Wettability alteration of calcite oil wells: Influence of smart water ions

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Further enhancement of crude oil recovery in the enhanced recovery stage from calcite oil wells is a major global challenge for oil industry. Experimental results suggest that ions present in sea water, also called smart water, have a significant influence on the wettability alteration (less oil wet) of calcite surface. In this paper, by utilizing Density Functional Theory (DFT) and Quantum Molecular Dynamics (QMD) simulations, we investigate the effect of additive ions of sea water in oil recovery by using acetic acid as a model compound of crude oil molecules. We find that Na+ ions precipitate to the calcite surface and form Na acetate. The binding energy of Na acetate is larger than original oil molecule (acetic acid), which reduces oil recovery. On the other hand, Mg2+ and SO42− ions can also reach to the calcite surface in proximity and modify the calcite surface. The binding energy of oil molecule on modified calcite surface is smaller than on pure calcite surface, which enhances oil recovery. Our results might help in understanding interaction among oil, water and additives ions of smart water for further experimental investigations.

Enhancement of crude oil recovery from oil wells is one of the global major challenges for oil companies. The enhancement of crude oil recovery can be achieved by injecting natural gases, bio-minerals, tap water, sea water, high pH solutions of surfactants, low salinity water, microbial and thermal methods1–13. Typically, there are three possible steps that can be applied during recovery of crude oil. These stages are: primary recovery, secondary recovery and enhanced recovery. In the primary recovery stage, due to large underground pressure of the oil reservoir, the crude oil can be extracted simply by drilling all the way to the reservoir where the recovery rate is up to 15%. When the underground pressures get down after the primary recovery stage, secondary methods are applied by injecting water or natural gases (air and carbon dioxide) to increase the reservoir pressure, which enhances the oil recovery rate by up to 45%. Finally, in the enhanced recovery stage, high pH solutions of surfactants, low salinity sea water are injected that cause the enhancement of oil recovery by up to 60%. This enhancement is believed to occur by wettability alteration of rock surfaces towards more hydrophilic.

In calcite oil wells, the calcite surfaces are more oil-wet than water-wet due to the presence of long-chain hydrocarbons ending with a carboxyl (–COOH) group. The typical binding energy of such hydrocarbons is larger than water molecules that induce more oil wet calcite surface14–18. Hence, in the enhanced recovery stage, when sea water is injected in the oil wells, contains of active sea water ions Mg2+, Ca2+, and SO42−. Earlier works show that injecting sea water in oil wells enhance the crude oil recovery up to 60%. For example, Zhanget al. have shown that injecting Mg2+ along with Na+ ions in oil wells enhance oil recovery to 20%. Since the temperature was kept constant when Mg2+ ion was injected in oil wells, the 20% oil recovery is caused by the activity of Mg2+ alone but not due to fluid expansion. Similarly, injecting Ca2+ ion along with SO42− ion enhances oil recovery up to 32%. The oil recovery is further enhanced up to 42% when Mg2+ ion along with SO42− ion is injected in oil wells. Similar enhancement of oil recovery due to pouring sea water in oil wells was observed by Fathi et al. Further, Fathi et al. showed that low salinity sea water (removing some of NaCl) also caused an enhancement of crude oil recovery. Sakumasetal. provided theoretical confirmations that additive ions of sea water act as a surface modifier of calcite (Mg2+ replaces Ca2+ and SO42− replaces CO32−), where relative binding of acetic acid (binding energy difference between water and acetic acid) as a representation of oil molecule is decreased. This cause enhancement of crude oil recovery due to less oil wet calcite surface. Our current work is different than Sakumasetal. in that the concentrations of Mg2+ is larger than SO42− ions in sea water, we show that additional Mg2+ can reach to the modified calcite surface and form Mg acetate, which is less sticky on the modified calcite surface. Also, theoretical predictions of enhancement of crude oil recovery due to pouring low salinity water in oil wells is not reported before.

