

Contents lists available at ScienceDirect

Journal of Cleaner Production



journal homepage: www.elsevier.com/locate/jclepro

# Kinetics and structure analysis of CO<sub>2</sub> mineralization for recycled concrete aggregate (RCA)



# Xinyu Zhu, Tao Wang<sup>\*</sup>, Zhenwei Yi, Zhouxin Zhu

State Key Laboratory of Clean Energy Utilization, Zhejiang University, Hangzhou, 310027, PR China

# A R T I C L E I N F O Handling editor: Lei Shi

Recycled concrete aggregate

Gas-solid reaction kinetics

CO<sub>2</sub> mineralization

Curing parameters

Carbon sequestration

Keywords:

#### ABSTRACT

CO<sub>2</sub> mineralization of solid waste in the construction industry for green concrete production is a promising approach for economically storing CO<sub>2</sub> and recycling solid waste. Recent investigations have underscored the significance of CO<sub>2</sub> sequestration and the augmentation of RCA performance engendered by the holistic reaction processes. While there is a pronounced interest in the optimization of macroscopic reaction conditions (e.g., temperature, pressure, etc.), the exploration and enhancement of the reaction kinetics stage often remains under explored. This study employed a reaction kinetics model to quantify the reaction rate unveiled two distinct reaction stages within the mineralization reaction. Early evaporation and pore formation established the groundwork for the diffusion mechanism of gas product layers in the middle and later stages, emphasizing the crucial role of water in connecting solid ion leaching and gas dissolution-diffusion in the reaction. The water content of the reaction has an optimal value (4%-6%), smaller particle size correlates with a higher optimal water content. Pre-soaking with a calcium hydroxide (CH) solution or suspension was employed to improve mineralization reaction kinetics, resulting in RCA with improved pore characteristics and strength. The crushing index decreased by 28.8% and 21.8%, the water absorption rate decreased by 11.1% for both coarse and fine RCA, and the cumulative total porosity of fine RCA decreased by 17.6%. This research aims to broaden the applications of waste concrete in the CO<sub>2</sub> capture, utilization and storage (CCUS) industry and produce low-cost, extensively processed, and high-strength RCA products while contributing to sustainable CO2 management.

#### 1. Introduction

The Paris Agreement established the objective of limiting the global average temperature increase to no more than 2 °C from the preindustrial revolution era. Recently, many countries have successively proposed strategies to achieve carbon neutrality in the near future (Lyu et al., 2022). However, Developing countries face significant CO<sub>2</sub> emissions from engineering construction and renovation annually (International Energy Agency (IEA), 2020) (International Energy Agency (IEA), 2022), which wil generate a large amount of waste concrete at the same time. In this context, CCUS technology hold significant promise for CO<sub>2</sub> sequestration and waste concrete recycling within the construction industry. For China, this technology will lead to the conservation of approximately 200 million tons of Sand and stone materials and the absorption of over 5 million tons of CO<sub>2</sub> annually (Saha et al., 2023) (Monkman and Shao, 2010).

Over the years, numerous scholars have investigated the  $CO_2$  mineralization reaction in recycled concrete aggregate (RCA). Key

factors influencing the CO<sub>2</sub> sequestration include RCA particle size, reaction humidity, moisture content, temperature, CO<sub>2</sub> pressure and concentration (Li et al., 2019; Jang et al., 2016; Voigt et al., 2018; Shi et al., 2018; Kisku et al., 2017; Fernández Bertos et al., 2004; Zhan et al., 2014). Particle size significantly affects the CO<sub>2</sub> sequestration rate, with smaller particles demonstrating a higher rate than larger particles (Zhan et al., 2014) (Shi et al., 2018) (Li et al., 2019), attributed to the larger specific surface area of small particles facilitating CO<sub>2</sub> diffusion. Water plays a crucial role in the mineralization reaction, serving as a solvent for both CO<sub>2</sub> and calcium ions (Fernández Bertos et al., 2004). Both components must first dissolve in the pore water to undergo ion reactions (Voigt et al., 2018). However, excessive water content can lead to a decrease in ion concentration, thereby affecting the rate and extent of the reaction (Jang et al., 2016). Therefore, there exists an optimal moisture content that allows for a thorough reaction. Zhan et al. (2016) determined that an optimal moisture content of approximately 5% yields the best material strength for the mineralization reaction. Additionally, maintaining a relative humidity between 50% and 70% in the

https://doi.org/10.1016/j.jclepro.2024.141571

Received 25 November 2023; Received in revised form 18 January 2024; Accepted 28 February 2024 Available online 9 March 2024 0959-6526/© 2024 Elsevier Ltd. All rights reserved.

<sup>\*</sup> Corresponding author. *E-mail address:* oatgnaw@zju.edu.cn (T. Wang).



Fig. 1. RCA samples with different diameters; (a) 0.15 mm-5mm; (b) 5-10 mm.

system is beneficial for stabilizing the reaction moisture (Pu et al., 2021) (John et al., 1990). The influence of temperature on mineralization reactions is primarily manifested in two aspects. Higher temperatures accelerate CO2 diffusion (Drouet et al., 2019) (Lekakh et al., 2008) while decreasing its solubility in water (Tai et al., 2006). As the mineralization reaction is exothermic, excessively high temperatures are not conducive to the reaction (Ouyang and Cao, 2023). Liu et al. (2001) observed that heating within the 20-60 °C range could increase the CO<sub>2</sub> sequestration rate, but temperatures exceeding 60 °C yielded a detrimental effect. The effect of CO<sub>2</sub> pressure and concentration on the reaction is mainly related to molecular diffusion (Mo et al., 2016) (Hyvert et al., 2010). In addition, increasing the CO<sub>2</sub> pressure at lower pressures promotes CO<sub>2</sub> diffusion and significantly improves the rate of CO<sub>2</sub> sequestration (Fang et al., 2017). However, as the reaction pressure increases, its impact on the enhancement of the CO<sub>2</sub> sequestration rate gradually decreases (Pan et al., 2017). This is mainly because high pressure accelerates the precipitation of CaCO<sub>3</sub> and blocks the original gas channel, which hinders the progress of the reaction (Liu et al., 2001). Moreover, when the CO<sub>2</sub> concentration is below 20%, increasing the concentration significantly enhances the rate of CO<sub>2</sub> sequestration. However, concentrations exceeding 50% only lead to relatively small improvements in the rate of CO<sub>2</sub> sequestration (Kisku et al., 2017) (Pu et al., 2021).

