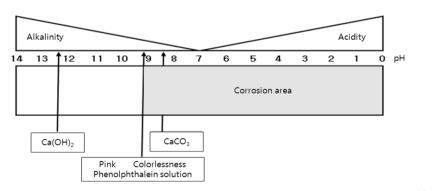# Chapter 2

Literature Review

2.1　Outline

In this chapter, literature review about definition and risk of a concrete carbonation, durability degradation mechanisms of a concrete carbonation, substance for evaluating carbonation quantitatively and TG/DTA was conducted in order to evaluate carbonation depth and predict service life of RC structure quantitatively.

2.2　Concrete Carbonation

2.2.1　Definition and Risk of a Concrete Carbonation

A concrete carbonation is a physiochemical reaction. Eq. 2.1 shows a representative carbonation equation (Ohgishi et al. 1983)[14] wherein a cement hydrate, $Ca(OH)_2$, which shows a strong alkali content in concrete, is reacted with CO_2 in the atmosphere and consequently generates $CaCO_3$. In this process, concrete loses alkalinity and becomes a low pH, shown in Fig. 2.1.
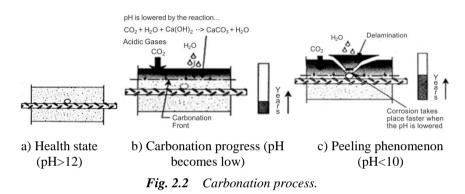
$$Ca(OH)_2 + CO_2 + H_2O \rightarrow CaCO_3 + 2H_2O \qquad \text{Eq. 2.1}$$

Fig. 2.1　*pH reduction by Carbonation process (Stark, J. and Whict, B. (1998)).[15]*

This concrete carbonation makes pH of concrete low because of losing Ca(OH)$_2$. Low pH circumstance makes rebar to be corroded and then volume of rebar begin to be expanded. So the expansion pressure on concrete around rebar makes concrete crack, subsequently detachment in happening. At last, this decreases the durability of RC structure rapidly. Fig. 2.2 shows carbonation process.

a) Health state   b) Carbonation progress (pH   c) Peeling phenomenon
(pH>12)   becomes low)   (pH<10)

Fig. 2.2   *Carbonation process.*

2.2.2   Durability Degradation Mechanisms of a Concrete Carbonation

High alkalinity resulted from the production of Ca(OH)$_2$ that is the result of hydration reaction. Because of producing Ca(OH)$_2$ that is the result of hydration reaction (Eqs. 2.2 - 2.7) make a high alkalinity.[13)]

$$2(C_3S) + 6H \rightarrow C_3S_2H_3 + 3CH \qquad \text{Eq. 2.2}$$

$$2(C_2S) + 4H \rightarrow C_3S_2H_3 + CH \qquad \text{Eq. 2.3}$$

$$C_4AF + 2CH + 2C\bar{S}H_2 + 18H \rightarrow C_8AF\bar{S}_2H_{24} \qquad \text{Eq. 2.4}$$

$$C_3A + C\bar{S}H_2 + 10H \rightarrow C_4A\bar{S}_2H_{12} \qquad \text{Eq. 2.5}$$

$$C_4AF + 4CH + 22H \rightarrow C_8AFH_{26} \qquad \text{Eq. 2.6}$$

$$C_3A + CH + 12H \rightarrow C_4AH_{13} \qquad \text{Eq. 2.7}$$

However, carbon dioxide penetrates from air as in Fig. 2.3 through porosity of concrete surface and interior capillary tube gap (Eq. 2.8). So carbon dioxide dissolves in solution on capillary tube and forms carbon. Because formed carbon is dissociated in solution on capillary tube, it becomes carbonic ion, (Eq. 2.9). Na$^+$, K$^+$ ion and OH$^-$ ion in solution on capillary tube accomplish equilibration and form high alkalinity. But, calcium hydroxide with highest solubility reacts with carbon dioxide according as carbonic ion is supplied in solution on capillary tube (Eq. 2.10) and creates insoluble calcium carbonate and deposit in capillary wall.

$$CO_2 + H_2O \rightarrow H_2CO_3 \qquad \text{Eq. 2.8}$$

$$H_2CO_3 \rightarrow 2H^+ + CO_3^{2-} \qquad \text{Eq. 2.9}$$

$$Ca^{2+} + CO_3^{2-} \rightarrow CaCO_3 \qquad \text{Eq. 2.10}$$
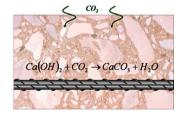

