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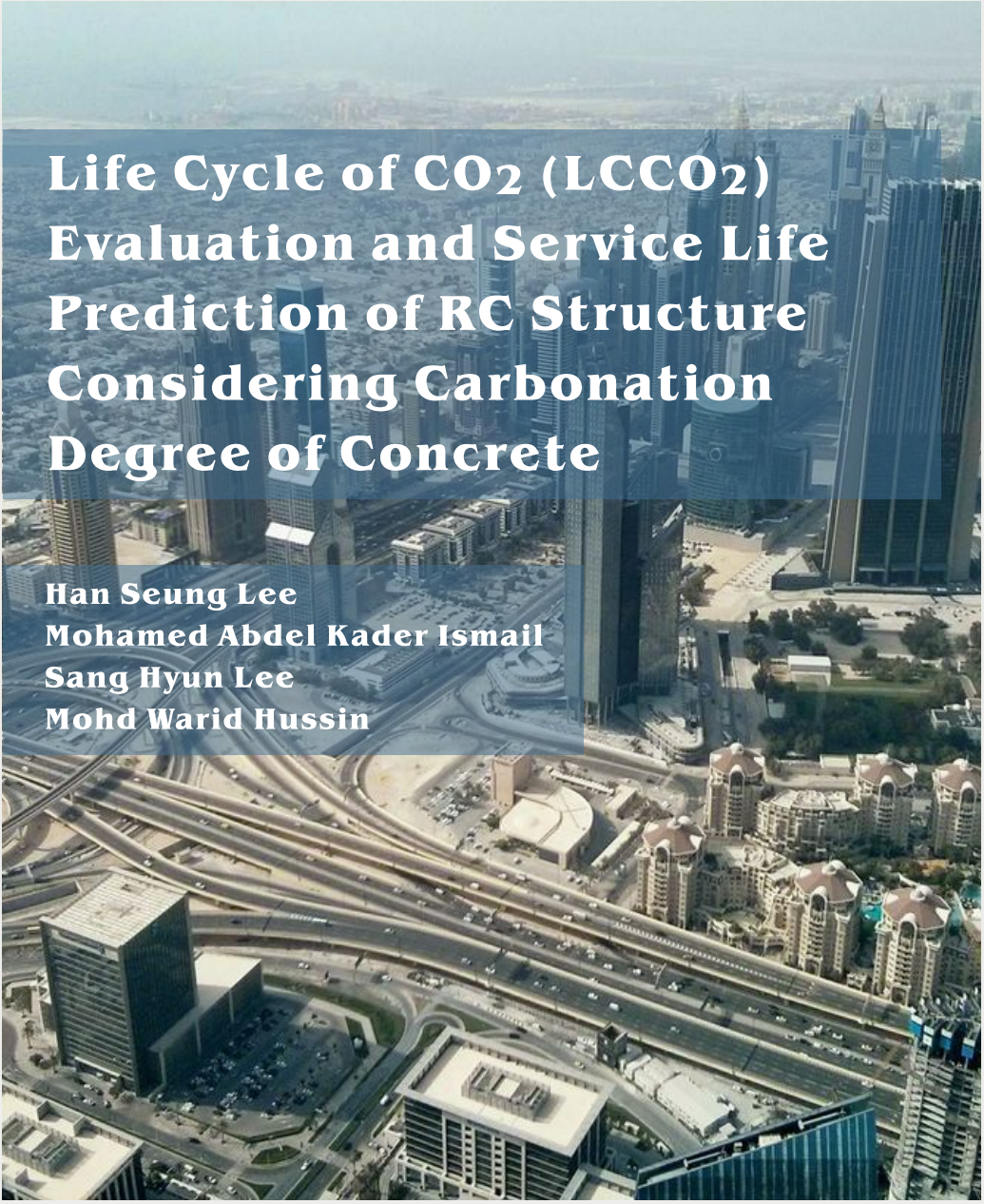

Life Cycle of CO_2 ($LCCO_2$) Evaluation and Service Life Prediction of RC Structure Considering Carbonation Degree of Concrete

Han Seung Lee
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Abstract

Life cycle of CO_2 ($LCCO_2$) evaluation and service life prediction of RC structure considering carbonation degree of concrete.

Building structure standard was modified in KOREA in 2012 in order to activate green development and new technology such as eco-friendly material and high strength concrete to be adopted to building. Because recently concerns about the sustainability of the globe highlight the need of CO_2 reduction and eco-friendly building and each country make and plan to commit the financial obligations of CO_2 emissions. As a result, design should consider using low CO_2 emissions and resource and CO_2 display of products has expanded.

On the other hand, there is still no formalized way in KOREA to display CO_2 emission of concrete that is a main building material. Especially, quantitative evaluating method for it is needed because it can be used as a reference day to decrease CO_2 emission by replacing cement with admixtures in concrete. Because cement emits much CO_2 in the process of making it but admixtures emits CO_2 much smaller than cement. Besides, concrete can absorb CO_2 through carbonation but there is still no reference data in KOREA to consider it.

Concrete carbonation decreases durability of concrete because it causes rebar to corrode. Therefore, quantitative evaluating method for amount of CO_2 absorption through carbonation should be considered under the condition that carbonation does not affect durability of RC structure.

Evaluating service life by carbonation has a limit that it uses an indicator. But that method is a qualitative method and has a limit not to consider carbonation degree. In the case of salt damage, quantitative evaluation method can be possible by measuring chloride ion concentration at the depth of rebar location but in the

case of carbonation there is still no quantitative evaluation method (evaluation materials, measurement position) and standard yet. Evaluation method by indicator has a qualitative assessment limit that instability color change may happen in the carbonation depth anytime. In addition, carbonation depth measurement method by the indicator has a problem that concrete color does not discolored in early progress of carbonation. Carbonation depth measurement method using an indicator may cause prediction error of service life of RC structure when measurement error by measurers has happened because of ambiguous boundary. Thus, evaluation method by indicator has a qualitative assessment limit that unstable color change may happen in the carbonation depth anytime. Therefore, a quantitative evaluation methods and standards for carbonation are required to overcome this problem.

So, this study proposed a quantitative evaluating method that overcomes the limitation of qualitative evaluation, which is carried out using the naked eye with respect to the color change boundary by spraying indicator. Carbonation depth becomes the basic data for estimating the residual life and durability of RC structures. To achieve this objective, the quantitative change of $Ca(OH)_2$ and $CaCO_3$ for each depth in concrete according to the carbonation process is measured using TG/DTA in order to propose a quantitative method and an evaluation basis. Another goal is to propose evaluating method of CO_2 absorption in the air through carbonation and how to evaluate $LCCO_2$ (emission – absorption of CO_2).

This study is composed of six chapters to evaluate $LCCO_2$ and service life prediction of RC structure considering carbonation degree of concrete and summarized contents of each chapter are as follows:

In chapter 1, necessity and objectives of this study are explained.

In chapter 2, review for carbonation and a quantitative evaluating method is

conducted to complement qualitative evaluating method by indicators.

In chapter 3, correlation between pH value and quantities of $Ca(OH)_2$, $CaCO_3$ is analyzed experimentally by carbonation weeks, concrete depths through accelerated carbonation experiment in order to propose a quantitative evaluating basis. Quantity of $Ca(OH)_2$ is important to predict service life of concrete against carbonation and cement hydration model can predict it quantitatively to any concrete mix. Therefore, validation for cement hydration model is verified by comparing prediction values and measured values of $Ca(OH)_2$.

In chapter 4, prediction model for carbonation based on FEM is used to predict the service life of RC structure. Required input parameters such as initial concentration of $Ca(OH)_2$, diffusion coefficient of CO_2, reaction velocity constant, CO_2 concentration in the air for FEMA are decided through literature review. The proposed quantitative evaluation basis in chapter 3 is used to evaluate and predict service life.

In chapter 5, CO_2 emission of concrete considering concrete mix and CO_2 absorption through carbonation during service life for unit volume concrete is calculated quantitatively. And then, CO_2 balance (emission-absorption of CO_2) and $LCCO_2$ is evaluated quantitatively to a real building.

In chapter 6, conclusions of this study are summarized and further study is proposed.

1. Proposal of a quantitative evaluation basis for carbonation depth

a) Carbonation depth is determined. Approximately 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.

b) 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.

c) 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.

2. Prediction of service life to all mixtures of concrete using carbonation degree

a) Hydration model is valid to estimate the amount of $Ca(OH)_2$ after comparing experimental value and predicted value.

b) Predicted value using a point where the concentration of $Ca(OH)_2$ is 60% value shows similar existing result after comparing exiting predicted model.

c) Prediction of service life for carbonation to all mixtures of concrete is possible by the result of FEMA using a hydration model and carbonation degree.

3. Proposing of evaluation method for concrete $LCCO_2$ by carbonation degree

a) In terms of CO_2 reduction, evaluation method of $LCCO_2$ and CO_2 balance for concrete with proposed carbonation can be used for determining the mix proportion of concrete and service life of structure.

This study is a limit that cannot be used as the method for quantitative

evaluation of concrete carbonation, because it is based on only the experimental result for water to cement ratio of 0.45, 0.55 and 0.65 with ordinary Portland cement. In future, an additional investigation for the concrete with fly ash and blast furnace slag will be needed.

