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# Molecular Dynamics Simulation of $CO_2$ Sequestration in $Ca^{2+}-CO_3^{2-}-NH_{4^{+}-}$ $Cl^--H_2O$ System

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Keywords: Steel slag; CO2 sequestration; CCUS; Molecular dynamics simulation



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# Article

# Molecular Dynamics Simulation of CO<sub>2</sub> Sequestration in Ca<sup>2+</sup>–CO<sub>3</sub><sup>2-</sup>–NH<sub>4</sub>+–Cl<sup>-</sup>–H<sub>2</sub>O System

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**Abstract:** A large amount of steel slag (SS) and CO<sub>2</sub> are generated in the steelmaking process. The indirect CO<sub>2</sub> capture using SS is a promising way for co-treatment of the wastes. Ammonium salt solution is widely used to extract Ca<sup>2+</sup> from the SS since it is recyclable. Several works have focus on improving the carbonation rate by adjusting various parameters (e.g., temperature and pH). However, there is little detail information about the associating behaviors and interaction strength between the various ions in the ammonia solution during the carbonation process. In this work, the Ca<sup>2+</sup>–CO<sub>3</sub><sup>2–</sup>–NH<sub>4</sub>+–Cl<sup>-</sup>–H<sub>2</sub>O system was established by using Material studio software. The effects of temperature and concentration of CO<sub>3</sub><sup>2–</sup> on CaCO<sub>3</sub> growth were explored at the atomic scale by calculating the binding energy, mean square displacement, and diffusion coefficient between particles. Furthermore, the microstructure, bonding characteristics, and occurrence behavior of each particle were studied though molecular dynamics simulation methods. The results showed that with the increase of temperature (20–80 °C), the binding ability and diffusion coefficients of Ca<sup>2+</sup> and CO<sub>3</sub><sup>2-</sup> increase in the system, which is beneficial to the formation of CaCO<sub>3</sub> clusters. With the increase of the concentration of CO<sub>3</sub><sup>2-</sup> (15–25 vol.%), the binding ability and diffusion coefficient of Ca<sup>2+</sup> and CO<sub>3</sub><sup>2-</sup> in the system are enhanced, which is beneficial to the formation of CaCO<sub>3</sub> clusters.

Keywords: steel slag; CO2 sequestration; CCUS; molecular dynamics simulation

#### 1. Introduction

(cc) (i)

The iron and steel industry is an energy-intensive industry [1], produces a large amount of CO<sub>2</sub> and steelmaking slag (SS) [2]. Globally, the steel industry produces about 130–200 million tons of SS every year [3]. In some major steel producing countries, such as China and India [4], the utilization rate of SS is still below 30% [5]. At present, the carbon capture, utilization, and storage (CCUS) process based on SS is an effective way to reduce  $CO_2$  emissions and waste utilization [6,7]. As early as the beginning of the 21st century, it was proposed [8] that  $CO_2$  can be sealed by indirect method with SS. The method includes selectively extracting Ca2+ [9,10] from SS with aqueous solutions such as acid (e.g., HCl, HNO<sub>3</sub>, CH<sub>3</sub>COOH, or HCOOH) and ammonium salt (NH<sub>4</sub>Cl, NH<sub>4</sub>NO<sub>3</sub>, or CH<sub>3</sub>COONH<sub>4</sub>). NH<sub>4</sub>Cl is more suitable as a Ca<sup>2+</sup> leaching agent for SS than strong and weak acids [13,14] because of its high Ca-selective, recyclability, and low cost [11,12]. Pilot-scale experiment work showed that the Ca-rich leaching solution can be produced by leaching SS with low concentration NH<sub>4</sub>Cl solvent (0.11  $mol \cdot L^{-1}$  (other elements Si, Mg, and Fe in SS are not significant or not detected) [15]. Thus, the leachate containing various ions (Ca2+, NH4+, Cl-, H2O) was obtained and then after for CO2 sequestration. However, the carbon capture efficiency of Ca<sup>2+</sup> in SS is very low, which leads to a low yield of calcium carbonate (CaCO<sub>3</sub>), so the CaCO<sub>3</sub> produced by SS cannot be used for large-scale industrialization. At present, a large number of experiments [16–19] have studied the formation of CaCO<sub>3</sub> in the NH<sub>4</sub>Cl

system. The results show that the formation of CaCO<sub>3</sub> is related to temperature [20,21], solution pH [22], NH<sub>4</sub>Cl concentration [23], and CO<sub>2</sub> flow rate [24]. Gadikotad et al. [25] concluded through experiments that the increase in temperature is beneficial to the formation of CaCO<sub>3</sub>. However, Ma et al. [26] proposed that the formation of CaCO<sub>3</sub> is not linear with the temperature. Therefore, the formation mechanism of CaCO<sub>3</sub> in solution should be further investigated.

