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Effect of injection brine composition on wettability and oil recovery in sandstone reservoirs



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HIGHLIGHTS

Bridging action of Ca²⁺ results in more oil-wet surface and limited oil recovery.
Wettability alteration and oil layer instability are the mechanism to EOR by LSF.

USF effect was investigated by surface force model in a cylindrical pore.

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ABSTRACT

Wettability alteration and enhanced oil recovery (EOR) of sandstone by low salinity waterflooding (LSF) have become the focus of many studies. However, there is no clear explanation of how the ion composition of brines influences the LSF effect. In this paper, imbibition, ζ -potential measurements, core displacement, and microscopic displacement experiments were adopted to investigate the effect of brine composition on the wettability and oil recovery of sandstone reservoirs and the Ca^{2+} bridge action between rock surface and the acidic components in crude oil. Besides, the surface force model in a cylindrical pore was also developed for investigating the mechanisms behind wettability alteration and EOR by LSF. The results show that Ca^{2+} in the brine acted like a bridge between the negatively charged sites on rock surface and dissociated acidic components in crude oil, and the acidic components in crude oil played an important role in the Ca^{2+} bridge action. Divalent cations (e.g. Ca^{2+}) in the brine hindered the low salinity effect, and thus the low-salinity brine without divalent cations showed optimal low salinity effect. Lowering the salinity of 1:1 electrolyte solution (e.g., NaCl solution) caused the expansion of the electrical double layer and increasing disjoining pressure between rock/brine and oil/brine interfaces, and thus the rock surface changed to be more water-wet and a thicker wetting-water film could be stable between rock surface and crude oil. When injecting low salinity NaCl brine, more water-wet state improves the ability of water imbibition in small pore and a thicker wetting-water film promotes destabilization of oil layers adhering to sandstone surface, thus resulting in EOR.

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1. Introduction

In the recent years, extensive laboratory and field tests have showed that LSF can act as an attractive enhanced oil recovery technology [1–6]. The popularity of this technology is mainly because of its efficiency in displacing crude oil, low investment, easy operation, ease of injection, and environmental protection, all of which bring economic benefits compared to other chemical EOR methods [7]. In most cases, the additional oil recovery from LSF was in the range of 5–20% of OOIP [7–9].

Over the last decades, the wettability alteration has been widely believed to be an important contributor to LSF [1,5,7,10]. Wettability alteration of sandstone rocks by LSF is related to the minerals on sandstone surface, the polar components in crude oil and the ion composition of injected water [8,11,12]. Many studies have been carried out on the wettability alteration of smooth mineral substrates (of quartz [10,13], glass [11], or mica [3,14]). The alteration was characterized by monitoring the bound oil residues and the macroscopic contact angle on the substrate in brines. High pH and low-salinity solutions can result in desorption of oil layer on



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substrates, and thus alter the wet state from oil-wet or neutral-wet to water-wet. Divalent cations (e.g. Ca²⁺) in the aqueous solutions act like a bridge between the negatively charged sites on substrate surface and negatively charged polar groups in crude oil, opposing desorption. From the field observation, LSF in the Omar field in Syria results in a more water-wet rock surface, which leads to an incremental recovery of 10–15% of the Stock Tank Oil Initially In Place (STOIIP) [1].

Low-salinity water expanding the electrical double layer was regarded as the main reason behind wettability alteration and EOR by LSF [3,10]. Lowering the salinity of injected brine, especially reduction of the multivalent cations, changes the electrical charges at both brine/rock and oil/brine interfaces to strongly negative, which causes higher repulsive forces between two interfaces, and as a result, the wet state is changed towards more water-wet and oil recovery is improved. Lager et al. [6] proposed that multicomponent ionic exchange (MIE) was responsible for the wettability alteration and EOR. MIE would allow for desorption of organic polar compounds and organo-metallic complexes from the rock surfaces and replacing them with cations in injection brines, thus resulting in more water-wet surfaces and an increase in oil recovery. Austad et al. [2] explained that a local increase in pH during LSF led to water-wet state and EOR which could be related to alkaline flooding. However, the theory based on salting-in effect has been proposed that lowering the salinity of brines could enhance the water structure around oil and thus increased the solubility of oil in water [8,15]; therefore the wettability changed to be more water-wet and oil recovery was enhanced during LSF.

