

The Effect of Low-salinity Water on Wettability and Oil Recovery by Core Flooding Test: A Case Study in the Shadegan Oil Field

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Abstract

In most carbonate reservoirs, the amount of oil recycled depends on the spontaneous uptake of brine in the matrix and oil extraction in that matrix towards the cracks. The injection of modified water makes this process possible by changing the wettability of the matrix block towards more water-wet. The rate of wettability change is one of the factors that makes the injection of low-salt water economically. Therefore, this study aims to identify the effect of ion type on the rate of wettability change to modify the composition of the water used for flooding into the reservoir so that the maximum use of this process is to increase oil production from the reservoir. The effect of sodium, magnesium, calcium and sulfate ions on oil recovery from carbonate reservoirs was investigated by a dynamic contact angle test. The results show that increasing the concentration of surfactants such as magnesium, calcium, and sulfate could rise (1) the wettability towards water-wet and (2) the rate of wettability change. In contrast, neutral ions, such as sodium ions, were resulted in a rate reduction in which surface ions change to wettability. Elimination of sodium ions would result in approximately the same amount of change in wettability but in a lesser time from 24 to 2 hrs. The results of the secondary injection showed that although the presence of sodium did not have a significant negative effect on oil recovery, the removal of sodium ions significantly could be improved the sweep efficiency of oil. In modified water, the sodium ion from +0.1 mol to +0.001 magnesium sulfate solution was eliminated. Instead, +0.1 mol sodium sulfate was added to enhance the breakthrough time from 0.31 to 0.43 seconds for injected pore volume. So, the second enhanced recovery was increased in compare to first EOR.

Keywords: Enhanced Oil Recovery, Wettability, Modified Water, Contact Angle, Core Flooding Test

Introduction

One of the most practical new methods in carbonate reservoirs is the modified seawater injection method. This method simultaneously increases the oil recovery percentage by changing the wettability of the matrix block to more water-wet and increasing the permeability of the matrix blocks. Reservoir rock wettability is one of the important parameters affecting capillary pressure, which is the driving force of the spontaneous imbibition process. So, the effects of surfactants behaviour in reducing surface adhesion (Inter Facial Tention; IFT) and changing in wettability in carbonate rocks have been discussed in the articles.

In this research, the effect of ions in seawater as surface-active ions for improving oil extraction from carbonate reservoirs was investigated. For this purpose, experiments measuring contact angle changes were performed to observe the change in wettability using solutions containing different amounts of ions in seawater. The effect of the mentioned factors has been investigated by measuring the change of contact angle on

the surface of reservoir rock samples (which have almost similar properties) in different solutions. Afterward, the effect of these results in the conditions of injection into the core was examined to evaluate the effectiveness dynamically. Smart water injection (SWI) was found to have some advantages over other enhanced recovery methods. First, smart water injection can achieve higher final oil recycling with minimal investment in common operations, assuming flooding infrastructure is already in place. Secondly, it can be injected at the beginning of the tank life cycle. Thirdly, the investment return is faster, even with a small increase in oil recovery. And finally, the SWI method is inexpensive and environmentally friendly. Also, it does not use expensive chemicals [1]. Some used chemical additives (quaternary ammonium cationic surfactants (R-N (CH₃)₃Br)) in injected water were used to change the wettability of carbonate rocks to more hydrophilic conditions [2]. In studies, the use of sulfate ions as a catalyst was found to be effective on wettability by cationic surfactants [3]. Subsequently, the experiments by Zhang et al. (2007) showed that sulfate

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alone could improve the wettability of carbonate rocks without the presence of expensive surfactants [4]. To obtain the self-priming mechanism of seawater in oil-friendly agile rocks, the effect of ions on the surface potential of seawater in the spontaneous imbibition process was investigated.

Their experiments were performed by changing the concentration ratio of Ca^{2+} and SO_4^{2-} ions as well as changing the temperature [5]. In another study, the oil recovery increased from 10% to 50% of the initial oil in place. That part was occurred when the concentration of SO_4^{2-} in seawater fluids varied from zero to four times that in normal seawater. Accordingly, it has been observed that sulfate in seawater is adsorbed on wet areas with a positive charge of the rock surface and reduces the positive charge of the surface [1,6]. Also, it has been observed that when the concentration of Ca^{2+} in seawater was changed from zero to 4 times its original concentration in seawater, oil recovery would be increased from 28-60% after 3 days of imbibition.

In that case, the concentration of sulfate is constant, and it is similar to its concentration in seawater. Excess Ca^{2+} will accumulate near the rock surface due to less electrostatic repulsion [1,6]. The effect of magnesium ions [3] on the surface in seawater and some other ions [7] present in seawater have also been investigated. Hence, it was concluded that the presence of sodium chloride salt by creating electrical layers prevents the access of active ions to the rock surface to change wettability and thus reduce oil recovery [7].

In another study, the ionic composition was determined by the effect of ions on improving oil recovery. The purpose of increasing the water wettability in the rock of the formation is to move the oil. Diluted seawater with low to medium salinity 2 to 10 times dilution or modified seawater was initiated. The reason was to discharge in monovalent ions but reinforced with sulfate (4 times) and ions (1-time calcium and magnesium) for flooding with smart water. They are most suitable in carbonate tanks [8].

Recently, much attention has been paid to the use of low salinity water (LSW) as a fluid to increase oil recovery. The change in oil recovery coefficient with LSW is attributed to relative permeability and capillary pressure changes using different salinity levels. Generally, flow functions and residual oil saturation change linearly with salt concentration [9]. It is shown by Shojaei et al. in 2015 that wettability changed from mixed to hydrophilic mode using LSW [9]. In addition, it was accomplished by them that improved oil recovery can be controlled by changing wettability and reducing IFT. Also, their findings have shown that in the LSW flooding process, the capillary pressure, like the relative permeability, depends on the salinity. Others performed flooding experiments on samples of dolomite saturated with crude oil from Iranian oil reservoirs by fluids with different salinities. Various measurements were conducted, including zeta potential, XRD, contact angle, and surface tension, to investigate the effect of ionic composition of brine and initial rock saturation on the change of wettability and oil recovery. Such analysis showed that the concentration of SO_4^{2-} ion in the injected water should be in the desired range for each case.

