Chapter 3

Evaluation of Concrete Carbonation

Degree Using a TG/DTA

3.1　Outline

In this chapter, at first, validation for hydration model effectiveness is conducted by comparing predicted values by model with measured one using TG/DTA before using it as a prediction model of initial concentration of $Ca(OH)_2$ to evaluate carbonation degree for all mixtures.

Secondly, correlation analysis between pH value and the amount of $Ca(OH)_2$, $CaCO_3$ using TG/DTA in cement or concrete specimen with carbonation time was conducted experimentally to deduct qualitative evaluation basis of service life for carbonation. Also, pH value and galvanic corrosion experiment using a potentiastat when the specimens were fully carbonated were tested to propose qualitative evaluation basis for carbonated depth.

3.2　Cement Hydration Model

Cement hydration model can predict hydration products and porosity quantitatively using a hydration equations and stoichiometric of reactants and products relationship during the hydration reaction. These hydration model researches began in Japan[33], U.S.[34], Netherlands[35] centered on the 1990s and have been actively studied to enhance the accuracy for prediction of the model. Fig. 3.1 is a process of calculating hydration products theoretically. The type and amount of oxide is different depending on the type of cement and the amount of compound is determined through Bogue's Eq[36]. Considering used cement; these cement compounds are combined with water to produce hydration products and the type and amount of it is determined with water to cement ratio, aggregate to cement ratio, hydration time.
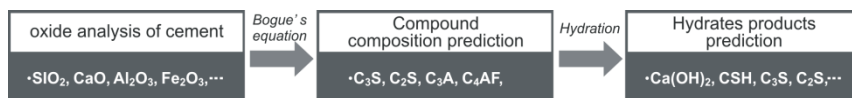
Fig. 3.1 *Calculation outline of hydration product.*

3.2.1 Prediction of Hydration Products

Portland cement has different composition of oxide depends on cement types. In the case of type I ordinary Portland cement, the composition with the kind of oxides is shown in Table 3.1.[37]

Table 3.1 *Oxide analysis of ordinary Portland cement (%).*

Oxide	SiO_2	Al_2O_3	Fe_2O_3	CaO	SO_3	Remains
Cement type I	21.1	6.2	2.9	65.0	2.0	2.8

The composition of cement compounds according to cement type can be calculated using a Bogue's equation (Eq. 3.1) and the analysis of cement oxide. Table 3.2 shows composition of cement compounds of type I ordinary Portland cement calculated from Eq. 3.1. Main compounds of type I ordinary Portland cement combines with water and hydration proceeds. The hydration process is shown in Eqs. 3.2 - 3.7. Herein, CH is calcium hydroxide, H is water (H_2O), $C_3S_2H_3$ is calcium silicate hydrate, CH_2 is gypsum. The hydration process of C_4AF, C_3A of reactants is affected by gypsum. So, Eqs. 3.4 and 3.5 are a hydration when the gypsum is, Eqs. 3.6 and 3.7 are when the gypsum is used up.

* Bogue's equations

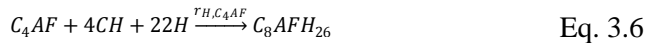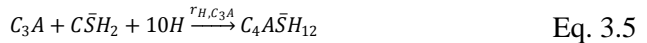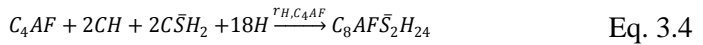$$C_3S = 4.071CaO - 7.600SiO_2 - 6.718Al_2O_3 - 1.430Fe_2O_3 - 2.852SO_3 \quad \text{Eq. 3.1}$$

$$C_2S = 2.867SiO_2 - 0.7544C_3S$$

$$C_3A = 2.650Al_2O_3 - 1.692Fe_2O_3$$

$$C_4AF = 3.043Fe_2O_3$$

Table 3.2   *Compound composition of ordinary Portland cement (%).*

Compound composition	ratio
C$_3$S(3CaO . SiO$_2$)	52.8
C$_2$S(2CaO . SiO$_2$)	20.7
C$_3$A(3CaO . Al$_2$O$_3$)	11.5
C$_4$AF(4CaO . Al$_2$O$_3$. Fe$_2$O$_3$)	8.8

$$2(C_3S) + 6H \xrightarrow{r_{H,C3S}} C_3S_2H_3 + 3CH \qquad \text{Eq. 3.2}$$

$$2(C_2S) + 4H \xrightarrow{r_{H,C23S}} C_3S_2H_3 + CH \qquad \text{Eq. 3.3}$$

$$C_4AF + 2CH + 2C\bar{S}H_2 + 18H \xrightarrow{r_{H,C4AF}} C_8AF\bar{S}_2H_{24} \qquad \text{Eq. 3.4}$$

$$C_3A + C\bar{S}H_2 + 10H \xrightarrow{r_{H,C3A}} C_4A\bar{S}H_{12} \qquad \text{Eq. 3.5}$$

$$C_4AF + 4CH + 22H \xrightarrow{r_{H,C4AF}} C_8AFH_{26} \qquad \text{Eq. 3.6}$$

$$C_3A + CH + 12H \xrightarrow{r_{H,C3A}} C_4AH_{13} \qquad \text{Eq. 3.7}$$

Initial molar concentration of main constituent can be calculated by Eqs. 3.8 and 3.9.

$$[i]_0 = \frac{m_i m_{cl} p_c (1-\varepsilon_{air})}{MW_i(1+\frac{wp_c}{cp_w}+\frac{ap_c}{cp_a})} \qquad \text{Eq. 3.8}$$

$$[C\bar{S}H_2]_0 = \frac{m_i m_{cl} p_c (1-\varepsilon_{air})}{MW_{gy}1+\frac{wp_c}{cp_w}+\frac{ap_c}{cp_a})} \qquad \text{Eq. 3.9}$$

$$F_i(t) = 1 - \frac{[i]}{[i]_0} = 1 - [1-k_H, t(1-n_i)]^{1/1-n_i} \qquad \text{Eq. 3.10}$$

([i]$_0$ is an initial molar concentration of constituent (i=C$_3$S, C$_2$S, C$_4$AF, C$_3$A))

Herein, mi is a compound composition of ordinary Portland cement in Table 3.2. In Eq. 3.10, m$_{cl}$ and m$_{gy}$ is the weight fraction of clinker, gypsum ($m_{gy} = 1 - m_{cl}$). ρ_C and ρ_w are the density of cement, water. w/c and a/c are the water to cement ratio, aggregate to cement ratio in concrete mixture. In Eq. 3.10, F_i, weight fraction of each compound in clinker with hydration time,

can be calculated by substituting k_H. i and n_i for value in Table 3.3 and the result is shown in Fig. 3.2. Eqs. 3.11 – 3.14[38] are used to calculate molar concentration of carbonatable substances in concrete at an arbitrary time after hydration and they are based on Eqs. 3.2 - 3.7.

Table 3.3   *Parameters of major constituent of ordinary Portland cement.*[38]

	C$_3$S	C$_2$S	C$_4$AF	C$_3$A	CH$_2$
Exponent n_i	2.65	3.10	3.81	2.41	-
Coefficient k_{ni} (20C)$\times 10^5$(s$^-$)	1.17	0.16	1.00	2.46	-
Molar weight MW$\times 10$ (kg/mol)	228.3	172.22	485.96	270.18	172.17

In Eq. 3.11, the molar concentration of $Ca(OH)_2$ can be calculated by consumed molar concentration of $Ca(OH)_2$ that is used in the process of hydration subtracted summing molar concentration of $Ca(OH)_2$ produced by hydration of each main compounds of cement. The molar concentration of CSH, C_3S, C_2S can be calculated using Eqs. 3.12 - 3.14 induced from Eqs. 3.2 - 3.7. The results of calculated molar concentration of each component with hydration time are shown in Fig. 3.3.