Fig. 2.3   *CO$_2$ penetration into concrete.*[16)]

Density of Ca^{2+} decreases if it is disappeared into the solution on capillary tube. Therefore, calcium hydroxide of solid state is melted in solution again. Because this process is repeated, calcium carbonate increases on solution interior as that carbonation is gone. pH value of solution is decided by OH$^-$ in equilibration with Na$^+$, K$^+$. Therefore, calcium hydroxide of solid state supplies OH$^-$ continually. Concrete pH falls sharply. Air time of exposure increases, calcium hydroxide in concrete be smelted and is disappeared. So, calcium carbonate is created and concrete pH value falls down.

Fig. 2.4 shows a correlation between pH of concrete and quantities of Ca(OH)$_2$, CaCO$_3$ in concrete from surface to the center by 1 cm depths. Concentration of Ca(OH)$_2$ becomes lower and that of CaCO$_3$ becomes higher according to exposure time expands and as a result pH value of concrete becomes low.

If pH becomes low and reaches 10.4 in these carbonation phenomenon, "passivating layer" of reinforcing rebar surface existed in (pH>12) high alkalinity state destroys. "Passivating layer" acts to prevent corrosion in connection with reinforcing rebar. Therefore, reinforcing rebar begins to corrode through the destroy of passivation layer.[17]
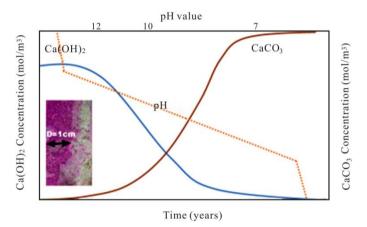

Fig. 2.4   *Change of Ca(OH)$_2$, CaCO$_3$ concentration and pH value with time.*

If reinforcing rebar corrodes, the volume of reinforcing rebar swells about 2.5 ~ 7 times. So, durability of reinforced concrete construction falls because of exfoliation and desquamation with concrete crack.

2.2.3   Changes in the Physical Properties of Concrete Subjected to Carbonation

Concrete carbonation decreases porosity in the concrete because the volume

of CaCO$_3$ that is a product from carbonation is bigger than that of Ca(OH)$_2$. As a result, the speed of carbonation progress into concrete becomes slow because diffusion speed of CO$_2$ slows down[18, 19]
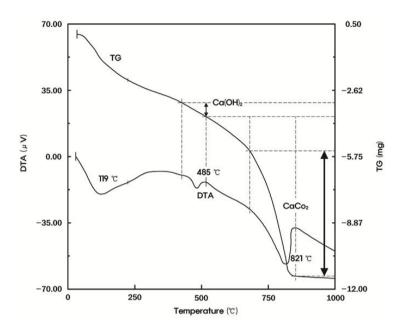
In case of plain concrete, carbonation is a merit that deceasing porosity in concrete so as to protect concrete by not to allow deteriorating ions to penetrate into concrete. But most structures have a rebar in concrete. Therefore, if pH value of concrete becomes low, it could cause rebar corrosion and concrete crack. So, generally carbonation can be a problem to RC structure in terms of durability.
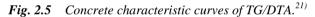
Also, concrete carbonation accompanies drying shrinkage and it may cause micro crack on concrete. But drying shrinkage becomes stable state after some time, and this is not a severe problem in terms of concrete performance.[20]

2.3 A Quantitative Evaluation Method of Ca(OH)$_2$, CaCO$_3$ Using a TG/DTA

Based on recent development in scientific analysis devices, studies on the measurement of the quantitative change of Ca(OH)$_2$ and CaCO$_3$ in concrete generated by carbonation have been conducted (Chang and Chen, 2006)[21] since mid of 1990s. And these studies tried to find out relation between carbonation depth by indicator and quantities of Ca(OH)$_2$, CaCO$_3$ measured by TG/DTA.

TG/DTA (Thermal Gravity/Differential Temperature Analyzer) is a device that measures the weight change of a substance in progress of heating it. This facilitates the quantitative analysis of the amount of components included in the subjective substance. Fig. 2.5 shows the analysis result of the component in concrete samples using the TG/DTA where the weight of samples continuously decreased during the heating process from 0 ℃ to 1000 ℃ (TG curve).