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In this paper, we consider acetic acid as a model compound of crude-oil molecule and investigate the influence of additive ions, Ca$^{2+}$, Mg$^{2+}$, SO$_4^{2-}$ and Na$^+$ in oil recovery. We use quantum mechanical calculations based on density functional theory (DFT) and Quantum Molecular Dynamics (QMD) simulations and find that the binding energy of acetic acid is larger than water molecule on pure calcite surface, which confirms that the calcite surface is oil wet. We further find that Na$^+$ ion reach to the calcite surface as a precipitate and form Na acetate that has larger binding energy than acetic acid. This provides an explanation for the experimental observations by Fathi et al. that injecting low salinity water (removing some of Na$^+$ and Cl$^-$ ions from sea water) in oil wells enhances oil recovery. As discussed by authors in refs 24, oil recovery is enhanced when Mg$^{2+}$ ion of sea water replaces Ca$^{2+}$ of calcite and SO$_4^{2-}$ ion of sea water replaces CO$_3^{2-}$ of calcite. In this case, on modified calcite,MgSO$_4$ surface, the binding energy of acetic acid decreases and water molecule increases. Such interplay causes an enhancement of crude oil recovery on modified calcite. MgSO$_4$ surface. In sea water, the concentration of Mg$^{2+}$ ions is the largest, about twice the concentration of SO$_4^{2-}$ and about four times the concentration of Ca$^{2+}$. There are also some left over Ca$^{2+}$ ions when Mg$^{2+}$ replaces Ca$^{2+}$. Hence, in this paper we find an additional role of Mg$^{2+}$ and Ca$^{2+}$ ions on modified calcite. MgSO$_4$ surface. Our study shows that Mg$^{2+}$ ions can approach near the oil molecule and form Mg acetate on modified calcite. MgSO$_4$ surface, that also cause enhancement of crude oil recovery.

**Computational Methods**

Density Functional Theory (DFT) calculations and Quantum Molecular Dynamics (QMD) simulations are performed under periodic boundary conditions, which are implemented in the Quantum Espresso software package. Ultrafast pseudopotentials and plane wave basis set with a kinetic energy and charge density cut-off at 60 Ry and 600 Ry are used. We include exchange and correlation effects within Perdew-Burke-Ernzerhof (PBE) Functional. Van der Waals interactions are also included with the Semiempirical Grimme’s DFT-D2 corrections term. For H$_2$O and acetic acid molecule on calcite surface, we use a 3.97 Å × 5.02 Å × 30.75 Å supercell that contains three layers (60 atoms) of orthorhombic (2 × 2) calcite slab model. For Ca and Mg acetates, we use a 7.95 Å × 5.02 Å × 30.75 Å supercell that contains three layers (120 atoms) of orthorhombic (2 × 2) calcite slab model. During geometry optimization, all atoms except the bottom layer are fully relaxed until the forces on atoms are smaller than 0.01 eV/Å. We have tested several k-point sampling. Calculation at Γ-point sampling fulfills convergence criteria. The optimized lattice constant of calcite is 3.97 Å along x-direction and 5.02 Å along y-direction which are in good agreement to the experimental data. Since initial configuration of a molecule is important for finding the global minimum energy configuration, we performed quantum molecular dynamics simulations to find a reasonable initial configuration of adsorbed molecules on calcite surface. To be sure that we eventually reached the overall minimum energy configuration, 21 possible initial configurations were tested and lower energies were selected to find binding energies of adsorbed molecule on calcite surface. The VESTA program was used to draw the molecular structure. The binding energy is calculated as:

$$E_b = E_{surf} + E_{mol} - E_{surf+mol},$$  \hspace{1cm} (1)

where $E_{surf+mol}$ is the total energy of adsorbed molecule on calcite surface, $E_{surf}$ is the total energy of calcite surface alone and $E_{mol}$ is the total energy of molecule in a vacuum. The total energies of free molecules are calculated in a large size of vacuum (20 Å × 20 Å × 20 Å) by using same k-point sampling at Γ-point. The distances between the molecule and the boundaries are kept more than 8 Å to avoid any artifact interaction between molecules. For Quantum Molecular Dynamics (QMD) simulations, we used 57 H$_2$O molecules in a (7.94 Å × 10.04 Å × 21.23 Å) size of supercell, which corresponds to the experimental density of water, 1 kg/L. For QMD, we have used 0.96 femo-second as an each ionic time step, temperature re-scales to 350 K and used the same k-point sampling and energy cut-off that were used for DFT calculation.

