A comparative dynamic study of seawater pretreatment using experimental and pilot bubble tower

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ABSTRACT

In the previous study, greenhouse gas CO₂ was successfully used as the precipitator to realize its carbonation by calcium ions in seawater with the help of magnesium oxide. In this study, the reaction process was firstly analyzed by a proposed reaction mechanism, and then the dynamic simulation of the gas–liquid–solid system was carried out via kinetic Monte Carlo simulation. Based on the reaction mechanism, the continuous experimental study was realized in a bubble column. The effects of air flow rate, carbon dioxide flow rate and temperature on the effectiveness evaluation indexes of decalcification efficiency, total mass transfer coefficient and carbon sequestration rate were studied. Finally, a bonnet tower with a diameter of 1 m and a height of 8 m was built to carry out the pilot test. In the laboratory experiments, the calcium removal rate reached 94%, the carbon sequestration rate reached 63.6%, and pure micron calcium carbonate products were obtained. The decalcification rate reached 95% in the pilot test, which is consistent with the results of the laboratory experiment.

Key words | carbon fixation, gas–liquid–solid system, Monte Carlo simulation, seawater decalcification

HIGHLIGHTS

- Reaction kinetics model in a gas–liquid–solid system is proposed.
- The continuous experimental study was realized in a bubble column.
- The basic data are provided for industrialization via laboratory and pilot tests.

GRAPHICAL ABSTRACT

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INTRODUCTION

With economic development, freshwater resources will become one of the biggest problems that plagues human development (José 2014). Seawater is considered as the most abundant raw material for freshwater production (Mahinpey et al. 2011). Now electrodialysis (Guillaume et al. 2018) and reverse osmosis (Lee et al. 2011) are being gradually developed as the environmentally friendly seawater desalination technologies. The large amount of calcium and magnesium ions in seawater will seriously affect the service life of the membrane (Tanaka et al. 2011).

Meanwhile, the development of new technologies for capturing and sequestering the emitted CO₂ is urgently required to restrain the effects of global warming. For this purpose, permanent fixation of CO₂ in the form of stable and environmentally benign carbonate minerals, such as magnesite (MgCO₃) and calcite (CaCO₃), through a mineral carbonation process has gained attention recently (Bobicki et al. 2012; Lu et al. 2016; Arias et al. 2017; Ebrahimi et al. 2018). The utilization of calcium ions in seawater to fix CO₂ in the form of calcium carbonate in the presence of alkaline sources has been studied by our group, and shows the potential characteristics of high reaction rate and energy saving. Sodium hydroxide was firstly chosen as a base source, and it is interesting to find that OH⁻ would precipitate in the form of Mg(OH)₂ and then Mg(OH)₂ would combine with CO₂ to form Mg₂CO₃ and meanwhile CaCO₃ would precipitate, rather than OH⁻ directly reacting with HCO₃⁻ to help the transformation of CO₂ to CaCO₃ (Zhao et al. 2013, 2016). Therefore, in order to reduce the operational cost, Mg(OH)₂ and even the base residual, which is the brine pretreatment waste of soda ash plant mainly containing Mg (OH)₂ and CaCO₃, were successfully tested as the alkali source (Zhao et al. 2017).

It is further proposed that MgO can act as the alkali source and the produced Mg₂⁺ and HCO₃⁻ can precipitate in the presence of NaOH (Zhao et al. 2019). The experiments demonstrated the sequestration can proceed at high speed, and pure CaCO₃ and MgCO₃·3H₂O can be produced as by-products, which can probably take place in a traditional chemical plant at minimal capital and energy expense.

Reaction kinetics is essential for the reactor and process analysis, design, simulation and control, as the state of the reactants and products over time can be obtained. Generally, the chemical reaction mechanism is firstly speculated and then a chemical reaction kinetics model is set up to make the dynamics simulation. The availability of the reaction mechanism can be effectively determined by comparing simulation results with the experimental results. Thus, the dynamic simulation is an indispensable part in the study of the chemical reaction mechanism.