That showed the reduction of the wettability of carbonate rock to an oil-friendly state by changing the composition of saltwater and reducing salinity. In addition, the initial water

saturation was involved in this process so that by increasing the SO_4^{2-} content in the desired range, oil recovery increases [10]. Low-salt water flooding (LSWF) has recently become a popular third-stage EOR injection method. Both fluid-fluid and rock-fluid interactions are recognized as effective mechanisms for LSWF effectiveness [11].

To grasp the mechanisms of oil movement from the porous media, knowledge of the role of wettability and fluid distribution at the pore scale is required. X-ray micro-CT technology provides opportunities to study the complex process of fluid displacement at the pore surface. All core samples became highly petroleum-friendly, regardless of post-impregnation cleaning methods with crude oil. The X-ray CT technique shows the rapid evolution of the saltwater contact angle, which is related to the changes in wettability to oil-friendliness after crude oil pumping. During the experiments in the Amute cell, the rate of oil recovery from the gently cleaned cores was observed, while no oil recovery rate was observed from the thoroughly cleaned cores.

The high rate of oil recovery from one of the samples was due to a fracture network observed under a CT scan [12]. So far, studies have been performed to obtain the mechanisms of change in the wettability of the surface of carbonate rocks. Still, more studies and experiments are needed to get an accurate and generalizable mechanism.

Those types of changes depend on the type and material of the reservoir rock system, crude oil, and water, it is necessary to study these changes and find the appropriate water composition for each specific system. In other words, for each specific reservoir, a combination of water should be obtained based on studies and experiments to be compatible with the reservoir conditions while creating the expected processes to increase the harvest and not cause problems such as destruction and sedimentation.

In the present study, the effects of two groups of solutions, one group including magnesium sulfate and sodium sulfate salts to study the effect of magnesium, sodium, and sulfate ions together on the change of wettability and another group including calcium sulfate and sodium sulfate salts to study the effect of calcium, sodium and sulfate ions together have been investigated. By the way, because of the importance of parametric wettability change, the time of such a change is also very important. Furthermore, the composition of the solutions used should also be studied in terms of the effect on the wettability change time. Subsequently, the rate of change in wettability and final wettability of carbonate samples was investigated. Those were compared by contact angle with considering the time of occurrence of wettability variations. Those are illustrated as follows.

Wetting of Carbonate Surfaces

Wettability is a term used to describe the relative affinity of a surface for fluid in the presence of other immiscible fluids. Wettability determines the position, distribution, and flow of fluids in the reservoir. Reservoir wettability plays an important role in reservoir estimation, reservoir development planning, and oil extraction behavior by affecting well chronology, relative permeability, capillary pressure, and reservoir water injection performance [13]. A fluid with a wettability property compared to the porous medium

(wetting fluid) occupies the small pores of the rock, and it is attached to the rock in large pores, and to produce it, a lot of effort is needed. In contrast, other fluids are located inside large pores (in the middle of large pores), making them easier to produce [14]. If a sample of rock only absorbs water spontaneously, it is called hydrophilic, and if it absorbs oil spontaneously, it is called oil-friendly.

Intermediate or neutral wettability is a state in which both oil and water tend to wet the surface (rock does not have a strong tendency to absorb water or oil by itself) [5,14,15]. In the reservoir conditions, the levels of carbonate rocks are positive. These positive charge sites form very strong bonds with the negative end of the carboxylic groups in the crude oil, leading the wettability of the carbonate rocks to the oil-wet condition.

Wettability tests performed on some carbonate reservoirs in southwestern Iran also confirm the oil-wet of their reservoirs. Also, contact angle measurements for 161 carbonate reservoir oil samples from geological areas around the world concluded that carbonate reservoirs are likely to be neutral to oil-friendly [15].

Wettability Measurement Methods

These methods to measure which are used to wettability, are divided into two main categories of quantitative and qualitative approaches. The qualitative wettability measurements encompass self-priming measurements, relative permeability measurements, capillary pressure diagrams, saturation and permeability measurements, buoyancy methods, microscopic examinations, reservoir logs, Nuclear Magnetic Resonance (NMR), color absorption, and some other methods. Those are all achievable in qualitative measurement methods. The most important quantitative methods for measuring wettability include contact angle measurement, Amot wettability index, and USBM wettability index measurements. Nevertheless, the contact angle measurement method in this study has been used

to measure wettability in different stages. In Table 1, a brief comparison of quantitative methods with their advantages and/or disadvantages for measuring wettability has been provided.

Contact Angle

Measuring the contact angle is the most accurate method for determining wettability for pure liquid and artificial rock samples. For a system consisting of two pure immiscible fluids lying on a smooth, homogeneous solid (Figure 1), there is an angle (θ), which is the contact angle. That angle is determined by Yang’s law (Yang, 1805) [16].

Based on Equation 1, the contact angle is obtained from the mechanical balance of force for surface or interfacial tension.

$$\sigma_{os} = \sigma_{ws} + \sigma_{ow} \cdot \cos \theta \tag{1}$$

where σ_{os} (N/m) is surface adhesion between oil and solid, σ_{sw} (N/m) is the surface adhesion between water and solid, σ_{ow} (N/m) is the surface adhesion between oil and water, and θ (Degrees) is the contact angle.

