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The Effect of Wettability Alteration of Carbonate Rock Using Cetyltrimethyl Ammonium Bromide on Acidizing with HCl 15%

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ABSTRACT

Most of the reservoirs in Iran are carbonate reservoirs that spend the second half of their life cycle, requiring acid stimulation processes for improved production rates. Acidizing is a well and reservoir stimulation method 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 aim to identify the optimal pre-flush fluid using a CTAB surfactant to enhance the acidizing process. Initially, the porosity test is conducted on the carbonate cores, and then they are acidized using 15 wt% HCl. Then, the contact angle test is performed to determine the optimal concentration of surfactant and the optimal time. Finally, the cores that we placed in contact with the pre-flush fluid were positioned in the vicinity of the acidic solution to assess the effectiveness of the pre-flush fluid. A CTAB surfactant solution with a concentration of 500 ppm in seawater, and a duration of 120 minutes, reduced the contact angle from 125 to 42.574, and was determined as the optimal pre-flush fluid. Also, the combination of 15 wt% HCl with seawater had the best performance.

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 exhibit high heterogeneity and porosity, characterized by numerous geological discontinuities, including fractures and faults. The complex physical and chemical conditions of 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. Matrix acidizing is the predominant method for mitigating or bypassing this damage [4]. Acidizing is one of the oldest and most practical techniques for boosting well productivity by improving near-wellbore permeability, a widely adopted method in the petroleum industry [5, 6]. Matrix acidizing is a highly effective, successful, and relatively low-

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cost method for enhancing well output in carbonate formations [7, 8]. Acidizing primarily aims to increase productivity in acid-soluble formations, such as dolomite, limestone, and chalk [5, 9, 10]. Typical matrix acidizing processes for oil-producing wells have three sequential stages: pre-flush, main acid treatment, and over-flush injection. The pre-flush stage prepares 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 crucial for preventing sludge and emulsion formation, as well as avoiding solid precipitation due to incompatibility between the 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 highly soluble chloride salts that 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 concentration; therefore, careful selection of the acid type and concentration is essential for a successful treatment [4]. In matrix acidizing carbonates, wormholes are formed due to 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. Oil clings to the rock surface in oil-wet rocks 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 thermophysical 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 has been used to acidize the carbonate core.

Materials and Methods

Materials

The crude oil used in this research is sourced from one of the wells in the Azadegan field, whose properties are listed in Table 1. This study utilized an Anton Paar rheometer and a CC27 spindle to determine viscosity. The maximum spindle rotation speed is 1200 rpm, and it can operate at a shear rate of up to 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 applied shear stress, calculating the viscosity. IP-143 analysis was employed to determine the asphaltene content of the crude oil. The hanging drop method measured the IFT between the oil sample and water.

Table 1. Crude oil properties

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

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

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

Seawater from the Persian Gulf was used in this research, and its brine composition analysis is presented in Table 3. Also, 30.2% HCl was used to prepare acidic solutions, which were diluted to 15 wt%, using distilled water and seawater

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). Initially, different concentrations of this surfactant were contacted with thin sections at varying times at a temperature of 70°C. Using the contact angle test, the optimal concentration of the surfactant and the optimal contact time were determined, which will be used in acidizing tests. In this work, surfactant concentrations of 250, 370, and 500 ppm will be used, and the thin section will be in contact with them for 60 and 120 minutes.

CTAB deionized water and seawater 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 Fig. 1.

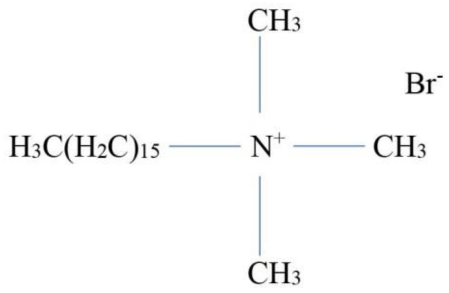

Fig. 1. A schematic of CTAB [17]

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 presented 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

Methods

One of the most important features of a rock is its porosity, which indicates the rock's ability to store fluids. Therefore, accurate porosity calculation is 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. Fig. 2 shows the schematic of the helium porosimeter device.