Meanwhile, as an important gas–liquid mass transfer reactor, the absorption tower such as the spray tower has a good application prospect in carbon dioxide fixation because of its high mass transfer efficiency and gas–liquid contact time (Kavoshi et al. 2015). For example, Ma and colleagues used ammonia water as an absorbent to absorb carbon dioxide in a bubble reactor and achieved good results (Ma et al. 2016). Möller found low gas holdup and large bubbles limited the mass transfer between gas and liquid, by comparing the performance between different orifice modes of ejectors (Möller et al. 2017).

Therefore, a kinetic Monte Carlo (KMC) simulation was firstly carried out with the help of Java software to simulate the changes in Ca²⁺ and Mg²⁺ concentrations and alkalinity with reaction time in presence of MgO, and the reaction mechanism was revealed. Then a bubble column was chosen as a reactor, in which a distributor with a cross-flow sieve tray with void diameter of 0.01 mm was added to strengthen the gas–liquid contact process. Finally, a bonnet tower with a diameter of 1 m and a height of 8 m was built to carry out the pilot test.

SIMULATION AND EXPERIMENTAL PROCEDURE

Simulation algorithm

The core algorithm in this work is the dynamic Monte Carlo simulation (KMC) algorithm developed by Gillespie (1976). The algorithm does not distinguish between series, parallel reaction and reaction order, whereas the reaction rate constants of each reaction need to be determined in the algorithm. The principle of the algorithm is to decide the reaction probability according to the reaction rate constant, and then the time interval and the length of the reaction types for the next step is determined by generating random numbers which uniformly distributed from 0 to 1. Then, according to the chemical reaction rate constant and a random number, the reaction time Δt is calculated and listed as below. Computing time is measured in Monte Carlo (MC) cycles (Gillespie 1976).

Δt = \( \left( \frac{1}{a_0} \right) \times \log \left( \frac{1}{R_1} \right) \)  \hspace{1cm} (1)
\[ a_0 = \sum_{i} k_i \cdot \prod_{j} X_{ij} \]  \hspace{1cm} (2)

where,
\( k_i \) is the reaction rate constant of reaction \( i \);
\( X_j \) is the number of particles of reactant \( j \) in reaction \( i \);
\( R_1 \) is a random number uniformly distributed between 0 and 1.

According to the calculated \( a_0 \) and another random number \( R_2 \), \( a_i \) is determined by the following calculation (Gillespie 1976).

\[
\begin{align*}
    a_i &= k_i \times \prod X_j \\
    \sum_{i=1}^{n-1} a_i &< R_2 \cdot a_0 \leq \sum_{i=1}^{n} a_i 
\end{align*}
\]

After the reaction types were determined, the number of particles of the reactants and products were adjusted accordingly.

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**Laboratory experiment**

The preparation and chemical composition of used artificial seawater are as given in the previous literature (Al-Anezi & Hilal 2006). All the raw materials mentioned in this study are of analytical purity. The experimental device is shown in Figure 1(a). The reactor is a glass column with an inner diameter of 14.8 cm and a height of 160 cm, which is separated by trays into six sections. The temperature was controlled in the range from 30 °C to 80 °C by the distributed control system (DCS).

A fixed amount of magnesium oxide with seawater was firstly added to the mixer and stirred into a uniform suspension at a certain temperature controlled by the DCS. The amount of magnesium oxide is twice as much as the moles of calcium ions. Carbon dioxide and air supplied by a CO₂

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![Figure 1](http://iwaponline.com/wst/article-pdf/83/4/803/850267/wst083040803.pdf)

**Figure 1** | (a) Laboratory scale experimental equipment diagram and (b) pilot plant photographs. b-1: Pilot technological process. b-2: Seawater feed tank. b-3: Seawater tank and magnesium oxide storage tank. b-4: Gas-liquid contact tower. b-5: Air blower and carbon dioxide cylinder.
cylinder and air blower were mixed quantitatively in a gas collecting device. Then, the collected gas was piped into a distributor which was laid at the bottom of the reactor. Meanwhile, the suspension was pumped into the reactor from the top.

