The effect of wettability alteration of carbonate rock using cetyltrimethyl ammonium bromide on acidizing with HCl 15%

ABSTRACT

Most of the reservoirs in Iran are carbonate reservoirs that spend the second half of their life and need acid stimulation processes for better production rate. Acidizing is one of the well and reservoir stimulation methods, which is used to increase oil and gas production from the fields due to its cost and efficiency. Acidizing of carbonate reservoirs is usually done in three stages: pre-flush, main acidizing, and post-flush. The pre-flush fluid is used to change the wettability of the rock from oil-wetting to water-wetting. In this work, we look for the optimal pre-flush fluid using CTAB surfactant to improve the acidizing process. At first, the porosity test is taken from the carbonate cores and then acidized using HCl 15 wt%. Then the contact angle test is performed to determine the optimal concentration of surfactant and the optimal time. Finally, the cores that we put in contact with the pre-flush fluid were placed in the vicinity of the acidic solution to determine the effectiveness of the pre-flush fluid. CTAB surfactant solution with a concentration of 500 ppm in sea water and a duration of 120 minutes was able to reduce the contact angle from 125 to 42.574 and determined as the optimal pre-flush fluid. Also, the combination of 15 wt% HCl with sea water had the best performance.

Keywords: Carbonate Acidizing, Hydrochloric Acid, wettability alteration, pre-flush fluid, CTAB

1. Introduction

It is estimated that carbonate reservoirs account for over half of the global oil reserves[1]. Approximately 50% of the world's proven oil reserves are located in the Middle East, with about 70% of these reserves found in fractured carbonate formations[1, 2]. Carbonate reservoirs are characterized by their high heterogeneity and porosity, featuring numerous geological discontinuities such as fractures and faults. The complex physical and chemical conditions present in these rocks often necessitate stimulation techniques to enhance oil production in the fields[3]. Near-wellbore damage, which can significantly hinder hydrocarbon production, may occur during various operations including drilling, cementing, perforation, completion, and stimulation. The predominant method for mitigating or bypassing this damage is matrix acidizing[4]. Acidizing is one of the oldest and most practical techniques used to boost well productivity by improving near-wellbore permeability, widely adopted in the petroleum industry[5, 6]. Matrix acidizing is a highly effective, successful, and relatively low-cost method for enhancing well output in carbonate formations[7, 8]. The primary objective of acidizing is to increase productivity in acid-soluble formations like dolomite, limestone, and chalk[5, 9, 10]. Typical matrix acidizing processes for oil-producing wells consist of three main sequential stages: pre-flush, main acid treatment, and over-flush injection. The pre-flush stage is crucial for preparing the rock surface for a more effective rock/acid reaction. During this phase, a nonreactive fluid (either water-based or diesel-based) is injected into the formation to alter the wettability of the oil-wet rock and to displace formation fluids (oil and high-salinity brine) away from the wellbore, thus limiting acid exposure. This pre-flush step is vital for preventing sludge and emulsion formation, as well as avoiding solid precipitation due to incompatibility between injected water and formation water[6, 11]. Research by Ayatollahi et al demonstrated that a CTAB surfactant solution met the optimization criteria for pre-flush fluids suitable for acidizing carbonate oil reservoirs[11]. The subsequent stage involves the main acid injection, typically performed with hydrochloric acid (HCl) in carbonate formations[6, 12]. Hydrochloric acid is favored as an acidizing fluid due to its cost-effectiveness and efficiency, as it generates chloride salts that are highly soluble in water and can dissolve minerals like calcite. The concentration of HCl used in acidizing ranges from 5% to 28%, with 15% being the most common[13]. Various factors influence reservoir acidizing, including temperature and acid concentration; thus, careful selection of acid type and concentration is essential for successful treatment[4]. In matrix acidizing of carbonates, wormholes are formed as a result of rock dissolution[14].