Contents

Chapter 1

Introduction

1.1 Background and Need of Research

1.1.1 Structural Standard Revision in Korea, 2012

Reinforced concrete is the most widely used structural material from the industrial era of increasing demand for housing so far.[1)] Structural standard of these reinforced concrete(hereafter RC) structures has been developed according to the needs of rationality, ensuring affordability, resource-saving, environmental protection, as shown in Fig. 1.1. In particular, the recent concerns about the sustainability of the global environment highlight the need of CO_2 reduction and green building in building industry and the financial obligations of carbon dioxide emissions is applied in some countries and will be applied to another more countries. Accordingly, structural standard was amended on the direction of activating green growth and new technologies such as high-strength and eco-friendly materials in KOREA, 2012.[2), 3)]

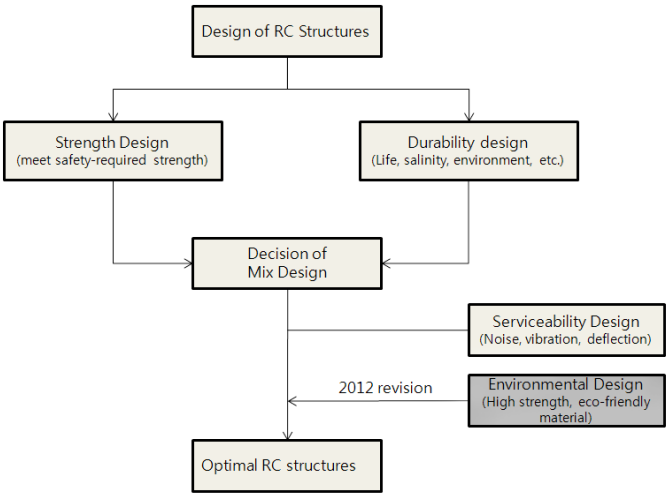


Fig. 1.1 *Design method of RC structure.*

1.1.2 A Qualitative Evaluation Limit of Concrete Carbonation Depth

Fig. 1.2 shows a process of durability deterioration by carbonation that is written in maintenance instructions of standard specification for concrete. This suggested that the life of RC structure is at the time of a rebar corrosion occurrence. Early degradation by this carbonation phenomenon such as acid rain, resulting from the rapid growth of the domestic industry since the 1970s and the increasing concentration of carbon dioxide in the atmosphere, have been reported recently.[5-8] Thus, in the case of urban corrosion initiation time by carbonation is important in terms of Durability.

In general, service life of RC structure by carbonation is evaluated at the time when the carbonation front (the color boundary between pink and colorless depth) reaches the depth of rebar in concrete using a phenolphthalein indicator considered the threshold of corrosion. Carbonation depth evaluation method using indicator could be clearly separated as shown in Fig. 1.3 (a) but in case of boundaries are ambiguous as shown in Fig. 1.3 (b) carbonation depth could be evaluated different by measurers. 10 mm carbonation depth measurement difference as shown in Fig. 1.4 causes a 25 years of service life prediction deviation.

Assessment methods between chloride attack and carbonation is compared in Fig. 1.5. In both cases, a qualitative evaluation method by using an indicator for measuring the depth of discoloration, progress of chloride attack and carbonation can be evaluated visually. In the case of salt damage quantitative evaluation can be possible by measuring chloride ion concentration at the depth of rebar location but in the case of carbonation there is still no quantitative evaluation method (evaluation materials, measurement position) and standard yet.

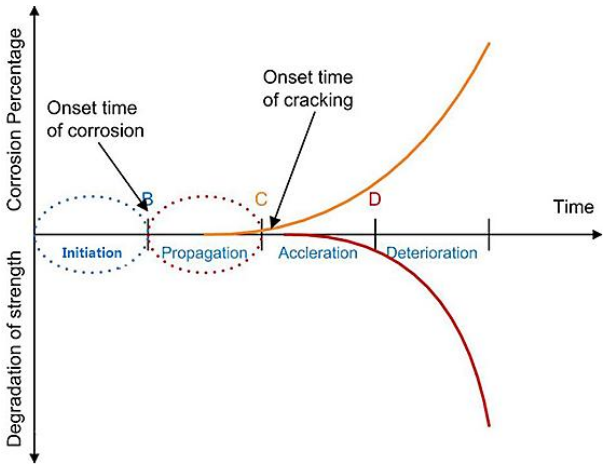
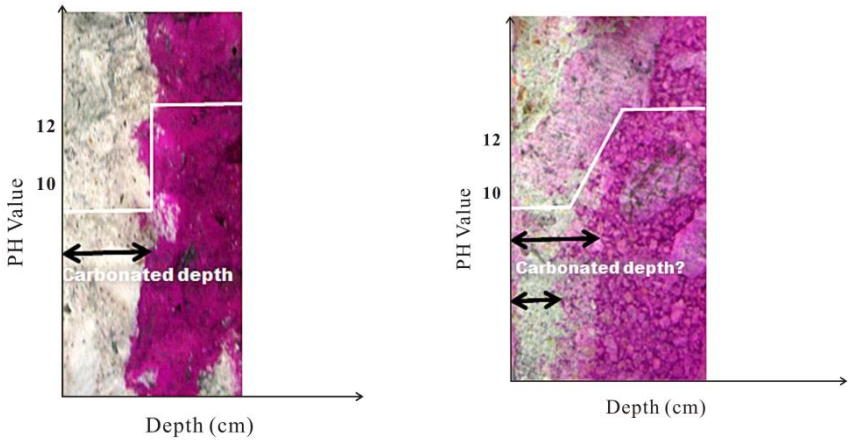


Fig. 1.2 *Deterioration by carbonation.*[4)]



a) If clarifies b) If the distinction is blurred

Fig. 1.3 *Carbonation depth evaluation by a phenolphthalein solution.*

Thus, evaluation method by indicator has a qualitative assessment limit that unstable color change may happen in the carbonation depth anytime. In addition, carbonation depth measurement method by the indicator has a problem that concrete color does not discolored in early progress of carbonation. Carbonation

depth measurement method using an indicator may cause prediction error of service life of RC structure when measurement error by measurers has happened because of ambiguous boundary. Therefore, a quantitative evaluation methods and standards for carbonation are required to overcome this problem.

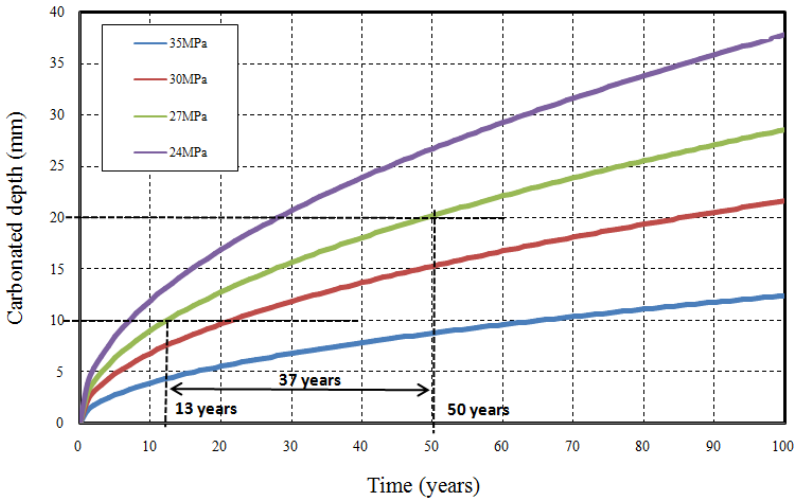


Fig. 1.4 *The service life prediction difference according to measurement error.*

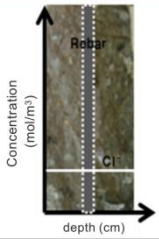
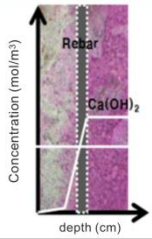
Item		Chloride Attack	Carbonation
Quantitative assessment	Figure		
	Indicator	$AgNO_3$ solution	1% phenolphthalein solution
	Measurement	Colored depth	Colored depth
Quantitative	Location	At the point of Rebar	?
	Material	Chloride ion	?
	Standard	1.2kg/m³	?

Fig. 1.5 *Comparison of evaluation methods for carbonation and salt attack.*

1.1.3 CO_2 Balance Evaluation of Concrete

Concrete carbonation is a phenomenon that indicating the strong alkali $Ca(OH)_2$ of cement hydration product in concrete reacts with CO_2 in the atmosphere to form a $CaCO_3$.

$$Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O \qquad \text{Eq. 1.1}$$

Fig. 1.6 shows the change in CO_2 concentration in the air in South Korea since 1999. The CO_2 concentration in the air has increased continuously by approximately 20 ppm from 1999 to 2007.[9] The 4th United Nations Intergovernmental Panel on Climate Change (IPCC) report stated that global warming is clearly upon us and that increased greenhouse gases due to human activity may be the main reason[10] and South Korea was the ninth largest producer of CO_2 gas emissions in 2004.[11]

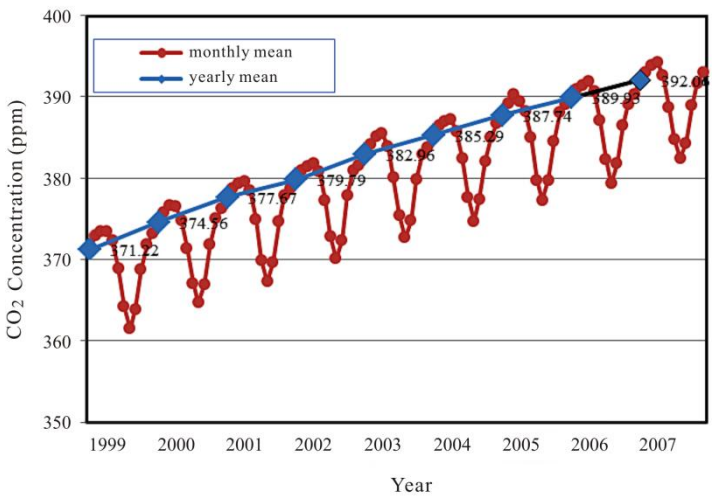


Fig. *1.6* *CO_2 concentration increase in South Korea.*

Especially, cement, which is a major constituent of concrete, emits a large quantity of CO_2 during the cement manufacturing process through

decarboxylation of limestone and this makes people consider that cement is not an eco-friendly building material.

