- Technical Paper -

THE STUDY ON THE CARBONATION PROMOTION PROCESS OF HARDENED CEMENT PASTE IN THE DRIPPING METHOD

Yaming JIN[*1], Dayoung OH [*2], Ryoma KITAGAKI[*3]

ABSTRACT

Various particle sizes of hardened cement paste powder (HCPW) were carbonated by dripping method to compare with HCPW under a constant relative humidity of 60% or 85%. And measure and analyze the impact of different drip intervals on the carbonation process by TGA, FTIR and SEM-EDS. The results indicate that after 1 day of carbonation, the rate of calcium hydroxide in HCPW with 0.3-0.6mm was less than 5% in the dripping samples, around 13% at RH60, and around 8% at RH85. After 28 days, the CO2 absorption of 0.15-0.3mm increased by 71%, 33% compared to RH60, RH85, respectively.

Keywords: CO_2 absorption, hardened cement paste powder, carbonation, particle size, dripping method

1. INTRODUCTION

The absorption of carbon dioxide (CO_2) has always been an important research topic in the field of building materials. In the past, a lot of research has been devoted to studying effects of carbonation on the durability of reinforced concrete [1]. However, people are now concerned about the substantial carbon sink represented by carbonation. According to Xi, F. et al., from 1930 to 2013, approximately 4.5 GtC of CO_2 was estimated to be reabsorbed by the carbonation of cement materials, which offset 43% of carbon dioxide emissions from the production of cement over the same period, not including emissions associated with fossil use during cement production [2]. Because concrete contains calcium hydroxide ($Ca(OH)_2$) and calcium silicate hydrate (C-S-H), which can absorb CO_2, research is being conducted on methods to absorb CO_2 using waste concrete [3,4].

In this study, to reabsorb as much CO_2 as possible, by dripping water to the HCPW to promote the dissolution of calcium and carbonate ions, and precipitation of calcium carbonate was induced through drying. This study focuses on determining the effect of particle size and dripping interval on the carbonation degree of HCPW. The carbonation progress of HCPW was investigated with Thermogravimetric analysis (TGA), Fourier transform Infrared spectroscopy (FTIR) and Scanning Electron Microscope- Energy Dispersive Spectroscopy (SEM-EDS).

2. MATERIALS AND METHODS

2.1 Raw materials and sample preparation

The cement the Japan Cement Association provided for cement paste with water-to-cement ratio of 0.6 are used. The cement paste was sealed curing for more than 6 months at 20°C.The hardened cement paste was crushed by a ball mill and sieved into two sizes, ranging from 0.15 to 0.3 mm and 0.3 to 0.6 mm. The chemical oxide composition of cement is shown in Table. 1.

2.2 Experimental methods

(1) Dripping method

Place HCPW with particle sizes of 0.15-0.3mm and 0.3-0.6mm respectively on the filter, and drip water continuously for 30 seconds every 12 hours (Drip12) or 24 hours (Drip24) on HCPW. The amount of each sample is 1.5g and the amount of dripping water is 3.5g. Additionally, to compare the degree of carbonation, place HCPW on the tray at a constant relative humidity of 60% (RH60) or 85% (RH85). This process was carried out at room temperature of 20°C, room humidity of 60% and CO_2 concentration of 0.04~0.05%.

(2) Thermogravimetric analysis

The amount of CO_2 absorption of HCPW was analyzed using thermogravimetric analysis (TGA). TGA was conducted after carbonation for 1, 3, 7, 14, and 28 days under each condition. TGA was performed with NEXTA STA200 under nitrogen atmosphere from 20°C

Table 1 Chemical composition of cement (wt%)

	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	Na_2O	K_2O	TiO_2	ig loss
Cement	21.41	4.84	3.20	65.01	1.08	2.02	0.33	0.43	0.24	0.97