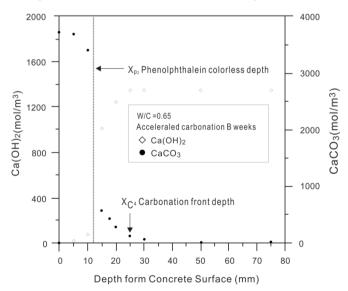**Fig. 2.5** *Concrete characteristic curves of TG/DTA.*[21]

Fig. 2.6 *Relationship between phenolphthalein colorless depth,
CaCO$_3$ and Ca(OH)$_2$ concentration distribution by TGA.*[21]

Eqs. 2.11 and 2.12 show the thermal decomposition of Ca(OH)$_2$ and CaCO$_3$, respectively. As shown in Table 2.1, this is due to the fact that some substances in a specific temperature range are evaporated by thermal decomposition, subsequently leading to reduction of its weight.

The quantitative measurement of each weight loss can be performed by measuring it around 500 ℃ for the weight loss (a) due to the evaporation of water, which is combined with Ca(OH)$_2$, and around 700 ℃ for the weight loss (b) due to the evaporation of carbon dioxide, which is combined with CaCO$_3$.

Using these measured values and the molecular weight of the matrix, the mass (x, y) of the substances, Ca(OH)$_2$ and CaCO$_3$, can be a quantitatively obtained. As shown in Fig. 2.6 of accelerated carbonation for 8 weeks, relation between carbonation depth by indicator and quantity of Ca(OH)$_2$, CaCO$_3$ according to depth. Concentration of Ca(OH)$_2$ is higher that of CaCO$_3$ in uncarbonated depth while concentration of CaCO$_3$ is higher that of CaCO$_3$ in carbonated depth.

$$Ca\,(OH)_{2(s)} \rightarrow CaO_{(s)} + H_2O_{(g)}$$

Molecular weight (g/mol)	74	18	Eq. 2.11
Measured weight (mg)	x	a	

$$CaCO_{3(s)} \rightarrow CaO_{(s)} + CO_{2(g)}$$

Molecular weight (g/mol)	100.09	44	Eq. 2.12
Measured weight (mg)	y	b	

Using a quantitative measuring method like above is expected to compliment the limitation of qualitative evaluation, which is carried out using the naked eye with respect to the color change boundary by spraying the conventional indicator.

Table 2.1 *Temperature range of hydrate decomposition during TGA measurements.*[22)]

	Temperature range	Decomposition of hydrates or carbonated products
1	25 to 430 ℃	Free and absorbed H$_2$O, H$_2$O from C-S-H, AFt, AFm, gypsum, and CO$_2$ absorbed in C-S-H
2	430 to 520 ℃	H$_2$O from portlandite Ca(OH)$_2$
3	520 to 650 ℃	OH- from structure of hydrates, structure H$_2$O, or CO$_2$ from vaterite, and C-S-H carbonation
4	650 to 720 ℃	CO$_2$ from calcite of carbonation
5	720 to 900 ℃	CO$_2$ from calcite of aggregates
6	900 to 1150 ℃	Other structural H$_2$O

2.4   Carbonation Degree

Fig. 2.7 represents the quantity change of Ca(OH)$_2$ and CaCO$_3$ with the passage of time. The quantity of Ca(OH)$_2$ in concrete increased due to hydration reaction during its aging period but decreased by the reaction with carbon dioxide in the air after exposure. However, the quantity of CaCO$_3$ gradually increased due to carbonation progress.
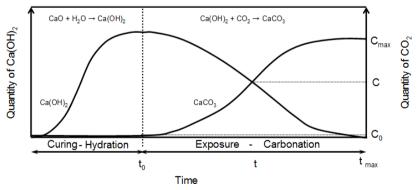

Fig. 2.7   *Quantity change of Ca(OH)$_2$ and CaCO$_3$ to time.*

The quantity of CO$_2$ in concrete shows a minimum level of C_o just after exposing it outdoors while the quantity of CO$_2$(C) in concrete gradually increased with the increase of CaCO$_3$, which is reacted with Ca(OH)$_2$, according

to the progress of concrete carbonation. The quantity where there is no more increase in the absorption of CO_2 after a considerable lapse of time in the outdoors is considered as the maximum carbonation time (t_{max}).

