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The Effect of Water-Soluble Compounds of Crude Oil on Wettability of Oil-Wet Calcite Surface in Low Salinity Water Injection

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INTRODUCTION

Water flooding in carbonate reservoirs due to oil or mixed wet rock surfaces leading to low water flood recoveries. Several researches have shown that modification of injected water by tuning either its salinity or ionic composition is capable of producing higher oil recovery. Among different effects of injected water on fluid/fluid and fluid/rock interactions, the wettability alteration is the most important factor which can improve the oil recovery [1–4].

In almost all previous studies, to recognize the effect of the saltwater ionic composition on wettability alteration, the oil-wet surface was contacted with saltwater, which only contained dissolved salt ions. However during water injection in oil reservoirs, after oil and saltwater contact, some amphiphilic components of crude oil can dissolve in the aqueous phase. These compo-

nents are surface active and can reduce the surface tension significantly [5–7].

Reviewing the preceding studies reveals obvious lack in experimental investigation of saltwater saturated with amphiphilic compounds of crude oil on the wettability alteration of the calcite surface. Therefore, to better understand the wettability alteration mechanisms and to represent reservoir real conditions, the dissolution of amphiphilic compounds in water after their contact with crude oil should be considered. In this study, we tried to investigate the effects of amphiphilic compounds on calcite surface wettability alteration.

METHODOLOGY

The effect of water-soluble amphiphilic compound of crude oil beside ionic composition of $MgCl_2$ and $CaCl_2$ salt, on wettability alteration of

oil-wet calcite surface was investigated. In this turn, distilled water and salt water of $MgCl_2$ and $CaCl_2$ with ionic strength of 0.5 molar were contacted to the crude oil for two weeks to be saturated with crude oil amphiphilic compounds. Moreover, the effect of these compounds on water properties are examined with pH and total organic carbon (TOC) tests. In the next step, the effect of on wettability alteration of oil-wet calcite surface was investigated with exposing the oil-wet surfaces to the saturated and pure (without contact with crude oil) water samples and measuring the contact angle of oil droplet on calcite surface.

RESULTS AND DISCUSSION

PH AND TOC TESTS

The results show that pH of water samples changes to acidic state after contacting with crude oil (Table 1). This reveals that the acidic compounds play the dominant role in pH determination. In other words, the acidic components were dissolved more than the basic components in the aqueous phase. The acidic compounds with low molecular weight and small structure can dissolve in water with pH upper than 5 [8]. However, presence of multifunctional groups on molecular structure increase solubility of compounds [9].

The total organic carbon test determines the amount of dissolved compounds in water. This value depends on ionic strength, pH value and divalent ions of water [10]. Results show that dissolution of organic compounds in distilled water is higher than salt waters (Table 2). The presence of salt ions and their structure reduce the solubility of organic compounds [11].

Table 1: pH and TOC results.

| Saturated water type | pH | TOC (ppm) |
|----------------------|-----------|-----------|
| Distilled water | 4.88±0.03 | 183 |
| $MgCl_2$ | 4.26±0.02 | 165 |
| $CaCl_2$ | 4.37±0.03 | 141 |

WETTABILITY

The aged calcite surfaces are exposed to the fresh and saturated water samples and wettability alteration of surfaces measured with contact angle. Tables 2 and 3 show the results of contact angle after exposing the oil-wet surface into pure and saturates salt waters respectively. The wettability of both surfaces which soaked to the pure and saturated waters altered toward water-wet. However, the changes in the presence of fresh waters are much more than saturated waters which indicate that the capability of freshwater in wettability alteration is more than that of saturated water. One of the main mechanisms that is active in wettability alteration is that the acidic compounds which have been constructed from the organic-ionic layer or have been adsorbed on the oil-wet carbonate surface leave the layer or carbonate surface and, consequently, dissolve in water during the soaking period. This could lead to wettability alteration toward water-wetness, whereas the presence of acidic compounds in the aqueous phase during the soaking period retarded their dissolution in the aqueous phase and restricted the capability of saturated water in wettability alteration.

The results reveal that as well as water-soluble amphiphilic compounds the presence of similar rock composition ions in water can prevent the wettability alteration. In this turn, the wettability alteration of surfaces exposed to the $CaCl_2$ salt waters (in both group of waters) was low and in saturated water was lower.

Table 2: Contact Angle Results for Samples Soaked in Fresh Water.

| Image of contact angle | Difference between contact angle before and after soaking in fresh water | Contact angle after soaking in fresh water | Brine |
|---|--|--|-------------------|
|  | 90.26 | 56.13 | Distilled |
|  | 104.07 | 47.17 | MgCl ₂ |
|  | 28.67 | 120.55 | CaCl ₂ |

Table 3: Contact Angle Results for Samples Soaked in Saturated Water.

| Image of contact angle | Difference between contact angle before and after soaking in saturated water | Contact angle after soaking in saturated water | Brine |
|---|--|--|-------------------|
|  | 17.62 | 136.76 | Distilled |
|  | 30.72 | 116.40 | MgCl ₂ |
|  | 23.22 | 130.23 | CaCl ₂ |

CONCLUSIONS

The contact of saltwater and distilled water with crude oil led to the dissociation and protonation of some amphiphilic compounds in the aqueous phase. The pH, TOC experiments elucidate some amphiphilic components of crude oil were dissolved in the aqueous phase, because partitioning of acidic compounds was more than that of basic compounds. The number of dissolved compounds in saturated water was not significant (on

the basis of TOC results); however, it has a considerable effect on the wettability behavior of oil-wet calcite. Both fresh and saturated water led to wettability alteration toward more water-wetness. However, the saturated water had lower capability in wettability alteration. Finally, on the basis of the contact angle results, it is concluded that the presence of amphiphilic components in saturated water impedes wettability alteration.

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