

## **Chapter 4**

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### **Prediction of the Service Life of RC Structures Considering Concrete Carbonation**



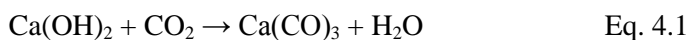
## 4.1 Outline

In this chapter, FEMA is used in order to predict carbonation depth quantitatively because it can predict the amount of Ca(OH)<sub>2</sub> at an arbitrary point in concrete. FEM program that is used in this study is LECCA2. FEMA requires input parameters to analyze and they are as follows. 1) the initial concentration of Ca(OH)<sub>2</sub>, 2) diffusion coefficient of CO<sub>2</sub> in concrete, 3) The reaction rate constant between Ca(OH)<sub>2</sub> and CaCO<sub>3</sub>, and 4) CO<sub>2</sub> concentration in the air. The values 1) and 2) are predicted by hydration model and 3) and 4) are determined through literature reviews. Prediction service life is determined using a newly proposed evaluation basis for carbonation. That is a point where the pH value of concrete in rebar position is 10.6 and at there, the amount of Ca(OH)<sub>2</sub> compared to the initial concentration of Ca(OH)<sub>2</sub> is a level of 60%.

## 4.2 Concrete Carbonation Model Using a FEMA

### 4.2.1 A Diffusion Equation of CO<sub>2</sub> in Concrete Based on the Chemical Reaction

A concrete carbonation is a physiochemical reaction that lowers pH in concrete because Ca(OH)<sub>2</sub>, which shows a strong alkali content in concrete, is reacted with CO<sub>2</sub> in the atmosphere and consequently generates CaCO<sub>3</sub>. As a result, rebar in concrete loses corrosion protection and it is easy to be corroded and this process is generally expressed in the following equation.



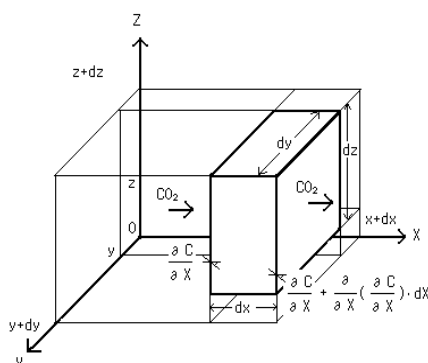
The model for CO<sub>2</sub> diffusion in concrete and carbonation reaction is based on

following assumptions:

1. Concrete is a semi-infinite fixed body and CO<sub>2</sub> flow in concrete is considered to flow in an only one direction (X-direction).
2. The CO<sub>2</sub> movement in concrete diffuses by Fick's first law.
3. Reaction between Ca(OH)<sub>2</sub> and CO<sub>2</sub> in concrete is a one-dimensional reaction.
4. The movement of Ca(OH)<sub>2</sub> in concrete is not considered.
5. Dense phenomenon of porosity in concrete through carbonation is not considered.

As shown in Fig. 4.1, considering a tiny section  $[x, x+\Delta x] \times [y, y+\Delta y] \times [z, z+\Delta z]$  in concrete, the amount of CO<sub>2</sub> entering by diffusion at plane  $X = x$  at time  $\Delta t$  is proportional to concentration gradient. So, when the concentration of CO<sub>2</sub>, the concentration change of CO<sub>2</sub> during time  $\Delta t$ , diffusion coefficient of CO<sub>2</sub> in concrete is expressed in  $C = C(x, t)$ ,  $\Delta t$ ,  $D$ , it can be showed in Eq. 4.2.

$$\Delta C \cdot dx \cdot dy \cdot dz = -D \cdot \frac{\partial C}{\partial x} \cdot dy \cdot dz \cdot \Delta t \quad \text{Eq. 4.2}$$



**Fig. 4.1** Migration and reaction of CO<sub>2</sub> in a tiny concrete section.

The amount of CO<sub>2</sub> coming out from plane  $X = x + \Delta x$  is expressed in Eq. 4.3.

$$\Delta C \cdot dx \cdot dy \cdot dz = -D \cdot \left( \frac{\partial C}{\partial x} + \frac{\partial}{\partial x} \left( \frac{\partial C}{\partial x} \right) dx \right) \cdot dy \cdot dz \cdot \Delta t \quad \text{Eq. 4.3}$$

Also, the amount of CO<sub>2</sub> being lost by reacting with Ca(OH)<sub>2</sub> in a tiny section can be expressed in Eq. 4.4 when the concentration of Ca(OH)<sub>2</sub> is  $C_a = C_a(x, t)$  and the reaction rate constant is  $k$ .

$$\Delta C \cdot dx \cdot dy \cdot dz = -k \cdot C \cdot C_a \cdot dx \cdot dy \cdot dz \cdot \Delta t \quad \text{Eq. 4.4}$$