Effect of Surfactants on the Wettability Changes

It was designated by Strand et al. in 2006 that the use of sulfate ions as a catalyst has been effective in changing wettability by cationic surfactants [3]. Subsequently, they obtain the Self-Priming mechanism of seawater in oil-wet agile rocks by investigating the effect of ions affecting the surface potential of seawater in the spontaneous vampire process. Therefore, they presented the same results by changing the concentration ratio of Ca^{2+} and SO_4^{2-} ions and the temperature of experiments. Based on their achievements, adsorption of SO_4^{2-} ion on the surface of the agile rock by changing the rock surface charge would help excrete negatively charged carboxylic materials.

Also, increasing the concentration of Ca^{2+} ion near the rock surface due to the co-adsorption of this ion in the presence of SO_4^{2-} ion would facilitate the reaction with carboxylic substances.

Table 1 Quantitative methods for wettability measuring.

Disadvantage	Advantage	Mechanism	Measurement Methods
Not considering surface roughness, rock homogeneity, and cavity structures	Very accurate	Static: The contact angle measurement on a rock surface	Contact Angle
Low sensitivity in neutral or highly hydrophilic conditions Lack of standard vampire time	Using of reservoir’s rock and fluid samples	Dynamics: based on the rate of absorption in Self-Priming measurements	Amott-Harvey
Limitation in sample size because of centrifuge	Using of reservoir’s rock and fluid samples Appropriate sensitivity Short time exp	Dynamics - vascular capillary pressure & centrifugal discharge	USBM

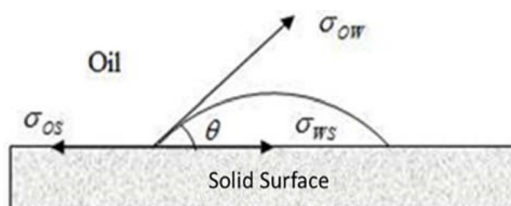
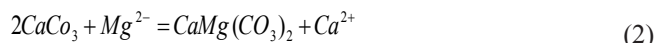


Fig. 1 Contact angle and surface adhesion (water drop on a wet surface).

Their Chromatographic experiments showed that the adsorption of sulfate ions on the surface of the rock increased with the mounting temperature and concentration of Ca^{2+} ions. In conjunction with other studies, the experiments carried out by Zhang et al. in 2007 indicated that sulfate alone could improve the wettability of carbonate rocks without the presence of expensive surfactants [4]. His experiment showed that with cumulative temperature, vapor velocity and oil extraction rate could be increased with an increase in absorption of SO_4^{2-} and Ca^{2+} ions on the rock surface. However, in earlier studies, Zhang and Austad (2006) showed that such kind of mechanism could be described by the adsorption of sulfate ions, increase in the negative surface charge, and surging the adsorption of calcium ions on the rock surface [3]. As a result, the separation of carboxylic substances from the surface following the reaction with Ca^{2+} ions was eased, and the formation of complexes with these ions was facilitated. They also investigated the effect of Mg^{2+} ions in seawater on spontaneous water drinking. Hence, relatively hydrophilic agile rocks and a chemical mechanism for all substances were affecting the active surface in seawater, was presented as SO_4^{2-} , Ca^{2+} , and Mg^{2+} . For such an analysis, chromatographic separation experiments were performed by them, and it was found out that at ambient temperature, Ca^{2+} ions tended to be more reactive than Mg^{2+} ions. But their results showed that at high temperatures (about 130 °C), the Mg^{2+} ions reacted by dolomitization, and those ions were substituted for Ca^{2+} ions according to Equation 2.



According to these observations, Mg^{2+} ions can have the ability to displace Ca^{2+} ions attached to carboxylic groups. In addition to affecting the surface potential, they were also found to be active in the process of improving wettability by seawater. Those kinds of analysis would be able Zhang and Austad to develop the chemical mechanism proposed by Strand et al. in 2006 based on the Self-Priming mechanism performed on a sample of agile rocks, as shown schematically in Figure 2. Considering Figure 2, Ca^{2+} ions can be reacted with adsorbed carboxylic groups on the rock surface and would separate them from the surface at low temperatures (Figure 2, Part A). Furthermore, at high temperatures, Mg^{2+} can separate the complex formed between Ca^{2+} ions and carboxylic groups (Figure 2, Part B) [4].

Materials and Methods

Material

The Individual materials which have been used for our analysis are being illustrated here.

Rock: The limestone rock which has been used in this study, is prepared from the Shadegan oil field. The XRD examination (Figure 3) of this rock showed that it is mainly composed of calcite. The petrophysical properties of the cores and the oil used are listed in Tables 2 and 3, respectively. The core sample was taken from the Asmari layer of this reservoir at a depth of 3050 meters.

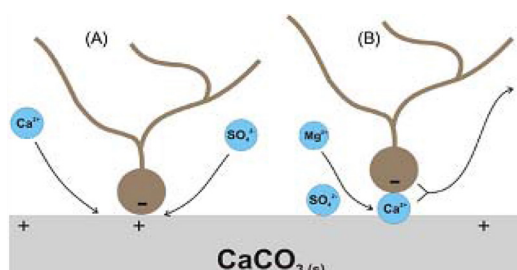


Fig. 2 Schematic model of the proposed mechanism for changing wettability by seawater injection. (A) The proposed model for the activity of Ca^{2+} and SO_4^{2-} ions at high and low temperatures. (B) Proposed model for the activity of Mg^{2+} and SO_4^{2-} ions at high temperatures [3].

Table 2 Petrophysical properties of cores

Secondary Injection	D ₄	D ₂
Length (cm)	7.1	7.05
Diameter (cm)	3.84	3.84
Porosity (%)	23.87	20.12
Permeability (cm ³)	9.39	7.61
Initial in-situ oil (cm ³)	15.95	13.2

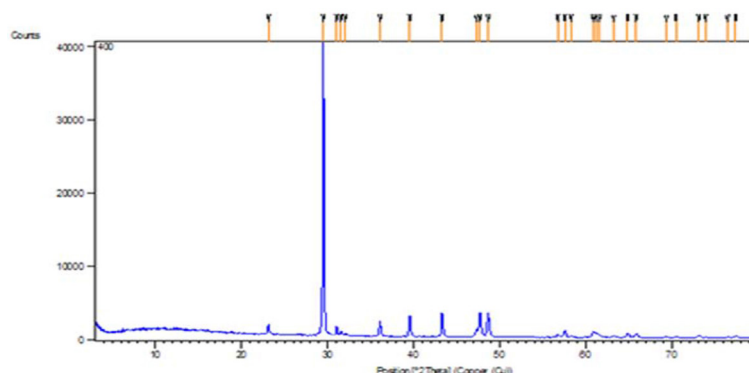


Fig. 3 Schematic model of the proposed mechanism.