Previous studies have predominantly focused on comparing the  $CO_2$  sequestration rate after the reaction under various conditions and the changes in the properties of mineralized RCA (Zhan et al., 2016; Pu et al., 2021; John et al., 1990; Drouet et al., 2019) (Wu et al., 2018) (Zhang et al., 2015) (Kou et al., 2014), with less emphasis on kinetic analysis of the reaction process. This article primarily assesses the aforementioned influencing factors in the mineralization process, analyzing the kinetic process throughout the entirety of the reaction process and exploring methods to enhance the reaction kinetic process.

#### 2. Materials and methods

## 2.1. Preparations of materials

The materials used in this study were sourced from the demolition of buildings in Hangzhou project by Hang Lung Properties Ltd (see Fig. 1); the contents of different chemical composition are shown in Table 1.The RCA were then sieved into three distinct grades based on particle size gradient: 0.15–2.5 mm, 2.5–5 mm, and 5–10 mm. Due to the relatively high moisture content of fine RCA, it is necessary to dry the RCA in an oven to absolute dryness before each experiment, and then adjust the moisture content of the RCA to the required level.

# 2.2. Experiments and methodologies

#### 2.2.1. $CO_2$ mineralization reaction

This study focused on the gas-solid two-phase chemical reaction between RCA and  $CO_2$ , with the primary reactions represented by Eq. (1) and Eq. (2) (Zhang et al., 2017).

$$CH + CO_2 \rightarrow CaCO_3 + H_2O \tag{1}$$

$$C-S-H + CO_2 \rightarrow CaCO_3 + SiO_2 \cdot nH_2O$$
<sup>(2)</sup>

Firstly,  $CO_2$  diffuses into the surface pores of the RCA and dissolves in the pore water. Substances such as CH and C–S–H then react with the dissolved  $CO_2$  to produce  $CaCO_3$  and silica gel. These products, having significantly lower solubility than the reactants, fill the voids within the RCA, thus enhancing its properties (Pu et al., 2023).

#### 2.2.2. Calculation method for CO<sub>2</sub> sequestration rate

This study developed a gas-solid two-phase reaction device for the  $CO_2$  mineralization of RCA (see Fig. 2). Open the reaction chamber before the start of the reaction, load the pre-weighed RCA, and close

Table I			
The chemical	composition	test results	of RCA

- 11

composition	СаО	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	SO <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	MgO	K <sub>2</sub> O
wt.%	19.72	53.17	11.71	0.662	5.82	2.20	3.29
composition wt.%	Na <sub>2</sub> O 1.78	TiO <sub>2</sub> 0.861	P <sub>2</sub> O <sub>5</sub> 0.223	MnO 0.138	ZnO 0.0252	BaO 0.0785	others 0.3223
wt.%	1.78	0.861	0.223	0.138	0.0252	0.0785	0.32



Fig. 2. Gas-solid two-phase reaction device.

# Table 2

Three common gas-solid reaction kinetic models.

Model basis	Kinetics function
Based on the diffusion mechanism of the product layer (HOUSE, 2007)	$[1-(1-\alpha)^{1/3}]^2 = kt$
Based on the surface chemical reaction mechanism (MONAZAM et al., 2011)	1- $(1-\alpha)^{1/3} = kt$
Based on the crystal nucleus growth mechanism (BARNES, 1980)	$[-\ln (1-\alpha)]^{1/3} = kt$

valves 2 and 3. Valve 1 is opened to introduce a specified amount of  $CO_2$  gas into the buffer tank, followed by closing valve 1. The reaction is initiated by introducing  $CO_2$  gas from the buffer tank into the reactor using valve 2. During the reaction process, gas can be supplied to the reaction chamber by controlling the opening and closing of valve 2 to maintain a constant reaction pressure. Simultaneously, a lifting switch controls the platform, immersing it in a water bath to maintain precise control over the reaction temperature. Temperature and pressure sensors enable real-time monitoring of gas data in both containers.

The reaction's CO<sub>2</sub> sequestration rate, denoted as  $\eta$ , is calculated using the gas method. Monitoring changes in pressure and temperature of the gas in the buffer tank and reaction chamber during the reaction process allows for the real-time calculation of  $CO_2$  consumption and  $CO_2$  sequestration rate, as expressed in Eq. (3) and Eq. (4).

$$m_{a} = P_{0}V_{1}M_{CO2}/(R \tau_{0} \gamma_{0}) - P_{1}V_{1}M_{CO2}/(R_{1} \tau_{1} \gamma_{1}) - P_{2}V_{2}M_{CO2}/(R \tau_{2} \gamma_{2})$$
(3)

$$\eta = m_a/m \tag{4}$$

Where *m* is the mass of added RCA (g),  $V_1$  is the volume of the buffer tank (L),  $V_2$  is the volume of the reaction chamber (L),  $M_{CO2}$  is the molar mass of CO<sub>2</sub> (g/mol). In the experiment,  $P_0$  is the initial pressure of the buffer tank before the reaction (Pa),  $\tau_0$  is the gas temperature of the buffer tank at this time (K), and  $\gamma_0$  is the compression factor of CO<sub>2</sub> at the pressure and temperature. During the reaction process, the recording point time was selected, where  $P_1$  is the pressure of the buffer tank at that time (Pa),  $P_2$  is the pressure of the reaction chamber (Pa),  $\tau_1$  and  $\tau_2$ are the temperature and temperature of the buffer tank and reaction chamber in that state (K),  $\gamma_1$ and and  $\gamma_2$  are the CO<sub>2</sub> compression factors of the two chambers in the corresponding state. *R* is the gas constant and is equal to 8.314 m<sup>3</sup>/(mol × K).

