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Research paper

Effects of low salinity water on calcite/brine interface: A molecular dynamics simulation study

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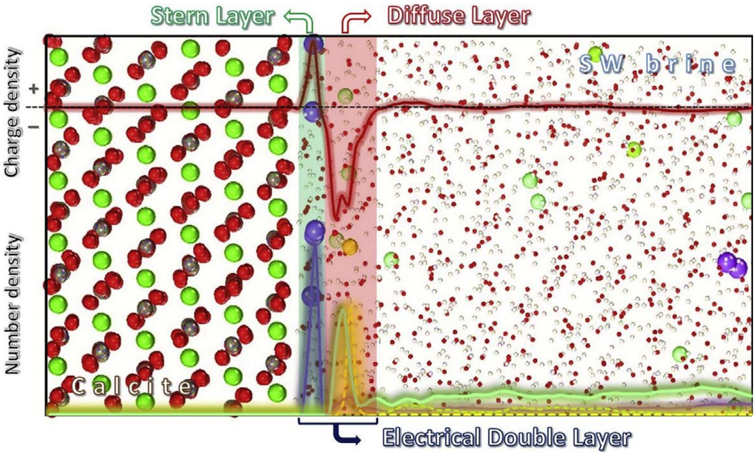
GRAPHICAL ABSTRACT



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ABSTRACT

Calcite is among the most abundant minerals organizing the oil reservoir formation and therefore its surface properties play a central role in the increase of the oil recovery efficiency. The effect of low-salinity water in carbonate rocks reveals that brine composition and salinity can improve the oil recovery in carbonates through wettability alteration. However, the specific mechanism for wettability changes that leads to improved oil recovery in calcite is not well understood. To obtain deeper insights at atomic level into the understanding the characteristics of the calcite-water interface, we performed classical molecular dynamics simulations in the presence of different ions in brine solutions in the oil reservoirs. The results showed highly ordered water layer in the vicinity of calcite surface, followed by subsequent layers rich in ions of brine. These layers form an electric double layer, with monovalent Na^+ ions in the Stern layer and anions in the diffuse layer. The results also indicated that divalent cations do not appear in the electric double layer. The appearance of ions at calcite/brine interface is more effective in wettability alteration for low saline brines such as seawater than high saline ones like formation water validating the applicability of low saline water injection method to improve oil recovery efficiency.

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1. Introduction

Calcite ($CaCO_3$) is one of the most dominant minerals on the earth's crust and is of critical importance in almost all geological systems. It is the main ingredient of chalk, dolomite, and limestone minerals which are recognized as the most significant source of major oil and gas reservoirs. Therefore, gaining knowledge about the molecular structure and the reactivity of calcite minerals with saline water initially occupying the oil and gas reservoirs would allow us to reach a consensus on some important issues such as ion exchange [1], contaminant migration [2,3], enhanced oil recovery (EOR) [4], biomineralization [5–7], and flocculation [8]. As a result, calcite has been considered as the topic of many experimental and theoretical studies [9–26]. In these studies calcite $(10\bar{1}4)$ surface was approved to be the most stable cleavage plane of the solid and therefore allocated the greatest portion of studies since now [20,21,27–37]. Studying the structure of calcite/water interface in order to understand the calcite surface specification is probably the most challenging subject among these researches [15,17]. Modeling studies have indicated that water molecules are significantly ordered near the calcite surface and adsorb uniformly on environmentally equivalent surface sites [38]. These researches in accordance with experimental studies have shown that water adsorbs onto calcite surface highly structured, forming at least one or two hydration layers. For instance, Fenter et al. [39] revealed that two considerable water density layers might form over a calcite surface with the peaks seen at 2.14Å and 3.44Å. The study conducted by Kerisit and Parker [13] illustrated the issue that the diffusion of water in the vicinity of calcite surface is anisotropic, such that the parallel diffusion coefficient parameter at the first and second layers was larger than diffusion coefficient in other directions.

These days the significance of water performance in oil reservoirs is due to injection of low salinity water (LSW) as a water flooding process in order to enhance oil recovery [40]. It is well understood that the reactivity of ions such as Na^+, Ca^{2+}, Mg^{2+}, Cl^- and SO_4^{2-} in seawater (SW) at the surface of carbonate reservoirs is responsible for wettability alteration from strongly oil wet toward more water wet states [41–44]. The proposed mechanism of LSW is wettability modification in which these ions must have a potent affinity for carbonate surface [45] and efficient oil recovery from imbibing the limestone cores with SW would be acquired [46]. Recently, Fattahi et al. [47] showed the fact that further 10% oil recovery was obtained by adjusting injection brine composition. Austad et al. [48] showed that the existence of sulfate is critical for wettability alteration following a smart water-flood stage as sulfate ions could act as a catalyst for wettability alteration. There are several experimental studies asserting that lowering brine salinity does not necessarily lead to interfacial tension (IFT) reduction between crude oil and injected brine, but there is a critical salinity in which the IFT between crude oil and brine is minimum [40,49]. Mahani et al. [50,51] observed through contact angle, IFT, and zeta potential measurements that a change in rock/brine and oil/brine interfaces toward more negative state caused electrical double layer expansion and wettability alteration as a result.

