

The Kinetic Study of Carbonation of BOF Slag at High Temperature: Impact of Particle Size Characteristics



Zhenghao Wang, Songming Zheng, Yue Lai, Huamei Duan, Dengfu Chen, Mujun Long, and Yandong Li

Abstract Basic oxygen furnace slag (BOFS) with high content of free CaO (f-CaO) can be utilized as a kind of building materials after carbonation. However, the degree of carbonation varies greatly depending on the particle size of slag. In this study, the carbonation process of BOFS with different particle sizes was evaluated in an autoclave. The highest CO₂ sequestration and f-CaO consumption reached 6.49% (64.9 g CO₂/kg slag) and 99.81%, respectively, when the particle size of BOF slag was less than 61 μm. Additionally, the size of particles had a minor impact on f-CaO consumption but significantly affected CO₂ sequestration. With CO₂ sequestration as an indicator, the results showed that the carbonation of BOFS was accurately described by the shrinking core model and the carbonation process was proved to be controlled by internal diffusion. The effectiveness and environmental benefits of this method make it worth promoting for the carbonation and stabilization of steel slag.

Keywords Basic oxygen furnace slag (BOF slag) · Direct carbonation · Free CaO consumption · CO₂ sequestration · Kinetic study

Introduction

The steel slag is a solid byproduct generated during the metallurgical industry's steel production process, representing approximately 15–20% of global steel production [1]. In 2022, the worldwide crude steel production was 1,885 million tons, with

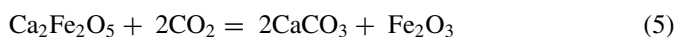
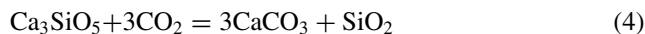
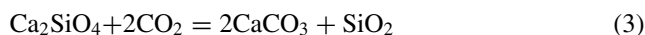
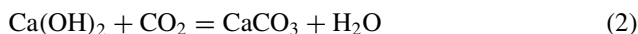
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China being the largest contributor. Each ton of steel production is associated with emissions equivalent to 1.8 tons of CO₂ on average. Consequently, CO₂ emissions from this industry account for about 6–7% of total global CO₂ emissions [2]. Notably in China, it ranks as the third-largest emitter after power and cement industries and contributes to around 10% of domestic CO₂ emissions [3].

Numerous valuable applications for steel slag has been identified, including road construction, cement manufacturing, and water engineering [4, 5]. However, the excessive presence of f-CaO in steel slag poses a challenge to its potential usage due to unfavorable expansion, thus hindering the sustainable and efficient utilization of steel slag [6]. Consequently, many studies have been conducted on reducing the f-CaO content through CO₂ reaction. The sequestration of CO₂ by steel slag can be classified into two main types: direct carbonation and indirect carbonation. Compared to indirect carbonation, direct carbonation is more convenient and has the potential for widespread application [7]. Direct carbonation can be achieved by the reaction of steel slag with CO₂ either in the aqueous or gaseous phase, without the need for solvent extraction of active components (such as Ca²⁺ or Mg²⁺) from the steel slag. The main chemical reactions of direct carbonation of steel slag can be expressed as follows [8, 9]:



The CO₂ sequestration by steel slag can be influenced by various factors, including reaction parameters and material properties. Among these properties, particle size plays a vital role in the carbonation process and is more important than the elemental composition of the initial material. Smaller particle size results in a larger surface area that benefits the extraction of calcium ions and carbonation of steelmaking slag, as it shortens the element diffusion distance from particle interior to surface [10, 11].

Baciocchi et al. [12] conducted a study on the carbonation process of stainless EAFS with varying grain sizes and observed a decrease in the carbonation reaction as the particle size increased. Renato et al. [12] conducted a study on the CO₂ storage capacity of different particle sizes of steel slag under mild operating conditions. The results indicated that the finest grain sizes had maximum CO₂ uptakes of 130 g CO₂/kg slag, which decreased with increasing particle size due to differences in reacting species availability and specific surface area. Liu et al. [13] carried out an experiment to investigate the impact of slag particles on the carbonation process of converter steel

