

Article

Development of Ultrafine Mineral Admixture from Magnesium Slag and Sequestration of CO₂

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Abstract: To upcycle magnesium slag solid waste (MS) as well as sequester CO₂, a new wet carbonation process was proposed to activate the volcanic ash activity of MS and use it as an ultrafine mineral admixture for cement. The effects of different carbonation times on the activity of MS were investigated, and the phase assemblage, as well as the changes in the microstructure and pore structure during the carbonation process, was also characterized using multiple techniques, such as TG-DTG, XRD, FT-IR, ²⁹Si NMR spectrum, SEM, and BET, to further reveal the carbonation activation mechanism of MS under wet carbonation. Moreover, the effects of MS before and after carbonation on the compressive strength of the composite cement paste were investigated to verify the feasibility of carbonated MS as an ultrafine mineral admixture. The results show that the products of MS generated after a short carbonation reaction were mainly highly polymerized calcium–silicate–hydrate gel and a large amount of calcium carbonate in the form of calcite and aragonite with a size of about 1 μm. The CO₂ sequestration rate of MS reached 22.14%. Compared to pure cement, carbonated MS can replace 30% of the cement clinker without compromising compressive strength. The above results offer potential possibilities for upgrading the utilization of MS and CO₂ sequestration in the cement industry.

Keywords: magnesium slag; wet carbonation; CaCO₃; microstructure; calcium–silicate–hydrate (C–S–H)



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1. Introduction

Cement, as one of the indispensable materials for modern urban construction, has a great role in the progress and development of society [1]. However, the production of cement requires large amounts of non-renewable energy as fuel and releases large amounts of harmful gases such as carbon dioxide (CO₂) [2–4]. This phenomenon has led to a gradual increase in the level of CO₂ in the atmosphere and, more seriously, to the greenhouse effect [5–9]. The environmental problems associated with global warming have prompted scholars to develop new mineral admixtures to reduce CO₂ emissions from the cement industry [10–14].

Various industrial solid wastes are used as mineral admixtures, such as fly ash (FA) [15–18], granulated ground blast furnace slag (GGBS) [17,19], silica fume [15,20,21], limestone [22], and sintering red mud [23], which greatly reduces the carbon emissions of the cement industry. In addition to these solid wastes, magnesium slag (MS) is a by-product produced during the magnesium refining process [24]. MS shows easy grinding characteristics, representing its great potential as a mineral admixture, but it still faces problems such as low activity and poor stability [25].

Many strategies have been developed to address these problems. For example, MS was ground into a fine powder to increase the particle size gradation while increasing its hydration activity [24,26]. As another option, chemical substances and microorganisms were added to further activate the MS [27]. However, these methods only improve the bulk

stability and hydration reactivity of MS to a certain extent and do not guarantee the safe and effective utilization of MS for a long time.

On the other hand, MS, like other solid wastes, contains significant amounts of calcium silicate minerals, which suggests that MS can react with CO_2 [28]. Using an accelerated carbonation method, Mo [29,30] found that the carbonation of steel slag generated a large amount of calcium carbonate and formed an amorphous SiO_2 gel with a high degree of polymerization. The results showed that the cement paste containing carbonated steel slag shows a great improvement in compressive strength. Similarly, there were many other studies on the carbonation of steel slag [31–33], furnace slag [34], fly ash [35–39], and slag [40]. When MS was exposed to a CO_2 -rich environment, it was easily carbonated to form calcite. Normally, both CaO and MgO contained in the MS can be converted to carbonate through a carbonation reaction with CO_2 . Therefore, MS has great application prospects as a new material for CO_2 mineralization. Mo [41] utilized the properties of MS, which was rich in CaO and MgO, to prepare a calcium carbonate binder using accelerated carbonation, and its compressive strength could reach 119.5 MPa. Calcium carbonate improved the performance of the cement both physically as a filler and chemically through nucleation. Meanwhile, amorphous silica gel shows volcanic ash activity. Therefore, MS carbonation activation products have the potential to be used as mineral admixtures.

Moreover, in some recent studies on wet carbonation, it has been found that using wet carbonation is better than other carbonation methods. Fang et al. [42,43] successfully produced calcite and alumina-silica from recycled cement paste through a new two-step wet carbonation method. Shen et al. [44] recovered nano-silica and calcium silicate-rich material from renewable cement powder. Lu et al. [45]. and Zajac [46–48] also prepared mineral admixtures with various crystalline forms of calcium carbonate as well as an amorphous gel as the main products. However, there is no detailed report on the wet carbonation of MS and its ability to sequester CO_2 after wet carbonation. The evolution of the reaction products and microstructures has not been revealed. Therefore, it is essential to explore the MS carbonation process and carbonation products for the preparation of highly active carbonated MS.

Therefore, this work aimed to explore the carbonation reaction process of MS in pure water and confirm whether MS after wet carbonation can be added to cement as a new mineral admixture. The carbonation process of MS was first explored by pH, conductivity, and temperature variations. The XRD, TG, FT-IR, NMR, SEM, and BET were also used to investigate the phase assemblage and microstructure of MS during wet carbonation, including the calcium-containing and silica phases. The carbonation activation mechanism of MS in pure water by CO_2 was also revealed, and the ability of MS to sequester CO_2 was discussed and analyzed. It is further shown that MS after wet carbonation can be used as a new mineral admixture.

2. Experimental Methodology

2.1. Materials

The MS of the Pidgeon method used in this work was obtained from Yulin City, Shaanxi Province, China. The MS is off-white after being dried and ground. The microscopic morphology and chemical composition of MS are shown in Figure 1 and Table 1. The XRD and particle size distribution are shown in Figures 2 and 3, respectively. The major chemical component of MS of the Pidgeon method is CaO, SiO_2 , Al_2O_3 , Fe_2O_3 , MgO, alkali, etc., and the content of CaO and SiO_2 are higher.

Table 1. The chemical composition of MS and OPC (wt.%).