$$[Ca(OH)_2] =$$
$$\frac{3}{2}\,[C_3S]_0 F_{C_3S} + \frac{1}{2}\,[C_2S]_0 F_{C_2S} - 4[C_4AF]_0 F_{C_4AF} - [C_3A]_0 F_{C_3A} + [C\bar{S}H_2]_0 \qquad \text{Eq. 3.11}$$

$$[CSH] = \frac{1}{2}\,[C_3S]_0 F_{C_3S} + \frac{1}{2}\,[C_2S]_0 F_{C_2S} \qquad \text{Eq. 3.12}$$

$$[c_3s] = [c_3s]_0(1 - F_{c_3s}) \qquad \text{Eq. 3.13}$$

$$[c_2s] = [c_2s]_0(1 - F_{c_2s}) \qquad \text{Eq. 3.14}$$
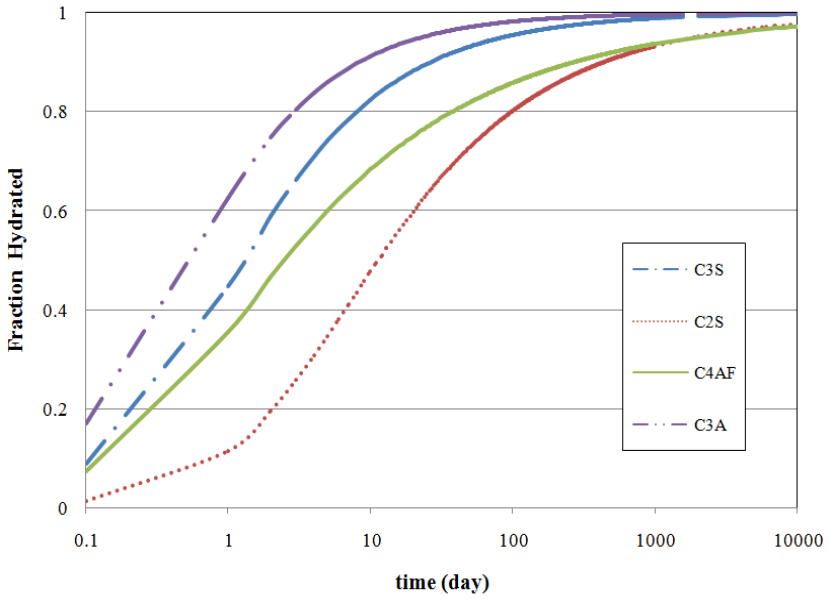
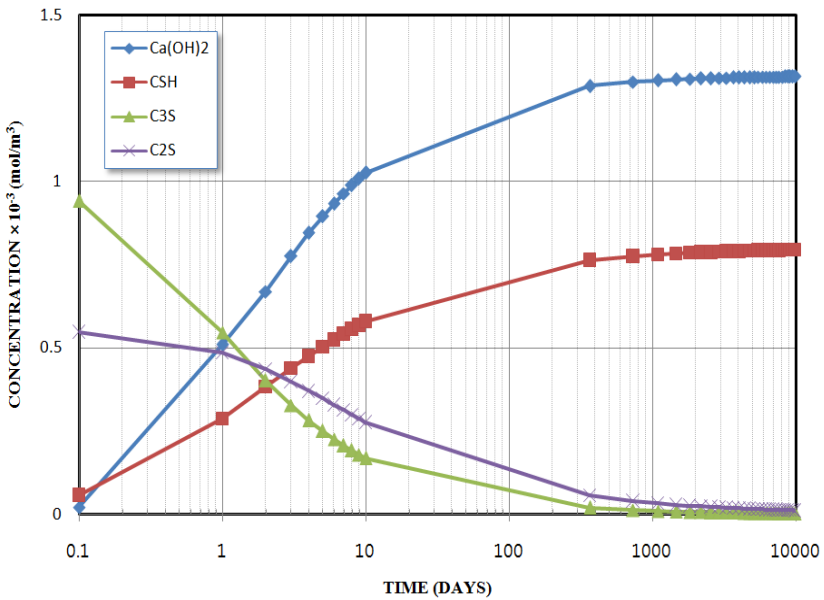***Fig. 3.2*** *Hydration speed of the four major constituents.*

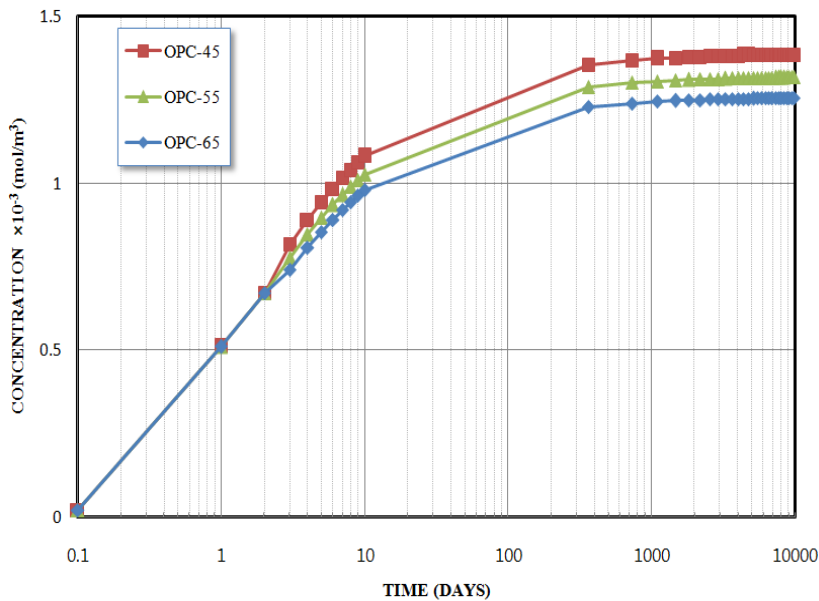***Fig. 3.3*** *Hydration product change with hydration time.*

Fig. 3.4 *Ca(OH)$_2$ quantity change with W/C ratio (a/c=3).*

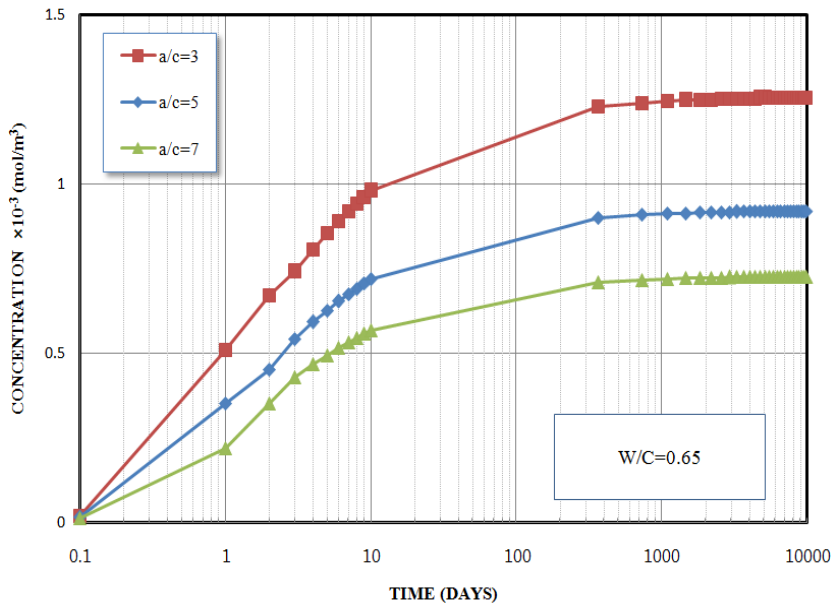***Fig. 3.5*** *Ca(OH)$_2$ quantity change with a/c ratio (w/c= 0.65).*

Hydration model can consider w/c, a/c. Figs. 3.4 and 3.5 show concentration change of $Ca(OH)_2$ with a/c, w/c respectively.

3.2.2 Prediction of Porosity Using a Cement Hydration Model

Porosity (ϵ_p) in concrete is defined as the ratio of porosity over concrete volume. Initial porosity in concrete is proposed by papadakis as a function of w/c, a/c as in Eq. 3.15. Porosity in concrete becomes smaller after hydration because of hydration products and at an arbitrary time t, it is expressed in Eq. 3.16.[39]

$$\epsilon_0 = \frac{\frac{w\rho_c}{c\rho_w}(1-\epsilon_{air})}{\left(1+\frac{w\rho_c}{c\rho_w}+\frac{a\rho_c}{c\rho_a}\right)} + \epsilon_{air} \qquad \text{Eq. 3.15}$$

$$\epsilon(t) = \epsilon_0 - \Delta\epsilon_H(t) \qquad \text{Eq. 3.16}$$

w/c: water to cement ratio

ρ_c, ρ_w, ρ_α: density of cement, water, aggregate

a/c: aggregate to cement ratio

ϵ_{air}: porosity in concrete

$\in(t)$: porosity in concrete at arbitrary time t

$\in_H(t)$: decreased porosity by hydration at time t

In Eq. 3.16, $\Delta_{\in H}(t)$ is a decrease in porosity with cement hydration time and can be expressed in Eqs. 3.17 and 3.18 because hydration products becomes bigger than cement in the process of Eqs. 3.2 - 3.7. Herein, t* is a time when gypsum that control hydration speed is used up. So, porosity with time can be calculated using Eqs. 3.17 and 3.18 when gypsum is / is used up respectively.