It is difficult to obtained more detailed information about the relationship between the particle interactions and independent parameters through lab-experiments. Molecular dynamics (MD) simulation is an effective method to explore the relationship between particles from the micro level. The research shows that the MD simulation method can be used to study the nano-scale particle system [26,27], which proves the accuracy of the MD simulation method at the micro level. Jing et al. [28] established the NaCl–CO<sub>2</sub>–H<sub>2</sub>O system by using the kinetic simulation method, and studied the action mechanism of NaCl as a hydrate inhibitor. Zhang et al. [29] established the LiCl–H<sub>2</sub>O system by kinetic simulation method, studied the dissociation pathway of LiCl. Li et al. [30] established CaO–H<sub>2</sub>O–CO<sub>2</sub> system by kinetic simulation method, and studied the effect of H<sub>2</sub>O on CO<sub>2</sub> capture by CaO. The above research shows that MD simulation has been widely used to study the microscopic behavior of particles in complex systems.

Based on the above researches, the Ca<sup>2+</sup>–CO<sub>3</sub><sup>2-</sup>–NH<sub>4</sub>+–Cl<sup>-</sup>–H<sub>2</sub>O system was established by using this simulation method. The effects of temperature and concentration of CO<sub>3</sub><sup>2-</sup> on CaCO<sub>3</sub> growth were explored at the atomic level by calculating the binding energy, mean square displacement, and diffusion coefficient between particles. Furthermore, the microstructure, bonding characteristics, and occurrence behavior of each particle were studied.

#### 2. Materials and Methods

# 2.1. Force field

Materials Studio (MS) simulation software was used to carry out MD simulation to simulate the microstructure variations during the binding process of Ca<sup>2+</sup> with CO<sub>3</sub><sup>2-</sup> which could not be directly evaluated by experiments. In the process of MD simulation, the choice of force field plays an important role in the accuracy of the results. The MS software provides users with various forms of force fields, among which COMPASS (condensed-phase optimized molecular potentials for atomistic simulation studies) force field is a molecular force field developed in recent years. The COMPASS force field is suitable for condensed matter systems or systems. The energy form of the system or system simulated or calculated by the COMPASS force field is relatively complete and the calculation accuracy is very high. The COMPASS force field has been proved by many studies [31] to be suitable for the system containing Ca<sup>2+</sup> and CO<sub>3</sub><sup>2-</sup>.

#### 2.2. Simulation model and procedure

The modules of Visualize, Amorphous Cell, and Forcite were used to simulate the interaction energy and particle distribution in a specific system, and the cluster behavior of CaCO<sub>3</sub> in a solution system was predicted.

Firstly, the ions and molecules in the system are drawn with the help of the "Visualizer" module in MS software. After that, the solution model of  $Ca^{2+}-CO_{3^2}-NH_{4^+}-Cl-H_2O$  system was constructed by using the "Amorphous cell" module, and the pH of the system was set at 12. When the model is established, Forcite is used to optimize the model and analyze the dynamics calculation. The chemical components of the system are established at different temperatures and different concentrations of  $CO_{3^{2-}}$  (refer to different  $CO_2$  concentrations in solution, ranging from 15 vol.% to 25 vol.%) are shown in Table 1.

Temperature/°C	Ca <sup>2+</sup>	$NH_{4^+}$	Cl	H <sub>2</sub> O	CO3 <sup>2-</sup>
20	200	400	400	224	144
50	200	400	400	224	144
80	200	400	400	224	144
80	200	400	400	224	108
80	200	400	400	224	180

Table 1. Composition of Ca<sup>2+</sup>–CO<sup>32</sup>–NH<sub>4</sub>+–Cl–H<sub>2</sub>O system at different temperature.

Geometry Optimization in "Forcite" module was used to optimize the geometry structure and energy of the initial model under different temperature conditions, which aimed to prevent the initial ion pairs and the formation of water molecules unreasonable overlap phenomenon. The specific optimization parameters are shown in Table 2.