Wettability refers to the tendency of one fluid to either spread or adhere to a solid surface in the presence of other immiscible fluids. In oil-wet rocks, oil clings to the rock surface due to electrostatic forces, forming a thin film over the surface. Carbonate rocks carry a positive charge in a neutral pH environment, leading to the adsorption of negatively charged components in crude oil, such as carboxylic acids, which render the rock surface oil-wet. During the acidizing process, this oil film acts as a barrier, reducing the reaction rate and preventing sufficient dissolution of the surrounding rock, ultimately diminishing treatment efficiency. Therefore, changing the wettability during the pre-flush stage is essential for enhancing the exposure of the rock surface to the injected acid[11, 15].

Moreover, a well-formulated pre-flush fluid can easily penetrate the rock due to its low interfacial tension (IFT) with oil. Interfacial tension is a thermos-physical property that dictates the behavior at the interface between two immiscible fluids[11, 16].

This study investigates the effect of pre-flush fluid on the acidizing process of the carbonate core. The pre-flush fluid used in this study is the cationic surfactant cetyltrimethylammonium bromide (CTAB). Also, 15%wt of hydrochloric acid have been used to acidize the carbonate core.

2. Materials and Methods

2.1 Materials

The crude oil used in this research is related to one of the wells in the Azadegan field, whose properties are given in Table 1. To calculate viscosity in this study, Anton Paar rheometer and CC27 spindle were used. The maximum spindle rotation speed is 1200 rpm and it can operate up to a shear rate of 1400 s^{-1}. To calculate viscosity with this device, the desired fluid is added to the special container of the CC27 spindle. Then the spindle is connected to the rheometer itself and the rheometer rotates under the shear stress applied to it and calculates the viscosity. IP-143 analysis was used to measure the asphaltene content of crude oil. The IFT between the oil sample and water was measured using the hanging drop method.

Table 1. Crude oil properties.

Asphaltene (%)	Viscosity (cp)	Density (gr/cc)	IFT
16.83	537	0.943	35.69

To investigate the effect of pre-flush fluid on rock wettability, carbonate rock outcrop samples were used. The XRF test results of the rock powder are given in Table 2. At first, several thin sections were prepared from the rock sample to be used for contact angle tests. Also, several cores with lengths of 0.8 to 0.9 cm were prepared for acidizing tests. The samples were first washed with methanol and then saturated with oil using a vacuum pump and kept in contact with oil for 48 hours at a temperature of 70ºC.

Table 2. XRF results of carbonate rock powder.

Compounds	%
L.O.I.	42.05
Na_2O	0.064
MgO	0.516
Al_2O_3	0.239
SiO_2	0.808
P_2O_5	0.059
SO_3	0.209
Cl	0.017
CaO	55.656
Fe_2O_3	0.21
Sr	0.172

Persian Gulf sea water was used in this research, whose brine composition analysis is shown in Table 3. Also, 30.2% HCl was used to prepare acidic solutions, which were diluted to 15%wt using distilled water and sea water.

Table 3. Brine composition analysis.

Brine	Chemical Formula	Concentration (ppm)	Molecular Weight (g/mol)
Sodium chloride	NaCl	28323	58.44
Sodium sulfate	Na_2SO_4	4936	142.04
Calcium chloride	$CaCl_2$	1630	110.98
Magnesium chloride	$MgCl_2$	10510	203.30
Potassium Chloride	KCl	1032	74.55

The surfactant used in this research is the cationic surfactant CTAB (Cetyltrimethylammonium Bromide). At first, different concentrations of this surfactant were contacted with thin sections at different times at a temperature of 70ºC, and then using the contact angle test, the optimal concentration of this surfactant and The optimal contact time has been obtained and will be used in acidizing tests. In this work, surfactant concentrations of 250, 370, and 500 ppm will be used and they will be in contact with the thin section for 60 and 120 minutes.

CTAB and deionized water and sea water were mixed using a magnetic stirrer until a homogeneous solution was obtained to prepare the surfactant solutions[17]. CTAB is a cationic surfactant whose schematic is shown in Figure 1.

