9 was significant, considering the heterogeneity of the geometry and the high mobility ratio. During the tertiary low-salinity waterfloods in Experiments 7 through 9, the low-salinity water gradually swept to the unswept region in the porous matrix and improved the sweep area, as demonstrated in the images in Fig. 13. Meanwhile, the residual-oil ganglion in the swept region during the high-salinity waterflood was not observed to mobilize (Fig. 13). These observations from the “reservoir-on-a-chip” model support the hypothesized mechanism that the low-salinity effect enhances the oil recovery by improving the sweep efficiency.

Experiments 7 through 10 show the positive correlation between the low-salinity effect and the incremental oil recovery. The tertiary flooding with lower salinity brings higher recovery that begins sooner: The tertiary oil recovery from the 3,000 ppm waterflood in Experiment 9 (10%) was lower than that from the DI waterflood in Experiments 7 (18%) and 8 (15%), and occurred much later.

Comparison of Experiment 6 with Experiments 7 and 8 shows that the incremental oil recovery from the tertiary DI waterflood in our idealized heterogeneous geometry (15 to 18%) was larger than that in our idealized homogeneous pore network (9%). Heterogeneity tends to decrease the sweep efficiency compared with the homogeneous porous medium, and the sweep-efficiency improvement was more significant in such a geometry. This observation also supports that the sweep efficiency is the primary cause of incremental oil recovery for our model systems.

Time-Dependent Behavior in the Reservoir-on-a-Chip Model. Time-dependent behavior was clearly presented in Experiments 7 and 9. A delay of tens of hours to days occurred before the oil saturation started to decrease during the tertiary low-salinity waterflood. Specifically, the delay in Experiments 7 through 9 was 10, 48, and 84 hours, respectively. In addition, the oil-saturation decrease resulting from the sweep improvement is a gradual and continuous process. The oil-saturation decrease or the sweep improvement in Experiments 7 through 9 lasted for tens of hours (39, 24, and 30 hours, respectively), showing a time-dependent effect.

Clearly, lower salinity results in faster recovery in the same pore geometry, as shown by the comparison of Experiments 8 and 9. The delay during the 3,000 ppm brine flood was significantly longer than the delay during the DI waterfloods. In addition, the delay in Experiment 7 was shorter than in Experiment 8. This is compatible with our theory because Experiment 7 has a larger throat/pore-body ratio, which corresponds to faster mass-transfer rate from water to oil.

The delay of tens of hours to days, as well as the continuous oil-recovery curves, agrees well with our observations and hypotheses formed from the pore-scale (subsection Single-Pore-Scale Observation: Oil Dewetting and Swelling) and pore-network-scale experiments (subsection Pore-Network Visualization: Pore/Pore Interactions and Upscaling). The delay times observed at all three scales are similar and all agree well with the estimated characteristic diffusion time using Eq. 3. Combining the three scales, the wettability change, the oil swelling, and the improved oil sweep are all time-dependent, dynamic processes.

Applications and Limitations: Core-Scale and Field-Scale Implications. The findings from our micromodel toolbox help to narrow the gap between the pore-scale and the larger-scale flow behavior. Our results can be used to explain certain phenomena, such as the time-delay behavior and oil-recovery improvement without clay, mentioned in several published coreflood studies. **Table 6** summarizes some published coreflood results and the reported and/or estimated delay time of the low-salinity effect. The delay of tens of hours to days agrees well with our observations at all three scales and the characteristic diffusion time estimated using Eq. 3. Our hypothesized mechanisms can be used to explain one type of low-salinity effect that is caused by the oil/brine interactions and requires the existence of active compounds in the oil phase. In addition, the oil swelling and the increase of flow resistance can explain the pressure-gradient increase reported in some coreflood and field tests (Zhang et al. 2007; Boussour et al. 2009; Austad et al. 2010; Robertson 2010; Masalmeh et al. 2014). A recent study (Collins et al. 2018) reported an increase of the aliphatic carboxylate acid in the produced oil during low-salinity waterflood and hypothesized that the release of aliphatic carboxylate acid (fatty acid) from the rock surface contributes to the wettability alteration. This finding and proposed mechanism agree with our theory that the release of polar compounds from the surface to the bulk oil resulted in the wettability alteration.

Literature	Experiment	Delay (PV/hours)	Change-Duration Time (PV/hours)	Improved Oil Recovery
RezaeiDoust et al. (2011)	Low-salinity flood in Fig. 8	2 PV/12 hours*	0.8 PV/4.8 hours*	2–3%
	Low-salinity flood in Fig. 10	2 PV/12 hours*	4 PV/24 hours*	7%
Masalmeh et al. (2014)	Tertiary low-salinity flood, Case 1	3 PV/25 hours	4 PV*/30 hours	3–4%
	Tertiary low-salinity flood, Case 2	4 PV/30 hours	6 PV*/50 hours	7%
Suijkerbuijk et al. (2014)	Tertiary low-salinity flood	3 PV/35 hours*	3 PV/35 hours*	6%

* Calculated from the data in the literature.

Table 6—Literature on the delay behaviors.

