Molecular dynamic simulations and DFT calculations on the effects of four inhibitors on the scaling of CaCO$_3$ molecules

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Abstract. Molecular dynamic simulations and DFT (with GGA and PBE functional) calculations were used to study two effects of four inhibitors on the scaling of CaCO$_3$. The first effect studied was the determination of the occurrence of the occupation of a position of a CaCO$_3$ molecule by an inhibitor molecule in the scaling of pipes. This phenomenon was shown to occur by the minimum distance between the scaling surface and the free molecules (the CaCO$_3$ or the inhibitors). The binding energy between the surfaces and free molecules showed that the intensity of adsorption of the inhibitors on the surfaces is stronger than the adsorption of CaCO$_3$ on the surfaces. The main connection mode between the inhibitor and the surfaces is an induction force (when the molecules are adsorbed on a Fe surface) or an electrostatic force and a hydrogen bond force (when molecules are adsorbed on a Fe$_2$O$_3$ and a calcite surface). The second effect studied in this work was the interaction between CaCO$_3$ molecule and the carboxyl of the inhibitor molecules. The values of the binding energy illustrate that this adsorption can occur spontaneously. The calcium ion of the CaCO$_3$ connects to the oxygen atom of the carbonyl of the carboxyl by a coordination bond. The carbonate ion of CaCO$_3$ connects to the hydrogen atom of the carboxyl by a hydrogen bond.

1. Introduction

Scaling in pipes is a main factor affecting the safety of oil and gas fields, and CaCO$_3$ is one of the main components of the scale that forms in the pipes. Chemical inhibitors are widely used in the oil industry to reduce the amount of scale formation. Four chemical inhibitors, polyacrylic acid (PAA), hydrolyzed polymaleic anhydride (HPMA), polyepoxysuccinic acid (PESA) and polyaspartic acid (PASP), are commonly used in CaCO$_3$ scale inhibition [1-5].

Scaling in the walls of pipes occurs in two steps. The first step is the formation of a CaCO$_3$ crystal nucleus, which can form on the walls in two ways: (1) the CaCO$_3$ molecules can adsorb on the active sites of the surface of the wall; or (2) the CaCO$_3$ can adsorb on suspended particles and can then be deposited on the surfaces of the wall [6,7]. The second step is CaCO$_3$ crystal growth. As the number of CaCO$_3$ molecules adsorbed on the crystal nucleus increases, the volume of the crystal becomes larger. In addition, according to Periodic Bond Chain theory, there are three types of crystal growth surfaces: K, S and F type growth surfaces. The adsorption of the CaCO$_3$ molecule on the different types of growth surfaces have different properties [8]. Sketches of the solid surfaces used in this paper are...
shown in figure 1.

![Figure 1. Sketches of the three types of growth surfaces (red part): K-type growth surface (a), S-type growth surface (b) and F-type growth surface (c).](image)

The effect of an inhibitor on the CaCO$_3$ scale formation has two modes: direct inhibition and indirect inhibition. In direct inhibition, the inhibitor molecules occupy active sites on the surfaces of the metal and the suspended calcites and prevent the adsorption of a CaCO$_3$ molecule on these surfaces. In indirect inhibition, the CaCO$_3$ molecules adsorb on the suspended segments of inhibitor molecules and cannot approach the active sites of the surfaces.

In this paper, three types of solid surfaces (i.e. Fe, Fe$_2$O$_3$ and calcite), CaCO$_3$ and four inhibitor molecules were first built using software. Then, molecular dynamic programs were used to simulate adsorption between the CaCO$_3$ and the inhibitor molecules on the active sites of the solid surfaces. The minimum distance between the molecules and each type of growth surface was measured by radial distribution functions to verify the inhibitor’s ability to occupy an active site of the surfaces. Then, the intensity of adsorption between the molecules and the surface was evaluated by the binding energy and the connection mode. Finally, the connection between the CaCO$_3$ and the inhibitor molecules were studied.