Fig. 2. A schematic of the helium porosimeter device

The contact angle between the rock and the oil drop, as shown in Fig. 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 greater than 105 degrees, the rock exhibits oil-wetting properties. Additionally, between 0 and 30 is highly water-wet, between 30 and 75 is water-wet, and between 75 and 105, neutral states occur. This research first conducted a contact angle test on the prepared thin sections, saturated with crude oil, to assess their wettability. Then, the thin sections are placed in contact with surfactant solutions of varying concentrations. Finally, the contact angle test is performed on the samples, allowing for the observation of the effect of different parameters on the alteration of wettability in the rock.

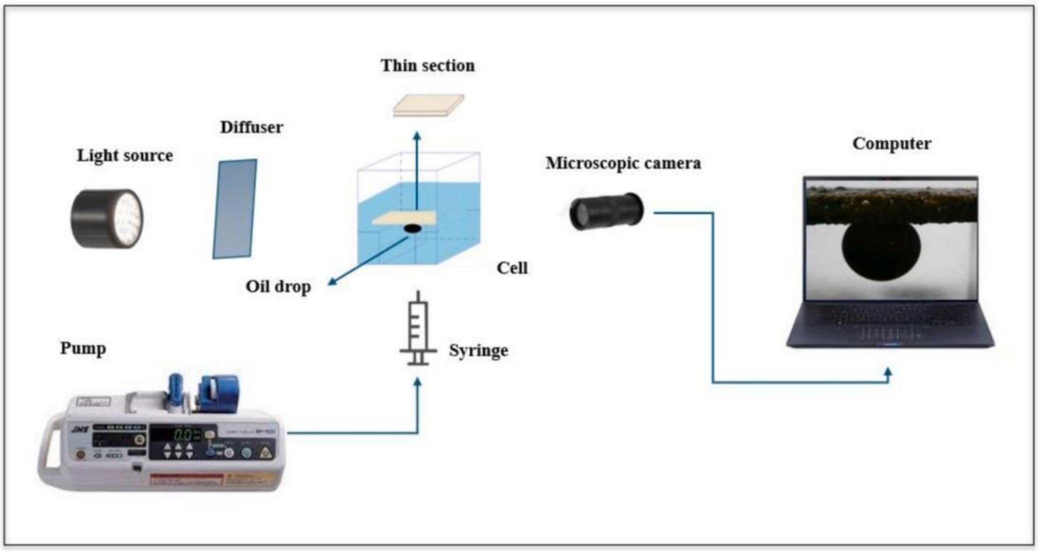

Fig. 3. Schematic of the Sessile drop technique for contact angle measurement [18]

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

Result and Discussion

Acidizing of Core Numbers 14 and 13 Using HCl 15 wt%

Core number 14 has an initial weight of 15.4541 grams. Fig. 4 shows the changes in core weight loss when in contact with 15 wt% HCl and 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 low, and the strength of the acid solution has decreased. The comparison of the initial and final weights of the core shows that the acidic solution of 15 wt% HCl with distilled water reduced the core's initial weight by 23.44% and achieved a final porosity of 40.49%. The reduction in porosity in this test can be attributed to the formation of sludge.

Core number 13 has an initial weight of 17.162 grams. Fig. 4 shows the changes in core weight loss in contact with HCl 15 wt% with seawater. The rate of reaction between the core and the acid solution was almost constant until the 8th minute, and the strength of the acid solution did not decrease. Different ions in the seawater have made the acidic solution more reactive in the last time intervals, and core 13 has a suitable weight loss. The comparison of the initial and final weights of the core shows that the acid solution of 15 wt% HCl with seawater was able to reduce the initial weight of the core by 30.97%. The final porosity of the core increased to 49.80%, indicating the positive efficiency of the 15 wt% HCl solution with seawater.