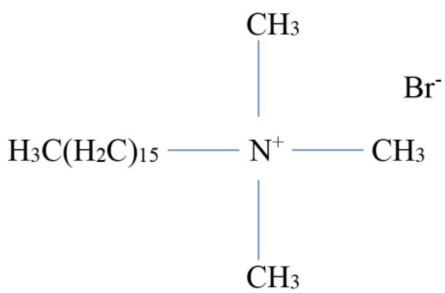

Figure 1. A schematic of CTAB[17].

In this research, carbonate cores with high porosity were used, the porosity of the core samples was measured using a helium porosimeter and the results are shown in Table 4. The porosity test was repeated three times for each core, with an error of less than 1%.

Table 4. Porosity test results of cores.

Core Number	Core Diameter (cm)	Core Length (cm)	Porosity (%)
4	3.81	0.9	43.04
6	3.81	0.9	43.52
13	3.81	0.85	45.06
14	3.81	0.8	46.01

2.2 Methods

One of the most important features of a rock is its porosity, which shows the capacity of the rock to store fluid. Therefore, accurate calculation of porosity is very important in estimating the amount of fluids inside the rock. In this research, the porosity of core samples was obtained using a helium porosimeter before and after acidizing. Figure 2 shows the schematic of the helium porosimeter device.

Figure 2. A schematic of helium porosimeter device.

The contact angle between the rock and the oil drop as shown in Figure 3 is measured by the sessile drop method and the wettability of the rock is determined. To measure the contact angle, the thin section was placed in a glass cell filled with distilled water and a drop of oil was placed on its surface with a needle. After 10 minutes, when the drop reached equilibrium on the surface, it was photographed under a microscope. Finally, the contact angle was determined using DigiMizer image analysis software. If the contact angle between the drop of oil and the rock is higher than 105, the rock has oil-wetting properties. Also, between 0 and 30 is highly water-wet, between 30 and 75 water-wet, and between 75 and 105 neutral state will happen. In this research, firstly, the contact angle test was conducted on the prepared thin sections that were saturated with crude oil to check their wettability. Then, the thin sections are placed in contact with the surfactant solution with different concentrations, and at the end, the contact angle test is taken from the samples, and the effect of different parameters on the wettability alteration of the rock can be seen.

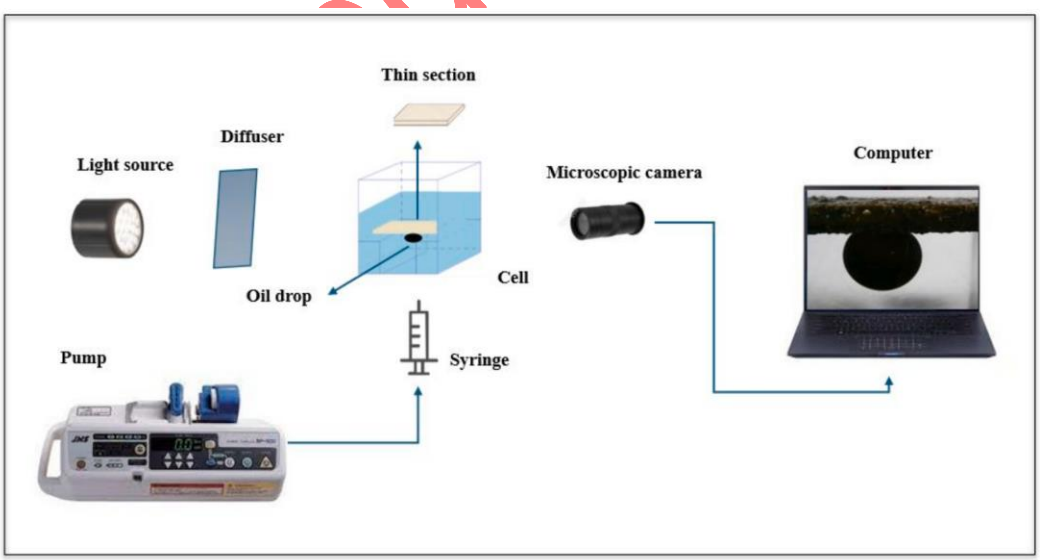

Figure 3. Schematic of Sessile drop technique for contact angle measurement[18].

