

## Wettability Alteration Due To $\text{SO}_4^{2-}$ Ions Absorption on the Calcite Surface: Molecular Dynamic Simulation

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**Abstract:** Recently, experimental studies of Wettability alteration is believed to occur in low salinity waterflooding of carbonate rocks. One possible justification for this wettability alteration is that various ions in the water phase (sulphate, calcium, magnesium, etc.) enter the formation water due to molecular dissolution. This creates a non-equilibrium state in the pore space that results in water-rock interaction in terms of dissolution/precipitation of minerals and/or changes in surface charge. In this study its tried to investigate the water-rock interaction on the model surface of calcite by means of molecular dynamics simulations. Persian Gulf seawater is simulated by constructing a 40000ppm synthetic brine by adding NaCl to distilled water. Pair correlation function,  $g(r)$ , is used to study the wettability alteration of calcite surface, due to adding different concentration of  $\text{Na}_2\text{SO}_4$  in the same condition of oil reservoirs at 100 C. The results showed that the absorption of  $\text{SO}_4^{2-}$  in the concentration of 10000 ppm of  $\text{Na}_2\text{SO}_4$  on the calcite surface is much more than other concentrations. In this concentration the ability of water attraction by calcite surface increased which caused the most wettability alteration on the surface of calcite slab.

**Key words:** Wettability alteration, molecular dynamics simulations, calcite surface, water-rock interaction

Date of Submission: 23-04-2018

Date of acceptance: 11-05-2018

### I. INTRODUCTION

Wettability is the most important factor that controls location and distribution of fluid in the carbonate reservoir rock [Anderson, W.G., 1986]. Remarkable wettability of a porous matrix to one liquid generally indicates stronger retention of that fluid and easier displacement of the other fluid. [Mugele, F. et al., 2015]. Recognizing the factors controlling wetting and alteration of wetting is always considered as a vital facet in studying most of the chemical enhanced oil recovery (EOR) techniques [Dehghan, A. et al., 2017, Karimaie, H. and Torsæter, O., 2007].

Two types of representative rock surfaces, namely, quartz and calcite, have been used by several researchers to study the low salinity water flooding performance. [Mugele F. et al., 2015, Aslan S. et al., 2016, Hirasaki, G. and Zhang, D.L., 2004]. Yousef et al. [Yousef A. et al., 2011, Yousef A. et al., 2011] investigated the effect of dilution of injection seawater on the wettability of carbonate reservoir. Their results revealed that the dilution of seawater can change the wettability of carbonate rock surface from oil-wet to water-wet state. Aslan et al. [Aslan, S. et al., 2016.] investigated the effect of NaCl and  $\text{MgCl}_2$  with varying concentrations in brine on the contact angle using two crude oil samples from two different reservoirs of a Chevron operated field on the quartz and calcite surfaces. They witnessed a non-monotonous trend from their contact angle data.

In addition, magnesium, calcium, sodium, sulphate ions have significant impact on recovery of crude oil from calcite oil reservoirs. The crude oil molecule consists of a long chain of hydrocarbons at one end and  $-\text{COOH}$  at the others [Fathi, T. et al., 2011]. To enhance oil recovery, several methods are being applied such as injecting natural gases, bio-minerals, tap water, sea water, high pH solutions of surfactant, low salinity water, microbial and thermal methods. These are some of the examples for possible ways of enhancing crude oil recovery [A. Rezaei-Doust, 2009].

In this paper, we perform molecular dynamic simulation to find the influence of additive ( $\text{SO}_4^{2-}$ ) ion of Persian Gulf sea water on the calcite surface model. The behavior of this ion in calcite/brine interface will be studied in the context of salinity effect. Several researchers believe that such studies will gain fundamental insight into the alteration of reservoir surface wettability.

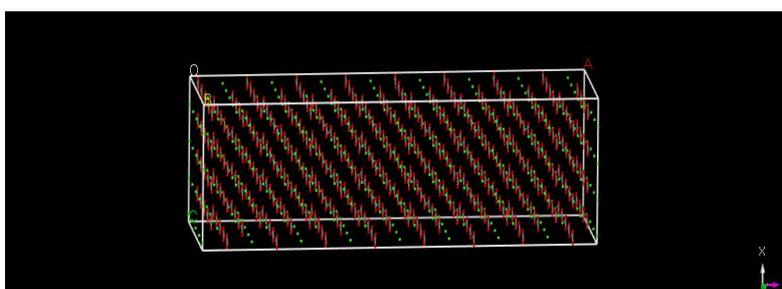
### II. MOLECULAR DYNAMIC SIMULATION

Four brine systems are simulated at the reservoir condition ( $T=100\text{ }^\circ\text{C}$ ) using the 'Materials Studio 2016' which the first one is a representative of Persian Gulf sea water and the rest are simulated by adding 2000 ppm, 5000 ppm and 10000 ppm of  $Na_2SO_4$  respectively. Excess information of systems is prepared as bellow:

**Table 1: systems properties**

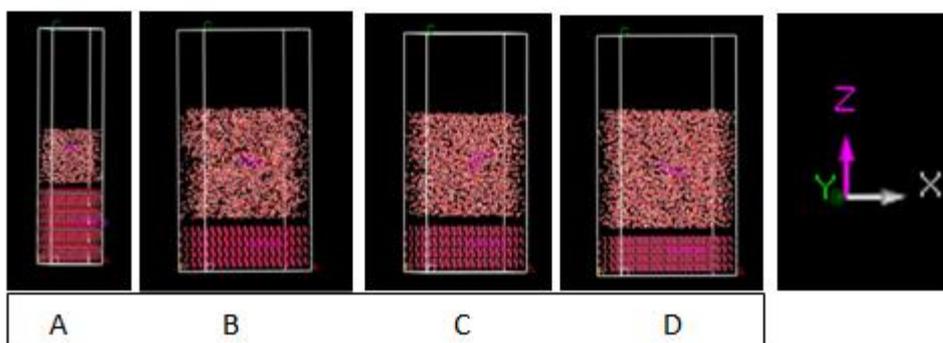
system	solvent	salt	Number of solvent molecules	Number of salt molecules	density	concentration
S1	water	NaCl	649	8	.991502	40000 ppm
S2	water	NaCl+ $Na_2SO_4$	2121	8+8	.993133	42000 ppm
S3	water	NaCl+ $Na_2SO_4$	2331	8+10	.995578	45000 ppm
S4	water	NaCl+ $Na_2SO_4$	2887	8+15	.999645	50000 ppm

These Simulations were dynamically relaxed at the canonical NVT ensemble (at a constant amount of substance (N), volume (V) and temperature (T)). Temperature was fixed at 373 K. A calcite slab is constructed, which contained 4 constrained atomic layers (with its normal axis in z direction) whose dimensions are  $68.2440 \times 19.9600 \times 20.4026 \text{ \AA}^3$  as shown in Figure 1.



**Figure 1:** Lattice parametrs of calcite slab

After creation of calcite rock, the brine systems are located at the calcite surface with a vacuum atmosphere of 52 Å, 32Å, 30.5Å and 28.5Å for second layers respectively. Figure 2 shows the simulation boxes with the brines systems and calcite slab.



**Figure 2:** constructed boxes demonstrate, A:system S1, B:system S2, C:system S3, D: system S4

Long-range electrostatic interactions were corrected by the Atom based summation method using Particle Mesh Ewald for the reciprocal part [Sun H., 1998.].The simulation boxes size were  $27.27 \times 121 \text{ \AA}^3$ ,  $40.40 \times 95 \text{ \AA}^3$ ,  $42.42 \times 93 \text{ \AA}^3$  and  $45.45 \times 92 \text{ \AA}^3$  respectively, which are adjusted according to the system density for bulk phase. The leapfrog method with a time step of 1fs was used to integrate the particle motion. A total simulation time of 50 ps was used to calculate the properties [Kim SK, 2015.].The COMPASS force field was applied in all cases [Sun H., 1998].The equation of COMPASS force field is represented as follows:

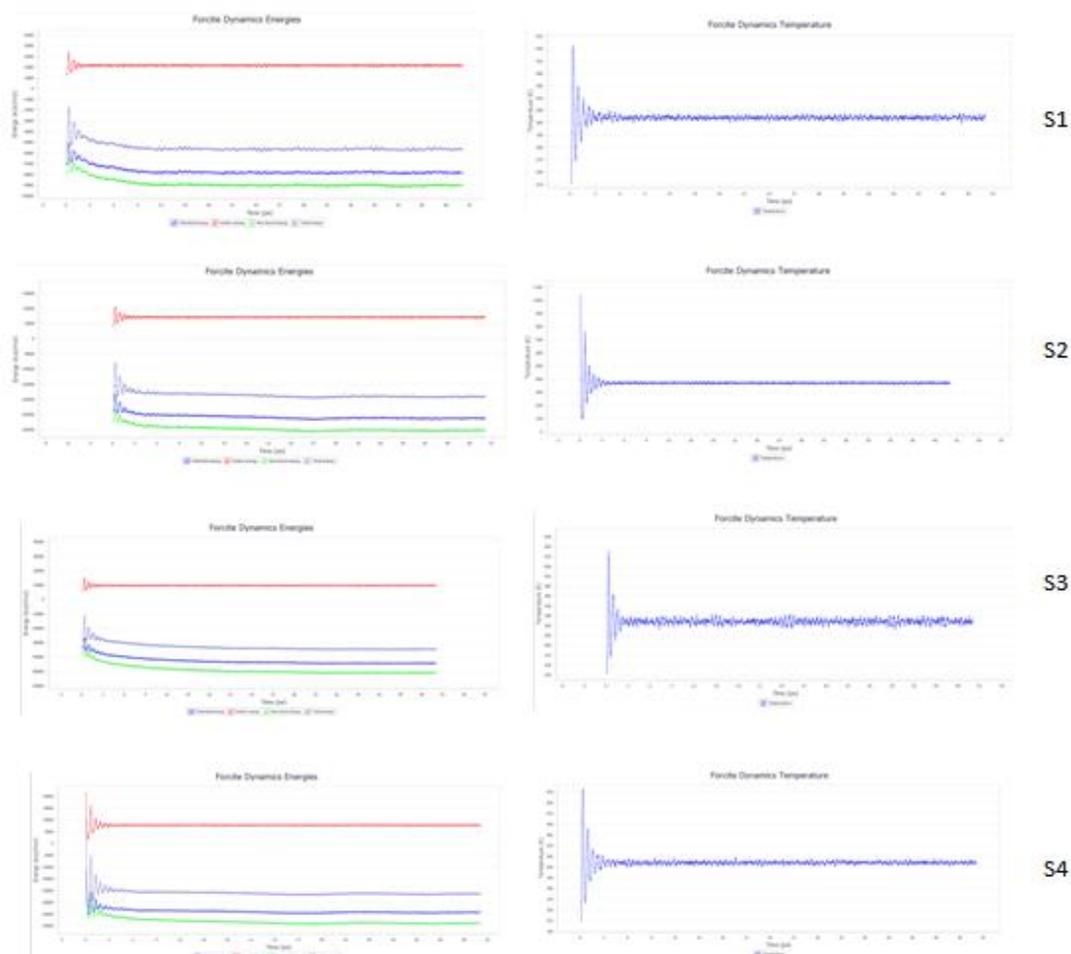
$$E_{total} = E_{bond} + E_{angle} + E_{oop} + E_{torsion} + E_{cross} + E_{elec} + E_l \quad 1$$

where  $E_{bond}$ ,  $E_{angle}$ ,  $E_{oop}$ ,  $E_{torsion}$  and  $E_{cross}$  represent bond stretching energy, angle bending energy, out-of-plane angle coordinates, bond torsion energy and cross-term interacting energy, respectively.

A van der Waals interaction cut-off distance of 12.5 Å was employed, and the Ewald summation method with an accuracy of 0.001 kcal/mol was used to account for the long-range electrostatic interactions for all boxes. The MD simulations were run at NVT ensemble at 373 K as an oil reservoir condition using a Nose thermostat.

### III. RESULT AND DISCUSSION

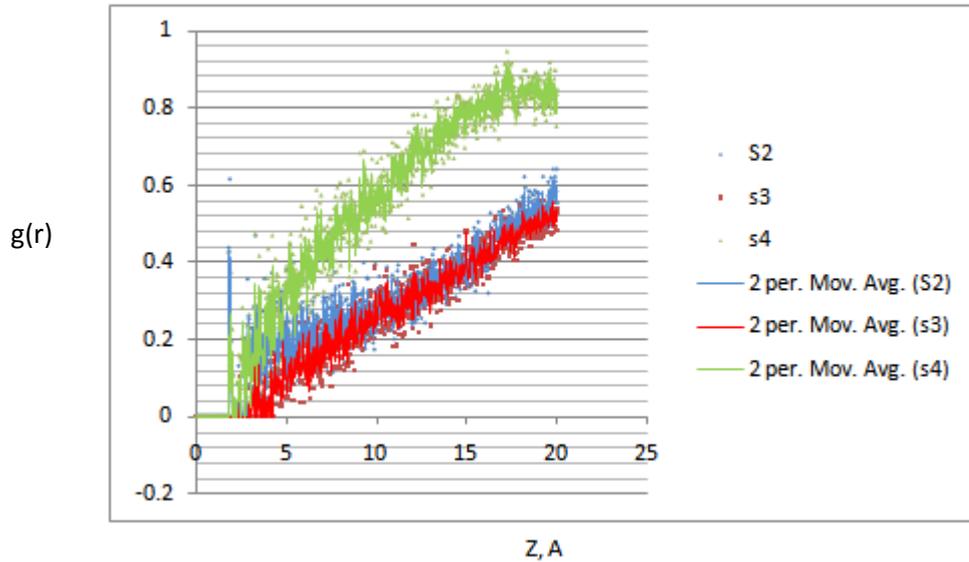
The equilibriums of systems are showed by total energies and temperature curves of the whole system. As you can see in Figure3