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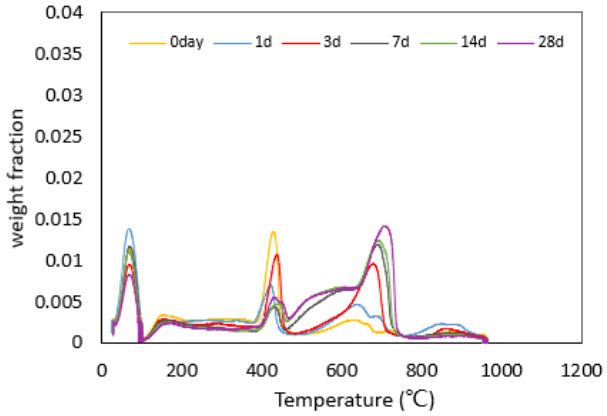
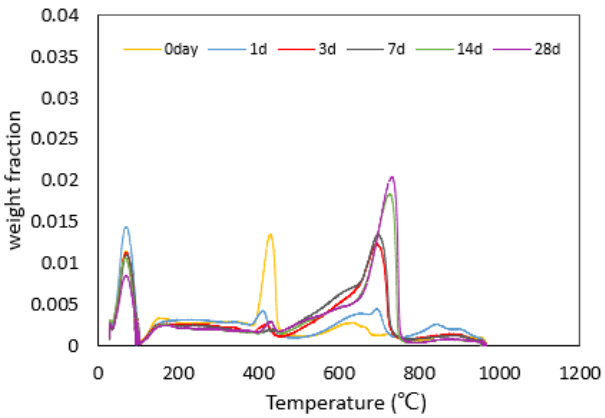
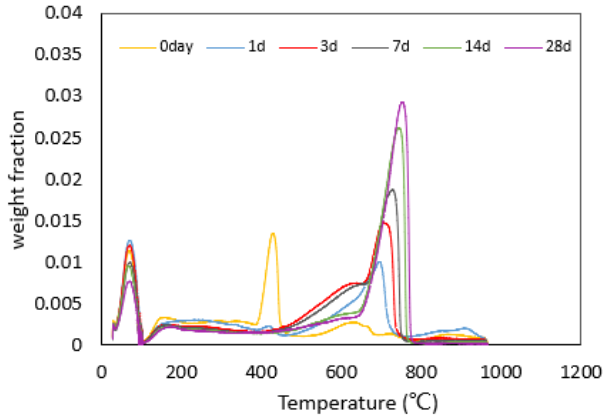


