

論文 Influence of Mixture Proportion on the Content of Carbon Dioxide Carbonated in Concrete

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ABSTRACT: Experimental results about the influence of mixture proportion on the content of CO₂ carbonated in concrete under accelerated carbonation exposure are presented in this paper. The content of CO₂ carbonated was evaluated by ignition loss of concrete. The depth of carbonation front was found to be about 2 to 4 times the depth of carbonation by phenolphthalein. The total amount of CO₂ carbonated in the concrete with water-cement ratio of 65 percent was about 2.6 times that in the concrete with water-cement ratio of 45 percent and the result was verified by theoretical analysis.

KEYWORDS: carbonation, content of CO₂ carbonated, water-cement ratio, ignition loss, Ca(OH)₂, accelerated carbonation

1. INTRODUCTION

Steel bars in concrete structures are protected by a thin oxide film that forms on their surface due to the high alkalinity of surrounding concrete which has a pH value around 12.5. Reducing the pH in concrete to a relative low value will destroy this protection and the corrosion of steel bars will be speeded. One of the most important causes of such a reduction of pH value in concrete is carbonation which is a chemical reaction between CO₂ that is present in the atmosphere at a small concentration and the hydrated cement minerals[1,2].

The most widely used method to measure the extent of carbonation is to treat a freshly broken surface of concrete specimen with 1 percent phenolphthalein solution; the portion having a high free Ca(OH)₂ (pH \geq 10) is colored pink while the uncolored portion is defined as the depth of carbonation. It has been reported that the corrosion rate of Fe at 40°C with a surrounding pH of 11 at which the concrete is considered as no carbonation by the phenolphthalein is larger than the corrosion rate at 20°C with a pH of 10[3]. A good understand of the carbonation progress, especially at the area where the pH is larger than 10, has a practical significance in a tropical climates such as Southern Kyushu area. Quantitative analysis of the content of CO₂ carbonated in concrete can give a more accurate description of the carbonation. In this study, an experiment was carried out to measure the content of CO₂ carbonated in concrete under accelerated carbonation exposure by ignition loss.

Much work has been done about the influence of mixture proportion, especially that of water-cement ratio on the depth of carbonation[4-7], but studies about how the mixture proportions affect the combination of CO₂ with hydrated cement minerals are few. The work presented here was tried to evaluate the influence of water-cement ratio on the distribution of CO₂ carbonated in concrete and the relationship between depth of carbonation indicated by 1 percent phenolphthalein solution and the content of CO₂ carbonated in concrete.

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2. EXPERIMENTAL DETAILS

2.1 MIXTURE PROPORTION AND SPECIMEN

An ordinary portland cement with a specific gravity of 3.16 was used in all the mixtures. The coarse aggregate used had a maximum size of 15mm and specific gravity of 2.58. All mixtures contained natural river sand which had a specific gravity of 2.57. The water-cement ratio of concrete was chosen to be 45, 55, and 65 percent. The unit weight of water was the same for all mixtures. **Table 1** gives the details of the mixture proportions. The slump of fresh concrete was designed as 8 cm.

| Table 1 Mixture Proportions | | | | | |
|-----------------------------|---------|----------------------------------|-----|-----|-----|
| W/C (%) | s/a (%) | Unit weight (kg/m ³) | | | |
| | | W | C | S | G |
| 45 | 45 | 180 | 400 | 780 | 918 |
| 55 | | | 328 | 800 | 955 |
| 65 | | | 277 | 820 | 978 |

Two batches of concrete were mixed for every proportion listed in **Table 1**. One was used for casting of specimens under natural exposure and the other was used for that under accelerated carbonation exposure. 20 specimens of 10×20 cm cylinder were cast from each batch. After casting and a moist curing of two days, the specimens under natural exposure were placed in the laboratory and those for accelerated carbonation test were moved into an accelerated carbonation chamber which had an average temperature of 21°C and a average relative humidity of 74 percent. The concentration of CO₂ was 0.07 percent in the laboratory and 10 percent in the accelerated carbonation chamber.