But concrete reabsorbs CO_2 gas in the air through carbonation during service life. Recently, some scientists have focused on concrete carbonation, such as carbon capture storage (CCS) and carbon capture reuse (CCR). Quantitative evaluations of CO_2 absorption through the carbonation of concrete have recently been reported in North America and northern Europe.[12, 13)]

However, there is no formula to calculate CO_2 absorption through carbonation yet. Even in case of equation 1.2, which is normally used, the ratio of CaO, which react with carbon dioxide is assumed different by researchers. (Claus Pade: 75%, Gajda: 32～37%) So, calculation result of CO_2 absorption is different by researchers.

$$CO_2 \text{ absorption}(\text{kg-}CO_2/\text{m}^3 \text{ concrete}) = 0.75 \times C \times CaO \times M_{CO2} / M_{CaO} \ (\text{kg/m}^3) \quad \text{Eq.1.2}$$

where,

M_i: the molecular weight of component M_i,

C: cement quantity of 1 m^3 concrete (kg/m^3),

CaO: CaO content of cement clinker (%).

In case of the above researchers, a maximum amount of carbon dioxide that concrete is capable of absorbing is calculated on the basis of concrete mix. But it is needed to know carbonation depth, degree considering service life of RC structure in order to calculate CO_2 absorption because CO_2 absorption is proportional to carbonation degree of concrete in a real condition.

1.2 Objectives of Research

The objective of this study is to establish a quantitative evaluating method that overcomes the limitation of qualitative evaluation, which is carried out using the naked eye with respect to the color change boundary by spraying indicator. Carbonation depth becomes the basic data for estimating the residual life and durability of RC structures. To achieve this objective, the quantitative change of $Ca(OH)_2$ and $CaCO_3$ for each depth in concrete according to the carbonation process is measured using TG/DTA in order to propose a quantitative method and an evaluation basis. Another one is to propose evaluating method of a CO_2 absorption quantity in the air through carbonation and how to evaluate $LCCO_2$ (emission-absorption of CO_2).

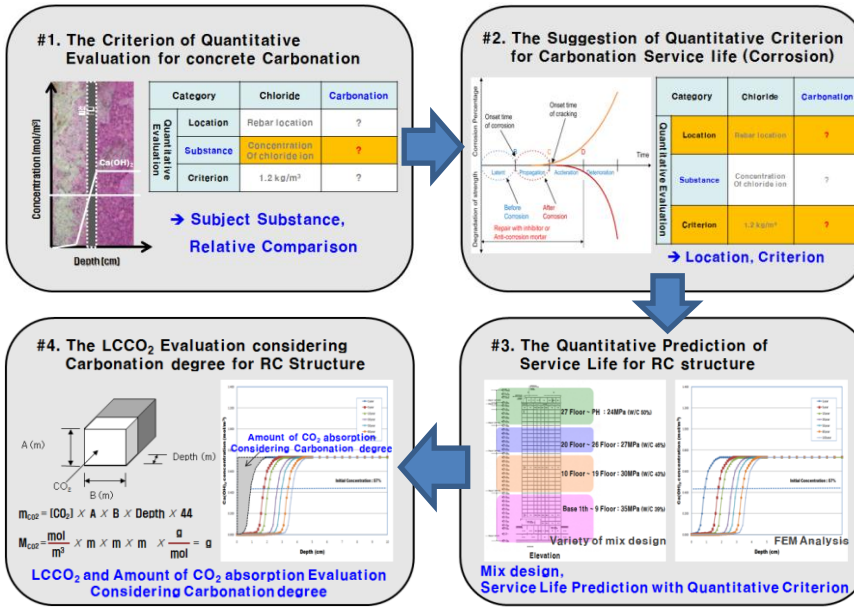


Fig. 1.7 *Correlation of research objectives.*

The specific goals of this study are the same as below, correlation between

each objective is shown in Fig. 1.7.

a) Proposal of a quantitative evaluation basis for carbonation depth

b) Proposal of an evaluation basis for service life of concrete against carbonation

c) Prediction of service life for carbonation using proposed basis

d) Evaluation for a CO_2 absorption quantity in the air through carbonation and $LCCO_2$ (emission-absorption of CO_2) during service life

1.3 Configuration and Contents of Research

This study is composed of six chapters as below and progressed sequentially in order to accomplish objectives.

Chapter 1. Introduction.

Necessity and objectives of this study are explained.

Chapter 2. Literature review.

Review for carbonation and a quantitative evaluating method is conducted to support qualitative evaluating method by indicators.

- Definition of concrete carbonation and mechanism.
- A quantitative evaluating method and substances for concrete carbonation
- Relation between carbonation and rebar corrosion.
- Prediction model of concrete carbonation.
- Cement hydration model.

Chapter 3. Deduction of a quantitative evaluating basis for carbonation through a quantitative evaluation experiment.

Correlation between pH value and quantities of $Ca(OH)_2$, $CaCO_3$ is analyzed experimentally by carbonation weeks, concrete depths through accelerated carbonation experiment in order to propose a quantitative evaluating basis.

Quantity of $Ca(OH)_2$ is important to predict service life of concrete against carbonation and cement hydration model can predict it quantitatively to any concrete mix. Therefore, validation for cement hydration model is verified by comparing prediction valued using it and measured values of $Ca(OH)_2$.

Chapter 4. Prediction of service life using a quantitative evaluation basis.

Prediction model for carbonation based on FEM is used to predict the service life of RC structure. Required input data such as initial concentration of $Ca(OH)_2$, diffusion coefficient of CO_2, reaction velocity constant, CO_2 concentration in the air for FEMA are decided through literature review. The proposed quantitative evaluation basis in chapter 3 is used to evaluate and predict service life.

Chapter 5. $LCCO_2$ evaluation of RC structure during service life.

CO_2 emission of concrete considering concrete mix and CO_2 absorption through carbonation during service life for unit volume concrete is calculated quantitatively. And then, CO_2 balance (emission-absorption of CO_2) and $LCCO_2$ is evaluated quantitatively to a real building.

Chapter 6. Conclusion

Conclusions of this study are summarized and further study is proposed.

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.

$$Ca(OH)_2 + CO_2 + H_2O \rightarrow CaCO_3 + 2H_2O \qquad \text{Eq. 2.1}$$

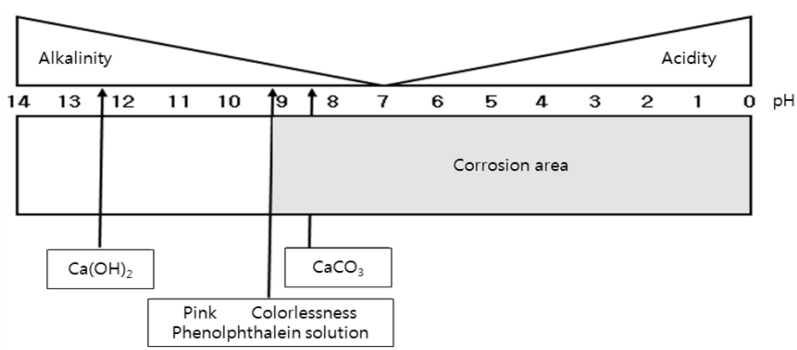
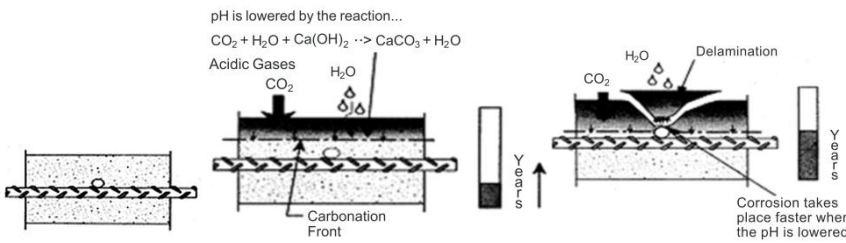


Fig. 2.1 *pH reduction by Carbonation process (Stark, J. and Whict, B. (1998)).*[15]

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 (pH>12) b) Carbonation progress (pH becomes low) c) Peeling phenomenon (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.

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

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

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

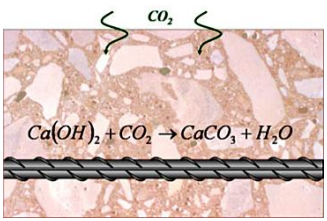


Fig. 2.3 *CO_2 penetration into concrete.*[16)]

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)]

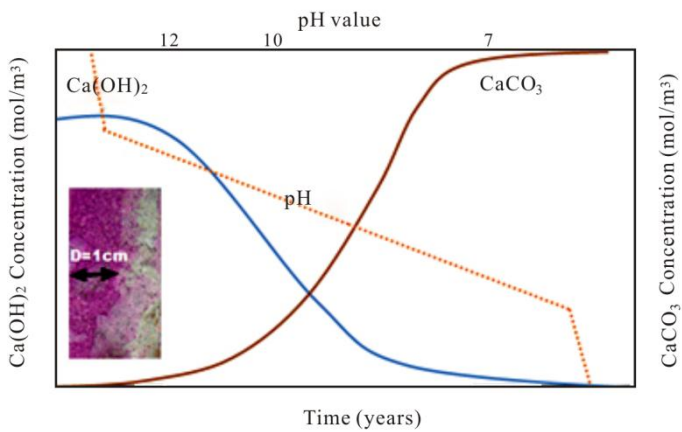


Fig. 2.4 *Change of $Ca(OH)_2$, $CaCO_3$ concentration and pH value with time.*

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).