2. Molecular models setup and simulation details

2.1. Modules and force field

Materials Studio 7.0 software packages, which include Discover, Forcite and DMol3 modules, were applied in this paper. The Discover module was used to optimize the structures of the system components. The Forcite module was used for simulation of the molecular dynamics of the system. The force field used in molecular dynamics simulation was the COMPASS force field, which is the first parameterized and validated ab initio force field [9-11]. The DMol3 module was used for investigating the interaction between the CaCO$_3$ and the inhibitor molecules. The functional and the basis set used in DMol3 were GGA and PBE and DNP (basis file is 3.5) respectively. The basis set used in DMol3 module was DNP. The basis file was 3.5.

2.2. Molecular models and simulation details

The (110) surface of Fe, (104) surface of Fe$_2$O$_3$ and calcite were selected in this paper [12-21]. Each solid surface contained three types of growth surfaces namely K, S and F type growth surface. All the solid surfaces were built by cleaving the surface of each crystal, which were imported from the structural database of Materials Studio software. The vacuum region distance of each surface was set to 120 Å. The dimensions of used Fe, Fe$_2$O$_3$ and calcite box were (79.436 Å, 79.436 Å, 126.0806 Å), (73.9709 Å, 75.525 Å, 127.2789 Å) and (80.9581 Å, 79.84 Å, 127.6306 Å) respectively. Then specific atoms were deleted in the K and S surfaces. The CaCO$_3$, PAA, HPMA, PESA and PASP molecules were built and moved on each surface manually. All the types of growth surfaces and inhibitor molecules used in this paper are shown in figures 2 and 3, respectively.
Figure 2. The K-type growth surfaces (a, d, g), S-type growth surfaces (b, e, h) and F-type growth surfaces (c, f, i) of Fe (a, b, c), Fe$_2$O$_3$ (d, e, f) and calcite (g, h, i). (Oxygen atom: red; iron atoms: blue; carbon atoms: gray; calcium atoms: green. For the interpretation of the references to color in this figure legend, the reader is referred to the web version of this article).

Figure 3. Molecular structure of PAA (a), HPMA (b), PESA (c) and PASP (d). (Oxygen atom: red; hydrogen atoms: white; carbon atoms: gray; nitrogen atoms: blue).
For the projects of the adsorption of a CaCO$_3$ or inhibitor molecule on the solid surfaces, all of the atoms of the surfaces were set to “fixed”, and the CaCO$_3$ or the inhibitor molecules were set to “free” [22]. For the projects of the interaction between a CaCO$_3$ and an inhibitor molecule, all the atoms were set to “free”. In all of the projects, the charge and force field types were assigned to each atom first; then, the energy minimization program was run using the smart minimizer method with the ultra-fine convergence level. The smart minimizer method begins with the steepest descent method, followed by the conjugate gradient method, and it ends with a Newton method. The minimization program step of each project was set to 20000.

After the energy minimization of each project was completed, the MD simulation was performed under the periodic boundary conditions and the NVT canonical ensemble with a time step of 1 fs. The temperature and run time were set to 343 K and 30 ps respectively. The figures of adsorption of CaCO$_3$, PAA, HPMA, PESA and PASP on the K-type surfaces of Fe$_2$O$_3$ and calcite are shown in figure 4.
Figure 4. The result of adsorption of CaCO$_3$ (a, b), PAA (c, d), HPMA (e, f), PESA (g, h) and PASP (i, j) on the K-type surface of Fe$_2$O$_3$ (a, c, e, g, i) and calcite (b, d, f, h, j).

3. Results and discussion

3.1. Equilibrium criteria
The equilibria of all the projects were simultaneously ascertained by the criteria of temperature and energy, limiting the extent of the fluctuations of temperature and energy to less than 10% [3,23,24].

The temperature and energy fluctuation curves of the adsorption of PASP on the K type surface of Fe$_2$O$_3$ and the interaction between the CaCO$_3$ and the PASP molecules were selected as examples and are shown in figures 5 and 6, respectively.