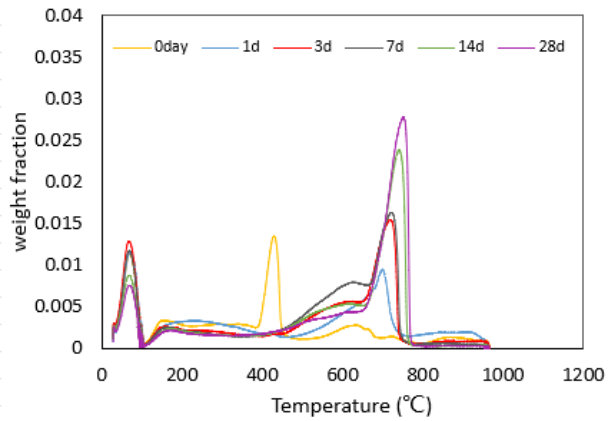
(a) RH60_0.3-0.6



(b) RH85_0.3-0.6

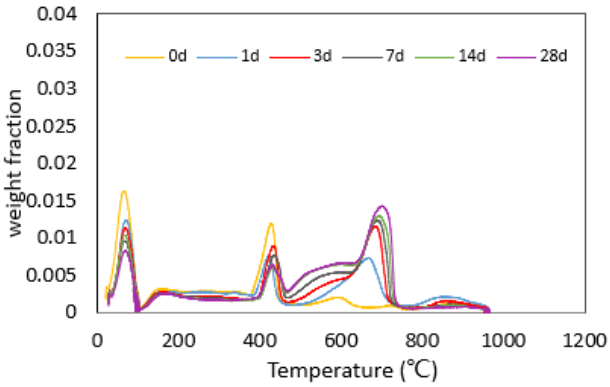


(c) Drip12_0.3-0.6

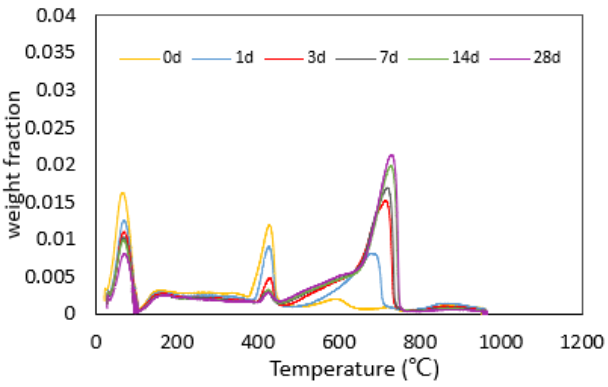


(d) Drip24_0.3-0.6

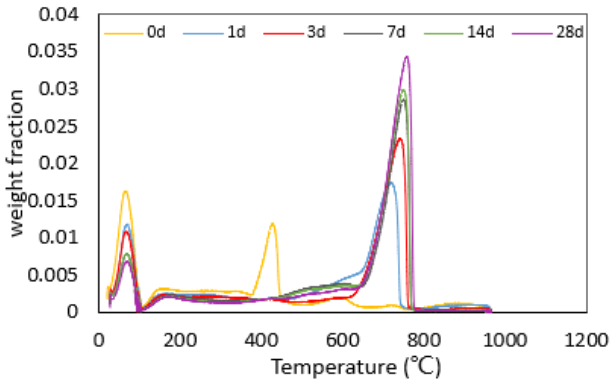
Fig.1 The results of TGA (0.3-0.6mm)



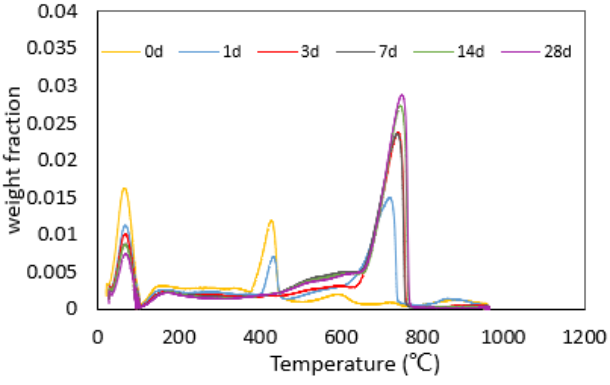
(a) RH60_0.15-0.3



(b) RH85_0.15-0.3



(c) Drip12_0.15-0.3



(d) Drip24_0.15-0.3

Fig.2 The results of TGA (0.15-0.3mm)

to 950°C. The heating rate was 10°C/min, and approximately 15 mg of each sample was analyzed. The amount of Ca $(OH)_2$ was quantified from the weight loss at around 460 °C using the tangential method [5]; similarly, the CO_2 absorption rate was calculated from the weight loss between 600 and 800 °C.

(3) Fourier transform Infrared spectroscopy (FTIR)

The molecular structures and compositions of HCPW was determined by Infrared spectroscopy. FTIR were collected in a spectral range from 400 to 7800 cm^{-1} and a resolution of 4 cm^{-1} with a FT/IR 4700 (JASCO) spectrometer. The average of 128 scans was taken.

(4) Scanning Electron Microscope- Energy Dispersive Spectroscopy

The elements present in the HCPW and their distribution are identified through Scanning Electron Microscope- Energy Dispersive Spectroscopy (SEM-EDS). SEM-EDS was conducted using the samples carbonated for 7 days under each condition.

