DIFFERENCE BETWEEN NATURAL AND ACCELERATED CARBONATION OF CONCRETE AT 2 % CO_2 AND 20 % CO_2

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In this study, the effect of CO_2 concentration on carbonation depth, semi-carbonated zone, pore size distribution and carbonation products in concrete were investigated. The CO_2 concentration was increased from 0.035 % to 2 % and 20 % at 70 % relative humidity and 20 °C. The results show that the carbonation process of 2 % CO_2 was more similar to natural carbonation than 20 % CO_2, as evidenced by the better linearity fitness of carbonation depth. The length of semi-carbonated zone was 6 mm at 2 % CO_2 and 8 mm at 20 % CO_2 within 16 weeks, a number that cannot be ignored when predicting the service life of concrete under carbonation. CH remained in a small amount in the completely carbonated zone instead of being completely consumed, and CH consumed at 20 % CO_2 is about 1.5-2.0 times that of 2 % CO_2. The content of $CaCO_3$ in the completely carbonated zone at 20 % CO_2 was higher than that of 2 % CO_2. $CaCO_3$ could fill in large pores between hydration products, so the porosity, average pore size and aperture decreased with CO_2 concentration.

Keywords: Concrete Carbonation; CO_2 Concentration; Carbonation Depth; Semi-carbonated Zone; Carbonation Products

1. Introduction

Concrete carbonation is one of the main factors of concrete reinforcement corrosion, which results in concrete neutralization and destruction of the alkaline protective membrane on the surface of steel [1, 2]. CO_2 is a reactant during concrete carbonation process, so the higher concentration of CO_2, the faster of the carbonation reaction. The amount of CO_2 concentration to be adopted in carbonation and carbonation products remains a controversial issue [3-9]. A concentration of 2 % CO_2 was recommended in the DuraCrete Project Document [10], while that of 20 % CO_2 was recommended by Test Method for Carbonation of Concrete [11]. In general, lower CO_2 concentrations of 1 %- 4 % were recommended in EU countries [12-14], with rare instances of the 20% CO_2 concentration common in China.

Further research is warranted to clarify the differences in concrete carbonation based on the CO_2 concentrations [15]. Castellote [3] and Bernal [16] show that higher CO_2 concentrations result in different carbonation products and lower pH values in concrete. During carbonation, portlandite (CH) is converted to $CaCO_3$ releasing water, and the calcium-silicate-hydrate (C-S-H) is decalcified leading to a phase with a lower Ca/Si-ratio [5, 17].

C-S-H gel may be completely carbonated at 100 % CO_2, and partial ettringite can be carbonated [3, 9]. The equilibrium pH for pore water at any CO_2 concentration is lower than 7; therefore all hydrated cement phases eventually become unstable [17].

Accelerated carbonation experiments at elevated CO_2 concentrations have been carried out to evaluate the carbonation resistance of concrete. This study compares natural and accelerated carbonation at 2 % CO_2 and 20 % CO_2, special attention is given to the change in semi-carbonated zones and quantitatively characterizing carbonation products at different CO_2 concentrations. The results will deepen the understanding of carbonation process and carbonation resistance of concrete.

2. Materials and methods

2.1. Materials and Mix Proportion

The mix proportion of concrete used was shown in Table 1. P·O 42.5 Portland cement was used. The fineness modulus of fine aggregate was 2.8 and the slump of the concrete was 120 mm. Specimens were concrete prisms of dimensions 100×100×400 mm^3. The internal faces of all molds were covered with a thin Teflon film to avoid the de-molding oil. Specimens were de-molded after

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Table 1

The mix proportion of concrete (kg/m^3)

Cement	Water	Fine aggregate	Coarse aggregate (5~10 mm)	Coarse aggregate (10~20 mm)
330	198	719	349	813

casting and curing at 20 °C and 95 % relative humidity (RH) for 1 day. Specimens were dried in the oven for 48 h at 50 °C after curing for 28 days in saturated $Ca(OH)_2$ solution at 20 °C. Two layers of aluminum foil tape were stuck to the surfaces of the dried concrete except for a middle zone of 80×160 mm^2 on a flat side.