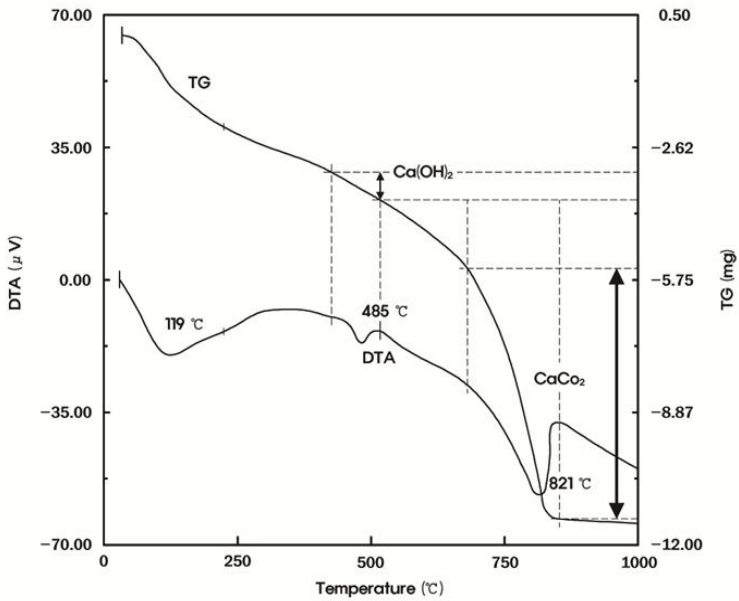


Fig. 2.5 *Concrete characteristic curves of TG/DTA.*[21)]

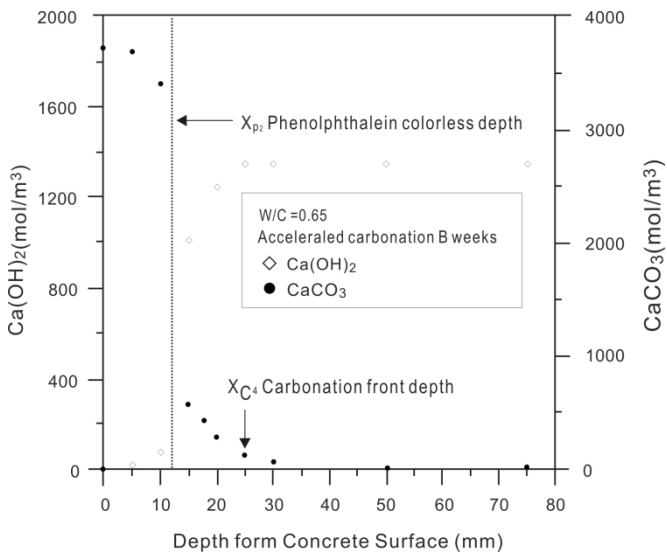


Fig. 2.6 *Relationship between phenolphthalein colorless depth, $CaCO_3$ and $Ca(OH)_2$ concentration distribution by TGA.*[21)]

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_2O, H_2O from C-S-H, AFt, AFm, gypsum, and CO_2 absorbed in C-S-H
2	430 to 520 ℃	H_2O from portlandite $Ca(OH)_2$
3	520 to 650 ℃	OH- from structure of hydrates, structure H_2O, 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_2O

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.

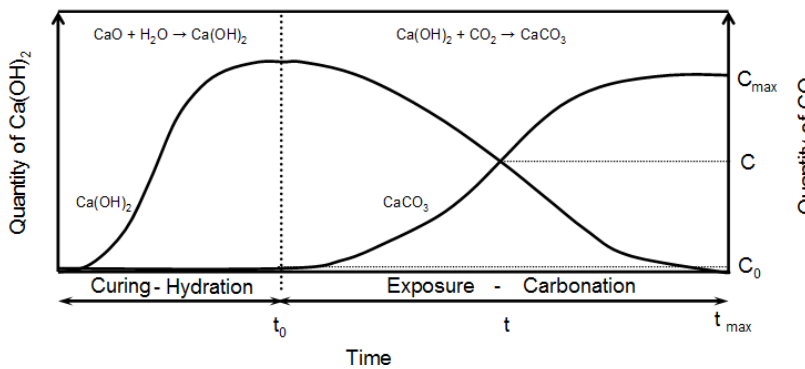


Fig. 2.7 *Quantity change of $Ca(OH)_2$ and $CaCO_3$ to time.*

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	Factors				
		W/C	Cement Type	Aggre. Type	Surr. Environ	Comp. Strengh
Hamada	$t = \frac{k}{R} C^2$	○	○	○		
Kishitani	$t = \frac{0.3(1.15+3x)}{R^2(x-0.25)^2} C^2$ (x≥0.6) $t = \frac{7.2}{R^2(4.6x-1.76)^2} C^2$ (x≤0.6)	○	○	○	○	
Sirayama	$t = \alpha\beta\gamma\delta\varepsilon \frac{5000}{(x-38)^2} C^2$	○	○	○	○	
Yoda	$t = \alpha\beta\gamma \frac{Pt^2}{(100x-Q)^2} C^2$	○			○	
Smolczyk	$x = 7.00\left(\frac{10\frac{W}{C}}{\sqrt{N_t}} - 0.175\right)\sqrt{t} - 0.50$	○				○
Wierjg	$x = \left(84.62 - \frac{\frac{W}{C}}{\sqrt{N_7}} - 0.64\frac{W}{C} - 1.63\right)\sqrt{t} + 0.9$	○				○
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	$\frac{2mm}{\sqrt{year}}$	$\frac{1.0mm}{\sqrt{year}}$	$\frac{0.75mm}{\sqrt{year}}$	$\frac{0.5mm}{\sqrt{year}}$
Buried	$\frac{3mm}{\sqrt{year}}$	$\frac{1.5mm}{\sqrt{year}}$	$\frac{1mm}{\sqrt{year}}$	$\frac{0.75mm}{\sqrt{year}}$
Exposed	$\frac{5mm}{\sqrt{year}}$	$\frac{2.5mm}{\sqrt{year}}$	$\frac{1.5mm}{\sqrt{year}}$	$\frac{1.0mm}{\sqrt{year}}$
Sheltered	$\frac{10mm}{\sqrt{year}}$	$\frac{6mm}{\sqrt{year}}$	$\frac{4mm}{\sqrt{year}}$	$\frac{2.5mm}{\sqrt{year}}$
Indoors	$\frac{15mm}{\sqrt{year}}$	$\frac{9mm}{\sqrt{year}}$	$\frac{6mm}{\sqrt{year}}$	$\frac{3.5mm}{\sqrt{year}}$

* 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 × A (m^2) per unit time (Eq. 2.15) is equal to one through micro section (Eq. 2.16).[25)]

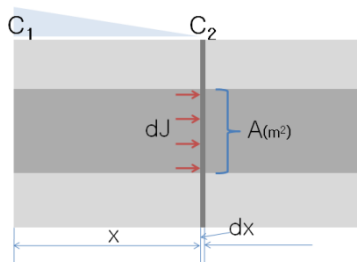


Fig. 2.8 *Carbonation Model.*

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

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

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

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

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

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)]	$\frac{\mathrm{d}}{\mathrm{dt}}\left(D_{CO_2}\frac{d[CO_2]}{dx}\right)+\frac{\mathrm{d}}{\mathrm{dt}}([Ca(OH)_2+3[\mathrm{C-S-H}]+3[C_3\mathrm{S}]+2[C_2\mathrm{S}])+\alpha=0$

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.

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

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.

$$[Ca(OH)_2] = \frac{3}{2}[C_3S]_0F_{C_3S} + \frac{1}{2}[C_2S]_0F_{C_2S} - 4[C_4AF]_0F_{C_4AF} - [C_3A]_0F_{C_3A} + [C\bar{S}H_2]_0 \quad \text{Eq. 2.22}$$

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)]

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

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.

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

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

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.

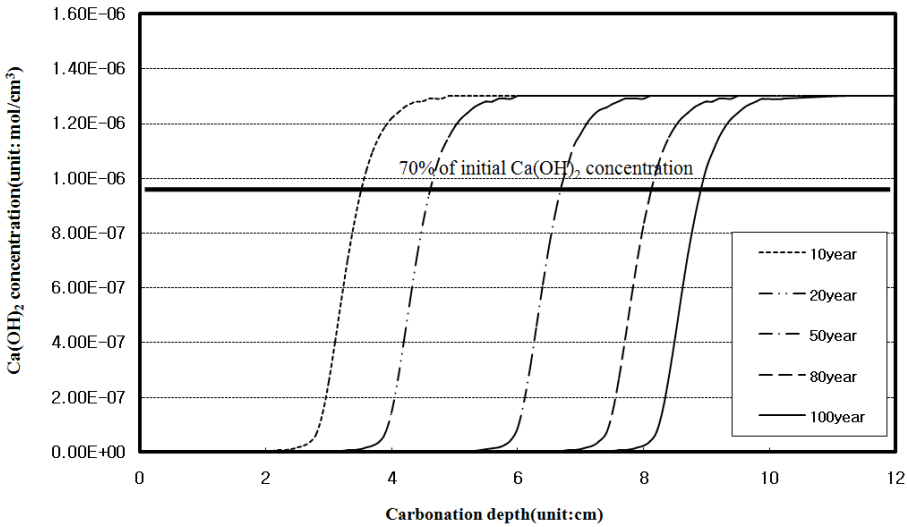


Fig. 2.9 *Carbonation model by using FEMA.*

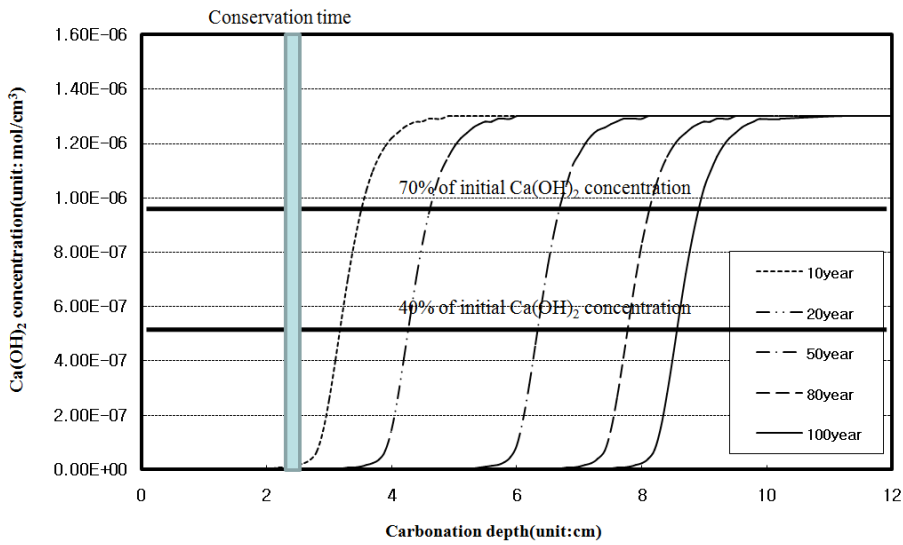


Fig. 2.10 *Carbonation model with using FEMA.*

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.