Table 3 Specifications of experiment oil

Total acid number mg KOH/g oil	S*	Ar*	Res*	As*	ρ of crude oil: (30°C) gr/ml	μ of crude oil: (30°C) mPa.s
0.14	63.96	25.33	9.06	1.65	0.873	13

Also, the crude oil used in this study is from the Bangestan Formation of the Shadegan field. This crude oil was used after refining by a 24-micrometer filter. At ambient temperature and atmospheric pressure, the density of this crude oil is equal to 0.82 g/cm^3 , and its viscosity is 8 cP. Slat: In this study, sodium sulfate, magnesium sulfate, and calcium sulfate salts were used to make solutions. All salts are of high purity, obtained from the German Merck company (Merck KGaA).

Methods

Solution Assemblies

To prepare the required solutions, test concentrations were first designed, and the amount of salt required to make these solutions was measured on an accurate laboratory scale. Afterward, the solutions were made using volumetric balloons and distilled water and transferred to special glass containers for storage and work. For solutions designing, two groups of solutions were generated:

1) Solution containing sodium sulfate and magnesium sulfate salts, and 2) a solution containing sodium sulfate and calcium sulfate salts. Group 1, which contains Mg^{2+} , SO_4^{2-} and Na^+ ions, has a total dissolved solids concentration of X, 2X, and 4X in a molar. The solutions were indicated as Group1, which they were naming D1, D2, D3, and D4, as details given in Table 4. The value of X here is considered to be 0.05 molar. Also, a solution in which the concentration of magnesium sulfate is determined as 2X, but it does not contain sodium sulfate salt.

The second group named C1 to C4 (Table 5), which includes Ca^{2+} , SO_4^{2-} and Na^+ , had a total dissolved solids concentration of X, 2X, and 4X in a molar. Also, a solution with the concentration of calcium sulfate salt was determined as 2X. But it does not contain sodium sulfate salt.

Table 4 Concentration (molar) of group one solutions.

	MgSO_4	Na_2SO_4
D ₁	0.5	0.5
D ₂	1.0	1.0
D ₃	2.0	2.0
D ₄	1.0	0.0

Table 5 Concentration (molar) of group 1 solutions

	CaSO_4	Na_2SO_4
C ₁	0.0025	0.05
C ₂	0.005	0.1
C ₃	0.01	0.2
C ₄	0.005	0.0

It should be noted that in both groups, the concentration of sodium sulfate was considered similar. In the first group, the concentration of two types of salt in each solution was equal. In contrast, for the second group, the concentration was not possible due to the limited solubility of calcium sulfate in water.

Salt solutions were prepared in group one, including sodium sulfate and magnesium sulfate (group D), and group two including sodium sulfate and calcium sulfate salts (group C). The concentration of group one salts is as shown in the below

table.

Rock Sample Preparations

A core with petrophysical properties, similar to described sample assets in Table 2, was cut into thin sheets by a core cutter. The cut samples were placed in an ultrasonic bath for 25 minutes for cleaning and then placed in an oven at 50°C for 24 hours to dry. After preparing the prepared rock samples, it is time to change their wettability and create a reservoir wettability. For this purpose, those samples were placed in the tank conditions and the tank fluid for a sufficient time to keep the wettability of the sample equal to the tank conditions. To do that, the cleaned and dried samples are placed in the crude oil of the target tank (Ahwaz-Bangestan) in a high-pressure cylinder piston system. Also, enough time (about a month) was given to the system to create a new balance on the rock surface. Thus, the sample wettability would be changed.

Contact Angle Measurement

To measure the contact angle, a DSA device made by the German company Kruss was performed. The general specifications of the equipment are given in Table 6. This measurement is also made in an aqueous medium so that each sample is placed in a small aquarium containing the same solution used to change wettability to measure the contact angle. Moreover, the oil drop was injected with a special needle. The injected volume was below the surface of the stone. The oil droplets that are injected below the surface of those samples were the same type of crude oil that has been used to oil the prototypes. After injecting each drop of oil, it was necessary to give the drop a suitable time when it would reach a stable state. To achieve this goal, the software was photographed at intervals of 10 seconds after the injection. Hence, the steady-state condition was created when the difference between the two measured contact angles was minimized.

Accordingly, in this case, the correct contact angle was the final measured angle. After injecting each drop of oil on a suitable surface, the drop must reach a stable state. To meet that purpose, the system would take photos after injecting each drop at intervals of 30 seconds.

Table 6 General specifications of the DSA device for measuring the wettability

Title	Values
Range of contact angle	Degrees 0.0-180
Measurement accuracy	Degrees 0.1
Created Droplets	Controlled by software
Syringe, Volume	microliters 450
Speed	to 1400 microliter in minutes 1

This steady-state condition was created when the difference between the two measured contact angles was minimized. As a result, the correct contact angle was the last measured angle. Contact angle tests were performed to minimize the effect of errors. For example, in each experiment, after measuring the initial contact angle and ensuring that the rock was completely oil-wet, the experiment was continued to evaluate the upshot of the solution. Also, in those experiments, to consider the effect of rock surface heterogeneity in each stage of the

experiment, more than one drop of oil was injected under the rock surface. Afterward, values from the closer contact angle values were selected as the answer.