3. RESULT

3.1 The results of TGA

The results of TGA shown in Fig. 1 and Fig. 2 represent the graphs of particle sizes 0.3-0.6mm and 0.15-0.3mm under four different conditions. CO_2 absorption rate and rate of $Ca(OH)_2$ are shown in Fig. 3 and Fig. 4 respectively. After 28 days of carbonation, in the case of particle sizes of 0.3-0.6mm, the CO_2 absorption rate was approximately 22% at Drip12, 21% at Drip24, 14% at RH60 and 17% at RH85, and in particle sizes of 0.15-0.3mm, the CO_2 absorption rate is 25% at Drip12, 23% at Drip24, 14% at RH60 and 18% at RH85. In the dripping method, the absorption of CO_2 increased by 71% compared to RH60 and 33% compared to RH85 in particle sizes of 0.15-0.3mm.

Under the same conditions, samples with smaller particle sizes exhibit greater CO_2 absorption than samples with larger particle sizes (see Fig.3). Comparing the CO_2 absorption rate after 3 days of carbonation, HCPW of 0.15-0.3mm absorbed 39%, 31%, 32%, and 33% more CO_2 than HCPW of 0.3-0.6mm at RH60, RH85, Drip12, and Drip24, respectively. This is because the smaller particle size, the greater the specific surface area in contact with atmospheric CO_2.

The data also clearly shows that $Ca(OH)_2$ was almost carbonated after 3 days of carbonation at Drip12 and Drip24 (see Fig.4), and further CO_2 absorption due to the carbonation of C-S-H was observed afterward (see Fig.3).

3.2 The results of FTIR

The FTIR spectra of the uncarbonated HCPW and the samples after 1, 3, 7, 14, 28 days of carbonation are shown in Fig. 5 and Fig. 6. Also, the vibration frequencies of calcium carbonate phases and C-S-H [6] are shown in Fig.5(a).

As carbonation proceeds, calcite and vaterite bands around 875 cm^{-1}, 1420 cm^{-1}, 1490 cm^{-1} gradually increased under all carbonation conditions. Bands observed at 713 cm^{-1}, and 746 cm^{-1} refer to the presence of calcite, and vaterite respectively [6]. These peaks appeared 7 days after carbonation at RH60, whereas in the case of Drip 12, they were observed 1 day after carbonation.

Meanwhile, when C-S-H is decomposed due to carbonation, $CaCO_3$ and SiO_2-gel are generated. In the case of dripping samples, the peak of SiO_2-gel was observed after 7 days of carbonation, regardless of dripping interval and particle size. Likewise, at RH60, as carbonation progressed regardless of particle size, C-S-H was decomposed, and a peak of SiO_2-gel was observed, whereas, at RH85, the peak of SiO_2-gel was almost not observed.

3.3 SEM-EDS images

The SEM-EDS images shown in Fig. 7 and Fig. 8 represent HCPW with particle sizes of 0.3-0.6mm and 0.15-0.3mm. As for particle size of 0.3-0.6mm, calcium ions in RH60 and RH85 are distributed inside the sample. However, in Drip12 and Drip24, calcium ions are distributed on the surface of the samples. And in Drip12 and Drip24, there are many pores inside the sample particularly in Drip12. Similarly, HCPW with particle size of 0.15-0.3mm has the same result.