To perform the acidizing test, the initial weight of the core was measured and then the core was placed in contact with an acidic solution and the core weight was measured at different time intervals and a core weight loss graph was prepared.

3. Results and Discussions

3.1 Acidizing of core number 14 and 13 using HCl 15 wt%

Core number 14 has an initial weight of 15.4541 grams. Figure 4 shows the changes in core weight loss in contact with HCl 15 wt% with distilled water. As shown in the figure, the rate of the acid solution reaction with the core is the highest at the beginning of the contact and gradually decreases. After 10 to 15 minutes, the core dissolution rate is very small and the strength of the acid solution has decreased. The comparison of the initial and final weight of the core shows that the acidic solution of HCl 15 wt% with distilled water was able to reduce 23.44% of the initial weight of the core and bring the final porosity to 40.49%. The reduction of porosity in this test can be caused by the formation of sludge.

Core number 13 has an initial weight of 17.162 grams. Figure 4 shows the changes in core weight loss in contact with HCl 15 wt% with sea water. The rate of reaction between the core and the acid solution has been almost constant until the 8th minute, and the strength of the acid solution has not decreased. The presence of different ions in the sea water has made the acidic solution to be more reactive in the last time intervals and core 13 has a suitable weight loss. The comparison of the initial and final weight of the core shows that the acid solution of HCl 15 wt% with sea water was able to reduce 30.97% of the initial weight of the core. The final porosity of the core increased to 49.80%, which shows the positive efficiency of the HCl 15 wt% solution with sea water.

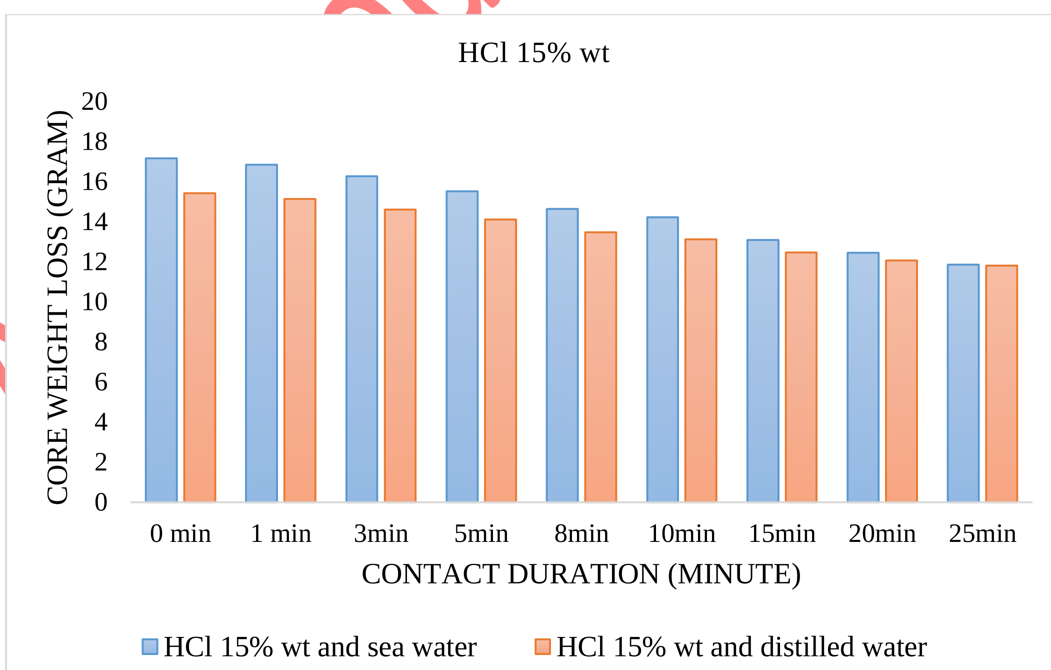

Figure 4. Core weight loss changes in contact with HCl 15wt%

3.2 Effects of Pre-flush Solutions on Wettability Alteration

First, the contact angle test was conducted on the thin sections saturated with oil in the presence of distilled water, and the angle between the rock and the oil was 125, which shows that the wettability of the rock is oil-wet. Figure 5 shows the contact angle between rock and oil in the initial state.

