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Abstract: The study of the mechanisms affecting the preparation parameters of carbonated steel slag is of great significance for the development of carbon sequestration materials. In order to elucidate the mechanism of the influence of moisture on CO_2 diffusion and particle cementation in steel slag, the effects of different water–solid ratios and water contents on the mechanical properties, carbonation products, and pore structure of steel slag after carbonation were investigated. The results show that increasing the water–solid ratio of steel slag can control the larger initial porosity and improve the carbon sequestration capacity of steel slag, but it will reduce the mechanical properties. The carbonation process relies on pores for CO_2 diffusion and also requires a certain level of moisture for Ca^{2+} dissolution and diffusion. Increasing the water content enhances particle cementation and carbonation capacity in steel slag specimens; however, excessive water hinders CO_2 diffusion. Reducing the water content can increase the carbonation depth but may compromise gelling and carbon sequestration ability. Therefore, achieving a balance is crucial in controlling the water content. The compressive strength of the steel slag with suitable moisture and initial porosity can reach 118.7 MPa, and 217.2 kg CO_2 eq./t steel slag can be sequestered.

Keywords: steel slag; carbon sequestration; water content; carbonation diffusion; pore

1. Introduction

Steel slag is a prominent by-product generated during the smelting process in the iron and steel industry, constituting approximately 8–15% of the total crude steel production [1–3]. In 2021, global crude steel production reached around 1.952 billion tons, resulting in an annual emission of steel slag exceeding 250 million tons [4]. Among these figures, China's crude steel production accounted for about 1.03 billion tons with a corresponding output of over 120 million tons of steel slag [5]. However, steel slag possesses drawbacks such as high free CaO content and low hydration activity [6], leading to its combined utilization rate remaining below 30% [7]. Consequently, it is primarily stockpiled or landfilled, posing significant environmental pollution concerns. Therefore, there is an urgent need to develop an efficient and environmentally friendly approach to the disposal of steel slag.

Meanwhile, the steel production process is accompanied by a substantial amount of carbon emissions. The carbon emissions of China's iron and steel sector account for approximately 15% of the national total [8]. Carbon Capture, Utilization and Storage (CCUS) is widely regarded as an optimal approach to achieve significant carbon emission reduction in the iron and steel industry [9,10]. By harnessing CO_2 , it becomes possible to convert the high calcium content present in steel slag into highly stable $CaCO_3$, thereby



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Copyright: © 2024 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). facilitating long-term carbon sequestration [11]. The CO_2 carbonation of steel slag has been acknowledged as the most favorable method for disposing of this by-product.

Steel slag can be classified into basic oxygen furnace slag (BOFS), electrical arc furnace slag (EAFS), argon oxygen decarburization slag (AODS), and ladle-refining slag (LFS) based on the production process [4,10]. Among these, LFS is a by-product generated during secondary or alkaline steelmaking [12], and it exhibits the highest calcium content among all types of slags [13]. The cooling process of the LFS results in the generation of a substantial quantity of the self-powdered γ -Ca₂SiO₄ (γ -C₂S) material phase, thereby conferring a powdery nature upon the LFS. The γ -C₂S enables a rapid reaction with CO₂ to form calcium carbonates (CaCO₃) and calcium silicate hydrates (C-S-H) [14,15]. Consequently, LFS holds great potential for application in CCUS technology.

The carbonation process of steel slag building materials typically involves mixing water with steel slag powder to form cubic blocks, which are then subjected to a direct gas–solid reaction by passing CO₂ gas through a closed stainless steel reactor [16,17]. Some researchers have also utilized liquid–solid reactions [18]. During the reaction between CO₂ and steel slag, CO_3^{2-} formed from dissolved CO₂ reacts with Ca²⁺ precipitated from the slag to produce stable CaCO₃ that provides high mechanical strength and permanently fixes CO₂ in the material [6]. Although the theoretical carbon fixation rate of steel slag ranges between 25% and 50%, various factors during carbonation limit its actual rate to about 15% [19]. Each ton of cement produced will emit 0.94 tons of CO₂ [20], so when carbonation of steel slag is applied in cementitious materials or aggregates to replace cement, the reduction in cement production and the amount of CO₂ absorbed by the steel slag makes it possible to achieve a carbon reduction of approximately 1.09 t of CO₂ for each ton of steel slag. This would be expected to achieve the carbon-negative production of building materials.