2.2. Test methods
2.2.1. Carbonation Experiment
Specimens were placed in carbonation chambers maintained at 20 °C and 70 % RH. Concentrations of 0.035%, 2.0%, and 20.0% CO_2 were employed. The carbonation depth and composition were measured at 2, 4, 8, and 16 weeks of carbonation.

2.2.2. Carbonation Depth
An indicator solution of 1% alcohol phenolphthalein (1 g phenolphthalein dissolved in a mixture of 95% ethanol (80 mL) and distilled water (20 mL)) was sprayed on the fresh fractured surface of specimens. The non-carbonated and semi-carbonated zones turned red, while the completely carbonated zone remained unchanged. The vertical distance from the interface of the two zones to the surface of the concrete is the carbonation depth. Carbonation depth measurement was conducted according to GB/T 50082-2009 [11].

2.2.3. Dynamic Thermal Mechanics Analyzer
DTA/TG (STA449c/3/G Dynamic Thermal Mechanics Analyzer, NETZSCH, Germany) was used for the quantitative analysis of CH and calcium carbonate ($CaCO_3$) at different carbonition depths. The length of the completely and semi-carbonated zones can be obtained from the change in CH and $CaCO_3$ content. Concrete specimens were cut into parallel slices and ground into powder. The first slice was 3 mm in width, and others were 2 mm in width. The experimental conditions were nitrogen atmosphere, 10-15 mg powder samples, 10 °C/min heating rate, and 20-1000 °C temperature range.

2.2.4. X-ray Diffractometer
An X-ray Diffractometer (D8 ADVANCE, German Brooke) was used to analyze the crystal structure of cement paste in carbonated concrete at 4 weeks. The target material is copper. The powder sample was pressed into the glass sheet with grooves and mounted on the sample stage. The scan angle is 5-70 °, minimum step length is 0.0001° and stability is 0.005%.

2.2.5 Mercury Intrusion Porosimetry
Pore size distribution analysis of cement paste in carbonated concrete was conducted using PoreMaster-GT60 (Quantachrome Instruments, USA). The test range of aperture is 0.003-360 μm, the accuracy is 1 % of the maximum pore volume. The maximum test pressure is controlled at 414 MPa, and the test atmosphere is nitrogen.

3. Results and Discussion

3.1. Carbonation depth
Figure 1 shows a linear relationship of carbonation depth between elevated and natural CO_2 concentrations. The carbonation depth increased with carbonation age and CO_2 concentration. In addition, the carbonation process was affected by the CO_2 concentration, and an increase in CO_2 concentration within a certain range can effectively accelerate the carbonation reaction [3, 5].
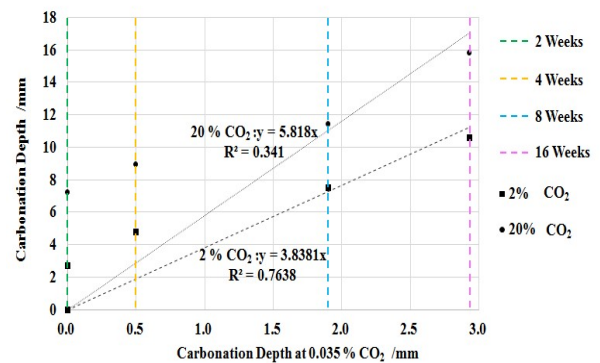

Fig.1 - The functional relation of concrete carbonation depth at different CO_2 concentration.

The correlation coefficients of the linear regression equation of 2 % CO_2 and 20 % CO_2 were 0.7638 and 0.341, respectively. The linearity fitness of 2 % CO_2 was better than 20 % CO_2. This means that the carbonation process of 2 % CO_2 was more similar to natural carbonation than 20 % CO_2. The regression coefficients indicate the accelerating rate of the carbonization reaction; thus, the carbonation rate was faster at 20 % CO_2 than 2 % CO_2. The accelerating rate increased from 3.8381 to 5.818, although the CO_2 concentration of the latter is 10 times that of the former, indicating that the multiple of CO_2 concentration does not respond to the accelerating rate of carbonation.

