Effect of Environmental Relative Humidity on Carbonation of Concrete
コンクリートの炭酸化に及ぼす相対湿度の影響

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1. Introduction

Deterioration of concrete structures due to corrosion of their reinforcement is one of the most serious problems facing concrete engineers presently. Reinforcement corrosion occurs only after depassivation due to carbonation of the surrounding concrete, penetration of chloride ions, or a combination of both. In urban environment, carbonation of concrete is the main mechanism that paves the way to initiation of reinforcement corrosion. It has been known that carbonation process is affected by environmental conditions such as relative humidity, temperature and concentration of CO_2. However, their effect on carbonation process which always related to evolution of carbonation depth has not been examined clearly. Experimental data obtained through accelerated carbonation test lead to ambiguous conclusion, especially the effect of environmental relative humidity. Those experments are different in concentration of CO_2, time measurement of carbonation depth, mix proportion of concrete (especially, water-cement ratio) and the procedure of water extraction. Those differences may be the factors which lead experimental results to ambiguous conclusion. If that presumption is correct, accelerated test results can not be applied directly to predict the effect of environmental relative humidity on carbonation of concrete in natural conditions. This paper discusses the factors affecting the influence of environmental relative humidity on carbonation of concrete and through mathematical modeling paves the ways to predict the evolution of carbonation depth in natural conditions.

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2. Carbonation Process

The physicochemical processes involved in carbonation of concrete are:

1. Hydration reactions from which carbonatable materials are produced.

2. Diffusion of atmospheric CO_2 in gaseous phase of the concrete pores.

3. Dissolution of solid $Ca(OH)_2$ in the pore water and the diffusion of dissolved $Ca(OH)_2$ in the aqueous phase of the pores.

4. Dissolution of CO_2 in the pore water and its reaction with dissolved $Ca(OH)_2$ and other solid carbonatable consituents of hardened cement paste.

5. The reduction of pore volume due to solid products of hydration and carbonation.

These processes are formulated into mathematical model for their quantitative descriptions. But, since carbonation process is very complex, not all these processes are included into the model. Some assumptions are needed in order to simplify the model, such as;

1. During carbonation process, hydration reaction of cement is neglected.

2. Carbonation of CSH is neglected.

3. Micro-structure of concrete is uniform before carbonation process.

4. The diffusion of $Ca(OH)_2(aq)$ is neglected.

5. Temperature of concrete is always constant.

Diffusion of atmospheric CO_2 into concrete

Penetration of CO_2 into concrete follows the Fick's second law.

$$\frac{\partial C}{\partial t} = \frac{\partial}{\partial x}\left(D_e \frac{\partial C}{\partial x}\right) \tag{1}$$

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where:

C: concentration of CO_2

D_e: effective diffusion coefficient which depend on porosity of concrete and relative humidity.

$$\sqrt{D_e} = B\varepsilon_p \,[1-(RH/100)] \quad \text{[5]} \qquad (2)$$
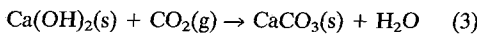
ε_p: porosity of concrete which depend on water-cement ratio and also reduced due to carbonation.

B : 1.2E-03 m/s$^{1/2}$

RH: Relative Humidity in concrete.

Carbonation of Ca(OH)$_2$

The overall reaction between $Ca(OH)_2(s)$ and $CO_2(g)$,

$$Ca(OH)_2(s) + CO_2(g) \rightarrow CaCO_3(s) + H_2O \qquad (3)$$

consists of several elementary steps which take place in the aqueous phase in the pore of concrete.

