Modeling of Carbonation based on Thermo-Hygro Physics with Strong Coupling of Mass Transport and Equilibrium in Micro-pore Structure of Concrete

Tetsuya Ishida
Associate Professor
Department of Civil Engineering, University of Tokyo
7-3-1 Hongo, Bunkyo-ku, Tokyo, 113-8656, Japan
E-mail: tetsuya.ishida@civil.t.u-tokyo.ac.jp

Chun-He Li
Assistant Professor
Department of Civil and Environmental Engineering, Gunma University
1-5-1 Tenjin-cho, Kiryu City, Gunma Prefecture, 376-8515, Japan
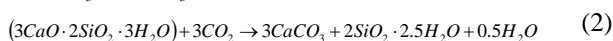E-mail: lichunhe@ce.gunma-u.ac.jp

1. Introduction

Carbonation of concrete is a phenomenon that causes corrosion of steel in reinforced concrete structures, and is recognized as an important problem for ensuring the durability of structures. Against this background, many researchers have proposed methods for predicting the progress of concrete carbonation under various environments. In this study, the authors aim to improve the accuracy and to extend the applicable range of existing models, not only for controlled acceleration environments, but also for low concentrations such as the carbon dioxide concentration in the atmosphere, and for various temperature histories, taking into account the application of the thermodynamic model to actual structures.

2. Modeling of carbonation based on thermo-hygro physics with strong coupling of mass transport and equilibrium in micro-pore structure of concrete

A carbonation model based on thermo-hygro physics at arbitrary temperature conditions is presented in this paper. Reaction of C-S-H gel was newly added to the existing model as well as calcium hydroxide reaction. These progresses of carbonation are expressed by the following Equations (1) and (2).

$$Ca^2 + CO_3^{2-} \rightarrow CaCO_3 \tag{1}$$

$$(3CaO \cdot 2SiO_2 \cdot 3H_2O) + 3CO_2 \rightarrow 3CaCO_3 + 2SiO_2 \cdot 2.5H_2O + 0.5H_2O \tag{2}$$

The law of mass conservation for carbon dioxide is the governing equation to be solved in numerical analysis of the carbonation phenomenon (Ishida et al. 2007). In the new model, relationship is proposed for the temperature dependent diffusivities of carbon dioxide in water and in air, based on values in the literature (CRC 2005).

From reaction equations (1) and (2), the consumption and generation of the following equivalent masses can be obtained: calcium hydroxide and C-S-H gel consumption, calcium carbonate, silica gel, and water generated at an arbitrary temperature condition. At an arbitrary stage during carbonation, the volume of each of these can be calculated in accordance with the Relational expression of mass and volume. The change in volume of hydrated products due to carbonation was obtained as the volumetric difference between the sum of calcium carbonate and generated silica gel and the sum of calcium hydroxide and consumed C-S-H gel. Figure 1 shows the concept of the change in porosity in the
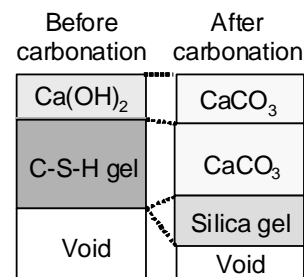

Fig.1 Concept of change in quantity of porosity in the proposed model

proposed model.

In the proposed model, the specific surface area of the gel increases due to carbonation, and it is assumed that as a result, the micro-pore structure distribution is changed. Referring to the experimental results (Kim et al. 1995), the relative change in the specific surface area of the gel due to carbonation is assumed to be a factor of 2. Thus, in the proposed model, the specific surface area of the carbonated C-S-H gel is roughly assumed to be $60m^2/g$, as a primary approximation.

3. Verification of the proposed carbonation model

Figure 2 shows the analytical results for pore size distribution before and after carbonation in case of water-to-cement ratio of 60%. From this figure, it can be seen that the current model calculates not only the reduction in porosity, but also the change in pore size distribution. From this, it is concluded that the newly proposed carbonation model is capable of reproducing the actual changes in porosity accurately.

Figure 3 shows the analytical results for postulated carbonation acceleration tests with a water-cement ratio of 60%, relative humidity 50%, and carbon dioxide concentration 10%, at 10°C temperature intervals over the range 10°C to 50°C. As shown in the figure, progress of the carbonation reaction is the fastest at 30°C, and progress tends to become slower when the temperature is above 30°C. It is considered that the temperature dependence of the carbonation reaction, which is known from previous research to a peak around 30°C, can be quantitatively predicted.

Generally, the mechanism by which the progress of carbonation shows a peak at a particular temperature is explained by the relationship of solubility and reaction rates to temperature canceling each other out. In other words, the solubility of carbon dioxide and calcium hydroxide are reduced by an increase in temperature, so the quantity available for reaction is reduced. On the other hand, as described by the Arrhenius law, the reaction rate coefficient itself becomes larger as the temperature rises. As a result of these two factors, the reaction rate is maximized at around 30°C. In the analysis using the proposed model, these factors were incorporated. Hence, different rates of progress of carbonation were predicted according to the temperature conditions.

4. Conclusion

In this study, carbonation reaction of C-S-H gel as well as that of calcium hydroxide was modeled for an arbitrary temperature environment based on the
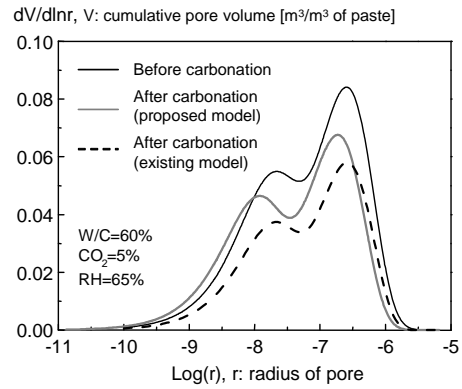

Fig.2 Change in computed pore size distribution due to carbonation
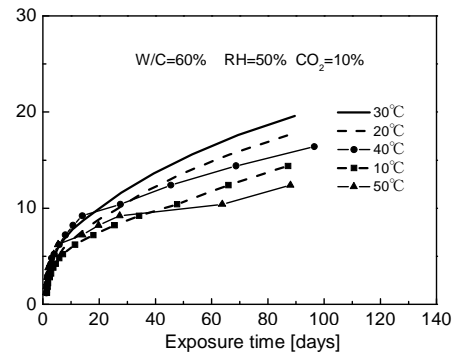

Fig.3 Effect of temperature on carbonation progress

microscopic mechanisms. The change in mass and volume of hydration products due to carbonation was directly applied to a micro-pore structure formation model, and the change in the microscopic structure was reasonably predicted. Furthermore, by appropriately taking into account the interactions among temperature, moisture state in pores, diffusion of carbon dioxide and carbonation reaction, it is possible to make good predictions of the progress of the carbonation under an arbitrary temperature environment and an arbitrary concentration of carbon dioxide.

References
Ishida, T., Maekawa, K. and Kishi, T. (2007). "Enhanced modeling of moisture equilibrium and transport in cementitious materials under arbitrary temperature and relative humidity history", *Cement and Concrete Research* 37, 565-578.
CRC Handbook of Chemistry and Physics, 85th Edition, CRC Press, Boca Raton, London, New York, Washigton, D.C.
Kim S., Taguchi, S., Ohba, Y., Tsurumi, T., Sakai, E. and Daimon, M. (1995). "Carbonation reaction of calcium hydroxide and calcium silicate hydrates", *Inorganic materials*, Vol. 2, No. 254, 18-25.