The changed amount of CO<sub>2</sub> in the region during time,  $\Delta t$  can be expressed in Eq. 4.5 from Eq. 4.2, 4.3 and 4.4.

$$\Delta C \cdot dx \cdot dy \cdot dz = D \cdot \frac{\partial^2 C}{\partial x^2} \cdot dx \cdot dy \cdot dz \cdot \Delta t - k \cdot C \cdot C_a \cdot dx \cdot dy \cdot dz \cdot \Delta t \quad \text{Eq. 4.5}$$

Eq. 4.6 is a diffusion equation of CO<sub>2</sub> showing one-dimension reaction between Ca(OH)<sub>2</sub> and CO<sub>2</sub> through dividing both sides of the above equation by  $dx \cdot dy \cdot dz$ .

$$\frac{\partial C}{\partial t} = D \cdot \frac{\partial^2 C}{\partial x^2} - k \cdot C \cdot C_a \quad \text{Eq. 4.6}$$

#### 4.2.2 The Progress of Carbonation Based on the Chemical Reaction

Calcium ion, Ca<sup>+2</sup>, second term on the right side in Eq. 4.6, shows the concentration of Ca(OH)<sub>2</sub> and this value decreases by reaction with CO<sub>2</sub>. Decreasing the value of  $C_a$  is a result of the reduction of the pH value in concrete and this shows concrete carbonation.  $C_a$  can be expressed as the amount of decreased CO<sub>2</sub> in a tiny section. Chemical reaction between CO<sub>2</sub> and Ca(OH)<sub>2</sub> is assumed in a one-dimension reaction and  $\Delta C_a$ , the amount of concentration change of Ca(OH)<sub>2</sub> during time  $\Delta t$  can be expressed as follows.

$$\Delta C_a = -k \cdot C \cdot C_a \cdot \Delta t \quad \text{Eq. 4.7}$$

Eq. 4.7 can be expressed in Eq. 4.8.

$$\frac{1}{Ca} \cdot \frac{dCa}{dt} = -k \cdot C \quad \text{Eq. 4.8}$$

when  $t = 0$ , Eq. 4.9 is obtained as the solutions of Eq. 4.8 because of  $Ca = Ca_t = 0$ .

$$Ca = Ca_{t=0} \cdot \exp\left(-k \cdot \int_0^t C(\tau) d\tau\right) \quad \text{Eq. 4.9}$$

Eq. 4.9 shows concentration of Ca(OH)<sub>2</sub> at an arbitrary point  $x$  in arbitrary time  $t$ . When  $Ca$  is reduced to a certain value, the concrete can be considered to be carbonated.

Substituting Eq. 4.6 in Eq. 4.9, the equation of concrete carbonation progress is obtained as Eq. 4.10 and this consider one-dimension reaction between Ca(OH)<sub>2</sub> and CO<sub>2</sub>. CO<sub>2</sub> diffusion in accordance with Fick's first law.

$$\frac{\partial C}{\partial t} = D \cdot \frac{\partial^2 C}{\partial x^2} - k \cdot Ca_{t=0} \cdot C \cdot \exp(-k \cdot \int_0^t C(\tau) d\tau) \quad \text{Eq. 4.10}$$

### 4.2.3 Boundary Conditions

In general, the boundary conditions for the diffusion equation can be given as follows when substance penetrates or diffuses in one direction in semi-infinite solid body.

[Initial conditions]

$$t = 0, 0 \leq x < \infty: C(x, t) = 0 \quad \text{Eq. 4.11}$$

[Boundary conditions]

$$t > 0, x = 0: C(x, t) = C_0 \quad \text{Eq. 4.12}$$

where  $C_0$  is an initial concentration at the surface of concrete. CO<sub>2</sub> concentration in the surface of the concrete is changed with time, but in this study, it is assumed to be a constant throughout the whole period.

#### 4.2.4 Approximation of the Equation by a Differential Equation

The indexes of paragraphs 1 and 2 of the right side in the left side of Eq. 4.10 can be expressed as shown in Eq. 4.15 respectively by difference approximation in Eq. 4.13.

$$\frac{\partial C}{\partial t} = \frac{C(x_i, t_{j+1}) - C(x_i, t_j)}{\Delta t} \quad \text{Eq. 4.13}$$

$$\frac{\partial^2 C}{\partial x^2} = \frac{C(x_{i+1}, t_j) + C(x_{i-1}, t_j) - 2 \cdot C(x_i, t_j)}{\Delta x^2} \quad \text{Eq. 4.14}$$

$$\exp\left(-k \cdot \int_0^t C(\tau) d\tau\right) = \exp\left(-k \cdot \sum_i^j = 1 C(x_i, t_i) \cdot \Delta t\right) \quad \text{Eq. 4.15}$$