Gas-solid carbonation is mainly restricted by reaction kinetics and CO₂ diffusion [4]; hence, researchers strive to study different conditions in this process for improved efficiency. Currently, there is a substantial body of mature research on the carbonation reaction of steel slag, which has revealed the effects of various conditions such as particle size, temperature, CO₂ pressure, and carbonation time on the carbonation results [21–25]. For instance, Ukwattage et al. improved the carbonation efficiency of steel slag by optimizing the three parameters of CO₂ pressure, temperature, and water–solid ratio [26]. Zhang et al. increased the carbon sequestration efficiency of steel slag to 16.65% by increasing the CO₂ pressure [27]. The study conducted by Tian et al. [28] concluded that temperature is the primary determinant influencing the direct gas–solid carbonation reaction of steel slag. However, it appears that the researchers overlooked the significance of moisture control in specimen preparation prior to carbonation. Steel slag not only needs water for Ca²⁺ dissolution and particle cementation during carbonation, but the carbonation reaction process also consumes a certain amount of water.

Furthermore, numerous unresolved issues persist in the investigation of the carbonation reaction mechanism of steel slag. For instance, there is a lack of synergistic studies on the water content and pore structure of specimens prior to carbonation. The alteration in pore structure during carbonation significantly impacts the compressive strength of specimens [14,29]. Secondly, existing research primarily focuses on pressed steel slag and lacks investigation into pouring molding commonly employed in cement-molding processes. Pouring molding can yield higher initial porosity compared to pressing molding, which theoretically results in higher carbon sequestration. The initial porosity of cast-molded specimens can be significantly controlled by manipulating the water–solid ratio, while the pore structure and porosity play a pivotal role in facilitating CO_2 diffusion. Thirdly, some researchers have observed that the center of the specimen has lower levels of carbonation than the surface part [30,31], but the mechanism underlying the microscopic effect remains elusive.

Considering the aforementioned issues, this study aims to utilize small poured cubic blocks of steel slag and manipulate different water–solid ratios to control their initial porosity. The water content is simultaneously regulated through air-drying of the steel slag. Initially, the impact of various water–solid ratios and water contents on the properties of steel slag is investigated, while microscopic analysis is employed to examine the carbonation products and pore structure of these. Consequently, a mechanism involving CO_2 diffusion and particle cementation is proposed by integrating the analytical findings with previous research studies. Notably, this research introduces a novel approach by employing three-dimensional pore structure analysis to explore the relationship between CO_2 diffusion and pore structure.

2. Materials and Methods

The ladle-refining slag (LFS) utilized in this study was obtained from a steel mill located in Guangxi, China. It underwent ball milling and sieving through a 100-mesh sieve to obtain a powder with an average particle size of 1.34 μ m, as depicted in Figure 1. Particle size analysis was performed using a Mastersizer 3000 laser particle sizer from Malvern Panalytical, EA Almelo, The Netherlands. LFS exhibits a significant composition of CaO (~71.23%) and SiO₂ (~21.31%) as presented in Table 1. The mineral composition of LFS is illustrated in Figure 2, where the primary mineral phases include calcio-olivine, akermanite, and fluorite, among others.



Figure 1. Particle size distribution of LFS powder.

Table 1. Chemical compositions of LFS (wt%).

Oxides	CaO	SiO ₂	Cr_2O_3	MgO	TiO ₂	Fe ₂ O ₃	Others
LFS	71.23	21.31	2.37	1.96	1.72	1.27	0.12



Figure 2. X-ray diffraction pattern of LFS powder.

The steel slag specimens were prepared by mixing water and LFS powder at different water–solid ratios of 0.25, 0.3, and 0.35. Subsequently, the resulting slurry was poured into a $20 \times 20 \times 20$ mm² steel film mold and allowed to cure through natural air-drying for a duration of 24 h at room temperature. Afterward, the cured steel slag specimens were divided into two groups, and uniform quality was ensured across all specimens. The first group of steel slag specimens underwent oven-drying until they reached a constant weight in order to determine their dry basis weight (M₀). Meanwhile, the second group of steel slag specimens was subjected to oven-drying at a temperature of 40 °C for t time to obtain their wet basis weight (M_t). The water content of each specimen was calculated using Equation (1). Throughout the weighing process and water content control procedures, efforts were made to maintain an error margin within ± 0.1 %. The control of water content change curve in relation to drying time.

