Computational Simulation about the Impact of High Voltage Electrostatic Field on Crystallization of Calcium Carbonate Aqueous Solution

D F Wang¹, a, D D Meng¹,2, b, *, X D Cui¹, c, F J Wang¹, d and Y Liu¹, e

¹College of Arts and Science, Qingdao Binhai University, Qingdao 266555, China
²Key Laboratory of New Metallic Functional Materials and Advanced Surface Engineering in Universities of Shandong, Qingdao Binhai University, Qingdao 266555, China
Shandong Provincial Natural Science Fund, ZR2019BA025, China
E-mail: *wdfsg2006@126.com, b*mengdongmail@163.com,
³cuixindong@163.com, ⁴wangfengjuna@126.com, ⁵lycsret0311@163.com
Corresponding Author: mengdongmail@163.com

Abstract. Computational simulation method was used in two models of calcium carbonate aqueous solution to explore the mechanism of anti-scaling under electrostatic field on the molecular level. The binding energy between the surface and ions indicated that the surface (104) was more favorable for the growth of the new crystal, while it was much easier to decompose under field strength 1300 V/m. The diffusion coefficients of Ca²⁺ and CO₃²⁻ revealed that the chemical reaction of Ca²⁺ and CO₃²⁻ ions in Model-II was much difficult to form calcium carbonate crystal under electrostatic field. The hydration degree of Ca²⁺ with O atoms from water molecules showed that the electric field could enhance the hydration degree of Ca²⁺ under certain field length, hence preventing the chemical reaction with CO₃²⁻ to produce crystal. In short, the scale inhibition effect under electrostatic field in Model-II was much better.

1. Introduction
In the process of industrial production and daily life, the occurrence of scaling not only caused enormous economic loss but also lots of serious security incidents. Over the past few decades, researchers had developed many kinds of methods for anti-scaling, one of which was using high voltage electrostatic field that originated in the United States [1]. This technique was developed in Japan in 1970s, which was firstly utilized in China in 1975.

In the past few years, the study of anti-scaling was almost about experimental method on the macro-quantitative level. However, the complexity of water system caused the great chanciness of experimental results [2]. In order to study the mechanism of anti-scaling under electrostatic field on the molecular level, and provide academic support for the application of anti-scaling using electrostatic field, computational simulation (molecular dynamics, MD) method was used in this paper to study the impact of high voltage electrostatic field on the crystallization of calcium carbonate aqueous solution.

In this paper, two types of aqueous solution of calcium carbonate that containing calcite crystal (1T0) surface and (104) surface (labeled as Model-I and II, respectively) were utilized to simulate the
impact of crystallization under high voltage electrostatic field, and then to explore the mechanism of anti-scaling. Through computational simulation, we analyzed the binding energy, diffusion value and hydration degree of two models to explore the impact of electrostatic field on crystallization of calcium carbonate aqueous solution, and found that the Model-II was much sensitive to the electric field so that the scale inhibition effect under high electrostatic field in Model-II was much better.

2. The Method of Computational Simulation

Molecular Dynamics Simulation is a computing physics method that widely used to simulate the classical multi-particle system. Materials Studio (MS) is an analog-computing software that developed by the Accelrys Company, which can be directly run on the PC for the simulation. The computing module—DISCOVER is used for simulation in this work, which is running on the server side, the data generated can be remotely shared with other PC in time. Discover module contains multiple force fields, among which the powerful force field—COMPASS will be used in the present work, that can be used to accurately predict the structure, conformation, vibration, and thermodynamic properties of various molecules in an isolated or condensed system under physical conditions. Complex potential energy functions are adopted by COMPASS, among which the bond stretching energy function adopting three stage series expansion and the non-bonding energy term adopting Lennard-Jones-9-6 function, as detailedly reported in our other works [3].

3. Parameters Setting and System Balanced Judgement

The crystals of CaCO₃ studied in this paper were composed of calcite structure with two main growth surfaces (1 1 0) and (1 0 4), respectively.