Substituting these expressions to Eq. 4.10, initial conditions  $C(x_i, t_i) = 0$  and boundary conditions  $C(x_l, t_i) = 0$  are used sequentially, the approximate solution of CO<sub>2</sub> concentration can be obtained.

$$C(x_i, t_{j+1}) = 1 - \frac{2D \cdot \Delta t}{\Delta x^2} - k \cdot C_{a_{t=0}} \cdot \Delta t \times C(x_i, t_j) \cdot \exp\left(-k \cdot \sum_i^j = 1 C(x_i, t_i) \cdot \Delta t\right) + \frac{D \cdot \Delta t}{\Delta x^2} \times C(x_{i+1}, t_j) + C(x_{i-1}, t_j) \quad \text{Eq. 4.16}$$

In addition, the distribution of Ca(OH)<sub>2</sub> can be obtained in Eq. 4.15 by assigning  $C_{a_i} = 0$ , the carbonation depth can be obtained at the point where Ca(OH)<sub>2</sub> concentration decreases 60% level compared to initial concentration of Ca(OH)<sub>2</sub>.

## 4.3 Deduction of Input Parameters for FEMA Through Literature Review

### 4.3.1 Outline

Carbonation prediction by using FEMA requires input parameters to analyze: 1) the initial concentration of Ca(OH)<sub>2</sub>, 2) diffusion coefficient of CO<sub>2</sub> in concrete, 3) The reaction rate constant between Ca(OH)<sub>2</sub> and CaCO<sub>3</sub> and 4) CO<sub>2</sub> concentration in the air. In this chapter, required parameters to FEMA are determined through literature reviews.

### 4.3.2 Diffusion Coefficient of CO<sub>2</sub> in Concrete

Concrete carbonation is a phenomenon where CO<sub>2</sub> in the air penetrates into the concrete and diffuses through porosity in concrete and combines with hydration product. Diffusion coefficient of CO<sub>2</sub> in concrete is affected by porosity structure in concrete and relative humidity affecting saturation degree of porosity. There are many researches to determine diffusion coefficient of CO<sub>2</sub> in concrete because it is an important variable that affects speed of concrete carbonation.

Papadakis expresses diffusion coefficient of CO<sub>2</sub> in concrete as a function of porosity and relative humidity in concrete as in Eq. 4.17.

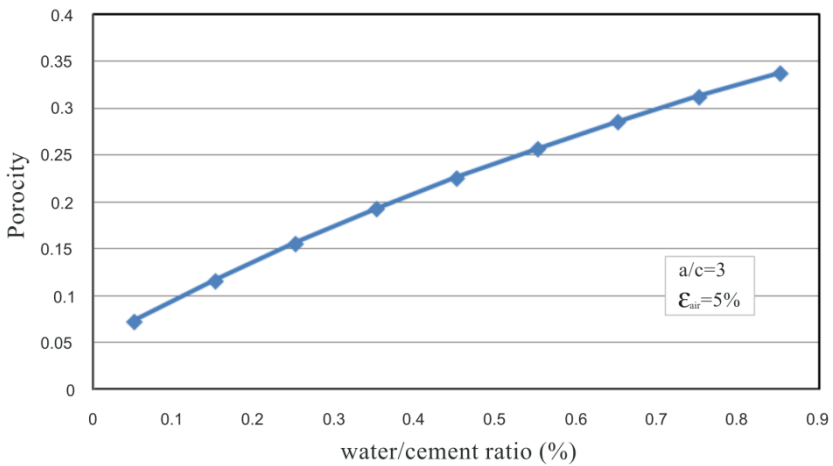
$$D_{e,CO_2} \approx 1.64 \cdot 10^{-6} \epsilon_p^{1.8} (1 - RH / 100)^{2.2} \quad \text{Eq. 4.17}$$

$D_{e,CO_2}$ : diffusion coefficient of CO<sub>2</sub> in concrete (m<sup>2</sup>/sec),  $\epsilon_p$ : porosity in concrete (%),  $RH$ : relative humidity (%).

In Eq. 4.17,  $\epsilon_p$  is the porosity in concrete and it is defined as a ratio of porosity over volume of concrete. Porosity of concrete in initial time of hydration



can be predicted using hydration model proposed by papadakis as in Eq. 3.15 in chapter 3. Porosity becomes smaller with hydration process because of increased volume of hydrated cement particles and porosity can be expressed in Eq. 3.16 at an arbitrary time  $t$  after hydration. Porosity with water to cement ratio and hydration time is shown in Fig. 4.2. Fig. 4.3 shows porosity with hydration time. Diffusion coefficient of CO<sub>2</sub> in concrete can be calculated using porosity of concrete with time as seen in Fig. 4.4. Fig. 4.5 shows a diffusion coefficient of CO<sub>2</sub> in concrete with hydration time and parameter change affected by relative humidity. Parameter becomes lower with increasing relative humidity from 0 to 100.