Oxide	SiO_2	Al_2O_3	CaO	Fe_2O_3	MgO	Others
MS	29.88	1.06	50.98	3.52	11.27	3.29
OPC	23.17	5.37	61.86	3.32	2.78	3.5

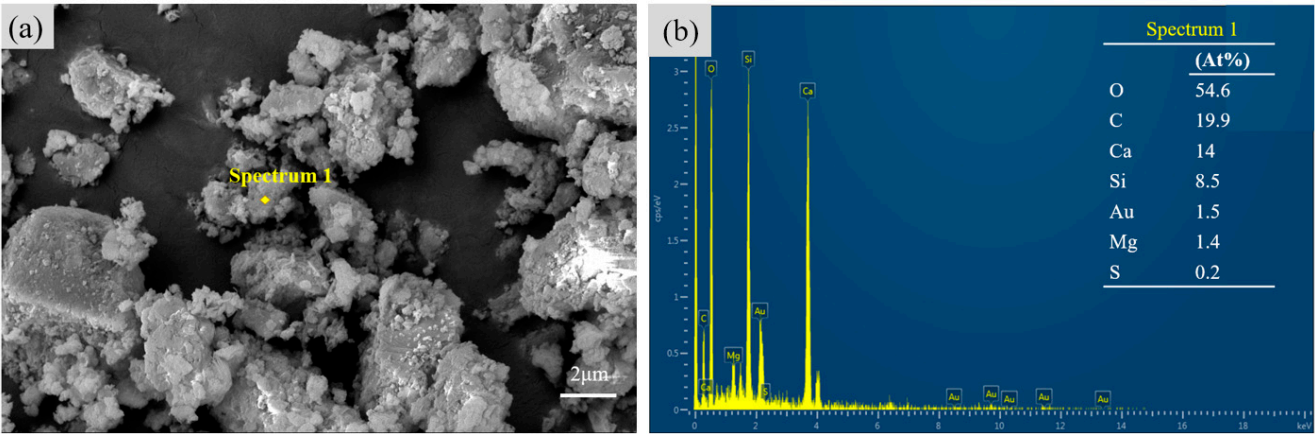


Figure 1. (a) SEM and (b) EDS spectrum of MS.

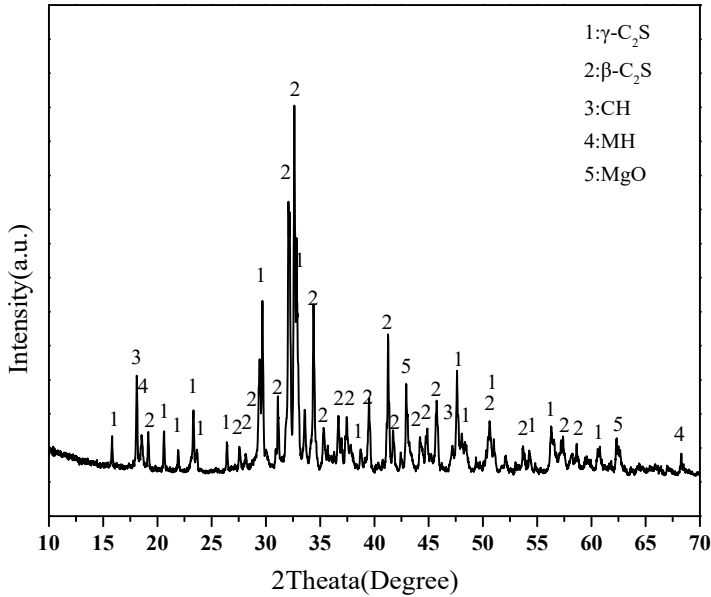


Figure 2. XRD spectrum of MS.

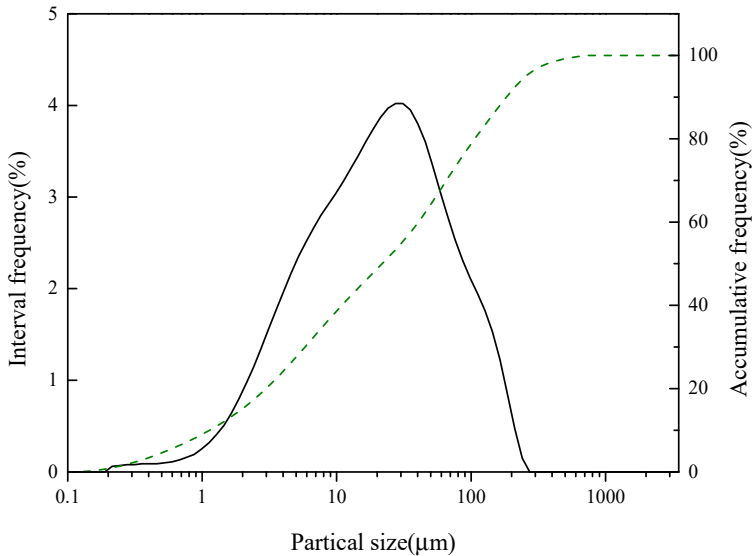


Figure 3. The particle size distribution of MS.

The specific surface area of the MS powder after milling was $724.4 \text{ m}^2/\text{kg}$, and the median particle size (D50) was $22.2 \text{ }\mu\text{m}$. The uncarbonated MS particles are mostly irregularly massive and surrounded by clusters of amorphous particles with complex composition but rich in silica and calcium elements. The mineral composition of the MS is mainly calcium silicate, with small amounts of magnesite and calcium oxide. The cement used in this work was ordinary Portland cement (OPC), and the chemical composition is shown in Figure 1.

2.2. The Wet Carbonation Process

For the wet carbonation process, MS powder was mixed with pure water in the container according to the ratio of 20:1, followed by stirring for 10 min with a stirring rate of 400 r/min [49]. Then, CO_2 gas was bubbled into the suspension at a CO_2 gas flow rate of 1 L/min/10 gMS using a flow meter. A pH meter was used to monitor the pH value of the suspension, and the temperature and conductivity were recorded. When the pH meter reading was less than 7 or the conductivity was stable, it represented the end of carbonation. The carbonated MS was obtained using vacuum filtration. After drying and grinding, the carbonated MS powder was obtained.

2.3. Preparation and Curing of Composite Cement Paste

Figure 4 shows the preparation process of composite cement paste. MS powders with different carbonation times (0, 10, 30, 120, and 480 min) were added to OPC at 30% substitution to prepare the cement paste blocks. The blocks were molded into $40 \times 40 \times 40 \text{ mm}$ in a constant temperature room, and the temperature was kept at a constant $20 \text{ }^\circ\text{C}$. The blocks were de-molded after 1 day and used to test the compressive strength. The remaining blocks were left to test their compressive strength at 3, 7, and 28 days.

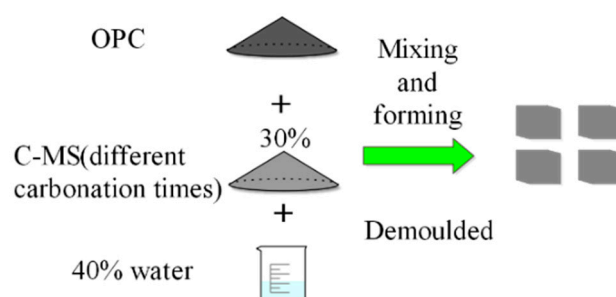


Figure 4. The preparation process of composite cement paste.