The bottom Layer of Model-I contained surface (1 1 0), the size was 1.996×1.706×1.008 nm³, including 7 layers of Ca²⁺ and CO₃²⁻ ions. The volume of calcium carbonate solution was 1.996×1.706×2.602 nm³, which was constructed by 300 water molecules, 2Ca²⁺ and 2CO₃²⁻ ions. The bottom Layer of Model-II was calcite surface (1 0 4) that composed of 4 layers of Ca²⁺ and CO₃²⁻ ions. The middle layer of the solution system was constructed by 300 water molecules, 2Ca²⁺ and 2CO₃²⁻ ions, and the volume was 2.429×1.996×1.828 nm³.

The high voltage electrostatic field was added to the 2 models by computer programming language BTCL, of which the field strength varying from 1000 V/m to 2000 V/m.

System balance conditions were \( \Delta E_{\text{converge}} \leq 0.001 \) (convergence parameter) and \( R \leq 0.001 \) (the ratio of total energy fluctuation to the kinetic energy fluctuation). If the system was not accordance with the two conditions, the calculating system would be optimized automatically and calculated repeatedly until satisfying the balance conditions.

4. Results and Discussion

4.1. The influence of electrostatic field on binding energy between the surface and Ca²⁺/CO₃²⁻ ions

The binding energy between surface (1 1 0)/(1 0 4) and Ca²⁺, CO₃²⁻ ions under the electrostatic fields were shown in Figure 1, respectively. The results showed that the variations of electrostatic field strength had no obvious effect on the binding energy in Model-I. While in Model-II, the binding energy dropped steeply to 3630 kcal/mol under the field strength 1300 V/m, revealing that the binding energy between surface (104) and ions was weakened by electric field. Viewed as a whole, the binding energy between ions and surface (104) (Model-II) was much stronger than that combining with (1 1 0) (Model-I). This result demonstrated that the ions were much easier to be adsorbed by surface (104), hence the surface (104) was more favorable for the growth of the new crystal. This result is the same as our previously reported temperature-dependent binding energies [3]. As the way of energy definition
was different, the binding energies that we calculated were larger than the reality. According to solid state physics theories, the influence of electrostatic field on atom’s energy mainly due to it’s impact on energy band. The present simulating results proved that electrostatic fields have no obvious effects on binding energies, in other words, the variation of field strength from 1000 V/m to 2000 V/m have no effect on the energy bands of Ca$^{2+}$, CO$_3^{2-}$ ions.

4.2. The diffusion of Ca$^{2+}$ and CO$_3^{2-}$ under the influence of electrostatic field

The influence on the diffusion coefficients of Ca$^{2+}$ and CO$_3^{2-}$ ions under different electrostatic field in Model-I and II were shown in Figure 2, respectively. As a whole, the diffusion of Ca$^{2+}$ in Model-I was affected more obviously than that in Model-II, field strengths 1100 V/m and 1600 V/m in particular, the diffusion values reached $3.750 \times 10^{-5}$ cm$^2$/s and $3.385 \times 10^{-5}$ cm$^2$/s, respectively. On the contrary, the diffusion of Ca$^{2+}$ in Model-II showed two pronounced anomalies under field strengths 1500 V/m and 1700 V/m that the values reached $2.750 \times 10^{-5}$ cm$^2$/s and $2.625 \times 10^{-5}$ cm$^2$/s, respectively, as shown in Figure 2 (up).

As shown in Figure 2 (down), CO$_3^{2-}$ in Model-I showed more diffusive on the whole than that in Model-II under different field strengths. The diffusion of CO$_3^{2-}$ in Model-I exhibited three pronounced
anomalies under field strengths 1400 V/m, 1600 V/m and 1900 V/m, respectively. While in Model-II, the diffusion showed faint variations under 1500 V/m, 1700 V/m and 1900 V/m, respectively.