slag. The findings suggested that changes in particle size of steel slag affected the transportation of gas and absorption of CO₂ in carbonated steel slag blended mortars during curing, thereby influencing microstructure, strength, and leaching properties. Additionally, in a study conducted by Li et al. [12], they investigated the effects of particle size on the environmental, economic, and engineering performances of aqueous carbonated steel slag powders. The findings indicated that reducing the particle size of steel slag had a positive impact on CO₂ sequestration (particle sizes ranging from 22.4 to 112.6 μm resulted in sequestering approximately 88.5–37.9 kg CO₂ per ton of steel slag) and enhanced the leaching process for mineralization due to improved extraction of metal ions. Wu et al. [14] conducted a study on the economic and rational grading of carbonated steel slag products. They formulated different ratios of steel slag micronized powder, coarse powder, and coarse particles. The weight gain and compressive strength were then analyzed after carbonation. The findings indicated that increasing the proportion of slag coarse powder to slag coarse particle up to 15% resulted in a decrease in the rate of carbonation. Similarly, the trend observed for compressive strength was consistent with that of the carbonation weight gain rate. Based on these results, it can be concluded that the most cost-effective gradation consists of 45 wt.% fine powder, 40 wt.% coarse powder, and 15 wt.% coarse granules.

However, there have been few studies on the direct carbonation of gas–solid reactions with low L/S above 500 °C under pressurized conditions. Additionally, the high f-CaO content in BOF slag poses challenges for its direct utilization, yet there is a lack of quantitative studies investigating the consumption of f-CaO after the carbonation reaction. This study is therefore aimed to examine the direct carbonation reaction of BOF slag of different particle size. The f-CaO consumption was analyzed using ethylene glycol method, while the CO₂ sequestration and reaction products were evaluated by Thermogravimetric analysis (TGA; TGA/DSC1/1600LF, Switzerland). The kinetics of f-CaO consumption and CO₂ sequestration were investigated using the shrinking core model to determine kinetic equations and the rate-limiting step in the carbonation process.

Materials and Methods

Basic Oxygen Furnace Slag (BOF Slag)

The BOF slag, obtained from Xinxing Pipes Corporation (Anhui, China), underwent a drying and calcination process at 800 °C for 30 min in an oven to eliminate moisture, hydroxide, and carbonate. Subsequently, the slag was ground and divided into four types based on particle size. D₁ had a particle size smaller than 61 μm, D₂ ranged from 61 to 75 μm, D₃ ranged from 75 to 100 μm, and D₄ ranged from 100 to 300 μm.

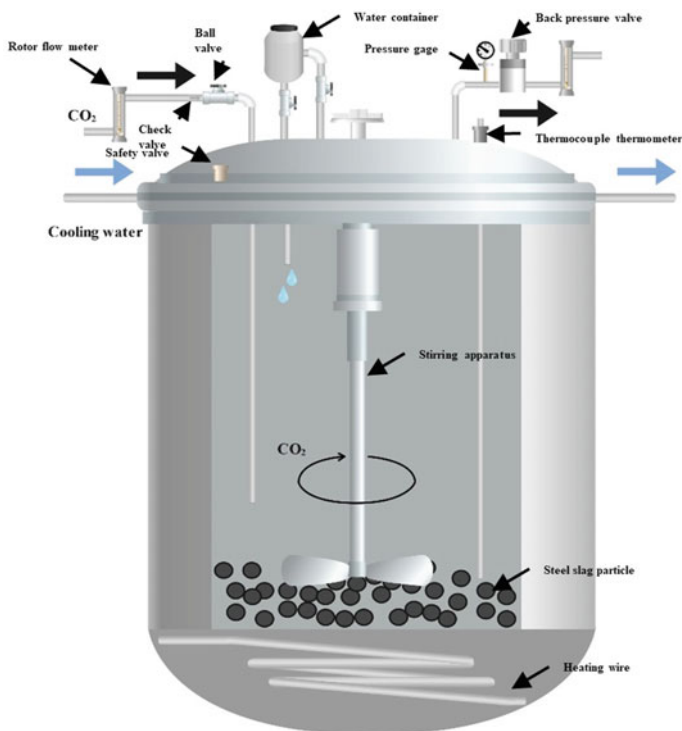


Fig. 1 Diagram of carbonation reaction equipment

Experimental Procedure

The carbonation experiment was conducted in a homemade autoclave reactor, as depicted in Fig. 1.

In each experiment, the crucible containing 25 g of slag was placed inside the reactor and heated to a temperature of 700 °C. Subsequently, CO₂ was introduced into the reactor to maintain a pressure of 0.35 Mpa. Following that, water was injected into the reactor with a liquid-to-solid ratio of 0.2 mL·g⁻¹ and the slag was stirred at a speed of 15 rpm. The entire reaction lasted for 75 min, during which six samples of slag were selected and analyzed at different time intervals.