Table 2. Specific optimization parameters of the system.

Parameter	Force field	Summation method	Truncation radius	Number of iteration steps	Quality	Optimization method
Settings	Compass	Ewald	12.5 Å	1000	Medium	Smart

The optimized system was simulated by using "Dynamics" in the "Forcite" module. The initial velocity of particles is random. The boundary condition of the system is periodic. The specific parameters of molecular dynamics simulation were shown in Table 3.

Table 3. Specific J	parameters of Mole	ecular Dynamics	simulation.
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Parameter	Force field	Ensemble	Temperature control method	Pressure control method	Step length	Analog time
Settings	Compass	NPT	Nose	Anderson	1 fs	1500 ps

# 2.3. Properties analysis

In this study, the interparticle interaction energies of CaCO<sub>3</sub> and H<sub>2</sub>O are calculated. The radial distribution function, mean square displacement, and diffusion coefficient of Ca<sup>2+</sup> and CO<sub>3</sub><sup>2-</sup> are analyzed. The interaction energy is the sum of the changes in kinetic energy and potential energy when particles in the system combine or separate. It is a negative value of binding energy numerically.

The calculation formula of binding energy is shown as Eq 1:

$$E_{\text{bind}} = E_{\text{AB}} - (E_{\text{A}} + E_{\text{B}}), \tag{1}$$

where  $E_{\text{bind}}$  is the binding energy of matter or system,  $E_{\text{AB}}$  is the total energy of matter or system,  $E_{\text{A}}$  is the energy of matter A, and  $E_{\text{B}}$  is the energy of matter B.

According to the above formula of binding energy calculation, the formula of binding energy between any two components in the three systems can be derived:

$$E_{A_1\&A_2} = \left(E_{A_1+B+A_2} - E_{A_1+B} - E_{A_2+B} - E_{A_1} - E_{A_2} + E_B + E_{A_1+A_2}\right)/2.$$
(2)

From the above formula, the binding energy formula of CaCO<sub>3</sub> and H<sub>2</sub>O in three systems CaCO<sub>3</sub>–NH<sub>4</sub>Cl–H<sub>2</sub>O can be obtained:

$$E_{\text{bind}} = \left(E_{\text{Total}} - E_{\text{CaCO}_3 + \text{NH}_4\text{Cl}} - E_{\text{H}_2\text{O} + \text{NH}_4\text{Cl}} - E_{\text{CaCO}_3} - E_{\text{H}_2\text{O}} + E_{\text{NH}_4\text{Cl}} + E_{\text{CaCO}_3 + \text{H}_2\text{O}}\right)/2$$
(3)

where *E*<sub>Total</sub> is the Total energy of the three system CaCO<sub>3</sub>–NH<sub>4</sub>Cl–H<sub>2</sub>O (kJ·mol<sup>-1</sup>), *E*<sub>bind</sub> is the binding energy of CaCO<sub>3</sub> and H<sub>2</sub>O (kJ·mol<sup>-1</sup>), *E*<sub>CaCO3+NH4Cl</sub> is the energy of CaCO<sub>3</sub> and NH<sub>4</sub>Cl (kJ·mol<sup>-1</sup>), *E*<sub>LaCO3+NH4Cl</sub> is the energy of H<sub>2</sub>O and NH<sub>4</sub>Cl (kJ·mol<sup>-1</sup>), *E*<sub>CaCO3+H2O</sub> is the energy of H<sub>2</sub>O and CaCO<sub>3</sub> (kJ·mol<sup>-1</sup>), *E*<sub>CaCO3+H2O</sub>, and *E*<sub>NH4Cl</sub> are the energy of CaCO<sub>3</sub>, H<sub>2</sub>O, and NH<sub>4</sub>Cl (kJ·mol<sup>-1</sup>).

In addition, the radial distribution function is used to study the orderliness of particles in the solution. The radial distribution function refers to the distribution probability of central particles and other particles in space when the coordinates of a certain particle are given. It can also be considered as the ratio of regional density to the average density of matter or system. And when the studied particle is an infinity away from the central particle, the regional density tends to be equal to the average density.

The radial distribution function is calculated as follows:

$$\rho \mathbf{g}(r)\pi r^2 \mathbf{d}r = \mathbf{d}\mathbf{N},\tag{5}$$

where  $\rho$  is the density of the substance or system (g/cm<sup>3</sup>), *r* is the distance from a given central particle (Å), and N is the number of molecules in the substance or system.