$$w\% = (M_t - M_0) / M_0 \times 100\%$$
(1)

After controlling the water content of the steel slag specimens, the sample was promptly introduced into the reaction vessel as depicted in Figure 3. This carbonation reactor is a single-layer stainless steel reactor with a volume of 20 L in a constant-temperature (25 °C) environment. The CO₂ pressure of the carbonation reactor can be controlled by adjusting the valve of the CO₂ gas tank. The reaction vessel was evacuated to -0.08 MPa and then carbonated at room temperature (25 °C) and a CO₂ pressure of 0.4 MPa for a duration of 24 h. The purity of CO₂ employed for this carbonation process was determined to be 99%. A schematic diagram for the preparation step is illustrated in Figure 4.



Figure 3. Carbonation reaction vessel.



Figure 4. Schematic diagram for the preparation step.

The compressive strength analysis was performed using a UTM5105 microcomputer control electronic universal material testing machine from Suns Technology Stock Co., Ltd., Shenzhen, China; the testing process was carried out in accordance with the Chinese standard GB/T 17671-2021 [32]. Thermogravimetric analysis was performed using the

STA 449 F5 thermal analyzer from NETZSCH, CO., Germany. The carbon sequestration rate of the specimens was calculated from the thermogravimetric analysis results using Equations (2) and (3) [15]. X-ray diffraction (XRD) analysis was performed using the X'Pert PRO X-ray diffractometer from Malvern Panalytical Ltd., The Netherlands. SEM analysis was performed using the S-4800 scanning electron microscope from Carl Zeiss AG, Germany. Three-Dimensional Computerized Tomography (3D CT) analysis was performed using a Xradia 510 Versa high-resolution 3D X-ray microscope from Carl Zeiss AG, Germany, equipped with a voltage of 100 kV, a pixel size of 3 μ m, and an exposure time of 2 s.

$$CO_2(wt.\%) = \frac{\Delta m_{CO2}}{m_{105^\circ C}} \times 100$$
 (2)

$$CO_2 uptake(wt.\%) = \frac{CO_{2carbonated} (wt.\%) - CO_{2initial} (wt.\%)}{100 - CO_{2carbonated} (wt.\%)} \times 100$$
(3)

where $CO_2(wt.\%)$ represents the rate of carbon dioxide loss; Δm_{CO2} denotes the rate of mass loss resulting from calcium carbonate decomposition in the specimen at elevated temperatures; $m_{105^\circ C}$ indicates the weight of the dried specimen; $CO_2uptake(wt.\%)$ signifies the rate of carbon sequestration; $CO_{2carbonated}(wt.\%)$ refers to the rate of carbon dioxide loss in the specimen after carbonation; $CO_{2initial}(wt.\%)$ represents the rate of carbon dioxide loss in the uncarbonated specimen.

3. Results

3.1. Regulation of Water Content Regulation

The variation rule of water content in specimens under different water–solid ratios at a 40 °C drying temperature was initially investigated, and the corresponding results are presented in Figure 5. Moisture loss from the specimen is evaporative moisture loss driven by the external environment, which is related to the relative humidity of the environment [33]. The higher the water–solid ratio, the greater the initial water content of the specimen observed. Additionally, a higher water–solid ratio leads to an accelerated overall drying rate due to decreased specimen density and increased porosity, facilitating easier drying. Initially, the drying rate was faster but gradually slowed down over time, possibly attributed to the difficulty in drying deeper internal water compared to surface and pore water. By adjusting different drying times, it was possible to control the water content of specimens according to fitted curves.



Figure 5. Variation in the water content of specimens with time at different water-solid ratios.

3.2. Compressive Strength

The steel slag specimens were prepared with varying water–solid ratios ranging from 0.25 to 0.35 and water contents ranging from 4% to 9%. These specimens were then carbonated using the aforementioned method for controlling water content. The resulting compressive strengths for each specimen are depicted in Figure 6. Notably, the compressive strength of the specimens exhibited a decreasing trend as the water–solid ratio increased. This was attributed to the fact that specimens with lower water–solid ratios tend to be denser and less porous, leading to an optimal compressive strength of 118.7 MPa observed at a water–solid ratio of 0.25 and a water content of 6%. The strength obtained by this specimen in 1 d exceeded the 28 d compressive strength value of the researcher's specimen [17]. However, a higher water–solid ratio offers improved pourability and moldability.