Analysis Method

The slag samples were heated from 25 °C to 900 °C at a rate of 10 °C·min⁻¹ under nitrogen. The mass loss between 500 °C and 900 °C was mainly due to CaCO₃ decomposition. The CO₂ weight (wt.%) and amount of CO₂ sequestration (wt.%)

were calculated using Eqs. (6) and (7):

$$\text{CO}_2(\text{wt.}\%) = \frac{\Delta m_{\text{CO}_2}}{m_{105^\circ\text{C}}} \times 100 \quad (6)$$

$$\text{CO}_2 \text{ sequestration}(\text{wt.}\%) = \frac{\text{CO}_{2\text{carbonated}}(\text{wt.}\%) - \text{CO}_{2\text{initial}}(\text{wt.}\%) }{100 - \text{CO}_{2\text{carbonated}}(\text{wt.}\%) } \times 100 \quad (7)$$

where $m_{105^\circ\text{C}}$ represents the dry weight of the slag measured at 105 °C, and Δm_{CO_2} is the CO_2 weight of the slag released from CaCO_3 decomposition between 500 °C and 900 °C.

The f -CaO content (wt.%) of initial and carbonated slag and the consumption of f -CaO content (%) were analyzed using a combination of ethylene glycol method [15] and TGA. Equations (8) and (9) are employed for quantifying, as follows:

$$f - \text{CaO}(\text{wt.}\%) = f - \text{CaO}_{\text{total}}(\text{wt.}\%) - \frac{\Delta m_{\text{H}_2\text{O}} \times M_{\text{CaO}}}{M_{\text{H}_2\text{O}} \times m_{105^\circ\text{C}}} \quad (8)$$

$$f - \text{CaO consumption}(\%) = \frac{f - \text{CaO}_{\text{initial}}(\text{wt.}\%) - f - \text{CaO}_{\text{carbonated}}(\text{wt.}\%) }{f - \text{CaO}_{\text{initial}}(\text{wt.}\%) } \quad (9)$$

where f -CaO_{total} can be determined using the ethylene glycol method, $\Delta m_{\text{H}_2\text{O}}$ represents the loss caused by $\text{Ca}(\text{OH})_2$ decomposition, and $M_{\text{H}_2\text{O}}$ is the molecular weight of H_2O .

Results and Discussion

The Impact of Particle Size on CO₂ Sequestration and f-CaO Consumption

The trend of f -CaO consumption and CO_2 sequestration over the reaction time is illustrated in Fig. 2. It can be observed that the particle size of BOF slag had a significant impact on CO_2 sequestration, with a dramatic increase as the particle size decreased. After reacting with CO_2 for 75 min, D_1 achieved a CO_2 sequestration rate of 6.49% (64.9 g CO_2 /kg slag), while D_4 only reached 1.45% (14.5 g CO_2 /kg slag) of CO_2 sequestration. Conversely, the influence of particle size on f -CaO consumption was relatively weak, and the highest f -CaO consumption was 99.81%, while the lowest f -CaO consumption was 85.14%.

According to Fig. 2, initially both CO_2 sequestration and f -CaO consumption increased rapidly. However, after 60 min, the value of CO_2 sequestration exhibited an obvious slower rise, indicating resistance throughout the entire process. Additionally, the carbonation process of large particle size BOF slag stopped increasing in less

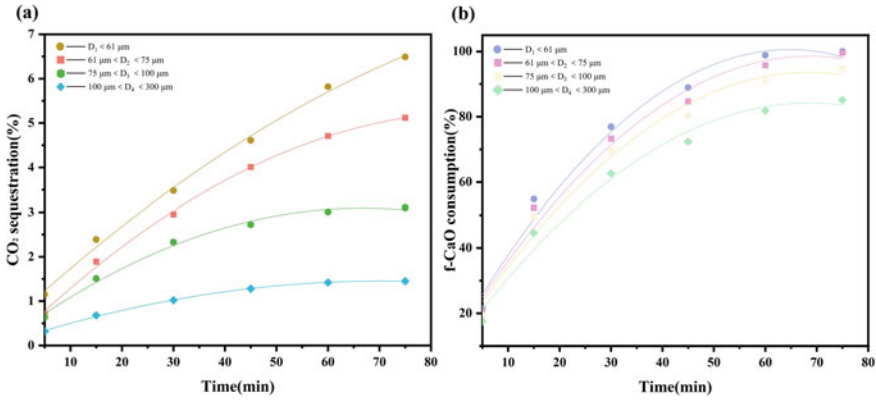


Fig. 2 Trends of a CO₂ sequestration; b f-CaO consumption over reaction time

than 60 min. Therefore, the Drozdov equation with a self-impeding coefficient was used to describe this CO₂ sequestration process [16], and the equation is as follows:

$$\frac{1}{t} \ln \frac{1}{1-x} - \beta \frac{x}{t} = k_m \tag{10}$$

where t is the reaction time, min; x is the leaching ratio, %; β is the self-impeding coefficient; and K_m is the reaction ratio constant.