Under the cited assumption, the carbonation degree (D_c) in concrete at an arbitral time after outdoor exposure can be presented as in Eq. 2.13, which shows the ratio of the amount of CO_2 maximally absorbed by the concrete (C_{max}-C_0) and the amount of CO_2 absorbed at an arbitral time(C-C_0) as Eq. 2.13.[23]

$$D_c = (C - C_0) \, / \, (C_{max} - C_0) X \, 100 \qquad \text{Eq. 2.13}$$

herein,

C: the amount of CO_2 in the sample,

C_0: the amount of CO_2 in the non-carbonated sample,

C_{max}: the amount of CO_2 maximally absorbed by the sample.

2.5   Prediction Models of Concrete Carbonation

2.5.1   Experimental Models

Eq. 2.14 is a generally used one and it explains that concrete carbonation depth is proportional to exposed time in the air. In this equation, b that is a function of water to cement ratio, strength, CO_2 concentration is a coefficient for carbonation rate of concrete and it is decided experimentally.

$$X_c = b\sqrt{t} \qquad \text{Eq. 2.14}$$

Xc: Carbonation depth in concrete.

b: Coefficient for carbonation rate of concrete.

t: Exposed time in the air.

Table 2.2 shows various equations based on experimental data proposed by researchers and their considered factors by equations.

Table 2.2 *Carbonation model equation.*[24)]

Researcher	Proposed model	W/C	Cement Type	Aggre. Type	Surr. Environ	Comp. Strengh
Hamada	$t = \dfrac{k}{R} C^2$	○	○	○		
Kishitani	$t = \dfrac{0.3(1.15+3x)}{R^2(x-0.25)^2} C^2$ (x≥0.6) $t = \dfrac{7.2}{R^2(4.6x-1.76)^2} C^2$ (x≤0.6)	○	○	○	○	
Sirayama	$t = \alpha\beta\gamma бε \dfrac{5000}{(x-38)^2} C^2$	○	○	○	○	
Yoda	$t = \alpha\beta\gamma \dfrac{Pt^2}{(100x-Q)^2} C^2$	○			○	
Smolczyk	$x = 7.00\left(\dfrac{10\frac{W}{C}}{\sqrt{N_t}} - 0.175\right)\sqrt{t} - 0.50$	○				○
Wierjg	$x = \left(84.62 - \dfrac{\frac{W}{C}}{\sqrt{N_7}} - 0.64\frac{W}{C} - 1.63\right)\sqrt{t} + 0.9$	○				○
Ko, Kyung Taek	$X = (2.823 - 0.584\log C)X(0.0303W/C - 1.0187)\sqrt{Ct}$	○			○	
Izumi	$C = 4.91 \cdot R_1 \cdot R_2 \cdot R_3 \cdot R_4 \cdot R_5 \cdot R_6 \cdot R_7\sqrt{t}$	○			○	

Table 2.3 is a coefficient for carbonation rate of concrete and Table 2.4 is correction factors for coefficient for carbonation rate of concrete and both of them are proposed values by concrete strength, exposed surroundings, types and replacement ratio of binders based on experiments and reviews using by Eq. 2.14

Table 2.3 *Suggested k-values for concrete surfaces with CEM I and exposed concrete surfaces.*[13]

Strength (MPa)	<15	15~20	25~35	>35
Wet/Submerged	$\dfrac{2mm}{\sqrt{year}}$	$\dfrac{1.0mm}{\sqrt{year}}$	$\dfrac{0.75mm}{\sqrt{year}}$	$\dfrac{0.5mm}{\sqrt{year}}$
Buried	$\dfrac{3mm}{\sqrt{year}}$	$\dfrac{1.5mm}{\sqrt{year}}$	$\dfrac{1mm}{\sqrt{year}}$	$\dfrac{0.75mm}{\sqrt{year}}$
Exposed	$\dfrac{5mm}{\sqrt{year}}$	$\dfrac{2.5mm}{\sqrt{year}}$	$\dfrac{1.5mm}{\sqrt{year}}$	$\dfrac{1.0mm}{\sqrt{year}}$
Sheltered	$\dfrac{10mm}{\sqrt{year}}$	$\dfrac{6mm}{\sqrt{year}}$	$\dfrac{4mm}{\sqrt{year}}$	$\dfrac{2.5mm}{\sqrt{year}}$
Indoors	$\dfrac{15mm}{\sqrt{year}}$	$\dfrac{9mm}{\sqrt{year}}$	$\dfrac{6mm}{\sqrt{year}}$	$\dfrac{3.5mm}{\sqrt{year}}$

* Strength class in cylinder strength values(C).

