

INVESTIGATION OF WETTABILITY ALTERATION OF CARBONATE ROCK IN PRESENCE OF SULFATE, CALCIUM AND MAGNESIUM IONS

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ABSTRACT

Wettability alteration (WA) is one of the principal challenges of oil wet carbonate reservoirs. During primary migration, oil would be replaced with formation brine which contains many cationic ions such as Ca^{2+} , Mg^{2+} that would boost calcite or dolomite surface charge to more positive, the amount of positive charge in rock/brine and oil/brine contacts region is high due to high cations concentration in formation brine during oil migration. In practice, after many years of migration process, because of negatively charged oil components, attractive forces will be active thus it would absorb the oil component to the calcite or dolomite surface consequently the wettability would change to oil wet. For more production in water flooding process in tertiary recovery processes, the rock wettability should change to more water wet conditions. Low salinity water injection comprising of SO_4^{2-} , Ca^{2+} , Na^+ and Mg^{2+} ions is known as a WA method that by dilution of seawater or other accessible brines. In this study, based on active ions in WA mechanism, variation of them in a baseline seawater shows tangible results for better water wetness in case when monovalent and divalent ions are used. In the experiments, WA of seawater with 3-time sulfate, 6-time calcium and magnesium (SW-3S-6C-M), (SW-3S-C-6M), (SW-6S-C-3M), (SW-6S-3C-M), (SW-3S-0C-0M), (SW-0S-3C-0M), (SW-0S-0C-3M) and seawater, the contact angles were measured. The results showed that by increasing the amount of sulfate, WA always seems to tend to be more water wet. As for calcite at low temperature in the presence of sulfate the WA happened while no change was noted in the absence of sulfate. Magnesium seemed to have an impact at elevated temperatures and in this case SW-3S-C-6M showed best (from 129° to 30°) in comparison with other brines. Finally, it was found that without refreshing the brine in each step, the results were not appreciable.

INTRODUCTION

Carbonate reservoirs contains the majority of the world's oil reserves. These oil reservoirs are characterized with two types of porous media namely i) matrix blocks and ii) natural fractures.

EOR methods for fracture reservoirs are usually designed to facilitate the transmission between matrix and fractures. Neutral to oil wet carbonate reservoir implies weak spontaneous imbibition of water. One of such methods for enhanced oil recovery from carbonate reservoirs is to use smart salinity water imbibition with the help of altering wettability from oil-wet to neutral or water-wet. Should a block matrix be surrounded by water, if existed in the fractures, then imbibition is expected to occur simultaneously during wettability alteration (at the moment of contact of cores with smart water as a wettability alteration agent, WA process will be started from all pores which are located on the surfaces of the cores and continuous to invading in core). Many factors such as pressure, temperature, oil composition, injection fluids properties would influence chemical wettability alteration under reservoir conditions.

Wettability alteration during water flooding by adjusting injection brine composition is becoming economically more viable thus a matter of much interest [1]. The main objective of EOR by ion exchange (chemical) mechanism is to improve mobility of trapped oil during water flooding [2]. In range of $\text{pH} < 9$, surface charge of carbonate rock are positive, thus by the use of diluted alkaline (Na_2CO_3) the surface charge will be altered to negative when an anionic surfactant is used [3]. The interaction between monomer of cationic surfactant and crude oil carboxylic materials forms a complex usually termed as “cationic surfactant”. negatively charged carboxylic material of crude oil will be adsorbed by the monomer of the cationic surfactant [4]. In low permeable rock such as carbonate matrix as a result of using surfactant and brine, the interfacial tension will be decreased (about 0.3-1.0 mN/m) and the imbibition rate is expected to decrease even though the capillary forces increase as a result of more water wetness [5].

By the use of diluted Persian Gulf seawater by 2, 10, and 20 times, the amount of oil recovery from composite limestone cores has been increased [6]. Nonetheless, in chalky cap rock flooded with diluted SW due to the decrease in surface active ions the recovery factor has been decreased [7]. Seawater includes potentially active ions such as Ca^{2+} , Mg^{2+} and SO_4^{2-} that control surface charge of carbonate rock to forming organic-metal complex and change the wettability to more water wetness and improve imbibition process and recovery factor. Negative charge of sulfate ions reduces the carbonate surface positive charge and let the positive ions to get closer to the carbonate rock. Carbonate rock positive charge would, in turn, lead to adsorption of negative charge and thus calcium and magnesium can get closer to the carboxylic component and separate them from carbonate rocks. Chemical activity and mobility of cationic ions strongly depend on temperature of the bulk of fluids which are in contact with the rock surface [8]. Magnesium is a potentially determining ion due to small size and high charge density. It may become more reactive because of partial dehydration as temperature increases [9]. Some criteria for the interaction which should exist for a successful wettability alteration process are as follows [10]:

1- Mixed wet condition

- 2- Existence of divalent cations
- 3- Initial formation water must be present
- 4- Oil must contain polar components

Overall, the utilization of smart water is a viable option to alter rock wettability to water wet at reservoir conditions but the key parameters that control the wettability alteration are potential influential ions such as sulfate, calcium and magnesium and high reservoir temperature conditions. The present study aims to determine the best optimum salinity with ions strength equal to seawater by foreseeing of concentration of sulfate, calcite and magnesium.

EXPERIMENTAL SET UP AND PROCEDURE

The following procedure was carefully performed to discern the optimum concentration:

1. Water from the nearest and the most accessible sea with known ions concentration were taken as sample.
2. All brines are synthetic and by adjusting the salts concentrations, and ion strength (the total number of moles of salt per liter) was kept constant with decreasing or increasing concentrations of sodium chloride.
3. Carbonate rock that have previously been studied were carefully cut into thin pieces before maintaining initially for 14 days in the formation brine at 75°C to achieve original positive charge as it would exist at the reservoir conditions. This method is reliable since the thin section would reach its maximum positive charge for attraction of negative charge oil components.
4. Thin sections were then kept in crude oil in 75°C and 2500 psi for 20 days or about 500 hrs. It should be pointed out that the amount of oil wetness would be changed due to difference of minerals in each section and different oil components. Reactive surface area of the thin section, those carbonate rock parts are that during aging process will react with carboxylic components of crude oil.
5. All solutions were of the same ion strength with different concentration ratios of sulfate, calcium and magnesium to determine the best interaction with carbonate rock minerals.
6. All the prepared thin sections in specified time interval of 0, 48, 120, 360 hrs were placed in the refresh synthetic brine before measuring the contact angle.

In this study, a drop shape analysis (DSA100, KRUSS, Germany) apparatus was used for measurement of contact angel, as shown in Fig. 1. In brief, for contact angle measurement, a micro syringe was fitted with a U-shape needle and loaded with the fluid with lower density (i.e., crude oil) the syringe was placed in a motor driven piston and the tip of the U-shaped needle was positioned in an optically clear vessel and immersed in the aqueous phase. A carbonate rock thin section with thickness of about 1.5 mm was placed on a rubber block, then the injection continued to the point at which the drop be big enough and leave the needle and stick to the rock surface. Finally, the image of the drop on the thin section is analyzed.



Figure 1: Drop shape analysis –DSA 100

RESULTS AND DISCUSSION

Diluted seawater with and without refreshing

Figures 2 and 3 show the best results for 5d-SW (5 times diluted sea water brine by distilled water) with respect to seawater and 3-time diluted seawater. The superiority of 5d-SW is probably due to the amount of concentration near the rock surface and more chance for active ions like sulfate, magnesium and calcium to reach to the carboxylic component which are stuck to the carbonate rock and separate them from carbonate rock and alter the wettability from oil wet to water wet condition. Table 1 shows salt concentration of synthetic brines. Furthermore, the results show just a marginal change when diluted brine without refreshing were used. This is because initially WA changes which, in turn results in concentration reduction of sulfate, calcium and magnesium as reported in Table 2.

Table 1: Properties of diluted brines-absolute concentration

composition	SW(gram/liter)	3dSW(gram/liter)	5dSW(gram/liter)
Na+	17	5.67	3.4
Ca ²⁺	0.55	0.18	0.11
Mg ²⁺	1.8	0.6	0.36
K+	4.3	1.43	0.86
SO ₄ ²⁻	3.2	1.07	0.64
HCO ₃ ⁻	0.75	0.25	0.15
Cl ⁻	23.25	7.75	4.65

Table 2: Measured contact angle of different diluted sea water with and without refreshing brine.