Wettability alteration and enhanced oil recovery of sandstone reservoirs by LSF have become the focus of many studies. However, the LSF effect for different ion compositions and how the ion composition of low-salinity brines influences wettability and oil recovery were barely studied in previous literature. In this paper, the effect of brine composition on wettability and oil recovery and the mechanism behind the effect in sandstone reservoirs were investigated. Analyzing the effect and understanding the underlying mechanism enable the optimization of injection brine composition for EOR.

2. Experimental section

2.1. Materials

2.1.1. Crude oil and mixing oil

The crude oil, obtained from Tarim oilfield, has a viscosity of 3.8 mPa·s (at 45 °C), a density of 0.829 g cm⁻³ (at 45 °C), API of 35.76, a n-C₇ asphaltene content of 0.54%, a resin content of 3.80%, and an acid number of 0.4 mg KOH/g oil.

Kerosene added to white oil at a 1:3 ratio by volume is as mixing oil. White oil and kerosene were supplied by Sinopec Corp. In order to remove impurities with interfacial activity, white oil and kerosene were treated by silica gel adsorption for 60 h under room temperature before use.

2.1.2. Brines

The ion composition of Tarim oilfield simulated formation water (SFW) is described in Table 1. Thus the ionic strength of SFW is 1.72 mol kg^{-1} . Other brines were prepared by dissolving desired amounts of salts in deionized water, the properties of

Table 2
Properties of brines.

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Brine	$CaCl_2$ (mol L ⁻¹)	NaCl (mol L ⁻¹)	Salinity (ppm)	Ionic strength (mol kg ⁻¹)	$\sigma_{ m OW} \ ({ m mN} \ { m m}^{-1})$
LS-1	0	0	0	0	22.5
LS-2	0	0.05	2925	0.05	21
LS-3	0	0.1	5850	0.1	17
LS-4	0	0.5	29,250	0.5	16.5
LS-5	0	1	58,500	1	13
LS-6	0	1.72	100,620	1.72	10.5
HS-1	0.017	0	1887	0.05	18.0
HS-2	0.573	0	63,603	1.72	16.0
HS-3	1.14	0	126,540	3.42	13.0

which are listed below in Table 2. All the reagents used in the study, such as NaCl, CaCl₂, MgCl₂, K₂SO₄ and FeCl₃, were of analytical grade.

2.1.3. Cemented quartz cores

Based on the technique of X-ray diffraction, the mineral contents of Tarim oilfield natural core were investigated. The result shows that the natural core is mainly composed of quartz and the quartz content is about 85%. Thus, in this study, the cemented quartz cores were used for imbibition and displacement experiments, and crushed for zeta potentials measurements. The artificial sandstone cores are cylindrical and their key parameters are presented in Table 3. In Table 3, the initial oil saturation (S_0) is percent content of crude oil in each core when the irreducible water saturation (S_w) is established, that is, $S_0 = 1 - S_w$.

2.2. Zeta potential measurement

DelsaTM Nano analyzer was used to measure the zeta potential of crude oil/brine and rock/brine interfaces at 45 °C. The oil/brine emulsions were prepared at volume ratio of 1:100, and the rock/ brine suspensions were prepared by adding 0.2 wt% of crushed core powder to the brine.

2.3. Displacement and imbibition experiments

The cores were first dried at 105 °C to constant weight, and were then saturated with SFW under vacuum. To calculate the absolute permeability, SFW was injected at a rate of 0.10 mL/min at 45 °C and the pressure drop was monitored. The cores were flooded and saturated with crude oil and the initial water saturation (irreducible water saturation, S_w) was established. The cores were then aged at 45 °C for sixty hours in the core holder. After aging, imbibition and displacement experiments were performed at 45 °C with prepared brines.

The displacement experiment was performed under the confining pressure of 10 MPa using a flow of 0.10 mL/min to simulate when the water flooding occurred. During waterflooding, the pressure drop across the cores was measured by a differential pressure transducer.

2.4. Microscopic displacement experiment

The microscopic displacement experiment was performed at room temperature as described in Ref. [16]. The experimental

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Ion composition of Tarim model formation water.

Ion	Ca ²⁺	Fe ³⁺	K ⁺	Mg ²⁺	Na ⁺	SO_{4}^{2-}	Cl ⁻
Mass concentration/mg L ⁻¹	5160.4	1.76	323.7	436.6	28983.9	398.3	55190.8

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