$$\Delta\epsilon_H(t) = [C_3S]_0 F_{C_3S} \Delta\bar{V}_{C_3S} + [C_2S]_0 F_{C_2S} \Delta\bar{V}_{C_2S}$$
$$+ [C_3A]_0 F_{C_3A} \Delta\bar{V}_{C_3A,\bar{S}} \qquad \text{Eq. 3.17}$$
$$+ [C_4AF]_0 F_{C_4AF} \Delta\bar{V}_{C_4AF,\bar{S}}, \qquad 0 \leq t \leq t^*$$

$$\Delta\epsilon_H(t) = [C_3S]_0 F_{C_3S} \Delta\bar{V}_{C_3S}$$
$$+ [C_2S]_0 F_{C_2S} \Delta\bar{V}_{C_2S}$$
$$+ [C_3A]_0 F_{C_3A}(t^*) \Delta\bar{V}_{C_3A,\bar{S}}$$
$$+ [C_3A]_0 \left(F_{C_3A} - F_{C_3A}(t^*) \right) \Delta\bar{V}_{C_3A} \qquad \text{Eq. 3.18}$$
$$+ [C_4AF]_0 F_{C_4AF}(t^*) \Delta\bar{V}_{C_4AF,\bar{S}}$$
$$+ [C_4AF]_0 \left(F_{C_4AF} - F_{C_4AF}(t^*) \right) \Delta\bar{V}_{C_4AF}, \qquad t \geq t^*$$

Where, $[i]_0$: initial concentration of compound i. (i = C$_3$S, C$_2$S, C$_4$AF, C$_3$A)

$[F]_i$: weight fraction of compound i with hydration time (i = C$_3$S, C$_2$S, C$_4$AF, C$_3$A)

$\Delta\bar{V}_i$: volume difference between reactants and products (I = C$_3$S, C$_2$S, C$_4$AF, C$_3$A)

Volume difference between reactants and products $\Delta\bar{V}_i$ uses a value in Table 3.4, initial porosity and change in porosity with hydration time, w/c are shown in Figs. 3.6 and 3.7.

Table 3.4 *Molar volumes differences.*[38)]

Hydration reaction	(1)	(2)	(3)	(4)	(5)	(6)
$\Delta\bar{V}$ X 10^6, m^3/mol	53.28	39.35	~220	155.86	~230	149.82
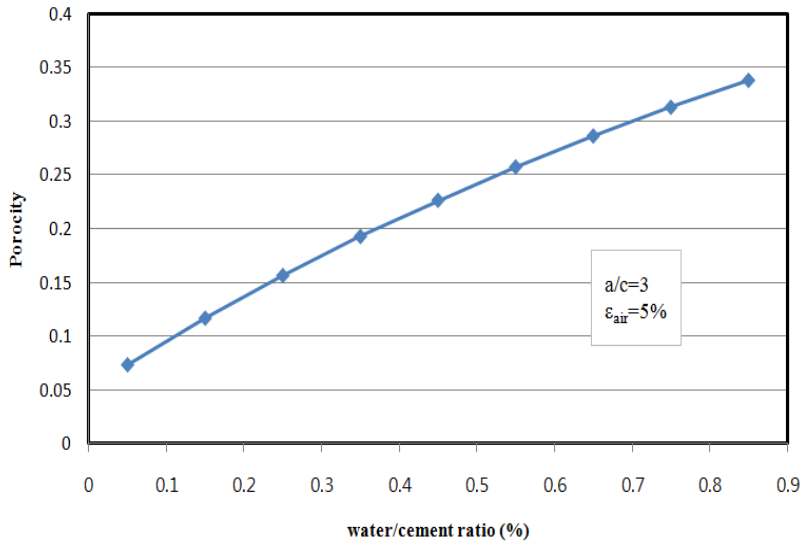
Fig. 3.6   *Porosity according to w/c ratio.*
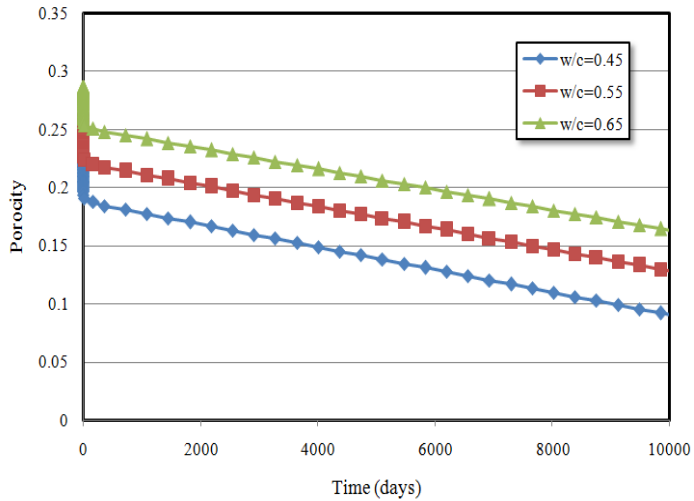
Fig. 3.7   *Porosity according to w/c ratio with time.*

3.3   Quantitative Evaluation Experiments of Ca(OH)$_2$ According to Hydration Time in Order to Verify Cement Hydration Model

3.3.1   Overview of Experiments

Cement hydration model has a merit that it can predict the amount of products quantitatively such as Ca(OH)$_2$ considering all mixtures. In order to investigate the suitability of hydration model as a method to calculate the amount of Ca(OH)$_2$ to an input data in FEMA, comparison between predicted values by model with measured one using TG/DTA is conducted.

So, in this chapter, the amount of Ca(OH)$_2$ in 3, 7, 28, 56 and 91 days after hydration of concrete and mortar are measured and the results are compared with ones that are calculated by hydration model. Also, correlation between pH value and the amount of Ca(OH)$_2$ in concrete are measured experimentally with hydration time.

3.3.2   Cast and Curing Method of Test Specimens

Concrete and mortar specimens were cast and the details of mix design is shown in Tables 3.5 and 3.6 according to water to cement ratio. The size of specimens in case of mortar is 5 cm $\times$ 5 cm $\times$ 5 cm of cube. Concrete specimens were fabricated in a cylinder shape and the size is Φ10 cm $\times$ 20 cm. Ordinary Portland cement is used as a binder and the properties are shown in Table 3.7. The properties of sand and aggregate are shown in Table 3.8.

Table 3.5 *Types of concrete specimens.*

No.	Index	W/C	Unit weight (kg/m^3)			
			W	C	S	G
1	C-OPC-45	0.45	216	480	751	866
2	C-OPC-55	0.55	206	375	863	866
3	C-OPC-65	0.65	202	311	944	850

Concrete and mortar specimens are made respectively in accordance with KS F 2403, KS L 5109. Forms for specimens were removed after 24 hours of casting, and they are cured at 20±3 ℃ water in 3, 7, 28, 56 and 91 days.

Table 3.6 *Types of mortar specimens.*

No.	Index	W/C	Weight mixing ratio		
			C	S	W
4	M-OPC-45	0.45	1	2.45	0.45
5	M-OPC-55	0.55	1	2.45	0.55
6	M-OPC-65	0.65	1	2.45	0.65

Table 3.7 *Physical property of cement.*

Specific gravity	Fineness (cm^2/g)	Stability (%)	Setting time (min)		Compressive strength (MPa)		
			Initial	Final	3 days	7 days	28 days
3.15	3,520	0.15	207	350	211	300	389

Table 3.8 *Physical Property of aggregates.*

	Specific gravity	Fineness modulus	Absorption (%)	Unit volume weight (Kg/m^3)	Passing rate through 0.08mm sieve (%)
sand	2.60	2.7	1.98	1,470	1.8
coarse aggregates	2.59	6.9	0.55	1,526	0.3

3.3.3   Measurement Items and Method

(1) A Quantitative Measurement of $Ca(OH)_2$

Sample for measurement of $Ca(OH)_2$ in hardened cement or concrete is crushed after water curing according to curing time. The crushed sample is dried for 24 hours in a dry oven at 105℃ after stopping hydration with an acetone. After that, the samples is crushed to powder until it can pass # 100 sieve and it is used to measure $Ca(OH)_2$ quantitatively using a TG/DTA.

(2) Measurement of pH[40)]

Powder samples for measurement of pH are same to one for TG/DTA. To measure pH of power, 5 g powder is mixed with 200 g of distilled water and the aqueous solution is tested with a pH meter. The measured value is determined with an average of 3 test results. The outline of an experiment is shown in Fig. 3.8.

| a) weighing material | b) mixing concrete | c) making specimens |
| d) curing specimens | e) TG/DTA measurement | f) pH measurement |

Fig. 3.8   Outline of experiment.

3.3.4 Experimental Results and Analysis

(1) The Analysis Results of Quantitative Measurement of Ca(OH)$_2$

Figs. 3.9 and 3.10 show a weight loss of $Ca(OH)_2$ and molar concentration of concrete that uses ordinary Portland cement and water to cement ratio of 0.45, 0.55. 0.65 according to curing time respectively. Regardless of water to cement ratio, the amount of $Ca(OH)_2$ is increased with curing time but the speed of increasing becomes slow, because of the fact that hydration proceed rapidly in initial times. As a result, the hydration degree reaches 90% in 3 months and the speed of hydration proceeds slow after 3 months. In case of water to cement ratio high, the amount of $Ca(OH)_2$ decreases because the amount of cement in concrete decreases as a result CaO that makes $Ca(OH)_2$ through hydration decreases in a high water to cement ratio.