2.4. Test Methods

2.4.1. Particle Size Distribution

The laser particle size analyzer used in this study was the Malvern Mastersizer 3000 E, and the dry method was chosen to test the particle size distribution of the samples.

2.4.2. The pH, Conductivity, and Temperature Changes

The REX PHS-3C type precision digital display pH meter was selected, the conductivity meter model was digital display DDS-11A type, and temperature changes were recorded using a digital display sensing thermometer.

2.4.3. Thermal Analysis (TG-DTG)

A comprehensive thermal analyzer (BJ-HCT-3, Beijing Hengjiu Scientific Instruments Factory, Beijing, China) was used. Before starting the test, the sample was first dried and ground. Temperature rise was set from room temperature to $1000 \text{ }^\circ\text{C}$ at $10 \text{ }^\circ\text{C}/\text{min}$. The

amount of calcium carbonate produced was further calculated from the weight loss on the TG curve according to Equation (1) [49,50].

$$Cc(\%) = \left(\frac{(M_{500^{\circ}\text{C}} - M_{800^{\circ}\text{C}}) \times \left(\frac{100}{44}\right)}{M_{800^{\circ}\text{C}}} \right) \times 100\% \quad (1)$$

where $M_{500^{\circ}\text{C}}$ is the mass loss at 500 °C, and $M_{800^{\circ}\text{C}}$ is the mass loss at 800 °C.

2.4.4. X-ray Powder Diffraction (XRD)

X-ray diffraction (XRD) was used to determine the mineralogical compositions of C-MS using X-ray diffractometer (Cu target, Smart Lab, Rigaku Corporation, Akishima City, Tokyo, Japan) with a step of 0.02 at 2/°min, an accelerating voltage of 45 kV, and a current of 200 mA [51,52].

2.4.5. Fournier Transform Infrared (FTIR) and ^{29}Si NMR Spectroscopy (NMR)

The V70 fully automatic switchable FTIR spectrometer was used to acquire the FTIR spectrum in the range of 400–4000 cm^{-1} using a solid powder total reflection method [50].

To better understand the chemical environment of Si in carbonated MS, the spectra of MS carbonated for 0, 30, and 480 min were tested using ^{29}Si MAS NMR on an Agilent 600 DD2 spectrometer (Agilent, New York, NY, USA, magnetic field strength 14.1 T) [51]. Solid-state ^{29}Si DD/MAS NMR spectra were recorded at a resonance frequency of 199.13 MHz. The powder samples were placed in a container with a diameter of 4.0 mm.

2.4.6. Scanning Electron Microscopy (SEM)

A Merlin compact SEM was used to capture SEM images at a high vacuum mode and a 15 kV accelerating voltage. To achieve adequate conductivity, the samples were coated with gold [50,52].

2.4.7. Pore Structure

The surface area and pores of the samples were measured and analyzed using a TriStar II 3020BET system manufactured by Micromeritics to study the pore structure evolution of the MS at different carbonation times. The total specific surface area and pore volume variation of the samples were investigated using calculation methods such as BET and BJH. The samples were degassed for 6 h at 45 °C to remove residual moisture and gaseous impurities.

3. Results and Discussion

3.1. The Changes in pH, Conductivity, and Temperature of MS Suspension

Figure 5 shows the changes in pH, conductivity, and temperature of the MS suspension during wet carbonation. It can be seen that the pH of the suspension rises rapidly to a final value of 11.5, which usually happens very quickly or even within a minute. This indicates that MS is very alkaline and seriously pollutes the environment, whereas, after CO_2 was injected, the pH of the suspension dropped quickly, which was divided into four main intervals. First, the pH of the suspension dropped rapidly to about 10 after the injection of CO_2 , and then the pH of the suspension rebounded briefly. In the third change interval, the pH dropped fast. Finally, the pH dropped slowly and gradually stabilized. The pH change of the suspension is explained as follows. The dissolution of MS in pure water gradually reached a steady state before the injection of CO_2 , and the suspension was filled with a large number of basic ions. When CO_2 was injected into the suspension, the dissolved minerals in the suspension reacted with the CO_2 to form a precipitate. The generation of carbonate precipitation consumed a large number of alkaline ions in the suspension, which, in turn, broke the ionic dissolution equilibrium and led to the continuous dissolution of the alkaline minerals. Due to the simultaneous generation of carbonates and dissolution

of minerals, the pH eventually reached stability in 20–35 min. As the reaction process continued, the dissolution of minerals in the suspension gradually ended, but precipitation continued to occur, so the pH of the suspension slowly decreased and finally stabilized at about 7.8. The whole carbonation process was generally completed within 6 h.