On the whole, the Ca\(^{2+}\) and CO\(_3^{2-}\) ions in Model-I were more active than that in Model-II under the influence of electrostatic field, and the anomalies driving electrostatic field strengths were universally lower than that in Model-II. The present results revealed that the chemical reaction of Ca\(^{2+}\) and CO\(_3^{2-}\) ions in Model-I was much easier, especially under the field strength 1600 V/m.

4.3. The influence of electrostatic field on the hydration degree of Ca\(^{2+}\) with O atoms from water molecules in the two models

The Radial-Distribution-Function (RDF) can provide a lot of information about the motional characteristics of particles in the system, which can be used to understand the "structure" of liquids. The RDF can be interpreted as the ratio of the regional density to the average density of the system [4]. The density of the region near the reference molecule is different from the average density of the system, but it should be the same as the average density when the distance from the reference molecule is long, this means that the value of the RDF should be close to 1 when the value is large [5].

![Figure 3. The influence of electrostatic field on RDF values (Ca\(^{2+}\)-O) in (a) Model-I and (b) Model-II.](image)

In the solution, a certain number of water molecules are arranged around Ca\(^{2+}\) and CO\(_3^{2-}\) to form hydrated ions, in which water molecules act as the ligand and bind with ions through coordination bonds. Obviously, the higher the hydration degree of Ca\(^{2+}\) and O atom is, the more difficult to form calcium carbonate crystals.

The RDF about hydration degree with particle length of Ca\(^{2+}\) in aqueous solution and O atoms from water molecules in the two models were shown in Figure 3 (a) and (b), respectively. One can see from the figures that the spike of RDF in Model-I showed variations under the influence of field length ~1200 V/m and 1700 V/m, which in Model-II exhibited obvious variations under field length 1300 V/m and 1800 V/m, as shown in the insets of Figure 3 (a) and (b). The present results indicated that the electric field could enhance the hydration degree of Ca\(^{2+}\) under certain field length, hence preventing the chemical reaction with CO\(_3^{2-}\) to produce calcium carbonate crystal.

On the other hand, the RDF spike values of Ca\(^{2+}\)-O in Model-II was significantly larger than that in Model-I. It demonstrated that the hydration degree of Ca\(^{2+}\) in Model-II was higher than that in Model-I. From this point of view, the scale inhibition effect of high voltage electric field in Model-II was much better.

5. Summary

Computational simulation (molecular dynamics) method was used to study the mechanism of anti-scaling under electrostatic field on the molecular level.
By analyzing the calculated binding energy data, one can know that the electrostatic field did not have an obvious influence on the binding energy between ions in aqueous solutions and crystal growth surface (110) (Model-I). The binding energy between ions and surface (104) (Model-II) was much stronger which demonstrated the ions were much easier to be adsorbed by surface (104), hence it was more favorable for the growth of the new crystal in Model-II. On the other hand, the binding energy dropped steeply under the field strength 1300 V/m in Model-II, revealing the Model-II was much sensitive to electric field.

The diffusion values of Ca$^{2+}$ and CO$_3^{2-}$ under electrostatic field revealed that the Ca$^{2+}$ and CO$_3^{2-}$ ions in Model-I were more active than that in Model-II under the influence of electrostatic field, hence the chemical reaction of Ca$^{2+}$ and CO$_3^{2-}$ ions in Model-I is much easier, especially under the specific field strengths.

The RDF about hydration degree of Ca$^{2+}$ in aqueous solution and O atoms from water molecules in the two models indicated that the electric field could enhance the hydration degree of Ca$^{2+}$ under certain field length and prevent the chemical reaction with CO$_3^{2-}$ to produce calcium carbonate crystal. Because the hydration degree of Ca$^{2+}$ in Model-II was higher than that in Model-I, the scale inhibition effect under high electrostatic field in Model-II was much better.

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