4. DISCUSSION

As mentioned above, the calcium layer was observed on the surface of samples of Drip12 and Drip24. From the TGA results, it was confirmed that $Ca(OH)_2$

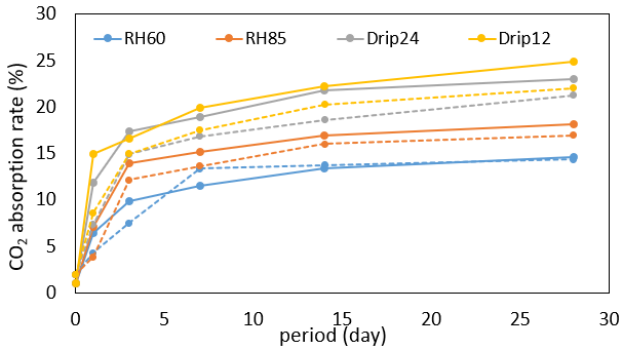


Fig.3 CO_2 absorption rate. Solid line: particle sizes 0.15-0.3mm. Dotted line: particle sizes 0.3-0.6mm

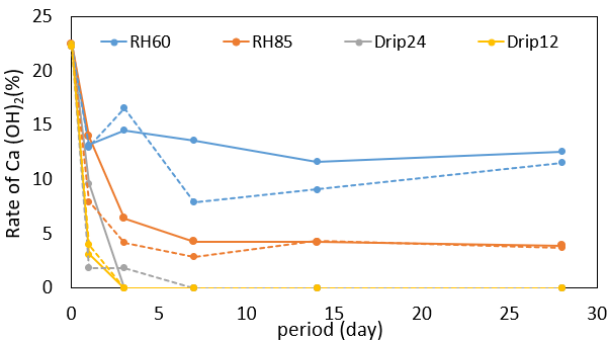
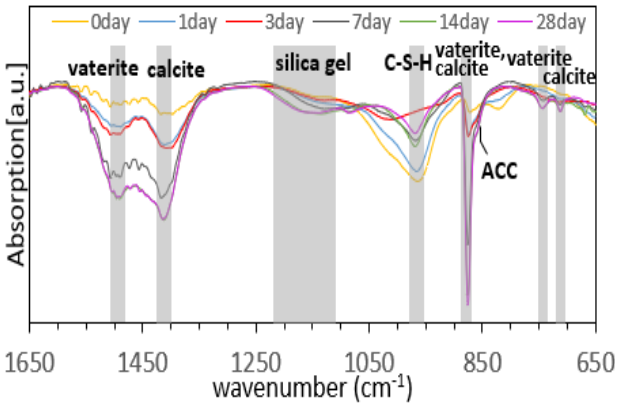
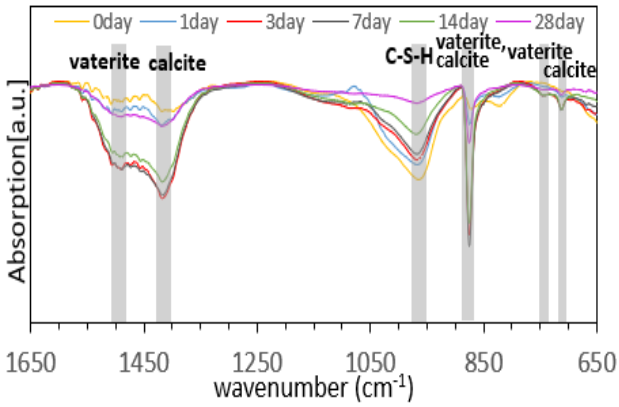


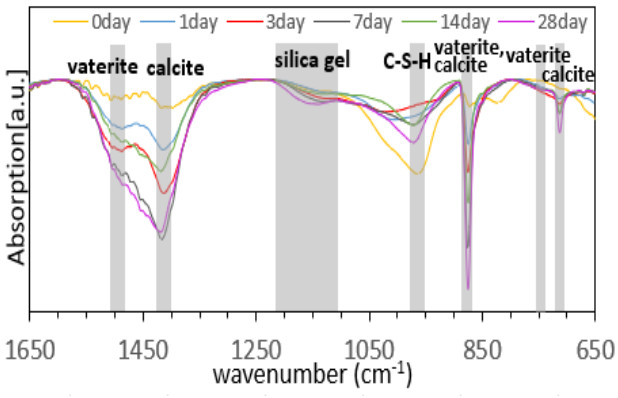
Fig.4 Rate of Ca $(OH)_2$. Solid line: particle sizes 0.15-0.3mm. Dotted line: particle sizes 0.3-0.6mm