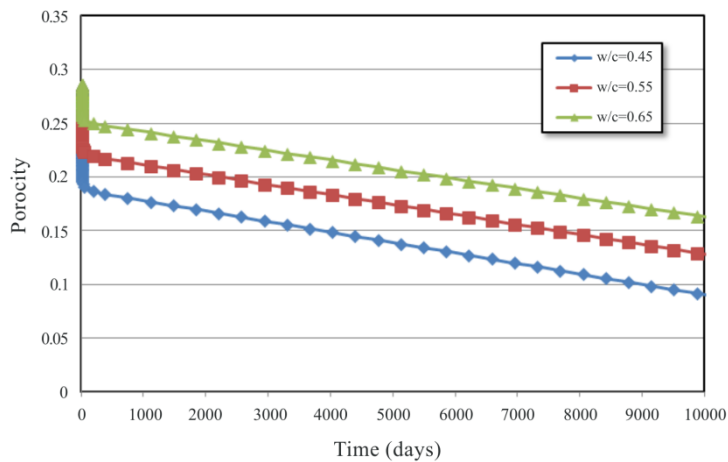


**Fig. 4.2** Porosity according to w/c ratio.

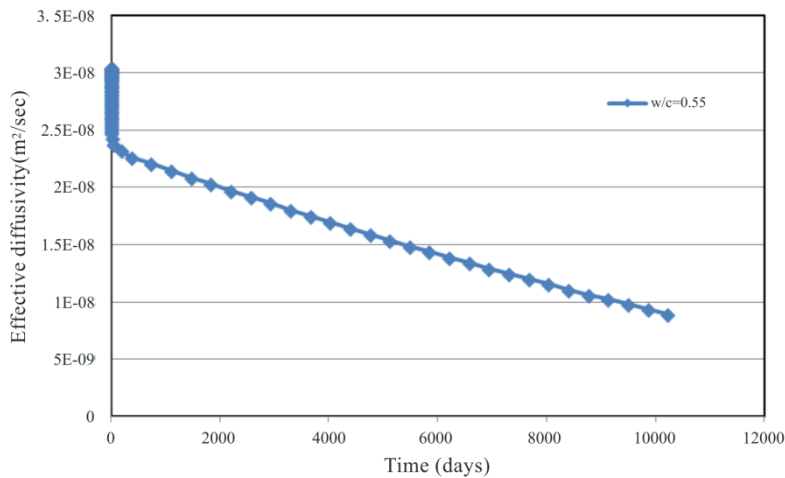
Especially, it shows 0 in case of 100% relative humidity and CO<sub>2</sub> diffusion in concrete does not happen under these conditions because the porosity, that is a flow channel of CO<sub>2</sub> gas, is filled with water. On the other hand, diffusion of gas in porosity is the fastest when relative humidity is 0.

Fig. 4.6 shows effective diffusivity of CO<sub>2</sub> with water to cement ratio change

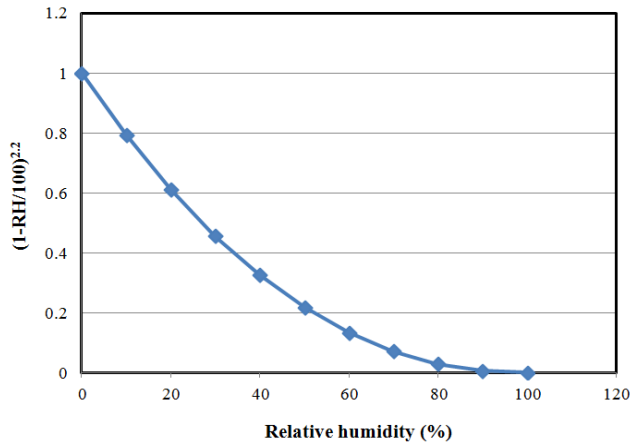
under the condition of 50% relative humidity in 3 months after hydration. Effective diffusivity becomes higher with increasing water to cement ratio because of increasing porosity at higher W/C.



