- Technical Paper -

PROPOSAL OF MISTING TECHNIQUE TO PROMOTE THE CARBONATION OF HARDENED CEMENT PASTE

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ABSTRACT

This study utilized the principle that wet-dry cycles promote carbonation and proposed a method to enhance the carbonation of hardened cement paste powder (0.6-1.18 mm) with a w/c ratio of 0.6 at ambient temperature and humidity by applying the misting technique. The results indicated that longer misting durations and shorter misting intervals led to higher carbonation, with the highest carbonation of 55% observed in mist30s after 28 days, which was 20% higher than in RH60. Additionally, $Ca(OH)_2$ was fully carbonated by misting, while 87% was consumed under RH60 after 28 days.

Keywords: CO_2 absorption, waste concrete, carbonation, technique, hardened cement paste

1. INTRODUCTION

Concrete serves as an essential material for a wide range of engineering and architectural applications owing to its remarkable durability, structural capabilities, and relatively low cost than other materials. As one of the key raw materials in concrete, cement consumption has been increasing steadily around the world. However, cement production involves the high-temperature calcination of clinker, which consumes significant energy and releases large amounts of CO_2. According to statistics, CO_2 emissions from cement production accounted for 8% of global total emissions [1], aggravating the greenhouse effect. To alleviate this situation and keep it in line with environmental goals, the use of the carbonation process of waste concrete to absorb CO_2 has become a popular topic. The carbonation process can be described in the Eq. (1)-(5) [2], primarily involving the carbonation of calcium-bearing phases in the concrete, allowing CO_2 to be converted into stable $CaCO_3$ and be stored for a long period.

$$Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O \quad (1)$$

$$3CaO \cdot 2SiO_2 \cdot 3H_2O + CO_2 \rightarrow 3CaCO_3 \cdot 2SiO_2 \cdot 3H_2O \quad (2)$$

$$3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 32H_2O + 3CO_2 \rightarrow CaCO_3 + 3CaSO_4 \cdot 2H_2O + 2Al(OH)_3 + 9H_2O \quad (3)$$

$$3CaO \cdot SiO_2 + 3CO_2 + nH_2O \rightarrow SiO_2 \cdot nH_2O + 3CaCO_3 \quad (4)$$

$$3CaO \cdot SiO_2 + 2CO_2 + nH_2O \rightarrow SiO_2 \cdot nH_2O + 2CaCO_3 \quad (5)$$

Among the various factors influencing carbonation, moisture is particularly crucial as it serves as a solvent for calcium and carbonate ions. Xu et al. report that carbonation occurs most rapidly in environments with a constant humidity of 50%-70% after 28 days of carbonation for a w/c ratio of 0.6 and CO_2 concentration of 20% [3]. Our previous study suggests that wet-dry cycles promote carbonation more effectively than maintaining constant humidity, particularly under wet-dry cycles of RH40-100 at a high w/c ratio of 0.6. [4]. Additionally, Oh et al. propose a new wet-dry cycle by periodically dripping water onto the samples and found that the carbonation after 7 days was twice as high in the dripping method compared to that at RH 85%, demonstrating the acceleration effect of the dripping technique on carbonation, which is attributed to the formation of macrocracks and the reorganization of C-S-H sheets. [5].

Therefore, accelerated carbonation under wet-dry cycles is a promising method for CO_2 absorption. This study proposes a new wet-dry cycling method: wetting the samples by misting. The misting process ensures that moisture is more evenly distributed throughout the sample in the wetting process, preventing clogging in certain areas and thereby promoting carbonation more effectively. The effects of misting duration and frequency on carbonation are investigated in this experiment. The carbonation degree and post-carbonation composition of the samples are analyzed using TGA and FTIR.

2. MATERIALS AND METHODS

2.1 Sample preparation

In this study, hardened cement paste powders (HCPWs) were manufactured using Ordinary Portland Cement with w/c ratios of 0.6. The cement paste was remixed every hour until bleeding and segregation were minimized. Subsequently, these specimens underwent

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sealed curing for over 3 months at 20℃. Following the curing process, the hardened cement pastes were pulverized using a ball mill to achieve particle sizes ranging from 0.6 to 1.18 mm.