# 2.2.3. Gas solid reaction kinetics model

During the reaction process, the reaction rate gradually diminished. Prior studies have offered limited exploration of the kinetic models related to mineralization reactions (Li, 2020) (Bracconi, 1992) (Miao et al., 2023). To understand the trend of these kinetic models, this study employed a gas method to detect rate changes in real-time under different reaction conditions and analyzed and compared the models involved in accordance with the physical mechanism of mineralization reactions.

The mineralization reaction of RCA is a gas-solid two-phase, irreversible and non-uniform reaction. Under high-pressure gas-solid reaction conditions, three distinct reaction models are primarily influenced by various factors, as detailed in Table 2.

#### 3. Results and analysis

#### 3.1. CO2 accelerated mineralization of RCA

#### 3.1.1. The influence of RCA particle size and moisture content

Fig. 3 (a) illustrates the initial rate of mineralization reaction of RCA, which exhibited a relatively rapid progression, stabilizing at approximately 4 h. Notably, more than 50% of the process was completed within the first 10 min of the reaction. As depicted in Fig. 3 (a), a



Fig. 3. Reaction process curves. (a) Different particle sizes; (b) Under different moisture contents.

#### Table 3

Comparison of conversion rates of three particle sizes of RCA in the first 10 min.

RCA size	$CO_2$ sequestration rate in 10min reaction (%)	$CO_2$ sequestration rate in 240min reaction (%)	Conversion rate in the first 10 min (CO $_2$ sequestration rate in 10min reaction to total CO $_2$ sequestration rate)
0.15–2.5 mm	2.70	3.08	87.7%
2.5–5 mm	1.93	2.82	68.4%
5–10 mm	0.91	1.69	53.8%

reduction in the particle size of the RCA was paralleled by a gradual increase in the  $CO_2$  sequestration rate of the RCA under equivalent conditions. Furthermore, Table 3 provides insights into how smaller RCA particle sizes facilitate higher conversion rates within shorter time intervals, while RCA with larger particles exhibited a significant increase in conversion rates during the mid-phase of the reaction, which might be attributed to the restriction on inward  $CO_2$  diffusion imposed by larger particle sizes.

The accelerated mineralization reaction between RCA and CO2 primarily involves a reaction between leached  $Ca^{2+}$  ions and dissolved  $CO_2$ within the pore water. The content of pore water in the RCA significantly influenced this process. As shown in Fig. 3 (b), for RCA of identical particle size, an increase in pore water content initially augmented CO<sub>2</sub> sequestration during the reaction since an optimal water quantity facilitated thorough Ca<sup>2+</sup> leaching. Conversely, excessive moisture content obstructed the RCA' pores, hindering the inward diffusion of CO2 and reducing the ion content in the pore water solution, thereby impeding the mineralization reaction (Šavija and Luković, 2016). The theory mentioned above implies the existence of an optimal moisture content for each particle size of the RCA. As illustrated in Fig. 4, the RCA were categorized into 8 levels based on their particle size. The mineralization reaction was conducted at room temperature and a CO<sub>2</sub> partial pressure of 1 MPa for 4 h. The detection of the CO<sub>2</sub> sequestration rate during the reaction revealed that as the particle size of the RCA decreased, the optimal water content progressively increased, attributed to a reduction in RCA particle size, which amplified the specific surface area, necessitating more pore water to achieve the same water film thickness.

#### 3.1.2. The influence of $CO_2$ partial pressure and reaction temperature

It is well-established that the gas pressure in the gas-solid reaction determines the rate and depth of inward diffusion of gas molecules. In the present study, RCA with a particle size of 2.5–5 mm were used, and the mineralization reaction was performed at different  $CO_2$  pressures for 4 h at 40 °C and a water content of 4%. The  $CO_2$  sequestration rate was measured as shown in Fig. 5 (a). As the  $CO_2$  pressure gradually increased, the  $CO_2$  sequestration rate was enhanced, but its effect on improving the reaction conversion rate weakened, suggesting there is an upper limit to the improvement effect of the reaction  $CO_2$  sequestration rate, which cannot exceed the theoretical maximum value.

Taking the CO<sub>2</sub> sequestration rates of the reaction at 0.5 MPa, 0.8 MPa, 1.0 MPa, and 1.5 MPa for 4 h, a curve illustrating the changes in CO<sub>2</sub> sequestration rate with pressure was generated, as shown in Fig. 5 (b). Using a negative exponential function to fit experimental data, Eq. (5) was obtained as CO<sub>2</sub> pressure increases, the carbon sequestration rate gradually increases and slowly approaches the theoretical maximum value. By evaluating the upper limit of this negative exponential function, it was determined that the theoretical maximum CO<sub>2</sub> sequestration rate was 2.91%, consistent with the CO<sub>2</sub> sequestration rate observed in RCA with particle sizes ranging from 0.15 to 2.5 mm in Section 3.1.1. It can be completely mineralized after 4 h of reaction under a CO<sub>2</sub> pressure of 1 MPa. This finding suggests that the CO<sub>2</sub> sequestration potential of this batch of RCA was approximately 2.9%. Moreover, taking into account the cost implications associated with high

pressure, it is worth noting that utilizing a pressure of 1 MPa could yield a CO<sub>2</sub> sequestration rate exceeding 90%. Hence, 1 MPa was the optimal pressure for the mineralization, curing, and regeneration of fine RCA.

$$y = 0.0291 \times [1 - e^{(-x/0.337)}]$$
(5)

Fig. 5 (c) illustrates the reaction process curve obtained by controlling the mineralization reaction at various temperatures over 4 h using RCA with particle sizes of 2.5–5 mm, a CO<sub>2</sub> pressure of 1 MPa, and a moisture content of 4%. As the reaction temperature increased from 20 °C to 40 °C, both the reaction rate and the final CO<sub>2</sub> sequestration rate experienced a significant boost, suggesting that appropriate heating enhances CO<sub>2</sub> diffusion and the reactivity of ions in the reaction, leading to an improved reaction rate and ultimately a higher CO<sub>2</sub> sequestration rate. However, when the temperature was further increased to 60 °C, the initial reaction rate continued to rise, but after 30 min, there was a sharp decline in the reaction rate, resulting in a final CO<sub>2</sub> sequestration rate



Fig. 4.  $CO_2$  sequestration rate curve with varying water content of RCA of different particle sizes.