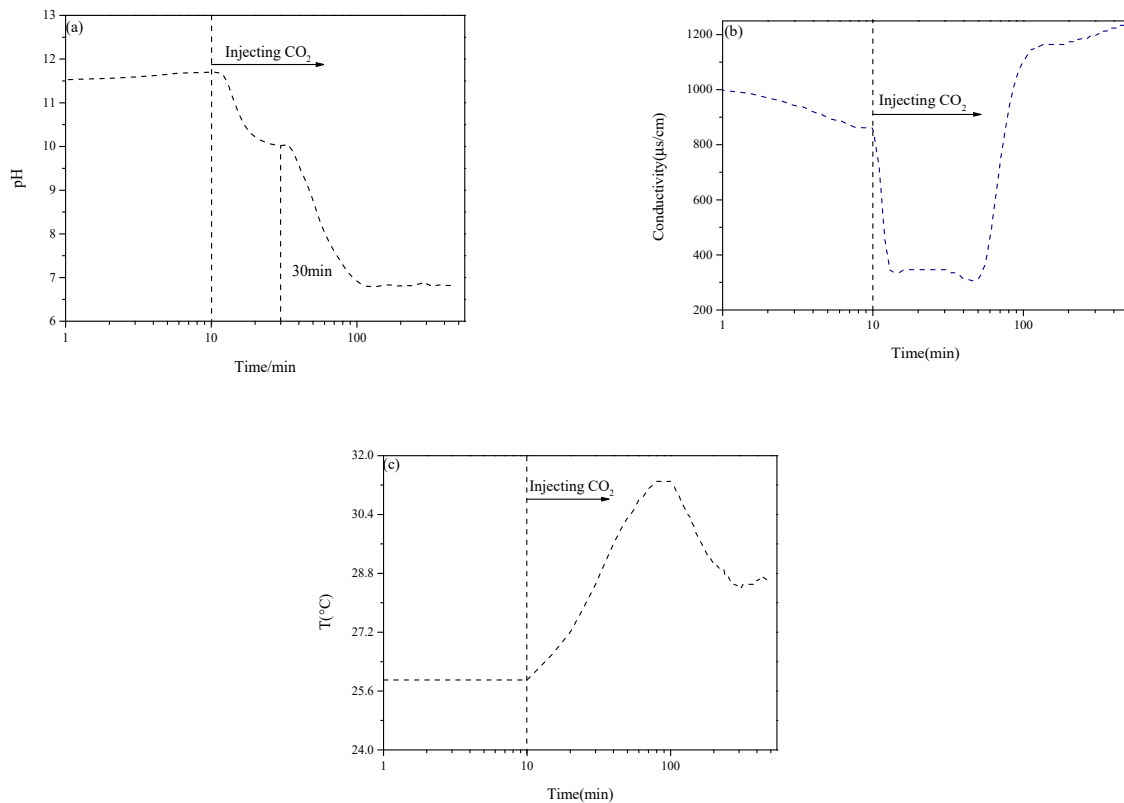


Figure 5. The changes in (a) pH, (b) conductivity, and (c) temperature of MS suspension during wet carbonation.

Figure 5b shows the changes in the conductivity of the suspension. The change in the conductivity curve is similar to the change in the pH curve. When CO₂ was not injected, the dissolution of minerals contained in the MS reached equilibrium, so the conductivity was maintained at about 900 μs/cm. The conductivity decreased rapidly after the injection of CO₂, and this phenomenon proves that the alkaline ions dissolved in the suspension can rapidly precipitate with CO₂ after the injection of CO₂. The dissolving equilibrium of the alkaline minerals was disturbed as the precipitation reaction progressed, and the ions were once again dissolved as the precipitation occurred. At this point, the dissolution and precipitation were nearly in balance, and the pH was restored in 20–35 min. The conductivity rose rapidly in the third stage. This is because the MS reaches a high degree of carbonation, and few basic ions can be bound to CO₂. The conductivity also equilibrated with the stabilization of pH, which proved that the carbonation of MS was completed at this time.

The temperature changes of the MS suspension during the carbonation process are shown in Figure 5c. It is obvious from Figure 5c that the temperature of the suspension gradually increases during the carbonation process. However, as the pH of the suspension stabilized, the temperature began to fall. The temperature of the suspension increased by about 3 °C throughout the carbonation process, indicating that the MS carbonation reaction is exothermic. This phenomenon was caused by the continuous dissolution of minerals in suspension (such as C₂S) and the heat generated by the formation of calcium carbonate precipitates. Under the same experimental conditions, MS was carbonated to different degrees and vacuum-filtered to obtain powder samples to reveal the phase assemblage.

The samples were dried and stored under seal at 105 °C and further characterized using XRD, TG, FTIR, NMR, SEM, and BET material testing methods.

3.2. Evolution of Calcium-Containing Phase

3.2.1. TG/DTG

The weight loss in Figure 6 can be used to calculate the CO₂ sequestration of MS at different carbonation times. The CaCO₃ content for different carbonation times can be subsequently determined using Equation (1). From Figure 6b, it indicates that the DTG curves are divided into three main peaks. Typically, dehydration of the gel water in C-S-H or silica gels occurs between 50 and 150 °C, while Ca(OH)₂ dehydrates between 350 and 500 °C to form CaO [53,54]. The third peak of mass loss at temperatures between 500 °C and 800 °C on the DTG curves represents the decomposition of calcium carbonated. From the above results, it can be seen that the weight loss peak belonging to CaCO₃ gradually shifts to the right as the carbonation reaction continues. This also indicates that the crystallinity will be better. It has been shown that the heat absorption peaks located at 550–680 °C, 680–780 °C, and 780–990 °C correspond to the different crystalline forms of CaCO₃, namely, amorphous calcium carbonate, aragonite, vaterite, and the better-crystallized calcite, respectively [55,56]. As the Mg content in MS micronized powder is significantly lower than γ -C₂S, the weight loss peak of hydro magnesite (Mg(OH)₂) at 390 °C due to dehydration is not obvious. From this study, the formation of amorphous CaCO₃ in an alkaline environment is more likely. However, the formation of CaCO₃ crystals is influenced more by the type of suspension and the pH of the growth environment. During the carbonation process, crystalline CaCO₃ is formed when the dissolved CO₂ in the suspension reaches saturation and the pH is below 7. Figure 7 shows the CaCO₃ content at different carbonation times. The CaCO₃ content reached 93.28% at 480 min as the carbonation reaction proceeded. This indicates that the calcium-containing minerals (C₂S) in suspension are essentially converted to CaCO₃.

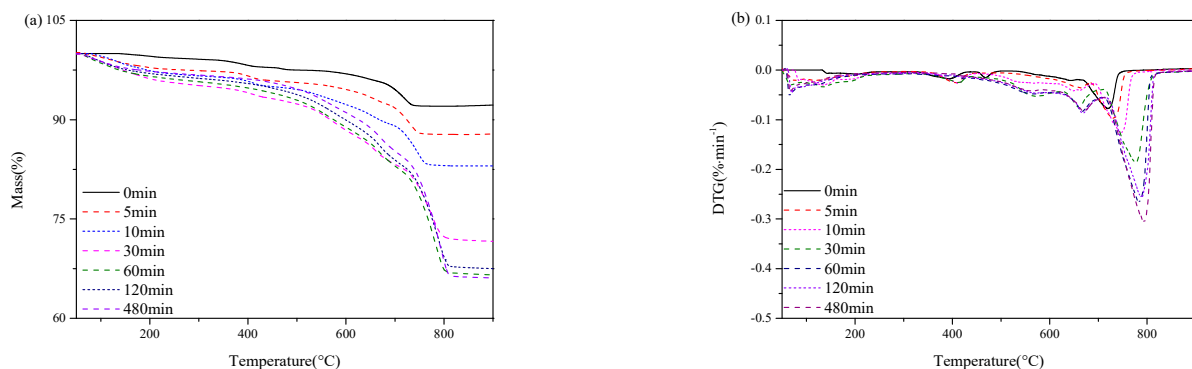


Figure 6. (a) TG and (b) DTG curves of MS with different carbonation duration.