Mean square displacement (MSD) refers to the average distance between all particles and their initial points when the motion time is *t*, which can be used to judge the speed and mode of particle motion in the system.

Mean square displacement is defined as follows:

$$MSD=\langle |\mathbf{r}(t)-\mathbf{r}(0)|^2 \rangle \tag{6}$$

where  $\langle |\mathbf{r}(t)-\mathbf{r}(0)|^2 \rangle$  represents the average of the system, *t* is the time, and MSD is the abbreviation of mean squared displacement, that is, the mean square displacement.

The most important function of mean square displacement is to use the calculated mean square displacement to calculate the diffusion coefficient according to Einstein equation. The corresponding relationship between the mean square displacement and the diffusion coefficient of particles is as follows:

$$\langle |\mathbf{r}(t) - \mathbf{r}(0)|^2 \rangle = 6Dt + C,$$
 (7)

where D and C are constants, where D is the diffusion coefficient.

When the studied system is liquid, the relationship between mean square displacement and diffusion coefficient is as follows:

$$D = \lim_{t \to \infty} \frac{1}{6t} \langle |\mathbf{r}(t) - \mathbf{r}(0)|^2 \rangle$$
(8)

In the process of molecular dynamics simulation, if the simulation time is long enough and in a cubic lattice, the diffusion coefficient is equal to one-sixth of the slope of the mean square displacement curve.

# 3. Results and discussion

# 3.1. Effects of temperature

# 3.1.1. Binding energy

The energy of each component of the system at different temperature conditions was studied, as shown in Table 4. It can be seen that the absolute value of the total energy of the system decreases with the temperature,. Using the Eq. 3, the binding energy of CaCO<sub>3</sub> and H<sub>2</sub>O at different temperatures can be calculated.

**Table 4.** Energy values of each component in  $Ca^{2+}-CO_{3}^{2-}-NH_{4}^{+}-Cl^{-}-H_{2}O$  system at differenttemperatures(kJ·mol-1).

Energy/kJ·mol <sup>-1</sup>	20 °C	50 °C	80 °C
E <sub>Total</sub>	-200885.32	-199381.04	-198523.37
$E_{CaCO_3+NH_4Cl}$	-138188.01	-137316.67	-136352.72
$E_{\rm H_2O+NH_4Cl}$	-68686.58	-67889.69	-67311.95
E <sub>CaCO3</sub>	-133390.83	-132855.18	-132724.31

			5
$E_{\rm NH_4Cl}$	-67266.41	-66959.19	-66086.94
$E_{\mathrm{H_2O}}$	-1349.42	-1098.47	-925.10
$E_{CaCO_3+H_2O}$	-197971.02	-197657.37	-196624.71
$E_{\rm bind}$	2469.38	2078.09	1688.48

Figure 1 is a histogram of the binding energy of CaCO<sub>3</sub> and H<sub>2</sub>O at different temperatures. The binding energy between CaCO<sub>3</sub> and H<sub>2</sub>O decreases with the temperature increase (cf. Figure 1). Under natural conditions, liquid water molecules are bonded by hydrogen bonds, and most of the hydrogen bonds between water molecules are in the network structure. This network structure can reduce the average gap between molecules in the system and hinder the thermal movement of Ca<sup>2+</sup> and CO<sub>3<sup>2-</sup></sub>. With the increase in temperature, some hydrogen bonds were broken between water molecules, thus the original spatial grid structure was destroyed in water molecules. The impediment of Ca<sup>2+</sup> and CO<sub>3</sub><sup>2-</sup> movement in the system is reduced. Ca<sup>2+</sup> and CO<sub>3</sub><sup>2-</sup> bind together under the action of electrostatic force. With the increase in temperature, the binding capacity of Ca<sup>2+</sup> and CO<sub>3</sub><sup>2-</sup> increases, while the binding energy of CaCO3 and H2O decreases. However, the hydration of Ca<sup>2+</sup> and CO<sub>3</sub><sup>2-</sup> decreases in the solution, which makes Ca<sup>2+</sup> and CO<sub>3</sub><sup>2-</sup> begin to polymerize, increases the chance of contact between Ca<sup>2+</sup> and CO<sub>3</sub><sup>2-</sup>, and is beneficial to the formation and polymerization of CaCO<sub>3</sub> clusters in the solution. Shashikant [32], in Ca<sup>2+</sup>–CO<sub>3</sub><sup>2–</sup>–NH<sub>4</sub><sup>+</sup>–Cl<sup>-</sup>–H<sub>2</sub>O system through experimental study on the effect of carbonization of SS, the results show that in 45–70 °C, increasing the temperature is beneficial to the formation of CaCO<sub>3</sub>. Similarly, Nielsen and Polettini obtained similar results at 10-60 °C[33] and 20-80 °C[34], which are also consistent with the simulation results of this study.