Fig. 5. Reaction process curves (a) Under different CO<sub>2</sub> pressures; (b) Fitting curve of CO<sub>2</sub> sequestration rate with pressure change; (c) Under different temperatures.

lower than that achieved at 40 °C. This decline was attributed to the rapid evaporation of water at excessively high temperatures. After 30 min, the moisture content decreased significantly, constraining the further enhancement of the reaction rate and the final  $CO_2$  sequestration rate. Consequently, excessive temperatures were detrimental to the reaction, highlighting the importance of utilizing the optimal temperature of 40 °C for the mineralization reaction of RCA.

# 3.1.3. Reaction kinetics

The conversion curves of the reaction for RCA with different particle sizes and water contents are shown in Fig. 6 (a) and 6 (b). The reactions took place at a temperature of 20 °C, a  $CO_2$  pressure of 1 MPa, and lasted 4 h. To facilitate comparison, the reaction time was presented in dimensionless form: t = reaction time/total time,  $\alpha =$  the carbon sequestration rate at this moment/the total carbon sequestration rate of the reaction under this condition. When comparing these curves to the three ideal models mentioned in Section 2.3, it was found that the kinetics of the mineralization reaction in RCA were consistent with the model dominated by gas product layer diffusion.

For RCA with a particle size in the range of 0.15–2.5 mm, the large

specific surface area facilitates rapid reaction. Consequently, the influence of  $CO_2$  initial dissolution and later water evaporation kinetics was more pronounced than gas product layer diffusion kinetics. In the case of RCA with particle sizes of 2.5–5 mm and 5–10 mm, there was ample space for gas diffusion within the product layer. In these RCA, gas diffusion within the product layer was the primary controlling factor. The mathematical representation of this kinetic conversion rate over time is given by Eq. (6), which can be transformed logarithmically into Eq. (7).

$$[1 - (1 - \alpha)^{1/3}]^2 = k t$$
(6)

$$\ln (1 - (1 - \alpha)^{1/3}) = (1/n) \times \ln t + (1/n) \times \ln k$$
(7)

where  $\alpha$  is the percentage of mineralization reaction at any given time (%). Its value is equal to the CO<sub>2</sub> sequestration rate at any time divided by the total CO<sub>2</sub> sequestration potential of 2.91%. *t* is the time of reaction (min), *k* is the reaction rate constant, and *n* is the model parameters, ideally set to 2.

Fig. 7 (a) shows the rate-fitting curves of RCA with different moisture contents during the mineralization reaction period under the curing conditions of 20  $^{\circ}$ C using a CO<sub>2</sub> curing pressure of 1 MPa. Using the



Fig. 6. Comparison between test curve and dynamic ideal model. (a) Different particle sizes; (b) Different moisture content.

segmented fitting method, it was found that the slope of the mineralization reaction curve during the early stage (30 min ago, ln t < 3) was significantly lower than the theoretical value (n = 2, slope = 0.5). The primary reason for this disparity is that during the early stage of the reaction, CO<sub>2</sub> gas molecules rapidly dissolve in the pore water of the RCA, creating a concentration gradient. During this stage, gas diffusion and the reaction are relatively intense. Additionally, due to the exothermic nature of the reaction, the heightened reactivity in the early stage may induce an unstable temperature gradient field, leading to partial evaporation or outward diffusion of pore water (Zhan et al., 2013). The evaporation of pore water and rapid heating jointly contribute to the deviation of the initial reaction slope.

During the later stage of the reaction (after 30 min, ln t > 3), the slope approached the ideal model with n = 2, given that the mineralization reaction completed in the previous stage constituted over 70% of the total reaction, resulting in the formation of a dense product layer of CaCO<sub>3</sub>. Consequently, the mineralization reaction entered a slower and more stable phase, with the product layer inhibiting and decelerating the inward diffusion of CO<sub>2</sub>, representing a diffusion-limited kinetic mechanism within the product layer (Wang et al., 2017).

During the reaction, the curve initially exhibited a slightly convex shape, signifying that the longitudinal intercept (i.e. reaction rate constant k) of the fitted curve gradually increased as the reaction progressed. This increase may be attributed to rapid heat generation during the early stages of the reaction, causing localized heating within the RCA. Simultaneously, the evaporation of water enhanced gas permeability, resulting in an escalation of the reaction rate constant. Beyond the 10-min mark, the curve assumed a concave shape, and the reaction equilibrium constant 'k' decreased. This process can be attributed to the deceleration of the reaction, heat loss, and the filling effect of the silica and calcium carbonate particles generated by the reaction within the RCA' pores, all of which contribute to the slowing down of the reaction rate constant (Huang et al., 2019).

Fig. 7 (b) and 7 (c) depict the rate-fitting curves of RCA with the same water contents during mineralization reactions conducted under varying  $CO_2$  pressures and temperatures. Utilizing a segmented fitting method, Table 4 and Table 5 present the parameters '*n*' and the rate constant '*k*' obtained from the fitting of the reaction process. In Table 5, the rate constant '*k*' remains relatively consistent under different partial pressures of CO<sub>2</sub>. However, there was a significant positive correlation between the rate constant '*k*' and temperature, indicating the influence of temperature on the reaction rate.