Table 2 shows the lengths of completely carbonated and semi-carbonated zones of concrete by DTA/TG. The completely carbonated

Table 2

Length of completely carbonated and semi-carbonated zones by DTA/TG

Carbonation age /weeks	Completely carbonated zone length / mm		Semi-carbonated zone length / mm	
	2 % CO$_2$	20 % CO$_2$	2 % CO$_2$	20 % CO$_2$
2	3	7	6	8
4	5	9	6	8
8	7	11	6	8
16	11	17	6	8

zone lengths were consistent with the carbonation depth measured by using 1% phenolphthalein. The length of semi-carbonated zone was 6 mm at 2 % CO$_2$ and 8 mm at 20 % CO$_2$ within 16 weeks, which was increased with CO$_2$ concentration. These results were also observed by Ji [5]. As can be seen, the length of semi-carbonated zone was more than the completely carbonated zone at 2 % CO$_2$ within 4 weeks, accounting for half of the length of completely carbonated zone of 2 % CO$_2$ and 20 % CO$_2$ at 16 weeks.

Non-carbonated concrete has an alkaline pH of about 12.6, the completely carbonated zone has a more neutral pH value of 8.3, and pH values of the semi-carbonated zone range from 8.3 to 12.6 [17]. Therefore, reinforcement begins to rust (pH≤11.5) when the length of the completely carbonated zone is less than the thickness of the protective layer. The length of the completely carbonated zone is currently used to predict the service life of concrete under carbonation. For the safety of concrete structures, the effect of the semi-carbonated zone length on predicting the service life of concrete under carbonation should be considered.

3.2. Composition analyses at different carbonation depth

As shown in Figures 2 and 3, the content of CH and CaCO$_3$ in the carbonated concrete was constant at a certain distance from the surface, corresponding to the completely carbonated zone and non-carbonated zone. The zone between the two zones was the partially carbonated zone, which is called the semi-carbonated zone [5], where the content of CH linearly increased and the content of CaCO$_3$ linearly decreased. CH remained in a small amount in the completely carbonated zone instead of being completely consumed. These were found to be coated with CaCO$_3$, preventing further dissolution [18]. In addition, CH in the completely carbonated zone at 20 % CO$_2$ was obviously lower than 2 % CO$_2$. While CaCO$_3$ in the completely carbonated zone at 20 % CO$_2$ was higher than 2 % CO$_2$, indicating more of the substance was carbonated.

In order to understand the effect of CO$_2$ concentration on carbonatable substances consumed and CaCO$_3$ generated, quantitative analysis of CH and CaCO$_3$ within 29 mm from the surface of concrete was carried out using Eqs. 1-4.
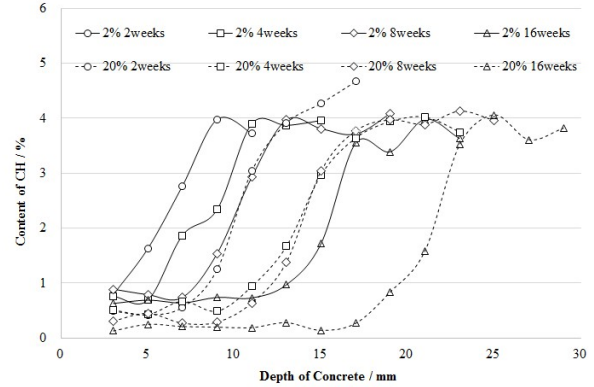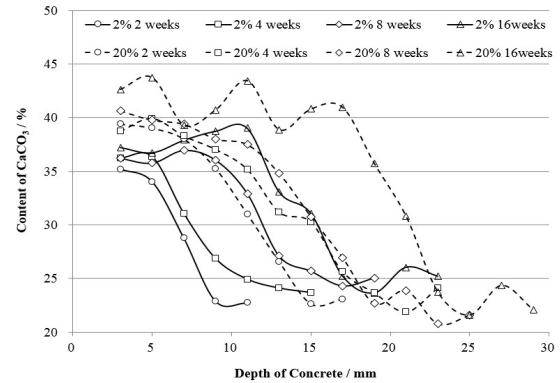

Fig. 2 - CH content of concrete at different depth.