**Pilot tests**

The pilot test was conducted in a gas–liquid contact tower with the diameter of 1 m and the height of 8 m, which was also equipped with several storage tanks: seawater feed tank (Φ2,000 × 2,000 mm), seawater tank (Φ3,000 × 3,000 mm), magnesium oxide storage tank (Φ1,000 × 1,000 mm), mixing tank (SV-5), air blower (ZG-65) and carbon dioxide cylinder (40 L), as shown in Figure 1(b).

**Calculation method**

The decalcification and carbon sequestration rates are calculated using the following methods.

The carbonization efficiency of calcium ions was studied from the rates of calcium removal $R_{Ca^{2+}}$ % and carbon sequestration $R_{CO_2}$ % calculated by Equations (5) and (6) respectively.

$$R_{Ca^{2+}} \% = \frac{C_{Ca^{2+}}^0 - C_{Ca^{2+}}}{C_{Ca^{2+}}^0} \times 100$$  \hspace{1cm} (5)

where $C_{Ca^{2+}}^0$ is calcium ion concentration in raw seawater (g·L$^{-1}$); $C_{Ca^{2+}}$ is calcium ion concentration in seawater after decalcification (g·L$^{-1}$).

$$R_{CO_2} \% = \frac{V \cdot \left( \frac{\rho_{CO_2} \cdot \rho_{air} \cdot \alpha_{CO_2}}{M_{Ca^{2+}} + M_{CO_2} + M_{HCO_3^-}} \right) \times 24.5}{(V_{CO_2} + V_{air} \cdot r_{CO_2}) \cdot \text{reaction time}} \times 100$$  \hspace{1cm} (6)

where V is the volume of seawater consumed per unit of time, L; $M_{Ca}$ is the molar mass of calcium ions, 40 g·mol$^{-1}$; $[CO_2]$ is the volume concentration of CO$_2$, mol·L$^{-1}$; $[HCO_3^-]$ is the volume concentration of HCO$_3^-$, mol·L$^{-1}$; $V_{CO_2}$ is the ventilation flow rate of carbon dioxide, L·min$^{-1}$; $V_{air}$ is the air ventilation flow rate, L·min$^{-1}$; $r_{CO_2}$ % is the proportion of carbon dioxide in the air.

The following is the calculation method of total mass transfer coefficient.

$D_{CO_2}$ is the diffusion coefficient of carbon dioxide calculated by Equation (7).

$$D_{CO_2} = \frac{7.4 \times 10^{-8} (\alpha M_B)^{0.5} T}{\mu V_A^{0.6}}$$  \hspace{1cm} (7)

Substitute $D_{CO_2}$ into Equations (8) and (9) (Wang et al. 2017) to get $k_L^0$ and $k_{g}$.

$$k_L^0 = \left( \frac{3 \pi^2}{2} \right) \left( \frac{Q h^2 W^2}{F} \right) \left( \frac{\rho}{\mu} \right)^{\frac{1}{2}} D_{CO_2}$$  \hspace{1cm} (8)

$$\frac{RTk_h h}{D_{CO_2}} = \phi = 1.075 \left( \frac{ReSc}{\Pi} \right)^{0.85}$$  \hspace{1cm} (9)

Plug $D_{CO_2}$ and $k_L^0$ into Equation (10) (Ma et al. 2016) and Equation (11) (Wang et al. 2017)

$$E_{CO_2} = \sqrt{\frac{kD_{CO_2} C_{int}}{k_L}}$$  \hspace{1cm} (10)

$$\frac{1}{k_L} = \frac{H}{E_{CO_2}^2}$$  \hspace{1cm} (11)