2.2 TEST PROCEDURES

At the ages of 28, 56, 91 days and 1 year, weight of specimen, compressive strength (JIS A 1108), depth of carbonation and content of CO₂ carbonated in concrete were measured. The depth of carbonation was determined by spraying 1 percent phenolphthalein solution to the broken surface of a specimen as soon as it was separated into two halves by a compressive load applied in its side surface. From each half of the specimen depths of carbonation at five points were measured. The average of all the 10 measurements from both halves was taken as the depth of carbonation of the specimen tested. The content of CO₂ carbonated in concrete was obtained by ignition test.

The content of CO₂ carbonated in concrete was measured in the following steps. At first, the upper 8 cm portion of the specimen was sliced into 10 pieces at a pitch of 8 mm and the rest of specimen was sliced into 8 pieces at a pitch of 15 mm. Then every piece was crashed and ground into powder repeatedly until all the powders could pass 0.105 mm mesh sieve. The powder sample about 2 grams was put into a muffle furnace to have the ignition test. Reduction of the sample weight at three temperature ranges, room temperature to 200°C, 200°C to 550°C, and 550°C to 950°C was measured. The content of CO₂ carbonated in concrete was calculated from the weight loss. When concrete was heated from room temperature to 950°C, its components, including hydrated cement minerals, aggregate, water, and CaCO₃ that is the product of carbonation, experience some chemical reactions. Two main reactions are given in Eq. (1) and Eq. (2).



From the ignition loss between 400~500°C and 650~950°C the content of CO₂ in the form of CaCO₃ inside concrete can be obtained. Because the other components also have their ignition losses between the two temperature ranges, this was taken into account by considering that the ignition loss of concrete between 400~500°C and 650~950°C was a combination of the losses of CaCO₃ and other components. The ignition loss without CaCO₃ could be obtained from the average loss of the samples in the middle portion of the specimen which could be regarded as no carbonation had occurred yet. By ignoring the movement of Ca(OH)₂ and CaCO₃ inside concrete and the anisotropy of specimen which might be caused during casting, the content of CO₂ carbonated can be obtained from the weight difference between the loss of samples at near top surface portion of the specimen and the average ignition loss of samples in the middle portion.

3. TEST RESULTS AND DISCUSSION

3.1 DEPTH OF CARBONATION

The rate of carbonation, as the following equation shows, is roughly proportional to the square root of exposed time.

$$X = K\sqrt{t} \quad (3)$$

In which X is the depth of carbonation (mm); t is exposed time (day), and K is carbonation coefficient ($mm/day^{1/2}$). By plotting the depth of carbonation vs. the square root of exposed time, values of K in this study are shown in **Table 2**. It can be found that the carbonation coefficient under accelerated carbonation exposure was about 6 to 7 times that under natural exposure. Theoretical study by considering carbonation as a diffusion-controlled process indicated that depth of carbonation is proportional to the square root of the ambient concentration of CO_2 [8,9]. The concentration of CO_2 in accelerated carbonation chamber is about 143 times higher than that in laboratory, so the theoretical carbonation coefficient of the former was 12 times that of the later. The decrease of pore volume in concrete due to rapid carbonation in the former made the diffusing of CO_2 into concrete slower than the theoretical calculation. Hence, the practical carbonation coefficient was smaller than that from calculation by considering the difference of CO_2 concentration. The influence of water-cement ratio on the depth of carbonation under accelerated carbonation exposure is illustrated in **Fig. 1**. It can be found that the relationship between depth of carbonation and water-cement ratio was a second order curve.

Table 2 Carbonation coefficient K
($mm/day^{1/2}$)

| W/C (%) | Accelerated Carbonation Exposure | Natural Exposure |
|---------|----------------------------------|------------------|
| 45 | 0.69 | 0.13 |
| 55 | 1.19 | 0.21 |
| 65 | 3.51 | 0.49 |

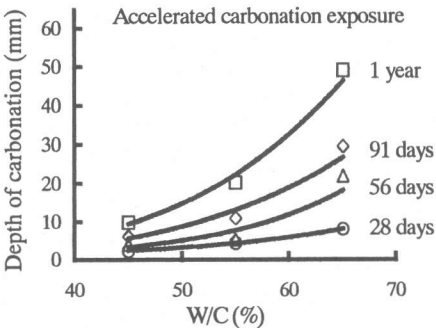


Fig. 1 Relationship between depth of carbonation and W/C

3.2 CONTENT OF CO_2 CARBONATED IN CONCRETE

(1) Test results

Test results on the content of CO_2 carbonated in concrete under accelerated carbonation exposure at the age of 56, 91 days and 1 year are shown in **Fig. 2** and **Fig. 3**. Depths of carbonation at the corresponding ages by phenolphthalein solution are also indicated in the two figures. The content of