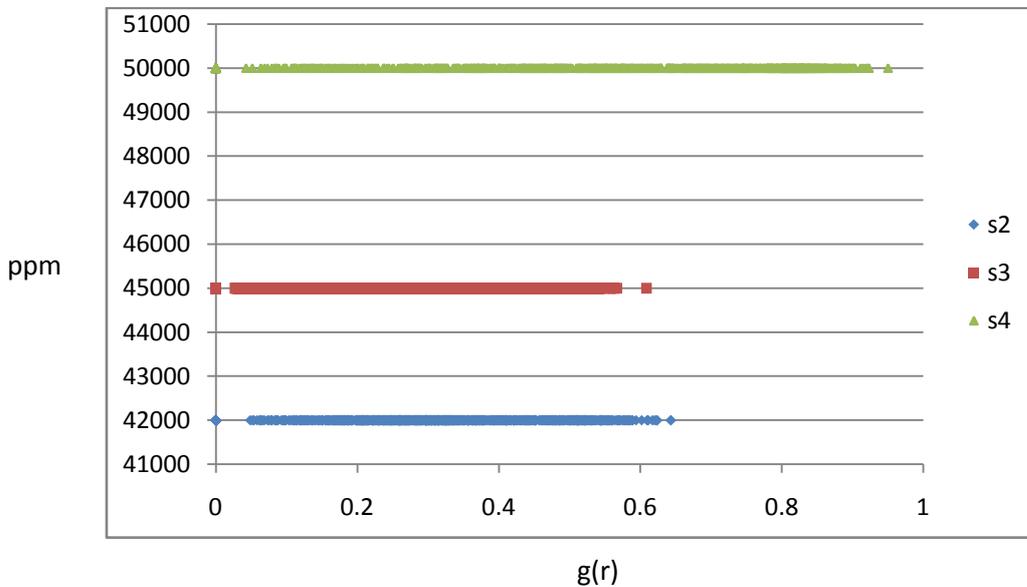
**Figure 3:** fluctuation curves of energy and temperature for four systems

The fluctuation curves of energy and temperature during the processes of energy minimization and anneal are shown in Figure 3. Potential energy, non-bond energy, kinetic energy and total energy rapidly decrease to a minimum state and keep stable; the temperature curves are stabilized at 373 K as the reservoir condition. The final results were calculated based on the simulation over 50 ps after the equilibration period.

In order to determine the ionic absorptions of  $so_4^{2-}$  on the calcite surface in 3 different concentrations of brines, Pair correlation function,  $g(r)$ , analysis over the ensemble trajectories through the simulation time steps are performed. With regard to RDF curves shown in Figure 4, the characteristic peaks of the radial distribution functions between  $So_4^{2-}$  and calcite surface for system s4 appear higher than that in systems S2 and S3. This means that in this concentration the adsorption of  $So_4^{2-}$  ions on the calcite surface is more. Note that the height of picks belongs to S2 system are higher than S3 system which cause a decreasing – increasing trend in adsorption of  $So_4^{2-}$  due to the systems concentrations (see Figure 4).



**Figure 4:** Pair correlation function between  $So_4^{2-}$  ions and calcite surface for systems S2, S3, S4



**Figure 5:** Concentration versus  $g(r)$  plot for  $So_4^{2-}$  absorption on the calcite surface.

Wettability between water and calcite rock may change due to the  $So_4^{2-}$  ions absorption on the calcite surface. To investigate this phenomenon the RDF analysis are performed between water molecules and calcite surface. With regard to results gained by Figures 6, 7, 8 and 9 the ability of watermolecules attraction in the system S4, by calcite rock is more than other systems.