where $k$ is the reaction rate constant of CO$_2$ absorption which is obtained by lg $k = 11.15 - 2.555/T$, mol·L$^{-1}$·s$^{-1}$; $\mu$ is viscosity measured by a Ukrainian viscometer, mPa·s. $H$ is Henry coefficient, Pa·cm$^{-3}$·mol$^{-1}$; $T$ is temperature, K; $Re$ is Reynolds number; $R$ is the universal gas constant, 8.31 J·mol$^{-1}$·K$^{-1}$; $Sh$ is Sherwood number; $Sc$ is Schmidt number; $d$ is diameter of tower, cm; $h$ is height, cm; $\Pi$ is 3.14; $g$ is 9.81; $C_{int}$ is calcium concentration, mol·L$^{-1}$; $k_L$ is liquid film mass transfer coefficient, mol·Pa$^{-1}$·cm$^{-2}$·s$^{-1}$; $D_{CO_2}$ is diffusion coefficient of carbon dioxide, cm$^2$·s$^{-1}$; $\rho$ is density, kg·m$^{-3}$; $W$ is column circumference, cm; $F$ is interface area, cm$^2$; $Q$ is flow rate, mL·s$^{-1}$; $\mu$ is viscosity, mPa·s; $M_B$ is molar mass of seawater, kg·kmol$^{-1}$; $V_A$ is molar volume of CO$_2$, cm$^3$·mol$^{-1}$.

In the mass transfer process between gas phase and liquid phase, there are mass transfer resistance of gas film (1/$k_g$) and mass transfer resistance of liquid film (1/$k_L$). The total mass transfer resistance (1/$K_G$) is generally calculated as Equation (12) (Wang et al. 2017):

$$\frac{1}{k_g} + \frac{1}{k_L} = \frac{1}{K_G}$$  \hspace{1cm} (12)

where $k_g$ and $K_G$ represent the gas film mass transfer coefficient, mol·Pa$^{-1}$·cm$^{-2}$·s$^{-1}$, and total mass transfer coefficient,
mol·Pa⁻¹·cm⁻²·s⁻¹; \( k_L^0 \) indicates the non-reactive liquid membrane mass transfer coefficient, cm·s⁻¹; \( E \) indicates the reaction enhancement factor (Dugas & Rochelle 2009; Ma et al. 2016).

**RESULTS AND DISCUSSION**

**Simulation**

**Speculation of reaction mechanism**

Based on the analysis on the concentration of residual ions in solution and the composition of solid precipitates, the main reactions for the CO₂ sequestration by Ca²⁺ in the presence of MgO were discussed in the previous study work (Zhao et al. 2016). The change of concentration of Ca²⁺ and Mg²⁺ in solution and the composition of solid precipitates with reaction time at 80 °C and under the condition that the mole ratio of added MgO is four times that of calcium in water are shown in Figure 2.

It can be found that before the injection of CO₂, alkali source MgO has already reacted with H₂O, and Mg(OH)₂ is created and ionized, which is generally called the digestion process of magnesium oxide as shown in Equations (13) and (14).

\[
\text{MgO} + \text{H}_2\text{O} \rightarrow \text{Mg(OH)}_2 \tag{13}
\]

\[
\text{Mg(OH)}_2 \leftrightarrow \text{Mg}^{2+} + 2\text{OH}^- \tag{14}
\]

Once the gas CO₂ is injected, Ca²⁺ would combine with CO₃²⁻ to form CaCO₃; meanwhile the concentration of Mg²⁺ increases. According to the simple thermodynamic analysis of standard molar reaction enthalpy change (kJ·mol⁻¹) and standard Gibbs free energy change (kJ·mol⁻¹), it is assumed that the reaction between MgO/Mg(OH)₂ and CO₂ occurs as listed in Equations (15)–(17).

\[
\text{CO}_2(\text{g}) \rightarrow \text{CO}_2(\text{l}) \tag{15}
\]

\[
\text{MgO} + \text{H}_2\text{O} + \text{CO}_2 \rightarrow \text{Mg}^{2+} + 2\text{HCO}_3^- \tag{16}
\]

\[
\text{Mg(OH)}_2 + \text{CO}_2 \rightarrow \text{Mg}^{2+} + 2\text{HCO}_3^- \tag{17}
\]

It is well known that CO₂ will dissociate in the water and in this system its dissociation occurs with the help of

![Figure 2](http://iwaponline.com/wst/article-pdf/83/4/803/850267/wst083040803.pdf) | The change of concentration of Ca²⁺ and Mg²⁺ in solution and the composition of solid precipitates with reaction time during the CO₂ sequestration by Ca²⁺ in the presence of MgO.
OH⁻, described as Equations (18)–(23).