**Results**

Oil recovery efficiency is determined by the competition between stickiness (or, the binding energies) of oil and water on the calcite surface in oil wells. Whether a calcite surface is oil-wet or water-wet is determined by the relative binding energy (binding energy difference) between water and oil molecules. For example, if the relative binding energy is negative (binding energy of oil molecule is larger than water molecule), then one can predicts more oil wet calcite surface. Decrease in relative binding energy due to low salinity water or additive ions of sea water turns calcite surface less oil wet that ultimately enhance crude oil recovery. We first calculate the binding energy of a water and an acetic acid molecules on a calcite surface. Figure 1(a,b) show the optimized water and acetic acid molecules on calcite surface with binding energies of 1.07 eV and 1.28 eV, respectively. These values are in agreement to ref 4. The binding primarily arises from the interaction between the O atom in water (acetic acid) and a Ca atom in calcite. There is also weak hydrogen bonding shown by dashed line in Fig. 1. The optimized structure of the dissociative adsorption of H$^+$ ion on a calcite surface is shown in Fig. 1(c). The two O atoms in an oil molecule (acetic acid) bind to two Ca atoms in a bidentate configuration. The non-dissociated acetic acid (acetic acid retains its hydrogen (Fig. 1(b))) is stable by 0.08 eV, compared to dissociated acetic acid (acetic acid loses its hydrogen to the calcite surface (Fig. 1(c))). The binding energy of a dissociated acetic acid, (E$_b$(RCOO$^-$)) is 2.10 eV, which suggest that the oil molecule is extracted in the form of non-dissociated acetic acid. Note that the binding of acetic acid is larger than water by 0.21 eV, which confirms that the calcite surface is oil wet (hydrophobic).

Fathi et al. in ref 3 reported that injecting low salinity sea water (removing some of NaCl from sea water) in oil wells enhances the oil recovery. We consider that Na$^+$ can reach to the calcite surface with a pre-adsorbed dissociated acetic acid and forms a Na acetate molecule. The optimized structure of Na acetate on the calcite surface is shown in Fig. 2. The binding energy of Na acetate on a calcite surface is 2.04 eV. Considering that it takes only 1.28 eV to desorb an oil molecule, the existence of Na$^+$ makes oil significantly stickier. This provides an...
explanation to the experimental results in that injecting low salinity sea water (or, removing some of NaCl from sea water) enhances oil recovery.

In ref.2 of Fig. 5, Zhang et al. reported that injecting Mg$^{2+}$ alone enhances oil recovery by approximately up to 20%. Note that in ref.2 of Fig. 5 on day 53, the temperature was kept constant, which suggest that the enhancement of crude oil recovery is not due to fluid expansion but due to the influence of Mg$^{2+}$ alone. Hence, we investigated the role of Mg$^{2+}$ ions in oil recovery. There are two possibilities for Mg$^{2+}$ ions in oil recovery: (i) Mg$^{2+}$ can reach to the calcite surface near the oil molecule and form Mg-acetate, as shown in Fig. 3(a) and (ii) Mg$^{2+}$ replaces Ca$^{2+}$ as shown in Fig. 3(b) (proposed in refs2-4). The binding energy of a Mg acetate molecule is 2.39 eV. As a Mg acetate contains two oil molecules, the effective binding energy of a Mg-modified oil molecule is 1.19 eV. Comparing with the binding energy of the original oil molecule (1.28 eV), oil molecule in the form of Mg-acetate is less sticky which benefits the oil recovery. As suggested in refs2-4, Mg$^{2+}$ of sea water may replaces Ca$^{2+}$ of calcite. In this case as shown in Fig. 3(b), the binding energy of acetic acid on modified calcite surface is 1.33 eV but at the same time, the binding energy of water molecule also increases to 1.15 eV, which is shown in Fig. 3(c). Hence, the relative binding energy (binding energy difference between water and oil molecule) on modified Mg-calcite surface is larger than the relative binding energy of acetic acid on modified Mg-calcite surface (−0.18 eV vs −0.21 eV), which is also beneficial for enhancing oil recovery. However the relative binding energy of Mg-acetate on pure calcite surface is larger than the relative binding energy of acetic acid on modified Mg-calcite surface (−0.12 eV vs −0.18 eV). Hence extracting oil molecule in the form of Mg acetate predicts the experimental result for the enhancement of crude oil by 20% due to having Mg$^{2+}$ alone in oil wells (see ref.2 of Fig. 5).

Figure 1. The atomic structures of the adsorption of (a) a H$_2$O molecule, (b) a dissociated acetic acid molecule, and (c) an acetic acid molecule.

