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# Investigation of Wettability Alteration due to Smart Water Injection into Carbonate Reservoirs by Zeta Potential and Contact Angle's Tests

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## Abstract

Nowadays, a wide-range of EOR methods are used to enhance oil recovery from carbonate reservoirs. They are the most scattered reservoirs all over the world. Smart water injection is one of the popular and newest methods in EOR. It controls the wettability of rocks. In this study, wettability alteration and the rate of wettability modification are investigated by zeta potential and contact angle experiments. Smart water is a kind of water with controllable salinity and ion concentration. In this regard, five different samples of smart water were synthesized by different concentrations of  $\text{SO}_4^{2-}$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$  ions, based on Persian Gulf seawater TDS. Then, the results were compared to those obtained from formation water and seawater, as the blank samples. The ability of the smart waters in controlling rock wettability was examined by pursuing of zeta potentials in the presence of different water samples at ambient condition. According to the results, the zeta potential of carbonate sands in the presence of water samples  $S_w\#4\text{SO}_4$ ,  $S_w\#2\text{SO}_4$ ,  $S_w$ , and formation water was  $-9.61$ ,  $-7.13$ ,  $-1.25$  and  $15.8$ , respectively. The data suggested that the samples  $S_w\#4\text{SO}_4$  and  $S_w\#2\text{SO}_4$  are the two most effective smart water samples in wettability alteration. After that, the most capable smart water samples with the most negative zeta potential was selected to be used for the contact angle experiment. The results showed that, in the presence of  $S_w\#4\text{SO}_4$ ,  $S_w\#2\text{SO}_4$ ,  $S_w$  and formation water, the final contact angle decreased from their initial values ( $144.23^\circ$ ,  $149.68^\circ$ ,  $136.63^\circ$ , and  $139.89^\circ$ ) to  $87.10^\circ$ ,  $105.17^\circ$ ,  $135.66^\circ$ , and  $143.13^\circ$ , respectively, which is in a good agreement with the results of zeta potential. These data showed that the amount of sulfate ions in the smart water can control the wettability of rock from oil to water-wet state.

**Keywords:** Smart Water, Wettability, Carbonate Reservoir, Contact Angle, Zetta Potential.

## INTROUDCTION

There are different ways to determine the degree of wettability of a surface relative to a fluid. If a surface is in contact with a fluid in such a way that the fluid completely covers the surface, the oppositely charged particles of the surface will close to the solid/liquid interface. Depending on the type of charge available at the surface, Zeta potential may have either positive or negative value. Since the calcite carbonate surface possesses positive zeta potential, those smart water sample which is able to negatively change the surface potential can shift the wettability of carbonate rocks from oil-wet to water-wet. The other index of surface wettability of rock stones can be considered as contact angle between the surface and the fluid in the presence of another incompatible fluid. Anderson has characterized the oil wettability of the rock from a strongly water-wet to a strongly oil-wet state by considering the contact angle. According to their work, the higher contact angle between the oil droplet and stone is, the lower water wettability properties the stone has [2, 3]. In 2010, Yusuf et al. carried out laboratory studies on the effect of smart water injection into carbonate reservoirs on the oil recovery [4]. In order to find a relationship between the effect of injected water ions on surface properties and the rate of recovery, Youssef et al. conducted an investigation on carbonate rocks [4]. In 2013, Alshabi et al. confirmed the results of Yousef et al. by computer simulation [5]. McGrae et al. (2005) attributed the increase in the recovery rate of oil to a change in wettability and reduced surface tension (IFT) in the presence of low salinity water [6]. Gonzalez and TravalloniL reported that hydrocarbon compounds containing nitrogen, sulfur, and oxygen (NSO) polar groups showed a tendency toward absorption on the surface of the rock, which causes the wettability of the rock to

become hemispherical [7]. In the meantime, heavy crude components such as asphaltene and resin have been shown to have the greatest effect on wettability [7]. Three  $\text{Ca}^{+2}$ ,  $\text{SO}_4^{-2}$  and  $\text{Mg}^{2+}$  ions at the carbonate surface have the capability to change surface potentials and alter surface charge (zeta potential) [8]. In the present study, the effect of the type of smart water injection on the wettability alteration of the reservoir rock was investigated in. In this regard, two important factors of zeta potential and contact angle were studied.

## EXPERIMENTAL

Formation and smart waters: formation water was chosen from a real sample (Formation water A). Smart waters were artificially made in different combinations, including a) seawater; b) seawater with a concentration of twice of magnesium ion; c) seawater with a concentration of twice of calcium ions; d) seawater with a concentration of twice of sulfur ion; and e) Seawater with four times higher sulfur concentration.

**Oil:** dead oil of reservoir (A) was applied. The oil API and the asphaltene content were 40% and 1.1%, respectively.

## POWDER AND SLICE

The carbonate sample, calcite type, was obtained from one of the western fields of Iran.