\[ \text{H}_2\text{O} \leftrightarrow \text{H}^+ + \text{OH}^- \]  
(18)

\[ \text{CO}_2 + \text{H}_2\text{O} \leftrightarrow \text{H}^+ + \text{HCO}_3^- \]  
(19)

\[ \text{HCO}_3^- \leftrightarrow \text{H}^+ + \text{CO}_3^{2-} \]  
(20)

\[ \text{CO}_2 + \text{OH}^- \rightarrow \text{HCO}_3^- \]  
(21)

\[ 2\text{HCO}_3^- \rightarrow \text{CO}_3^{2-} + \text{CO}_2 + \text{H}_2\text{O} \]  
(22)

\[ \text{CO}_3^{2-} + \text{H}_2\text{O} \leftrightarrow \text{HCO}_3^- + \text{OH}^- \]  
(23)

With the generation of carbanion, calcium ions in the residual solution will decrease as CaCO₃ precipitates as shown in Equation (24) and magnesium ions in the residual solution will increase as shown in Equations (16) and (17).

\[ \text{CO}_3^{2-} + \text{Ca}^{2+} \rightarrow \text{CaCO}_3 \]  
(24)

However, when the calcium ions in the residual solution are not enough to form calcium carbonate, the form and dissolution of calcium carbonation (Equation (25)) will come to level off.

\[ \text{CaCO}_3 \leftrightarrow \text{Ca}^{2+} + \text{CO}_3^{2-} \]  
(25)

**Simulation procedure**

Our KMC algorithm consists of the following steps, shown in Figure 3.

As shown in Figure 3, the whole procedure can be described as the following.

(a) Set the particle numbers of each ion according to its concentration and related reaction rates by Equations (2) and (3).

(b) Generate random numbers R₁ and R₂ uniformly distributed between 0 and 1.

(c) Update computing time from \( t \to t + \Delta t \), \( \Delta t \) is defined by Equation (1).

(d) Perform the adsorption of \( \text{CO}_2 \) according to its gas-liquid mass transfer model and calculate the particles of liquid \( \text{CO}_2 \).

(e) The reactions are divided into three categories: fast reaction, controlled speed reaction and equilibrium reaction. Perform the KMC algorithm respectively:

For the controlled speed reactions, such as Equations (13), (16), (17), (21), (22) and (24), the reaction type \( i \) is firstly decided by Equations (3) and (4), and the number of particles of the reactant in the related reaction \( i \) is subtracted by 1 but those of the reaction products in the related reaction \( i \) are added by 1. For example, when Equation (13) is performed, if the number of particles of MgO and \( \text{H}_2\text{O} \) is each greater than or equal to 1, the reaction can occur; then the number of particles of MgO and \( \text{H}_2\text{O} \) is subtracted by 1 but the number of particles of Mg(OH)₂ is added by 1: Mg(OH)₂ + 1. If the number of particles of MgO or \( \text{H}_2\text{O} \) is less than 1, the reaction cannot occur, and the KMC algorithm is skipped for the next step.

For the rapid reactions of Equations (18) and (20), and equilibrium reaction of Equations (14), (19), (23) and (25), if \( K > K_{sp} \), the number of particles of the reactant in the related reaction \( i \) is subtracted by 1 but those of the reaction products in the related reaction \( i \) are added 1. If \( K < K_{sp} \), the reverse reaction event happens: the number of the reactants increases by 1, and those of the products decrease by 1. If \( K = K_{sp} \), skip the event.

(f) Repeat the algorithm until the concentrations of \( \text{Ca}^{2+} \) and \( \text{Mg}^{2+} \) reach equilibrium.

The correlated kinetic constants

Some relative reaction rate constants \( k_i \) are obtained from the previous literature and some equilibrium constants \( K_i \) are calculated by HSC 6.0 The correlated kinetic constants of the main reactions are shown in Table 1.