(2) The Results of pH Measurement

Fig. 3.11 shows the relationship between pH value and the amount of $Ca(OH)_2$ in a hardened cement or concrete. In case of uncarbonated concrete, pH value is over 13 in some research papers because they measure it in pore solution in concrete. However, in this experiment, pH value is measured in the aqueous solution that is mixed with distilled water and powder. As a result, the value is lower than 13 but positive correlation between pH value and the amount of $Ca(OH)_2$ is confirmed experimentally.

3.3.5 Comparison Between Quantitative Prediction and Experimental Result of Ca(OH)$_2$

Figs. 3.12 – 3.14 show comparison results of $Ca(OH)_2$ between predicted

values using hydration model and measured values from TG/DTA experiment
with water to cement ratio 0.45, 0.55 and 0.65 for a concrete that uses ordinary
Portland cement. Regardless of water to cement ratio, the measured value of
Ca(OH)$_2$ is less than that of predicted value but the difference between them
becomes lesser with hydration and is predicted to be much less over 3 months
hydration.
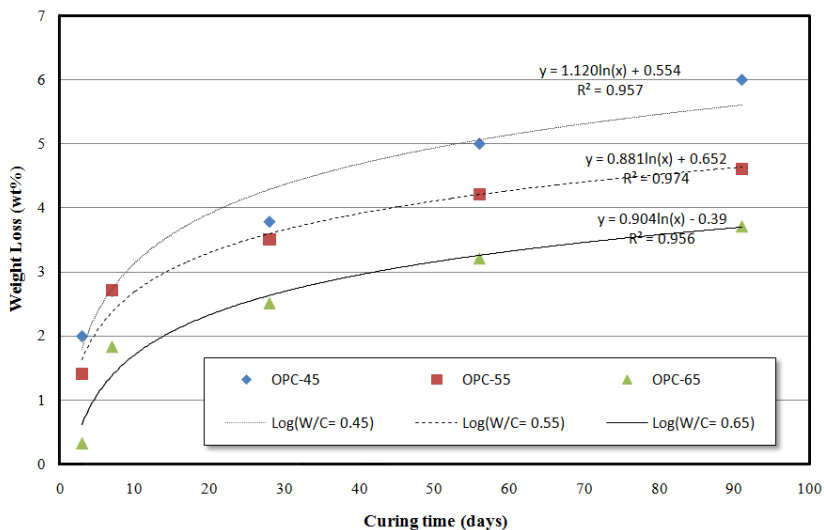
Fig. 3.9 *Weight loss of concrete according to w/c ratio with time.*
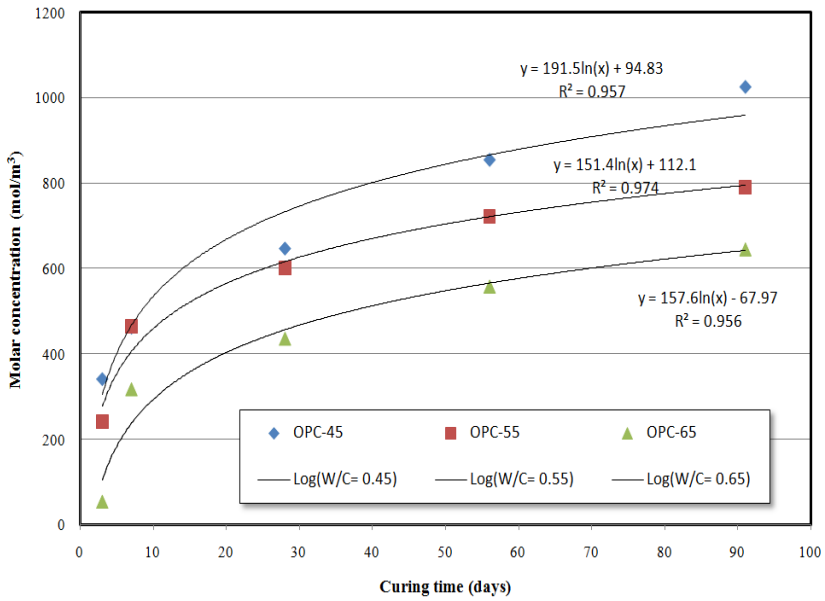
Fig. 3.10 *Molar concentration of concrete according to w/c ratio with time.*
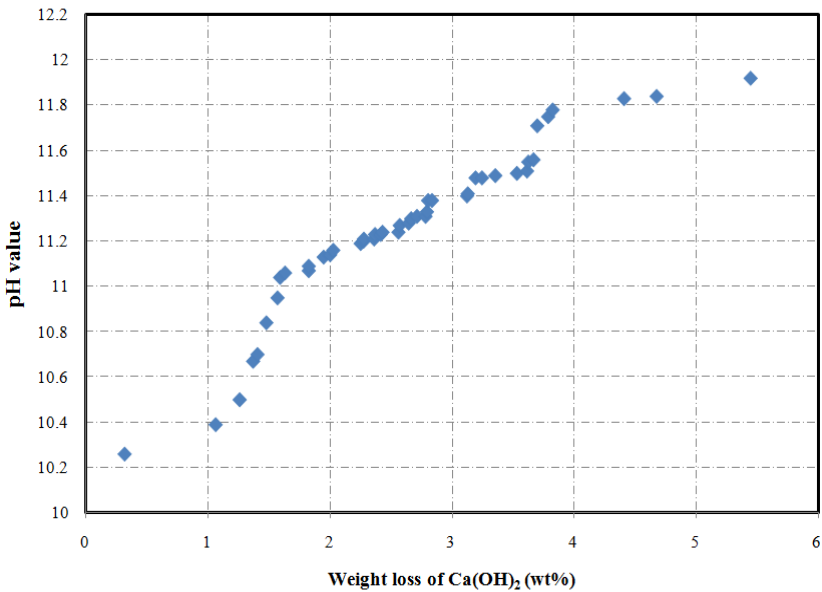
Fig. 3.11 *Relation between pH value and the amount of Ca(OH)$_2$.*
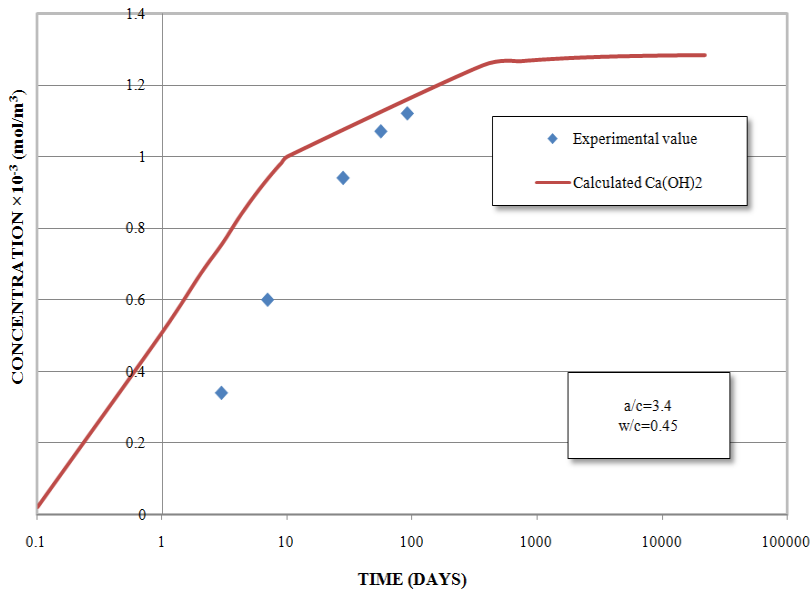
Fig. 3.12 *Comparison between experiment and calculated values of Ca(OH)$_2$ (w/c= 0.45).*
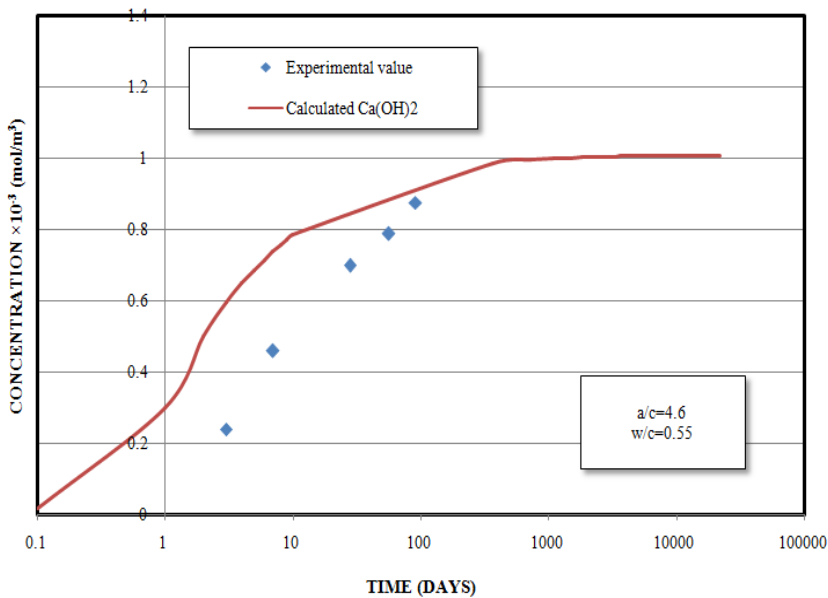
Fig. 3.13 *Comparison between experiment and calculated values of Ca(OH)$_2$ (w/c= 0.55).*
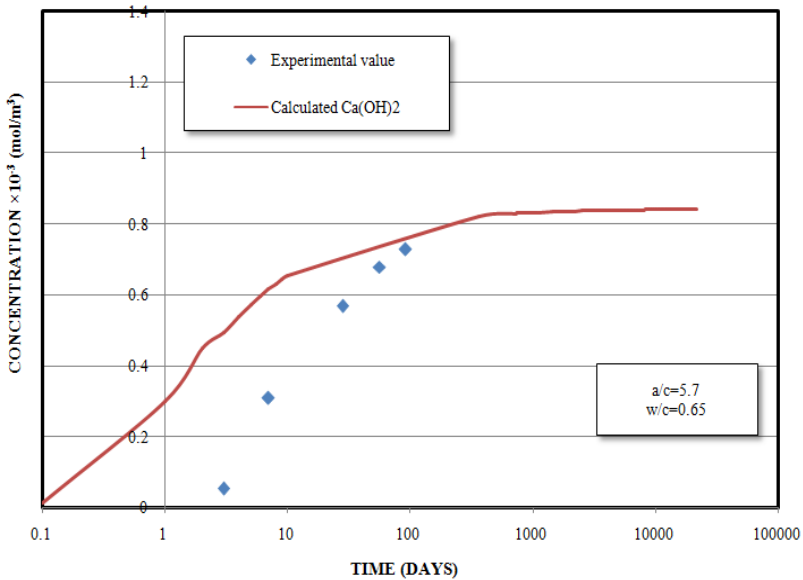
Fig. 3.14 *Comparison between experiment and calculated values of*
$Ca(OH)_2$ (w/c = 0.65).