2.2 Experimental conditions

The misting experimental setup is shown in Fig. 1. In its upper part there was a mesh where the experimental samples could be placed. The lower part was fitted with a misting device, and it was connected with a timer. When the designated time was reached, the device started to mist the sample. The experimental ambient temperature and relative humidity were 20°C, 60%, and the CO_2 concentration was 400-500ppm. There are 3 duration and 2 intervals for misting. The experiment conditions are shown in Table 1.

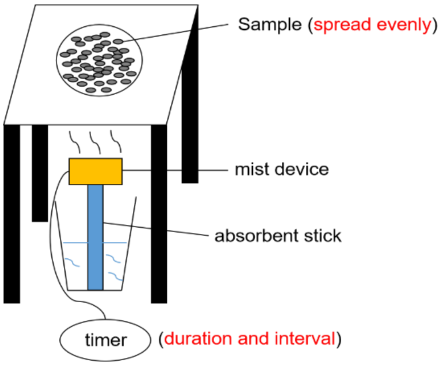

Fig.1 Misting experimental setup

Table 1 Experiment conditions

W/C ratio	0.6
Temperature and Relative humidity	20°C, 60 % RH
Misting solution	Distilled water
Misting interval	12-hour interval, 24-hour interval
Misting duration	10s, 20s, 30s
Period	1d, 3d, 7d, 14d, 28d
CO_2 concentration	400-500 ppm (air environment)

2.3 Analyze methods

(1) Thermogravimetric analysis (TGA)

In this study, after a carbonation process for 1, 3, 7, 14, and 28 days, the carbonated HCPWs were dried in a vacuum desiccator at 30°C for at least 3 days. The amounts of absorbed CO_2 and the $Ca(OH)_2$ ratio were determined through TGA conducted under a nitrogen (N_2) atmosphere. TGA measurements were performed over a temperature range from 20°C to 950°C with a heating rate of 10°C/min, during which the temperature was held at 105°C for 30 minutes for drying and at 950°C for one hour to dehydrate C-S-H.

(2) Fourier transform Infrared spectroscopy (FTIR)

The FTIR spectra of all samples were acquired using an FT/IR 4700 instrument (JASCO). The spectra spanned the range of 4000 to 650 cm^{-1}, with a resolution of 4 cm^{-1}, and each spectrum was generated from 32 scans. The data were recorded in % Transmission.

3. RESULTS

3.1 TGA results

The TGA results from 1 day to 28 days are shown in Fig. 2. According to Fig. 2a, after one day of carbonation, the $Ca(OH)_2$ peaks for all samples had little difference, showing similar carbonation at this stage. It formed in a low-temperature range for calcite peaks of 660-680 °C. After 3 days of carbonation (Fig. 2b), carbonation under mist30s was higher than others, particularly for mist30s_12h, while it was lowest under mist10s_12h and mist20s_12h. Metastable $CaCO_3$ (vaterite or aragonite, which has occurred mass loss at around 500-650 °C) was formed at this stage, including in mist10s_12h and mist20s_12h, though in very small amounts. Additionally, the calcite peaks moved to higher temperatures, but there were two ranges for 3 days: 705 °C for mist10s_12h, mist20s_12h, and mist10s_24h; 730 °C for mist30s_12h, mist20s_24h, and mist30s_24h. When samples were carbonated for 7 days (Fig. 2c), compared to 1 day and 3 days, the $Ca(OH)_2$ peaks almost disappeared under mist30s_12h, mist20s_24h, mist30s_24h and had a large decrease for the rest of the samples of mist10s_12h, mist20s_12h, and mist10s_24h, showing the significant carbonation at this stage. In addition, metastable $CaCO_3$ was formed in all samples. The calcite peaks continuously shifted to higher temperatures of 735-740 °C. The results of 14 days of carbonation were shown in Fig. 2d, similar to those of 7 days of carbonation. Due to the progress of carbonation, the $Ca(OH)_2$ peaks of mist10s_12h, mist20s_12h, and mist10s_24h decreased further. At the same time, the calcite peaks moved to around 745-750 °C. After 28 days of carbonation, all samples had no $Ca(OH)_2$ peaks, meaning the complete consumption. And the calcite peaks further moved to 750-755 °C (Fig. 2e).