Figure 6. The effects of different water–solid ratios and water content on the compressive strength of the samples.

The initial compressive strength of the specimens demonstrated an increase, followed by a decline as water content increased. This phenomenon is attributed to the fact that γ -C₂S requires a certain amount of water to dissolve Ca²⁺ during the carbonation reaction (see Equation (4)) [34]. An increase in water content provides more water for the carbonation reaction, which makes γ -C₂S and the other reactive constituents more susceptible to carbonation, thus increasing the strength. Excess water may obstruct the pores of the steel slag specimens, resulting in the hindered diffusion of carbon dioxide [35].

$$Ca_2SiO_4 + 4H_2O \rightarrow 2Ca^{2+} + H_4SiO_4 + 4OH^-$$
(4)

The higher the water–cement ratio, the greater the optimal water content required for achieving maximum compressive strength in the specimen. This is attributed to the fact that specimens with higher water–cement ratios possess a more porous structure, thereby rendering it more challenging for water to hinder the carbonation process compared to specimens with lower water–cement ratios. This was consistent with the discussion in Wang et al.'s study [36].

3.3. Carbon Sequestration

The thermogravimetry (TG) and DTG results of carbonated LFS with varying watersolid ratios and water contents are presented in Figure 7. The DTG results reveal that the mass loss peak between 400 and 800 °C represents the decomposition peak of CaCO₃. By employing Equations (2) and (3), the rate of mass loss over the temperature range can be used to calculate the carbon sequestration rate, as demonstrated in Figure 7a. It is observed ratio, in contrast to the result of compressive strength presented in Figure 7b. Although a higher water–solid ratio results in increased porosity, leading to lower densification and strength, these pores facilitate greater penetration of CO_2 during the curing process. The carbon sequestration rate of LFS samples, characterized by a 0.35 water–solid ratio and 8% water content, amounts to 21.72%, indicating that each ton of LFS can effectively absorb and fix approximately 217.2 kg of CO_2 . This is much higher than the average carbon sequestration rate value of 15% proposed by researchers [19]. From the TG plot, it can be inferred that the carbonated LFS with a higher water–solid ratio is less influenced by the water content, suggesting that an increase in pore space mitigates the adverse effects of water on CO_2 diffusion. The carbonated LFS exhibits an increasing then decreasing trend of the carbon sequestration rate with respect to water content, which is consistent with the compressive strength results presented in Figure 6. The current findings imply that maintaining an adequate water supply is crucial to ensure proper dissolution and solidification of CO_2 , yet an excessive increase in water content beyond a certain threshold potentially leads to adverse effects on CO_2 .



Figure 7. (**a**) Carbon sequestration rate of carbonated LFS with different water–solid ratios and different water contents; (**b**) TG and DTG results of carbonated LFS with 0.25 water–solid ratio; (**c**) TG and DTG results of carbonated LFS with 0.3 water–solid ratio; (**d**) TG and DTG results of carbonated LFS with 0.35 water–solid ratio.

In order to observe the distribution of water in samples with different water contents, the center of samples with a water–solid ratio of 0.3 and different water contents was cut to obtain a profile, and phenolphthalein powder was evenly sprayed on the profile. The LFS, a highly alkaline substance, would show color in the presence of water, as shown in the upper part of Figure 8. The sample with 0% water content did not show color due to the absence of water, which proved the feasibility of the test method. The increase in water content was observed to be accompanied by a progressively more pronounced coloration of the specimen's cut surface.



Figure 8. Sample center profiles of LFS before and after carbonation.

After carbonation, the sample was uniformly covered with standard phenolphthalein solution on the central profile to indicate the carbonation depth, as shown in the bottom part of Figure 8. The sample with 16% water content has a darker color before carbonation and almost covers the whole sample. After carbonation, it was found that the sample also showed a darker color in the phenolphthalein solution, indicating that the degree of carbonation of the sample was small. This was because the excessive water content led to the hindered diffusion of CO₂ during the carbonation process. With the decrease in water content, the color of the sample before carbonation became lighter and lighter. This proves that the moisture inside and outside the sample was reduced, and the resistance of CO₂ diffusion was reduced. So when the water content were fully carbonated to the inside. When the water content was 7%, the obstruction effect of water on CO₂ diffusion became very small, and there was enough water to dissolve Ca²⁺ and CO₂. After carbonation, phenolphthalein drops in the sample did not show color, the carbonation degree was high, and tightly packed cementation products could be clearly observed.