3.4 Quantitative Measurement of $Ca(OH)_2$ and $CaCO_3$ According to Carbonation

3.4.1 Outline

In chapter 3, the amount of $Ca(OH)_2$, $CaCO_3$ in carbonated concrete is measured quantitatively by 5 mm depth from surface to internal direction with carbonation times. Also, colored section by indicator, measured pH and loss ratio of $Ca(OH)_2$, $CaCO_3$ are compared in each carbonation time in order to create quantitative evaluation basis for carbonation. As a result, quantitative evaluation basis for carbonation is proposed as a remaining ratio of $Ca(OH)_2$ compared to initial concentration of $Ca(OH)_2$.

3.4.2 Cast and Curing Method of Test Specimens

Specimen that is used in carbonation test is the same as mentioned in 3.3.

3.4.3 Accelerated Carbonation Test Method of Concrete and Mortar

In KS F 2584, the size of specimen for concrete is $100 \times 100 \times 400$ mm, it should be cured in 20 ℃ and relative humidity 60% in the air for 28 days after water curing for 28 days. But in this experiment, the specimens are cured in water for 3 months and are cured in air dry for 1 month. The specimens are coated with epoxy on four surfaces so that CO_2 penetrates into concrete in one way as shown in Fig. 3.15. Although the accelerated carbonation condition is determined by a temperature of 20 ℃, 60% of relative humidity, 5% of carbon dioxide in the KS F 2596, but this experiment used a modified set of parameters: temperature of 20 ℃, 60% of relative humidity, 10% of carbon dioxide to accelerate the carbonation reaction. Using the accelerated carbonated specimens for 1, 4, 8, 13, and 26 weeks, measurements of the carbonation depth were carried out by spraying a 1% phenolphthalein solution at the cutting surface of the specimens by 5 mm depths after cutting them using a high-speed cutter. The process of experiment is shown in Fig. 3.16.

3.4.4 Carbonation Depth Measurements by Phenolphthalein Indicator

(1) Carbonation depth measurement method

In accordance with KS F 2596, measurements of the carbonation depth were carried out by spraying a 1% phenolphthalein solution at the cutting surface of the specimens after cutting them using a high-speed cutter. In case of concrete,

the carbonation depths were determined by the average value of 30 points as shown in Fig. 3.17: ten points (the depth from the surface of the concrete to the purple colored region) for three specimens. In case of mortar, the carbonation depths were determined by the average value of 15 points: five points (the depth from the surface of the concrete to the purple colored region) for three specimens as shown in Fig. 3.18.

a) size of specimen   b) painting side with epoxy
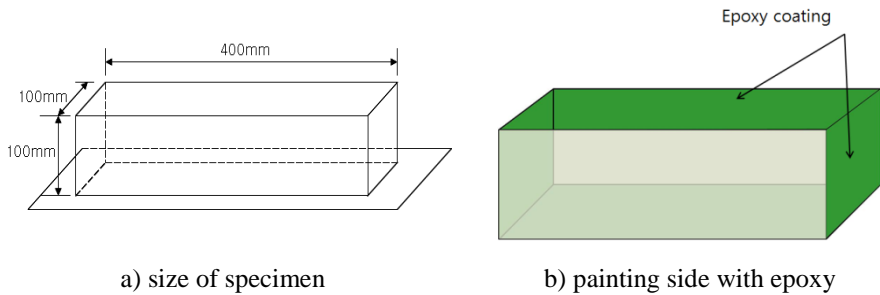
Fig. 3.15   *Preparation of carbonation specimen.*

a) Epoxy application

b) Carbonation acceleration test

c) Splitting specimen

d) Carbonation depth measurement

e) Sampling according to depth

f) TG/DTA analysis
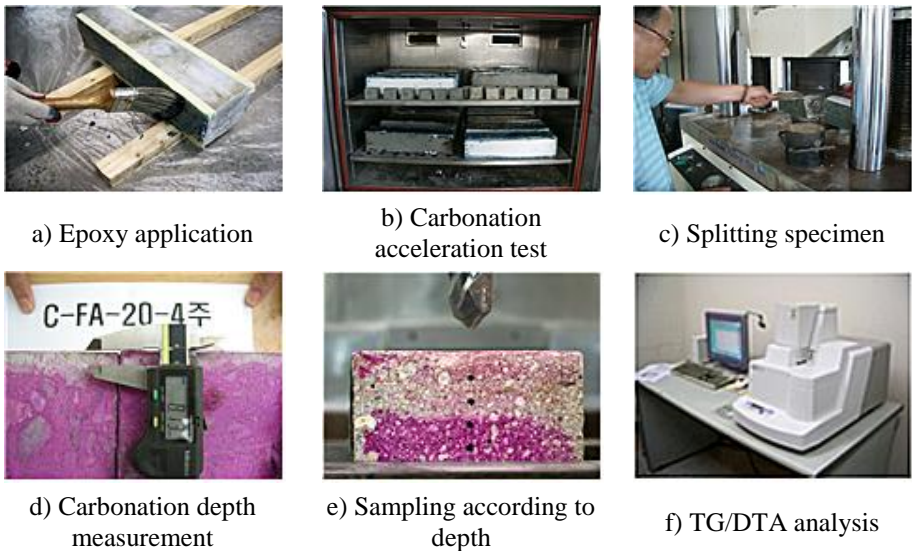
Fig. 3.16   *Experiment outline and process.*
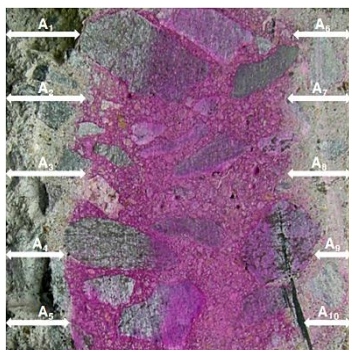
$$^0X_P = \frac{\sum_{i=1}^{10} A_i + \sum_{i=1}^{10} B_i + \sum_{i=1}^{10} C_i}{30}$$

i = measurement position,
A, B, C = types of specimen

Fig. 3.17 *Carbonation depth
measurement of concrete.*
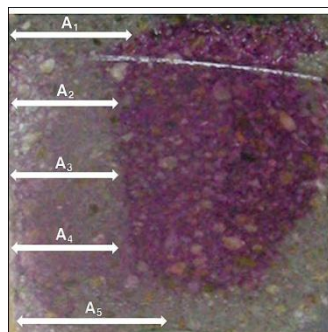
$$^0X_P = \frac{\sum_{i=1}^{5} A_i + \sum_{i=1}^{5} B_i + \sum_{i=1}^{5} C_i}{15}$$

i = measurement position,
A, B, C = types of specimen

Fig. 3.18 *Carbonation depth
measurement of mortar.*

3.4.5 Experimental Results and Analysis

(1) Results and analysis of the carbonation depth by W/C and age by using a phenolphthalein indicator

The carbonation depth presented by color change by spraying an indicator for each specimen with and the type of W/C ratio in concrete and mortar is shown in Tables 3.9 and 3.10.

