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Effect of the Type and Concentration of Salt on Production Efficiency in Smart Water Injection into Carbonate Oil Reservoir Rocks

Huxiong Li, Fatemeh Razavirad, Abbas Shahrabadi,* and Andrew Binley
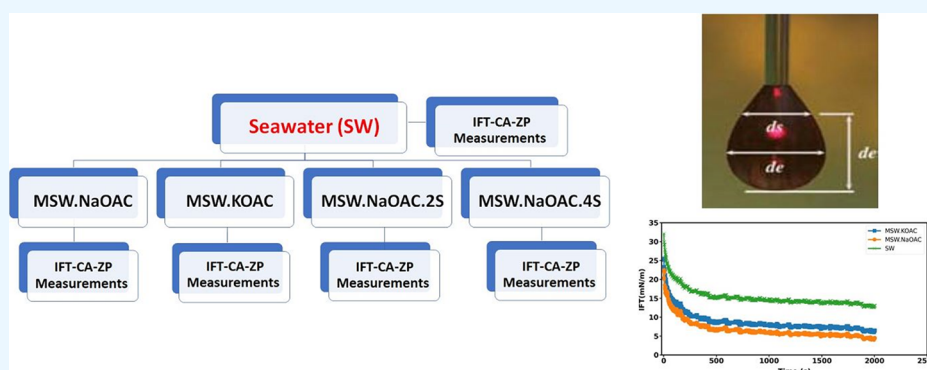
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ABSTRACT: Smart waterflooding is one of the most practical emerging methods of enhanced oil recovery in carbonate reservoirs. In this study, the effect of salt type and its concentration in smart water on oil recovery from a carbonate reservoir rock is investigated. A series of experimental measurements, including zeta potential (ZP), interfacial tension (IFT), and contact angle (CA), were conducted to examine the effect of ions on the oil/brine/rock interaction. IFT, ZP, and CA were also used as screening methods to select effective solutions for flooding experiments. The results of the study show that synthesized brines containing sodium acetate and potassium acetate salts have a significant effect on the reduction of IFT; however, rock surface wettability due to such brines is insignificant. The presence of organic salts in the injected water can alter the properties of the fluid and rock surface, leading to improved oil recovery. The salts can reduce the interfacial tension between the oil and water phases, making it easier for the water to displace and mobilize trapped oil. This effect is particularly beneficial in reservoirs with high oil−water interfacial tension as it enhances the capillary forces and improves the sweep efficiency. Smart water with sodium acetate (MSW.NaOAc) caused a 7% increase in oil production in the tertiary injection process due to IFT and CA reduction. The secondary injection of MSW.NaOAc led to an oil production efficiency of 76%, which is 10% higher than that of the secondary injection of seawater (SW), confirming the effectiveness of acetate ions in enhancing oil recovery. Doubling the concentration of sulfate ions in modified SW (MSW.NaOAc.2S) caused a 19% increase in oil production in tertiary injections after SW flooding. The secondary injection of MSW.NaOAc.2S produced a 13% increase in the recovery factor compared to SW flooding in the secondary mode. The main driving mechanism for oil mobilization was found to be wettability alteration, which is supported by the analyses of CA and ZP. This study confirms that the salt type and concentration present in a brine solution play a vital role in the movement of trapped oil in carbonate reservoirs.

1. INTRODUCTION

Carbonate formations are the largest oil reservoirs, globally. Due to the properties of carbonate reservoirs, such as oil-wetness, low matrix permeability, natural cracks with high permeability, and heterogeneity of rocks, the oil recovery factor is normally below 30%.[1,2] Any method that has the capability of changing the rock-wetting state from hydrophobic to hydrophilic could be effective in improving oil production from carbonate reservoirs. Enhanced oil recovery (EOR) is of major importance in the oil industry, particularly given the increasing demand for energy. Hence, methods with the aim of enhancing

crude oil production from reservoirs in secondary or tertiary stages are likely to be attractive to the oil industry. The EOR methods for secondary mode, such as immiscible gas injection and waterflooding, are used to stabilize the reservoir pressure[3]

as a result of pressure drop after primary oil production. A number of studies have shown that oil recovery from sandstone reservoirs is higher than carbonate reservoirs due to the complexity of carbonated reservoirs and the presence of fracture networks and an oil/mixed-wet matrix.[4−67] To reduce the residual oil in porous media, numerous methods of EOR have been developed.[8−101112] EOR methods at the secondary stage are commonly described as low salinity waterflooding,[13,14] smart waterflooding,[15−1718] advanced ion management,[19,20] or ion tuning,[21,22] aimed at enhancing oil production through reducing salinity and/or modifying the ionic content of injected brines.[23−25262728293031] An essential step to improving oilfield development is finding an appropriate method to enhance oil production.

Smart water refers to tuning the ionic composition and salinity of the injected water, which results in the alteration of the initial equilibrium of porous media. Its use has attracted interest for application to secondary or tertiary recovery processes.[16,32] Due to its cost-effectiveness and easy accessibility for oil recovery enhancement compared to conventional seawater (SW) injection, smart waterflooding is one of the most practical methods of EOR.[7] However, the formation damage due to the incompatibility of the injected water with the reservoir water is a potential limitation of the method.[33,34] Water salinity alteration, or changing its ionic composition, is able to enhance oil recovery of sandstone and carbonate reservoirs by about 5−25%.[35] However, the main mechanisms that lead to the effectiveness of this method are still unclear.[24,31,36,37]

