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Research paper

Investigating Calcium and Magnesium Ion Effects on Improving Oil Recovery during Smart Water Injection in Carbonate Oil Reservoirs

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A b s t r a c t

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It is widely accepted that different brines with various compositions can increase the oil recovery during water flooding in carbonate reservoirs. The concept of preparing a kind of smart water for these cases is an interesting subject whose underlying mechanisms have not been fully understood yet. It is still required to consider the crude oil/rock/brine interactions. To understand a typical smart water flooding process, it was decided to evaluate the effect of the two most important ions in a water flooding process. Calcium and magnesium, known as the hard ions, can be very effective, especially in the case of changing the reservoir rock surface behaviour and the fluids interactions. To understand these parameters, some solutions and carbonate rock samples were prepared; the fluids interfacial tensions (IFT) and the rock wettabilities were monitored by changing the ions concentration in aqueous phase. Contact angle measurement results showed that increasing the concentration of each of these ions can improve the water-wet tendency of the initially near oil-wet rock surfaces. This impact was more dominant for the case of having calcium ions. Interfacial tensions also reduced up to 20% while the concentration of these ions approached to that of typical carbonate formation water. The order of change for the case of calcium ion was more dominant (around 3%) than the other ion. The results of these experiments can be applied for real water flooding in carbonate reservoirs which are subject to the injection process, especially while the produced water is going to be used as the re-injecting agent.

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1. Introduction

Water is an efficient injection agent for displacing oil of light to medium gravity, which is relatively easy to inject into oil-bearing formations. Since water is available, and most importantly, inexpensive with low operating costs, favorable economics compared to other EOR methods could be obtained during a water flooding process.

In many cases, the wetting condition for oil displacement is not optimal with the available source of injection water [1]. The wetting condition can, however, be improved by modifying the ionic composition of the injected fluid. The water flood, then becomes a tertiary oil recovery method. Injection of seawater into high temperature chalk reservoirs [2-5], and low salinity water flooding of sandstone reservoirs [6] are some successful examples in this criteria. The idea is to inject chemistry-optimized water in terms of salinity and ionic composition into the reservoir, instead of any available water that may currently be injected or planned to be injected.

The chemical mechanism for this wettability modification by seawater is now documented and well-understood [4-7]. The symbiotic interaction between SO_4^{2-}, Ca^{2+}, and Mg^{2+}, which are all components of seawater, will remove some of the carboxylic material from the chalk surface, and thereby, will increase the capillary forces to promote spontaneous imbibition of water into the matrix blocks. The formation water may be of high salinity, and it is usually rich in Ca2+. On average, the oil recovery from carbonates is well below 30% due to low water wetness, natural fractures, low permeability, and inhomogeneous rock properties.

At relevant reservoir conditions, the carbonate surface is positively charged. The carboxylic material in crude oil, as determined by the Acid Number, AN (mgKOH/gr oil), is the most important wetting parameter for carbonate systems. Crude oil components containing the carboxyl group, -COOH, are mostly found in the heavy end fraction of crude oils, i.e. in the resin and asphaltene fraction [8]. The bonds between the negatively charged carboxylic group, -COO-, and the positively charged sites on carbonate surface are very strong, and the large molecules will cover the carbonate surface. The imbibitions rate and oil recovery decreased dramatically as the AN of the oil increased [9]. The chemical properties of the carboxylic material in the crude oil also affect the wetting properties [10]. Rao [11] pointed out that high temperature carbonate reservoirs appeared to be more water-wet, compared to low temperature reservoirs. It is further known that the AN and the reservoir temperature are not independent variables. The AN of the crude oil appears to decrease as the reservoir temperature increases due to increased decarboxylation of the acidic material at high temperatures. The decarboxylation process is even catalyzed by solid CaCO3 [12].

There are examples of limestone reservoirs that are completely oil-wet, even though the crude oil present in the reservoir has a very low AN. Experimental work showed that it is impossible to obtain wettability modification in this type of rock material using different techniques [13]. Obviously, the reservoir must be exposed to organic materials before the present oil invade the reservoir because the oil and formation brine which are in contact with a new water-wet carbonate do not change the wetting properties significantly.

This paper investigates the effect of the two most effective ions in the oil reservoir brine, i.e., calcium and magnesium, to change the order of rock surface wetness and the fluids interfacial tension in typical carbonate reservoirs.

2. Experimental Works

2.1. Experimental Apparatus

Two main apparatuses were used in performing the experiments and getting the relevant results: Sigma-700, and a contact angle measurement device. The Sigma-700 apparatus is designed to measure the interfacial tension in the range of medium to high values by a method known as the ring method; its circle-like probe is able to measure the disjointing force between two phases, as it moves up and down in the media across the interface. The contact angle measurement tool is also available for measuring the fluid contact angle on a rock surface as it is placed on it using a Dino microscope.