**Simulation results**

The simulation program ran \( 3.23 \times 10^9 \) MC cycles. In order to reduce computer’s memory footprint, data were recorded every \( 10^7 \) cycles, and a total of 323 sets of data were output, including ‘machine time, MT’, ‘\( \text{Ca}^{2+} \) particle number’, ‘\( \text{Mg}^{2+} \) particle number’ and ‘total alkalinity’, where the total alkalinity is calculated using the intermediate variables of \( \text{OH}^- \), \( \text{CO}_3^{2-} \) and \( \text{HCO}_3^- \) in the program.

Figure 4(a) shows the simulation results of \( \text{Ca}^{2+} \) and \( \text{Mg}^{2+} \) particle number along with the change of machine time. It can be seen that \( \text{Ca}^{2+} \) particle count drops rapidly when the machine time is 0–5 MT, and then it goes down like a ladder within 5–35 MT, which is speculated to be due to the nature of the KMC algorithm for only a reaction can occur at each time step, and there are multiple ways for the generation of \( \text{CO}_3^{2-} \), the restriction of number of
particles leading to the step-down. Within 5–35 MT, the reduction rate of Ca$^{2+}$ particle number gradually decreases, and finally drops to the lowest point at about 35 MT. After that, the concentration remains unchanged, but it does not reach the theoretical value of 0, nor does it reach the value at the dissolution equilibrium of CaCO$_3$.
Mg$^{2+}$ particle number increased rapidly within 0–5 MT, and then the particle number of Mg$^{2+}$ did not increase.

In the KMC algorithm, the MT generated by the random number of CPU is not one-to-one correspondence with the natural reaction time, so the machine time needs to be corresponded with the natural reaction time. By comparison, 1 MT is equal to 0.2143 min.

The simulation results of the Ca$^{2+}$ and Mg$^{2+}$ concentrations with time are shown in Figure 4(b) and can be compared with experimental data. We can obviously draw the conclusion that the simulation results of Ca$^{2+}$ are in accordance with the experimental data; at about 7 min, Ca$^{2+}$ concentration basically reached the lowest value which can elucidate the mechanism proposed in Table 1. The simulation results of Mg$^{2+}$ concentration change are close to the experimental results, and Mg$^{2+}$ concentration increases gradually during 10 min. It is inferred that the difference of simulation results with the experimental results could be because the simulation only considers the ideal adsorption of CO$_2$ into the system, but does not take into account the actual gas-liquid mass transfer during CO$_2$ bubbling and the change of the specific surface area of MgO and Mg(OH)$_2$. Meanwhile, sampling and analysis preparation time is required for the offline analysis of the basic ions in the experiments, and probably there is still going on the solvation of the CO$_2$, thus causing certain deviation between the experimental result and the simulation value. After 10 min, Mg(OH)$_2$ completely disappeared in the system. At this point, CO$_2$ and CO$_3^{2-}$ and HCO$_3^-$ were in the state of reaction equilibrium and dissolution equilibrium, so the total alkalinity would not continue to increase.

Based on the above analysis, the dynamic simulation by using the KMC algorithm is basically consistent with the experimental results.

### Laboratory experiment

Based on the above mechanism studies, it can be concluded that the reaction between magnesium oxide and carbon dioxide theoretically depends on the reaction between gas...
(CO₂) and solid (MgO), rather than the hydrolysis of magnesium oxide and the ionization of magnesium hydroxide. Therefore, it is proposed in this paper that there is no need for digestion after adding magnesium oxide. Moreover, the column spray tower is used to enhance the mass transfer rate between the vapor, liquid and solid, thus reducing the reaction time and realizing continuous reaction. In this part, the influence of air flow, temperature and carbon dioxide concentration on the decalcification rate and carbon sequestration rate were investigated. Meanwhile, the corresponding total mass transfer coefficients were calculated.

**Influence of air flow**

The influence of air flow on the decalcification rate was firstly investigated, in which the flow rate of CO₂ was maintained but the air flow rate was increased.