Hoegnesen[38] used smart waterflooding in a study of the impact of ionic composition changes, that is, the concentration of SO_4^{2-} ions at various temperatures, on the oil recovery from a carbonate reservoir. A researcher found that higher temperature and SO_4^{2-} concentrations led to a spontaneous imbibition rate increase.[39] He investigated the influence of symbiotic behavior of different ion concentrations (SO_4^{2-}, Mg^{2+}, and Ca^{2+}) on the compatibility, surface charge, wettability alteration, and interfacial tension (IFT) reduction. They determined an appropriate concentration of divalent ions during their smart waterflooding in a coated carbonated micromodel. Flooding the reservoir rock with enriched SW with Ca^{2+} has been shown to provide the highest oil recovery.[8,39−41] The electrostatic repulsion between calcium (Ca^{2+}) ions and the positively charged carbonate surface could be reduced by the adsorption of sulfate (SO_4^{2-}), leading to their reaction with the adsorbed carboxylic oil components, detaching them from the rock surface.[842] Some researchers investigated the influence of diluted smart waters on oil production. They found that excess amounts of SO_4^{2-} and magnesium (Mg^{2+}) improved the wettability alteration toward more water-wetness and IFT reduction, leading to an increase in the final oil recovery.[43] Smart waterflooding was designed by changing the concentrations of cations (mainly SO_4^{2-}, Ca^{2+}, and Mg^{2+}) with the same level of total dissolved solids (TDS) as seawater. They observed the wettability alteration due to the increase in the concentration of SO_4^{2-} ions, which accelerated the rate of reaction in the crude oil−brine−rock system. However, the effectiveness of Mg^{2+} ions in wettability alteration is higher than that of Ca^{2+}.[44] Oil-containing chalk cores with neutral wetting conditions were studied using a series of long-term spontaneous imbibition experiments at 70, 100, and 130 °C. It was concluded that the excess amount of SO_4^{2-} ions in the imbibing fluid improves the oil recovery

significantly due to the wettability alteration of the chalk to a more water-wet state.[41] It was found that Mg^{2+} ions present in seawater, as well as Ca^{2+} and SO_4^{2-}, are able to increase the positive surface charge density of chalks leading to wettability alteration to water-wetness during water injection.

A large number of studies have been carried out to explain the mechanisms acting on oil in smart waterflooding. These mechanisms include the reduction of the IFT between aqueous and oleic phases,[45−4748] rock surface wettability alteration toward more water-wetness,[40,49−51] electrical double layer expansion at the rock surface in contact with the aqueous phase,[52−54] migration of fines,[55,56] variations in interface viscoelasticity,[57−596061] formation of microdispersions,[62,63] and multi-component ionic exchange.[44,64] As mentioned above, a number of studies have investigated the effects of various divalent ions on the recovery process. Findings from such studies have demonstrated that wettability alteration,[8,44,49,65−676869670] IFT reduction[42,51,71,72] electrical double layer expansion,[54,73−75] rock dissolution,[65,73,76,77] and change the surface electrical charge according to zeta potential measurement[8,48,78] play a key role in oil production from carbonated rocks. However, much of the literature claims that the wettability alteration is the most efficient mechanism in waterflooding processes.[5,8,36] Double-layer expansion is considered an important mechanism in wettability alteration.[37] Wettability alteration may also occur due to the dissolution of calcite[46,73,79,80] or anhydrite.[68,71] A study investigated the impact of different divalent and monovalent ions on IFT and found that Mg^{2+} is the most effective ion on IFT reduction in the presence of a large amount of resin. For a more detailed overview and discussion on the mechanisms behind the waterflooding, the reader is referred to 81.

In recent years, researchers have conducted extensive studies on the composition of smart water with a focus on the effects of mineral salts and ions. Based on initial experiments and positive results regarding the significant reduction of IFT, this study specifically examines the effects of organic salts, particularly sodium acetate and potassium acetate. Furthermore, the study investigates the impact of increasing the sulfate ion concentration in the presence of sodium acetate. Therefore, the aim of this research is to experimentally investigate the effect of different synthetic smart water formulations, prepared by modifying seawater and adding organic salts, on enhancing oil recovery during the water flooding process in the carbonate reservoirs. Building on this research, in this study, following preliminary tests and the positive results using organic salts (i.e., sodium acetate and potassium acetate) on IFT and CA reduction, a series of flooding experiments using synthesized smart water, including such salts, were performed. In these experiments, the effect of excess amount of sulfate ion concentration in the presence of sodium acetate salt was examined. In the initial stage, to investigate rock-fluid and fluid−fluid reactions, IFT, contact angle, and zeta potential experiments were performed for different water compositions; these experiments were also used as screening methods to determine the optimal solutions for core flooding experiments. The overall objectives of the study are to improve our understanding of mechanisms affecting the efficiency of oil recovery using smart water flooding and to assess the efficiency of such a process in comparison to the more traditional use of seawater.

2. MATERIALS AND METHODOLOGY

2.1. Fluids. In this section, the fluids used in the experiments are introduced.

2.1.1. Brines. Synthetic brines and seawater (SW), were used in the study. The brines were made by mixing pure salts (Merck grade) including NaCl, $CaCl_2 \cdot 2H_2O$, $MgCl_2 \cdot 6H_2O$, Na_2SO_4, $NaHCO_3$, $NaOAc \cdot 3H_2O$, and KOAc with distilled water. Synthetic seawater (SW) was prepared based on seawater components with a TDS of 41,461 ppm. In order to investigate the effect of sodium acetate ($NaOAc \cdot 3H_2O$) as an organic salt on residual oil saturation (S_{or}) and relative permeability curves, brines containing varied concentrations of this salt were prepared, allowing for an assessment of the optimal concentration of sodium acetate. Four types of smart water were synthesized with the same TDS as SW: (1) MSW.NaOAc is modified seawater which is made by removing sodium chloride (NaCl) from seawater and adding trihydrate sodium acetate ($NaOAc \cdot 3H_2O$) equivalent to the ionic concentration of NaCl; (2) MSW.KOAc is modified seawater, which is made by replacing NaCl with potassium acetate (KOAc) equivalent to the ionic concentration of sodium chloride; (3) MSW.NAOAc.2S and (4) MSW.NAOAc.4S are seawater modified with sodium acetate with 2 and 4 times the concentration of sulfate ions, respectively. Specifications of the seawater and synthetic brines used in this study are given in Tables 1 and 2, respectively.

Table 1. Salt Compositions and TDS of Seawater

ion compositions	concentration (ppm)
Na^+	13,110
Cl^-	23,040
Ca^{2+}	500
Mg^{2+}	1640
Ba^{2+}	0.6
SO_4^{2-}	3070
HCO_3^-	92
Sr^{2+}	4.7
Fe^{2+}	<0.05
CO_3^{2-}	4
Li^+	0.1
TDS (ppm)	41,461
pH	7.85

2.1.2. Crude Oil. The dead crude oil used was obtained from an Iranian oil reservoir and used as an oleic phase for all of the experiments. The crude oil specifications and corresponding standard test methods are given in Table 3, while live oil compositions are given in Table 4.