The degree of carbonation was calculated by Eq. (6)-(9) [6], and the results are shown in Fig. 3.

$$m_{CH,norm} = m_{CH} / m_{950} \times m_{950,cem} \quad (6)$$

$$m_{CC,norm} = m_{CC} / m_{950} \times m_{950,cem} \quad (7)$$

$$DoC_{CH} = (m_{CH0,norm} - m_{CH,norm}) / m_{CH0,norm} \times 100 \quad (8)$$

$$DoC_{HCP} = (m_{CC,norm} \times 56 / 100) / m_{CaO,cem} \times 100 \quad (9)$$

Where, $m_{CH,norm}$ was the amount of $Ca(OH)_2$ per 100 g of cement; m_{CH} was the amount of $Ca(OH)_2$ per 100 g of HCP; $m_{950,cem}$ was the ignited mass of cement at 950°C (0.981 g per 1 g of cement), and m_{950} was the ignited mass of each sample. where DoC_{CH} and DoC_{HCP} were the degrees of carbonation for $Ca(OH)_2$ and HCP, respectively; $m_{CaO,cem}$ was the weight fraction of CaO in cement (65.01% in this study); and $m_{CH0,\ norm}$ was the amount of $Ca(OH)_2$ per 100 g of cement before carbonation.

The DoC results are shown in Fig. 3. Fig. 3a shows the overall carbonation. After one day, all six misting samples had low carbonation (10%—12%), but it was higher than RH60 (8%) and increased significantly until seven days.

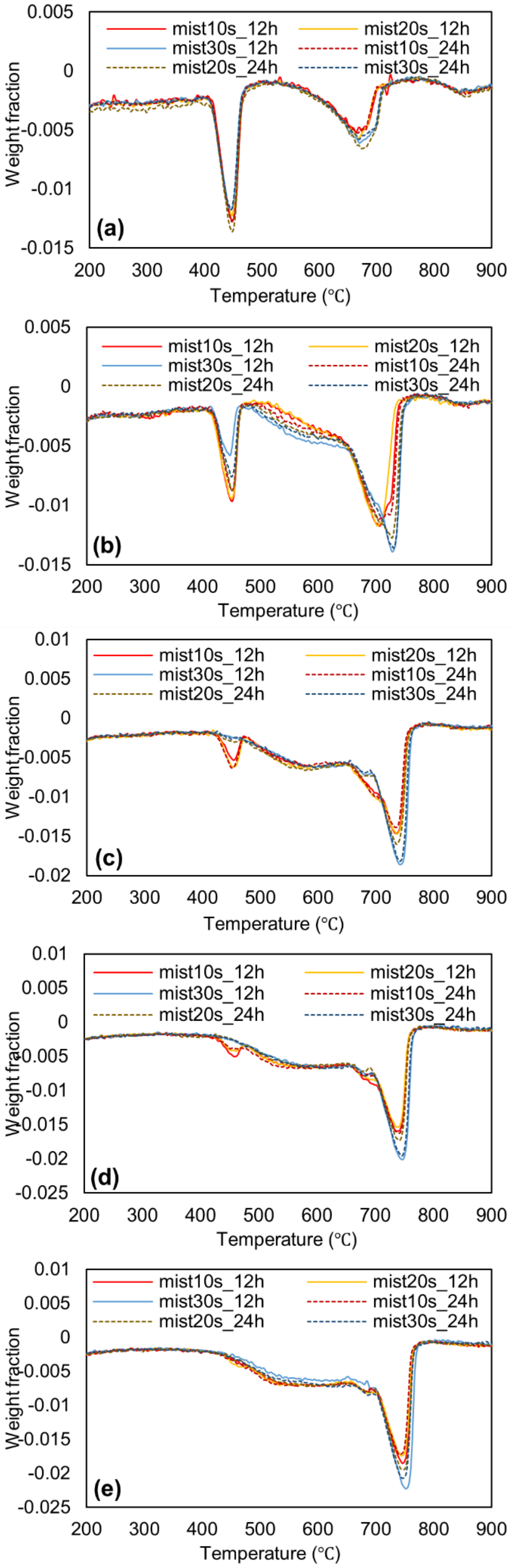

Fig. 2 TGA results for 1, 3, 7,14, and 28 days (a to e)