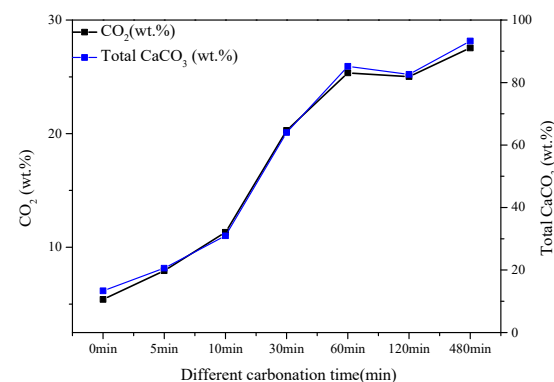


Figure 7. Total content of CaCO₃ and sequestered CO₂ in MS with different carbonation duration.

3.2.2. XRD

The phase assemblage of the sample was further investigated using XRD, and the results are shown in Figure 8. The phase assemblage of the MS before carbonation is mainly composed of C_2S and a small amount of MgO . However, the results also show the presence of a small amount of calcite, indicating that the MS was slightly carbonated. Figure 8b shows that the $CaCO_3$ diffraction peak at $2\theta \approx 29.42^\circ$ gradually increases as the carbonation reaction continues, which is consistent with the results of the TG analysis. As the carbonation reaction continued, the diffraction peaks of C_2S disappeared completely after 30 min. This indicates that C_2S was converted to calcite after the carbonation reaction. In addition, the diffraction peak of MgO disappeared when the carbonation reaction proceeded to 30 min, indicating that MgO was converted to Mg carbonate or Mg calcite. However, it was reported that the diffraction peaks of Mg calcite and calcite overlapped, so it was difficult to distinguish [57].

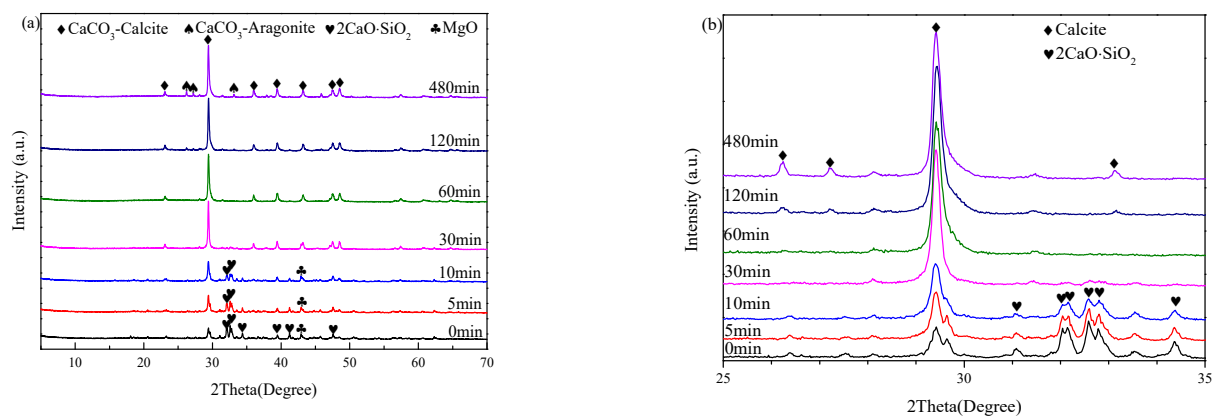


Figure 8. (a) XRD patterns of MS with different carbonation duration and (b) Enlarged XRD patterns at $25\text{--}35^\circ$.

The semi-quantitative (QXRD) analysis results of the MS after different carbonation times are shown in Table 2. This result proves that the calcite content continues to increase as the carbonation reaction continues, with the calcite content up to 93.2% at 60 min. However, when the carbonation time reached 120 min, the diffraction peaks of aragonite appeared on the XRD pattern, indicating that the carbonation of MS produced not only calcite but also aragonite. This result also appeared in the DTG analysis.

Table 2. The QXRD data of Cc in carbonated MS.

Time/min	0 min	5 min	10 min	30 min	60 min	120 min	480 min
Cc wt. %	7.9	30.6	43.5	92.8	93.2	90.2	83.2

3.3. Evolution of Silica Phases

3.3.1. FTIR

The FTIR results can further characterize the structural changes of the products during the carbonation process. The spectra were observed mainly in the range of $800\text{--}1600\text{ cm}^{-1}$. The asymmetric stretching vibration (ν^3), out-of-plane bending vibration (ν^4), and in-plane bending vibration (ν^2) of the carbonate group correspond to 1420 , 876 , and 712 cm^{-1} , respectively, as shown in Figure 9. The presence of these peaks indicates the presence of calcite in the sample, and the amount of calcite can also be indicated by the variation in the intensity of these peaks. The absorption peak found around 1000 cm^{-1} represents the vibration of the Si-O bond (ν^3).

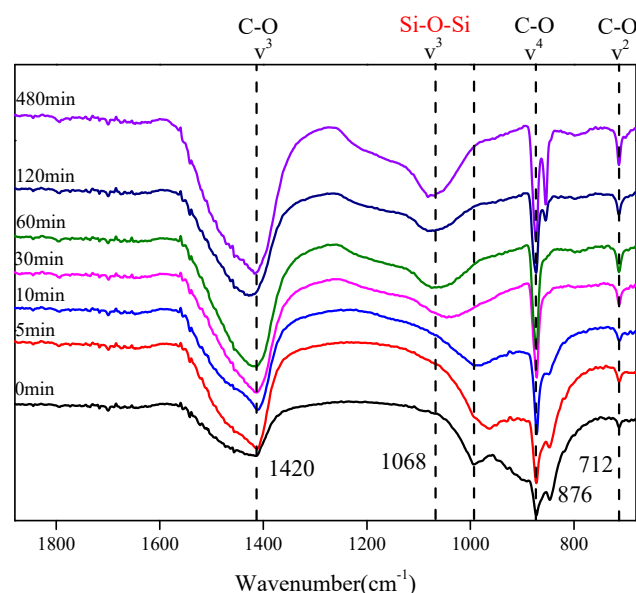


Figure 9. The FTIR spectra of MS with different carbonation duration.

The FTIR spectra show that slight calcite vibrational peaks were also present in the MS, representing the presence of a small quantity of CaCO_3 in the MS as well, which is consistent with the XRD analysis. In addition, the peaks located at these three positions were significantly enhanced with the continuation of the carbonation reaction. It is obvious from the spectrum that the yield of calcium carbonate was very high when the carbonation reaction proceeds for only 5 min, and this result is consistent with the early change pattern of pH and conductivity. As the carbonation reaction continued, the quantity of carbonate generated showed an increasing trend, but the rate of growth decreased, which is similar to the DTG and XRD results.