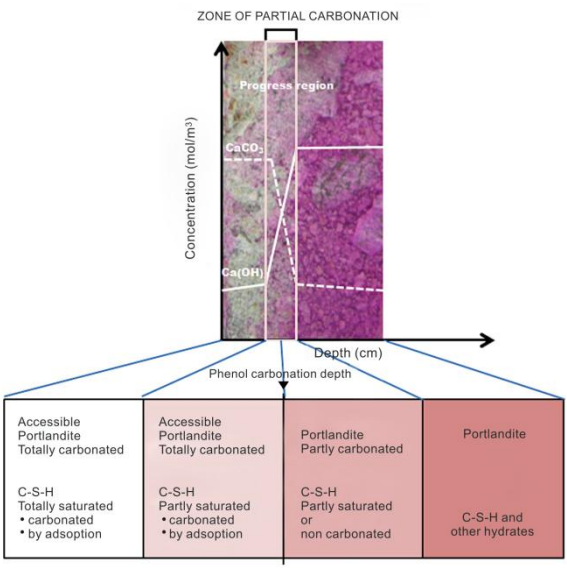


Fig. 2.11 *Outline of four zones exhibiting various levels of carbonation in concrete.*[22]

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.

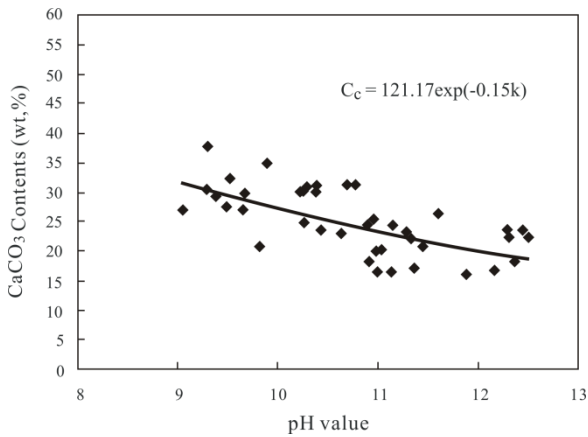


Fig. 2.12 *pH value according to the contents of calcium carbonate.*[29]

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.

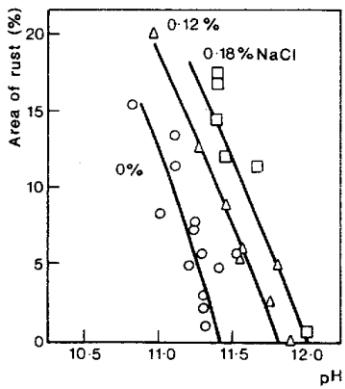


Fig. 2.13 *Effect of pH upon corrosion of steel in carbonated mortar.*[31]

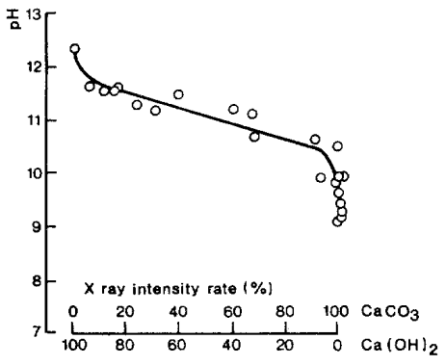


Fig. 2.14 *pH value versus X-ray diffraction intensity.*[14]

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.

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.

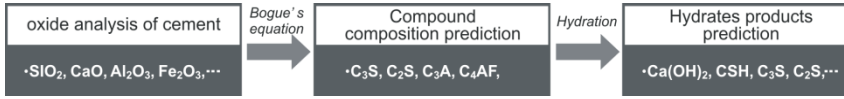


Fig. 3.1 *Calculation outline of hydration product.*

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
$C_3S(3CaO.SiO_2)$	52.8
$C_2S(2CaO.SiO_2)$	20.7
$C_3A(3CaO.Al_2O_3)$	11.5
$C_4AF(4CaO.Al_2O_3.Fe_2O_3)$	8.8

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

$$2(C_2S) + 4H \xrightarrow{r_{H,C2_3S}} C_3S_2H_3 + CH \qquad \text{Eq. 3.3}$$

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

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

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

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

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

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

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

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

($[i]_0$ is an initial molar concentration of constituent (i=C_3S, C_2S, C_4AF, C_3A))

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_3S	C_2S	C_4AF	C_3A	CH_2
Exponent n_i	2.65	3.10	3.81	2.41	-
Coefficient k_{ni} (20C)×10^5(s^{-1})	1.17	0.16	1.00	2.46	-
Molar weight MW×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.

$$[Ca(OH)_2] = \frac{3}{2}[C_3S]_0F_{C_3S} + \frac{1}{2}[C_2S]_0F_{C_2S} - 4[C_4AF]_0F_{C_4AF} - [C_3A]_0F_{C_3A} + [C\bar{S}H_2]_0 \quad \text{Eq. 3.11}$$

$$[CSH] = \frac{1}{2}[C_3S]_0F_{C_3S} + \frac{1}{2}[C_2S]_0F_{C_2S} \quad \text{Eq. 3.12}$$