**Buried concrete is concrete in the ground not in direct contact with atmosphere.

Table 2.4 *Binder correction factors based on strength classes% in weight of binder.*[13]

Amount in wt. (%)	<10	10~20	20~30	30~40	40~60	60~80
Limestone		k X 1.05	k X 1.10			
Silica fume	k X 1.05	k X 1.10				
Fly ash		k X 1.05		k X 1.10		
GBFS	k X 1.05	k X 1.10	k X 1.15	k X 1.20	k X 1.25	k X 1.30

The above equations and tables can predict carbonation depth considering types and replacement ratio of binder, exposure condition but there is a limit that the values are based on Sweden in order to adopt in Korea and colored depth data by indicator qualitatively and they cannot consider water to cement ratio and aggregate to cement ratio.

2.5.2 Carbonation Prediction Models Using a Fick's Diffusion Law

This model predict concrete carbonation using diffusion equation by

concentration gradient of CO_2 based on Fick's law because concrete carbonation is a phenomenon by CO_2 diffusion in concrete.

Gas diffuses from the point of high concentration to the point of low concentration. Fig. 2.8 shows concentration gradient of CO_2 between C_1 that is concrete surface and C_2 that is at any point in concrete. Equation 2.17 can be derived based on assumption that CO_2 gas diffuses from C_1 to C_2 and the dJ, the flux through volume $X \times A$ (m^2) per unit time (Eq. 2.15) is equal to one through micro section (Eq. 2.16).[25]
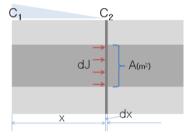

Fig. 2.8 *Carbonation Model.*

$$\frac{dJ}{dx} = \frac{D \cdot A \cdot (C_1 - C_2)}{x}$$ Eq. 2.15

$$\frac{dJ}{dx} = a \cdot A$$ Eq. 2.16

C_1: CO_2 concentration on the surface

C_2: CO_2 concentration in x+dx point from concrete surface

a: CO_2 absorption capability per unit volume of concrete (kg/m^3)

D: diffusion coefficient of CO_2 in concrete

t: time

$$x = \sqrt{\frac{2 \cdot D \cdot (C_1 - C_2)}{a}} \cdot \sqrt{t}$$ Eq. 2.17

$$a = 0.6 \times 0.6 \times C \times \frac{M_{CO_2}}{M_{CaO}} = 0.3C[kg / m^3] \qquad \text{Eq. 2.18}$$

a: CO$_2$ absorption capability per unit volume of concrete (kg/m^3)

C: cement amount of unit volume concrete (kg/m^3)

0.6: hydration degree (%)

0.63: content of CaO in cement (%)

Considering first term of right side in Eq. 2.17, Eq. 2.17 can be simplified to the form of Eq. 2.11 eventually. *a*, denominator of Eq. 17, is a variable presenting absorption capacity of CO$_2$ unit volume of concrete. It is proportional to the amount of Ca(OH)$_2$ that is hydration product in concrete like Eq. 2.19. This is why most CO$_2$ in the air combine with Ca(OH)$_2$ like Eq. 2.20. Therefore, absorption capacity of CO$_2$ in concrete is proportional to the amount of Ca(OH)$_2$ and it is proportional to the amount of CaO in cement. Herein, a is a absorption capacity of CO$_2$, it is proportional to the amount of CaO in cement, cement hydration and considering each values 0.6, 0.63 and molecular weight ratio of CO$_2$ and CaO, the value a can be Eq. 2.18.

$$CaO + H_2O \rightarrow Ca\,(OH)_2 \qquad \text{Eq. 2.19}$$

$$Ca(OH)_2 + CO_2 \rightarrow CaCO_3 \qquad \text{Eq. 2.20}$$

Eq. 2.20 has an advantage that can predict carbonation considering coefficient of CO$_2$ and cement quantity in concrete. But there is a limit that it does not consider whole mixture of concrete such as aggregate to cement ratio, water to cement ratio. Also, there is a limit that carbonation depth is evaluated qualitatively by phenolphthalein indicator. Table 2.5 is a model using Fick's law proposed by Papadakis.