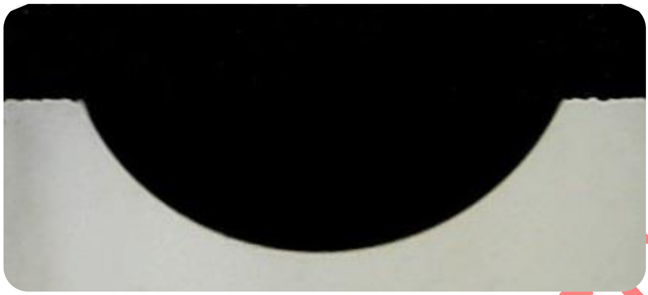

Figure 5. Contact angle between rock and oil in the initial state

Next, the thin sections were placed in contact with different concentrations of CTAB surfactant at different times and the optimal concentration and optimal time were determined. We used CTAB surfactant in concentrations of 250, 370, and 500 ppm and put them in contact with the desired thin sections at 70ºC for 60 and 120 minutes. Surfactant solutions were prepared in distilled water and sea water to determine the effect of ions in sea water on wettability.

The contact angle tests for the thin sections that were in contact with the surfactant solution with distilled water show that the wettability of the rock has become neutral in the best conditions and the surfactant solution could not change the wettability to the water-wet state. The wettability of the rock changed to 95.215, 92.22 and 89.676 for 60 minutes and concentrations of 250, 370 and 500, respectively. Also, the wettability of the rock changed to 106.2585, 101.1135 and 97.043 for 120 minutes and concentrations of 250, 370 and 500, respectively. Figures 6 and 7 show the change of wettability of thin sections in contact with different concentrations of CTAB along with distilled water during 60 and 120 minutes.

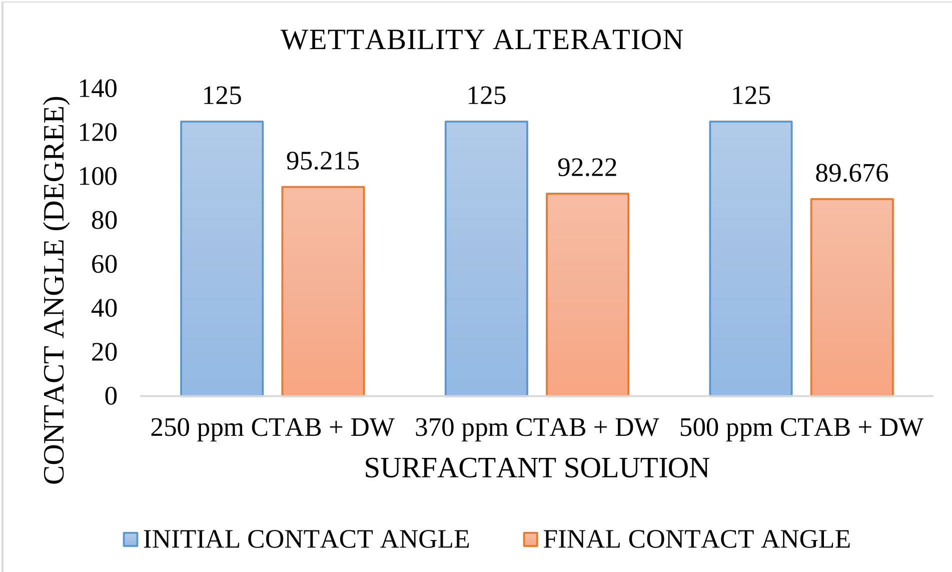

Figure 6. Wettability alteration of thin sections in contact with different concentrations of CTAB along with distilled water for 60 minutes.