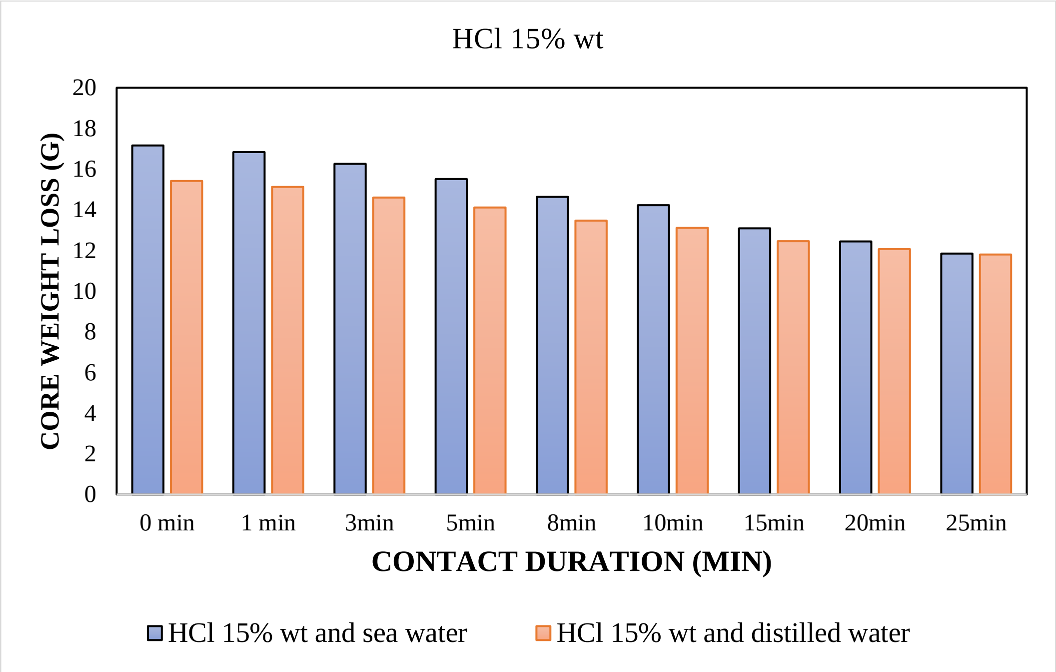

Fig. 4. Core weight loss changes in contact with HCl 15 wt%

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°, indicating that the wettability of the rock is oil-wet. Fig. 5 shows the initial state's contact angle between rock and oil.

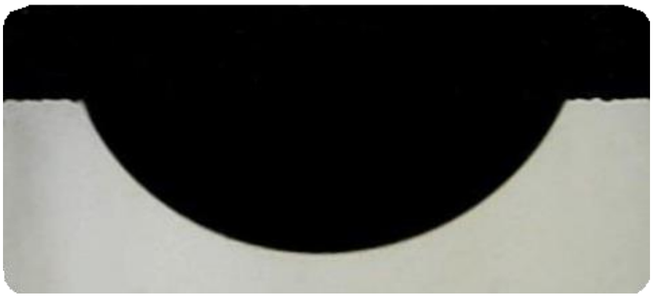

Fig. 5. Contact angle between rock and oil in the initial state

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 at concentrations of 250, 370, and 500 ppm and placed them in contact with the desired thin sections at 70 °C for 60 and 120 minutes. Surfactant solutions were prepared in distilled water and seawater to determine the effect of ions in seawater on wettability.

The contact angle tests for the thin sections that were in contact with the surfactant solution and distilled water indicate that the wettability of the rock has become neutral under the best conditions, and the surfactant solution was unable to alter the wettability to a 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. Figs. 6 & 7 show the wettability change of thin sections in contact with different concentrations of CTAB and distilled water during 60 and 120 minutes.