3.4. Mineralogical Compositions

The X-ray diffraction patterns and semi-quantitative mineral-phase analyses of samples with 6–8% water content and varying water–solid ratios are presented in Figure 9. The semi-quantitative analytical procedure exclusively considers calcium oxides and represents a corrected outcome. The predominant constituents in the LFS feedstock were calcio-olivine and akermanite, denoted by the chemical formulas γ -C₂S and Ca₂Mg(Si₂O₇), respectively. $Ca_2Mg(Si_2O_7)$ is a mineral-phase variant of $3CaO \cdot 2SiO_2(C_3S_2)$, primarily formed due to the incorporation of Mg^{2+} ions into the C_3S_2 lattice, replacing some of the Ca^{2+} ions during the high-temperature melting process of LFS. It shares similar properties to C₃S₂. Previous studies have demonstrated the significant carbonation activity of γ -C₂S and C₃S₂ [37]. Therefore, the primary sources of carbonation activity in the LFS were calcium silicate and akermanite. In contrast, fluorite does not react with CO_2 and was included in the analysis solely for comparative purposes with other phases. Additionally, the presence of other trace substances in the LFS was not analyzed; thus, the results of this semi-quantitative analysis should be considered as a reference only. The primary product of the reaction between steel slag and CO_2 is $CaCO_3$ [38], and the three primary crystalline forms of laboratory-generated CaCO₃ are calcite, aragonite, and vaterite [39]. γ -C₂S carbonated at low temperatures produces CaCO₃, primarily in the form of calcite [33]. Moreover, it can be discerned from Figure 9a that a prominent calcite diffraction peak appeared subsequent to carbonation, while no diffraction peaks of aragonite or vaterite were detected.



Figure 9. LFS with different water–solid ratios and water contents: (**a**) X-ray diffraction pattern; (**b**) semi-quantitative mineral-phase analysis.

From Figure 9b, it can be discerned that an increase in the water–solid ratio results in a corresponding elevation of calcite generation following carbonation. The generation of calcite demonstrates an initial rise followed by a decline as water content increases, in line with the findings of carbon sequestration and thermogravimetry presented in Figure 7. Upon carbonation, the contents of calcium silicate and akermanite decrease as the degree of carbonation intensifies, thereby indicating that γ -C₂S and Ca₂Mg(Si₂O₇) serve as the primary active agents in the carbonation of LFS, which are transformed into stable calcite upon carbonation, concurrently fixing CO₂ within the calcite. However, calcium silicate and akermanite do not experience complete carbonation, likely due to the challenges associated with CO₂ penetration within the particles of LFS.

3.5. Morphology

The microscopic morphology of LFS after carbonation with a water-solid ratio of 0.3 and a water content of 6–8% is shown in Figure 10, magnified by 20,000 times. It can be observed that as the water content increases, the size of carbonation products initially increases and then decreases. Additionally, specimens with higher degrees of carbonation exhibit larger and denser calcium carbonate crystals. The formation of calcite crystals on the particle surface can be observed in specimens with a water content of 6%. These fine particles, approximately $0.3 \,\mu m$ in size, are cemented to the larger matrix as depicted in Figure 10a. At a water content of 7%, calcite exhibits enhanced crystallinity and grows in rock-like layers, while some small clusters of calcium carbonate crystals fill pores and increase compactness (Figure 10b). This may explain why specimens with a water content of 7% possess higher strength compared to others. Figure 10c reveals that small calcium carbonate crystals measuring around 0.2 µm are cemented together to form larger particles measuring approximately 1.2 µm; however, these cemented particles fail to continue growing due to certain limitations, resulting in low crystallinity levels. This phenomenon could be attributed to an abundance of surface moisture hindering CO_2 diffusion on high-water-content specimen particles. Pores associated with high-watercontent samples are smaller than those found in low-water-content samples but occur at a greater frequency.



Figure 10. SEM images of carbonated LFS with (**a**) 6% water content; (**b**) 7% water content; (**c**) 8% water content.