Dissolution of $Ca(OH)_2(s)$ and $CO_2(g)$ is the crucial step in these reactions. It has been found that the rate expression

$$r_{CH} = HRTk_2 \,[OH^-]_{eq} \,[CO_2] \quad \text{[1]} \qquad (4)$$

provides a good approximation for pH value above ten. In the above expression, $[CO_2]$ is the molar concentration of CO_2 in the gas phase of the pores (in moles of $CO_2(g)$ per unit volume of pore air); H=34.2 mol/m^3. atm (at 25°C) is Henry's constant for the dissolution of CO_2 in water; R=8.206E-05 m^3. atm/mol. K is the gas constant; T is the absolute temperature in K; and k_2=8.3 m^3/mol. sec (at 25°C) is the rate constant for the reaction of CO_2 and OH$^-$; $[OH^-]_{eq}$ is the molar concentration of OH$^-$ in the aqueous phase at saturation, equal to 43.2 mol/m^3 at 25°C. Obviously, water plays a key role in carbonation process. It blocks the pores and thus hinders diffusion of CO_2 through the pores. On the other hand, it provides a medium for reaction between CO_2 and $Ca(OH)_2$. Therefore, it is unavoidable to include water evaporation process into carbonation process model.

3. Mathematical Model

Mathematical model constructed is a nonlinear-coupling problem which considers interaction between diffusion of CO_2 into concrete and diffusion of water from concrete. Differential equations can be formulated as follows,

$$\frac{\partial C_1}{\partial t} = \frac{\partial}{\partial x}\left(D_1 \frac{\partial C_1}{\partial x}\right) + f\,(K(t)) \qquad (5)$$

$$\frac{\partial C_2}{\partial t} = \frac{\partial}{\partial x}\left(D_2 \frac{\partial C_2}{\partial x}\right) \qquad (6)$$

$$\frac{\partial C_3}{\partial t} = -K(t) \qquad (7)$$

where subscripts 1, 2, 3 represent carbon dioxide, water and calcium hydroxide.

C: concentration

D: diffusion coefficient

D_1 is affected by amount of water in concrete and reducing porosity of concrete due to carbonation.

D_2 is adopted from nonlinear water diffusion model by Bazant.

K: reaction rate between $Ca(OH)_2$ and CO_2 which depends on amount of water and concentration of CO_2.

To solve equations (5)~(7), numerical method has to be used since the problem is strongly nonlinear. Using Finite Element Method these equations can be solved simultaneously time by time. By calculating distribution of $Ca(OH)_2$ concentration inside concrete time by time, the evolution of carbonation depth can be known.

4. Calculation Results

Some calculation results have been obtained in order to examine the factors affecting influence of environmental relative humidity on carbonation of concrete.

In this paper, the value of environmental relative humidity from 30% to 70% are choosen. Figure 1 shows that in 1%~10% CO_2 which represent high concentration of CO_2 in accelerated test, decrease of environmental relative humidity will increase carbonation depth. But, in
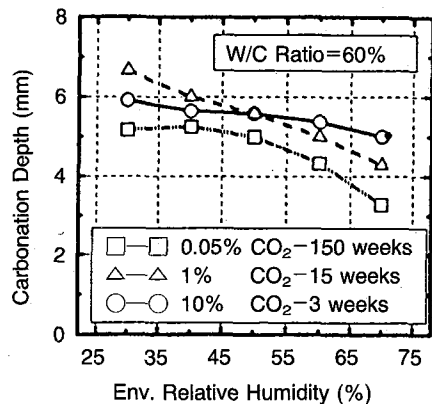

Fig. 1 Effect of CO_2 Concentration

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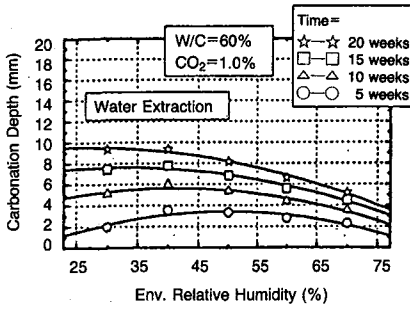

Fig. 2a　Carbon. Depth vs Env. RH without Water Evap.
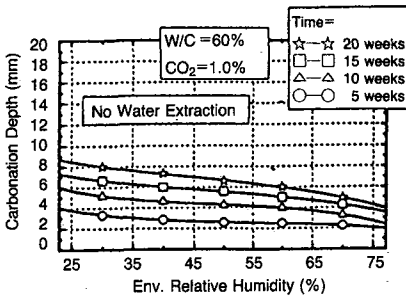

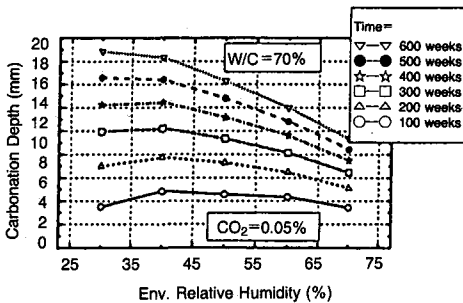Fig. 2b　Carbon. Depth vs Env. RH with Water Evap.