Figure 1. Binding energy of CaCO3 and H2O at different temperature.

#### 3.1.2. Microstructure of particles

Table 5 shows the peak position and peak value of the  $Ca^{2+}-CO_{3^{2-}}$  radial distribution function diagram in the system under different temperature conditions. It can be seen that with the increase in temperature, the peak position of the highest peak is similar, which indicates that the interaction distance between  $Ca^{2+}$  and  $CO_{3^{2-}}$  does not change with the change of temperature. Figure 2 shows the radial distribution function of  $Ca^{2+}-CO_{3^{2-}}$  in the system at different temperatures. It can be seen from the figure that under different temperature conditions, the radial distribution function of  $Ca^{2+}-CO_{3^{2-}}$  appears sharp peaks around r=4.07 Å, and with the increase in distance, the graph becomes flat and approaches 1. In the range of r=4.07 Å, the binding strength of  $Ca^{2+}$  and  $CO_{3^{2-}}$  is higher, and the two ions interact directly at this distance. With increasing temperature, the peak value of the  $Ca^{2+}-CO_{3^{2-}}$  radial distribution function increases, and the peak shape tends to be sharp. This indicates that increasing the temperature is beneficial to enhance the association between  $Ca^{2+}$  and  $CO_{3^{2-}}$ , and is



beneficial to the formation of CaCO<sub>3</sub> pre-nucleation clusters. As can be seen from Figure 2, Ca<sup>2+</sup> and CO<sub>3</sub><sup>2-</sup> are in a cluster structure with short-range and medium-range order and long-range disorder.

Figure 2. Radial distribution function diagram of Ca<sup>2+</sup>–CO<sub>3</sub><sup>2-</sup> in system at different temperatures.

Table 5. Peak positio	on and peak valu	ie of radial d	distribution	function	diagram	of Ca <sup>2+</sup> –CO <sub>3</sub> <sup>2</sup>	in system
at different temperat	tures.						

Temperature/°C	Peak position/Å	Peak value/ —
20	4.07	4.51
50	4.03	5.39
80	4.09	6.11

Figures 3 and 4 are the mean square shifts of  $Ca^{2+}$  and  $CO_3^{2-}$  in the system at different temperatures, respectively. It can be seen that the mean square shift of  $CO_3^{2-}$  and  $Ca^{2+}$  has a good linear relationship with time. At different temperatures,  $CO_3^{2-}$  and  $Ca^{2+}$  are rapidly stabilized after a short relaxation of the system and then keep a relatively stable diffusion state. With the increasing temperature, the slope of the mean square displacement curve of  $Ca^{2+}$  and  $CO_3^{2-}$  increases, that is, the diffusion coefficients of  $CO_3^{2-}$  and  $Ca^{2+}$  increase with the increasing temperature. This also shows that in this study, high temperature can accelerate the diffusion of  $Ca^{2+}$  and  $CO_3^{2-}$  in the system, and increase the probability of collision and combination between them in the system, which is beneficial to the formation of  $CaCO_3$  crystals. The effect of temperature on the carbonation of steel slag at 20–100 °C [27,38] has been investigated experimentally, and it is considered that the increase of temperature is one of the reasons for the increase in ion diffusion rate in the system. The experimental study at 20–60 °C [34] also reached the same conclusion, which is also consistent with the results obtained by theoretical analysis [37–39].



Figure 3. Mean square displacement of Ca<sup>2+</sup> at different temperatures.



Figure 4. Mean square displacement of CO<sub>3<sup>2-</sup></sub> at different temperatures.