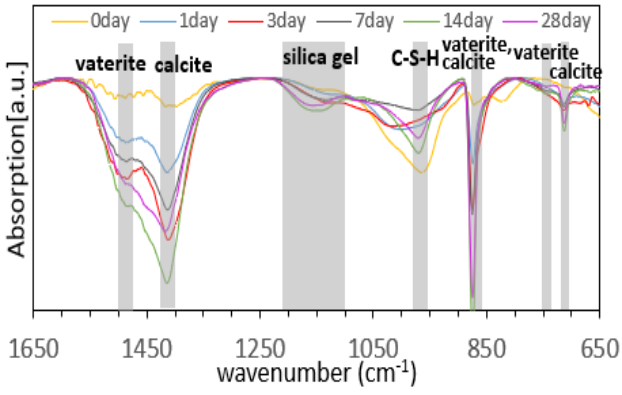
(a) RH60_0.3-0.6



(b) RH85_0.3-0.6

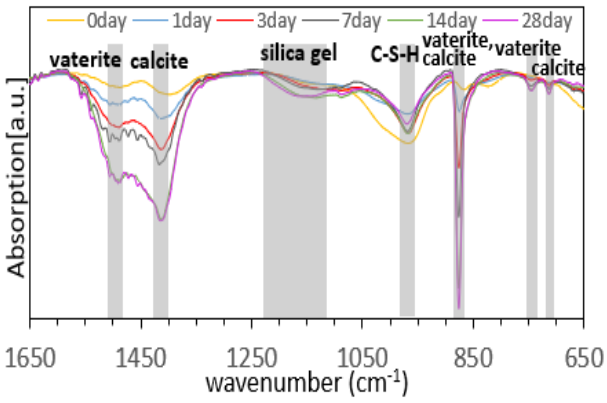


(c) Drip12_0.3-0.6

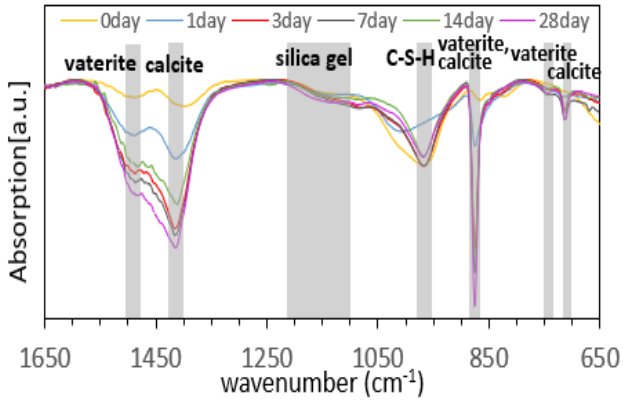


(d) Drip24_0.3-0.6

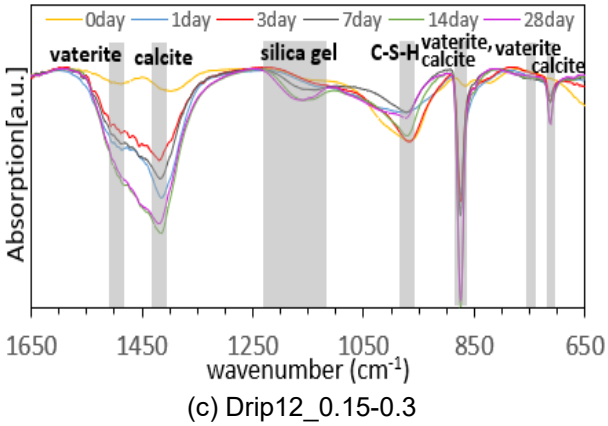
Fig.5 The results of IR (0.3-0.6mm)