Fig. 3 - CaCO$_3$ content of concrete at different depth.

$$C_{CH,c} = \frac{3}{29}\left(C_{CH,N} - C_{CH,3}\right) + \frac{2}{29}\int_0^{29}\left(C_{CH,N} - C_{CH,x}\right) \tag{1}$$

Where $C_{CH,c}$ is the CH consumed within 29 mm (the maximum carbonation depth tested) from the surface of concrete in %, $C_{CH,N}$ is the CH content in the non-carbonation zone, which is the mean value of the CH content at different carbonation depths within the non-carbonation zone in %, $C_{CH,3}$ is the CH content at 3 mm carbonation depth in %, $C_{CH,x}$ is the CH content at a certain carbonation depth in %, and x (>3) is carbonation depth in mm.

$$C_{Ca,CH} = \frac{100}{74} \times C_{CH,c} \tag{2}$$

Here, $C_{Ca,CH}$ is the CaCO$_3$ generated from CH carbonation in %, 100 is the molar mass of CaCO$_3$, and 74 is the molar mass of CH.
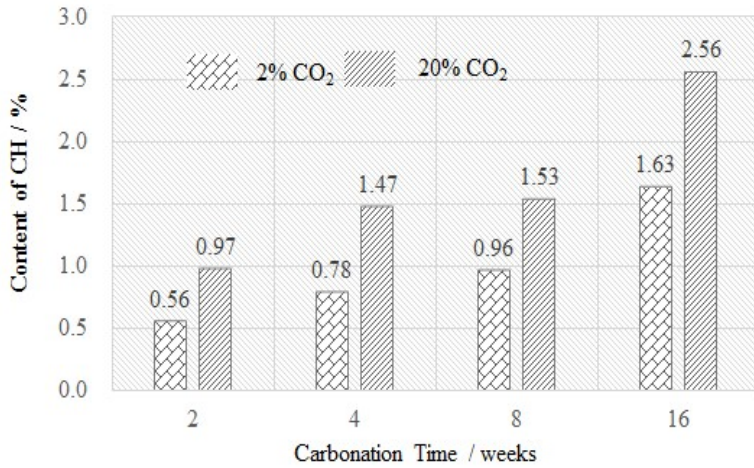
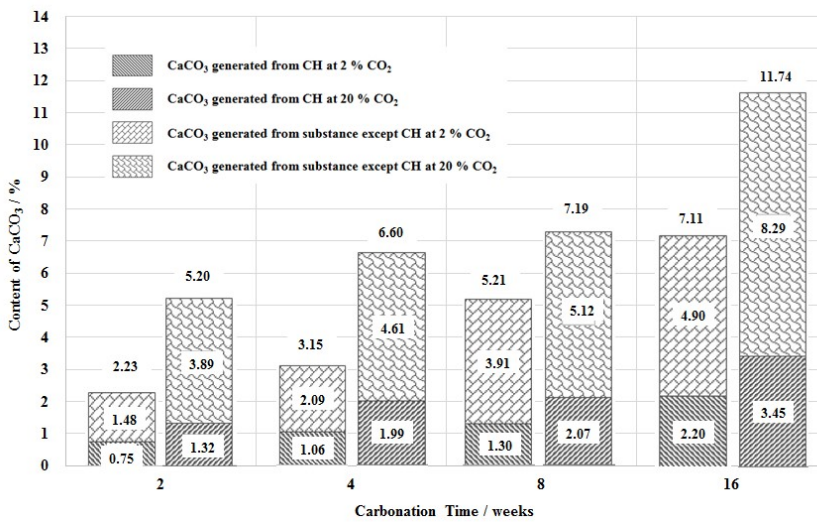Fig. 4 - CH consumed within 29 mm from the surface of concrete.