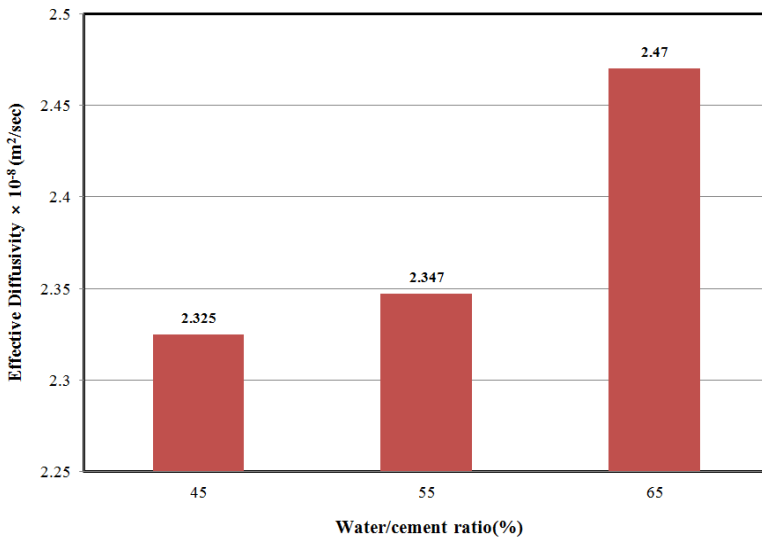
**Fig. 4.3** Porosity according to w/c ratio with time.



**Fig. 4.4** Effective diffusivity change with time (RH=50%).



**Fig. 4.5** Effective diffusivity of CO<sub>2</sub> according to relative humidity.



**Fig. 4.6** Effective diffusivity according to w/c ratio.

(RH=50%, Curing time= 90 days).

### 4.3.3 Reaction Rate Constant Between Ca(OH)<sub>2</sub> and CO<sub>2</sub>

Reaction rate constant between Ca(OH)<sub>2</sub> and CO<sub>2</sub> in concrete is affected by temperature, humidity, porosity and water to cement ratio. Carbonation speed is

proportional to reaction rate constant but it is difficult to estimate reaction rate constant quantitatively so the value is estimated through the inverse analysis by comparing experimental results with analytical result assuming reaction rate constant.

Masuda (1991)<sup>41)</sup> proposed reaction rate constant between Ca(OH)<sub>2</sub> and CO<sub>2</sub> in concrete through the inverse analysis by comparison experimental results with analysis results assuming reaction rate constant. The result with water to cement ratio is shown in Table 4.1.

**Table 4.1** Reaction velocity coefficient.

W/C	k(1/day)
0.45	300,000
0.55	420,000
0.65	750,000

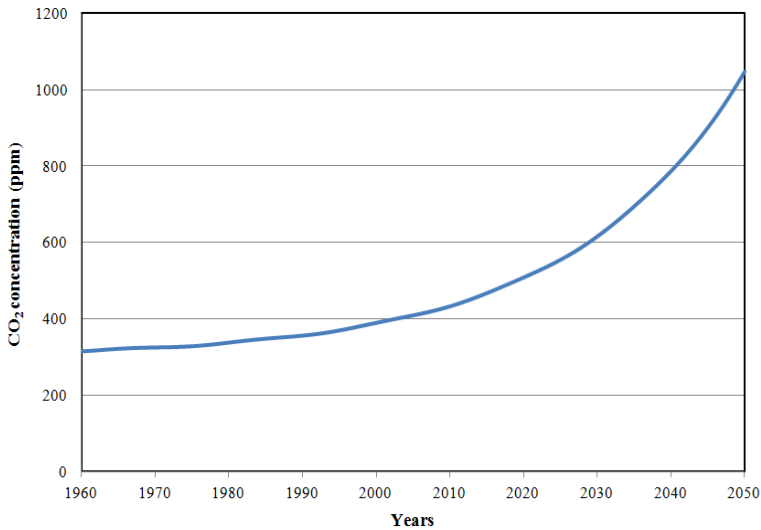
#### 4.3.4 Concentration of Carbon Dioxide in the Atmosphere

Concrete carbonation is a phenomenon where CO<sub>2</sub> diffuses from the point of high concentration to the point of low concentration and the flow rate is proportional to concentration gradient. Therefore, CO<sub>2</sub> concentration change in the air affects CO<sub>2</sub> diffusion in concrete.

Hukusima proposed CO<sub>2</sub> concentration in the air as in Eq. 4.18 based on parameters measured in Hawaii, United States Marine Weather Bureau and the result are shown in Fig. 4.7.

$$C(t) = 14.4128 \exp(0.00357t) + 1.9946 \sin(01.9867 + 0.553958t) + 300.7913 \quad \text{Eq. 4.18}$$

Where t: month



*Fig. 4.7 Expectation of CO<sub>2</sub> concentration change.*

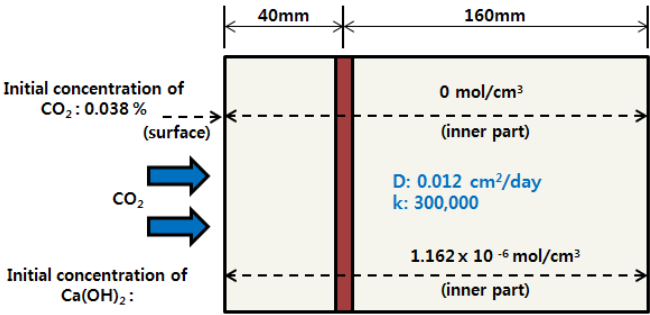
## 4.4 Prediction for Concrete Carbonation Progress Using FEMA