# 3.1.3. Agglomeration behavior

Figure 5 shows the motion trajectory of each particle in the system with time when the solution temperature is 80 °C and the concentration of  $CO_{3^{2-}}$  is 20 vol.%. It can be seen from the figure that  $Ca^{2+}$  and  $CO_{3^{2-}}$  in the solution system are irregularly dispersed at the initial moment. With the increase of simulation time,  $Ca^{2+}$  and  $CO_{3^{2-}}$  form clusters through the interaction force between ions.



**Figure 5.** Motion trajectories of particles in the system with  $CO_{3^2}$  concentration of 20 vol.% at different simulation times (T=80 °C). (a) 0 ps; (b) 150 ps; (c) 300 ps. Red: O; Green: Ca; Grey: C; Blue: H.

Figure 6 shows the characteristics of the largest cluster particles in the system at different temperatures. The trajectories of particles are different with different temperatures, which also leads to the different degrees of particle clusters in the system.



**Figure 6.** Characteristics of the largest cluster particles in  $Ca^{2+}-CO_{3}^{2-}-NH_{4}^{+}-Cl^{-}-H_{2}O$  system at different temperatures. (a) 20 °C; (b) 50 °C; (c) 80 °C.

As can be seen from Figure 6, with the gradual increase of temperature, the number of atoms contained in the largest cluster particles in the solution system increases, and the degree of agglomeration becomes larger and larger. This shows that in the temperature range of 20–80 °C, high temperature is beneficial to the association between  $Ca^{2+}$  and  $CO3^{2-}$  and the formation of large clusters.

#### 3.2. Effects of concentrations of CO<sub>3<sup>2-</sup></sub>

#### 3.2.1. Binding energy

In this simulation experiment, with the help of the "Forcite" module in MS software, the energy of each component of the system under different concentrations of  $CO_{3^{2-}}$  was studied at 20 °C, and the results are shown in Table 6. It can be seen from the table that with the increase in the concentration of  $CO_{3^{2-}}$  in the system, the absolute value of the total energy of the system decreases. The proportion of  $CO_{2}$  in the exhaust gas from iron and steel enterprises is 15 vol.%–25 vol.%. Therefore, using the formula 3, the binding energy of CaCO<sub>3</sub> and H<sub>2</sub>O under different CO<sub>2</sub> concentrations (15 vol.%–25 vol.%) of  $CO_{3^{2-}}$  can be calculated.

**Table 6.** Energy calculation of each component in  $Ca^{2+}-CO_{3}^{2-}-NH_{4}^{+}-Cl^{-}-H_{2}O$  system under different concentrations of  $CO_{3}^{2-}$  (kJ·mol<sup>-1</sup>).

Energy/kJ·mol⁻¹	15 vol.%	20 vol.%	25 vol.%
$E_{\mathrm{Total}}$	-189592.61	-199381.04	-213739.43
$E_{CaCO_3+NH_4Cl}$	-123302.42	-137316.67	-150464.40
$E_{\rm H_2O+NH_4Cl}$	-68686.58	-67889.69	-66684.57
$E_{CaCO_3}$	-120190.84	-132855.18	-146846.78
$E_{\rm NH4Cl}$	-67266.41	-66959.19	-69376.41
$E_{\mathrm{H_2O}}$	-1349.42	-1098.47	-959.42
$E_{CaCO_3+H_2O}$	-184432.24	-197657.37	-212247.99
$E_{\rm bind}$	2751.18	2078.09	1169.74

Figure 7 is a histogram of binding energy between CaCO<sub>3</sub> and H<sub>2</sub>O under different concentrations of CO<sub>3</sub><sup>2-</sup>. It can be seen from the figure that with the gradual increase in the concentration of CO<sub>3</sub><sup>2-</sup>, the number of CO<sub>3</sub><sup>2-</sup> in the system increases, and the binding energy between CaCO<sub>3</sub> and H<sub>2</sub>O decreases. With the increase in the concentration of CO<sub>3</sub><sup>2-</sup>, the concentration of [35] CO<sub>3</sub><sup>2-</sup> in the system increases. The increase of CO<sub>3</sub><sup>2-</sup> concentration will break the network structure of hydrogen bonds between water molecules. The breakdown of the grid structure reduces the number of hydrogen bonds in the system and the interaction force between water molecules, which leads to

the decrease of the binding energy between CaCO<sub>3</sub> and H<sub>2</sub>O. This indicates that high CO<sub>3</sub><sup>2-</sup> concentration will make Ca<sup>2+</sup> and CO<sub>3</sub><sup>2-</sup> start to polymerize, increase the chance of contact between Ca<sup>2+</sup> and CO<sub>3</sub><sup>2-</sup>, and facilitate the formation and polymerization of CaCO<sub>3</sub> clusters in solution. A large number of experiments [37,40] at the concentration of 10 vol.%–100 vol.% CO<sub>2</sub> show that the increase of CO<sub>3</sub><sup>2-</sup> concentration is beneficial to the formation of CaCO<sub>3</sub>, which is the same as the simulation results in this study, which verifies the credibility of the simulation results from the side.