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

$$[c_2s] = [c_2s]_0(1 - F_{c_2s}) \quad \text{Eq. 3.14}$$

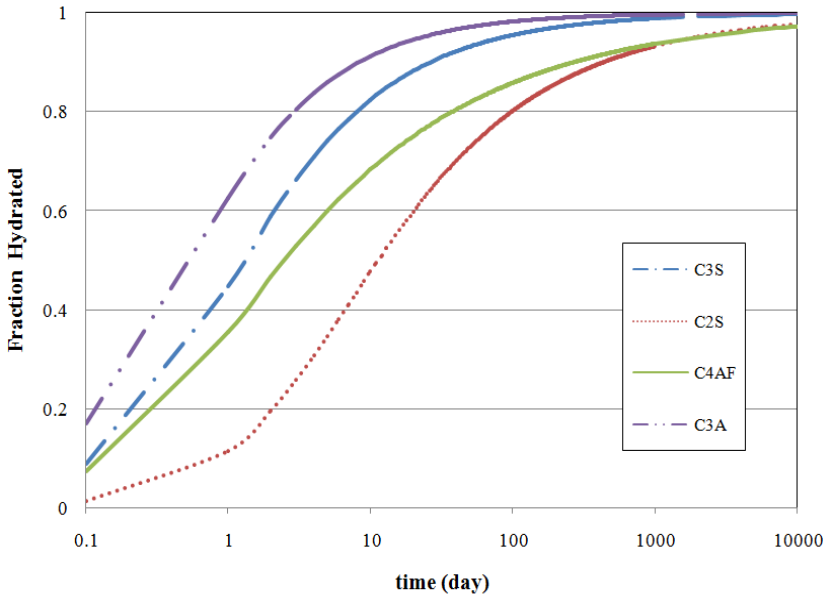


Fig. 3.2 *Hydration speed of the four major constituents.*

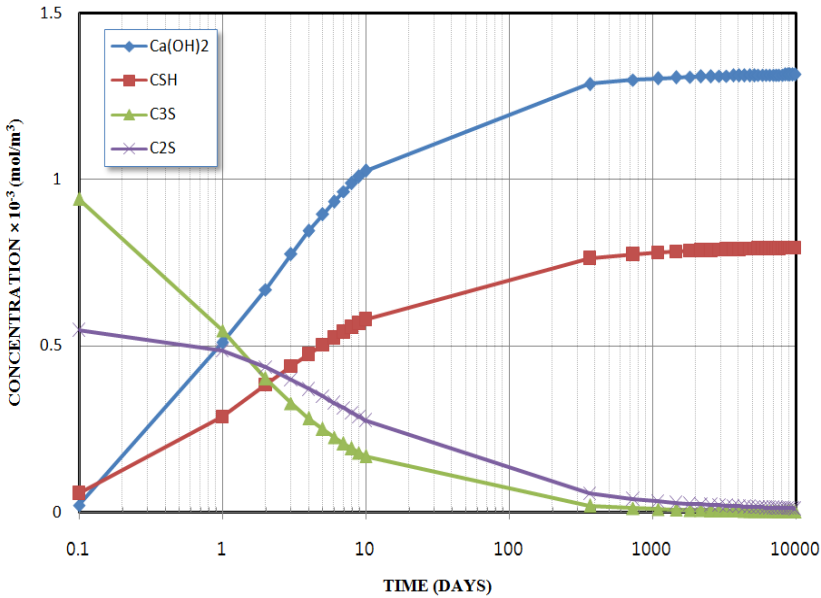


Fig. 3.3 *Hydration product change with hydration time.*

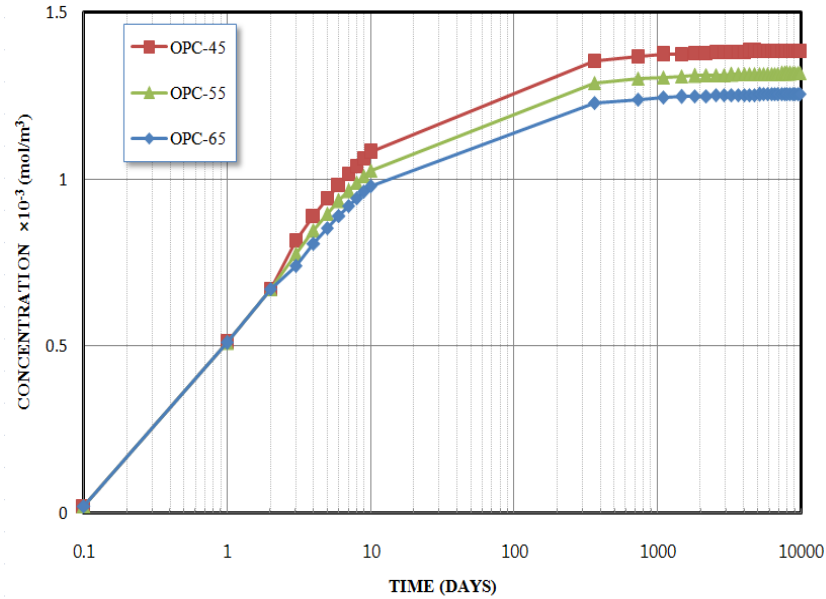


Fig. 3.4 *$Ca(OH)_2$ quantity change with W/C ratio (a/c=3).*

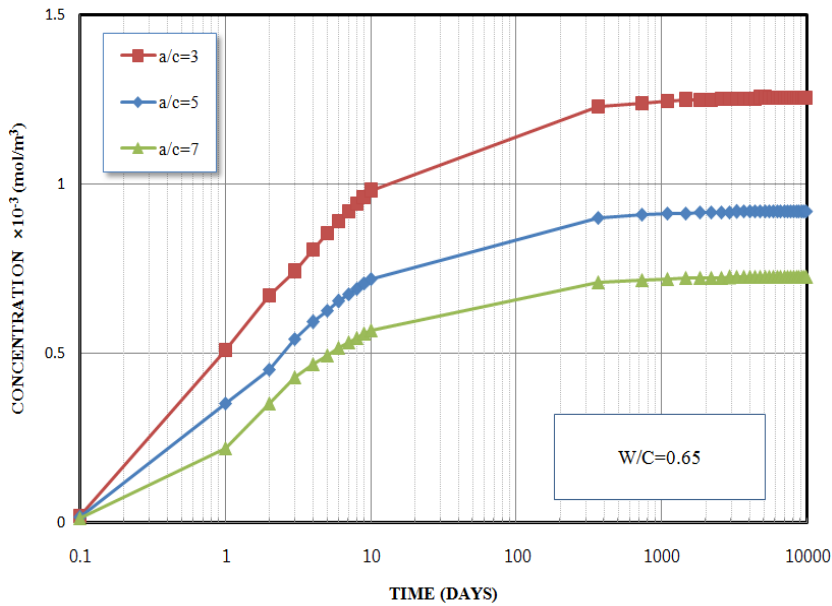


Fig. 3.5 *$Ca(OH)_2$ quantity change with a/c ratio (w/c= 0.65).*

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.

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

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

Where, $[i]_0$: initial concentration of compound i. (i =C_3S, C_2S, C_4AF, C_3A)

$[F]_i$: weight fraction of compound i with hydration time (i=C_3S, C_2S, C_4AF, C_3A)

$\Delta\bar{V}_i$: volume difference between reactants and products (I = C_3S, C_2S, C_4AF, C_3A)

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

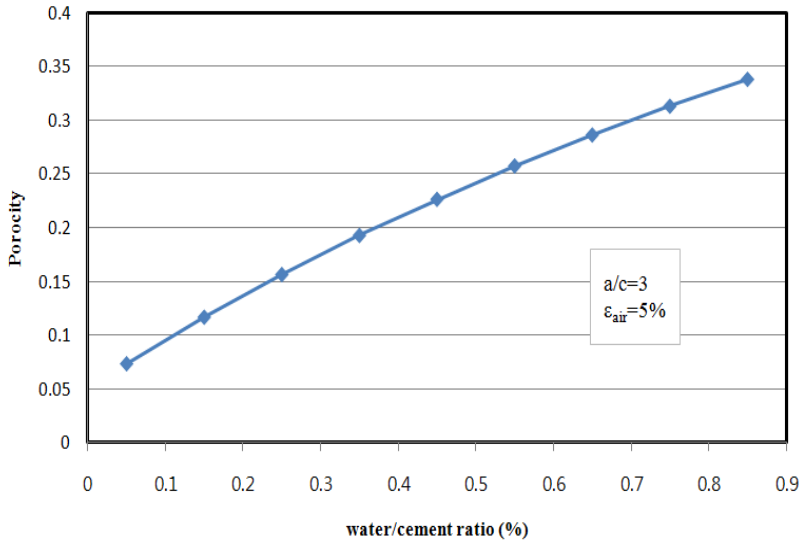


Fig. 3.6 *Porosity according to w/c ratio.*

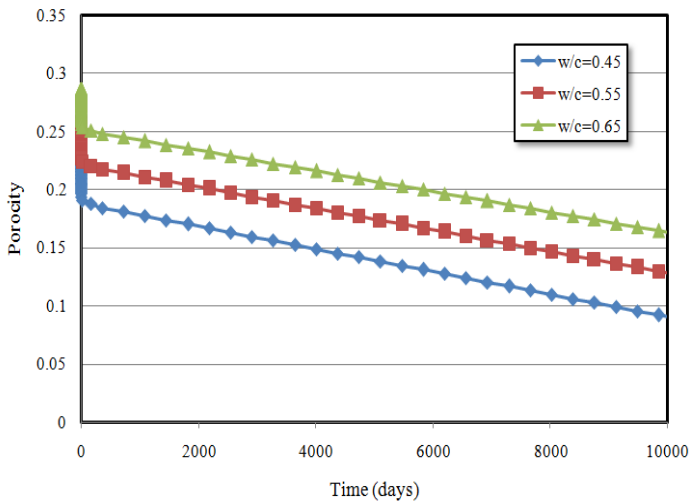


Fig. 3.7 *Porosity according to w/c ratio with time.*

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 × 5 cm × 5 cm of cube. Concrete specimens were fabricated in a cylinder shape and the size is Φ10 cm × 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.