Figure 2. The atomic structure of Na acetate on a calcite surface. The binding energy of Na acetate is 2.04 eV, which is larger than original oil molecule (acetic acid) (2.10 eV vs 1.28 eV). Hence, Na$^+$ ions of sea water makes oil molecule more sticker that reduce the crude oil recovery.
In Fig. 4(a), we consider that either replaced Ca\(^{2+}\) ions by Mg\(^{2+}\) ions during surface modification or excess Ca\(^{2+}\) ions of sea water can also reach to the calcite surface and forms Ca acetate. The binding energy of a Ca acetate molecule is 2.52 eV. As a Ca acetate contains two oil molecules, the effective binding energy is 1.26 eV per modified oil molecule. Comparing to the 1.28 eV binding energy of the original oil molecule, the existence of Ca\(^{2+}\) ions in seawater make oil less sticky. However, as the energy difference is negligibly small, the effect in oil recovery may not be useful. In ref.\(^{2}\) of Fig. 5, Zhang et al. also reported that injecting Ca\(^{2+}\) along with sulfate ions on day 43 enhances oil recovery by approximately up to 24%. Note that sulfate ions alone have no effect in the oil recovery but oil recovery enhances when sulfate ions along with Ca\(^{2+}\) ions injected. Hence, we investigated the role of Ca\(^{2+}\) along with sulfate ions in oil recovery. Similar to Fig. 4(a), we consider that Ca\(^{2+}\) ions reach to the calcite surface.

| Surface       | \(E_b\) (HO) | \(E_b\) (acetic acid) | \(E_b\) (Mg acetate) | \(E_b\) (Ca acetate) |
|---------------|--------------|-----------------------|----------------------|----------------------|
| calcite       | 1.07         | 1.28                  | 2.39                 | 2.52                 |
| calcite.Mg    | 1.15         | 1.33                  | 2.38                 | 2.57                 |
| calcite.SO\(_4\) | 0.96       | 1.09                  | 2.30                 | 2.45                 |
| calcite.MgSO\(_4\) | 1.13     | 1.22                  | 2.31                 | 2.47                 |

Table 1. Binding energies (eV) of water, acetic acid, Mg acetate and Ca acetate on pure calcite and modified calcite surfaces. The relative binding energy (i.e., the binding energy difference between water and oil molecule) is used in Eq. (3) to calculate the contact angle.
and forms Ca acetate and then SO$_4^{2-}$ ion replaces CO$_3^{2-}$. The optimized structure of Ca acetate on modified calcite, SO$_4$ surface is shown in Fig. 4(b). The binding energy of Ca acetate on modified calcite.SO$_4$ surface is 2.45 eV and its effective value per modified oil molecule is 1.22 eV. Since the binding energy of original oil molecule is larger than Ca modified oil molecule (1.28 eV vs 1.22 eV), the crude oil recovery is expected to be enhanced.

Finally, we explore the interplay effect of Mg$^{2+}$, Ca$^{2+}$ and SO$_4^{2-}$ ions on oil recovery. Experimental observations in ref. 2 of Fig. 5 by Zhang et al. reported that injecting Mg$^{2+}$ along with SO$_4^{2-}$ ions leads the enhancement of crude oil recovery by approximately up to 32%. Hence, there are three possibilities for the role of Mg$^{2+}$ and SO$_4^{2-}$ ions in oil recovery: (i) Mg$^{2+}$ replaces Ca$^{2+}$ and SO$_4^{2-}$ replaces CO$_3^{2-}$ ref. 24, (ii) the replaced Ca$^{2+}$ ions from calcite and additional Ca$^{2+}$ ions present in sea water can form Ca acetate on modified calcite.MgSO$_4$ surfaces, and (iii) the additional left over Mg$^{2+}$ ions that could not find CO$_3^{2-}$ ions during surface modification forms Mg acetate on modified calcite.MgSO$_4$ surfaces. In Fig. 5, we have presented the optimized structure of acetic acid (Fig. 5(a)), Ca acetate (Fig. 5(b)) and Mg acetate (Fig. 5(c)) on modified calcite.MgSO$_4$ surface. To compare the binding energy difference between water and oil molecule on modified calcite.MgSO$_4$ surface, we present the optimized relaxed structure of water molecule on modified calcite.MgSO$_4$ surface in Fig. 5(d) that has binding energy of 1.13 eV. The binding energies of acetic acid, Ca acetate per oil molecule and Mg acetate per oil molecule are 1.22 eV, 1.23 eV and 1.15 eV, respectively. By comparing to the binding energy of original oil molecule on pure calcite surface (1.28 eV), the extracted oil molecules in the form of acetic acid, Ca acetate and Mg acetate from the modified calcite.MgSO$_4$ surfaces are all helpful for enhancing crude oil recovery. But, oil extraction in the form of Mg acetate from modified calcite.MgSO$_4$ surface maximize the enhancement of crude oil recovery because of its lowest binding energy of 1.15 eV.