Figure 7. Binding energy of CaCO3 and H2O under different CO32- concentrations.

#### 3.2.2. Microstructure of particles

Table 7 shows the peak position and peak value of the Ca<sup>2+</sup>–CO<sub>3</sub><sup>2-</sup> radial distribution function diagram in the system under different concentrations of CO<sub>3</sub><sup>2-</sup>. It can be seen from the table that under the conditions of 15 vol.%, 20 vol.%, and 25 vol.% CO<sub>3</sub><sup>2-</sup> concentration, the radial distribution function of Ca<sup>2+</sup>–CO<sub>3</sub><sup>2-</sup> forms its peak at r=4.03 Å, r=4.09 Å and r=4.05 Å, respectively. However, with the increase in the concentration of CO<sub>3</sub><sup>2-</sup>, the peak position of the highest peak is similar, which indicates that the interaction distance between Ca<sup>2+</sup> and CO<sub>3</sub><sup>2-</sup> does not change with the change of the concentration of CO<sub>3</sub><sup>2-</sup>. Ca<sup>2+</sup> and CO<sub>3</sub><sup>2-</sup> show short-range, medium-range ordered and long-range disordered cluster structures.

**Table 7.** Peak position and peak value of  $Ca^{2+}-CO^{3^{2-}}$  radial distribution function diagram in the system under different concentrations of  $CO^{3^{2-}}$ .

CO <sub>3</sub> <sup>2-</sup> concentration/vol.%	Peak position/Å	Peak value/—
15	4.03	5.01
20	4.09	6.11
25	4.05	8.00

Figure 8 shows the radial distribution function of  $Ca^{2+}-CO_3^{2-}$  in the system under different concentrations of  $CO_3^{2-}$ . It can be seen from the figure that under the condition of different concentrations of  $CO_3^{2-}$ , the radial distribution function of  $Ca^{2+}-CO_3^{2-}$  has a similar peak position at r=4.05 Å, and has a second peak near r=5.21 Å, which is close to 1 in the remote range. In the range of the first peak, the binding force between  $Ca^{2+}$  and  $CO_3^{2-}$  is strong, which is due to the direct interaction between  $Ca^{2+}$  and  $CO_3^{2-}$  in this range. With the increase of  $CO_3^{2-}$  concentration, the peak value of  $Ca^{2+}-CO_3^{2-}$  radial distribution function increases, and the peak shape tends to be sharp. This phenomenon shows that the increase of  $CO_3^{2-}$  concentration is beneficial to the formation of  $CaCO_3$  clusters due to the enhancement of the association between  $Ca^{2+}$  and  $CO_3^{2-}$ .



**Figure 8.** Binding Radial distribution function diagram of  $Ca^{2+}-CO^{3^{2-}}$  in system under different concentrations of  $CO^{3^2}$ .

Figures 9 and 10 are the mean square shifts of  $Ca^{2+}$  and  $CO_3^{2-}$  in the system under different concentrations of  $CO_3^{2-}$ , respectively. It can be seen from the figure that the mean square shift of  $CO_3^{2-}$  and  $Ca^{2+}$  has a good linear relationship with time. Under the condition of different concentrations of  $CO_3^{2-}$ , both  $CO_3^{2-}$  and  $Ca^{2+}$  reached stability rapidly after a short relaxation of the system and then kept a relatively stable diffusion state all the time. The slope of mean square displacement curve of  $Ca^{2+}$  and  $CO_3^{2-}$  also increases, which indicates that the diffusion coefficients of  $CO_3^{2-}$  and  $Ca^{2+}$  increase with the increase in the concentration of  $CO_3^{2-}$ . This also shows that in this study, high concentration of  $CO_3^{2-}$  can accelerate the diffusion of  $Ca^{2+}$  and  $CO_3^{2-}$  in the system and increase the probability of collision and combination between them in the system which is beneficial to the formation of  $CaCO_3$  crystals.