#### 3.1.4. The effect of additive on reaction kinetics

During the mineralization reaction process, the concentration of  $Ca^{2+}$  ions played a key role. Therefore, the RCA involved in the reaction were pre-treated by soaking in a CH solution, and the moisture content was then adjusted to the desired state (w/b = 4%). Fig. 8 displays the kinetic profiles of the reaction after soaking and slight stirring in four different concentrations of CH solutions for 24 h. The curve in the figure revealed that RCA soaked in clean water experienced ion loss, which was not conducive to subsequent mineralization reactions. After soaking in a 0.01 mol/L CH solution, the reaction kinetics closely resembled those of the unsoaked RCA, suggesting that when the concentration of the CH solution was less than 0.01 mol/L, it resulted in the dissolution and loss of  $\mathrm{Ca}^{2+}$  ions in the RCA, which was not conducive to subsequent mineralization reactions. Increasing the solution concentration appropriately could enhance the conversion rate of the reaction (the concentration of a CH-saturated solution at room temperature was about 0.02 mol/L). However, if the concentration became excessively high and a suspension was formed (0.04 mol/L), the kinetics were initially improved but were significantly inhibited during the later stage since higher concentrations of the soaking solution led to higher Ca<sup>2+</sup> content in the surface pores of the RCA after soaking, which, in turn, improved the conversion rate of the mineralization reaction. Nevertheless, when the concentration of the CH solution became excessively high, the rapid reaction in the early stage generated CaCO<sub>3</sub> fillings that made the RCA' surface denser. This density hindered the inward diffusion of CO<sub>2</sub> gas, resulting in a slower reaction rate in the middle and later stages of the reaction. Data shown in Table 6 also corroborated this theory. As the CH concentration increased from 0 to 0.02 mol/L, the apparent rate constant 'k' gradually rose. However, when the concentration was increased to 0.04 mol/L, 'k' actually decreased. An excessively high CH concentration was detrimental to the RCA' reaction. Throughout the entire reaction process, a concentration of 0.02 mol/L proved to be the most effective, consistent with the concentration of CH employed by Pan et al. (2017).

#### 3.2. Mechanical performance

By controlling the reaction time of RCA under optimal conditions, the mechanical properties of mineralized RCA were measured as a function of the degree of reaction (as shown in Fig. 9). A positive correlation was observed between the improvement of mechanical properties of RCA and the degree of reaction. The most significant



Fig. 7. Linear fitting relationship between ln [1-  $(1-\alpha)^{1/3}$ ] and ln t. (a) At different moisture contents; (b) At different CO<sub>2</sub> pressures; (c) At different temperatures.

Table 4
Fitting results of the apparent kinetic curve parameter $n$ in Fig. 7 (b) (c).

Variable	Pressure (MPa)				Temperature (°C)		
	0.5	0.8	1.0	1.5	20	40	60
n (The first curve)	3.91	3.14	3.02	3.33	4.28	3.71	4.34
R <sup>2</sup>	0.998	0.995	0.990	0.991	0.994	0.999	0.977
n (The second curve)	2.26	2.13	2.16	1.99	1.95	2.02	2.27
R <sup>2</sup>	0.989	0.995	0.978	0.989	0.991	0.989	0.990

# Table 5

Fitting results of the apparent kinetic curve parameter k of the second curve in Fig. 7 (b) (c).

Variable	Pressure (MPa)				Temperature (°C)		
	0.5	0.8	1.0	1.5	20	40 °C	60
$k/10^{-3} \min^{-1}$ R <sup>2</sup>	1.123 0.989	1.165 0.995	1.173 0.978	1.248 0.989	0.943 0.991	1.384 0.989	1.643 0.990

enhancement effect was observed in the crushing index of both coarse and fine RCA, with reductions of 19.5% and 17.8%, respectively. The improvement in water absorption of coarse and fine RCA was relatively modest, with decreases of 2.2% and 2.7%, respectively. However, after pre-soaking in a 0.02 mol/L CH solution followed by mineralization reaction, the performance improvement of RCA was remarkably significant. The crushing index decreased by 28.8% and 21.8%, and the water absorption rate decreased by 11.1% for both coarse and fine RCA. Pan et al. (2017) used 0.01 mol/L calcium hydroxide immersion in their study, and the crushing index of the aggregate decreased from 18% to 13%, a decrease of 27.8%, which is consistent with the improvement measured in this study (see Fig. 10).

# 3.3. Physical and chemical evolution

Fig. 11 (a) provides a comparative analysis of the X-ray diffraction patterns of RCA with particle sizes of 2.5–5 mm before and after the mineralization reaction. It was found that one of the main active substances in the RCA, CH, underwent a reaction (around  $18^{\circ}$ ), and its diffraction peak was significantly reduced. However, it did not



**Fig. 8.** Linear fitting relationship between ln  $[1 - (1-\alpha)^{1/3}]$  and ln *t* at different CH concentrations.

**Table 6** Fitting results of the apparent kinetic curve parameter n and parameter k in Fig. 8.

0					
CH concentration/(mol/L)	No soaking	0	0.01	0.02	0.04
<i>n</i> (The second curve) $k/10^{-3}$ min <sup>-1</sup> (The second curve)	2.02 1.587	1.94 1.336	2.12 1.519	2.02 2.295	2.05 1.826
$R^2$	0.984	0.989	0.988	0.981	0.974

completely disappear, indicating that the mineralization reaction of the RCA was not fully complete, which may be due to the presence of certain dense areas inside the RCA, which prevented gas molecules from

penetrating. This also explained why the final CO<sub>2</sub> sequestration rate of fine RCA (in section 3.1) was higher than that of coarse aggregate in the experimental data. Indeed, it is highly conceivable that grinding it into fine powder allows it to react with CO<sub>2</sub> completely upon contact. The peak representing ettringite (around 55°) disappeared after mineralization, indicating a near-complete reaction. Meanwhile, the peaks (around 29.5° and 39.5°) representing calcite (mainly composed of CaCO<sub>3</sub>) significantly increased, suggesting that calcite was the main component in the mineralization reaction products of RCA. The basic peak values representing C2S and C3S also decreased to some extent, indicating that a certain amount of calcium silicate, dicalcium silicate, and other substances were consumed during the reaction process. However, their degree of reaction and contribution to the CO<sub>2</sub> sequestration process of RCA mineralization reaction are smaller than those of CH. The peaks representing SiO<sub>2</sub> (around  $60^{\circ}$  and  $67^{\circ}$ ) showed a significant increase, and the SiO2 in these reaction products likely



**Fig. 10.** Comparison of crushing index and water absorption before and after the mineralization reaction.



Fig. 9. Changes in RCA' properties with degree of reaction.