Figure 11 shows the $5000 \times$ -magnification electron image, and the EDS surface scan results are shown in Figure 10b. The dense structure of the 7%-water-content specimen can be observed in the electron image. A large number of overlapping regions of Ca, Mg, C, and O elements can be found, which further proves that the carbonation products of the LFS are calcium/magnesium carbonates and predominantly CaCO₃, which is consistent with the results in Figure 9. The areas exhibited smaller crystalline structures and high brightness corresponding to CaCO₃ products, whereas the larger particles with darker regions represent uncarbonated calcium silicate. This distinction arose from the fact that calcium carbonate could solely precipitate on the surface of calcium silicate particles, leading to a higher number of small calcium carbonate crystals formed on larger calcium silicate particles. Carbonation was more challenging for larger calcium silicate particles compared to their smaller counterparts.



Figure 11. EDS result of carbonated LFS with 7% water content.

3.6. Pore Structure

In order to investigate the distribution of pore structures within carbonated LFS samples with a water–solid ratio of 0.3 and varying water contents, a high-resolution threedimensional X-ray microscope was employed to analyze the central region of the samples. Pore identification is achieved through grayscale threshold segmentation, wherein the lower density of water compared to solids enables direct pore recognition during analysis. The porosity can be determined by reconstructing the test results in three dimensional Cross-sections of samples with different water contents. It is evident that most curves exhibit overall flatness, with only a few positions displaying significant fluctuations attributed to large pore size defects present in the original samples. However, these defects remain within acceptable limits and do not undermine the value of our findings. Furthermore, it was observed that all samples exhibited reduced porosity after carbonation compared to their pre-carbonation state. This reduction in porosity correlates with changes in compressive strength, carbon sequestration rate, and physical phase content as discussed elsewhere in this paper. Notably, as the water content approaches 7%, higher degrees of carbonation lead to increased generation of calcium carbonate, which fills up pores and contributes to enhanced strength.



Figure 12. Axial pore size distribution of carbonated LFS with different water contents.

The test results were reconstructed in three dimensions, classifying holes based on connectivity into open and closed categories. The rendered results are presented in Figure 13. The upper section of the figure illustrates cut sections of the samples with varying water contents, while the lower section showcases the three-dimensional rendering. In the lower half of the 3D rendering, only the original shape is displayed, whereas in the upper half, both open and closed pores are visible with a priority given to displaying closed pores. It can be observed that micropores are distributed throughout the specimen, while closed pores are predominantly concentrated in its central region. Following carbonation treatment, there was a significant increase in closed pores within the specimen. This phenomenon may be attributed to calcium carbonate production blocking connecting pores and leading to an increased formation of closed pores.



Figure 13. Cutaway and 3D rendering of 3D CT of specimens with (**a**) uncarbonated; (**b**) 6% water content; (**c**) 7% water content; (**d**) 8% water content.

The results of total porosity, open porosity, and closed porosity obtained through calculation are presented in Table 2. In total, 98.71% of the pores in the uncarbonated specimen are classified as open pores (Figure 13a), which facilitates favorable conditions for CO_2 diffusion during the carbonation process. The variation in water content shows a similar trend between open porosity and total porosity, indicating that carbonation generates calcium carbonate that fills most of the open pores, enhancing overall compactness but reducing pore connectivity. Closed pores consistently increase with increasing water content. Notably, specimens with 8% water content exhibit higher levels of closed pores compared to those with 7% water content; however, they show lower levels of carbonation. This observation suggests that higher-water-content specimens possess more bridging water between particles and result in calcium carbonate deposition within particle gaps, leading to increased formation of closed pores. Consequently, this impedes CO_2 diffusion pathways and affects later-stage carbonation progress. At a water content of 7%, although more closed pores are formed, there are still interconnected pores within the specimen allowing CO₂ penetration (Figure 13c). Beyond a water content threshold above 7%, closed pores occupy almost all internal spaces within the specimen (Figure 13d), resulting in incomplete carbonation and subsequent reductions in strength and carbon sequestration rate.

Table 2. Porosity of carbonated LFS with different water contents (%).