Enhancement of crude oil recovery is usually determined by measuring contact angle of oil molecule on calcite surface. Contact angles of water droplets on calcite surface in oil wells provides ideal situation to examine the energetics of solid surface. Using Young's equation$^{24-26}$, from schematic of Fig. 6(a), the contact angle for three phases (calcite surface-oil-water) system can be calculated by the Young's equation:

\[
\theta = \gamma_{so} \sin \theta + \gamma_{sw} \cos \theta - \gamma_{ow}
\]

where $\theta$ is the contact angle, $\gamma_{so}$, $\gamma_{sw}$ and $\gamma_{ow}$ are the interfacial tensions of solid surface-oil, solid surface-water and oil-water respectively.
where $\gamma_{os}$ is the interfacial tension between oil and calcite surface, $\gamma_{ws}$ is the interfacial tension between water and calcite surface, $\gamma_{ow}$ is the interfacial tension between oil and water. For acetic acid as a model compound of oil molecule, $\gamma_{ow} = 0.001$ eV/Å$^2$ is used. The change in interfacial tension, $\Delta \gamma$ caused by additives Mg$^{2+}$ and SO$_4^{2-}$ ions substitution in proximity, is estimated by the changes in the binding energy (for numerical values, see Table 1) per unit area for oil and water molecule on pure calcite and on modified calcite surfaces as:

$$\theta = \gamma_{os} - \gamma_{ws} \cos \theta = 0,$$

where $\gamma_{os}$ is the interfacial tension between oil and calcite surface, $\gamma_{ws}$ is the interfacial tension between water and calcite surface, $\gamma_{ow}$ is the interfacial tension between oil and water. For acetic acid as a model compound of oil molecule, $\gamma_{ow} = 0.001$ eV/Å$^2$ is used. The change in interfacial tension, $\Delta \gamma$ caused by additives Mg$^{2+}$ and SO$_4^{2-}$ ions substitution in proximity, is estimated by the changes in the binding energy (for numerical values, see Table 1) per unit area for oil and water molecule on pure calcite and on modified calcite surfaces as:

$$\Delta \gamma = \frac{\Delta E_{os} - \Delta E_{ws}}{\gamma_{ow} A},$$

where $A$ is the surface area. Since, additive ions Mg$^{2+}$ and SO$_4^{2-}$ present parts per million in sea water, we made approximation that only 5% additive ions participate in the wettability alteration of calcite surface. In Fig. 6(b), the contact angle change on modified calcite surface due to additives Mg$^{2+}$ and SO$_4^{2-}$ ions of sea water from the reference value of the contact angle, $\theta = 90^\circ$ (mixed oil-water-wet) is shown. In Fig. 6(b), it can be seen that maximum oil recovery can be achieved for a case when Mg$^{2+}$ replaces Ca$^{2+}$ and SO$_4^{2-}$ replaces CO$_3^{2-}$ (contact angle change $\approx 74^\circ$). This result explains the experimental observations by Zhang et al.$^2$ of Fig. 5 in that the interplay between Mg$^{2+}$ and SO$_4^{2-}$ ions in wettability alteration of calcite enhances crude oil recovery. The wettability alteration depends on the presence of Mg$^{2+}$ and SO$_4^{2-}$ ions in sea water. For example, in Table 2, we summarize the

| Surface         | Contact angle for water | Contact angle for acetic acid |
|-----------------|-------------------------|-------------------------------|
| Calcite.Mg      | 84.9° (water wet)       | 98.4° (oil wet)               |
| Calcite.MgSO$_4$| 86.2° (less water wet)  | 79.9° (water wet)             |

Table 3. Change in contact angle for Solid-Liquid-Vapor (SLV) phases by considering 10% of wettability alteration due to additive ions of sea water and ideal case for initial mixed oil wet calcite surface, $\theta = 90^\circ$.  

\[ \gamma_{os} = \gamma_{ws} - \gamma_{ow} \cos \theta = 0, \]  
\[ \Delta \gamma = \frac{\Delta E_{os} - \Delta E_{ws}}{\gamma_{ow} A}, \]
contact angle change by considering 1% and 10% coverage of these additive ions in oil wells. Here, it is clear that the contact angle changes from hydrophobic (oil wet) to mixed oil wet (θ < 135°) calcite surface.