It is worth mentioning that the samples were tested in crude oil after the required time to check their wettability status at zero time. Hereafter, according to the method mentioned above, the contact angle of the oil drop on the rock surface was measured. After confidence of oil-wetting for the sample, it was placed in a special solution to perform the process of changing the wettability on it. In the next step, measuring contact angle by DSA device at different times was accomplished.

At approximate diversity times of $t_1 = 1$, $t_2 = 2$, $t_3 = 2_4$, and $t_4 = 72$ hours, and a new drop was injected below the rock surface at each of these times to record the rate of change in wettability of the rock surface. The droplet measurement was removed, and the sample was resuspended in its solution. At $t_5 = 168$ hours, the contact angle was measured to obtain the final wettability of the rock surface. If this number was close to the value obtained after three days, the number of wettability changes was stable. Here, the times reported above are cumulative. Therefore, in those experiments, more than one drop of oil was injected below the rock surface at each stage of the experiment to consider the effect of heterogeneity of the rock surface. Again, the values close to each other were selected as appropriate, and the others were acceptable in all cases. The errors of calibration of those tests were also measured and announced by the software analysis system. In all test cases also, they were less than one degree. Furthermore, to reduce the error after injecting each drop of oil on the surface at the appropriate time, the drop is needed to reach a stable state. To achieve this goal, after injecting each drop at intervals of 30 seconds, the system takes pictures. This steady-state condition was created when the difference between the two measured contact angles was minimized. In such a case, the correct contact angle was the last measured angle.

Core Flooding Experiment

For this stage of the experiment procedure, a flooding device has been used for the core sample. The specifications of the core flooding apparatus are given in Table 7. First, the Shadegan carbonate core was placed in a saxophone device to remove any organic substances. Then the core was put in the oven and would let to dry. In the next step, the dried kernels were placed under a vacuum in the brine for two days in a desiccator. From the difference between the wet and dry weight of the kernel, the amount of space and consequently the percentage of porosity were obtained. The desired core was placed in the retaining core, and its permeability to the formation water was measured. The desired brine was injected into the aging core with a flow rate of 0.2 cc/min. To eliminate the final capillary effect, the injection flow rate was increased from 0.2 to 0.4 and then to 0.6 cc/min. Throughout the flood, the amount of oil produced and the pressure drop at both ends of the core was measured. This phase was continued until the stage of no more oil production and a constant state of pressure drop would be reached.

Table 7 Specifications of flooding device to the core

Title	Values
Hesler Core Holder	1.0
Maximum core dimensions	1.5 inches of diameter and the maximum length of 3 inches
Maximum operation pressure	400 bars
Maximum enclosing pressure	700 bars
Pressure difference transmitter	The amount of 2 with the accuracy of 0.1%
Maximum operation temperature	100 °C
Cylinder of fluid holder	3.0
Hydraulic pump	1.0

Results and Discussion

Contact Angle Analysis

The results of changes in the surface wettability of carbonate rocks have been measured by low salinity modified solutions. That has been done by measuring the contact angle. The results of changes in wettability on the surface of carbonate rocks by low salinity solutions were measured by estimating the contact angle. The ions of Na^+ were observed in water with low salinity on changes in wettability. The D_1 sample contains sodium sulfate salts with a concentration of 0.05 mol and magnesium sulfate with a concentration of 0.05 mol. In contrast, sample D_2 contains 0.1 mol sodium sulfate and 0.1 mol magnesium sulfate salts. The D_3 sample contains 0.2 mol sodium sulfate and 0.2 mol magnesium sulfate salts. The D_4 sample contains 0.1 mol magnesium sulfate salt. Group two consists of four concentrations of sodium sulfate and calcium sulfate salts. Furthermore, in samples C_1 to C_3 , the concentrations are varied by a factor of X, 2X, and 4X. This kind of arrangement was presented to observe the effect of the salinity of the water. This type of active ions was included to do changes in the wettability of carbonate samples and also the time of change in wettability of these samples. In the C_4 solution, the concentration of magnesium sulfate with the size of the C_2 solution was determined. That was performed to compare the results of samples to observe the effect of the presence of ions Na^+ in water with low salinity on changes in wettability.

The C_1 sample contains sodium sulfate salts with a concentration of 0.05 mol and calcium sulfate with a concentration of 0.0025 mol. The C_2 sample includes sodium sulfate salts with a concentration of 0.1 mol and calcium sulfate with a concentration of 0.005 mol.

The C_3 sample contains sodium sulfate salts with a concentration of 0.2 mol and calcium sulfate with a concentration of 0.01 mol. The C_4 sample contains calcium sulfate salt with a concentration of 0.005 mol. To conclude, Fig. 4 to Fig. 11 demonstrate the contact angle value for the samples of D_1 to D_4 and C_1 to C_4 in respect to time, correspondingly.

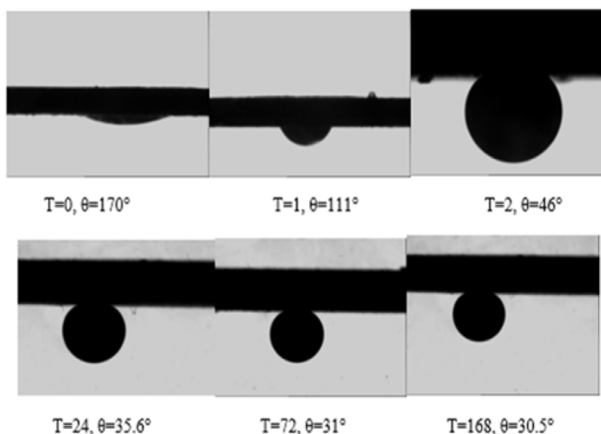


Fig. 4 Oil droplets below the rock surface and the size of the contact angle against the time: sample D₁.