By comparing the system S1 which contains merely  $Na^+$  and  $Cl^-$  ions with other systems that encompass addition different concentrations of  $So_4^{2-}$  ions, the waterwettability decreased by adding  $So_4^{2-}$  ions and increasing the concentration of brine to 45000 ppm, then it increased after that the concentration reached to 50000 ppm.

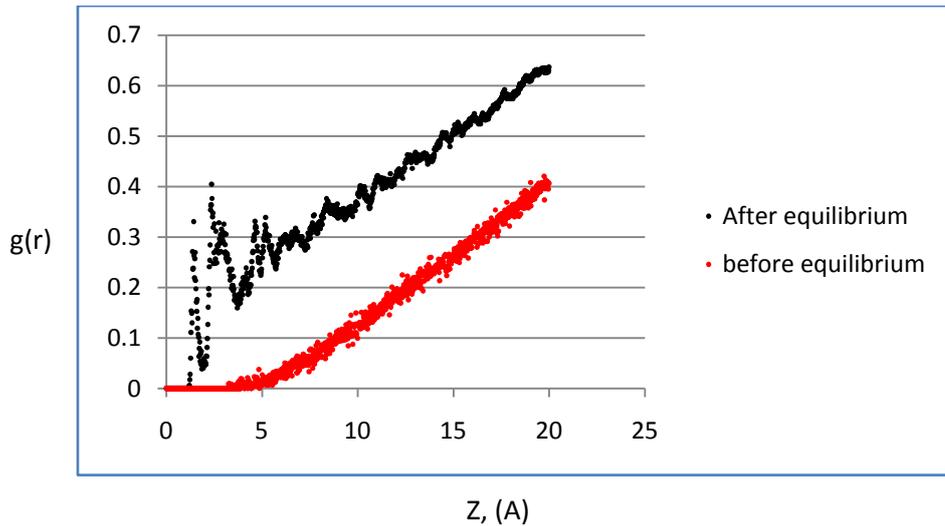


Figure 6: Pair correlation function between H<sub>2</sub>O molecules and calcite surface for system S1 before and after the equilibrium the system.