Interestingly, as the carbonation reaction continues, the Si-O vibrational peak located between 900 and 1200 cm^{-1} not only shifted position to a higher wave number (1068 cm^{-1}), but the intensity of this peak also increased. This phenomenon indicates the dicalcium silicate in MS undergoes a carbonation reaction to produce a calcium–silicate–hydrate gel with a high polymerization degree. However, this phenomenon occurred only after 30 min and coincided with the pH change of the suspension. The FTIR analysis shows that CaCO_3 forms more easily than calcium–silicate–hydrate gel in the carbonation products of C_2S and requires certain environmental conditions to improve the calcium–silicate–hydrate gel polymerization.

3.3.2. ^{29}Si NMR

Figure 10 represents the ^{29}Si NMR spectrum results of MS with different carbonation duration. For the MS, the Q^1 and Q^0 sites appeared in the range of -83 and -70 ppm, respectively, indicating the existence of C_2S in the MS. After 30 min of carbonation, the peak at -83 ppm decreased, and the peak of Q^4 sites appeared at -110 ppm, suggesting the formation of the amorphous silica phase with a high polymerization degree [58]. The above results show that the polymerization of the silica gel started at 30 min of carbonation. After 480 min of carbonation, the peaks of the $\text{Q}^3(\text{OH})$ and Q^4 sites generated by the Ca-modified silica gel became increasingly intense as the carbonation period increased. This phenomenon occurs because the MS suspension is alkaline and the injected CO_2 dissolves rapidly in the alkaline suspension, increasing the solubility of the hydrogen ions in the suspension. It not only lowers the pH of the suspension but also promotes the dissolution rate of calcium ions from C_2S minerals. The highly polymerized silica gel was created at this point through the condensation process of the $[\text{SiO}_4]$ group when Ca^{2+} finally mixes with CO_3^{2-} in the suspension to produce a CaCO_3 precipitate.

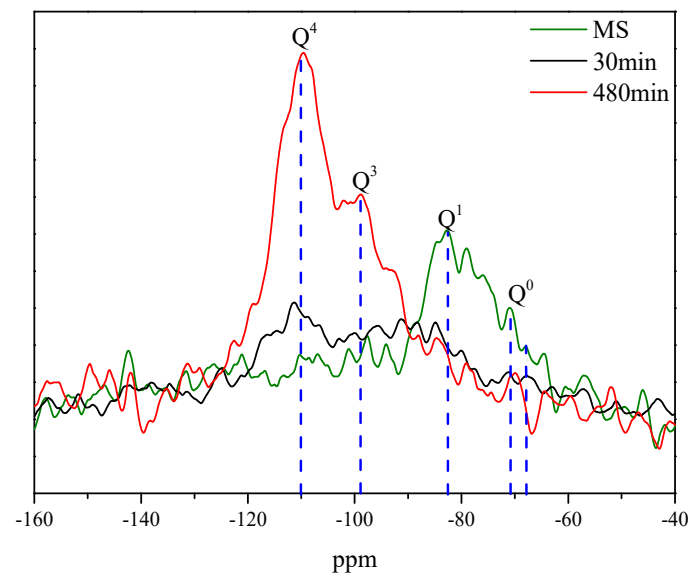


Figure 10. The ^{29}Si NMR spectra of MS with different carbonation duration.

3.4. Microstructure of MS

Figure 11 shows the SEM and EDS images of MS with different carbonation duration. It can be seen that the morphology of the MS particles did not change much at the beginning, but small particles of calcium carbonate were formed. When the carbonation reaction continued up to 10 min, a large number of calcite particles were observed, although the size of these particles was very small. After 30 min, the particle morphology changed dramatically. The plate-like calcite particles were attached around the MS particles, and the size of the calcite particles increased significantly compared to the initial stage of the reaction.

As the carbonation time increased, the microstructure of the MS changed significantly after 60 min. The acidity of the suspension reached neutralization at this time, and the microscopic morphology of the C-MS was mostly hexagonal calcite crystals with a size of about $1\ \mu\text{m}$. This is due to the continuous growth of the small calcite initially covering the surface of the MS particles through the carbonation reaction. In addition, there are even smaller calcite sizes between these grains. These generated carbonate products and calcium–silicate–hydrate gels are the main factors in the strength growth of the specimens [59,60].

The size of the calcite particles continues to grow as the carbonation reaction continues. Interestingly, when the carbonation reaction proceeded to 120 min, some CaCO_3 in the form of aragonite crystals appeared, and when the carbonation reaction continued to 480 min, the amount of aragonite had increased significantly. This result is following the XRD and TG-DTG results.