Fig. 11. Microscopic testing of RCA. (a) X-ray diffraction patterns; (b) SEM photos; (c) Pore size distribution; (d) Accumulated pore volume.

emanated from the mineralization reaction transformation of silicon components in materials such as calcium silicate and dicalcium silicate.

As shown in Fig. 11 (b1), SEM revealed a large number of hydration products (such as flaky tobermorite and needle-like ettringite) before the mineralization reaction, with structures mostly resembling loose needle-like formations, which significantly limited the strength of the RCA (Morandeau and White, 2015). As shown in Fig. 11 (b2), after the mineralization reaction, structures, such as flaky tobermorite and acicular ettringite, were partially consumed, and a significant amount of granular calcium carbonate (aragonite) and other substances were generated and filled the original acicular and flaky structures, improving the original porosity (Groves et al., 2005) (Morandeau et al., 2014); some of the aragonite was converted into calcite, stabilizing the structure and resulting in enhanced overall mechanical compressive performance of the RCA.

Fig. 11 (c) and 11 (d) display the pore size distribution of fine RCA before and after the mineralization reaction. It was found that the pore reduction of RCA due to the mineralization reaction primarily occurred in the range of 30–200 nm, primarily attributed to the strong filling effect of aragonite and calcite generated by the reaction on pore sizes larger than 30 nm. However, the filling effect on pore sizes smaller than 10 nm was weaker, leading to some pore sizes larger than 10 nm shrinking to below 10 nm after filling, thereby increasing the number of

pores smaller than 30 nm after mineralization. When the reaction pressure was excessively high (1.5 MPa, orange line in Fig. 11 (c) (d)), a structural collapse occurred during the consumption of needle-shaped and flake-shaped crystals in the reaction, generating new granular crystals. Small pores merged to form larger pores, with more large pores observed under 1.5 MPa reaction conditions than other conditions.

On the other hand, after soaking with an appropriate concentration of CH (purple line in Fig. 11 (c) (d)), the mineralization reaction effectively promoted the transformation and filling of small pores. After this reaction, the abundance of pores smaller than 15 nm was lower than in other groups, and the cumulative total porosity was also the least (decreased by 17.6%), substantiating that the mineralization reaction of RCA soaked in additives yielded greater benefits in improving the performance of RCA.

# 4. Conclusions

In the present study, the  $CO_2$  mineralization kinetics of RCA under different conditions were examined, and the influence of additives on the kinetic process was explored. The findings of our study are summarized as follows:

- (1) The  $CO_2$  mineralization of RCA follows a diffusion-limited kinetics reaction. There are two reaction processes with distinct characteristics. The pores formed by water evaporation during the early stage lay the foundation for the diffusion mechanism of gas in the product layer in the middle and later stages. The model also indicates that water is vital in linking solid ion leaching and gas dissolution diffusion in the reaction. The water content of the reaction has an optimal value (4%–6%), which is related to the particle size of the RCA. Smaller particle size correlates with a higher optimal water content.
- (2) The addition of CH additives significantly impacts the kinetics of the reaction. On one hand, it rapidly increases the speed of the early stage of the reaction. However, it also obstructs pores due to the generation of more reaction products, affecting the kinetics of the later stage of the reaction. Therefore, the optimal soaking concentration for CH is 0.02 mol/L.
- (3) Mineralization can enhance the mechanical properties of RCA to varying degrees, particularly when soaked in a suitable concentration of CH solution before undergoing the mineralization reaction, significantly improving the material's porosity and mechanical performance. The crushing index decreased by 28.8% and 21.8%, the water absorption rate decreased by 11.1% for both coarse and fine RCA, and the cumulative total porosity decreased by 17.6% for fine RCA.

The mineralization regeneration of waste concrete connects the path of transforming demolished concrete into recycled building materials, effectively addressing the challenges of solid waste utilization, raw material supply, and high carbon emissions during production, thereby promoting the advancement of the circular economy in the construction sector.

#### CRediT authorship contribution statement

Xinyu Zhu: Writing – review & editing, Writing – original draft, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. Tao Wang: Writing – review & editing, Resources, Project administration, Methodology, Investigation, Funding acquisition, Conceptualization. Zhenwei Yi: Writing – review & editing, Validation, Supervision, Methodology, Conceptualization. Zhouxin Zhu: Writing – review & editing, Supervision, Methodology, Conceptualization.

# **Declaration of Competing interest**

This paper is novel and has not been published previously. No conflict of interest exits in the submission of this manuscript. All authors approved the manuscript and this submission.

## Data availability

No data was used for the research described in the article.

# Acknowledgements

This study is supported by the National Key R&D Program of China (2022YFB4102104), Pioneer R&D Program of Zhejiang Province China (2023C03016) and the Fundamental Research Funds for the Central Universities (2022ZFJH04).

# References

- Barnes, P.A., 1980. Comprehensive chemical kinetics. In: Bamford, C.H., Tipper, C.F.H. (Eds.), Reactions in the Solid State, vol. 22. Elsevier, Amsterdam, p. 340. Thermochimica Acta, 42(2) (1980) 249-250.
- Bracconi, Pierre, 1992. Modeling of the kinetics of chemically controlled double solid-gas reactions. Solid State Ionics 51 (Issues 3–4), 261–272. https://doi.org/10.1016/ 0167-2738(92)90208-7.