The results of the fitting are shown in Fig. 3 and Table 1, which clearly demonstrate a strong linear correlation (correlation coefficient > 0.999) between $\ln[1/(1-x)] \cdot t^{-1}$ and $x \cdot t^{-1}$. Additionally, it was found that both the self-impeding coefficient and reaction ratio constant increased as the particle size decreased. Notably, particles smaller than 61 μm exhibited the highest reaction ratio constant and lowest self-impeding coefficient, reaching values of 0.0022 and 0.9894, respectively.

According to previous studies [17, 18], the small particle size of BOF slag results in a larger surface area, which provides more contact areas with CO₂ and facilitates the carbonation process and leads to higher CO₂ sequestration and f-CaO consumption. However, compared to other alkaline constituents in BOF slag, the content of f-CaO was relatively low, approximately 5% by mass in this study. Therefore, the differences in particle size had limited influence on it.

The Kinetic Study of Carbonation Process

In this study, the carbonation kinetics of BOF slag were investigated using the shrinking core model, which has been previously validated for the carbonation process of BOF slag [19]. If the rate-limiting step is determined by the diffusion

Fig. 3 Relationship between $\ln[1/(1-x)] \cdot t^{-1}$ and $x \cdot t^{-1}$ for various particle sizes in the CO₂ sequestration process

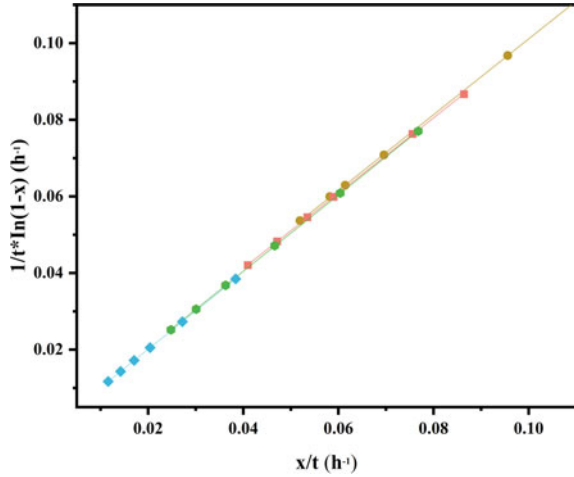


Table 1 Detailed information of fitting results

| Particle size (μm) | Reaction ratio constant | Self-impeding coefficient | Correlation coefficient |
|--------------------|-------------------------|---------------------------|-------------------------|
| <61 | 0.0022 | 0.9894 | 0.99997 |
| 61–75 | 0.00192 | 0.98267 | 0.99995 |
| 75–100 | 0.000566 | 0.99716 | 0.99997 |
| 100–300 | 0.000119 | 0.99877 | 0.99997 |

of reactants through the CaCO₃ layer, then Eq. (10) can be used to express the relationship between reaction time (t , min) and CO₂ sequestration (X , %). On the other hand, if it is determined by a chemical reaction between reactants, then Eq. (11) can illustrate this relationship.

$$t = \frac{\rho_B R^2}{6bD_e C_{Ag}} \left[1 - 3(1 - X)^{\frac{2}{3}} + 2(1 - X) \right] = \tau \left[1 - 3(1 - X)^{\frac{2}{3}} + 2(1 - X) \right] \tag{11}$$

$$t = \frac{\rho_B R}{bk'' C_{Ag}} \left[1 - (1 - X)^{\frac{1}{3}} \right] = \tau \left[1 - (1 - X)^{\frac{1}{3}} \right] \tag{12}$$

where the term ρ_B is the molar density of the solid, mol·cm⁻³. R is the radius of the slag particle, cm. D_e is the effective diffusivity of the gaseous reactant in the CaCO₃ layer, cm²·s⁻¹. C_{Ag} represents the concentration of CO₂, mol·cm⁻³. K'' represents the first-order rate constant for the surface reaction, s⁻¹.

To identify the step that limits the rate of carbonation in this study, Fig. 4 illustrates the relationships between $1 - 3(1 - X)^{2/3} + 2(1 - X)$ and t , as well as $1 - (1 - X)^{1/3}$ and

t. The fitting results indicate that the carbonation process was governed by internal diffusion, with R^2 values ranging from 0.9403 to 0.9866.