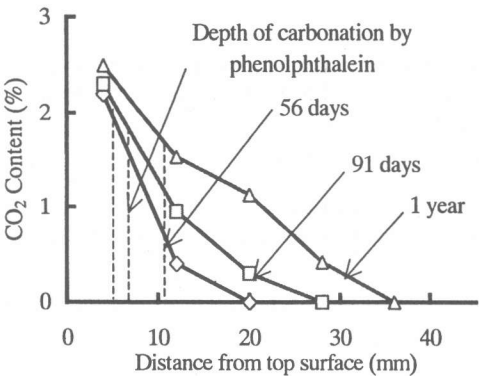


Fig. 2 Distribution of CO_2 carbonated in concrete and depth of carbonation (W/C=45%)

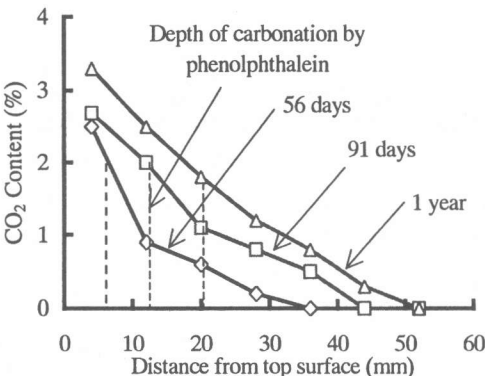


Fig. 3 Distribution of CO_2 carbonated in concrete and depth of carbonation (W/C=55%)

CO₂ is expressed as the percentage of the weight of CO₂ obtained from ignition test to the weight of concrete. Distributions of the content of CO₂ carbonated in concrete with water-cement ratio of 45, 55 and 65 percent after 1 year exposure are illustrated in Fig. 4.

From Fig. 2 and Fig. 3 it can be found that the content of CO₂ carbonated in concrete increased with the age and the near surface portion in concrete specimen had the highest content. Fig. 2 and Fig. 3 show that from the position indicated by phenolphthalein solution as the depth of carbonation towards the interior part of specimen, there still existed the CO₂ carbonated in concrete at some extents. It also can be found from the two figures that the depth of carbonation front, known as the position at which the content of CO₂ carbonated in concrete became zero, was about 2 to 4 times the depth of carbonation[10].

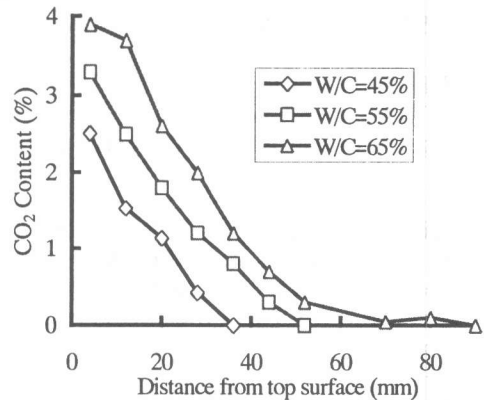


Fig. 4 Content of CO₂ carbonated in concrete at age of 1 year

The unit weight of cement in the concrete with water-cement ratio of 65 percent was 277 kg/m³, less than the other two concretes, thus the content of substance available for carbonation in hydrated cement minerals was also lower than that in other concrete. However, the results given in Fig. 4 shows that until the age of 1 year a higher CO₂ content in the concrete with water-cement ratio of 65 percent can be seen at each portion from the top surface to the interior part of the specimen. Table 3 gives the total amount of CO₂ carbonated in the concrete specimen at the age of 1 year. The total amount of CO₂ carbonated in the concrete with water-cement ratio 65 percent was about 2.6 times that in the concrete with water-cement ratio of 45 percent. The carbonation coefficient of the concrete of 65 percent water-cement ratio under accelerated carbonation exposure given in Table 2 was about 5 times that of the concrete of 45 percent water-cement ratio. It can be said that water-cement ratio was a major parameter influencing the content of CO₂ carbonated in concrete. However, the influence of water-cement ratio on the content of CO₂ carbonated in concrete was less than its influence on the carbonation coefficient.