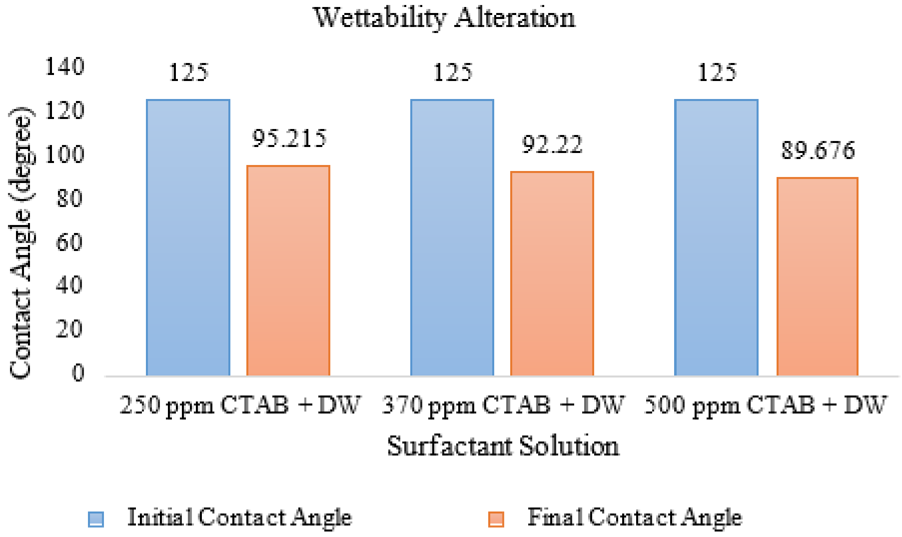

Fig. 6. Wettability alteration of thin sections in contact with different concentrations of CTAB along with distilled water for 60 minutes

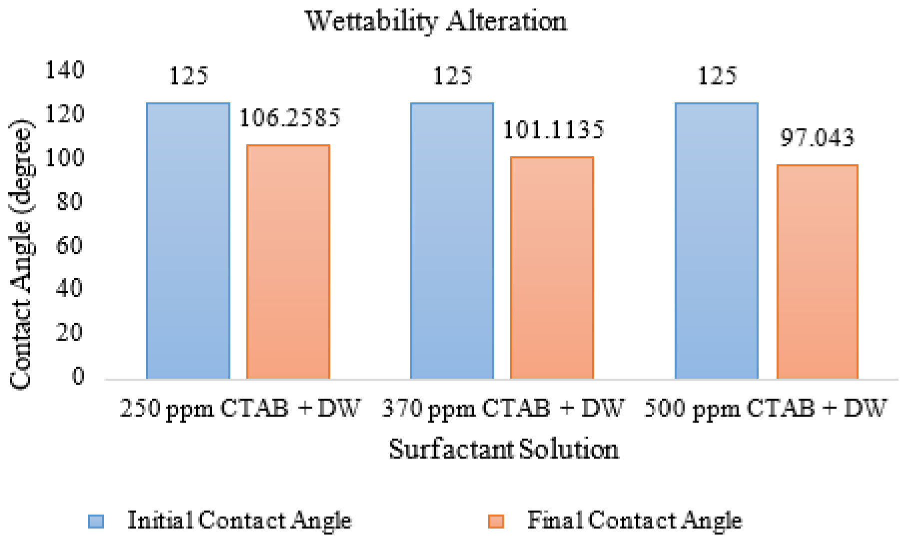

Fig. 7. Wettability alteration of thin sections in contact with different concentrations of CTAB, along with distilled water for 120 minutes

The contact angle tests for the thin sections in contact with the surfactant solution, as well as seawater, showed that the contact angle decreased in all solutions with varying concentrations and times. Additionally, the surfactant solutions, along with seawater, were able to alter the wettability from a water-wet state. Figs. 8 & 9 show the wettability change of thin sections in contact with different concentrations of CTAB along with seawater during 60 and 120 minutes.