Thereafter, the increase in carbonation began to level off and reached stability after 28 days of carbonation, at which point most of the samples had more than 50% carbonation in addition to mist10s_24h and RH60. The highest carbonation, approximately 55%, was observed in mist30s_12h, mist30s_24h, and mist20s_24h, about 20% higher than the lowest carbonation of 45% in RH60. Among the samples, mist30s consistently resulted in the highest carbonation, with mist30s_12h showing higher carbonation levels than mist30s_24h throughout the carbonation period. These results highlighted that misting duration and interval were critical factors in controlling moisture levels, directly influencing the carbonation process. Longer misting durations and shorter intervals led to higher carbonation degrees. However, increasing the duration or shortening the interval for HCPWs could not be continuously adjusted, as excessive moisture may saturate samples and clog the pores. While the increase in moisture enhances the dissolution of calcium ions, it hinders CO_2 diffusion, inhibiting carbonation [7].

The carbonation of $Ca(OH)_2$ is shown in Fig. 3b. For constant humidity, the consumption of $Ca(OH)_2$ under RH60 condition was significantly lower than that under misting conditions from 3 days to 28 days. It was observed that $Ca(OH)_2$ was consumed slowly (12% for 3 days) and could not be completely consumed even after 28 days of carbonation (87%). However, for misting conditions, $Ca(OH)_2$ was consumed rapidly, and after 7 days of carbonation, it was completely depleted in mist30s and mist20s_24h. In contrast, 81% of $Ca(OH)_2$ was consumed in mist10s_12h, 90% of $Ca(OH)_2$ was consumed in mist10s_24h, and only 55% was consumed in RH60 at this stage. After 14 days of carbonation, $Ca(OH)_2$ in mist10s_24h was also completely consumed while it remained in mist10s_12h and RH60.

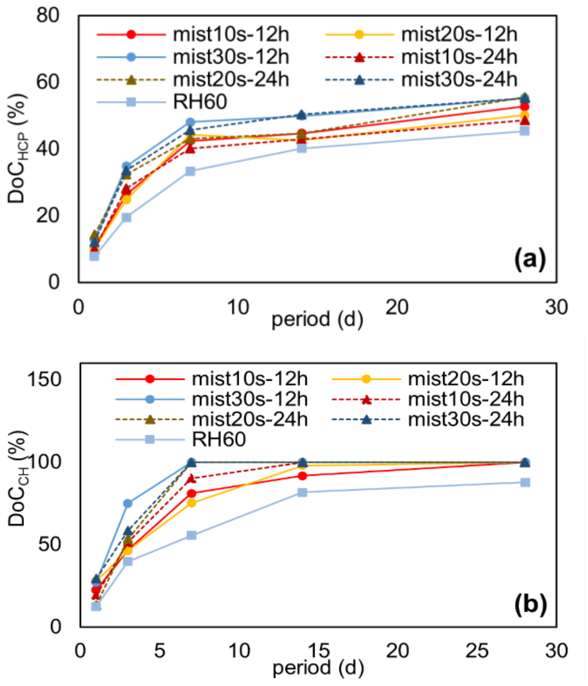

Fig. 3 The degree of carbonation from 1 day to 28 days

3.2 FTIR results

To study the phases of $CaCO_3$ after the carbonation and the decomposition of C-S-H, FTIR was measured. The vibration frequencies of different phases are shown in Table 2, and the results are shown in Fig. 4. After 1 day of carbonation, the TG results in Fig. 3a did not show clear peaks, making it difficult to determine the presence of vaterite. However, the FTIR results in Fig. 4a confirmed the formation of vaterite after 1 day, showing the existence of both calcite and vaterite though at the early stage. And due to the early carbonation, all samples had low carbonation, and the intensity of peaks was at a low level. Based on the bands at 876 cm^{-1} and 1490 cm^{-1}, which correspond to vaterite, and the bands at 713 cm^{-1}, 874 cm^{-1}, and 1420 cm^{-1}, which correspond to calcite, a significant increase in carbonation was observed after 3 days. Fig. 4c to Fig. 4e were the results for 7, 14, and 28 days, the carbonation further increased, and all the peaks were similar to the data for 3 days, showing the co-existence of vaterite and calcite. The initial wavenumber (non-carbonated) for C-S-H was approximately 960 cm^{-1}. However, after 7, 14, and 28 days of carbonation, the C-S-H peaks shifted to a higher wavenumber of 969 cm^{-1}. This shift was attributed to a reduction in the Ca/Si ratio, as calcium was consumed during carbonation [8].