- Drouet, Emeline, Poyet, Stéphane, Le Bescop, Patrick, Torrenti, Jean-Michel, Bourbon, Xavier, 2019. Carbonation of hardened cement pastes: influence of temperature. Cement Concr. Res. 115, 445–459. https://doi.org/10.1016/j. cemconres.2018.09.019.
- Fang, Xiaoliang, Xuan, Dongxing, Poon, Chi Sun, 2017. Empirical modelling of CO2 uptake by recycled concrete aggregates under accelerated carbonation conditions. Mater. Struct. 50, 200. https://doi.org/10.1617/s11527-017-1066-y.
- Fernández Bertos, M., Simons, S.J.R., Hills, C.D., Carey, P.J., 2004. A review of accelerated carbonation technology in the treatment of cement-based materials and sequestration of CO2. J. Hazard Mater. 112 (3), 193–205. https://doi.org/10.1016/j. jhazmat.2004.04.019.
- Groves, Geoffrey W., Brough, Adrian, Richardson, Ian G., Dobson, Christopher M., 2005. Progressive changes in the structure of hardened C3S cement pastes due to carbonation. J. Am. Ceram. Soc. 74, 2891–2896. https://doi.org/10.1111/j.1151-2916.1991.tb06859.x.

HOUSE, J.E., 2007. Principles of Chemical Kinetics, second ed.

- Huang, H., Guo, R., Wang, T., Hu, X., Garcia, S., Fang, M., Luo, Z., Maroto-Valer, M.M., 2019. Carbonation curing for wollastonite-Portland cementitious materials: CO<sub>2</sub> sequestration potential and feasibility assessment. J. Clean. Prod. 211, 830–841. https://doi.org/10.1016/j.jclepro.2018.11.215.
- Hyvert, N., Sellier, A., Duprat, F., Rougeau, P., Francisco, P., 2010. Dependency of C–S–H carbonation rate on CO2 pressure to explain transition from accelerated tests to natural carbonation. Cement Concr. Res. 40 (11), 1582–1589. https://doi.org/ 10.1016/j.cemconres.2010.06.010.

International Energy Agency (IEA), 2020. Energy Technology Perspectives. International Energy Agency (IEA), 2022. WorldEnergyOutlook2022.

- Jang, J.G., Kim, G.M., Kim, H.J., Lee, H.K., 2016. Review on recent advances in CO2 utilization and sequestration technologies in cement-based materials. Construct. Build. Mater. 127, 762–773. https://doi.org/10.1016/j.conbuildmat.2016.10.017.
- John, J., Hirai, K., Mihashi, H., 1990. Influence of environmental moisture and temperature on carbonation of mortar. Concrete Research Technology 1, 85–94.
- Kisku, N., Joshi, H., Ansari, M., Panda, S.K., Nayak, Sanket, Dutta, ekhar Chandra, 2017. A critical review and assessment for usage of recycled aggregate as sustainable construction material. Construct. Build. Mater. 131, 721–740. https://doi.org/ 10.1016/j.conbuildmat.2016.11.029.
- Kou, Shi-Cong, Zhan, Bao-jian, Poon, Chi-Sun, 2014. Use of a CO2 curing step to improve the properties of concrete prepared with recycled aggregates. Cement Concr. Compos. 45, 22–28. https://doi.org/10.1016/j.cemconcomp.2013.09.008.
- Lekakh, S.N., Rawlins, C.H., Robertson, D.G.C., Richards, V.L., Peaslee, K.D., 2008. Kinetics of aqueous leaching and carbonization of steelmaking slag. Metall. Mater. Trans. B 39 (1), 125–134. https://doi.org/10.1007/s11663-007-9112-8.
- Li, Zhenshan, 2020. General rate equation theory for gas–solid reaction kinetics and its application to CaO carbonation. Chem. Eng. Sci. 227, 115902 https://doi.org/ 10.1016/j.ces.2020.115902.
- Li, Yang, Zhang, Shuai, Wang, Ruijun, Zhao, Yun, Men, Chuangshe, 2019. Effects of carbonation treatment on the crushing characteristics of recycled coarse aggregates. Construct. Build. Mater. 201, 408–420. https://doi.org/10.1016/j. conbuildmat.2018.12.158.
- Liu, L., Ha, J., Hashida, T., Teramura, S., 2001. Development of a CO2 solidification method for recycling autoclaved lightweight concrete waste. J. Mater. Sci. Lett. 20, 1791–1794. https://doi.org/10.1023/A:1012591318077.
- Lyu, Yizheng, Gao, Hanbo, Yan, Kun, Liu, Yingjie, Tian, Jinping, Chen, Lyujun, Wan, Mei, 2022. Carbon peaking strategies for industrial parks: model development and applications in China. Appl. Energy 322, 119442. https://doi.org/10.1016/j. apenergy.2022.119442.
- Miao, Endong, Du, Yi, Zheng, Xufan, Zhang, Xuguang, Xiong, Zhuo, Zhao, Yongchun, Zhang, Junying, 2023. CO2 sequestration by direct mineral carbonation of municipal solid waste incinerator fly ash in ammonium salt solution: performance evaluation and reaction kinetics. Separation and Purification Technology 309, 123103. https:// doi.org/10.1016/j.seppur.2023.123103.
- Mo, Liwu, Zhang, Feng, Deng, Min, Panesar, Daman K., 2016. Effectiveness of using CO2 pressure to enhance the carbonation of Portland cement-fly ash-MgO mortars. Cement Concr. Compos. 70, 78–85. https://doi.org/10.1016/j. cemconcomp.2016.03.013.
- Monazam, E.R., Shadle, L.J., Siriwardane, R., 2011. Equilibrium and absorption kinetics of carbon dioxide by solid supported amine sorbent. AIChE J. 57 (11), 3153–3159. https://doi.org/10.1002/aic.12516.
- Monkman, S., Shao, Y., 2010. Integration of carbon sequestration into curing process of precast concrete. Can. J. Civ. Eng. 37, 302–310. https://doi.org/10.1139/L09-140.
- Morandeau, A., White, C., 2015. In situ X-ray pair distribution function analysis of accelerated carbonation of a synthetic calcium-silicate-hydrate gel. J. Mater. Chem. A 3 (16), 8597–8605. https://doi.org/10.1039/C5TA00348B.
- Morandeau, A., Thiéry, M., Dangla, P., 2014. Investigation of the carbonation mechanism of CH and C-S-H in terms of kinetics, microstructure changes and moisture properties. Cement Concr. Res. 56, 153–170. https://doi.org/10.1016/j. cemconres.2013.11.015.
- Ouyang, Mingwei, Cao, Yan, 2023. Utilizations of reaction exothermic heat to compensate the cost of the permanent CO2 sequestration through the geological mineral CO2 carbonation. Energy 284, 128626. https://doi.org/10.1016/j. energy.2023.128626.
- Pan, Ganghua, Zhan, Mimi, Fu, Minghua, Wang, Yaping, Lu, Xiaojun, 2017. Effect of CO2 curing on demolition recycled fine aggregates enhanced by calcium hydroxide presoaking. Construct. Build. Mater. 154, 810–818. https://doi.org/10.1016/j. conbuildmat.2017.07.079.
- Pu, Yunhui, Lang, Li, Wang, Qingyuan, Shi, Xiaoshuang, Luan, Chenchen, Zhang, Guomin, Fu, Ling, Abomohra, Abd El-Fatah, 2021. Accelerated carbonation