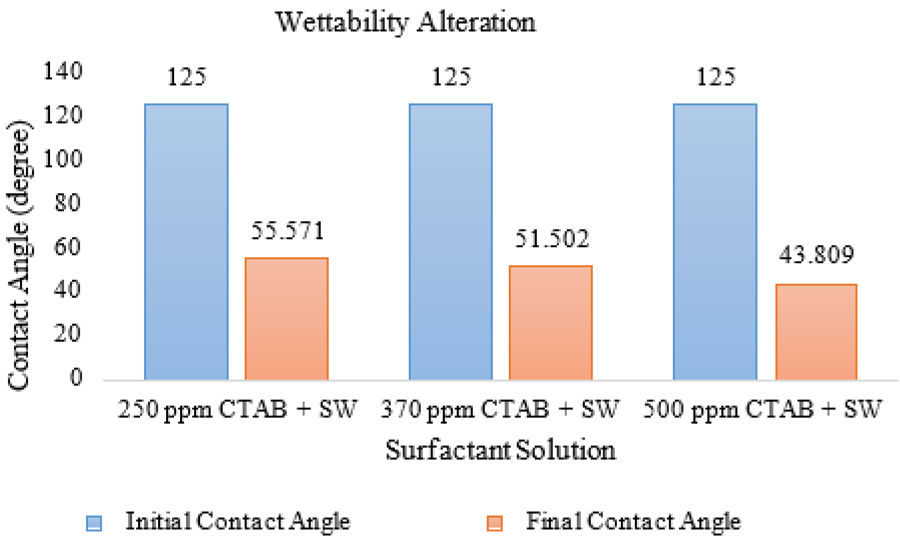

Fig. 8. Wettability alteration of thin sections in contact with different concentrations of CTAB along with seawater for 60 minutes

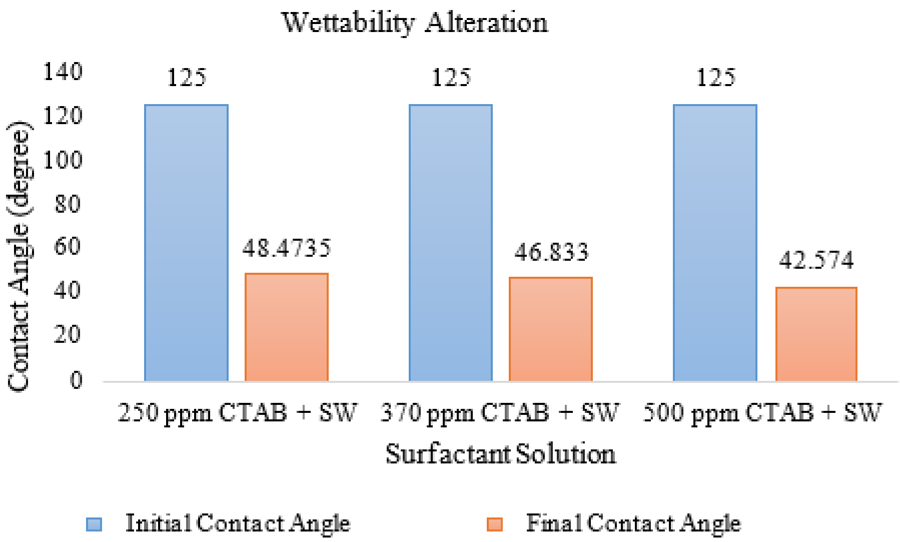

Fig. 9. Wettability alteration of thin sections in contact with different concentrations of CTAB along with seawater during 120 minutes

The contact angle between the oil drop and the rock, using a CTAB surfactant solution and seawater, decreased to a greater extent with increasing contact time to 120 minutes. The CTAB solution, combined with seawater at a concentration of 500 ppm, demonstrated the best performance among the different solutions and was identified as the optimal solution.