Table 2.5   *Carbonation model using Fick's law.*

Researcher	Proposed model
Papadakis[19]	$\dfrac{d}{dt}\left(D_{CO_2}\dfrac{d[CO_2]}{dx}\right)+\dfrac{d}{dt}([Ca(OH)_2+3[C-S-H]+3[C_3S]+2[C_2S])+\alpha=0$

2.5.3   Integrated Carbonation Prediction Model Considering the Hydration

Concrete carbonation is a phenomenon where concentration of $Ca(OH)_2$ is decreased by changing it into $CaCO_3$ by combining it with CO_2 in the air through carbonation. Therefore, it is important to estimate concentration of $Ca(OH)_2$ in the uncarbonated concrete. The concentration of $Ca(OH)_2$ is varied by hydration degree, concrete mixture and cement types that used in concrete. As a result, the researches to estimates concentration of $Ca(OH)_2$ considering concrete mixtures has studied by many researchers because it can estimate carbonation based on the concentration of $Ca(OH)_2$ considering various mixtures.

Eq. 2.21 is an equation that estimates the concentration of $Ca(OH)_2$ in concrete considering amount and hydration degree of cement.

$$C_a = 0.3\ Q.\ \alpha\ /\ 74 \qquad\qquad \text{Eq. 2.21}$$

C_a: concentration of $Ca(OH)_2$ in concrete (mol/m^3)

Q: quantity of ordinary Portland cement in concrete (kg/m^3)

α: hydration degree of ordinary Portland cement (%)

74: molar concentration of $Ca(OH)_2$ (g/mol)

Papadakis[26] calculated molar concentration of $Ca(OH)_2$ quantitatively like Eq. 2.22 with hydration time by summarizing multiplied values between concentration all kinds of compounds and fraction ratio related to concentration

of $Ca(OH)_2$ that consumes and produces through hydration process based on hydration equations in terms of $Ca(OH)_2$ concentration.

$$[Ca(OH)_2] =$$
$$\frac{3}{2}[C_3S]_0 F_{C_3S} + \frac{1}{2}[C_2S]_0 F_{C_2S} - 4[C_4AF]_0 F_{C_4AF} - [C_3A]_0 F_{C_3A} + [C\bar{S}H_2]_0 \qquad \text{Eq. 2.22}$$

Especially Eq. 2.22 has a merit that it can predict the concentration of $Ca(OH)_2$ quantitatively considering all mixtures based on kinds of oxides and composition ratio of binders compared to Eq. 2.21.

Papadakis proposed prediction equation for carbonation depth like Eq. 23 that is proportional to the concentration and the diffusion coefficient of CO_2 in the air and is in reverse proportional to the molar concentration of substances that are hydration products in concrete and react with CO_2 penetrating from the air in terms of concentration change of substances that can react with CO_2 in concrete with time.[25]

$$x_c = \sqrt{\frac{2D^C_{e,CO_2}[CO_2]^0}{[Ca(OH)_2]^0 + 3[CSH]^0 + 3[C_3S]^0 + 2[C_2S]^0}} \qquad \text{Eq. 2.23}$$

x_c: carbonation depth (mm)

D^c_{e,CO_2}: effective diffusion coefficient of CO_2

$[CO_2]^0$: concentration of CO_2 in the air

$[Ca(OH)_2]^0 + 3[CSH]^0 + 3[C_3S]^0 + 2[C_2S]^0$: the initial concentration of carbonatable substances.

Effective diffusion coefficient of numerator is affected by pore size, distribution and saturation degree and saturation degree is affected by relative humidity in the air in Eq. 2.23.

Eq. 2.24 is proposed by Papadakis and it shows effective diffusion coefficient is a function of relative humidity and porosity.[27]

$$D_{e,CO_2} \approx 1.64 \cdot 10^{-6} \varepsilon \in_p^{1.8} (1 - RH \: / \: 100)^{2.2} \qquad \text{Eq. 2.24}$$

ϵ_p: porosity in concrete after hydration (%)

RH: relative humidity (%)

ϵ_p in Eq. 2.24 is porosity in concrete after hydration and it is a function related to water to cement ratio, densities of compounds and porosity of air like Eq. 2.25. Porosity in concrete is a function of time and it decreases by carbonation and hydration because of volume expansion of reactant products with time and it can be calculated like Eq. 2.26 considering volume changed result from hydration and carbonation.