For idealistic case of solid-liquid-vapor (air) phase, we can express Eq. (2) in terms of work of adhesion,

\[ W_{SL} = \gamma_{LV}(1 + \cos \theta), \]

where \( W_{SL} = \gamma_{SV} - \gamma_{SL} \). Here S, V, L corresponds to solid, vapor and liquid phases. By writing work of adhesion in terms of binding energy per unit area, we can express Eq. 4 as

\[ 1 + \cos \theta = \frac{E_b}{A \gamma_{LV}}. \]

The contact angle change for water and acetic acid oil molecule is listed in Table 3. Here we have used \( \gamma_{LV} = 72.8 \text{ dyn/cm} \) for water vapor phase and \( \gamma_{LV} = 27.3 \text{ dyn/cm} \) for acetic acid vapor phase. Here we have applied a concept that the larger binding energy on modified calcite surface for water turn the surface towards hydrophilic, while as the larger binding energy for acetic acid turns the surface towards hydrophobic. From Eq. 5, we have estimated the contact angle change and listed in Table 3. Here we also find that the contact angle change for acetic acid turns towards hydrophilic when wettability alterations occur due to Mg\(^{2+}\) and SO\(_4^{2-}\) ions.

A comment on the molecule extracted in the form of Mg and Ca acetates. In aqueous conditions, these acetate molecules dissociate into acetate ions. Then Mg\(^{2+}\) and Ca\(^{2+}\) ions can again reach to the oil molecule near the calcite surface and again modify oil molecules in the form of Mg and Ca acetate, which process is acting as a catalyst. Dissociation of Mg and Ca from Mg-acetate and Ca-acetate in water at different temperatures are reported by a number of authors in refs\(^{27,28}\).

We have so far investigated the wettability alteration of calcite surface due to additive ions of sea water that has greater influence in the enhancement of crude oil recovery. Now, using quantum molecular dynamics simulations, we investigate the probability of forming the oil molecule as Na, Mg, Ca acetates on the pure calcite and modified calcite(Mg, calcite.SO\(_4\), calcite.MgSO\(_4\)) surfaces. We use the following reaction mechanism:

\[
\text{calcite} \cdot \text{RCOOH} + \text{Na}^+(\text{H}_2\text{O})_n \rightleftharpoons \text{calcite} \cdot \text{RCOONa} + H^+(\text{H}_2\text{O})_n. \tag{6}
\]

\[
\text{calcite} \cdot (\text{RCOOH})_2 + \text{Mg}^{2+}(\text{H}_2\text{O})_n \rightleftharpoons \text{calcite} \cdot \text{Mg(RCOO)}_2 + H^+(\text{H}_2\text{O})_nH^+, \tag{7}
\]

\[
\text{calcite} \cdot \text{RCOOH} + \text{Mg}^{2+}(\text{H}_2\text{O})_n \rightleftharpoons \text{calcite} \cdot \text{MgRCOOH} + \text{Ca}^{2+}(\text{H}_2\text{O})_n, \tag{8}
\]

\[
\text{calcite} \cdot (\text{RCOOH})_2 + \text{Ca}^{2+}(\text{H}_2\text{O})_n \rightleftharpoons \text{calcite} \cdot \text{Ca(RCOO)}_2 + H^+(\text{H}_2\text{O})_nH^+, \tag{9}
\]

\[
\text{calcite} \cdot (\text{RCOOH})_2 + \text{SO}_4^{2-} + \text{Ca}^{2+}(\text{H}_2\text{O})_n \rightleftharpoons \text{calcite} \cdot \text{SO}_4\text{Ca(RCOO)}_2
\]
\[+\text{CO}_3^{2-} + H^+(\text{H}_2\text{O})_nH^+. \tag{10}\]