Table 3 Total amount of CO₂ carbonated in concrete (age: 1 year)

| W/C(%) | 45 | 55 | 65 |
|-------------------------------|------|-------|-------|
| Amount of CO ₂ (g) | 8.44 | 14.99 | 21.86 |

(2) Theoretical analysis

Carbonation can be regarded as a diffusion process in which some of the diffusing CO₂ molecules become immobilized due to the irreversible carbonation reaction with hydrated cement minerals as diffusion proceeds, thus the equation of diffusion takes the form of

$$\partial C / \partial t = D(\partial^2 C / \partial x^2) - KC \quad (4)$$

where C is concentration of diffusing CO₂; D is diffusion coefficient of CO₂ in concrete, K is reaction rate constant. By considering concrete as a semi-infinite, homogenous medium, solution of Eq. (4) at the initial condition and boundary conditions

$$\begin{aligned} t=0; \quad x < 0 \quad C=C_s, \quad x > 0 \quad C=0 \quad (C_s: \text{concentration of ambient CO}_2) \\ \text{all } t; \quad x=0 \quad C=C_s, \quad x \rightarrow \infty \quad C=0 \end{aligned}$$

can be obtained from Laplace transformation[11]

$$\frac{C}{C_s} = \frac{1}{2} \exp\left\{-x\sqrt{K/D}\right\} \operatorname{erfc}\left\{\frac{x}{2\sqrt{Dt}} - \sqrt{Kt}\right\} + \frac{1}{2} \exp\left\{x\sqrt{K/D}\right\} \operatorname{erfc}\left\{\frac{x}{2\sqrt{Dt}} + \sqrt{Kt}\right\} \quad (5)$$

The total amount of CO₂ diffusing into concrete M_T through a unit area at a given exposed period T is

$$M_T = Cs\sqrt{D/K}\left\{(KT + 0.5)\text{erf}(\sqrt{KT}) + \sqrt{KT/\pi} \exp(-KT)\right\}. \quad (6)$$

Using Eq. (6) to estimate the content of CO₂ carbonated in concrete, information about the value of Cs (mol/m³), D (m²/day), and K (day⁻¹) must be known. Cs, as an external factor, is easy to determine. As the concrete in Fig. 4 had the same environmental condition, the rate constant K was regarded as having the same value and in this study it was taken as 0.15 day⁻¹. It has been pointed out that the diffusion coefficient of a gas in concrete is a function of its pore volume and for oxygen it takes the form of [12,13]

$$D = 0.43 \times (3.62 \times 10^{12})^{V_g} (\text{cm}^2 / \text{day}) = 0.43 \times 10^{-4} \times (3.62 \times 10^{12})^{V_g} (\text{m}^2 / \text{day}) \quad (7)$$

where V_g is the volume of gaseous phase pores inside concrete. Diffusion coefficient of a gas is proportional to the mean velocity of its molecules, which is inversely proportional to the square root of its molecular weight, and the mean free path of its molecules, which is inversely proportional to the cross sectional area of the molecules. By considering the difference in molecular weight and diameter of O₂ and CO₂ and the effect of temperature on diffusion process, diffusion coefficient of CO₂ in concrete is deduced as

$$D = 0.21 \times 10^{-4} \times (3.62 \times 10^{12})^{V_g} \times \left(\frac{T}{T_0}\right)^n \quad (8)$$

where T₀=293(K), n=0.79 is the cohesion coefficient of CO₂ at normal atmospheric pressure at T.

Table 4 gives the total amount of CO₂ M carbonated in concrete from calculation by Eq. (6). The volume of gaseous phase pores V_g in **Table 4** used for the calculation of diffusion coefficient D

was the total volume of entrapped air and capillary pore which could be obtained from the method proposed by A. M. Neville [14]. M in **Table 4** was approximated to the test result given in **Table 3**. The concrete with a high water-cement ratio had a larger pore volume than that with low water-cement ratio and a large pore volume made the diffusing of CO₂ into concrete easier.