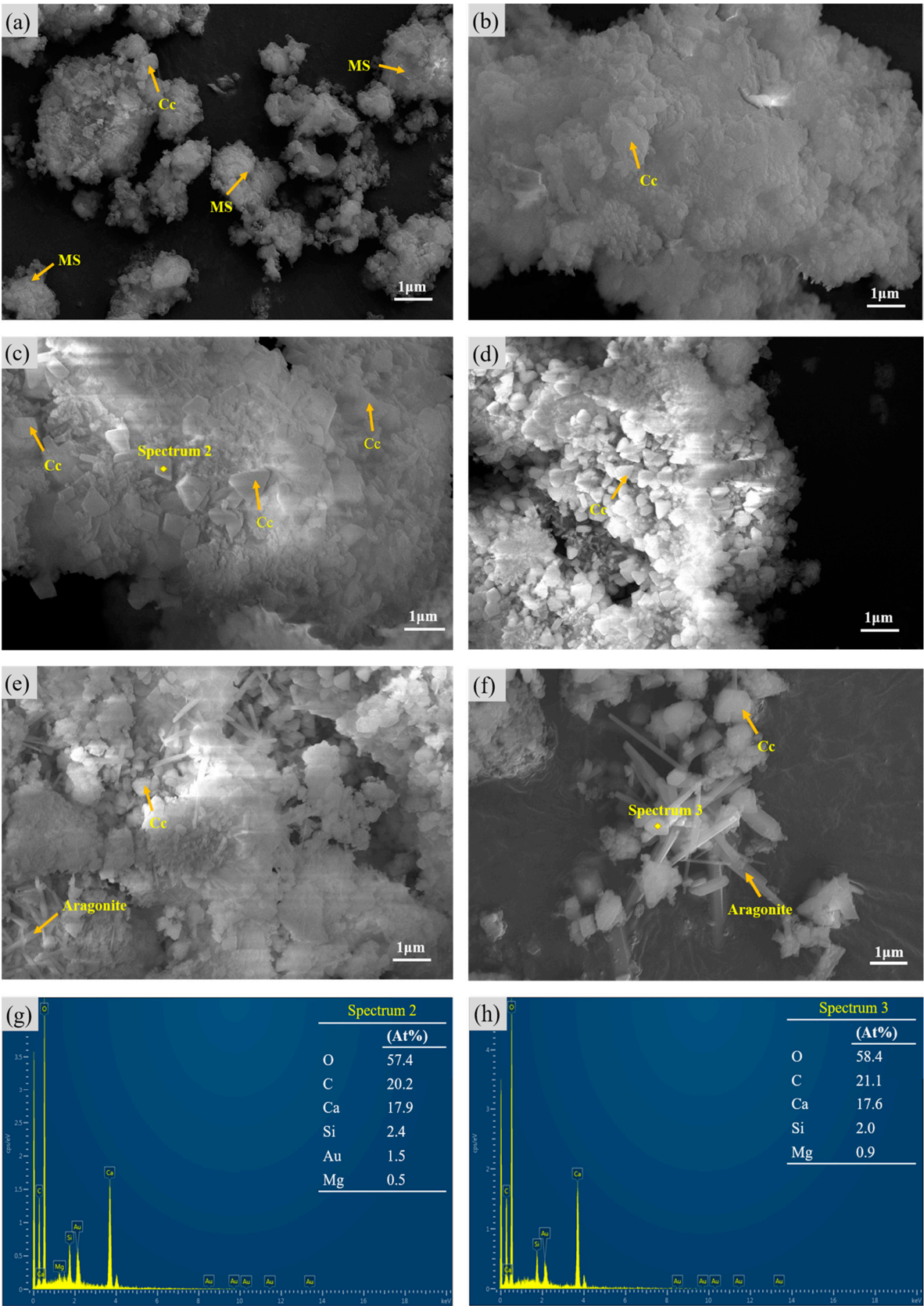


Figure 11. SEM and EDS images of MS with different carbonation duration: (a) 5 min; (b) 10 min; (c) 30 min; (d) 60 min; (e) 120 min; (f) 480 min; (g) EDS of spectrum 2; (h) EDS of spectrum 3.

3.5. Pore Structure Evolution of MS

The pore structure of MS was tested using the BET method, as shown in Figure 12. According to the IUPAC nomenclature, all isotherms can be identified as type 2 isotherms [61]. It can be observed from Figure 12a that the isotherm starts to change when the carbonation is at 5 min. From the above results, it can be seen that the absorbed nitrogen content increases with the continuation of the carbonation reaction when the relative pressure is in the range of 0.7–1. Along with the continuous carbonation reaction, the nitrogen uptake of the samples after the carbonation time of more than one hour increased rapidly at the relative pressures of 0.45 to 1.0, and the relative pressure range also gradually expanded. This phenomenon was also consistent with the pore size distribution in Figure 12b.

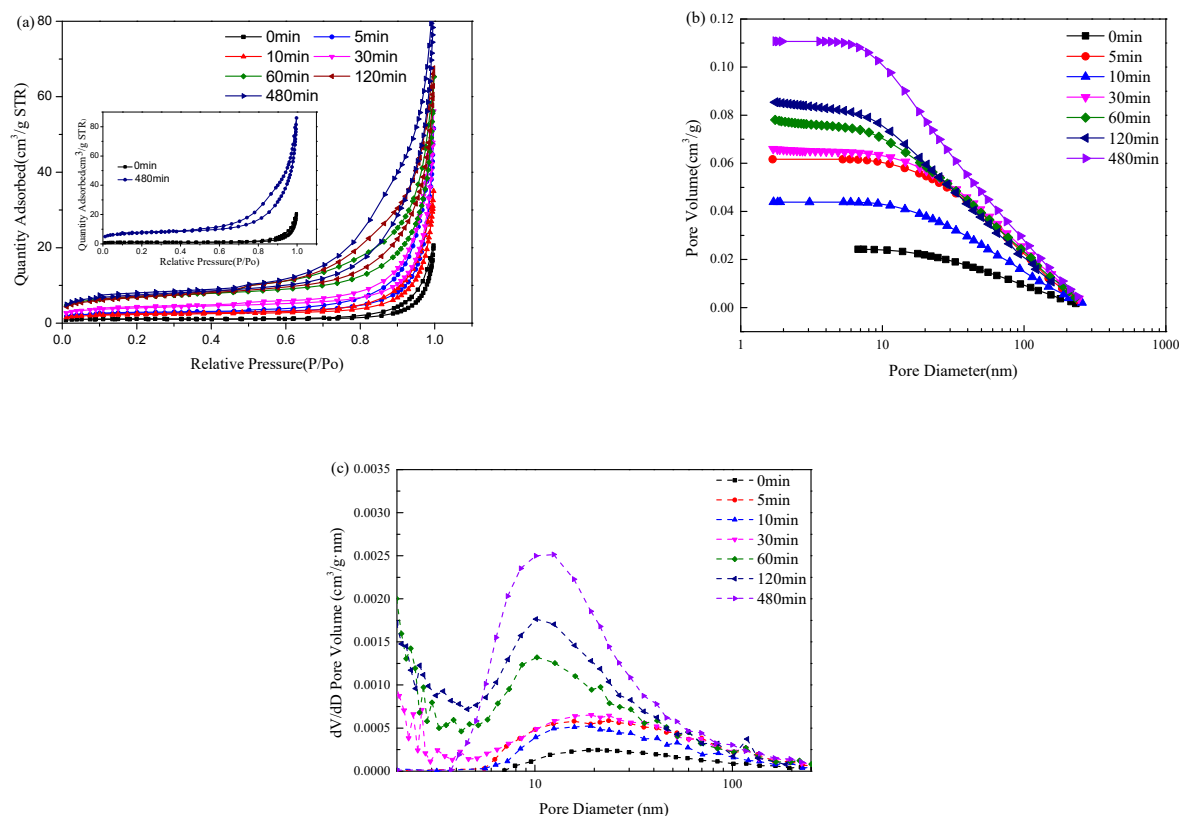


Figure 12. BET results of MS with different carbonation duration: (a) N₂ adsorption and desorption isotherm, (b) pore volume, (c) pore diameter.