Figure 5. The temperature fluctuation curve of the adsorption of PASP on the K-type surface of Fe$_2$O$_3$ (a) and the interaction between CaCO$_3$ and PASP molecule (b).

As shown in figure 5, the temperature fluctuation of the adsorption project and the interaction project in the last 5 ps of the simulation periods were 315 K-365 K and 314 K-371 K, respectively. These results indicate that the temperature fluctuation reached the equilibrium criterion, because the initial temperature was 343 K and that the extent of temperature fluctuation was less than 34 K. As
shown in the example in figure 6, the total energy fluctuation in the last 5 ps of the simulation period for the first project ranged from -611 to -589 kcal mol\(^{-1}\) and from -974 to – 961 kcal mol\(^{-1}\) for the second project. The total energy fluctuation curves of each project in the last 5 ps period had a relatively flat trajectory, which indicates that the simulation projects had reached energy equilibration and the results of the projects are reliable.

**Figure 6.** The total energy (the upper blue curve), kinetic energy (the red curve), non-bond energy (the green curve) and potential energy (the under blue curve) of the adsorption of PASP on the K-type surface of Fe\(_2\)O\(_3\) (a) and the interaction between the CaCO\(_3\) and the PASP molecules (b).

### 3.2. Interaction between free molecules and solid surfaces

To understand the interactions between the CaCO\(_3\) and the inhibitor molecules with the solid surfaces, two aspects were analyzed. The first aspect was the measurement of the minimum distance between the molecules and the solid surfaces to determine if the inhibitors’ occupation of the active sites of the solid surfaces prevents the CaCO\(_3\) molecules from entering the space between the inhibitors and the surfaces. The second aspect was to calculate the binding energy between the molecules and the solid surfaces to determine the tendency and intensity of the adsorption of the CaCO\(_3\) and the inhibitor molecules on the solid surfaces.

**3.2.1. The minimum distance between the molecules and the solid surfaces.** The minimum distance between the inhibitor molecule and the growth surface is the key factor in confirming the inhibitor molecule’s occupation of the active site on the growth surface.

The atoms of the red surface in figure 1 were selected as the active site of each solid surface. The K type and the S type growth surfaces were divided into three and two parts, respectively, as shown in figure 7. The distance between the molecules and each part of the surface was measured individually by the radial distribution function (RDF). The minimum distance between the molecules and the growth surfaces are shown in table 1.

**Figure 7.** Parts of the K-type growth surface (left) and the S-type growth surface (right).
Table 1. Minimum distance between molecules and growth surfaces (Å).

|                  | CaCO$_3$ | PAA | HPMA | PESA | PASP |
|------------------|----------|-----|------|------|------|
| **Fe$_2$O$_3$ (104) surface** |          |     |      |      |      |
| K-type-A         | 2.49     | 3.43| 2.49 | 2.88 | 3.05 |
| K-type-B         | 2.19     | 1.70| 1.61 | 1.66 | 1.72 |
| K-type-C         | 2.97     | 2.70| 2.86 | 3.07 | 2.61 |
| S-type-A         | 2.08     | 1.57| 1.79 | 1.72 | 1.62 |
| S-type-B         | 3.41     | 2.65| 2.75 | 1.62 | 2.17 |
| F-type           | 2.44     | 1.55| 1.66 | 1.59 | 1.62 |
| **Fe (110) surface** |          |     |      |      |      |
| K-type-A         | 2.89     | 2.15| 2.41 | 2.49 | 2.99 |
| K-type-B         | 3.31     | 2.67| 1.87 | 2.53 | 2.53 |
| K-type-C         | 2.97     | 2.37| 2.07 | 2.23 | 2.37 |
| S-type-A         | 2.85     | 2.49| 2.51 | 1.79 | 2.53 |
| S-type-B         | 2.95     | 2.45| 2.43 | 2.11 | 2.79 |
| F-type           | 2.67     | 2.17| 1.85 | 2.25 | 1.87 |
| **Calcite (104) surface** |          |     |      |      |      |
| K-type-A         | 1.89     | 2.49| 1.35 | 1.25 | 1.37 |
| K-type-B         | 3.41     | 1.47| 1.35 | 1.29 | 1.39 |
| K-type-C         | 1.93     | 1.37| 1.43 | 1.37 | 1.27 |
| S-type-A         | 1.95     | 1.25| 1.27 | 1.29 | 1.29 |
| S-type-B         | 1.93     | 1.37| 1.27 | 1.31 | 1.51 |
| F-type           | 1.91     | 1.33| 1.25 | 1.27 | 1.25 |