Brine	CA-0hr	CA-48hr	CA-120hr	CA-360hr
3d-Sea W-R	149.3	120.0	112.2	102.0
3d-Sea W-WR	116.0	-	-	110.0
5d-Sea W-R	142.9	107.6	90.2	87.4
5d-Sea W-WR	125.0	-	-	113.0
Sea W-R	147.6	115.1	106.33	106
Sea W-WR	128.1	-	-	122.3

REFRESHING BRINE

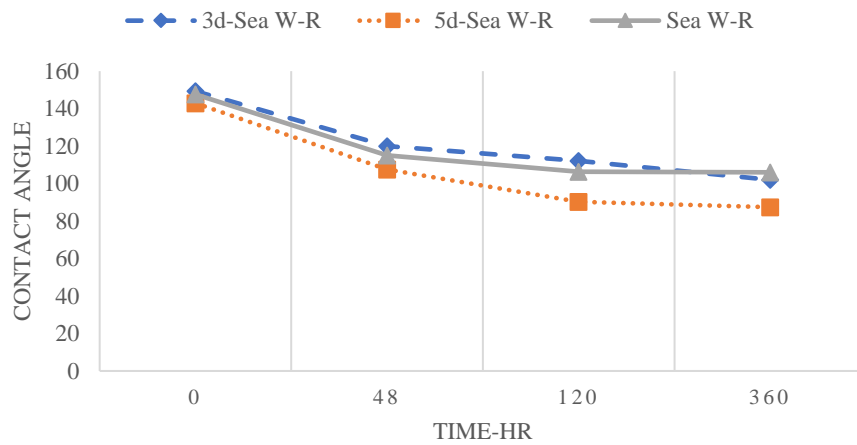


Figure 2: Wettability alteration trend in each step-refreshing brine

WITHOUT REFRESHING BRINE

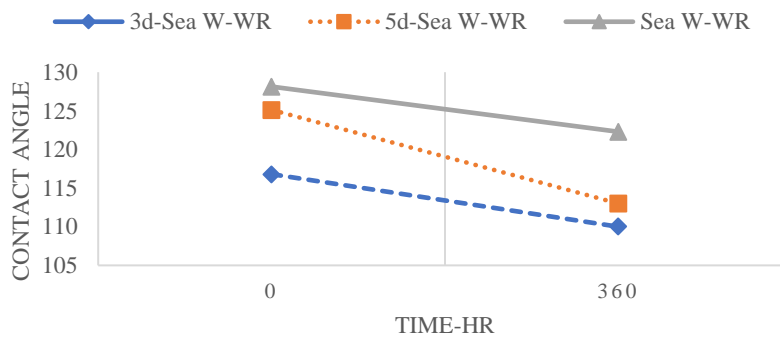


Figure 3: Wettability alteration trend –without refreshing brine

Contact angel of synthetic brines with different ratios of active ions

Different concentration ratios of active ions (Table 3) for similar ion strength show the importance of the divalent cations during completion of wettability alteration process. As it can be seen from the above figure that Sea W-3S-C-6M has the maximum wettability alteration from 129.2 to 30.1 degrees as shown in Figure 5 and all changes of contact angle are reported in Table 4. The most important ion is sulfate because of its role in decreasing surface positive charge and allowing the cations to get closer to the carbonate surface and react with crude oil carboxylic components that are stuck to the rock surface.

As shown in Figure 4, in comparison to 6-time sulfate samples, wettability alteration for magnesium due to its chemical activity and surface density charge for SW-6S-C-3M (Figure 5) is more than SW-6S-3C-M (Figure 6). This implies that the concentration of sulfate ions must not exceed from an optimal because at high concentrations, the possibility of cations accessibility to the carbonate rock will be decreased.

Table 3: properties of brines with similar ion strength-absolute concentration

Composition	SW-6S-3C-M (gram/liter)	SW-6S-C-3M (gram/liter)	SW-3S-6C-M (gram/liter)	SW-3S-C-6M (gram/liter)
Na ⁺	17.93	13.76	15.88	5.02
Ca ²⁺	0.53	1.57	3.13	0.53
Mg ²⁺	1.81	5.43	1.81	10.84
K ⁺	0.43	0.43	0.43	0.43
SO ₄ ²⁻	19.85	19.85	9.93	9.93
HCO ₃ ³⁻	0.74	0.74	0.74	0.74
Cl ⁻	21	25.11	27.94	32.94

Table 4: Measured contact angle of different active ions (sulfate, calcium, magnesium).