Table 2 Wavenumbers of $CaCO_3$ and C-S-H [9]

Mode	C-S-H	Vaterite	Calcite
Wavenumber (cm^{-1})	960	876, 1490	713, 874, 1420

4. DISSCUSSION

4.1 Carbonation of different calcium-bearing hydrates

Fig. 5 shows the proportion of $CaCO_3$ for each calcium-bearing material after carbonation, which was calculated by Eq. (10)-(11). The consumption of C-S-H could be observed even after 3 days of carbonation for misting and constant humidity conditions. Beyond the overall degree of carbonation, a key distinction between the two carbonation methods was the consumption of $Ca(OH)_2$. Under misting conditions, the carbonation primarily involved $Ca(OH)_2$, which was rapidly consumed and eventually depleted. As the carbonation of $Ca(OH)_2$ progressed and it was gradually consumed, the slower carbonation rates of C-S-H caused it to become the dominant source of carbonation in the later stages. In contrast, under RH60, the carbonation of $Ca(OH)_2$ was higher than that of C-S-H throughout the process, but as mentioned in 3.1, $Ca(OH)_2$ did not be depleted. In addition, it was found that the decalcification of C-S-H in RH60 was higher than that by the misting technique during the later stage (15.2% for 28 days).

$$CC_{CH} = (CH0 - CH) \times 100 / 74 \quad (10)$$

$$CC_{CSH} = CC - CC_{CH} - CC_0 \quad (11)$$

Where, CC_0, CH_0: initial proportion of CC and CH; CC, CH: proportion of CC and CH after carbonation; CC_{CH}, CC_{CSH}: CC from CH and CSH carbonation.

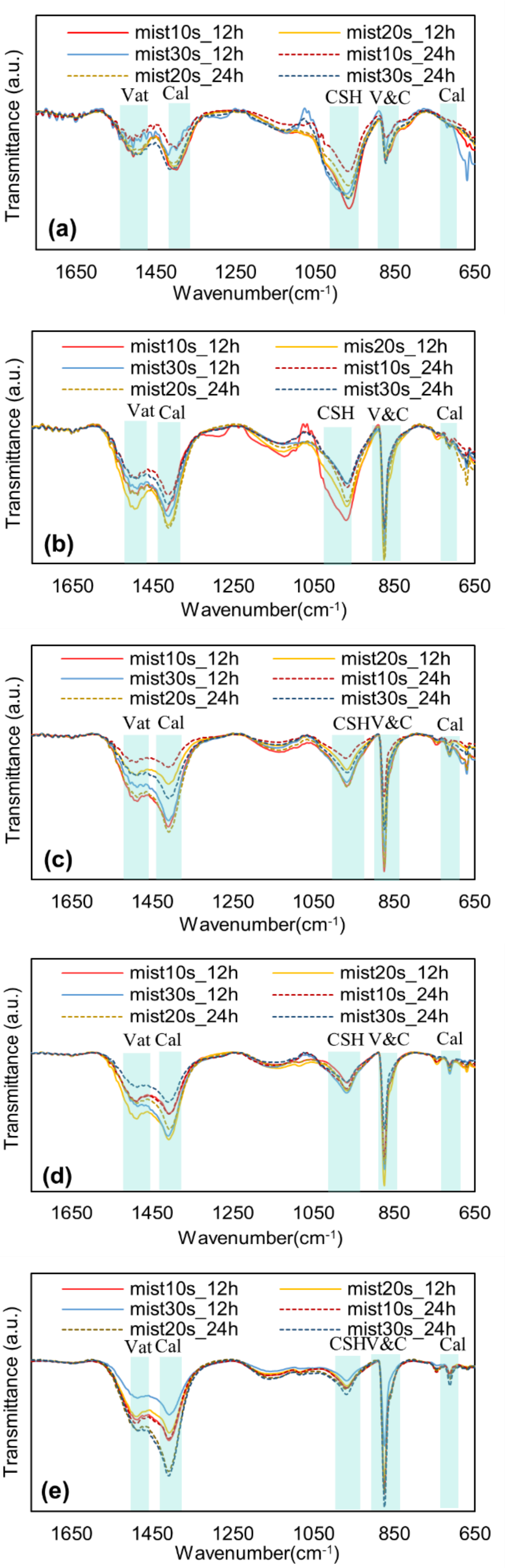

Fig. 4 FTIR results for 1, 3, 7,14, and 28 days (a to e)