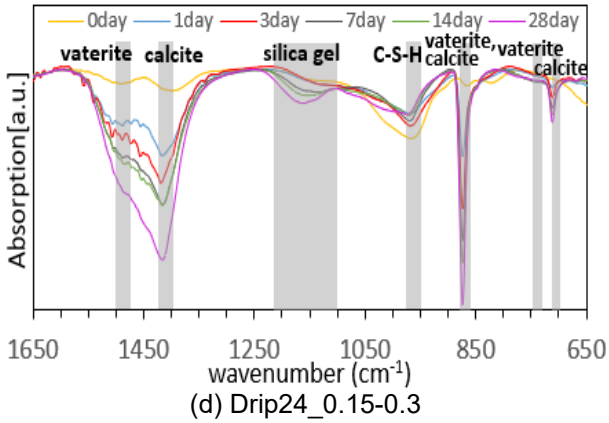
(a) RH60_0.15-0.3



(b) RH85_0.15-0.3

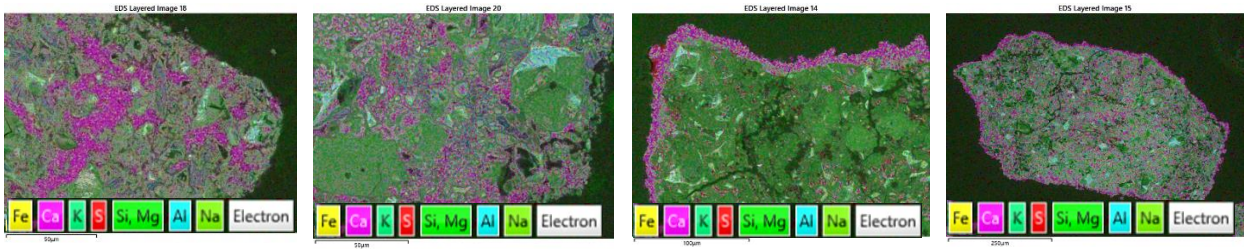


(c) Drip12_0.15-0.3



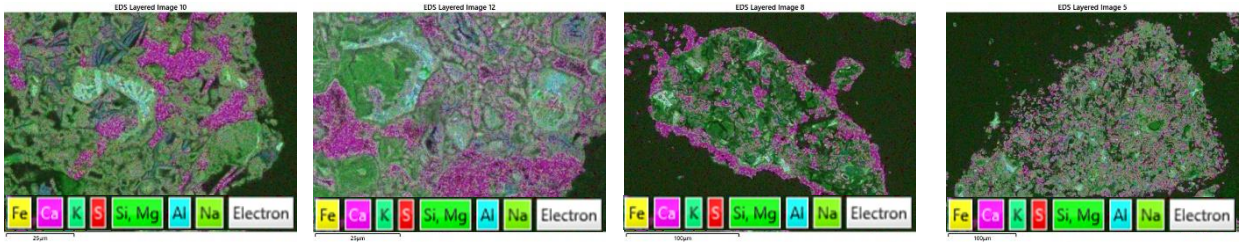
(d) Drip24_0.15-0.3

Fig.6 The results of IR (0.15-0.3mm)