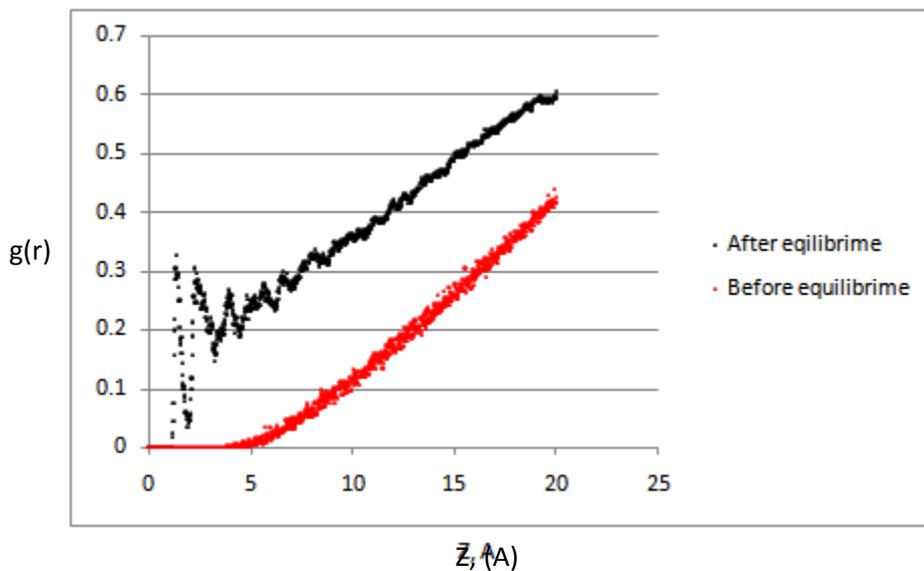
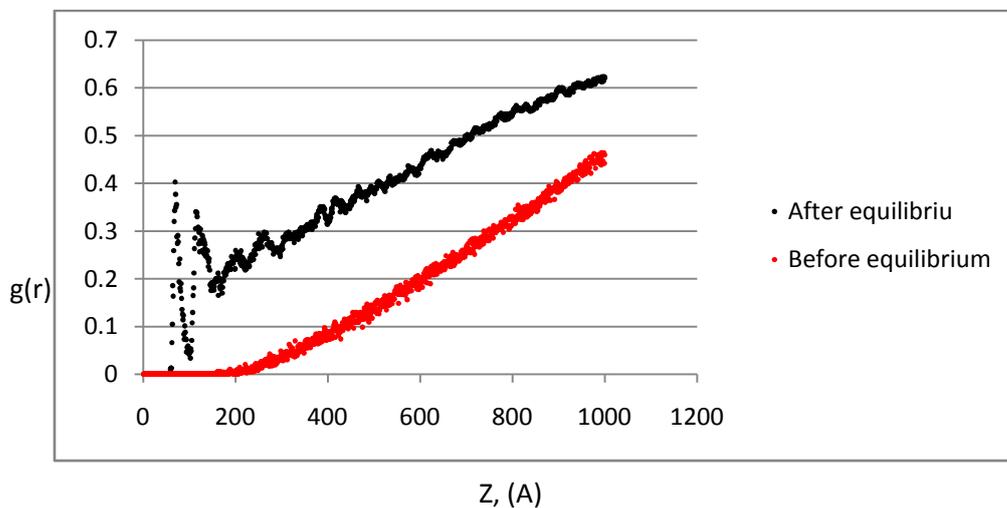
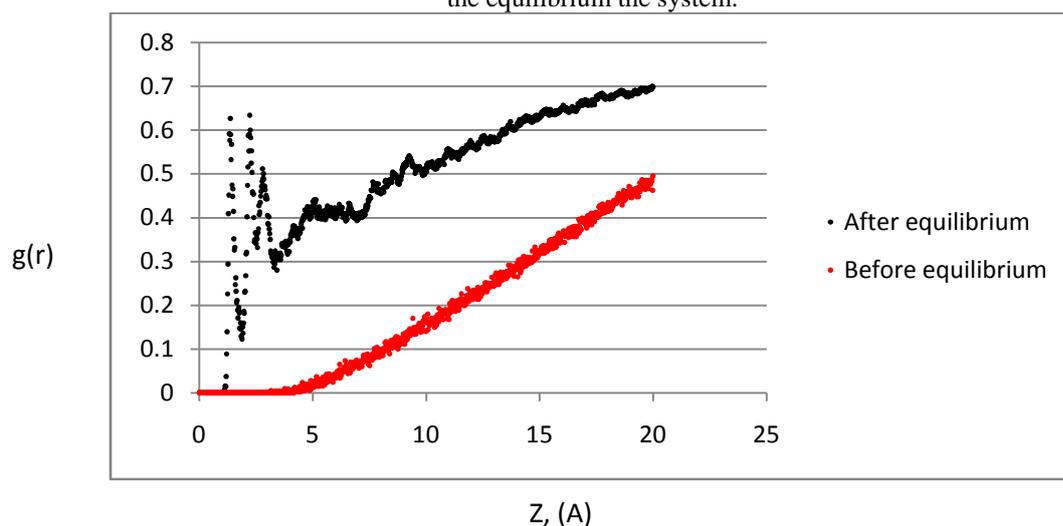


Figure 7: Pair correlation function between H<sub>2</sub>O molecules and calcite surface for system S2 before and after the equilibrium the system.



**Figure 8:** Pair correlation function between H<sub>2</sub>O molecules and calcite surface for system S3 before and after the equilibrium the system.



**Figure 9:** Pair correlation function between H<sub>2</sub>O molecules and calcite surface for system S4 before and after the equilibrium the system.

#### IV. CONCLUSION

In this paper, by simulation the Persian Gulf seawater ppm by addition of NaCl salt as the representative component of water injecting to oil reservoirs and considering rock surface as a perfect calcite crystal surface, the structure of interface adsorption system and the wetting action are investigated at micro molecular level. It was found that:

- By addition the  $SO_4^{2-}$  ions to the brine and increase the concentration to 50000 ppm, the maximum absorption of  $SO_4^{2-}$  ions is reached.
- The maximum water wetting of calcite surface occurred when the concentration of brine was 50000ppm (40000 ppm of seawater+10000ppm of  $Na_2SO_4$ ).
- $SO_4^{2-}$  ion is a convenient agent for altering the wettability of calcite surface in the reservoir condition.

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IOSR Journal of Engineering (IOSRJEN) is UGC approved Journal with SI. No. 3240, Journal no. 48995.

Mohammad Joharifarda "Wet ability Alteration Due To  $SO_4^{2-}$  Ions Absorption on the Calcite Surface: Molecular Dynamic Simulation" IOSR Journal of Engineering (IOSRJEN), vol. 08, no. 5, 2018, pp. 61-68.