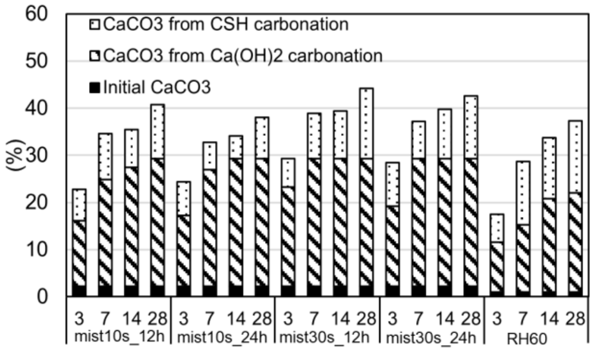

Fig. 5 $CaCO_3$ in HCPWs from the carbonation of calcium-bearing materials

In this study, periodic misting introduced wet-dry cycles during carbonation, notably expected to cause shrinkage, especially in the C–S–H sheets. During the drying phase, the evaporation of pore water leads to substantial changes in capillary tension, driving deformation and shrinkage of the C–S–H sheets [10]. This rearrangement of the C–S–H sheets leads to the formation of numerous capillary pores, facilitating the diffusion of CO_2 and water from the ambient air into the samples. The CO_3^{2-} ions then react with Ca^{2+}, promoting the consumption of $Ca(OH)_2$ and C–S–H, and thereby enhancing the overall carbonation process.

4.2 The potential for reusing carbonated HCPWs.

Dripping technology is a wet-dry cycle carbonation technology similar to misting. When using the dripping technique, the carbonation degree decreases at some point because the calcium carbonate generated on the surface comes off by the dripping solution or might pass through the filter with the solution [5]. On the other hand, the carbonation degree did not decrease with the increase in the number of misting times in the misting technology, so it is thought that the $CaCO_3$ generated by carbonation was precipitated inside or remained on the surface of the particles.

The primary reusable component of waste concrete was the residual cement paste, which contained microcracks and exhibited higher porosity. Incorporating these materials into new concrete would have a detrimental effect on the properties [11]. In this study, the misting technique was utilized to accelerate carbonation, leading to a substantial amount of CO_2 absorption. Furthermore, the carbonation process is expected to significantly reduce porosity by reducing the harmful pore size, due to the $CaCO_3$ generated inside the waste concrete particles. These alterations can provide favorable conditions for the potential reuse of HCPWs for new concrete. According to Jiang's study, when 20% of the fine aggregate was replaced with carbonated HCPWs, the compressive strength of the resulting new concrete was comparable to that of ordinary concrete [12], demonstrating the potential of this method.

5. CONCLUSIONS

(1) The misting technique accelerated the carbonation rate and enhanced the degree of carbonation for HCPWs more than RH60. For overall carbonation, longer misting durations and shorter misting intervals were more effective in accelerating the carbonation process. The highest carbonation was about 55% in mist30s_12h_28d, 20% higher than in RH60.

(2) In addition to overall carbonation, carbonation under misting conditions significantly enhanced the consumption of $Ca(OH)_2$. After 28 days of carbonation, all $Ca(OH)_2$ in misting samples was completely depleted, compared to 87% consumption in RH60.

(3) It is expected that the hardened cement paste particles carbonated by misting technology have $CaCO_3$ precipitated inside or remaining on the particle surface. This may provide favorable conditions for the reuse of HCPW in new concrete.

Currently, the water-cement ratio of concrete in the construction industry is generally between 0.4 and 0.6. In addition, as the particle size increases, the specific surface area decreases, slowing the carbonation rate. Therefore, further research on various particle sizes and w/c ratios is needed to optimize the CO_2 absorption efficiency.

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