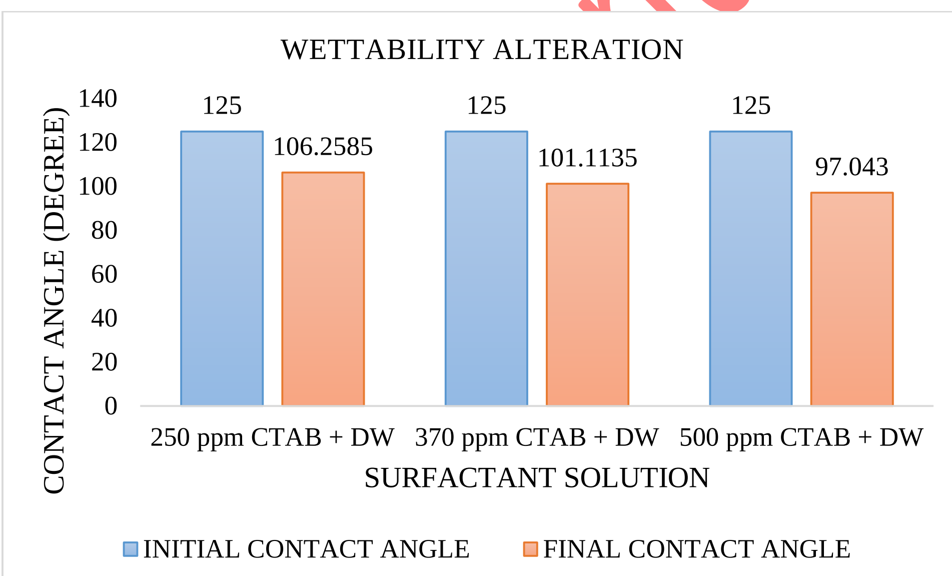

Figure 7. Wettability alteration of thin sections in contact with different concentrations of CTAB along with distilled water for 120 minutes.

The contact angle tests for the thin sections that were in contact with the surfactant solution along with sea water showed that the contact angle decreased in all solutions with different concentrations and different times and the surfactant solutions along with sea water were able the wettability change to the water-wet state. Figures 8 and 9 show the change of wettability of thin sections in contact with different concentrations of CTAB along with sea water during 60 and 120 minutes.

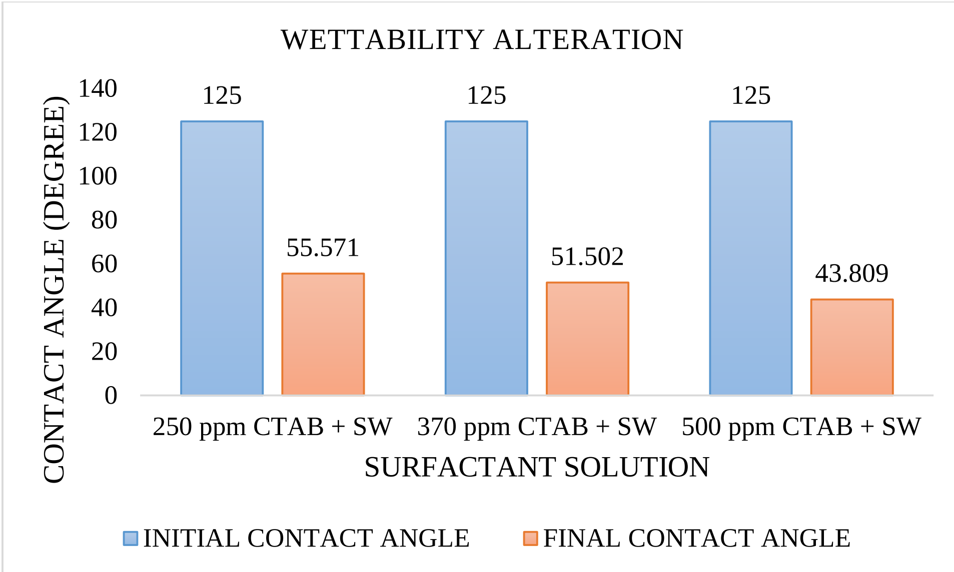

Figure 8. Wettability alteration of thin sections in contact with different concentrations of CTAB along with sea water for 60 minutes.