2.2. Fluid/Rock Properties

Two carbonate rock samples from a real oil reservoir were provided with the following properties (Table 1). These core samples were initially cleaned, then sliced in thin pieces with 1 cm thickness. Depending on the type of the experiments, they were just washed and cleaned, or initially aged in the crude oil for 14-days at 80 ^{oC} to be oil-wet. Afterwards, the contactable tests with the relevant solutions were performed on them. The prepared dead crude oil sample was also quite light with 26^{o} API from the same reservoir. All the experiments were performed at ambient conditions in order to be able to quantitatively compare the results and bring them on a scale for similarity.

Table. 1: Core plug properties

sample	porosity, %	perm., md	Diameter, cm	Length, cm	grain density (gr/cm^3)	description
A	11	15	3.81	12.5	2.8	dolomite, grey
B	9	28	3.81	12.5	2.84	dolomite, grey

The composition of the injected water to the mentioned reservoir was prepared, and the synthetic water, based on its composition, was made (the water composition is shown in Table 2). To investigate the various injection conditions, considering the effect of the hard ions, different solutions of this synthetic water with various ion concentrations were prepared, and the interfacial tension, contact angle of these aqueous solutions, and the crude oil were measured to compare the fluid-fluid interactions (the mixtures' compositions are shown in Table 3).

Table. 2: Injection water composition

ion	Na	K	Ca	Mg	Li	Ba	Fe	Sr	SO_4	CO_3	HCO_3	Cl
Conc., (ppm)	12650	460	500	1642	0.1	0.6	<0.05	4.7	3070	4	92	23042

Table. 3: Prepared water composition

Solution No.	Na	K	Ca	Mg	Li	Ba	Fe	Sr	SO_4	CO_3	HCO_3	Cl
1	12650	460	500	1642	0.1	0.6	<0.05	4.7	3070	4	92	23042
2	12650	460	500	2737	0.1	0.6	<0.05	4.7	3070	4	92	>23042
3	12650	460	10000	1642	0.1	0.6	<0.05	4.7	3070	4	92	>23042
4	12650	460	19300	1642	0.1	0.6	<0.05	4.7	3070	4	92	>23042
5	12650	460	19300	2737	0.1	0.6	<0.05	4.7	3070	4	92	>23042

3. Results and Discussions

The main focus of the experiments and the expected results are on the performance of two kinds of the ions that are believed to have the most influential impact on the fluids' interaction, and considerably change in different media. These ions are calcium and magnesium whose order of change from injected to the produced water is important.

3.1. Interfacial Tension

Initially, to calibrate the Sigma-700 apparatus, the interfacial tension of the distilled water and air was measured, then, each set of the chemicals was loaded into the device. The order of changes in different sets of the solutions is as follow:

Table. 4: IFT values of the different water solutions

Solution no.	1	2	3	4	5
IFT (mN/m)	12.5	11.3	10.8	10.3	9.9

The obtained results in Table 4 clearly showed that the solution composition has some influence on the fluids interfacial tension values. According to the results, increasing the hard ion concentration in each case reduced the target for IFT values. At this condition, having more hard ions in the media attracts more water molecules around their boundary which will cause the hard hydrogen bonds to be weakened, and more contact possibility between the two phases to happen. Besides, the IFT variation in this domain is very low. The schematic of these numbers are shown in Fig. 1, which shows a variation up to 20% from solution numbers 1 to 5.

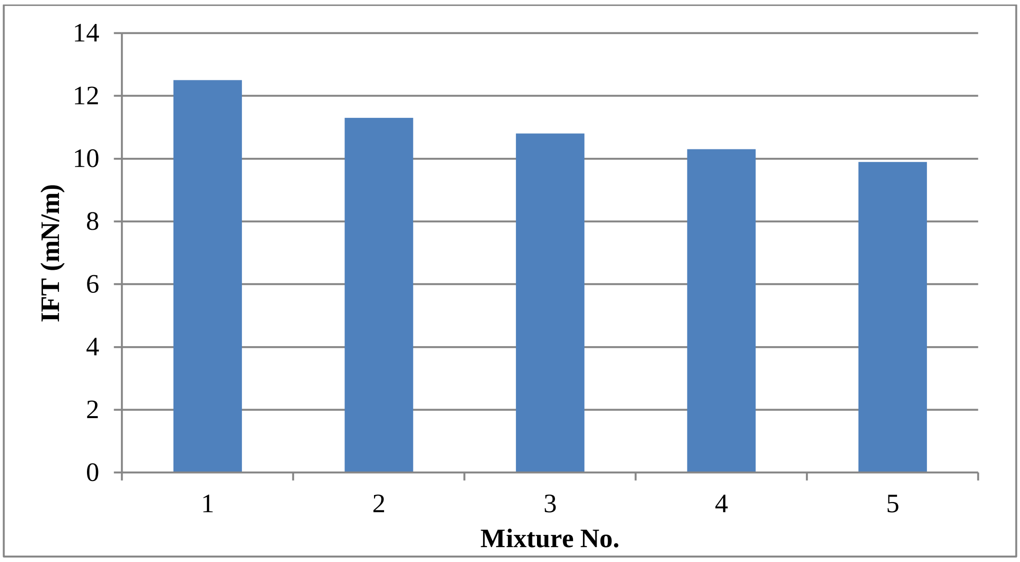

Fig. 1: IFT variation in different provided aqueous solutions and the crude oil

So, the electrostatic forces which effect on the two phase interfaces have a minimum value at maximum calcium and magnesium concentration solutions. It is obvious that these values are case dependent, and can be modified for each set of the aqueous and oil solutions if the concentration of other ions, like Sulphates, is going to change substantially.