Fig. 5 - CaCO$_3$ generated within 29 mm from the surface of concrete

$$C_{Ca} = \frac{3}{29}(C_{Ca,3} - C_{Ca,N}) + \frac{2}{29}\int_0^{29}(C_{Ca,x} - C_{Ca,N}) \tag{3}$$

Here, C$_{ca}$ is the CaCO$_3$ content within 29 mm from the surface of concrete in %, C$_{Ca,N}$ is the CaCO$_3$ content of non-carbonation zone, which is the average value of CaCO$_3$ at different carbonation depths within the non-carbonation zone in %, C$_{Ca,3}$ is the CaCO$_3$ content at 3 mm carbonation depth in %, C$_{Ca,x}$ is the CaCO$_3$ content at certain carbonation depths in %, and x (> 3) is carbonation depth in mm.

$$C_{Ca,O} = C_{Ca} - C_{Ca,CH} \tag{4}$$

Here, C$_{Ca,O}$ is the CaCO$_3$ generated from carbonatable substances except CH.

As shown in Figures 4 and 5, the content of CH consumed at 20 % CO$_2$ was about 1.5-2.0 times of 2 % CO$_2$ at the same carbonation time. The content of CaCO$_3$ generated at 20 % CO$_2$ was about 2 times that of 2 % CO$_2$ at 2 weeks and 4 weeks, and 1.5 times at 8 weeks and 16 weeks.

The total CaCO$_3$ generated at a certain CO$_2$ concentration was 3.0 ~ 4.0 times that of CaCO$_3$ generated from CH, indicating that C-S-H and other phases play an important role in concrete carbonation.

3.3. Pore size distribution in carbonated concrete

Table 3 shows the change of pores in concrete. The porosity, average pore size and most probably aperture decreased with CO$_2$ concentration. The effect at 20 % CO$_2$ was more obviously. Fig. 6 shows the pore size distribution of cement paste in carbonated concrete at different CO$_2$ concentrations. The content of pores under 20 nm (harmless to concrete) increased with the CO$_2$ concentration; carbonation has little effect on content of pores between 20-50 nm (less-harmful to concrete) and 50-200 nm (harmful to concrete), the pores which greater than 200 nm (serious harmful to concrete) decreased significantly. Carbonation products CaCO$_3$ could fill in the large pores between hydration products. As can be

seen, carbonation can reduce the porosity of concrete and make the microstructure more compact, resulting in a reduced of CO_2 diffusion rate.
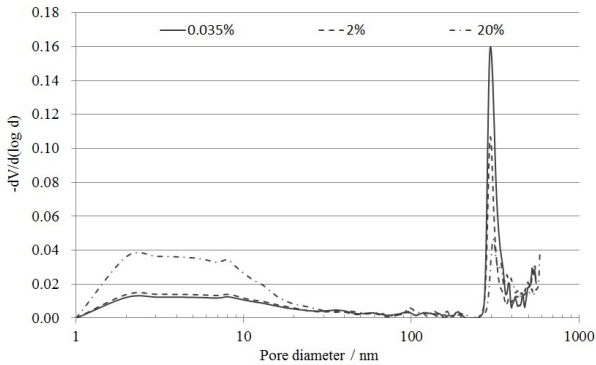

Fig. 6 - Pore size distribution of cement paste in carbonated concrete

3.4. CaCO₃ in carbonated concrete

Figure 7 shows that the crystal of cement paste in carbonated concrete at 0.035 % CO_2 was mainly hydration products CH and non-hydration mineral calcium silicate (C_3S), $CaCO_3$ crystals were not observed. At 2.0 % CO_2 and 20 % CO_2, carbonation products $CaCO_3$ was found to exist in carbonated concrete; the content of CH decreased compared with the carbonated concrete at 0.035 % CO_2, which was in agreement with thermal analysis. The crystal of $CaCO_3$ was mainly calcite and aragonite at 2.0 % CO_2, vaterite was rare. However, $CaCO_3$ was mainly calcite and vaterite of

equal proportions at 20 % CO_2, aragonite was rare. This indicates that the CO_2 concentration affects the crystal structure of the carbonation product $CaCO_3$.