It shows that carbonation depth increases with accelerated carbonated time for the same water cement ratio and according to the increase of W/C ratio for the same carbonation time.

Table 3.9 *Carbonation depth measurement of concrete by accelerated carbonation time.*
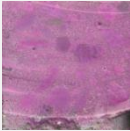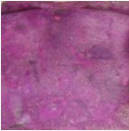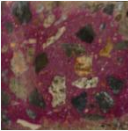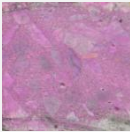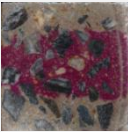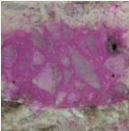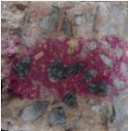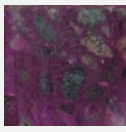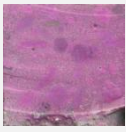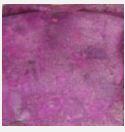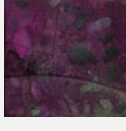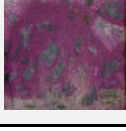
time W/C	scale	1 week	4 weeks	8 weeks	13 weeks
C-OPC-45	5				
C-OPC-55	5				
C-OPC-65	5				

Table 3.10 *Carbonation depth measurement of mortar by accelerated carbonation time.*

time W/C	scale	1 week	4 weeks	8 weeks	13 weeks
C-OPC-45	5				
C-OPC-55	5				
C-OPC-65	5				

Figs. 3.19 and 3.20 show the carbonation depth of concrete and mortar respectively by spaying an indicator. The carbonation speed in concrete is evaluated about 1.8 times faster than that in mortar experimentally.
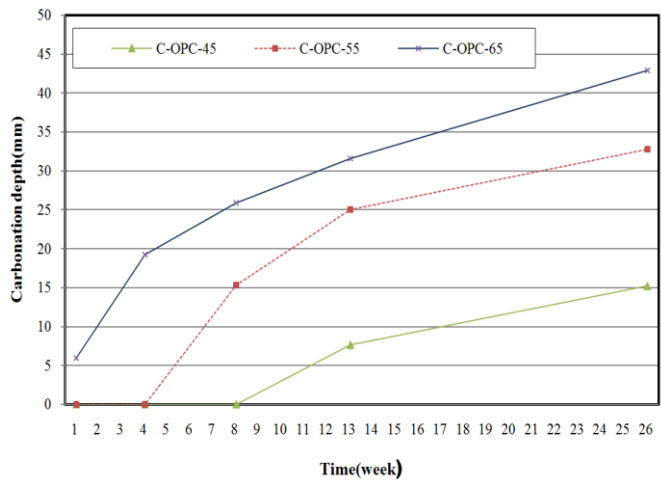

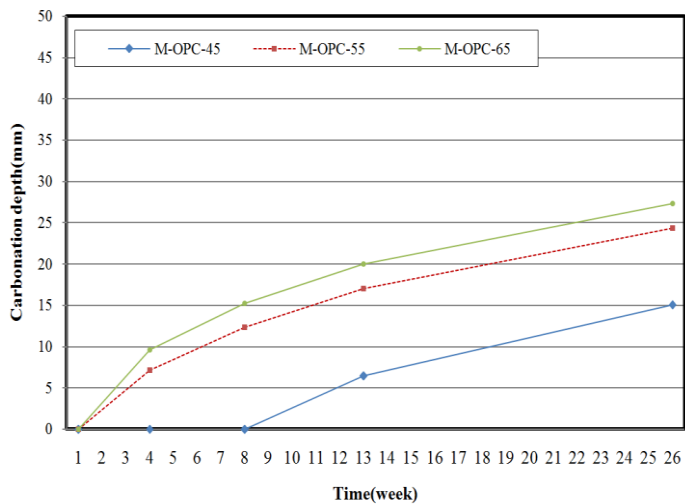**Fig. 3.19**   *Carbonation depth measurement of concrete by accelerated carbonation time.*

Fig. 3.20   *Carbonation depth measurement of mortar by accelerated carbonation time.*

(2) Results and analysis of quantitative changes of Ca(OH)$_2$ and CaCO$_3$ by W/C and carbonation weeks with using a TG/DTA

To measure the change of Ca(OH)$_2$ and CaCO$_3$ according to the depth of each carbonation time, 5 mm samples were collected from the surface of the specimen to the internal direction according to the mixture and carbonation times. Then, Ca(OH)$_2$ and CaCO$_3$ in samples were quantitatively measured using TG/DTA. Figs. 3.21 - 3.23 show the measurement results of Ca(OH)$_2$ and CaCO$_3$ in carbonated mortar in 1, 4 and 8 carbonation weeks with water to cement ratio of 0.45, 0.55 and 0.65.

Fig. 3.23 shows the relationship between the carbonated depth using an indicator for the specimen of W/C=0.55 and the quantities of Ca(OH)$_2$ and CaCO$_3$ measured using TG/DTA according to each 5 mm depth. It shows a tendency for CaCO$_3$ to increase from the inside of specimen to the surface of specimen. It was recognized that the point where the mass ratios of Ca(OH)$_2$ and CaCO$_3$ is about 1:3 agreed with the color change zone by the phenolphthalein solution. It was also verified to be the same as the cases of W/C=0.45 and 0.65 as shown in Figs. 3.23 - 3.25.

Fig. 3.24 shows the weight loss ratio of the amount of Ca(OH)$_2$, CaCO$_3$ at each depth in mortar with carbonation time. The weight loss ratio of the amount of Ca(OH)$_2$ and CaCO$_3$ with carbonation time increases much in a nearer depth from surface and this tendency is measured apparently in a higher water to cement ratio.
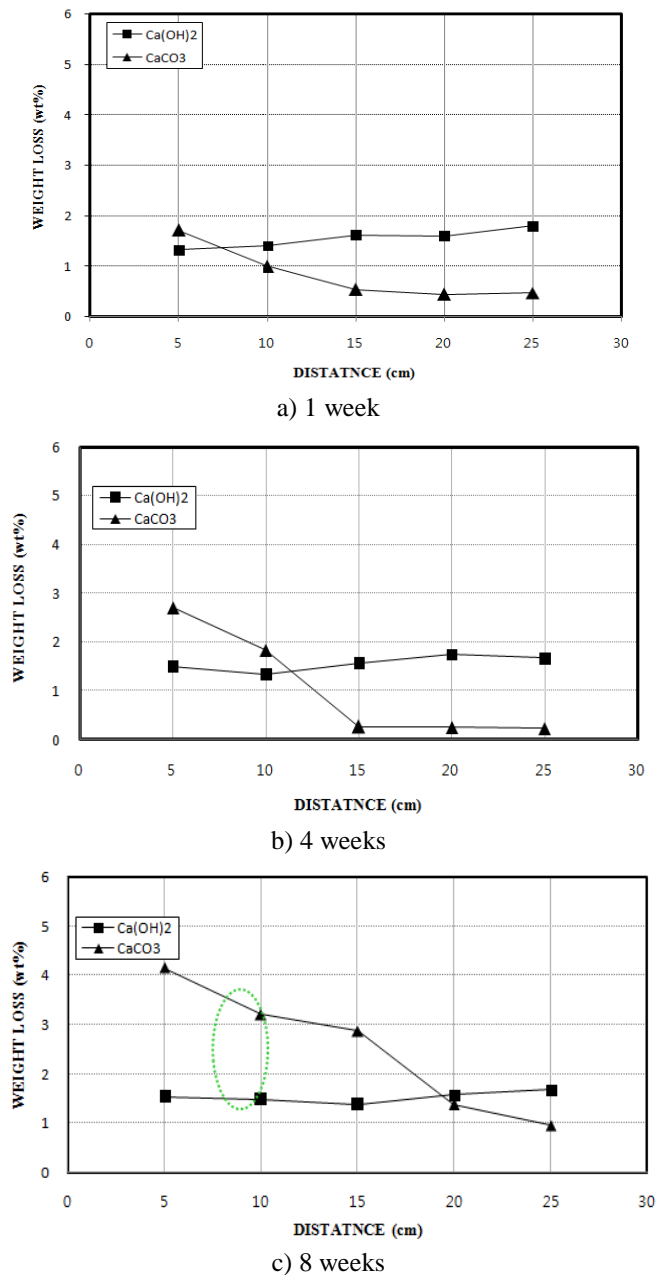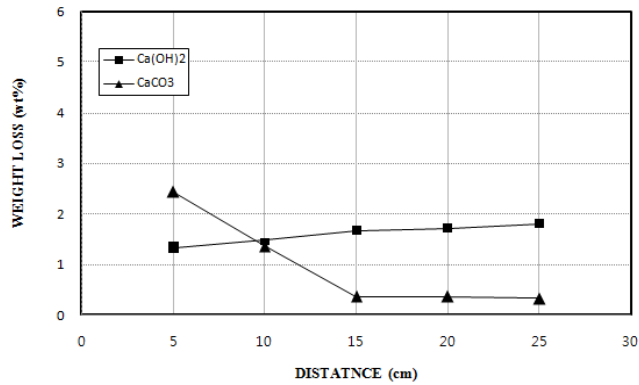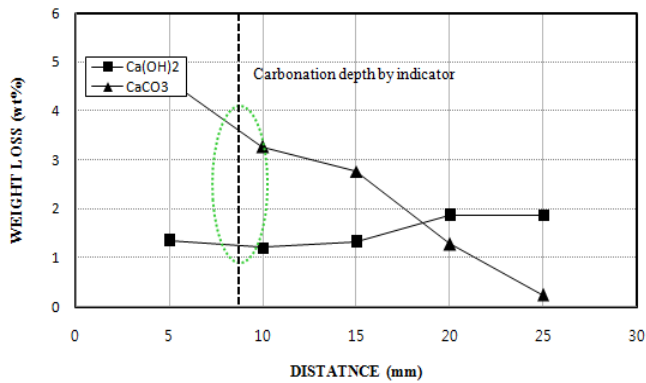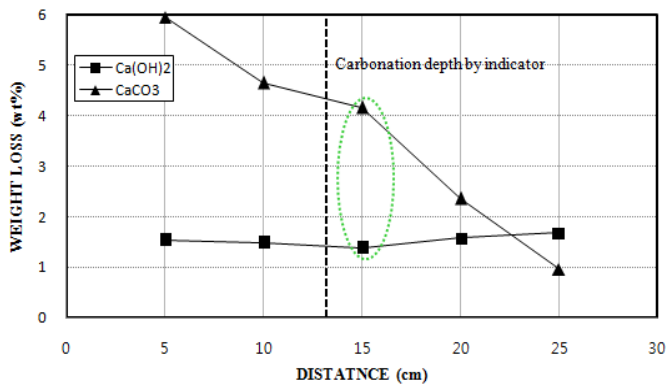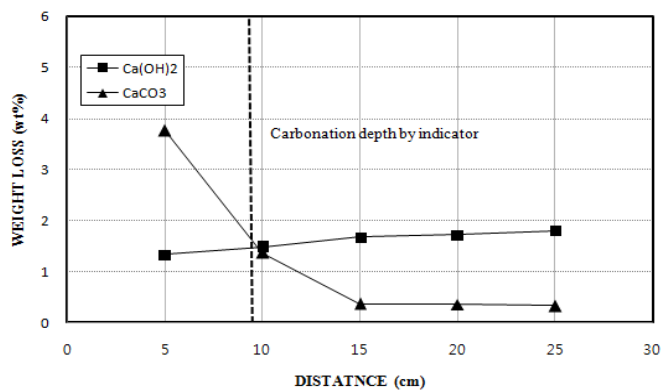
a) 1 week