Figure 5(a) shows the change of calcium removal rate under different air flow rates. As the air flow increased from 4 L·min⁻¹ to 8 L·min⁻¹, the calcium removal rate gradually decreased. Keon et al. (2020) found that the formation of bubbles is unstable under large gas flow, and the rising speed of large bubbles in solution is faster than that of small bubbles. Then it is speculated that a reduction in the carbon dioxide ratio is not conducive to the gas–liquid exchange, as the proportion of carbon dioxide decreases and air flow increases. The surface area of the mass transfer interface was calculated by taking the tray aperture as the average diameter of the bubble to calculate the total mass transfer coefficient (K_G).

As shown in Figure 5(b), K_G decreases with the increase of air flow, which can also be explained from Equation (12); when 1/k_L is fixed, the increases of 1/k_G of CO₂ with increasing air gas flow, which is caused by the decrease of CO₂ proportion, would lead to the decrease of K_G. And it also verifies that the mass transfer is reduced but the total gas–liquid contact area increases with the increase of air flow. Thus, the decalcification rate decreases with increasing the air flow, as shown in Figure 5(a). To further verify this conclusion, the carbon sequestration rate was calculated, as shown in Figure 5(c).

From Figure 5(c), it can be seen that carbon sequestration rate decreases gradually with the increase of air flow rate. It is speculated that excessive air flow leads to shorter residence time, and the reduction of carbon dioxide proportion is not conducive to absorption.

**The effect of temperature**

The influence of temperature was then investigated, since theoretically the temperature will affect gas–liquid mass transfer and the reaction between gas and solid.

Figure 6(a) shows the change of calcium removal rate at different temperatures. By comparing the five temperatures, it is found that the conversion rate at 30 °C is lower than...
75%, but the decalcification rate can increase to 90% at 40 °C, and then the temperature brings little increase when it continues to increase. Based on kinetic theory (Liu et al. 2013), the increase in temperature will accelerate the thermodynamic movement of gases and the percentage of activated molecules; then the reaction rate increases between CO₂ and MgO. As the temperature rises, the gas molecules
become too active, causing them to escape from the liquid. Therefore, 50 °C can be chosen as the optimal reaction condition. As shown in Figure 6(b), the total mass transfer coefficient first increases and then decreases with the rise of temperature. The mass transfer coefficient is highest at 50 °C. But the carbon sequestration rate decreases with increasing temperature (as can be seen in Figure 6(c)), and it can be explained that high temperatures lead to the escape of CO₂ molecules from seawater and a decrease in the solubility of carbon dioxide (Abuin et al. 2014).

Influence of carbon dioxide concentration

The influence of carbon dioxide concentration was then investigated by changing the CO₂ flow rate while the flow rate of air was kept constant, since the concentration of CO₂ may affect gas–liquid mass transfer and the adsorption between gas and solid.

The effect of carbon dioxide flow rate on calcium removal rate is shown in Figure 7(a). From Figure 7(a), we can see that the decalcification rate is the highest when the carbon dioxide flow rate is 60 L·h⁻¹, and the decalcification rate is lowest when the carbon dioxide flow rate is 80 L·h⁻¹. The change of carbon dioxide flow has no effect on the total mass transfer coefficient, as listed in Figure 7(b). From Figure 7(c), it can be seen that carbon sequestration rate decreases with the increase of carbon dioxide flow rate. It is inferred that the change of carbon dioxide has little effect on the gas–liquid mass transfer, mainly because the increase of carbon dioxide flow has little change on the total gas volume, and the change of kᵫ can be ignored. But higher flow rate leads to lower adsorption of CO₂, and then there is an optimal CO₂ flow concentration.

The detailed process analysis under optimal experimental condition

According to the above comparation of experimental conditions, the process was analyzed in detail under the optimal experimental condition, in which the air flow rate was 4 L·min⁻¹, CO₂ flow rate was 60 L·h⁻¹ and the temperature was 50 °C.