Several studies have shown that carbonation could increase the strength of concrete [19-21]. Carbonation products $CaCO_3$ have a lower specific surface area and poor mechanical properties compared with hydration products C-S-H [21]. Compared with the carbonated concrete at 0.035% CO_2, C_3S content was less at 2.0 % CO_2 and 20 % CO_2; thus, the reduced amount of C_3S may be in a reaction of hydration or carbonation. As we known, carbonation can lead to the pH of concrete solution neutralization, so the concentration of hydroxide ion was reduced. According to the chemical reaction equilibrium equation, the reaction which increased the concentration of hydroxide ion will be promoted. While the reaction of C_3S hydration generates hydroxide ion and C-S-H, so the carbonation could promote the reaction of C_3S hydration, resulting in more C-S-H generation and higher strength, this requires more experiments to demonstrate.

4. Conclusions

The following conclusion can be drawn for the concrete mix and the CO_2 concentration used in this study:

(1) The carbonation process of 2 % CO_2 was more similar to natural carbonation than 20 % CO_2, shown by the better linearity fitness of

Table 3

The pore size distribution in concrete

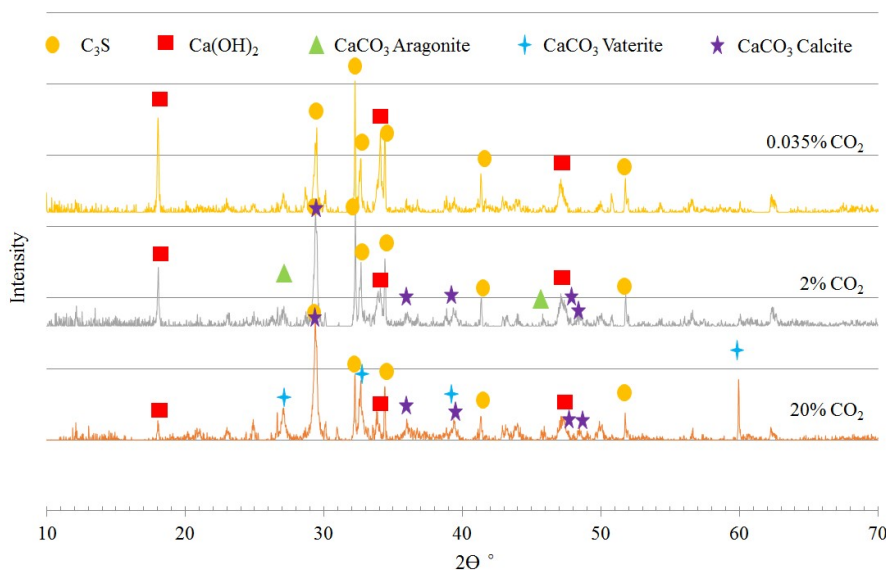| Specimen No .	Porosity /%	Average pore size /nm	Most probably pore size /nm
0.035 % CO₂	18.74	31.36	4.075
2 % CO₂	14.03	26.67	4.051
20 % CO₂	12.19	21.21	3.037

Fig.7 - XRD spectrum of cement paste in carbonated concrete.

carbonation depth. The length of semi-carbonated zone was 6 mm at 2 % CO$_2$ and 8 mm at 20 % CO$_2$ within 16 weeks, a value that cannot be ignored when predicting the service life of concrete under carbonation.

(2) The content of CH and CaCO$_3$ in the semi-carbonated zone linearly increased and linearly decreased, respectively. CH remained in a small amount in the completely carbonization zone instead of completely consumed, and CH consumed at 20 % CO$_2$ is about 1.5-2.0 times of 2 % CO$_2$.

(3) The content of CaCO$_3$ in completely carbonated zone at 20 % CO$_2$ was higher than 2 % CO$_2$. CaCO$_3$ could fill in the large pores between hydration products, so the porosity, average pore size and most probably aperture decreased with CO$_2$ concentration.

(4) The CO$_2$ concentration affects the crystal structure of carbonation product CaCO$_3$. The CaCO$_3$ crystal was calcite and aragonite at 2.0 % CO$_2$, while it was calcite and vaterite at 20 % CO$_2$.

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