Figure 9. Mean square shift of Ca<sup>2+</sup> under different concentrations of CO<sub>3</sub><sup>2</sup>.



Figure 10. Mean square shift of CO<sub>3<sup>2-</sup></sub> under different concentrations of CO<sub>3<sup>2</sup></sub>.

#### 3.2.3. Agglomeration behavior

Figure 11 shows the characteristics of the largest cluster particles in the system under different concentrations of  $CO_{3^{2-}}$ . With the change in the concentration of  $CO_{3^{2-}}$ , the number of anions and cations in the system also changes, which also causes the difference of particle cluster degree in the system. It can be seen from the figure that with the increase in the concentration of  $CO_{3^{2-}}$ , the number of atoms contained in the largest cluster particles in the solution system also increases, and the degree of agglomeration is increasing. This phenomenon shows that in the range of 15 vol.%–25 vol.%  $CO_{3^{2-}}$  concentration, high concentration of  $CO_{3^{2-}}$  is beneficial to the formation of large clusters and the association between  $Ca^{2+}$  and  $CO_{3^{2-}}$ .



**Figure 11.** Characteristics of the largest cluster particles in the system under different concentrations of CO<sub>3<sup>2-</sup></sub>. (a) 15 vol.%; (b) 20 vol.%; (c) 25 vol.%.

It shows that in the CaCO<sub>3</sub>–NH<sub>4</sub>Cl–H<sub>2</sub>O system, increasing concentration of CO<sub>3</sub><sup>2-</sup> is beneficial to the formation of large clusters of CaCO<sub>3</sub>. Ca<sup>2+</sup> and CO<sub>3</sub><sup>2-</sup> further improve the association degree, inhibit the hydration of Ca<sup>2+</sup> and CO<sub>3</sub><sup>2-</sup>, and enhance the stability of the association structure of Ca<sup>2+</sup> and CO<sub>3</sub><sup>2-</sup>.

#### 4. Conclusions

The crystallization behavior of CaCO<sub>3</sub> in the Ca<sup>2+</sup>–CO<sub>3</sub><sup>2-</sup>–NH<sub>4</sub><sup>+</sup>–Cl–H<sub>2</sub>O system at different temperatures and different concentrations of CO<sub>3</sub><sup>2-</sup> was simulated by molecular dynamics simulation method using Materials Studio software. In this work, the crystallization behavior of CaCO<sub>3</sub> in the temperature range of 20–80 °C was simulated. The results show that the Ca<sup>2+</sup> bonding to CO<sub>3</sub><sup>2-</sup> at a distance of r=4.07 Å, which the bonding energy between Ca<sup>2+</sup>–CO<sub>3</sub><sup>2-</sup> increased with the temperature (20–80 °C). This reasons behind of the phenomenon may be the destruction of the hydrogen bonding network between water molecules by a higher temperature. In addition, the diffusion coefficients of

Ca<sup>2+</sup> and CO<sub>3</sub><sup>2-</sup> are increased with the temperature. Furthermore, the effect of the concentration of CO<sub>3</sub><sup>2-</sup> on CaCO<sub>3</sub> is studied in the range of 15 vol.%–25 vol.%. It was found that the changes of the concentration of CO<sub>3</sub><sup>2-</sup> and temperature have an insignificant of the binding distances between Ca<sup>2+</sup>– CO<sub>3</sub><sup>2-</sup>, which the first CO<sub>3</sub><sup>2-</sup> shell around Ca<sup>2+</sup> with a distance of 4.05 Å. In addition, the intensity of the first peak of Ca<sup>2+</sup>–CO<sub>3</sub><sup>2-</sup> increased remarkably with the CO<sub>3</sub><sup>2-</sup> concentration, indicating a higher binding capacity of Ca<sup>2+</sup> and CO<sub>3</sub><sup>2-</sup> with the increase in the concentration of CO<sub>3</sub><sup>2-</sup>. The mean square displacement of Ca<sup>2+</sup> and CO<sub>3</sub><sup>2-</sup> increases with increasing concentration of CO<sub>3</sub><sup>2-</sup>, which beneficial to the formation of the large CaCO<sub>3</sub> cluster. However, a high concentration of CO<sub>3</sub><sup>2-</sup> in the solution system may require a higher CO<sub>2</sub> content in the industrial waste gas or gas flow rate.

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