This model has a merit that it can predict carbonation depth considering all mixtures by calculating the molar concentration of carbonatable substances. Also, it can predict carbonation depth more concisely considering porosity change with time dependent character resulting from hydration and carbonation. But there is also a qualitative evaluating limit that uses a datum measured by indicator and various inspectors to verify accuracy of prediction values.

$$\in_0 = \frac{\frac{wp_c}{cp_w}(1 - \epsilon_{air})}{(1 + \frac{wp_c}{cp_w} + \frac{ap_c}{cp_a})} + \in_{air} \qquad \text{Eq. 2.25}$$

$$\in (t) = \in_{(0)} - \Delta\in_{H(t)} - \Delta\in_c \qquad \text{Eq. 2.26}$$

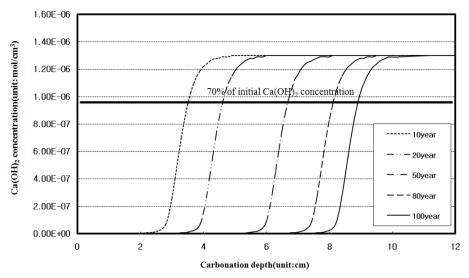### 2.5.4 Carbonation Prediction Model Using a FEM Analysis

Masuda, Tanano[28] used this FEMA in order to predict carbonation quantitatively. Fig. 2.9 is a result of FEMA with concrete depth, carbonation time. It shows molar concentration distribution of $Ca(OH)_2$ in concrete.
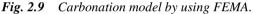
They estimated carbonation depth in concrete as a point where the concentration of $Ca(OH)_2$ reaches 40 ~ 70% compared to the initial concentration of $Ca(OH)_2$ as an evaluation basis for carbonation depth in concrete. Concentration gradient of $Ca(OH)_2$ is affected by diffusion coefficient of CO_2 in concrete, reaction rate constant (K) between $Ca(OH)_2$ and CO_2.

This FEMA has a merit that it substitutes qualitative method by indicator with evaluating the concentration of $Ca(OH)_2$ with depth in concrete quantitatively. But it is an important to decide which point carbonation depth is compared to the initial concentration of $Ca(OH)_2$ as an evaluation basis for carbonation depth in concrete. Masuda Tanano (1991) derived relation between colored depth by indicator and the amount of $Ca(OH)_2$ compared to the initial concentration of $Ca(OH)_2$ with carbonation time. As a result, the amount of $Ca(OH)_2$ compared to the initial concentration of $Ca(OH)_2$ is in a range of 40 ~ 70% and it becomes an evaluation basis for carbonation depth by FEMA. But there is a problem that there is a wide range to decide carbonation depth in concrete result in wide range for evaluating a service life of RC structure and it reduces the accuracy for prediction as shown in Fig. 2.10.

In domestic researches, Lee, H.S and Lee, S.H (2007)[29] evaluated carbonation depth at a point that the concentration of $Ca(OH)_2$ reaches 70% compared to the initial concentration of $Ca(OH)_2$ in predicting service life of RC structures. They reported it is important to decide limit depth for carbonation as an evaluating basis in order to evaluate service life of RC structure more accurately: which ratio is suitable to carbonated depth compared to the initial concentration of $Ca(OH)_2$ related to rebar corrosion in concrete in a corrosion circumstances.

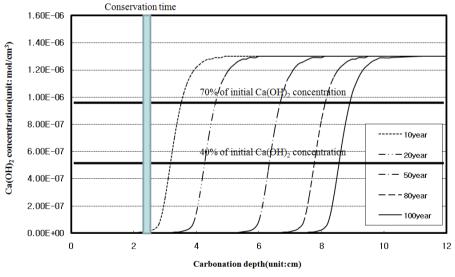***Fig. 2.9***   *Carbonation model by using FEMA.*

Fig. 2.10   *Carbonation model with using FEMA.*

FEMA evaluates the amount of Ca(OH)$_2$ quantitatively at an arbitrary point in concrete with depth and carbonation time. However, the range of Ca(OH)$_2$ amount compared to the initial concentration of one as an evaluating basis for

carbonation depth is needed to propose more concisely when FEMA is used to evaluate carbonation depth.