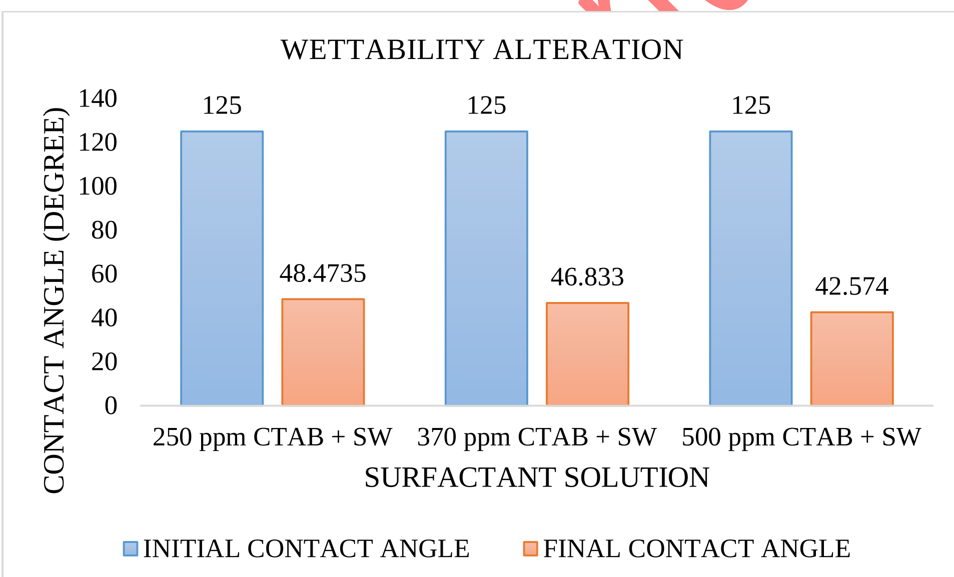

Figure 9. Wettability alteration of thin sections in contact with different concentrations of CTAB along with sea water during 120 minutes.

The contact angle between the oil drop and rock with CTAB surfactant solution along with seawater decreased to a greater extent by increasing the contact time to 120 minutes. CTAB solution together with sea water with a concentration of 500 ppm was able to have the best performance among different solutions and was identified as the optimal solution.

3.3 Acidizing of core number 6 and 4 using HCl 15 wt% after pre-flush with surfactant solution

The presence of oil on the surface of the rock creates a barrier against the acid, which delays the arrival of the acid to the surface of the rock and increases the consumption of acid before it reaches the surface of the rock. To change the wettability of rock from oil-wetting to water-wetting, CTAB surfactant solution with a concentration of 500 ppm was used along with sea water for 120 minutes. First, we put core number 6 in contact with the surfactant solution at 70ºC. Then this core was placed in contact with HCl 15 wt% and distilled water and its weight loss was measured in different time intervals. The initial weight of the core is 18.1535 gr and its initial porosity is 43.529%. Figure 10 shows changes in core weight loss in contact with HCl 15 wt% with distilled water.