According to the assumptions of this model, the product (carbonate) layer acts as a barrier for reactant diffusion, thus becoming the rate-limiting step in carbonation process. What's more, the kinetic equation of BOF slag of D_1 was determined through a series of experiments conducted at temperatures ranging from 400 °C to 700 °C. The results are illustrated in Fig. 5a.

$$\ln K = \frac{-1232}{T} + 1.332 \tag{13}$$

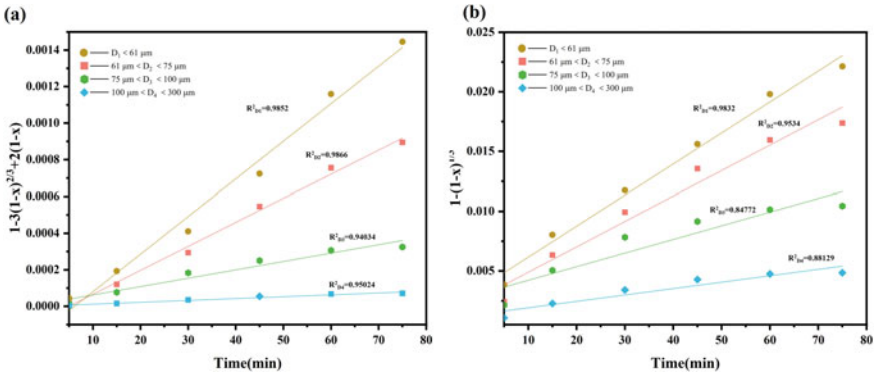


Fig. 4 Fitting results of CO₂ sequestration using shrinking core model: **a** Internal diffusion control; **b** interface chemical reaction control

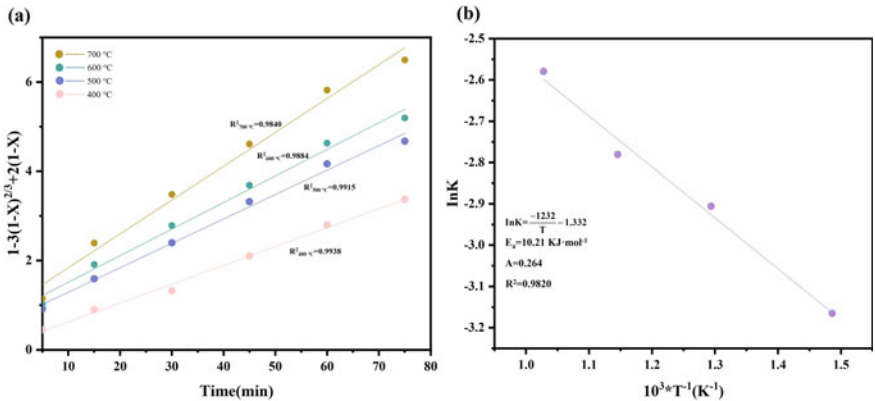


Fig. 5 **a** Fitting results of CO₂ sequestration using shrinking core model under different temperatures; **b** kinetics equation of carbonation process of BOF slag of D_1 . **b** shows the kinetic equations for CO₂ sequestration and f-CaO consumption, which could be expressed as Eq. 13

Conclusions

The results showed that smaller particle size of BOF slag led to higher CO₂ sequestration and f-CaO consumption. The highest CO₂ sequestration and f-CaO consumption of 6.49% (64.9 g CO₂/kg slag) and 99.81%, respectively, were achieved when the particle size was less than 61 μm. The Drozdov equation was used to describe the carbonation process, and the results showed that the self-impeding coefficient and reaction ratio constant increased with decreasing particle size. This was consistent with the experimental results. In addition, the particle size of BOF slag of less than 61 μm had the optimum self-impeding coefficient and reaction ratio constant of 0.0022 and 0.9894, respectively.

However, the impact of particle size on CO₂ sequestration was more pronounced due to the lower content of f-CaO in BOF slag and f-CaO is the most reactive alkaline constituent in BOF slag and readily reacts with CO₂. Therefore, there is no need to grind BOF slag into the finest powder if the purpose is only to stabilize the slag.

Additionally, the kinetics of the carbonation process could be accurately described by a shrinking core model. This model revealed that the formation of carbonate is the main reason why there was no further increase in CO₂ sequestration. Furthermore, this study has proven that reactant diffusion is the rate-limiting step in the carbonation process, and a kinetic equation has been derived. As a result, this approach showed significant potential for widespread implementation as an efficient method to eliminate f-CaO, stabilize BOF slag, and capture CO₂.

Acknowledgements The authors gratefully acknowledge the financial support provided by the Sichuan Science and Technology Program, project No. 2022YFQ0037, the National Natural Science Foundation of China, project No. 51904035, Fuling Science and Technology Project, project No. FLKJ,2022CBZ4061.

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