### 4.4.1 Analysis Outline

Carbonation prediction using FEMA requires input parameters to be analyzed: 1) the initial concentration of Ca(OH)<sub>2</sub>, 2) diffusion coefficient of CO<sub>2</sub> in concrete, 3) The reaction rate constant between Ca(OH)<sub>2</sub> and CaCO<sub>3</sub> and 4) CO<sub>2</sub> concentration in the air. The values 1) and 2) are predicted by hydration model and 3) and 4) is determined through literature review. Required input parameters are assumed as shown in Table 4.2 in this study with water to cement ratio and concrete mix proportion. Model for analysis is a one-dimensional model that consider only horizontal direction diffusion and material was assumed a homogeneous isotropic. Fig. 4.8 shows input data used in FEMA in case of water to cement ratio of 0.45.

**Table 4.2** Assumptions of variable for analysis.

W/C	initial concentration of Ca(OH) <sub>2</sub> ×10 <sup>-6</sup> (mol/cm <sup>3</sup> )	CO <sub>2</sub> concentration (%)	reaction rate constant (1/day)	diffusion coefficient (cm <sup>2</sup> /day)	Ca(OH) <sub>2</sub> loss rate (%)
0.45	1.162	0.38	300,000	0.012	60
0.55	0.876	0.38	420,000	0.02	60
0.65	0.732	0.38	750,000	0.05	60



**Fig. 4.8** FEM carbonation analysis model (w/c=0.45).

#### 4.4.2 Prediction of Concrete Carbonation Depth with W/C Using FEMA

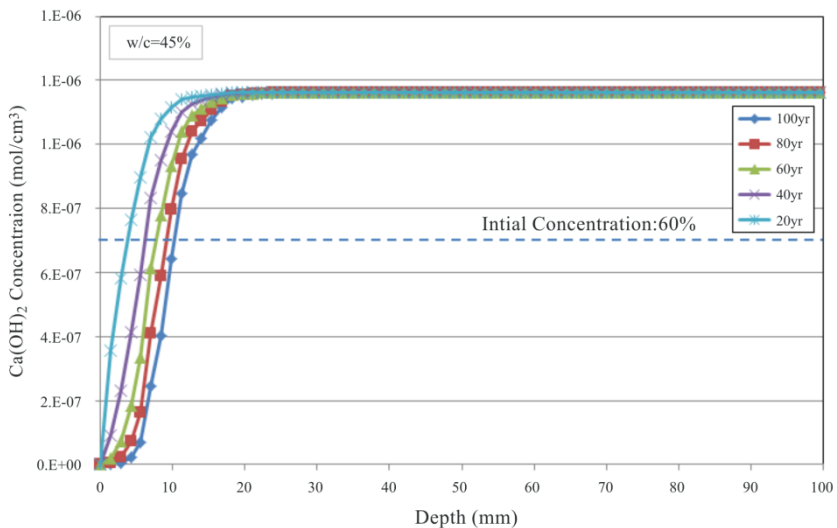
Figs. 4.9 - 4.11 show the results of prediction of Ca(OH)<sub>2</sub> distribution in concrete with time by the water to cement ratio. Concrete carbonation depth is assumed to the point where pH value is 10.6. This point is determined as a point where the concentration of Ca(OH)<sub>2</sub> reaches 60% compared to the initial concentration of Ca(OH)<sub>2</sub> as a quantitative evaluation basis for carbonation depth in concrete proposed in chapter 3. As a result, carbonation depth increases with increasing water to cement ratio and passing time.

Carbonation depth becomes deeper with the increase of water to cement ratio because diffusion coefficient of CO<sub>2</sub> in concrete becomes higher, as a result concentration gradient of Ca(OH)<sub>2</sub> is sweeper. On the other hand, carbonation

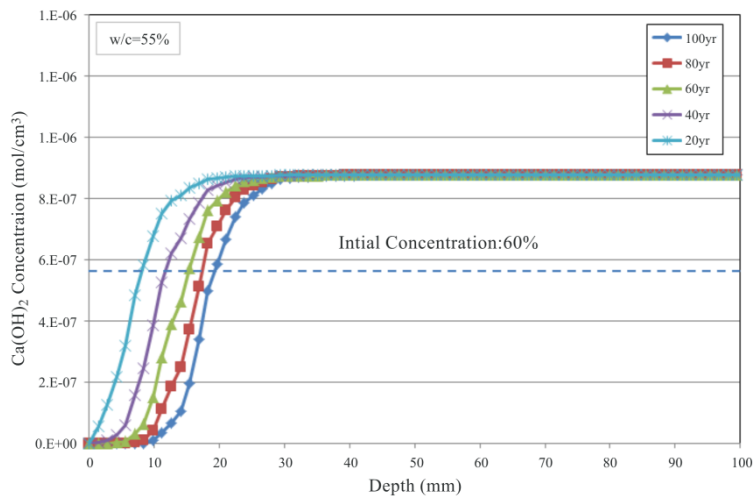
depth becomes shallower as water to cement ratio becomes lower because diffusion coefficient of CO<sub>2</sub> in concrete becomes lower, as a result concentration gradient of Ca(OH)<sub>2</sub> is steeper.