Despite such observations, the role of ions in wettability alteration is still ambiguous at the atomic level. It is believed that ion-binding or specific interactions between surface sites and ions is one of the main categories of crude oil/brine/solid interactions identified [52]. Based on this mechanism, ions can bind at both oil/solid and oil/water interfaces and/or bridge between them through columbic interactions [53]. Such dominant electrostatic interactions depend on the brine characteristics (ionic strength and composition). Chiappa et al. reported that the change in ionic strength causes a slight alteration in the adsorption of charged molecules. However, a very different behavior is observed with changing brine composition. They showed the effect caused by the presence of a divalent cation rather than a monovalent one. The Ca^{2+} cation enhanced adsorption of organic molecules through bridging/charge coordination mechanism. Thus it is preferable to operate with low-salinity brines containing monovalent ions toward more water-wet characteristics [54].

Another aspect, which has not been studied previously, is the compositional effect of brine which directly affects wettability alteration process. Knowing also that sulfate has a strong affinity toward $CaCO_3$, it is to be expected that sulfate will influence the surface charge of carbonates [55], and in that case, it will also have an impact on the wetting state of the rock [56]. It was also suggested that the lonely sulfate ion could reduce the adsorption of long-chain carboxylic acids onto calcite as well as displace the long-chain carboxylic acids adsorbed on a calcite surface [57]. However, the presence of Ca^{2+} or Mg^{2+} ions as well as SO_4^{2-} ion is required to change the wettability of carbonate rock at temperatures greater than 90 °C. Fathi et al. [58] reported that the removal of NaCl from SW can significantly improve the oil recovery from carbonates. In a very recent report, these authors observed that Ca^{2+} did not improve oil recovery from carbonates until the temperature is 120 °C, while SO_4^{2-} can increase the oil recovery in lower temperature ranges [58]. Contrary to these mechanisms, a recent report suggested that the wettability alteration of carbonate rock, triggered by a change of surface charges [59], supports the smart water flooding. Therefore, additional studies are needed to better understanding of the roles that the key ions play during oil recovery with smart-water. The results showed that the absence of SO_4^{2-} in the SW could significantly increase the amount of adsorbed acid, while Ca^{2+} and Mg^{2+} did not markedly affect its adsorption. Consequently, the increase of the SO_4^{2-} ion content of smart-water makes the carbonate reservoirs more water-wet [60].

Yousef et al. [61] showed that increasing levels of SO_4^{2-} were effective in wettability alteration from oil-wet toward water-wet. Zhang and Austad [62] also found that an increase of the SO_4^{2-} ion concentration in SW has a positive effect on the oil recovery. However, Karoussi and Hamouda [63] suggested that SO_4^{2-} works only in the presence of Mg^{2+} or Ca^{2+} ions. The presence of SO_4^{2-} without Mg^{2+}/Ca^{2+} in SW and formation water (FW) was found to have a negative effect for both SW and FW. Hence to improve the oil recovery, sulfate must act together with either Ca^{2+} or Mg^{2+} [64]. In these studies, an increase of SO_4^{2-}/Ca^{2+} has often led to higher oil recovery (or less oil wetting conditions) [50]. Chen et al. [65] simulated calcite-hydrocarbon interactions in concentrated brine solutions and verified the density of monovalent ions (Na^+ and Cl^-) to be significantly considerable in calcite/brine interface. Quite the reverse, divalent cations (Ca^{2+} and Mg^{2+}) did not appear at the interface.

In spite of all these observations, lack of molecularly interpreted studies to basically understand the process at solid/brine interface and salinity effect is obvious. In this paper, we aim to study the interactions between the surface of calcite and monovalent/divalent ions present in high and low salinity water at the atomic level of investigation using molecular dynamics simulation. The impact of sulfate ion is also verified in this study. The behavior of these ions in calcite/brine interface will be studied in the context of salinity effect. We and several others [66] believe that such studies will gain fundamental insight into the alteration of reservoir surface wettability and leads to the clarification of mechanism responsible for low salinity effect in enhanced oil recovery process.

2. Methods and simulation details

The system studied consists of a brine aqueous solution over a calcite slab. We have chosen to study calcite slab terminated by $(10\bar{1}4)$ plane because this low index surface has been shown to exhibit the lowest surface energies amongst stable cleavage planes of calcite. The calcite surface contained six atomic layers (with its normal axis in z-direction) whose dimensions are $24 \times 24 \times 17.5 Å^3$.

For our studies the impact of existence of SW fluid with total salinity of 46000 ppm (46 g/L) containing ionic components of 10 Na^+, 2 Mg^{2+}, 1 SO_4^{2-} and 12 Cl^- ions on calcite surface was considered. In a