3.2. Contact Angle Measurements

To investigate the effect of the contact angle measurement, as a result of these solutions, initially the after-aged non-treated contact angle of a rock slice was measured (Fig. 2). Then, each of the after-aged core slices were soaked in the provided solutions for 14 days. Then, the contact angle value was measured.

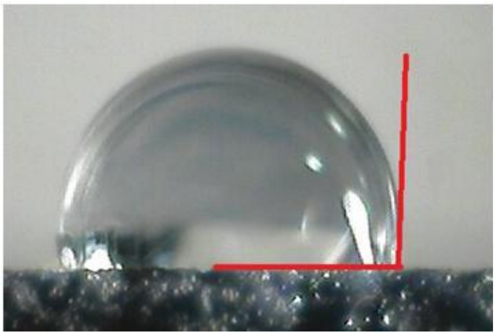

Fig. 2: schematic of the rock-fluid contact angle at initial conditions

A schematic of the droplets' shape in any case is shown in Fig. 3. As it could also be seen in Table 5, the order of changes in the contact angle values is descending. It means that the presence of both calcium and magnesium ions is in a way that reduces the amount of the contact angle. Since the order of change in the hard ion concentration was such that the real concentration of hard ions in the reservoir formation water be obtained, the final results can be an indicator of what is going to happen in real cases.

Table. 5: Contact angle values of the different water solutions

Solution no.	Initial state	1	2	3	4	5
Degree	99	88	85	83	75	65

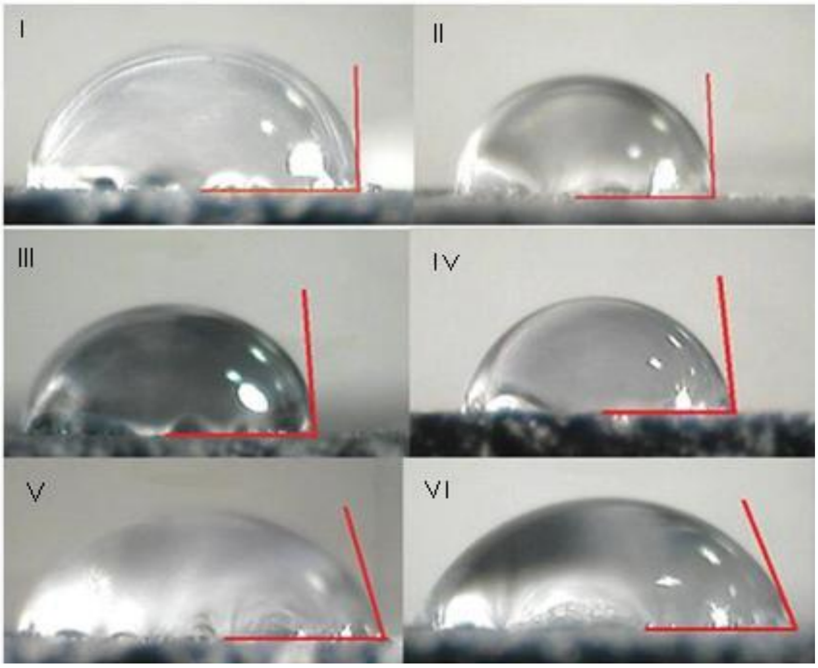

Fig. 3: A schematic of the rock-fluid contact angle after soaking the rock samples in the provided solutions: I) initial state before soaking, II) after soaking in solution1, III) (after soaking in solution2, IV) after soaking in solution3, V) after soaking in solution4, VI) after soaking in solution5

These results showed that both ions can improve the water wetness tendency of the rock surface. However, the synergistic effect of both ions is more considerable and interesting in case of changing the rock surface charges and providing water-wet surfaces. Presumably, these small cations with high surface charges prepare a better condition for adhesion to the rock surface, the places where some fatty/heavy oil molecules were previously attached. In general, the injected water composition during water flooding process can be changed in many ways in which the process performance improves. All of these treatments can be called as providing a suitable smart water composition for a nominated hydrocarbon reservoir.

4. Conclusions

According to the results of the experiments which focused on the individual effect of the calcium and magnesium ions, it is concluded that:

- The presence of these small hard ions in the injected sea water solution can improve the water-wet tendency of the rock surfaces,
- The interfacial tension between the crude oil and aqueous solution is somewhat affected by the presence of the calcium and magnesium ions,
- Simultaneous increase of these two ions cannot be so effective on reducing the IFT values, after a certain amount,
- The contact angle value reduces considerably by gradual increase of these ions' concentration,
- The calcium ions have more positive effect on the parameter improvement. Besides, the obtained results can be helpful to improve the water flooding efficiency in carbonate reservoirs.

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