## RESULT AND DISCUSSIONS

The results of the Zeta potential are given at Figure 1. Since the rock sample is of calcite type, accumulated with positively charged calcium ions, the presence of negative ions in the sternlayer is expectable. Hence, the higher tendency of sulfate ion toward adsorption on the surface, comparing with other anions, is quite expected.

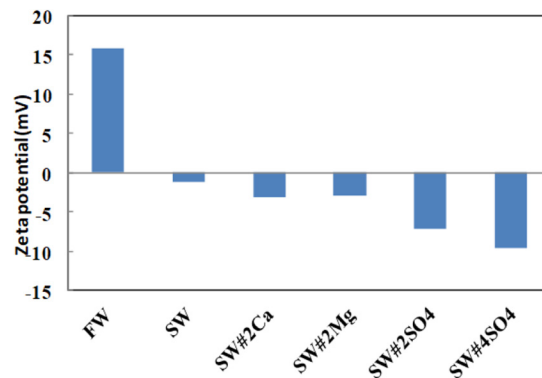


Figure 1: The results of the Zeta potential versus the type of smart water and formation water.

Since the carboxylic group is bonded to the calcium atoms via a polar bond, at the carbonate surface, a sort of competition between the calcium-sulfate and calcium-carboxylic bond should take place. The bond between sulfate ions and calcium ions is much stronger than polar bonds; therefore, calcium atoms tend to exhibit a strong tendency toward attaching to sulfate groups. Meanwhile, with the removal of electrostatic forces, active calcium ions in the bulk can detach freely from the surface and form a chemical bond with the carboxyl groups. By increasing the concentration of sulfate ions, they can approach to the carbonate surface more easily. It means that the more negative zeta potential on the surface is, the higher the capability of the smart water, to improve oil recovery, is reached.

Contact angle variations in the presence of water formations, seawater, and two smart water

samples were investigated over time (Figure 2). In all cases, it is evident that the change in wettability at the early hours is higher. In other words, at the start, the interaction between water, oil, and rock rapidly increased and the contact angle reduced gradually. The process moves towards the equilibrium, and the contact angle remains unchanged at longer contact time. Due to the low concentration of sulfate ions in the water, i.e. 360 ppm, the surface concentration of sulfate ions on the carbonate stone should be insignificant. Therefore, there is no intense competition between the processes of forming sulfate-calcium and calcium-carboxylic couples. However, carboxylic groups still do not stick to the surface of the carbonate sample. As a result of the presence of carboxylic groups on the surface of the rock, the tendency of oil drops toward leaving the surface is reduced, and thus the contact angle does not change at a long time.

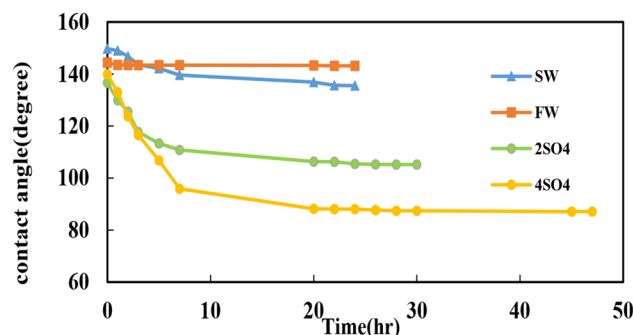


Figure 2: contact angle versus time for the formation and smart waters.

In fact, by increasing the concentration of sulfate ions, their ability to move from the bulk to the surface of the rock is increased due to the attraction force with the oppositely charged calcium species. As a result, this process involves the formation of ionic bonds between the surface calcium ions and sulfate ions in the bulk, releasing carboxylic groups from the surface. Removing carboxylic groups, the interaction between the rock surface and oil phase is reduced dramatically, which is very important in oil droplets removal from the carbonate surface. This can be confirmed by reducing the contact angle between the water droplet and rock surface. The trends observed in Figure 2 indicate that the capability of the water samples toward changing the carbonate reservoir wettability is along with the Zeta potential data in figure 1.

## CONCLUSIONS

The effect of injecting process of smart water on the wettability characteristics of carbonate reservoirs has been studied. Five different types of smart seawater, based on Persian Gulf water, were prepared with different concentrations of  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ , and  $\text{SO}_4^{2-}$  active surface ions. The capability of the smart waters toward surface wettability alteration was determined via measuring the Zeta potential of the carbonate stone. According to the results, it was discovered that the mentioned ions can change the surface of carbonate reservoirs into a hydrophilic surface. Among the three active ions, sulfate ion was more active than the others in term of changing the surface potential of carbonate reservoirs. Also, the smart seawater with four times of sulfate concentration was found as the most effective sample in shifting the contact angle of the oil droplet toward the hydrophilic range, which is in a complete agreement with the mechanism proposed by Loger et al [9].

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