2.2. Rock Samples. In flooding experiments, to assess type/ion composition effects on residual oil saturation and to ensure that the petrophysical properties of the core have no effect on oil production, core plug samples with similar

Table 3. Physical Properties of Crude Oil at Ambient Conditions

crude oil	API (deg)	asphaltenes (wt %)	density (g/cm³)	specific gravity	viscosity @ 25 °C (cp)
Oil	41.84	<0.5	0.8307	0.8163	4.77

Table 4. Crude Oil Sample Composition

components	reservoir oil (mole %)
H_2S	0.00
N_2	0.00
Co_2	0.00
C_1	0.00
C_2	1.11
C_3	1.88
iC_4	0.80
nC_4	2.93
iC_5	1.69
nC_5	2.91
C_6	7.85
C_7	8.10
C_8	8.98
C_9	7.69
C_{10}	6.67
C_{11}	5.32
C_{12}	44.07
total	100

porosity and permeability from the same rock type are required. The core plug samples investigated were collected from a carbonate reservoir in the southwest of Iran.

X-ray diffraction (XRD) analysis can be used to identify the type of rock and its constituent minerals. The mineral composition estimated from XRD of the tested core plug samples used in this study confirms a carbonate rock consisting of a high proportion of calcite mineral. The porosity and permeability of the investigated core plug were also measured by using a helium porosimeter and permeameter, respectively. Table 5 lists the core plug physical properties.

Table 5. Petrophysical Properties of the Core Plugs

plug no.	length (cm)	diameter (cm)	porosity (%)	absolute permeability (md)	irreducible water (S_{wi}) (%)
1	5.215	3.81	17.26	2.216	17
2	5.214	3.80	16.46	2.177	16.4
3	5.214	3.81	17.10	2.612	16.7
4	5.214	3.80	16.30	2.260	17.9

2.3. IFT Measurement. IFT refers to the tension at the interface of two immiscible phases, which is considered as the indication of the energy at the interface of the two immiscible fluids and so is a fundamental parameter for the EOR process.
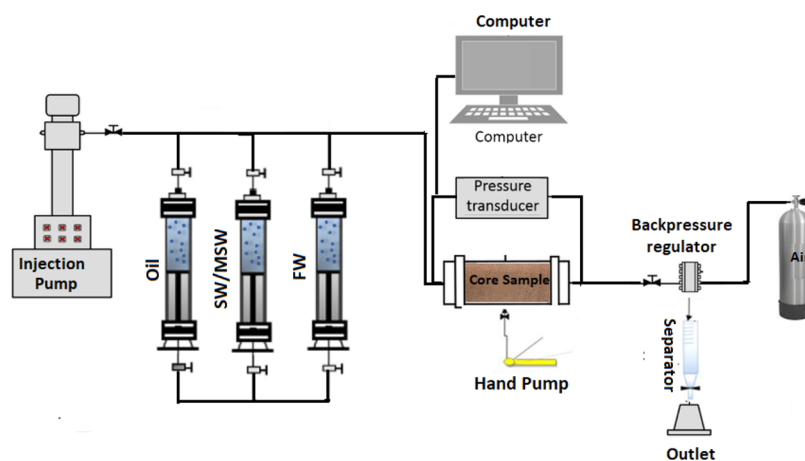
Table 2. Brine Composition of Synthetic Smart Water

brine\salt concentration	NaCl	$MgCl_2 \cdot 6H_2O$	$MgSO_4$	$CaCl_2 \cdot 2H_2O$	Na_2So_4	$NaHCO_3$	$NaOAc \cdot 3H_2O$	KOAc	TDS (ppm)
SW	32,350	7247	3851	1834		127			45,409
MSW.NaOAc		7247	3851	1834		127	75,360		88,419
MSW.KOAc		7247	3851	1834		127		54,375	67,434
MSW.NaOAc.2S		13,751		1834	9090	127	66,600		91,402
MSW.NaOAc.4S		13,751		1834	18,180	127	66,600		100,492

Figure 1. Schematic representation of core flood apparatus.

The successful agents in EOR processes, such as surfactants, polymers, and low salinity water, tend to reduce the IFT between oil and the displacing fluid and thus produce more oil. The pendant-drop technique is commonly used to measure the liquid−liquid IFT. In this method, an oleic phase droplet is allowed to hang from the tip of a capillary tube (e.g., a needle) in a visual cell filled with the aqueous phase. The shape of a liquid droplet under static conditions, controlled by the balance of gravity and surface forces, is determined and related to the liquid−liquid IFT. The drop shape image is computed, and the IFT is calculated by solving the Laplace equation. The apparatus used in this study, called IFT 700, is designed to determine the IFT and contact angle (CA) and is composed of a drop injector (inner diameter ranging from 0.4 to 1.0 mm), a viewing cell with an internal electrical heater, a back pressure regulator, two supply tanks and corresponding electrical heaters; and one charged-coupled device camera with a macro-lens. The IFT was measured when the immersed pendent dropped in equilibrium. The dynamic IFT measurement experiments were conducted at least three times at ambient temperature and pressure. Figure 1 illustrates the schematic diagram of the IFT and contact angle apparatus.

2.4. Wettability Measurement. Wettability significantly affects a variety of measurements critical to describing oil reservoirs such as capillary pressure, relative permeability, fluid displacement flooding behavior, and electrical properties.[82] Therefore, to investigate the wettability due to interactions between the rock surface and pore fluids in both sandstones and carbonates, a large number of studies have been carried out by others.[8,44,49,65−67,69,70] Wettability represents a balance of forces that occur at the interface between three phases, including oleic and aqueous phases in contact with a solid. The contact angle (CA) measurement is a common way to determine the wettability of rock samples. The measurements are generally made on a polished surface that simulates the reservoir material. Due to the adsorption of carboxylic groups of crude oil on a carbonate rock surface, they have mostly neutral or oil-wet wettability.[83] Since core preparation affects the initial wettability of carbonate rocks, aging process must be accomplished to restore the initial wettability. To do so, the core slabs were prepared from core plugs and treated following the same procedure performed on core plugs during flooding tests (discussed later in Section 2.6). To assess the effect of synthetic brines on surface wettability alteration, CA measurement by means of the Sessile drop method was used. The aged core slabs were placed in a transparent cell filled with a synthetic brine solution, and then an oil droplet was injected from the bottom of the cell using a needle that was positioned vertically. As soon as the oil drop touched the core slab, photographs were taken by a camera, and the CA between the oil drop and the rock was measured. The experiment was operated at ambient temperature and pressure. Due to surface preparation, equilibration of the solid and liquids, and surface roughness, CA measurements can show significant variation.