Although the mechanisms we proposed in this work are time delayed rather than instantaneous, they are not prohibitively slow (i.e., making the process uneconomic at the field scale). The time scale for the response is in days, which is not long compared with the time scale in reservoir operations (months to years) but is also not negligible compared with timesteps used in a simulator. Many recent low-salinity models assume an instantaneous wettability change and therefore an instantaneous relative permeability change when the salinity decreases (Al-adasani et al. 2012; Jackson et al. 2016; Qiao et al. 2016; Al-Ibadi et al. 2019), where timesteps as small as

approximately 0.1 days are applied. Therefore, during the first tens of timesteps after a location experiences a salinity change, the accuracy of the wettability and relative permeability calculation triggers concerns given our experimental results on time dependency. Incorporating contact time as a parameter in relative permeability functions or using a much larger timestep might address this problem. The effect of time dependency of wettability alteration and oil swelling on field-scale behavior needs further investigation with numerical modeling and other large-scale tools.

Our model system is idealized, such as the pure-glass surface, artificially designed pore networks, and the limited geometry scaleup to inches (although still near or above the REV scale). Thus, on the basis of our experiments, we do not exclude the possibility that other mechanisms can also contribute to the low-salinity effect in field applications. To test the proposed hypotheses in coreflood, it is necessary to use a design where the interactions and performance are analyzed by analyzing the oil recovery, pressure drop, and oil characteristics in real time. For other complex systems, additional assumptions and conditions (such as the oil type and brine salinities) need to be examined. Limitations of the microfluidics platform on enhanced-oil-recovery (EOR) study are discussed in the Supplemental Material.

Nevertheless, the idealization reduced complications and focused on the first-order effect resulting from the fluids' interactions. Following the model framework from the single-pore scaleup to the intermediate-pore-network scale and then up to a "reservoir-on-a-chip" model, we showed how the pore-scale behaviors affect macroscale parameters. The use of such a microfluidic toolbox demonstrated a possible method to narrow the gap between observations at the micrometer/pore scale and the understanding of porous-media-flow behaviors by qualitative and quantitative analysis.

Conclusions

To better understand the mechanisms of improved recovery caused by low-salinity waterflooding, microfluidic experiments were conducted on single-pore scale, pore-network scale, and reservoir-on-a-chip scale. Micrometer-scale observations and theories are scaled up to a porous-medium-scale model, which explains one type of low-salinity effect with delayed oil recovery and in the absence of clay.

In the subsection Single-Pore-Scale Observation: Oil Dewetting and Swelling, observations on the single-pore scale reveal a considerable dewetting and swelling of crude oil in contact with low-salinity water. This can be explained from the interplay between the water chemical potential and the polar compounds in the oil phase. In the subsection Pore-Network Visualization: Pore/Pore Interactions and Upscaling, flow experiments on the pore-network scale (with approximately 10^2 pores) show that the oil dewetting and swelling under low-salinity waterflooding leads to a redirection of flooding liquid from the swept region to the unswept region, and thus helps to recover originally unswept oil. In the subsection Reservoir-on-a-Chip Validation: Delayed Increase in Oil Recovery, flooding experiments on the heterogeneous porous micromodel ("reservoir-on-a-chip," containing approximately 10^4 pores) with 2D connectivity support the hypothesis that sweep efficiency (not the mobilization of capillary-trapped residual oil) is the primary cause of incremental oil recovery, and this low-salinity effect is time dependent. The response time after low-salinity-water injection remains at the same order of tens of hours, but regardless of that, the experiment is scaled up from 1 to approximately 10^4 pores. This time dependency agrees with the estimated characteristic time of the water in the oil-diffusion process. A 10 to 18% incremental oil recovery is obtained during tertiary low-salinity waterfloods in this model system.

The time-dependent oil dewetting/swelling-induced sweep-efficiency improvement can explain some observations in published corefloods, such as the pressure-gradient increase and the delay/long tail of coreflood-recovery curves. In addition, this observation also shows that the presence of clay is not necessary for low-salinity waterflooding to be effective, although additional mechanisms might exist between low-salinity water and clays.

Nomenclature

- A_p = pore-throat cross-sectional area, m^2
- C = water concentration in oil, kg/m^3
- C_a = capillary number, dimensionless
- D_p = etching depth of the micromodel, m
- D_{r1} = relative diffusion factor (ratio of water-diffusion factor in Diluted Oil 1 compared with that in the original crude oil), dimensionless
- D_w = water-diffusion coefficient in oil, m^2/s
- H_p = pore-body depth, m
- H_t = pore-throat depth, m
- L_p = characteristic pore-body length, m
- L_t = characteristic throat length, m
- q_w = water-injection rate, m^3/s
- t_c = characteristic time, seconds
- V = volume of one pore, m^3
- γ_{os} = interfacial tension between oil and solid, N/m
- γ_{wo} = interfacial tension between oil and water, N/m
- γ_{ws} = interfacial tension between water and solid, N/m
- η_0 = viscosity of the original crude oil, cp
- η_1 = viscosity of Diluted Oil 1, cp
- η_w = water viscosity, cp
- θ = contact angle, radian
- ϕ = porosity of the micromodel, dimensionless

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SI Metric Conversion Factors

$$\begin{array}{ll} \text{cp} \times 1.0 & \text{E-03} = \text{Pa}\cdot\text{s} \\ \text{psig} \times 1.45 & \text{E-04} = \text{Pa} \end{array}$$

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