It is noted that most of the values of the distance between the inhibitors and the surfaces were less than the values of the distance between the CaCO$_3$ and the surfaces, i.e., no CaCO$_3$ could enter the space between the inhibitor and the solid surface. However, most of the values of the distance between the inhibitors and part A of the K type growth surfaces of the solid were larger than the values of the distance between the CaCO$_3$ and these surfaces, especially between PAA and part A of the K type growth surface of Fe$_2$O$_3$. Therefore, an atom of CaCO$_3$, which was farthest from part A of the K type growth surface of the solid, was selected. The distances between these atoms of CaCO$_3$ and the solid surfaces were calculated and are shown in table 2.

Table 2. Largest distance between an atom of CaCO$_3$ and part A of the K type growth surface of the solid.

| surface         | Atom of CaCO$_3$ | Distance (Å) | The angle to the normal (°) | Normal distance (Å) |
|-----------------|------------------|--------------|-----------------------------|---------------------|
| Fe (110)        | O                | 5.101        | 15.633                      | 4.912               |
| Fe$_2$O$_3$ (104) | Ca              | 6.433        | 32.762                      | 5.410               |
| Calcite (104)   | O                | 4.399        | 31.165                      | 3.764               |

As shown in table 2, all of the values of the normal distance were larger than the values of the distance between the inhibitor and the surface minus the values of the distance between the CaCO$_3$ and the surface, which means that the CaCO$_3$ cannot enter the gap between the inhibitor and part A of the K type growth surface.

3.2.2. Binding energy and connection mode between the molecules and the solid surfaces. The binding energy is an important factor that was used to determine the tendency and intensity of the interactions.

The binding energy was calculated by equations (1) and (2) [25]:

\[ \Delta E = E_{\text{two components}} - (E_{\text{first component}} + E_{\text{second component}}) \]  \hspace{1cm} (1)
\[ \Delta E_b = -\Delta E \]  \hspace{1cm} (2)
where $\Delta E$ is the interaction energy between the two components, $E_{\text{two components}}$ is the energy of the system that contains these components, and $E_{\text{first component}}$ and $E_{\text{second component}}$ are the single point energy of each component. The binding energy, $\Delta E_b$, was calculated as the negative value of the interaction energy and is shown in Table 3.

### Table 3. The binding energy between the molecules and the surface (kcal mol$^{-1}$).

|                        | CaCO$_3$   | PAA      | HPMA     | PESA     | PASP     |
|------------------------|------------|----------|----------|----------|----------|
| **Fe$_2$O$_3$ (104) surface** |            |          |          |          |          |
| K type                 | 118.313    | 138.274  | 188.277  | 273.208  | 407.776  |
| S type                 | 87.293     | 122.969  | 228.138  | 286.879  | 309.661  |
| F type                 | 40.869     | 80.705   | 141.762  | 164.132  | 229.371  |
| **Fe (110) surface**   |            |          |          |          |          |
| K type                 | 32.876     | 351.287  | 507.103  | 842.422  | 1175.883 |
| S type                 | 31.347     | 347.522  | 653.798  | 891.529  | 1137.326 |
| F type                 | 26.008     | 318.62   | 675.055  | 552.603  | 1190.445 |
| **Calcite (104) surface** |           |          |          |          |          |
| K type                 | 255.833    | 312.739  | 780.453  | 1186.546 | 917.913  |
| S type                 | 287.908    | 442.586  | 891.726  | 1218.547 | 1178.755 |
| F type                 | 118.394    | 160.499  | 348.941  | 454.104  | 561.119  |