2.5. Zeta Potential Measurement. Since wettability refers to the adsorption of a fluid, in the presence of immiscible fluids, onto a rock surface, zeta potential measurements are an effective way to measure wettability. The rock wettability is influenced significantly by the electrical surface charge at the solid−liquid interfaces. Therefore, a change in zeta potential plays a key role in explaining wettability alteration and the release of previously trapped oil during controlled salinity waterflooding. The zeta potential measurement is used to define the surface charge of rock minerals. When a solid particle is dispersed in water, the charged particles attract a layer of counterions from the aqueous phase and form a thin layer that is firmly bound to the particle surface, named the Stern layer. The second layer, named the diffuse layer, is loosely associated with the particle surfaces, which are made of free ions that move in the fluid. The Stern and diffuse layers create an electrical double layer. Hence, the zeta potential is defined as a potential difference between the bulk fluid and the layer of fluid containing the oppositely charged ions that are bound to the particle surface. Particles, with a high surface charge, form a large double layer, which prevents particles from approaching each other because of the electrostatic repulsion between them due to identical charges.

In this study, zeta potential measurements were made to determine the surface charge of the calcium carbonate particles in the presence of various brines. The treatment of core plugs before ZP measurements was as follows. (i) First, the carbonate rock powder with a size of less than 30 μm was prepared by grinding the rock. (ii) To wash the prepared rock powder, it was placed in an ultrasonic bath for 30 min followed by heating in the oven to a temperature of 90 °C. (iii) To restore the initial wettability of the core plug, the ageing process must be accomplished. To do so, the rock powder was put in contact with oil at a temperature of 90 °C for 2 weeks. (iv) In the next step, 0.1 g of rock powder was immersed in 9.9
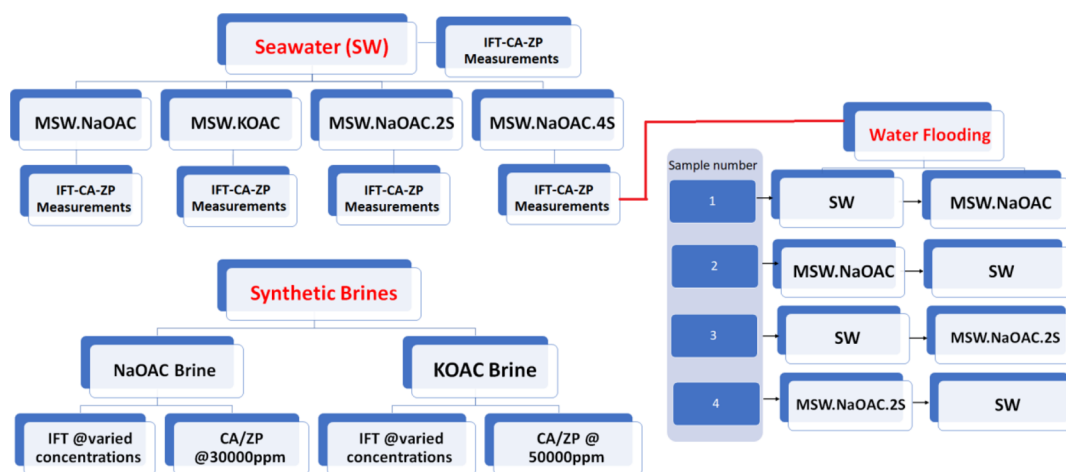
Figure 2. Experimental procedure.

g of brine for 24 h, stirred, and ultrasonicated in order to be ready for ZP measurements.

2.6. Core Flood Setup and Procedure. The core flood apparatus, which is capable of flooding experiments at high pressure and temperature, consists of a double screw volumetric pump (specially designed to inject continuous flow at constant pressure and flow rate), a core holder, an oven, four transfer vessels, a back pressure regulator, a hydraulic jack for confining pressure, a pressure transducer, and an effluent collective system. The pressure drop between the inlet and outlet sides by means of a digital pressure recorder can be captured. A schematic representation of the apparatus is shown in Figure 1. The temperature of the displacement experiments was set at 85 °C with an overburden pressure of 500 psi (3447.38 kPa). The core flood procedure adopted was as follows: (1) prior to conducting core flooding experiments, core plugs were cleaned with methanol and toluene and then placed in an oven to dry. Then, the physical properties of core plugs including length (L), diameter (D), dried weight (W_{dry}), and bulk volume were measured. To saturate the core plug, we placed it inside a cylinder that was connected to a vacuum pump through a valve above the cylinder. After 30 min of vacuuming, the vacuum pump was shut off and the valve closed. Formation water (FW) was then injected into the cylinder through a valve placed at the bottom of the cylinder. To overcome the capillary pressure and ensure that the entire pore space, even small pores were saturated with FW, a pressure of 3000 psi (20684.27 kPa) was applied to the cylinder for 72 h. Then, the saturated weight (W_{wet}) of the core plug was measured, and therefore, porosity and the pore volume were determined gravimetrically. (2) To measure the absolute permeability of the core plug, it was flooded with a single-phase fluid until a steady-state flow condition was attained. The saturated core plug was placed into the core holder, and the FW injection was repeated at various flow rates. A constant pressure drop of the flowing fluid across the core plug was observed when the steady-state condition was attained. The absolute permeability was then calculated based on Darcy's law. (3) To reach the irreducible water saturation (S_{wi}), the saturated core plug was then flooded with dead crude oil until no water was produced. The process was followed by ageing core plugs with crude oil for 4 weeks at a pressure of 1000 psi (6894.76 kPa) and a temperature of 85 °C, respectively. (4) After ageing of each core plug with dead

crude oil, it was placed in the core holder, and crude oil was injected at a frontal advance rate of 3 cc/h. (5) In order to investigate the effect of brines on oil production, three synthetic brines, including SW, MSW.NaOAc, and MSW.NaOAc.2S (given in Table 2), were chosen based on IFT, contact angle, and zeta potential results. Four flooding scenarios have been defined, as shown in Figure 2. The synthetic water injection was conducted at a relatively low flow rate (3 cc/h).