Acidizing of Core Numbers 6 and 4 Using HCl 15 wt% after Pre-flush with Surfactant Solution

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

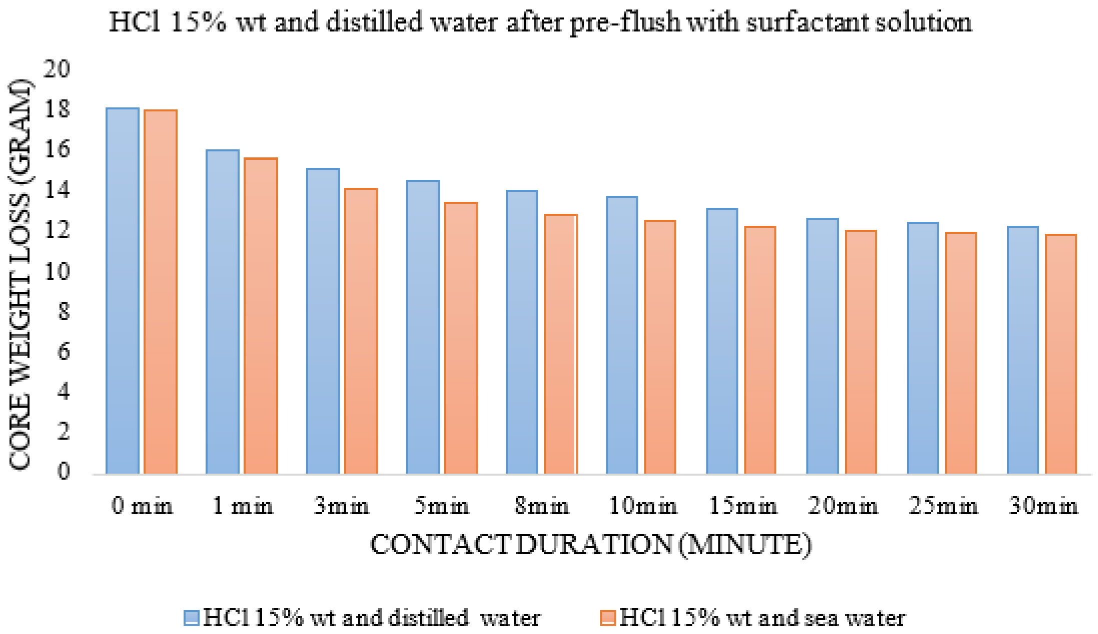

Fig. 10. Core weight loss changes in contact with HCl 15 wt% after pre-flush with surfactant solution

Considering that the wettability of the core has changed to a water-wet state, the acidic solution reaches the rock's surface earlier. It has a significant dissolution rate in the first period. The core dissolution rate is 2.1527 g/min from 0 to 1 minute, then decreases drastically in the subsequent periods. Comparing the initial and final weights of the core reveals that the acid solution reduced the core's weight by 32.47%. The final porosity of the core increased to 47.425%. The comparison between core number 6 and core number 14 reveals that the surfactant solution had a positive impact on the acidizing performance.

We placed the core in contact with a CTAB surfactant solution at a concentration of 500 ppm and seawater for 120 minutes at 70 °C. Then, this core was placed in contact with an acidic solution of HCl 15 wt% and seawater, and its weight loss was measured at different time intervals. The initial weight of the core is 17.9949 g, and its initial porosity is 43.04%. Fig. 10 shows the changes in core weight loss in contact with HCl 15 wt% with seawater. According to Fig. 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 than in core 6, which is caused by the presence of ions in the seawater. Comparing the initial and final core weights reveals that the acid solution reduced the core weight by 33.88%. The final porosity of the core increased to 48.257%, indicating the effect of the surfactant solution as a pre-flush fluid.

Conclusion

A 15 wt% solution of HCl in seawater yielded better results than a 15 wt% solution of HCl in distilled water, likely due to the presence of ions in seawater. A CTAB surfactant solution mixed with distilled water altered the wettability of the rock to a neutral state. A CTAB solution and seawater with a concentration of 500 ppm, when used for 120 minutes, performed best among the different solutions and was identified as the optimal surfactant solution. Both acidic solutions of HCl (15 wt%) with distilled water and HCl (15 wt%) with seawater, after preflushing with a surfactant solution, increased the porosity, demonstrating the effective efficiency of the pre-flush fluid.

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