Fig. 3　Carbon. Depth vs Env. RH (various time)
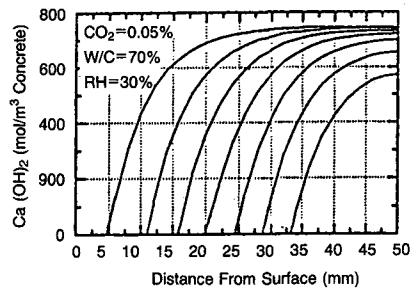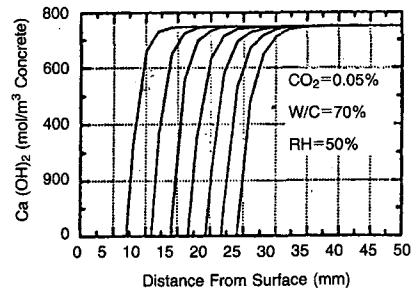

Fig. 4a　Formation of Carbonation Front in low RH

Fig. 4b　Formation of Carbonation Front in high RH
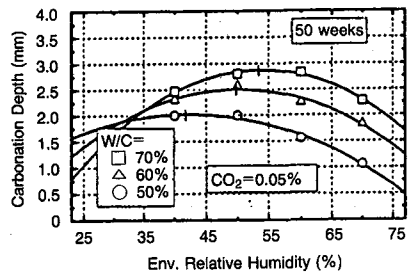

Fig. 5　Carbon. Depth vs Env. RH (various W/C Ratio)

0.05% CO_2 which represents normal concentration of CO_2 in natural conditions, there is a maximum (peak) value of carbonation depth around 40% of environmental relative humidity. This phenomenon is due to water evaporation in concrete since extraction water is not applied or the initial condition of hardened concrete is completely wet. Water evaporation in concrete is relatively slow compared to carbonation process in high concentration of CO_2. Therefore, in short period of time, relative humidity in concrete is still much higher than environmental relative humidity so that diffusivity of CO_2 becomes the determining factor in carbonation process. Figures 2a and 2b show that in high concentration of CO_2,

the existing of water extraction affects the results. The peak value of carbonation depth can only be seen when water extraction process is applied. Therefore, the uncomplete water extraction should affect experimental results. Figure 3 shows that in the normal concentration of CO_2, the critical value of environmental relative humidity decreases with time and finally disappears. The formation of carbonation front can explain that behaviour (shown in figure 4a and 4b). In low relative humidity, reaction rate is relatively slow and penetration of CO_2 is relatively fast. Therefore, CO_2 can penetrate to the deeper part of concrete and reacts with $Ca(OH)_2$ although the outer part has not yet been carbonated completely. Therefore, the relatively slow reaction rate

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only causes the decrease of carbonation depth at early stage. At late stage, progression of carbonation depth is relatively fast because $Ca(OH)_2$ content has been reduced from the beginning. Figure 5 shows that in normal concentration of CO_2 and relatively short time, decrease of water-cement ratio decreases critical value of environmental relative humidity. It is caused by the difference of water content in hardened concrete with different water-cement ratio.

5. Conclusions

Based on these calculation results, the following conclustions can be obtained:

1. Concentration of CO_2, period of time, existing of water extraction and water-cement ratio affect the influence of environmental relative humidity on progression of concrete carbonation depth.

2. Influence of environmental relative humidity on progression of carbonation depth in natural conditions can not be predicted merely based on accelerated test results.

3. In the normal concentration of CO_2, lower en-

vironmental relative humidity ($\leq 30\%$) causes higher carbonation depth at late stage.

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