3. RESULTS AND DISCUSSION

In this section, the effect of the type and concentration of salt on oil displacement during the smart water injection process in carbonate cores are presented.

3.1. IFT Measurement. The IFT measurements between dead oil and smart waters at ambient conditions were carried out. Figure 3 shows the measured IFT between crude oil and
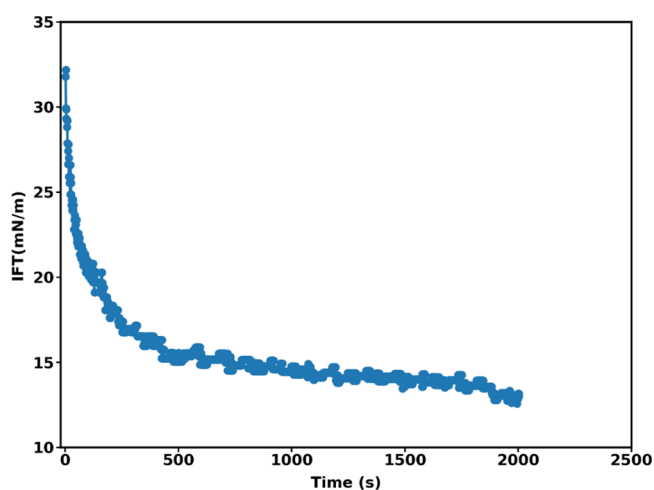

Figure 3. Dynamic and equilibrium IFT between the crude oil and seawater at ambient conditions.

seawater. As shown, the initial value of the IFT is about 26 dyn/cm, which decreased over time and reached the final value of 12.5 dyn/cm.

In the first series of IFT experiments, the effect of varied concentrations of sodium acetate (NaOAc) and potassium acetate (KOAc) on the IFT was investigated. In order to
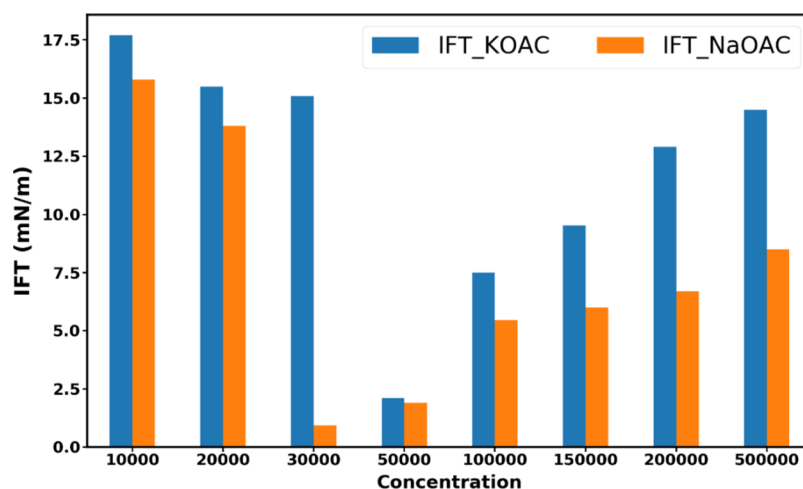
Figure 4. Effect of different concentrations of sodium acetate and potassium acetate on the interfacial tension.

compare the effect of these salts and define the optimal concentration (the concentration of salt that provides the lowest IFT), brines containing different concentrations of NaOAc and KOAc were synthesized. The IFT measurements between crude oil and NaOAc and KOAc solutions are compared in Figure 4. As can be seen, the measured IFT value between NaOAc and KOAc solutions and crude oil is a function of salt concentration; specifically, the IFT values decrease with the increase of salt concentration until they reach a specific concentration (30,000 and 50,000 ppm for NaOAc and KOAc salts, respectively), and then the IFT value increases with an increase in salt concentration. However, at equal concentrations, the effect of NaOAc brine on the IFT is more significant than that of KOAc brine. The optimum concentration of NaOAc salt for lowering the value of IFT (0.94 dyn/cm) occurred at a concentration of 30,000 ppm. The IFT value between KOAc and crude oil at optimum salt concentration, that is, 50,000 ppm, is 4.42 dyn/cm. Hence, to reduce the IFT, sodium acetate salt is more effective.

Recent studies have shown that the IFT between oleic and aqueous phases decrease due to chloride ion reduction from seawater.[45−4748] Hence, regarding the positive effect of chloride ion reduction in seawater on the oil recovery factor and the capability of NaOAc and KOAc salts in lowering IFT, the impact of seawater containing these salts in the absence of NaCl salt on oil production was investigated. The result of measured IFT between crude oil and different brines including synthetic SW, MSW.NaOAc, and MSW.KOAc is shown in Figure 5. It can be seen that the IFT between crude oil and SW is 12.5 dyn/cm, while for MSW.NaOAc and MSW.KOAc, it is 4.40 and 6.33 dyn/cm, respectively. From this, it can be concluded that the IFT reduction can be considered an effective mechanism for increasing oil recovery.

In the next series of IFT experiments, to investigate the effect of sulfate ion concentration in the presence of NaOAc salt, the synthetic seawater was modified with 2 and 4 times the concentration of the sulfate ions in the absence of NaCl salt, that is, MSW.NaOAc.2S and MSW.NaOAc.4S, respectively. A comparison of the results shows that the addition of sulfate ions to modified seawater (MSW.NaOAc) increases the IFT (Figure 6).

3.2. Wettability Measurement. Contact angle measurements have been used as a screening method to select effective solutions for flooding experiments. In order to investigate the
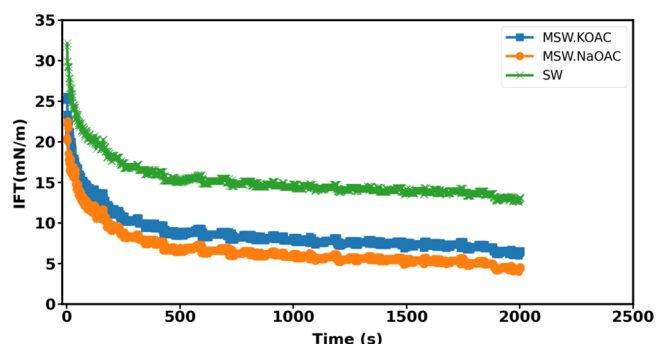