#### X. Zhu et al.

technology for enhanced treatment of recycled concrete aggregates: a state-of-the-art review. Construct. Build. Mater. 282, 122671 https://doi.org/10.1016/j. conbuildmat.2021.122671.

- Pu, Yunhui, Lang, Li, Shi, Xiaoshuang, Wang, Qingyuan, Abomohra, Abdelfatah, 2023. Recent advances in accelerated carbonation for improving cement-based materials and CO2 mitigation from a life cycle perspective. Construct. Build. Mater. 388, 131695 https://doi.org/10.1016/j.conbuildmat.2023.131695.
- Saha, Sayan, Sau, Debasis, Hazra, Tumpa, 2023. Economic viability analysis of recycling waste plastic as aggregates in green sustainable concrete. Waste Management 169, 289–300. https://doi.org/10.1016/j.wasman.2023.07.023.
- Šavija, Branko, Luković, Mladena, 2016. Carbonation of cement paste: Understanding, challenges, and opportunities. Construct. Build. Mater. 117, 285–301. https://doi. org/10.1016/j.conbuildmat.2016.04.138.
- Shi, Caijun, Wu, Zemei, Cao, Zhijie, Ling, Tung Chai, Zheng, Jianlan, 2018. Performance of mortar prepared with recycled concrete aggregate enhanced by CO2 and pozzolan slurry. Cement Concr. Compos. 86, 130–138. https://doi.org/10.1016/j. cemconcomp.2017.10.013.
- Tai, Clifford Y., Chen, W.-R., Shih, Shin-Min, 2006. Factors affecting wollastonite carbonation under CO2 supercritical conditions. AIChE J. 52, 292–299. https://doi. org/10.1002/aic.10572.
- Voigt, Martin, Marieni, Chiara, Clark, Deirdre E., Gíslason, Sigurður R., Oelkers, Eric H., 2018. Evaluation and refinement of thermodynamic databases for mineral carbonation. Energy Proc. 146, 81–91. https://doi.org/10.1016/j. egypro.2018.07.012.

- Wang, Tao, Huang, Hao, Hu, Xutao, Fang, Mengxiang, Luo, Zhongyang, Guo, Ruonan, 2017. Accelerated mineral carbonation curing of cement paste for CO<sub>2</sub> sequestration and enhanced properties ofblended calcium silicate. Chem. Eng. J. 323, 320–329. https://doi.org/10.1016/j.cej.2017.03.157.
- Wu, Junyong, Zhang, Yunsheng, Zhu, Pinghua, Feng, Jincai, Hu, Kun, 2018. Mechanical properties and ITZ microstructure of recycled aggregate concrete using carbonated recycled coarse aggregate. J. Wuhan Univ. Technol.-Materials Sci. Ed. 33 (3), 648–653. https://doi.org/10.1007/s11595-018-1873-1.
- Zhan, Baojian, Poon, Chisun, Shi, Caijun, 2013. CO2 curing for improving the properties of concrete blocks containing recycled aggregates. Cement Concr. Compos. 42, 1–8. https://doi.org/10.1016/j.cemconcomp.2013.04.013.
- Zhan, Baojian, Poon, Chi Sun, Liu, Qiong, Kou, Shicong, Shi, Caijun, 2014. Experimental study on CO2 curing for enhancement of recycled aggregate properties. Construct. Build. Mater. 67 (A), 3–7. https://doi.org/10.1016/j.conbuildmat.2013.09.008.
- Zhan, Baojian, Xuan, Dongxing, Poon, Chisun, Shi, Caijun, 2016. Effect of curing parameters on CO2 curing of concrete blocks containing recycled aggregates. Cement Concr. Compos. 71, 122–130. https://doi.org/10.1016/j. cemconcomp.2016.05.002.
- Zhang, Jiake, Shi, Caijun, Li, Yake, Pan, Xiaoying, Poon, Chi-Sun, Xie, Zhaobin, 2015. Influence of carbonated recycled concrete aggregate on properties of cement mortar. Construct. Build. Mater. 98, 1–7. https://doi.org/10.1016/j. conbuildmat.2015.08.087.
- Zhang, Duo, Ghouleh, Zaid, Shao, Yixin, 2017. Review on carbonation curing of cementbased materials. J. CO2 Util. 21, 119–131. https://doi.org/10.1016/j. icou.2017.07.003.