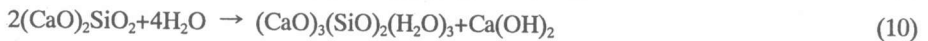
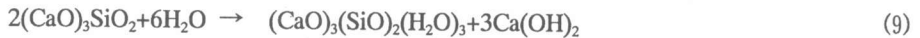
Table 4 Total amount of CO₂ carbonated in concrete calculated by Eq. (6) (age: 1 year)

| W/C (%) | V _g (m ³ /m ³) | D (m ² /day) | M (g) |
|---------|--|-------------------------|-------|
| 45 | 0.083 | 0.00023 | 9.94 |
| 55 | 0.105 | 0.00044 | 13.7 |
| 65 | 0.141 | 0.00124 | 22.9 |

Note: Cs=3.09 mol/m³ K=0.15 day⁻¹

(3) Concentration of CO₂ carbonated in concrete and Ca(OH)₂

One of the main reaction in concrete carbonation is the reaction between CO₂ and Ca(OH)₂ which is a product of the hydration of C₃S and C₂S



From the above two equations the theoretical content of Ca(OH)₂ W_{Ca} produced by the hydrated cement minerals can be obtained if the chemical composition of cement and hydration degree are known. The C₃S and C₂S content in the portland cement used are 50 percent and 26 percent, respectively. According to Eq. (9) and (10), the theoretical concentration of Ca(OH)₂ is about 30.2 percent of cement weight. W_{Ca} in the unit of mol/m³ takes the form of

$$W_{Ca} = 0.302 \beta W_c \times 1000 / 74 = 4.08 \beta W_c \quad (11)$$

where W_c is the unit weight of cement (kg/m³), and β is the degree of hydration of cement. Fig. 5 gives the theoretical concentration of Ca(OH)₂ calculated by Eq. (11) at age of 91 days (β=0.95) and the concentration of CO₂ carbonated in the first slice cut from the concrete specimens. The concentration of CO₂ is the mole numbers

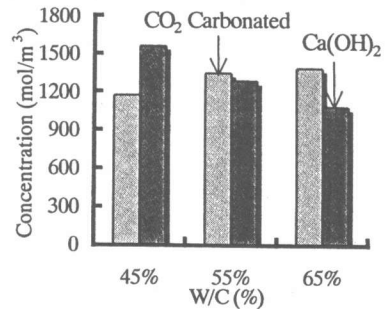


Fig. 5 Concentration of CO₂ carbonated and theoretical concentration of Ca(OH)₂ (age: 91 days)

of CO_2 per unit volume of concrete. For the concrete with water-cement ratio of 45 percent, the concentration of CO_2 carbonated was about 75 percent of the theoretical concentration of $\text{Ca}(\text{OH})_2$, whereas for the concrete with water-cement ratio of 55 and 65 percent it was about 105 and 126 percent of the theoretical concentration of $\text{Ca}(\text{OH})_2$, respectively. The molar concentration of CO_2 carbonated in concrete was higher than the molar concentration of $\text{Ca}(\text{OH})_2$ in concrete showed that besides $\text{Ca}(\text{OH})_2$, other hydrated cement minerals also took part in the carbonation process[2].

4. CONCLUSIONS

From the results of this study, the following conclusions can be drawn.

1. The difference between the carbonation coefficients under accelerated carbonation exposure and natural exposure was smaller than that from theoretical calculation by considering the difference of the CO_2 concentration in two exposures. Relationship between depth of carbonation and water-cement ratio was a second order curve. The carbonation coefficient of concrete with 65 percent water-cement ratio was about 5 times that of the concrete with 45 percent water-cement ratio.

2. The depth of carbonation front at which the content of CO_2 carbonated in concrete became zero, was about 2 to 4 times the depth of carbonation by phenolphthalein. The total amount of CO_2 carbonated in concrete with water-cement ratio 65 percent was about 2.6 times that in concrete with water-cement ratio of 45 percent and theoretical analysis showed an approximate result.

3. Molar concentration of CO_2 carbonated in concrete might be higher than the molar concentration of $\text{Ca}(\text{OH})_2$ in concrete. Besides $\text{Ca}(\text{OH})_2$, other hydrated cement minerals also took part in the carbonation process.

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