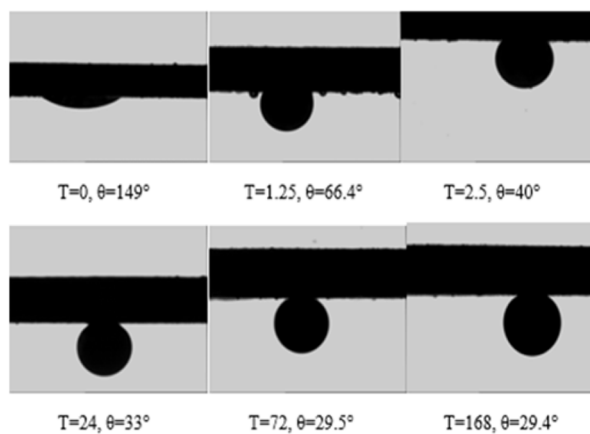


Fig. 8 Oil droplets below the rock surface and the size of the contact angle against the time: Sample C₁.

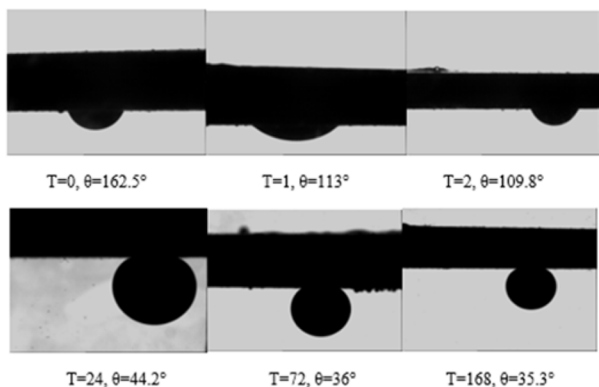


Fig. 5 Oil droplets below the rock surface and the size of the contact angle against the time: Sample D₂.

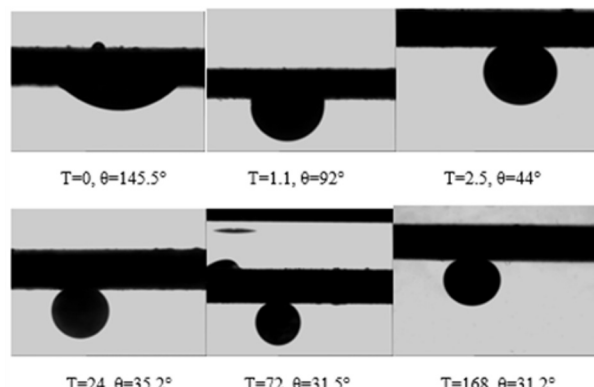


Fig. 9 Oil droplets below the rock surface and the size of the contact angle against the time: Sample C₂.

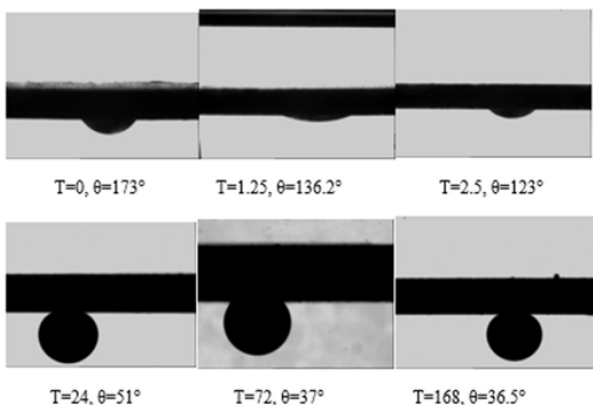


Fig. 6 Oil droplets below the rock surface and the size of the contact angle against the time: Sample D₃.

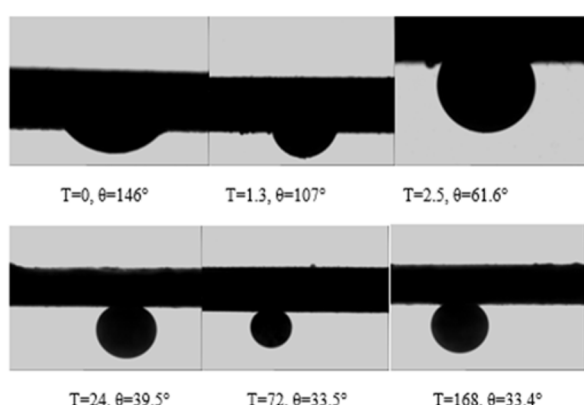


Fig. 10 Oil droplets below the rock surface and the size of the contact angle against the time: Sample C₃.

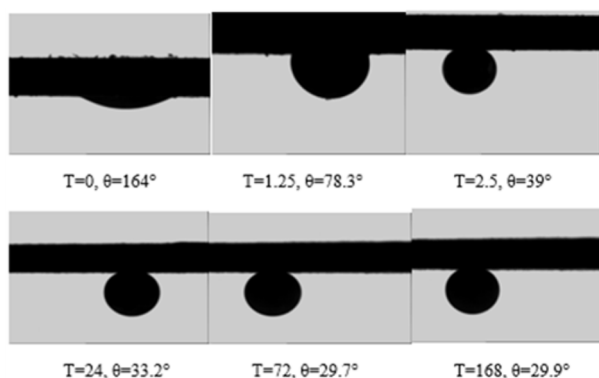


Fig. 7 Oil droplets below the rock surface and the size of the contact angle against the time: Sample D₄.

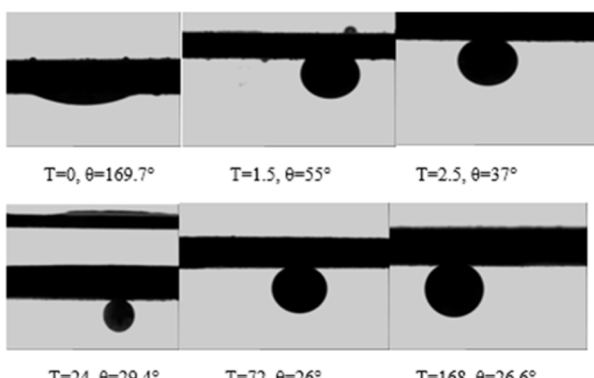


Fig. 11 Oil droplets below the rock surface and the size of the contact angle against the time: Sample C₄.