All of the values in Table 3 are positive, which means that all of the adsorptions occur spontaneously. In addition, the values of the binding energy between the inhibitors and the solid surfaces were larger than the values of the binding energy between the CaCO$_3$ and the solid surfaces. This result means that the tendency and the intensity of the adsorption of the inhibitors on the solid surfaces were stronger than the CaCO$_3$, i.e., the inhibitor molecules can occupy the active sites on the solid surfaces and prevent the CaCO$_3$ crystal nucleus formation and growth.

Since all of the atoms on the Fe surface were electroneutral and the molecules (the CaCO$_3$ and the inhibitors) were polar, the main interactive force between the Fe surface and the free molecules was the van der Waals force, especially the induction force. For the Fe$_2$O$_3$ and the calcite surfaces, all of the atoms on these surfaces had charge. Therefore, the electrostatic force was the main force between the molecules and these surfaces. In addition, there were many oxygen atoms on the surfaces and carboxyl groups in the inhibitor molecules; hence, when an inhibitor molecule adsorbed on the surface, a hydrogen bond formed. Thus, a hydrogen bond is the other main force between the inhibitor and the surfaces, as shown in Figure 8.

**Figure 8.** Hydrogen bonds (blue dotted line) when PESA adsorbs on the Fe$_2$O$_3$ surface (a) and PASP adsorbs on the calcite surface (b).

### 3.3. Interaction between the CaCO$_3$ and the Inhibitor Molecules

The mode of the interaction between the CaCO$_3$ and the inhibitor is the indirect inhibition mode, i.e., the CaCO$_3$ adsorbs on the inhibitor molecule’s chain rather than adsorbing onto the solid surface. The
molecular dynamic simulation results of the interaction between the CaCO$_3$ and the inhibitor molecules are shown in figure 9.

![Figure 9. The interaction between CaCO$_3$ and PAA (a), HPMA (b), PESA (c) and PASP (d).](image)

It can be seen from figure 9 that the CaCO$_3$ molecules interact preferentially with the carboxyl groups of the inhibitor molecules, which the Ca$^{2+}$ ions of the CaCO$_3$ interact with the oxygen atoms of the carbonyl of the carboxyl groups, while the oxygen ions of the CaCO$_3$ interact with the hydrogen atoms of the carboxyl group. The calculated quantum parameters for interaction between inhibitor and CaCO$_3$ molecule are shown in table 4.

**Table 4.** The calculated quantum parameters for interaction between inhibitor and CaCO$_3$ molecule.

|                  | PAA     | HPMA    | PESA    | PASP    |
|------------------|---------|---------|---------|---------|
| Binding energy   | 123.034 | 164.412 | 171.534 | 207.144 |
| Ca-O Bond length | 2.186   | 2.174   | 2.242   | 2.227   |
| Ca charge change | 0.21    | 0.22    | 0.21    | 0.21    |
| O charge change  | -0.16   | -0.16   | -0.16   | -0.14   |
| H-O Bond Mulliken population | 0.46 | 0.46 | 0.48 | 0.49 |
| H-O Bond length  | 1.048   | 1.043   | 1.025   | 1.012   |
| H charge change  | -0.08   | -0.05   | -0.07   | -0.07   |
| O charge change  | -0.08   | -0.04   | -0.05   | -0.08   |

All of the values of the binding energy between CaCO$_3$ and inhibitor molecules are positive, which means these reactions occur spontaneously. The value of binding energy between CaCO$_3$ and PASP was largest, which means the adsorption of CaCO$_3$ on PASP was strongest.