The alkali oxide of MgO is difficult to dissolve, but from the simulation it is speculated that MgO reacts with CO₂ to form Mg²⁺. Therefore, the concentration of Mg²⁺ in solution with operation time was measured and compared with the theoretically maximum Mg²⁺ concentration, as it is the sum of the magnesium in the original seawater and MgO, shown in Figure 8(a). As can be seen, the magnesium ion concentration stabilizes after 40 minutes of operation time. After stabilization, the Mg²⁺ concentration reaches its theoretically maximum concentration, indicating magnesium oxide is completely ionized after experimental stabilization.
After the samples were collected, crystals were allowed to grow for 24 hours under the optimal conditions to see whether the decalcification changed. From Figure 8(b), the decalcification rate has a small increase to 95% after crystal growing time of 24 h. Thus, it is concluded that the gas–liquid–solid contact time in the column is sufficient to ensure their complete reaction.

Figure 9(b) shows the electron microscope image of the solid after the reaction at different magnification. The particles are about 5 microns in size and have the shapes of particles, columnar and spindles. In order to determine the composition of the solid phase after the reaction, X-ray diffraction (XRD) is used and the diffraction pattern is shown in Figure 9(a).

Pilot scale test

The pilot test device was designed and developed on the basis of the small test. As shown in Table 2, the optimal conditions of the small test were compared with those of the pilot test. Based on the limitation of the site and equipment of the pilot test, the scale of the pilot plant is 244 times that
of the laboratory. Through the comparison, it was found that the air flow increased by 333.33 times, the sea water flow increased by 330.12 times, and the carbon dioxide flow increased by only 150 times. This is because a higher gas volume greatly increases the total gas–liquid contact area in the pilot scale, and the height of the tower increases the gas–liquid contact time and makes the reaction more complete, so a better effect is achieved. The samples were allowed to stand for 24 hours for analysis of calcium removal rate at different operation times, as shown in Figure 10.

![Figure 9](image.png)

**Figure 9** (a) XRD diffraction pattern and (b) transmission electron microscopy images of calcium carbonate.

| Temperature | CO₂ flux m⁻³h⁻¹ | Air flux m⁻³h⁻¹ | Seawater flux m⁻³h⁻¹ | Magnesium oxide flux m⁻³h⁻¹ |
|-------------|-----------------|-----------------|----------------------|-----------------------------|
| Optimal conditions for small trials | 50 | 0.36 | 4 | 0.498 | 0 |
| Optimal conditions for pilot test | 50 | 9 | 80 | 15 | 1.44 |

Table 2 | Pilot test data sheet

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As can be seen, the decalcification rate reached 90% at 6 minutes and was maintained at 95% after 10 minutes, indicating that the seawater has filled the tower and aerated steadily within 10 minutes. The results of the pilot test were consistent with those of laboratory tests.

CONCLUSION

In this study, based on the reaction mechanism, the dynamic simulation of the reaction process was carried out, and then continuous laboratory experiments were done to establish the optimal experimental conditions and its pilot tests. The main conclusions are as follows.

i. A simulation model of the decalcification reaction was established, and the simulation of the gas–liquid–solid reaction kinetics process was realized through the KMC algorithm. Through simulation, the relationship of the concentration of Ca$^{2+}$ and Mg$^{2+}$ ions, and the total alkalinity with reaction time were obtained. Through a comparison, the simulation results were basically consistent with the experimental results.

ii. In the laboratory experiments, the optimal operating conditions were obtained from the three aspects of temperature, carbon dioxide flow and air flow. The calcium removal rate reached 94% and the carbon sequestration rate reached 63.6% under the considered optimal experimental condition. It can continuously produce micron-sized calcium carbonate with uniform particle size whose crystal type is aragonite.

iii. On the basis of the laboratory test, the pilot test was expanded in the pilot bonnet tower by about 300 times. The results showed that the absorption effect of gas and liquid was better, and the calcium removal rate was consistent with the results of laboratory test.

iv. Continuous decalcification and carbon sequestration experiments were carried out in the column and bonnet tower for the first time, which greatly saves raw materials and can achieve decalcification efficiency of about 95% at lower temperatures. The produced calcium carbonate has high purity and can be continuously produced as a product.

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DATA AVAILABILITY STATEMENT

All relevant data are included in the paper or its Supplementary Information.

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