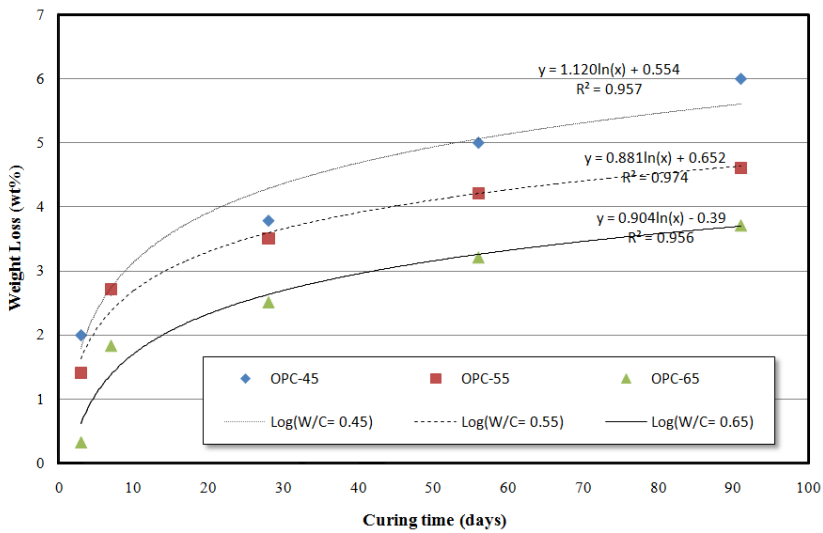


Fig. 3.9 *Weight loss of concrete according to w/c ratio with time.*

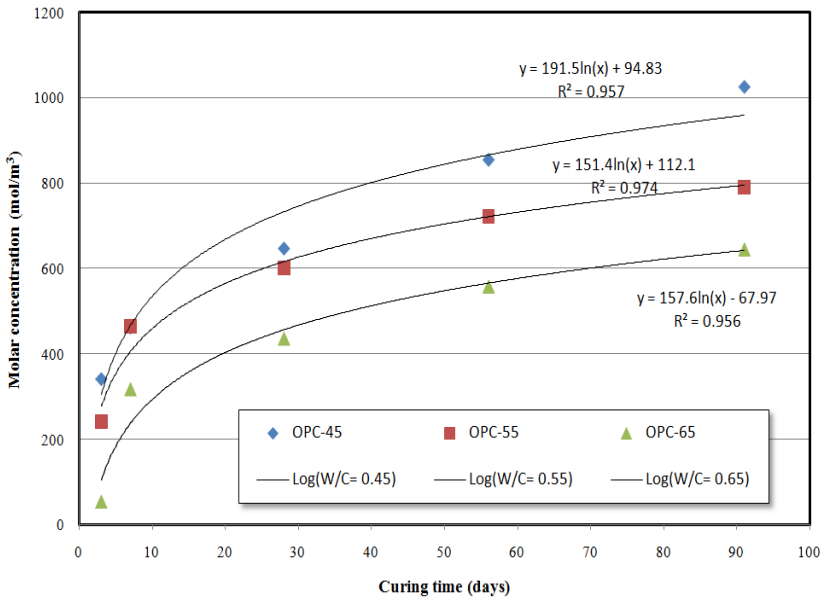


Fig. 3.10 *Molar concentration of concrete according to w/c ratio with time.*

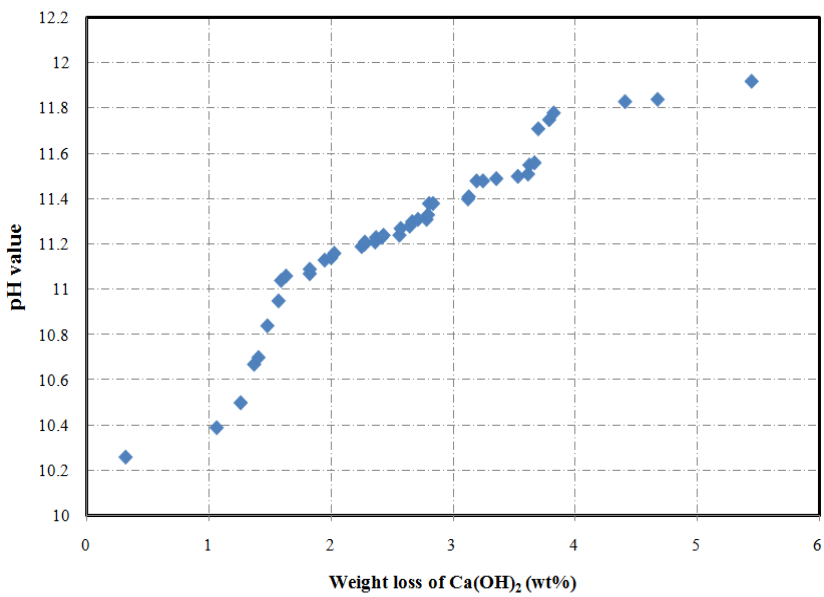


Fig. 3.11 *Relation between pH value and the amount of $Ca(OH)_2$.*

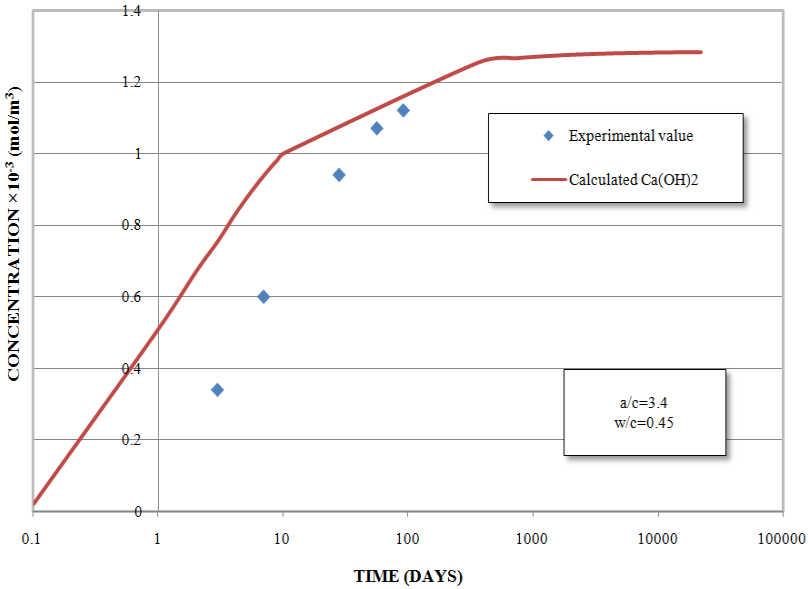


Fig. 3.12 *Comparison between experiment and calculated values of $Ca(OH)_2$ (w/c= 0.45).*

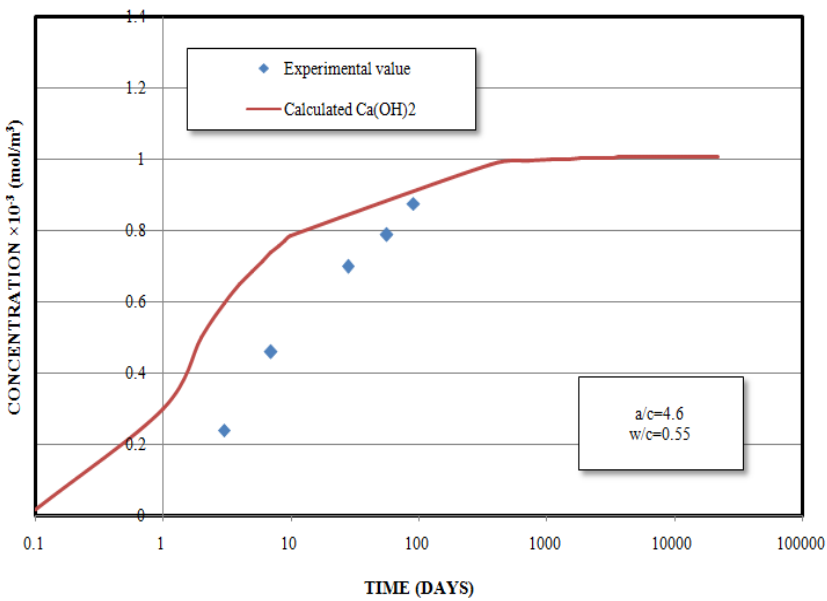


Fig. 3.13 *Comparison between experiment and calculated values of $Ca(OH)_2$ (w/c= 0.55).*

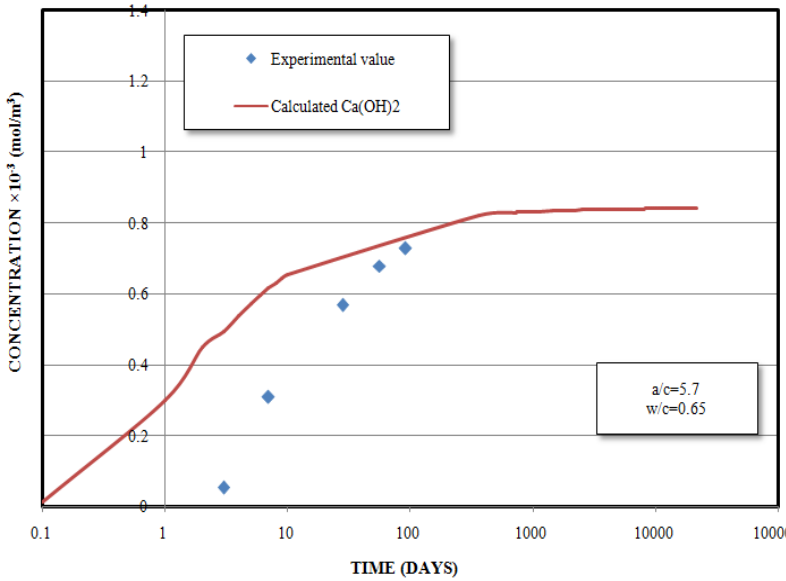


Fig. 3.14 *Comparison between experiment and calculated values of $Ca(OH)_2$ (w/c = 0.65).*

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

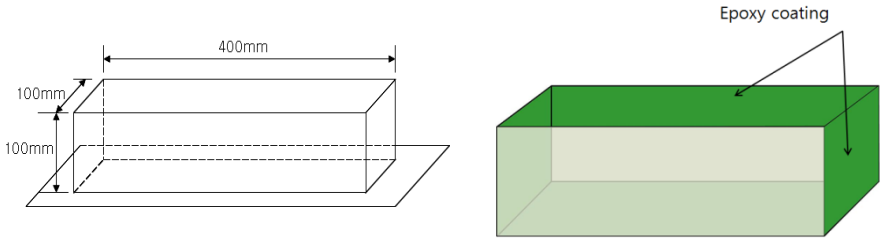
In KS F 2584, the size of specimen for concrete is 100 × 100 × 400 mm, it should be cured in 20 ℃ and relative humidity 60% in the air for 28 days after water curing for 28 days. But in this experiment, the specimens are cured in water for 3 months and are cured in air dry for 1 month. The specimens 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.



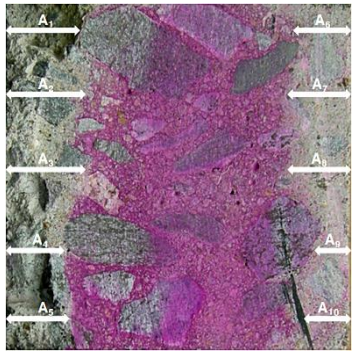
a) size of specimen b) painting side with epoxy

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

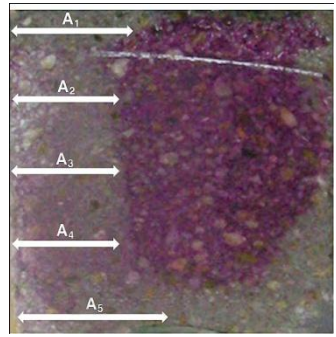
Fig. 3.16 *Experiment outline and process.*



$$^{0}X_P = \frac{\sum_{i=1}^{10} A_i + \sum_{i=1}^{10} B_i + \sum_{i=1}^{10} C_i}{30}$$

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

Fig. 3.17 *Carbonation depth measurement of concrete.*



$$^{0}X_P = \frac{\sum_{i=1}^{5} A_i + \sum_{i=1}^{5} B_i + \sum_{i=1}^{5} C_i}{15}$$

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.*

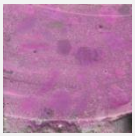
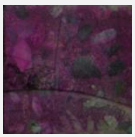
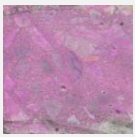
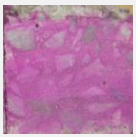
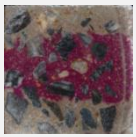
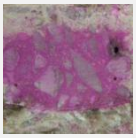
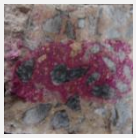
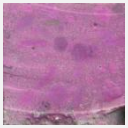
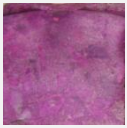
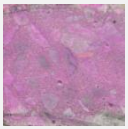
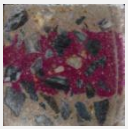
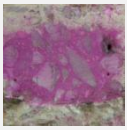
time / W/C	scale	1 week	4 weeks	8 weeks	13 weeks
C-OPC-45	 5				
C-OPC-55	 5				
C-OPC-65	 5				

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.