From the results in Figure 12b, it can be found that the pores smaller than 10 nm are increasing, indicating that finer particles were formed during the carbonation process. From the FTIR results, it was discovered that the silica gel began to polymerize only when the carbonation period reached 30 min, and the number of gel holes kept rising as the carbonation time increased. From the results in Figure 12c, the proportion of pore structures from 5 to 10 nm increases considerably. This result indicates that the pore size of C-MS gradually decreases with the continuation of the carbonation reaction.

Table 3 shows the BET results. This result shows the increasing trend of the pore volume and specific surface area of the sample along with the continuation of the carbonation reaction. The C₂S minerals contained in the MS continued to dissolve and decalcify as the carbonation reaction proceeded to 120 min. This severely disrupted the initial structure of the MS, resulting in an increase in the cumulative pore volume from the initial 0.024245 to 0.085418 cm³/g. The surface area rose to 24.5005 m²/g when the carbonation time reached 480 min from 0 min, which indicated that the MS particles after the carbonation reaction had a high surface area and small particle size.

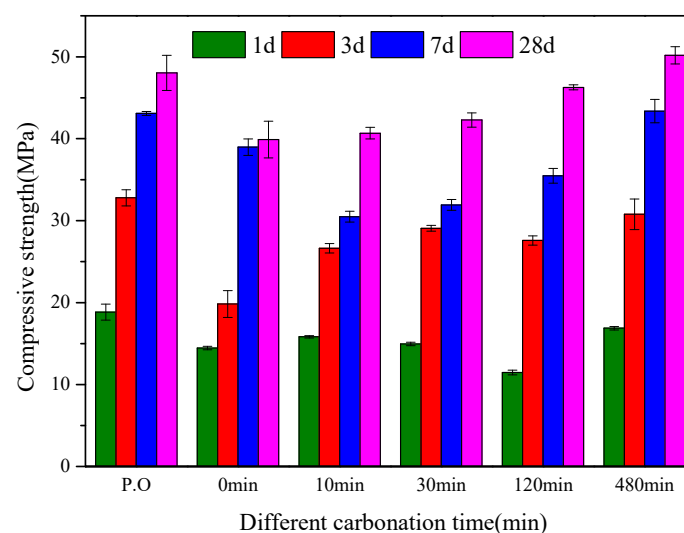
Table 3. The BET results of carbonated MS.

Carbonation Time	Surface Area ^a (m ² /g)	Pore Volume ^b (cm ³ /g)
0 min	3.5305	0.024245
5 min	8.4097	0.061703
10 min	7.3247	0.043953
30 min	13.1911	0.066004
60 min	22.7523	0.078075
120 min	22.8674	0.085418
480 min	24.5005	0.110765

^a BET surface area. ^b BJH adsorption cumulative pore volume of pores between 1.7000 and 300.0000 nm diameter.

3.6. Feasibility of Using Carbonated MS as Mineral Admixtures

Figure 13 shows the effect of C-MS with different carbonation duration on the compressive strength of cement paste. The results show that when the curing age was 1 d and 3 d, the compressive strength of the specimens with 30% MS was only 76.75% and 60.48% of the control group. Unlike the blocks using C-MS as the mineral admixture, the compressive strength at 1d and 3d showed an overall increasing trend with increasing carbonation time. When the curing time was 7 d, the compressive strength of the blocks increased significantly with the increase in carbonation time. When the carbonation time of MS was 480 min, the compressive strength of the blocks could almost reach the same effect as the control group and tended to exceed the strength effect of the control group, and this phenomenon was reflected in all curing ages. After the curing time reached 28 d, the compressive strength of the blocks showed an overall increasing trend. The block strength could reach 96.32% of the control group when the carbonation time of MS reached 120 min. However, the compressive strength reached its highest at a carbonation time of 480 min, with an increase of 4.45% compared to the control group. The compressive strengths of the cement paste with 30% C-MS were 43.38 and 50.18 MPa at 7 and 28 days, respectively, which were 11.3 and 25.8% higher than those of the cement paste with 30% MS. This result illustrates the great potential of MS after wet carbonation for highly reactive mineral admixtures.

**Figure 13.** Effect of C-MS with different carbonation duration on the compressive strength of cement paste.

3.7. CO₂ Uptake

The current methods of producing low-carbon concrete products are mainly classified as direct emission reduction, indirect emission reduction, and CO₂ mineral carbonation. However, accelerated carbonation using CO₂ is considered to be one of the most promising approaches to reducing CO₂ emissions and achieving low-carbon strategies. The CO₂

uptake during the carbonation of MS was further calculated from the TG curve, as shown in Equations (2) and (3).

$$CO_2 = M_{500^{\circ}C} - M_{800^{\circ}C} \quad (2)$$

$$CO_2 \text{ uptake} = CO_2 \text{ after} - CO_2 \text{ before} \quad (3)$$

where CO_2 is the mass loss of CO_2 in the samples. $M_{500^{\circ}C}$ is the mass loss at $500^{\circ}C$. $M_{800^{\circ}C}$ is the mass loss at $800^{\circ}C$. CO_2 uptake is the CO_2 sequestration rate during carbonation. CO_2 after is the mass loss of CO_2 in the samples after wet carbonation. CO_2 before is the mass loss of CO_2 in the samples due to the air carbonation.

The CO_2 capture storage (CCS) shown in the TG results was $22.14 \text{ g } CO_2/100 \text{ g MS}$. This result shows that the wet carbonation method not only enables the reuse of solid waste MS but also reduces CO_2 emissions by sequestering CO_2 . In addition, the carbonated products of the MS can be used as building materials. It can not only solve the saturation problem of mineral admixtures applications but also solve the current environmental pollution problem of MS.

4. Conclusions

In this work, the reaction process of MS in wet carbonation was investigated, and the main carbonation products of MS and the phase assemblage under different reaction stages were analyzed and studied. The effect of C-MS with different carbonation duration on the compressive strength of cement paste was compared. Some conclusions were summarized as follows:

- (1) The process of the carbonation reaction of MS in pure water occurs very rapidly. Within the first 30 min of carbonation, about 50% of Cc has been formed. The morphological changes were closely related to the pH evolution of the suspension.
- (2) The carbonation pretreatment of MS generated a large amount of Cc, including calcite and aragonite, and SiO_2 gel with a high degree of polymerization, which improved the compressive strength of the cement paste containing C-MS mineral admixtures.
- (3) The compressive strengths of the cement paste with 30% C-MS were 43.38 and 50.18 MPa at 7 and 28 days, respectively, which were 11.3 and 25.8% higher than those of the cement paste with 30% MS.

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