\[
\text{calcite} \cdot \text{RCOOH} + \text{Mg}^{2+}(\text{H}_2\text{O})_n + \text{SO}_4^{2-} \rightleftharpoons \text{calcite} \cdot \text{MgSO_4RCOOH}
\]
\[+\text{CO}_3^{2-} + \text{Ca}^{2+}(\text{H}_2\text{O})_n. \tag{11}\]

\[
\text{calcite} \cdot (\text{RCOOH})_2 + \text{Ca}^{2+}(\text{H}_2\text{O})_n + \text{Mg}^{2+}(\text{H}_2\text{O})_n + \text{SO}_4^{2-} \rightleftharpoons \text{calcite} \cdot \text{MgSO_4Ca(RCOO)}_2 + \text{CO}_3^{2-} + H^+(\text{H}_2\text{O})_nH^++\text{Ca}^{2+}(\text{H}_2\text{O})_n, \tag{12}\]

\[
\text{calcite} \cdot (\text{RCOOH})_2 + 2\text{Mg}^{2+}(\text{H}_2\text{O})_n + \text{SO}_4^{2-} \rightleftharpoons \text{calcite} \cdot \text{Mg}_2\text{SO_4RCOOH}_2 + \text{CO}_3^{2-} + H^+(\text{H}_2\text{O})_nH^++\text{Ca}^{2+}(\text{H}_2\text{O})_n. \tag{13}\]

In Fig. 7, total energy vs simulation time of left hand side of reactions [(7)-(13)] are shown by solid black lines and right hand side of reactions [(7)-(13)] are shown by red dotted lines. For charged systems, we used a compensating jellium background; which is widely used for total energy calculations of charged systems.

From Fig. 7, it is clear that the reactions (8), (9), (10), (12) are endothermic. It means these reactions do not take place in normal reservoir conditions and thus the additive ions of sea water in the form of calcium acetate and magnesium acetate on pure calcite surface, calcium acetate on calcite.S04 and calcite.MgSO4 do not take place. This suggest that the products formed in these reactions may not be energetically preferred and may not have much influence in oil recovery.

On the other hand, from Fig. 7, it is clear that the reactions (6) may be exothermic, where good amount of Na\(^+\) can reach to the calcite surface and form Na acetate. Since the binding energy of Na acetate is larger than original oil molecule, having Na\(^+\) ions in sea water clearly reduce the oil recovery. Similarly, from Fig. 7, it is also clear that the reactions (7), (8), (13) may also be exothermic. Hence Mg\(^{2+}\) and SO\(_4^{2-}\) ions of sea water modify the calcite surface, where the binding energy of oil molecule on these modified calcite surface is smaller than on for pure calcite surface, which enhance the crude oil recovery.
Conclusions
In summary, using quantum mechanical calculations based on density functional theory, we investigated the role of Na\(^+\), Ca\(^{2+}\), Mg\(^{2+}\) and SO\(_4^{2-}\) ions of sea water on oil recovery at the atomic scale. We find that Na\(^+\) ions form Na acetate with oil molecules that make calcite surface more oil-wet which, is harmful to oil recovery. On the other hand, Mg\(^{2+}\) and SO\(_4^{2-}\) ions of sea water modify the calcite surface and the additional left over Mg\(^{2+}\) ions that could not find SO\(_4^{2-}\) ions during surface modification, form Mg acetate on modified calcite. MgSO\(_4\) surfaces. This makes the original oil molecule much less sticky on the modified calcite surface. This enhance the crude oil recovery. Finally, by using Quantum Molecular Dynamics simulations, we have shown that having Na\(^+\) ion in sea water may reach to the calcite surface and form NaNacetate (exothermic). We have also shown that surface modification occurs due to having Mg\(^{2+}\) and SO\(_4^{2-}\) in sea water (exothermic).

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Acknowledgements
S.P. and R.M. were supported by the Natural Sciences and Engineering Research Council (NSERC) of Canada, the Canada Research Chair (CRC) program. R.M. was supported by the Bizkaia Talent Grant under the Basque Government through the BERC 2014–2017 program, as well as Spanish Ministry of Economy and Competitiveness MINECO: BCAM Severo Ochoa excellence accreditation SEV-2013-0323. S.P. was partially supported by NSF under Grants No. Phy-1415600.

Author Contributions
S.P. and R.M. proposed the idea and wrote the manuscript.

Additional Information
Competing Interests: The authors declare that they have no competing interests.

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