Figure 5. Interfacial tension (IFT) variations over time as a function of the salt type.
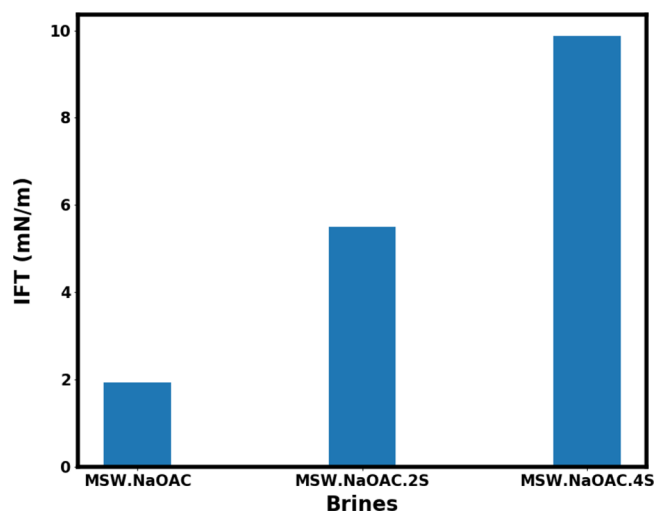
Figure 6. Investigation of the effect of the sulfate ion concentration on IFT.

effect of sodium acetate (NaOAc) and potassium acetate (KOAc) salts, synthetic brines containing the optimum concentration of NaOAc and KOAc (30,000 and 50,000 ppm, respectively) were investigated. The contact angle measurements were carried out on synthetic SW and MSW.NaOAc to study the effect of NaOAc salt on wettability alteration. The capability of sulfate ions with different concentrations to change rock wettability was also investigated.

The results of wettability alteration using SW and MSW.NaOAc are shown in Figure 7. The images on the left
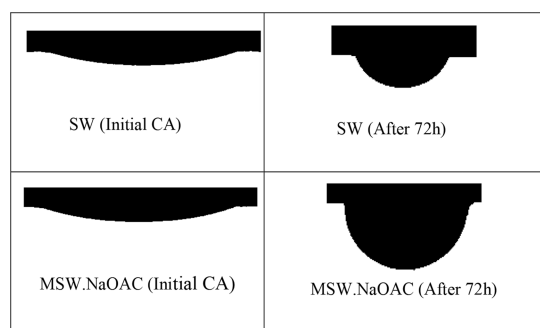
Figure 7. Contact angle measurement initially and after soaking in smart waters for 72 h.

side of the figure show the initial contact angle measured on the aged rock slab, while the effect of synthetic brines on the rock wettability, which was measured after soaking the rock slab in synthetic brines for 72 h, is seen on the right side of the figure.

As can be seen in Figure 7, the contact angles of the rock slab in contact with SW and MSW.NaOAc are decreased to 120° and 90°, respectively, indicating that modified seawater is more effective than seawater on wettability alteration. The contact angle changes due to soaking rock slabs in varied synthetic brines are given in Table 6. As shown, modified

Table 6. Measured Contact Angle for the Synthesized Brines

brine	initial CA	final CA (after 72 h)	CA changes
NaOAc (c = 30,000 ppm)	176	125	51
KOAc (c = 50,000 ppm)	176	155	21
SW	170	120	50
MSW.NaOAc	175	90	85
MSW.KOAc	170	135	35
MSW.NaOAc.2S	176	72	104
MSW.NaOAc.4S	170	90	80

seawater with sulfate ions (MSW.NaOAc.2S) is able to change the wettability greatly. However, brines containing KOAc and NaOAc salts as well as MSW.KOAc have the least ability to alter the wettability. A comparison between MSW.NaOAc.2S and MSW.NaOAc.4S reveals the higher ability of the MSW.NaOAc.2S in wettability alteration. Due to the fact that wettability alteration is considered one of the main mechanisms in the process of oil recovery enhancement, hence, SW, MSW.NaOAc, MSW.NaOAc.2S are suitable candidate brines for flooding experiments.

3.3. Zeta Potential Measurement. To investigate the effect of organic acetate ion on oil displacement, first, the zeta potential of NaOAc and KOAc solutions at optimum concentrations, obtained from IFT measurement, was measured. Then, the effect of modified seawater, that is, MSW.NaOAc and MSW.KOAc, on the zeta potential was also studied. Since the sulfate ion is an effective ion in recovery processes due to the rock wettability alteration, zeta potential experiments were also conducted on MSW.NaOAc.2S and MSW.NaOAc.4S brines.

Figure 8 illustrates the zeta potential measurements conducted on aged calcite powder in the presence of different synthetic brines solutions. SW provides a negatively charged surface (-2.25 mV) related to the ratio of divalent anion and cations concentrations. The sulfate (SO_4^{2-}) concentration is 2 times higher than Mg^{2+} and 6 times higher than Ca^{2+} in SW (3070, 1640, 500 ppm, Table 1), confirming the negative value of SW on the calcite surface charge. The oil-wet calcite powder was dispersed in seven different types of smart water solutions in which a Stern layer of adsorbed ions was formed while the hydrated ions stayed in solution. Therefore, different ions in the aqueous phase modify the calcite powder surface charge due to a double layer with a variable thickness. According to results shown in Figure 8, the lowest zeta potential values are related to 2 and 4 times the excess amount of divalent anions (SO_4^{2-}), that is, MSW.NaOAc.2S (-5.6 mV) and MSW.NaOAc.4S (-8.3 mV). This indicates the ability of the sulfate ions to penetrate the electric double layer. Therefore, it can be concluded that SO_4^{2-} is an effective ion in providing a negatively charged surface, resulting in the required repulsion for the separation of oil from the rock surface. Zeta potential experiments also confirmed the contact angle results in which
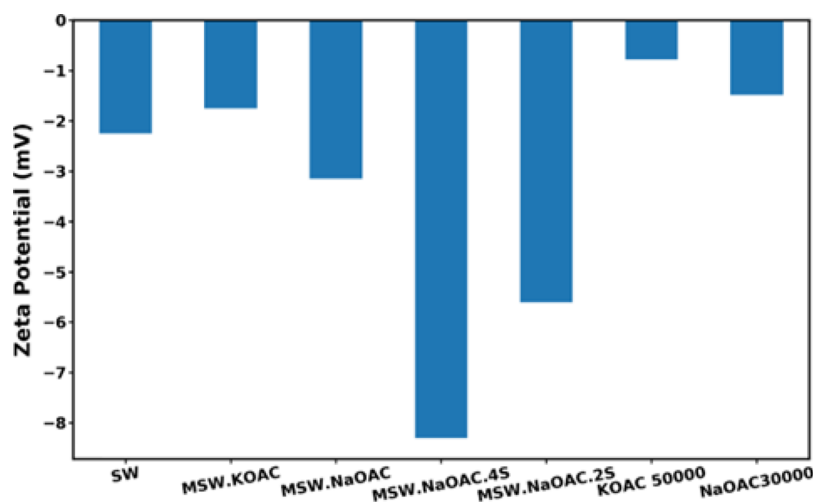
Figure 8. Results of measuring the zeta potential of solution and carbonate rock powder.