Brine	CA-0hr	CA-48hr	CA-120hr	CA-360hr
Sea W-3S-6C-M	123.8	100	93.7	88
Sea W-3S-C-6M	129.2	100.1	50.6	30.1
Sea W-6S-M-3M	126.7	106	92	90
Sea W-6S-3C-M	118.5	101.2	92.4	90

WETTABILITY ALTERATION

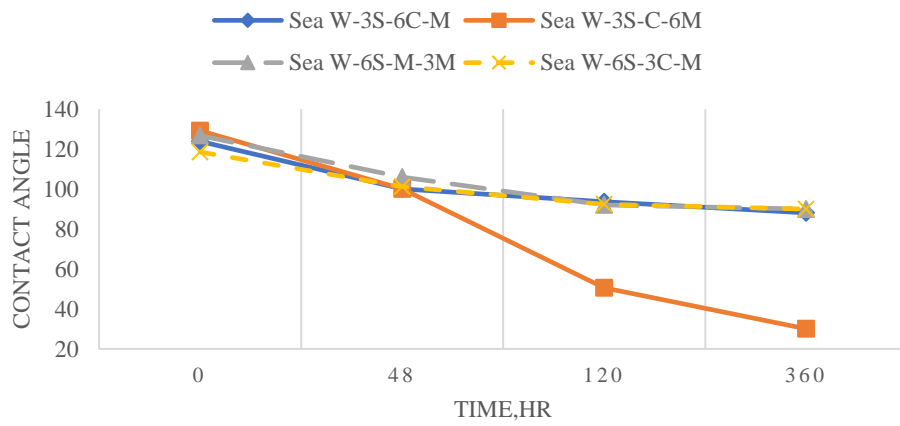


Figure 4: Wettability alteration trend at different time intervals

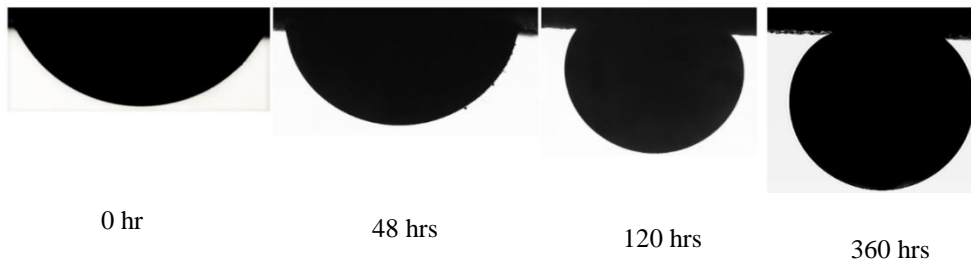


Figure 5: Contact angle of synthetic brine SW-3S-C-6M at different time intervals of 0, 48, 120, 360 hrs.

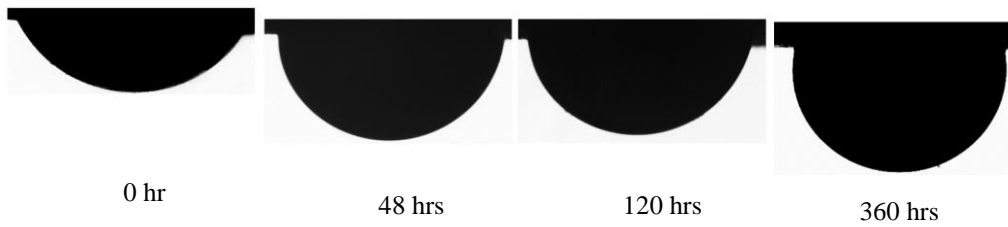


Figure 6: Contact angle of synthetic SW-3S-6C-M at different time intervals of 0, 48, 120, 360 hrs.

CONCLUSIONS

- During the experiments as time elapsed, the ion concentration remained constant with refreshing brine which provided enough number of ions to react with crude oil carboxylic components thus more WA would be expected to occur as time elapses.
- Due to the size of oil wet carbonate rock surface area which was in contact with brine at different time intervals, the degree changes in WA faded as time elapsed.
- Sulfate accessibility to carbonate rock surface in competition with other monovalent ions will be increased by dilution of brine.
- For brines with ion strength close to seawater, the concentration of sulfate ions must be at optimal so that to assure that calcium and magnesium ions would be able to reach near the carbonate surface.
- Synthetic brine (SW-3S-C-6M) is the optimum active ions concentration for WA with ion strength equal to 0.63.
- For all synthetic brines, magnesium with compared to calcium played a more important role in WA.

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