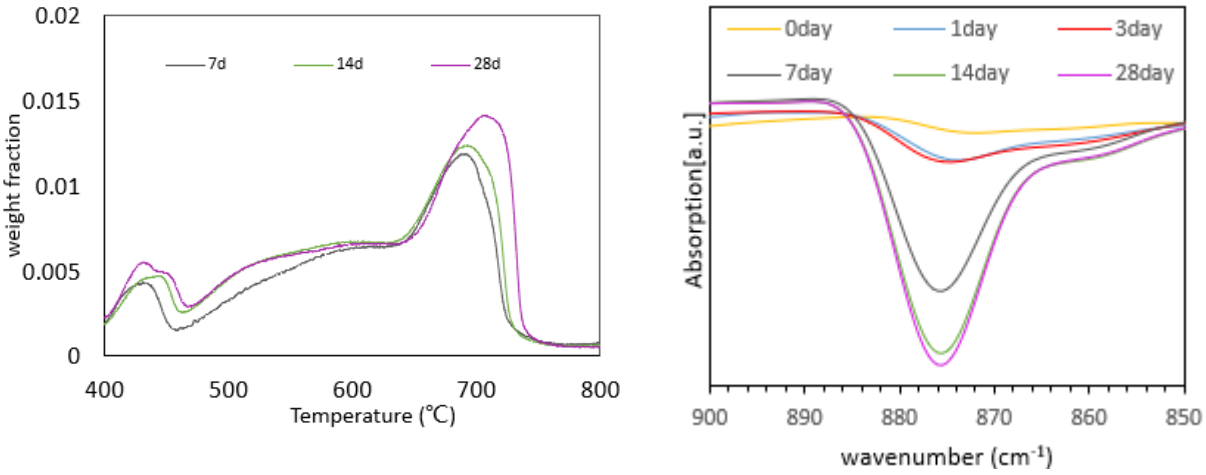
(a) RH60_0.3-0.6_7d (b) RH85_0.3-0.6_7d (c) Drip12_0.3-0.6_7d (d) Drip24_0.3-0.6_7d

Fig.7 SEM-EDS mapping images (After 7 days of carbonation, particle size: 0.3-0.6mm)



(a) RH60_0.15-0.3_7d (b) RH85_0.15-0.3_7d (c) Drip12_0.15-0.3_7d (d) Drip24_0.15-0.3_7d

Fig.8 SEM-EDS mapping images (After 7 days of carbonation, particle size: 0.15-0.3mm)



(a) RH60_0.3-0.6 (b) RH60_0.3-0.6

Fig.9 Part of TGA and FTIR result

was completely decomposed in the dripping sample after 7 days of carbonation, so the calcium layer of the dripping samples was the $CaCO_3$ layer. Unlike RH60 and RH85, as the surface dried, calcium ions released by dripping water reacted with carbonate ions, and $CaCO_3$ was precipitated on the particle surface, which is the liquid/vapour interface.

From the TGA results, it was found that the decomposition speed of $Ca(OH)_2$ in the dripping sample was faster than that of RH60 and RH85. Additionally, from the FTIR results, it can be seen that in the case of the dripping samples, the speed at which C-S-H is decomposed and SiO_2-gel was produced was faster than that of RH85. (The agglomerative SiO_2-gel in the dripping sample can also be observed from the SEM-EDS mapping image.) As a result, it can be seen that the CO_2 absorption speed was prompted, as shown in Fig. 3.

Meanwhile, TGA results showed that the $Ca(OH)_2$ rate increased after 7 days of carbonation at RH60. The reason is that another peak was observed in the decomposition region of $Ca(OH)_2$, which overestimated the amount of $Ca(OH)_2$ (see Fig. 9). From the FTIR results, it was found that the ACC peak was generated at RH60 after 7 days of carbonation. This suggests that the peak at around 450 degrees in the TGA result may be due to ACC.

5. CONCLUSIONS

(1) TGA and FTIR results showed that the decomposition of $Ca(OH)_2$ and C-S-H increased by the dripping method compared to RH60 and RH85. As a result, in samples with a particle size of 0.15-0.3 mm carbonated through the dripping method, CO_2 absorption increased by 71% compared to RH60 and 33% compared to RH85 after 28 days of carbonation.

(2) Under the same conditions, samples with smaller particle sizes absorb more CO_2 than samples with

larger particle sizes because smaller particle sizes have a greater specific surface area in contact with atmospheric CO_2.

(3) As carbonation proceeds, $CaCO_3$ was precipitated on the particle surface, which is the liquid/vapour interface by the dripping method.

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