SO_4^{2-} alters the wettability of the rock surface toward more water-wetness.

3.4. Waterflooding Experiments. This section compares the effectiveness of alterations in ion compositions of seawater on oil production during smart waterflooding. Based on static experiments including IFT, CA, and zeta potential measurements, appropriate synthetic brines, that is, MSW.NaOAc and MSW.NaOAc.2S, were chosen as agents for smart waterflooding. SW flooding was also conducted as a reference. The flooding scenario is shown using a chart in Figure 2. In this experimental design, the influence of ion exchange on the investigated carbonate reservoir and its potential to release the trapped oil from the rock surface was examined. All flooding experiments were conducted in secondary and tertiary modes and at a temperature of 85 °C. It should be noted that the ion compositions and salinity of SW were considered as references, and synthetic brines investigated in this study were prepared with respect to SW. These brine samples were chosen in order to quantify the effects of acetate and SO_4^{2-} ions in the absence of NaCl on the oil recovery factor.

As shown in Figure 2, in the first scenario, SW was injected into core plug 1 in secondary mode, followed by reformed SW with NaOAc (MSW.NaOAc) injection in the tertiary state. The next flooding experiment (the second scenario) was conducted on core plug 2 in which MSW.NaOAc was first injected followed by SW flooding. To study the effectiveness of divalent anions (SO_4^{2-}) to release the trapped oil, a synthetic brine with 2 times the excess amount of divalent anions (SO_4^{2-}), that is, MSW.NaOAc.2S was synthesized and injected into core plugs 3 and 4 in secondary and tertiary modes, respectively (the third and fourth scenarios). The core plugs were flooded with investigated brines until no oil production was observed at each step.

3.4.1. Comparison of Seawater and Reformed Seawater. As mentioned in the former section, in order to investigate the effects of sodium acetate salt, SW was first injected into core plug 1 in secondary mode, followed by MSW.NaOAc in the tertiary state. Then, the reverse of this process was carried out in core plug 2. The water imbibition flooding results are listed in Figure 9.

The oil recovery of 66.6% was observed during SW injection in secondary flooding over core plug 1 (Figure 9). After reaching the stable production profile, SW was replaced by MSW.NaOAc flooding in tertiary mode and flooding continued until no more oil production was observed.
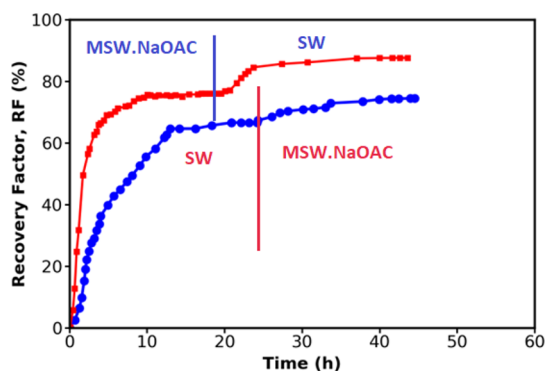
Additional oil production was observed when MSW.NaOAc is 9.5% of the original oil in place. Therefore, the recovery factor during tertiary flooding reached 76.1%.

In the second scenario, core plug 2 was flooded by MSW.NaOAc in secondary mode, followed by SW flooding. It was observed that SW flooding in the tertiary state provides an additional oil recovery factor of 11.5%, in comparison to SW flooding in the secondary mode. Furthermore, an enhancement of 7% in the oil recovery factor was observed during MSW.NaOAc flooding in secondary mode. The comparison of the final oil recovery factors of these two core plugs shows that the MSW.NaOAc brine, in comparison to SW, is able to release more trapped oil from the carbonate rock during the secondary flooding. It can be said that scenario 2 (MSW.NaOAc flooding followed by SW injection) is more suitable, that is, leads to higher oil production.

At the beginning of the water injection, the production is mostly influenced by the reduction of IFT, and the comparison of the results of the injection at the secondary state of two brines reveals that the IFT reduction has a significant effect on the amount of production. With the passage of time and the effect of smart water on the surface wettability alteration, the production will continue under the influence of the change of wettability, and the comparison of the final production of these two injection processes shows that both the mechanism of IFT reduction and wettability alteration are effective mechanisms in the process of smart water injection. The results of the zeta potential measurements show that replacing chloride ions with acetate ions provides a negatively charged surface, resulting in the separation of oil from the rock surface. The experiments conducted in this study following scenarios 1 and 2 confirmed this.

3.4.2. Investigating the Effect of Adding Sulfate Ions. The next experiments were conducted on core plugs 3 and 4, with a procedure similar to that performed on core plugs 1 and 2, aimed at comparing SW to the MSW.NaOAc.2s brines. The experimental sequences of brine injections for core plug 3 was SW → MSW.NaOAc.2S, while MSW.NaOAc.2S → SW was considered for core plug 4. The experiment was started by injecting SW and continued until no more oil was produced. In the next stage, SW was replaced by MSW.NaOAc.2S during tertiary flooding, which causes a further oil recovery factor of 19%. The overall oil recovery factor during tertiary flooding of core plug 3 was found to be 86% (Figure 10).
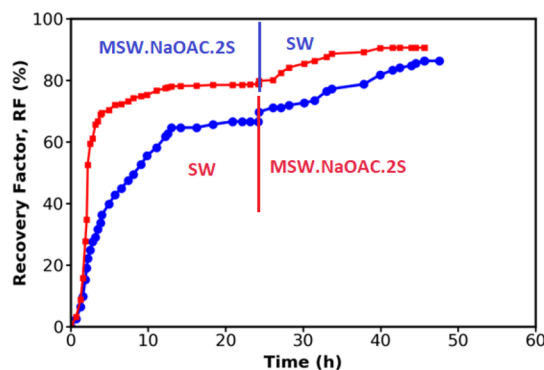
Figure 9. Oil recovery factor versus time during waterflooding. The blue line shows the oil recovery factor for core plug 1; the red line shows the oil recovery factor for core plug 2 in reverse operation.