Fig. 4.12 shows a predicted carbonation depth with water to cement ratio and carbonation time using a quantitative evaluation basis that carbonation depth is a point where the concentration of Ca(OH)<sub>2</sub> reaches 60% compared to the initial concentration of Ca(OH)<sub>2</sub> and also mass reduction rate of Ca(OH)<sub>2</sub>, CaCO<sub>3</sub> is 1:3 at there.

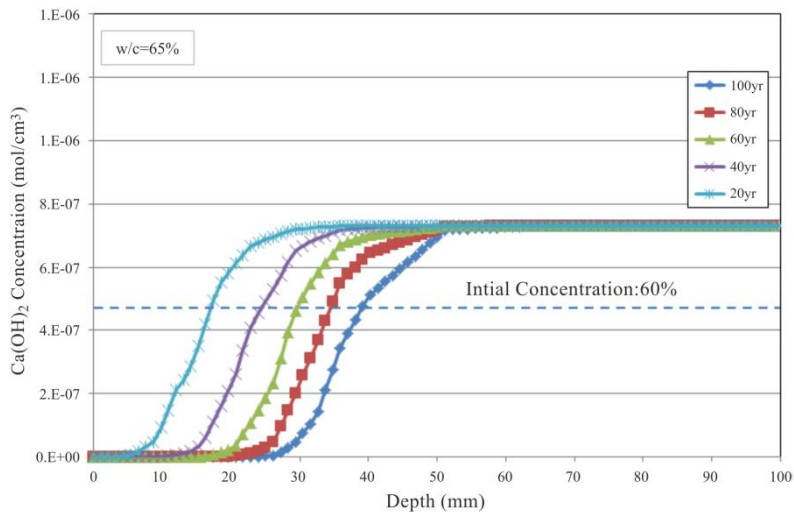
Predicted carbonation depth in this study is compared with carbonation depth predicted by Ko, KyeongTaek, Kishitani, JSCE with water to cement ratio and the result is shown in Fig. 4.13 ~ 4.15. Carbonation depth predicted using a quantitative evaluation basis shows a similar result compared with predicted ones by Kishitani, JSCE.