2.6 Relationship Between pH Value and the Amount of $Ca(OH)_2$ and $CaCO_3$

Geraldine et al. (2006)[22] divided carbonation area into four steps with concrete depth as in Fig. 2.11 through evaluating $Ca(OH)_2$ quantitatively using TG/DTA from exiting division between carbonated area and uncarbonated area by indicator. But there is also limit that it evaluates carbonation depth by color change using indicator and it may vary by various inspectors because of qualitative evaluation method.
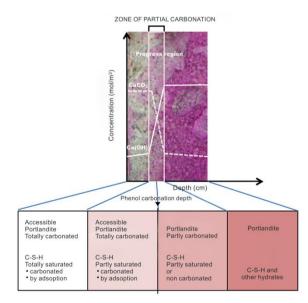

Fig. 2.11 *Outline of four zones exhibiting various levels of carbonation in concrete.*[22]

In order to increase accuracy of predicting carbonation depth using TG/DTA, evaluation basis for carbonation depth through a qualitative analysis method

such as TG/DTA is needed based on experimental correlation data between pH value and quantity of $Ca(OH)_2$ and $CaCO_3$ that rebar corrosion occurs.

Concrete has a strong alkalinity (over 13 in pH value) right after hydration by the influence of Na^+, K^+ from hydroxide ion binding substance such as $Ca(OH)_2$.[29] But pH drops because calcium carbonate (pH = 8.5 ~ 10) is produced by dissolving $Ca(OH)_2$ that has a high alkalinity in concrete through carbonation according to using time of RC structures.

Lee, J.K[30] (2003) evaluated pH value and the amount of $CaCO_3$ in sample specimens of concrete that is cored from 70 civil structures in Korea. As a result, relation that how pH value decreases with increasing the amount of $CaCO_3$ is derived experimentally as in Fig. 2.12.
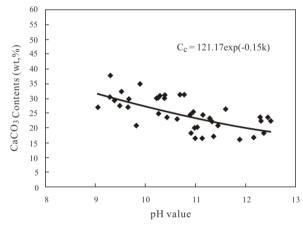

$$C_c = 121.17\exp(-0.15k)$$

Fig. 2.12 *pH value according to the contents of calcium carbonate.*[29]

Saeki N et al. (1984) reported that the corrosion of rebar in carbonated mortar begins at 11.4 of pH value as in Fig. 2.13.[31] This experimental data means that rebar corrosion may begin faster than 8 ~ 10 of pH value using phenolphthalein indicator. It is expected that corrosion area to be much more than 20% of rebar surface area in case of carbonation depth by indicator reaches rebar location.

Ohgishi S. and Ono. H. (1983)[14] reported relation between pH value and the amount of $Ca(OH)_2$, $CaCO_3$ as in Fig. 2.14.

Choi, J, Y *et al.* (2007)[32] reported experimentally correlation between pH value and the amount of $Ca(OH)_2$, $CaCO_3$ in mortar specimen with water to ratio, carbonation time and depth.

However, researches about correlation of pH value and the amount of $Ca(OH)_2$, $CaCO_3$ in cement or concrete specimen when rebar corrosion begin are not enough. So research about this theme is essential and needed to propose qualitative evaluation basis for carbonated depth and service life.
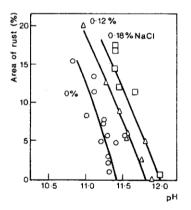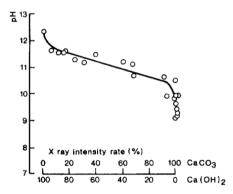

Fig. 2.13 *Effect of pH upon corrosion of steel in carbonated mortar.[31]*

Fig. 2.14 *pH value versus X-ray diffraction intensity.[14]*

2.7 Summary

In this chapter, researches about study trend for carbonation, quantitative evaluation method, pH and prediction method of service life are reviewed and the summarized conclusions are as follows.

1. Complementary methods that can evaluate carbonation degree quantitatively needed to complement qualitative evaluation method for carbonation depth if the distinction is blurred by indicator.

2. Research about correlation of pH value and the amount of $Ca(OH)_2$, $CaCO_3$ in cement or concrete specimen using TG/DTA when rebar corrosion begins is essential and needed to propose qualitative evaluation basis for carbonated depth and service life.

3. Hydration model proposed can predict initial concentration of $Ca(OH)_2$ considering all mixtures. So, validation is needed to ensure hydration model effectiveness before using it as a prediction model of initial concentration of $Ca(OH)_2$ in this research.