Figure 10. Diagram of the oil recovery process of seawater injection and modified seawater with twice the concentration of sulfate ions. The blue line shows the oil recovery for core plug 3; the red line shows the oil recovery factor for core plug 4 in reverse operation.

In the last scenario, the waterflooding started with MSW.NaOAc.2S. As can be seen in Figure 10, MSW.NaOAc.2S provided a 14% increase in oil recovery in the secondary injection process compared to SW flooding in scenario 3. The flooding continued by SW during the tertiary stage in which overall oil recovery reached 90.66%, which is an increase of 4.66% compared to the contrasting case, that is, scenario 3. By comparing the results of these processes, it can be seen that the highest amount of oil recovery in the secondary injection process is related to MSW.NaOAc.2S. As mentioned before, the CA measurement showed that MSW.NaOAc.2S is able to change the wettability of oil-wet carbonate rock surface greatly which is consistent with the zeta potential measurement of this brine.

4. SUMMARY AND CONCLUSIONS

In this research, the effect of organic salt compounds on the rate of oil recovery from calcite carbonate rocks at ambient temperature and pressure was investigated. To gain a better insight regarding liquid/liquid and solid/liquid interactions and mechanisms involved during low salinity waterflooding, a series of sub-pore tests (IFT, CA, and ZP tests) followed by flooding experiments within carbonate rock samples were carried out. The key findings are as follows.

1. The results from IFT experiments show that acetate ions have a significant effect on reducing the IFT between the aqueous and oleic phases. Compared to SW, modified SW with both sodium acetate and potassium acetate provides a noticeable decrease in IFT. Nevertheless, this IFT reduction is more significant for SW modified with sodium acetate. The IFT measurement conducted on MSW.NaOAc.2S and MSW.NaOAc.2S reveals that the addition of sulfate ions to modified SW (MSW.NaOAc) increases the IFT. The higher the sulfate ion concentration, the higher the IFT.

2. The CA experiment results show that wettability alteration due to brines containing KOAc and NaOAc salts, as well as MSW.KOAc, is insignificant. It was also observed that modified SW with sulfate ions (MSW.NaOAc.2S) is able to change the wettability greatly. Comparison between MSW.NaOAc.2S and MSW.NaOAc.4S reveals the higher ability of the MSW.NaOAc.2S in wettability alteration.

3. The results of zeta potential measurements conducted on aged calcite powder in the presence of different synthetic brines solution indicate that the lowest zeta potential values are related to 2 and 4 times the excess amount of divalent anions (SO_4^{2-}), that is, MSW.NaOAc.2S (-5.6 mV) and MSW.NaOAc.4S (-8.3 mV). This indicates the ability of sulfate ions to penetrate the electric double layer and provide a negatively charged surface, resulting in the required repulsion for the separation of oil from the rock surface. This confirms the capability of SO_4^{2-} to alter rock surface wettability.

4. The secondary imbibition experiments using the SW and the MSW.NaOAc brine injection demonstrate that MSW.NaOAc brine is more effective than SW for displacing oil in porous media. The oil recovery factors of SW and the MSW.NaOAc brine flooding in the secondary mode were 66.66 and 76.1%, respectively. MSW.NaOAc followed by SW floodings provided oil recovery of 87.66% (the second scenario), while the oil recovery factor due to SW injection and the subsequent MSW.NaOAc flooding (the first scenario) resulted in a 74.5% recovery.

5. The results of secondary smart waterflooding experiments in carbonate rocks reveal that both elimination of inactive monovalent ions (Na^+ and Cl^-) and adding acetate ions, as well as an increase in the amount of SO_4^{2-} ions, improved oil recovery significantly, leading to a 79.1% recovery factor, which is 3% higher than the oil recovery factor due to MSW.NaOAc injection at the secondary mode. Hence, the ultimate oil recovery factor according to the MSW.NaOAc.2S followed by SW flooding (the last scenario) was 90.66%.

This study confirms that the salt type and concentration present in brine solution play vital roles in the movement of trapped oil. According to the findings of these experiments, it is recommended that the effect of temperature and pressure on the IFT and CA of a solution containing sodium acetate salt should be investigated. It is also recommended that the effectiveness of smart waters containing sodium acetate in sandstones is also studied. Ionic analysis of the outlet brines from the flooding experiments can provide a better understanding of the effective mechanisms in the production process. Spontaneous imbibition experiments with different combinations of smart waters containing varied organic salt ions in order to compare the results of flooding tests may also be beneficial in further enhancing our knowledge of relevant mechanisms.

■ ASSOCIATED CONTENT

ⓢ Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.3c04888.

> Schematic representation of core flood apparatus, experimental procedure, dynamic and equilibrium IFT, effect of different concentrations of sodium acetate and potassium acetate on interfacial tension, investigation of the effect of sulfate ion concentration on IFT, contact angle measurement, results of measuring the zeta potential of solution and carbonate rock powder, oil recovery factor versus time during waterflooding, and oil recovery process of seawater injection and modified seawater (PDF)

■ AUTHOR INFORMATION

Corresponding Author

Abbas Shahrabadi − Petroleum Engineering Department, Research Institute of Petroleum Industry (RIPI), Tehran 1485733111, Iran; ⓞ orcid.org/0009-0002-0549-8664; Email: shahrabadia@ripi.ir

Authors

Huxiong Li − Institute of Artificial Intelligence, School of Mechanical and Electrical Engineering, Shaoxing University, Shaoxing 312000, China

Fatemeh Razavirad − Institute of Artificial Intelligence, School of Mechanical and Electrical Engineering, Shaoxing University, Shaoxing 312000, China; Structural Dynamics and Geotechnic, Aarhus University, 8000 Aarhus, Denmark

Andrew Binley − Lancaster Environmental Centre, Lancaster University, Lancaster LA1 4YQ, U.K.

Complete contact information is available at:
https://pubs.acs.org/10.1021/acsomega.3c04888

Notes

The authors declare no competing financial interest.

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