Samples	Water Content	Total Porosity	Open Porosity	Closed Porosity
а	uncarbonated	20.44%	20.18%	0.26%
b	6%	17.69%	16.90%	0.79%
С	7%	10.60%	7.14%	3.46%
d	8%	13.61%	8.52%	5.09%

4. Discussion

Previous studies have demonstrated that γ -C₂S undergoes low-temperature carbonation to produce calcite and silica, with the silica encapsulating uncarbonated γ -C₂S particles and the calcite filling the pores [40,41]. Similar structural characteristics are observed in steel slag carbonation as well [42]. Figure 14 illustrates the cementation mechanism of LFS, primarily composed of γ -C₂S, under a carbonation environment based on the findings presented in this paper. Distinguishing itself from previous studies, this mechanism provides a comprehensive understanding of the carbonation reaction behavior by focusing on pore and particle cementation, particularly in relation to both open and closed pores. For clarity purposes, γ -C₂S particles are used instead of LFS particles.

This study describes the differentiation between <7% and >7% water content during carbonation behavior. At <7% water content, γ -C₂S particles exhibit reduced formation of bridging water, facilitating easy diffusion of CO₂ between and within the particles through interconnected pores (see Figure 14a). The enhanced contact area between CO₂ and the particles enables a greater carbonation extent for γ -C₂S particles. This leads to easier interior carbonation of specimens with lower water content, as demonstrated in Figure 8. However, complete carbonation of steel slag due to inherent particle size constraints leads to the presence of a porous carbonate layer in its products [43].

At >7% water content, there is sufficient bridging water to cement the particles; however, the presence of this bridging water hinders CO_2 diffusion into the interior. Calcium ions are released into the bridging water and react with CO_2 , resulting in precipitation of calcium carbonate. This process leads to the solidification of the bridging water and closure of gaps between particles, transforming original open pores into closed ones after carbonation (see Figure 14b). Consequently, this impedes subsequent particle gaps and internal carbonation.



Figure 14. Carbonation cementation mechanism of LFS particles with (**a**) <7% water content; (**b**) >7% water content.

In summary, at <7% water content, the specimens were susceptible to interior carbonation due to the prolonged presence of open pores. At >7% water content, the specimens formed closed pores as a result of bridging water hardening, thereby hindering the carbonation process. At the optimum water content, although closed pores were also formed alongside open holes in the carbonated specimen, they did not impede carbonation from reaching the interior. Furthermore, Figure 14b illustrates a significantly more cemented structure with an appropriate amount of enhancing strength.

5. Limitations and Future Directions

This paper specifically addresses the significant impact of moisture on the carbonation reaction, without establishing correlations with other influencing factors. Future investigations should aim to comprehensively explore the carbonation mechanism of steel slag by concurrently studying moisture, temperature, CO_2 pressure, and other relevant variables. The objective of this paper is to emphasize the importance of moisture in the carbonation mechanism through controlled manipulation of its content; however, implementing such control measures in practical engineering scenarios may prove challenging based on the methods employed herein. Therefore, it is imperative for researchers to develop a suitable approach for regulating water content.

6. Conclusions

- 1. A method was developed to control the water content of steel slag specimens, and the significant influence of moisture and pore space on the carbonation reaction of steel slag specimens was innovatively identified. The carbonation process relies on pores for CO₂ diffusion and also requires a certain level of moisture for Ca²⁺ dissolution and diffusion. Increasing the water content enhances particle cementation and carbonation capacity in steel slag specimens; however, excessive water hinders CO₂ diffusion. Reducing the water content can increase the carbonation depth but may compromise gelling and carbon sequestration ability. Therefore, achieving a balance is crucial in controlling the water content;
- 2. The pour-molding process was employed to enhance the porosity of steel slag specimens. The increase in pores reduces the density of the steel slag specimens but enhances their CO₂ diffusion capacity. This is different from the common compression-molding process, achieving the absorption and fixation of approximately 217.2 kg of CO₂ for each ton of LFS at a 0.35 water–solid ratio and optimum water content. This carbon sequestration capacity is at an industry-leading level;

3. An innovative three-dimensional pore structure analysis method was used to analyze the connected and closed holes, and it was found that steel slag particles with low water content have a minimal impact on pore connectivity during cementation, allowing most of the pores to remain open. Conversely, steel slag particles with higher water content result in the formation of more closed pores that hinder CO₂ diffusion into the interior of the steel slag specimens, leading to a lower degree of carbonation compared to their surfaces. This study reveals the key mechanisms by which pore space and moisture affect carbonation reactions.

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