The electron distribution of an oxygen atom is $1s^2\ 2s^2\ 2p^4$. For the oxygen atom of the carbonyl, the electron orbitals are sp2 nonequivalent hybrids: one sp2 hybrid orbital has one electron, one p orbital has one electron, and two sp2 hybrid orbitals have two electrons. The electron distribution of Ca$^{2+}$ ion is $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^0$. It can be seen from table 4 that when oxygen atom of the carbonyl interacting
with \( \text{Ca}^{2+} \) ion, the charge of \( \text{Ca}^{2+} \) ion increased and the charge of oxygen atom decreased, means electronic transfer from \( \text{Ca}^{2+} \) ion to oxygen atom and form bond. For the interaction between the oxygen ions of the \( \text{CaCO}_3 \) interact with the hydrogen atoms of the carboxyl group, the charge of these atoms both decreased, mean there are electrons accumulations on these atoms.

Thus, bond exists between the \( \text{Ca}^{2+} \) ion and the oxygen atom of the inhibitor since the electrons of \( \text{Ca}^{2+} \) ion are transferred to oxygen atom. The stability of the coordinate bond was estimated by the energy gap between the Highest Occupied Molecular Orbital (HOMO) and the Lowest Unoccupied Molecular Orbital (LUMO) of the coordination compound. The \( \text{Ca}—\text{O} \) coordinate bond, the HOMO and the LUMO of the coordinate bond and the energy gap are shown in figures 10-12 and table 5, respectively.

![Image](https://via.placeholder.com/150)

Table 5. The HOMO, LUMO and energy gap of the coordinate bonds.

|       | HOMO (au) | LUMO (au) | Energy gap (au) |
|-------|-----------|-----------|-----------------|
| \( \text{Ca-PA} \)  | -0.094607 | -0.08701  | 0.007597        |
| \( \text{Ca-HPMA} \) | -0.100599 | -0.095294 | 0.005305        |
| \( \text{Ca-PESA} \) | -0.095754 | -0.074945 | 0.020809        |
| \( \text{Ca-PASP} \) | -0.09956  | -0.078605 | 0.020955        |

As seen in figures 11 and 12, for the \( \text{Ca}—\text{O} \) coordinate bond, the HOMO are mainly from the 4s orbital of \( \text{Ca}^{2+} \) ions, and the LUMO are mainly from the 2p orbital of the O atoms of the inhibitor. The values of the energy gap of these coordinate bonds were small, which means the coordinate bonds formed between \( \text{Ca}^{2+} \) ions and inhibitors were not very stable. The values of the energy gap of \( \text{Ca-PESA} \) and the \( \text{Ca-PASP} \) are larger than the \( \text{Ca-PA} \) and the \( \text{Ca-HPMA} \), meaning the coordinate bonds between the \( \text{Ca}^{2+} \) ions and the O atoms of the PESA and the PASP are more stable.

For the carbonate ions of the \( \text{CaCO}_3 \) and the carboxyl of the inhibitors, it can be speculated from figure 9 and the distance values in table 4 that the carbonate ion connection to the hydrogen of carboxyl is formed through a hydrogen bond, as shown in figure 13.
Figure 13. Hydrogen bonds (blue dotted line) between the carbonate ion and the H atom of PAA, HMPA, PESA and PASP (from left to right).

4. Conclusion
The two effects of the four inhibitors on the adsorption of the CaCO$_3$ on Fe, Fe$_2$O$_3$ and calcite surfaces have been investigated by the molecular dynamics simulation method. The first effect, the occupation of an inhibitor molecule on the active site of a solid surface, was verified by studying the minimum distance between the free molecule and the solid surface. The binding energy between the free molecules and the solid surfaces showed that the tendency and intensity of adsorption of the inhibitor on the active sites of the surfaces were stronger than the adsorption of the CaCO$_3$ on these sites. The second effect was the CaCO$_3$ adsorption on the suspended segments of the inhibitor molecule, which was verified by the formation of a coordinate bond between the Ca$^{2+}$ ion of the CaCO$_3$ and the O atom of the carbonyl of the carboxyl of the inhibitor molecule as well as the hydrogen bond formation between the O atom of the CaCO$_3$ and the H atom of the carboxyl of the inhibitor molecule.

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