Core Flooding Examination

At the first stage, D_2 and D_4 were injected in core 1 and core 2, respectively. That was executed to investigate the effect of surfactants presentation as well as sodium ions in the oil material. Secondly, the D_2 solution injection test was accomplished while it consisted of 0.1 mol of magnesium sulfate salts and 0.1 mol of sodium sulfate salts to core1. The core was also oil-wet and oil-saturated. Lastly, the D_4 solution injection test was accomplished while it consisted of 0.1 mol of magnesium sulfate salts with no sodium sulfate salts to core 2. The core was also oil-wet and oil-saturated. In Figures 12 and 13, the oil recovery in contrast to injection cavity volume for that analysis is being illustrated for both D2 and D4 types.

Inquiry and Discussions

The solutions which have been used in groups of one and two were in the low-salinity water range. For that reason, the final contact angles were estimated for the different samples. The measurements were conducted in the highly hydrophilic range with a slight difference. In disparity, the reaching time to final contact angle (i.e., change in wettability) was dissimilar for unlike solutions.

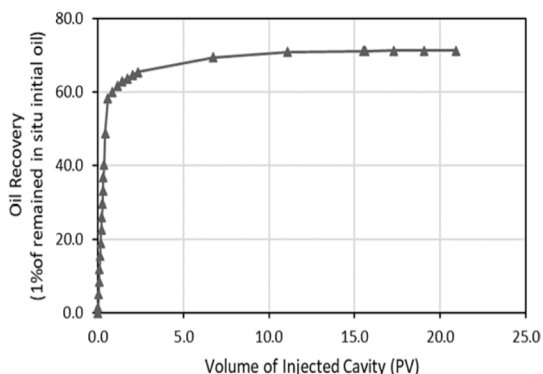


Fig. 12 Oil recovery during secondary injection of D_4 solution in limestone core with mixed wettability against the volume of the injected cavity.

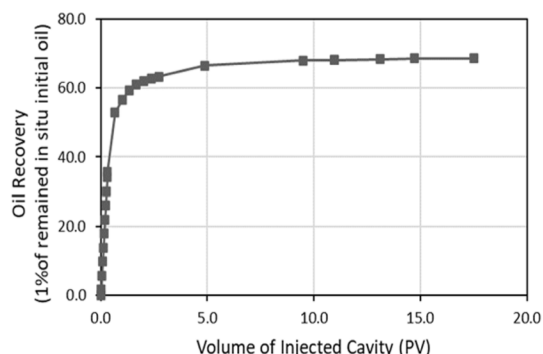


Fig. 13 Oil recovery during secondary injection of D_2 solution in Shadegan oil field (i.e., limestone) with mixed wettability against the volume of injected space

Based on experimental proceedings, it was observed that the changes in wettability could change rapidly in the early hours of the process. Also, by considering the occurrence of major changes in the early hours, the contact angle was recorded at times t_1 and t_2 at one-hour intervals. Therefore, the rest of the measurement intervals of 24 and 72 hours were performed. Then, the final estimations were made after one week to ensure the stability of the contact angle and to avoid

repeated changes. In group one, the contact angle at the 24 and 72 hours was estimated. The outcome indicated that by increasing the concentration of each salt from 0.05 to 0.2 mol in solutions of D_1 to D_3 , the rate of change in wettability would drop. In Figure 14, the changes in contact angle size over time are shown. Based on the figure, the faster the contact angle size decreases, the faster the wetting changes can occur.

As shown in Figure 14, removing sodium ions from the medium in the D_4 solution caused the fastest decrease in the contact angle size. It designates the fastest change in the wettability of the rock surface in this group. That can be described based on the most changes in the first 24 hours of the experiment.

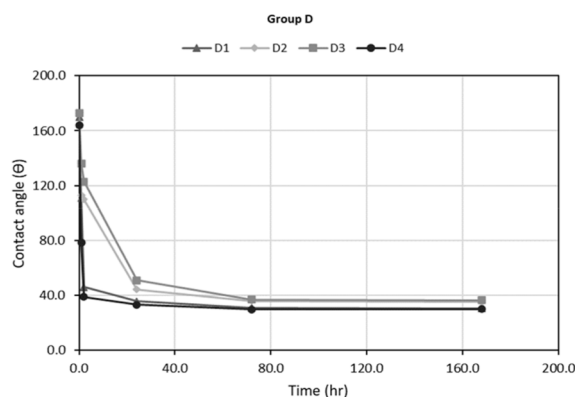


Fig. 14 Contact angle variations over time: group D

Moreover, that part is considered as a transition area to make a vibrant comparison of the fluctuations that can be seen. Such an area is shown in Figure 15. Similar to group one, the time of wettability vagaries was reduced in group two as well. Such a diminishing was occurred by increasing the concentration of each salt in solutions C_1 to C_3 from 0.05 to 0.2 for sodium sulfate salt and from 0.0025 to 0.01 for calcium sulfate salt. In Figure 16, the nominated changes over time are shown.

In group two, the fastest changes in wettability were created by removing sodium ions from the medium in the C_4 solution. Figure 17 also shows the first 24 hours of the experiments for better result comparison.