b) 4 weeks

c) 8 weeks

Fig. 3.21   *Weight loss of Ca(OH)₂ and CaCO₃ in mortar specimen according*
to accelerated carbonation time (w/c=0.45).

a) 1 week

b) 4 weeks

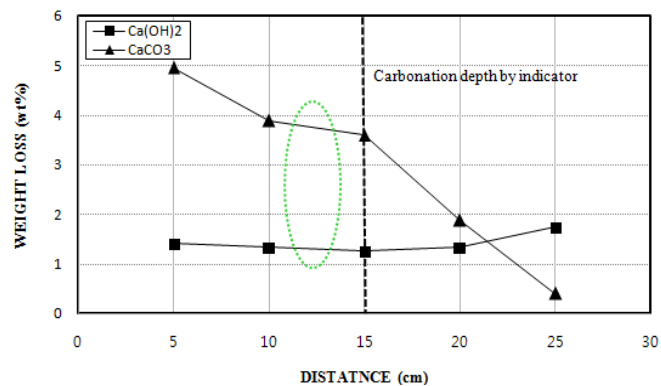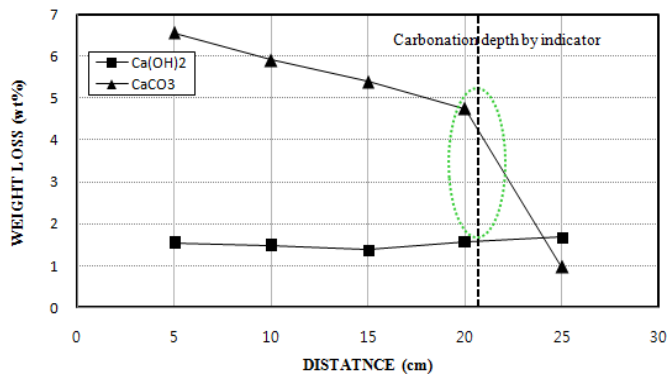

c) 8 weeks

Fig. 3.22 *Weight loss of Ca(OH)$_2$ and CaCO$_3$ in mortar specimen according to accelerated carbonation time (w/c=0.55).*
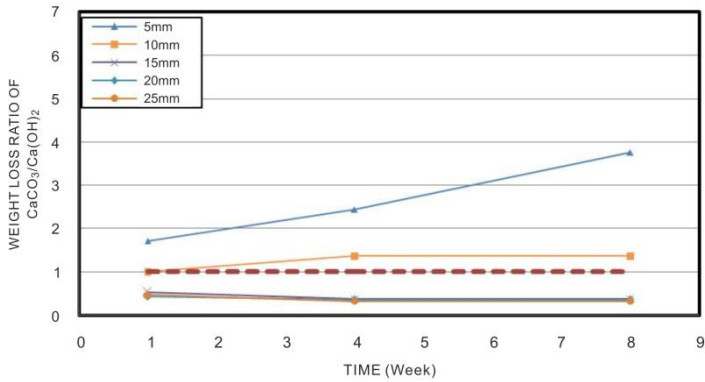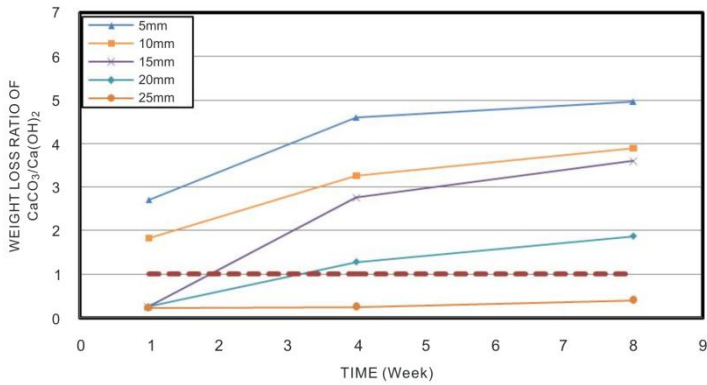
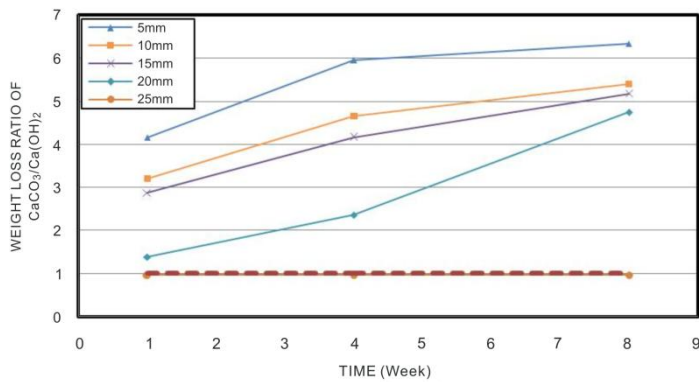a) 1 week

b) 4 weeks

c) 8 weeks

Fig. 3.23   *Weight loss of Ca(OH)$_2$ and CaCO$_3$ in mortar specimen according*
to accelerated carbonation time (w/c=0.65).

a) w/c=0.45

b) w/c=0.55

c) w/c=0.65%

Fig. 3.24 *Weight loss ratio of Ca(OH)$_2$/CaCO$_3$ according to depth with carbonation time.*

3.5   Evaluation of Concrete Carbonation Degree

3.5.1 C_o and C_{max} Evaluation of the Carbonation Degree

In order to propose a quantitative evaluation basis for carbonation degree, C_0, C_{max} as standard data are needed. Dapkus, Stankevisius[23] proposed that the value of C_0 and C_{max} are 2%, and 16%. In this study, mortar specimens is carbonated in 100% CO_2 chamber and the amount of $Ca(OH)_2$, $CaCO_3$ and pH value is measured in every week in order to measure or decide C_0, C_{max} experimentally and the result is shown in Figs. 3.26 - 3.27. As a result, C_0 and C_{max45} are measured to 1.0, 27.9%. The pH value under maximum carbonated condition is 10.6.