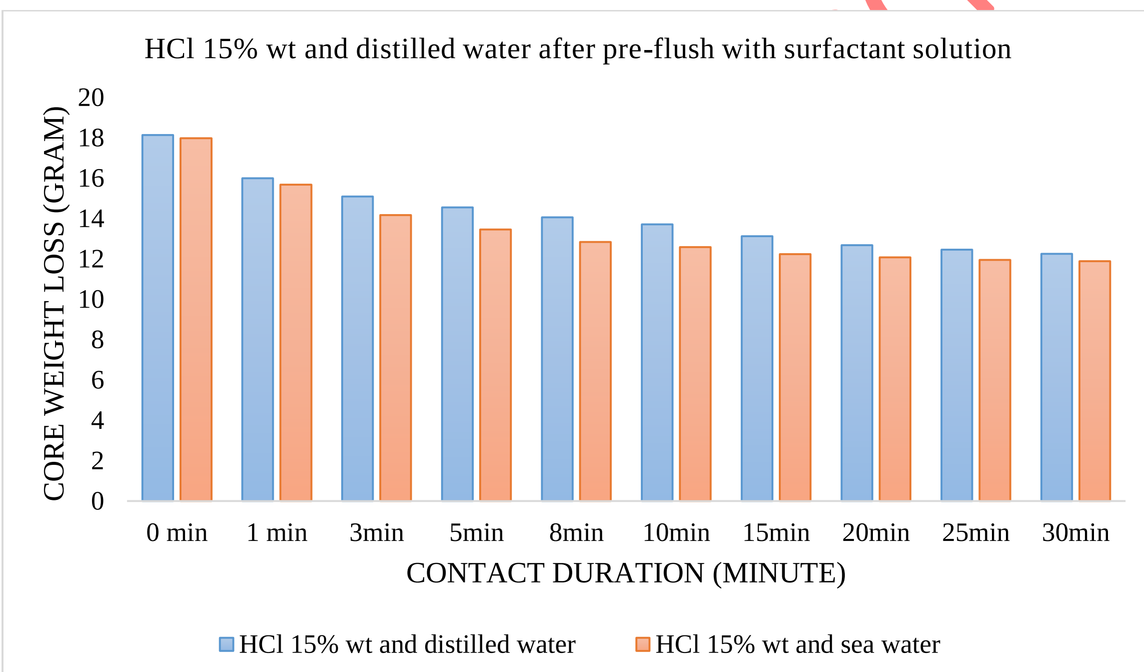

Figure 10. Core weight loss changes in contact with HCl 15wt% after pre-flush with surfactant solution

Considering that the wettability of the core has changed to a water-wet state, the acidic solution reaches the surface of the rock earlier and has a significant dissolution rate in the first period. The core dissolution rate is 2.1527 g/min in the period from 0 to 1 minute and it decreases drastically in the following periods. Comparing the initial weight and the final weight of the core shows that the acid solution was able to reduce 32.47% of the initial weight of the core. The final porosity of the core increased to 47.425%. The comparison between core number 6 and core number 14 shows that the surfactant solution was able to have a positive effect on the acidizing performance.

we placed the core in contact with CTAB surfactant solution with a concentration of 500 ppm along with sea water for 120 minutes at 70ºC. Then, this core was placed in contact with an acidic solution of HCl 15 wt% and sea water, and its weight loss was measured at different time intervals. The initial weight of the core is 17.9949 gr and its initial porosity is 43.04%. Figure 10 shows the changes in core weight loss in contact with HCl 15 wt% with sea water. According to figure 10, the dissolution rate of the core in the period from 0 to 1 minute is 2.3125 g/min. The high dissolution rate in this period is due to the absence of oil, which acts as a barrier against acid. The dissolution rate in the later periods was higher compared to core 6, which is caused by the presence of ions in the sea water. Comparing the initial and final core weights shows that the acid solution was able to reduce 33.88% of the core weight. The final porosity of the core increased to 48.257%, which indicates the effect of the surfactant solution as a pre-flush fluid.

4. Conclusion

- 15 wt% of HCl with sea water gave better results than 15 wt% of HCl with distilled water due to the presence of ions in seawater.
- CTAB surfactant solution with distilled water changed the wettability of the rock to a neutral state.
- CTAB solution together with sea water with a concentration of 500 ppm in a period of 120 minutes was able to have the best performance among different solutions and was known as the optimal surfactant solution.
- Both acidic solutions of HCl 15 wt% with distilled water and HCl 15 wt% with sea water after pre-flush with surfactant solution were able to increase the porosity, which shows the effective efficiency of the pre-flush fluid.

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