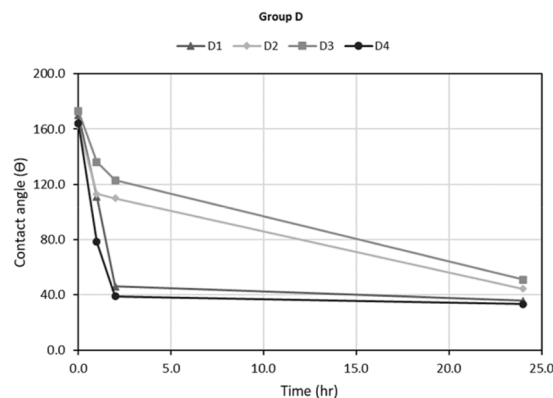


Fig. 15 Changes in contact angle overtime in the first 24 hours: group D

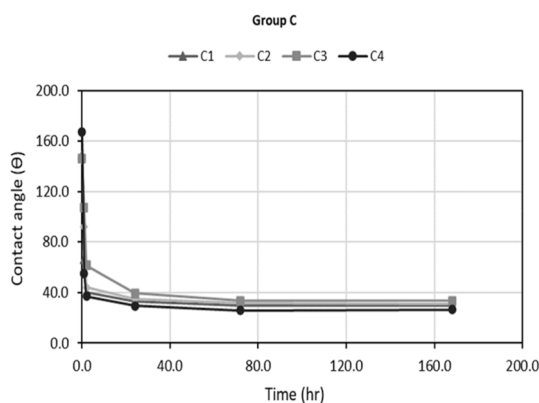


Fig. 16 Contact angle variations over time: group C.

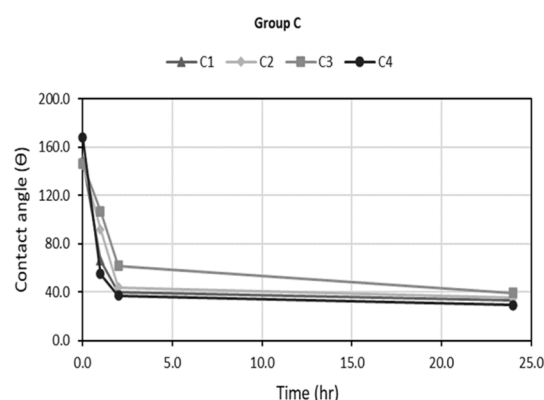


Fig. 17 Changes in contact angle overtime in the first 24 hours for group C.

Both groups of one and two would contain ions active in the wettability process (i.e., magnesium, calcium, and sulfate ions). To change the wettability, these active ions must be able to reach the rock surface [17]. The presence of inactive ions such as sodium ions in the bilayer (i.e., the charged surface that is in contact with the brine) prevents those kinds of active ions from easily reaching the rock surface and reacting to the rock later [18,19]. In this study, the concentrations of surface-active ions increased in samples D_1 to D_3 and C_1 to C_3 . But there was a decrease in the rate of change of wettability because of the increase in inactive sodium ions in those solutions. From this observation, it can be concluded that the simultaneous increase in active ions and inactive ions in the environment, even in equal amounts, does not necessarily neutralize each other. In the experiments made for the mentioned substances and conditions, the increase in sodium ion concentration had a greater effect in comparison with calcium, magnesium, and sulfate ions. The access of active ions to the surface and the reaction were accelerated in samples C_4 and D_4 by removing sodium ions from the environment. Consequently, it had the highest rate of change of wettability which caused the rate of wettability change to be increased. After the oil recovery behavior in the early hours was considered, it was found out by us that the sweeping efficiency of solution D_4 was higher than solution D_2 . As shown in Figure 18, the breakthrough time in the second injection of D_4 is longer than in D_2 . Also, the curve of oil recovery for D_4 is being in higher positions than D_2 at the 5-pore volume injection (5 PV). This would make the D_4 injection more economical than the D_2 . In other words, by removing monovalent ions such as sodium, divalent ions will

play their role as more potentially determining ions, and they will increase the rate of wettability change. As a result, the sweeping efficiency was improved too.

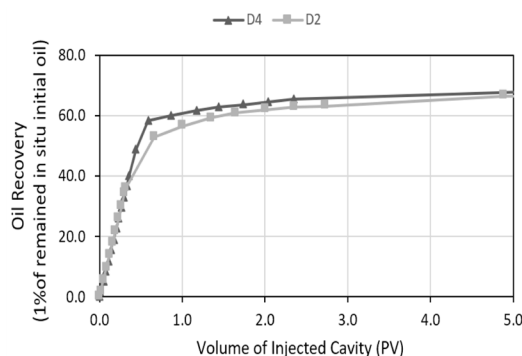


Fig. 18 Comparison of oil recovery during secondary injection of solution D_2 and D_4 in the limestone core with the wettability of the mixture against the volume of injected cavity in the early times.

In secondary injection, D_2 and D_4 were 68.5 and 71.2, respectively. The proximity of oil recovery in those two injections was indicated that the difference between the two solutions was not significant on the final recovery. However, the D_4 solution has slightly improved oil recovery compared to the D_2 solution, which can be attributed to the higher wettability of the D_4 solution.

Conclusions

Smart water can be used as a suitable solution to change the wettability of carbonate reservoirs. The rate of wettability changes can be varied for diverse water compositions. Major changes were reached in the early times, and the speed of change was much faster in that wettability interval. So, those kind of results is clearly replicated from the slope of the contact angle curve versus time. As the water salinity increases in these solutions, the rate of wettability variation decreases. Sodium-ion hurts the process and prevents surface-active ions from reaching the double layer to perform the reaction. Also, the simultaneous increase in active ions and inactive ions in the environment, even in equal amounts, does not necessarily neutralize each other.

The results of core injection showed that by eliminating monovalent ions such as sodium, divalent ions could play a more prominent role as potential determinants of ions and increase the rate of wettability change. As a result, sweeping efficiency is improved. The final recovery is approximately the same at the low salinity range. However, the removal of sodium ions will improve the sweeping efficiency of the modified water injection. Ultimately, using low-salinity water can increase the oil recovery in comparison to normal conditions.

Nomenclatures

LSW: Low salinity water
 LSWF: Low-salt water flooding
 SWI: Smart water injection
 Res : Resine
 As : Asphalt
 Ar : Aromatic
 S : Saturation

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