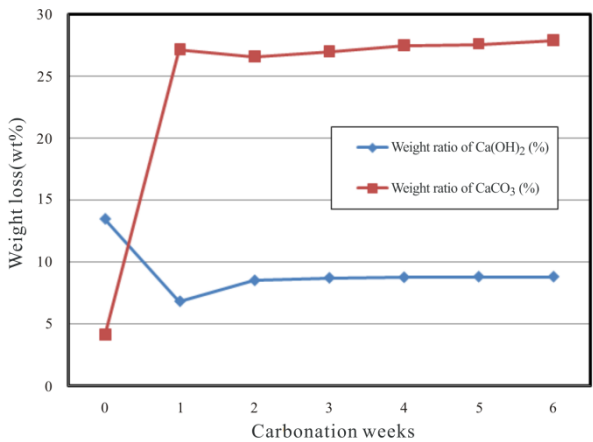**Fig. 3.25**   *Measurement of pH value.*

Fig. 3.26   *Weight loss of $Ca(OH)_2$ and $CaCO_3$ according to accelerated carbonation time (CO_2:100%).*
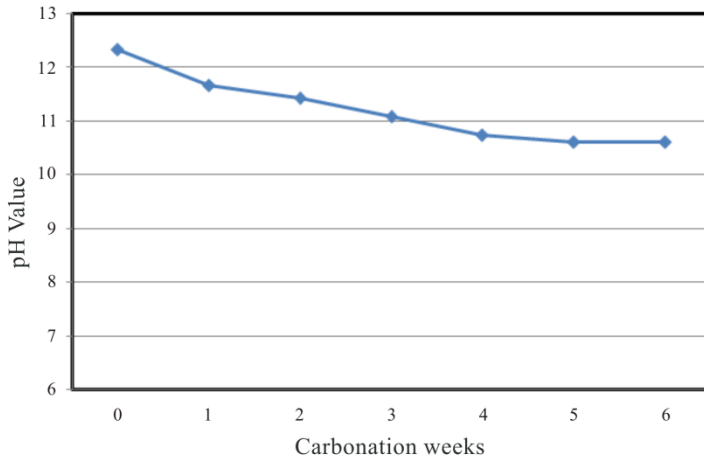
Fig. 3.27 *pH value according to accelerated carbonation time (CO₂:100%).*

3.5.2 Evaluation of Carbonation Degree

Figs. 3.28-3.30 show a carbonation degree calculated by Eq. 3.15. In case of OPC-45, measurement of carbonation depth is impossible in accelerated carbonation after 1, 4 and 8 weeks by indicator because the color does not change. However, even in a first carbonation week, carbonation degree can evaluate quantitatively that it is 9.5% carbonated in a 5 mm from the surface as shown in Fig. 3.28. Also, carbonation degree increases in a same position with a carbonation times.

$$D_C = (C - C_0) / (C_{max} - C_0) \text{ x } 100 \qquad \text{Eq. 3.15}$$

where, C is CO_2 content in sample, C_0 is CO_2 content in an uncarbonated sample, C_{max} is the max CO_2 content that sample can absorb.
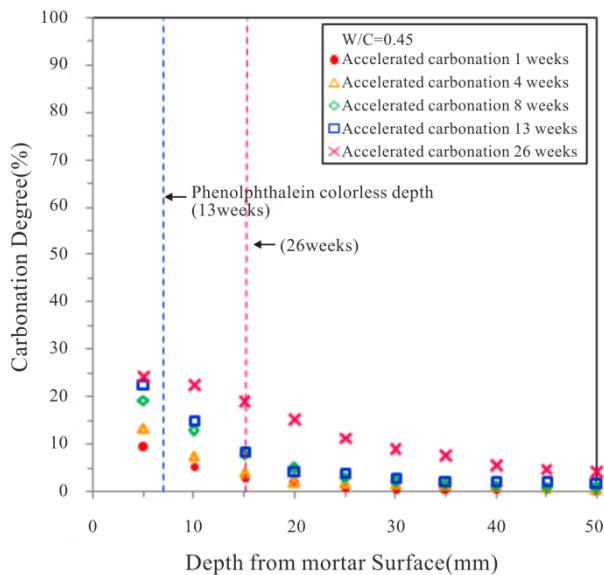
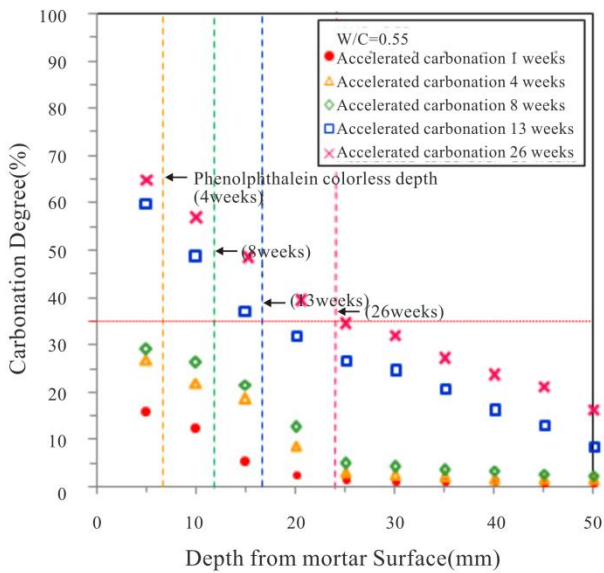**Fig. 3.28** *Relation between carbonation degree and phenolphthalein colorless depth with carbonation time (W/C=0.45).*

Fig. 3.29 *Relation between carbonation degree and phenolphthalein colorless depth with carbonation time (w/c=0.55).*
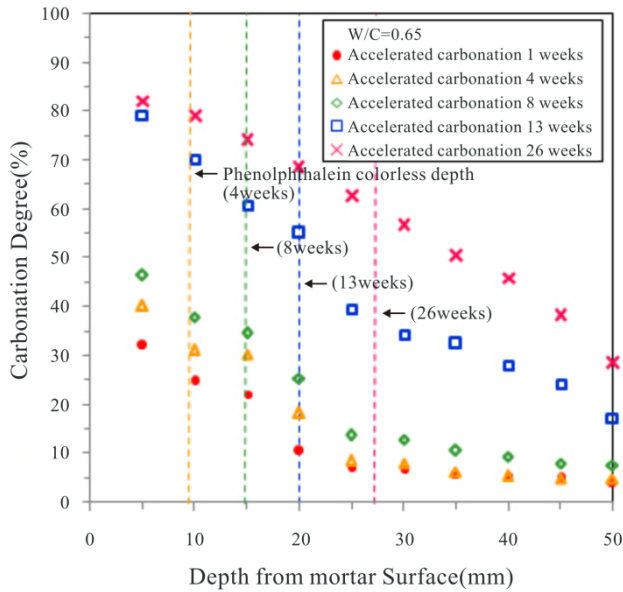
Fig. 3.30   *Relation between carbonation degree and phenolphthalein colorless depth with carbonation time (W/C=0.65).*

3.6   Proposal of a Quantitative Evaluation Standard for Carbonation Depth of Concrete

Carbonation depth is determined approximately at 60% level of the initial concentration of $Ca(OH)_2$ and the point where the ratio of $CaCO_3$, $Ca(OH)_2$ 1:3 is matched the colored point by indicator. pH value does not decrease fewer than 10.6 in 100% CO_2 chamber. As a result, a quantitative evaluation standard for carbonation is proposed as shown in Table 3.11.

Table 3.11   *Volume ratio of Ca(OH)₂ and CaCO₃ according to weight loss ratio.*

Weight loss ratio (Ca(OH)₂: CaCO₃)	ratio compared to initial concentration of Ca(OH)₂	pH value
1: 3	60	10.6

3.7 Summary

From the analysis of experimental result for the amount of $Ca(OH)_2$, $CaCO_3$ and pH value with hydration and carbonation time, the summarized conclusions are as follows.

1. Hydration model is evaluated to be valid to estimate the amount of $Ca(OH)_2$ after comparing experimental value and predicted value during hydration as an input parameter.

2. Carbonation depth is determined approximately at 60% level of the initial concentration of $Ca(OH)_2$ and the point where the ratio of $CaCO_3$, $Ca(OH)_2$ 1:3 is matched the colored point by indicator.

3. C_0 is the mass loss rate of sample using TG/DTA after 3 months hydration and the value is 1.0% and it is expected to the lowest because the sample is not carbonated yet. C_{max} is the mass loss rate of sample using TG/DTA when the value does not rise up more in a chamber of 100% CO_2 gas in the air so the sample is expected to be fully carbonated and the value is 27.15%. pH value at that time is 10.6 and this value is expected sample to be fully carbonated experimentally.

4. Proposed quantitative evaluation method considering carbonation degree for carbonation can evaluate even in 1 week carbonation time even though method by indicator cannot evaluate because of uncolored concrete. Carbonation degree with water to cement ratio of 0.45, 0.55, 0.65 is evaluated $D_{c45} = 23.3\%$, $D_{c55} = 64.8\%$, $D_{c65} = 82.1\%$ in 26 carbonation weeks at 5% of CO_2 concentration.