**Fig. 4.9** FEM carbonation analysis ( $w/c=0.45$ ).

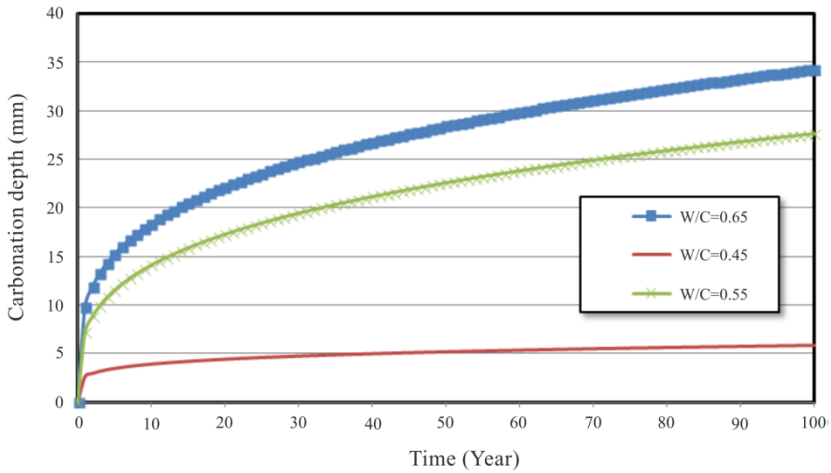


**Fig. 4.10** FEM carbonation analysis (w/c=0.55).

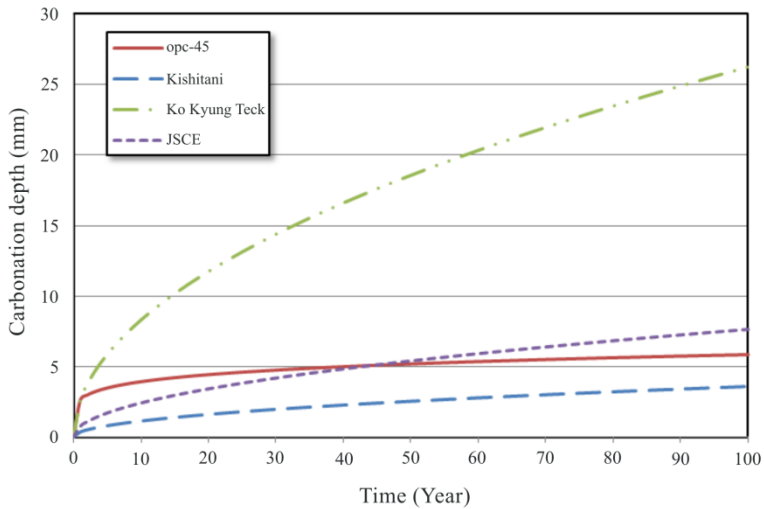


**Fig. 4.11** FEM carbonation analysis (w/c=0.65).

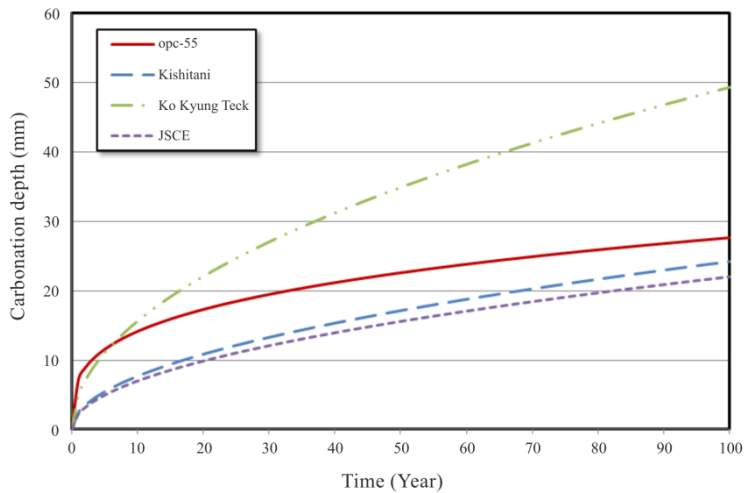




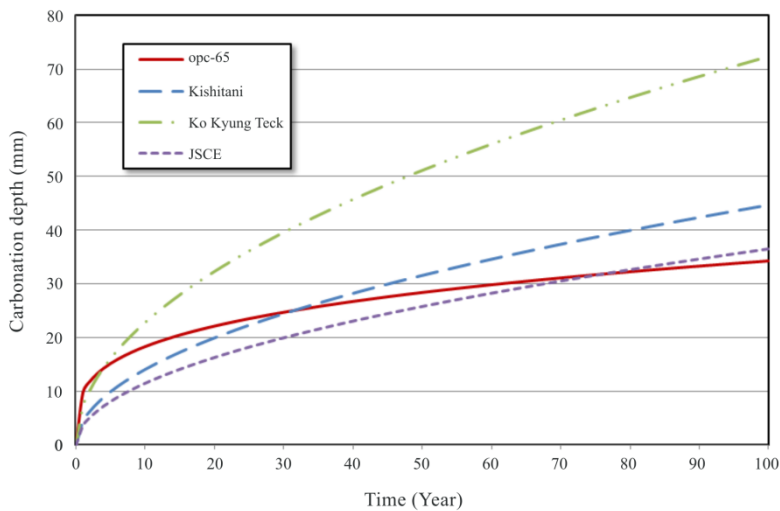
**Fig. 4.12** FEM carbonation analysis result according to w/c ratio.



**Fig. 4.13** Comparison between other carbonation depth expectation models (w/c=0.45).



**Fig. 4.14** Comparison between other carbonation depth expectation models ( $w/c=0.55$ ).



**Fig. 4.15** Comparison between other carbonation depth expectation models ( $w/c=0.65$ ).

## 4.5 Summary

In this chapter, at first, the required input parameters is determined through literature review and experiments result in order to predict carbonation depth using a FEMA. Secondly, carbonation depth by FEMA is predicted using a proposed quantitative evaluation basis. After comparing predicted carbonation depth of this study with other researcher's findings, conclusions in this chapter can be drawn as follows:

1. Predicted carbonation depth with carbonation time using a quantitative evaluation basis that carbonation depth is a point where the concentration of Ca(OH)<sub>2</sub> reaches 60% compared to the initial concentration of Ca(OH)<sub>2</sub> and also mass reduction rate of Ca(OH)<sub>2</sub>, CaCO<sub>3</sub> is 1:3 is similar to ones proposed by Kishitani and JSCE.
2. From the FEMA, the carbonation depth in concrete is the point where the concentration of Ca(OH)<sub>2</sub> reaches 60% compared to the initial concentration of Ca(OH)<sub>2</sub> and it becomes deeper with carbonation times.