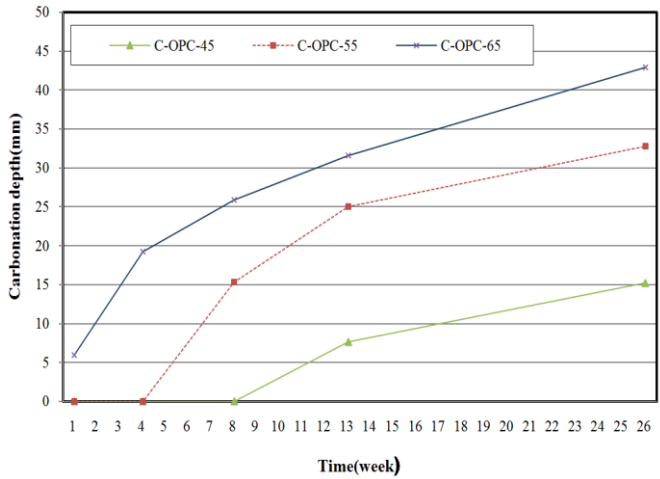


Fig. 3.19 *Carbonation depth measurement of concrete by accelerated carbonation time.*

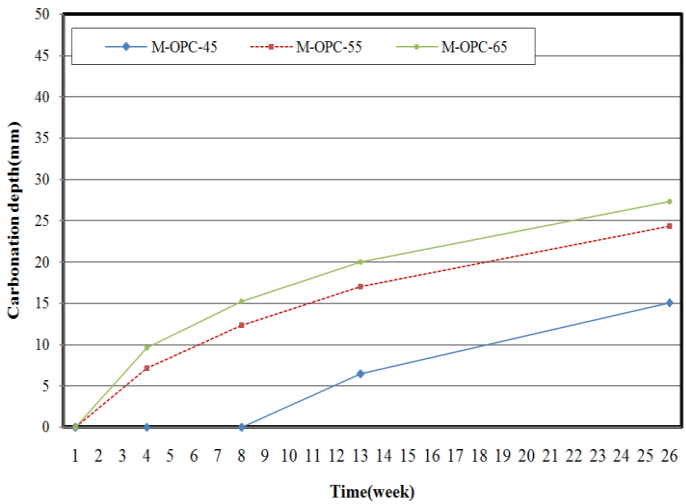


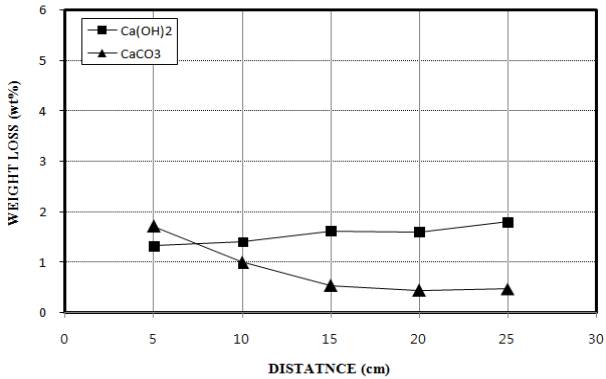
Fig. 3.20 *Carbonation depth measurement of mortar by accelerated carbonation time.*

(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

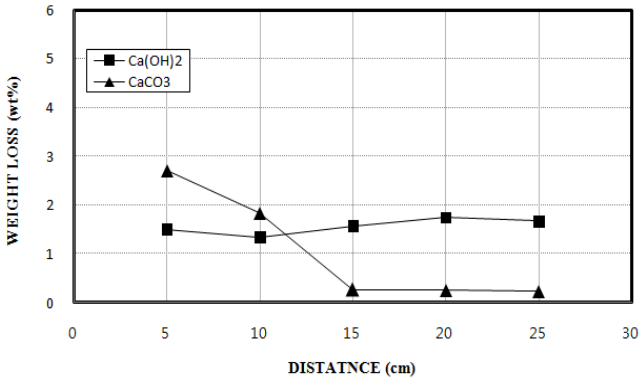
To measure the change of $Ca(OH)_2$ and $CaCO_3$ according to the depth of each carbonation time, 5 mm samples were collected from the surface of the specimen to the internal direction according to the mixture and carbonation times. Then, $Ca(OH)_2$ and $CaCO_3$ in samples were quantitatively measured 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.

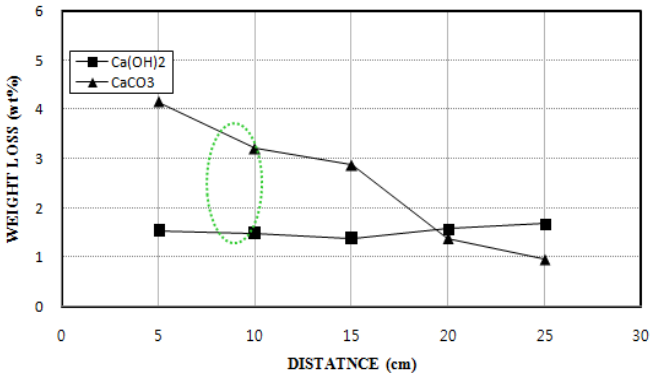
Fig. 3.24 shows the weight loss ratio of the amount of $Ca(OH)_2$, $CaCO_3$ at each depth in mortar with carbonation time. The weight loss ratio of the amount of $Ca(OH)_2$ and $CaCO_3$ with carbonation time increases much in a nearer depth from surface and this tendency is measured apparently in a higher water to cement ratio.



a) 1 week

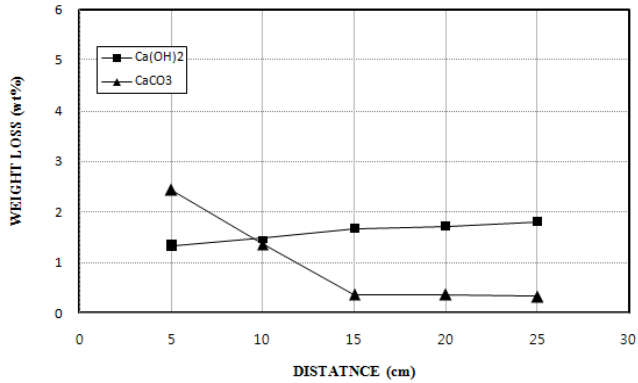


b) 4 weeks

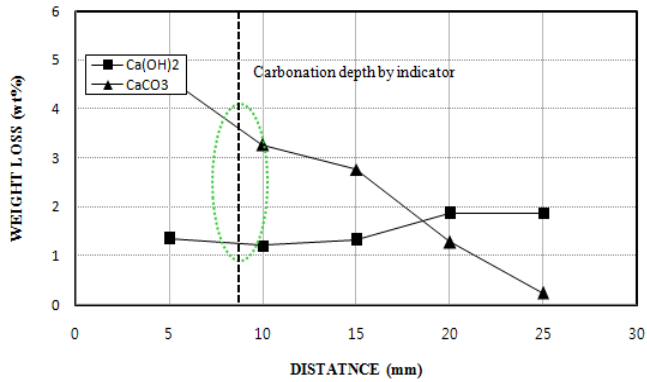


c) 8 weeks

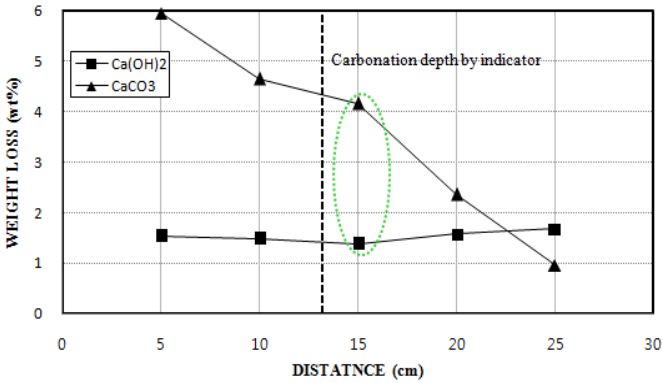
Fig. 3.21 *Weight loss of $Ca(OH)_2$ and $CaCO_3$ in mortar specimen according to accelerated carbonation time (w/c=0.45).*



a) 1 week

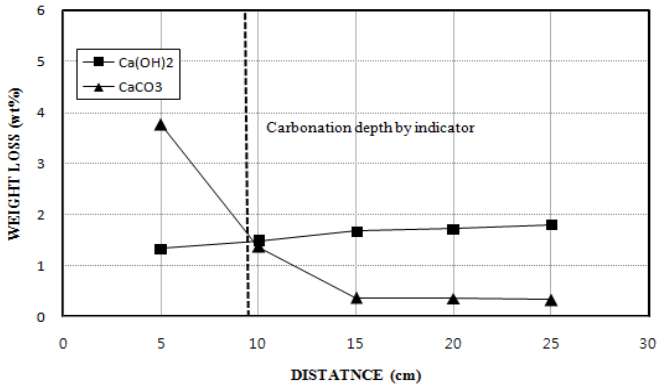


b) 4 weeks

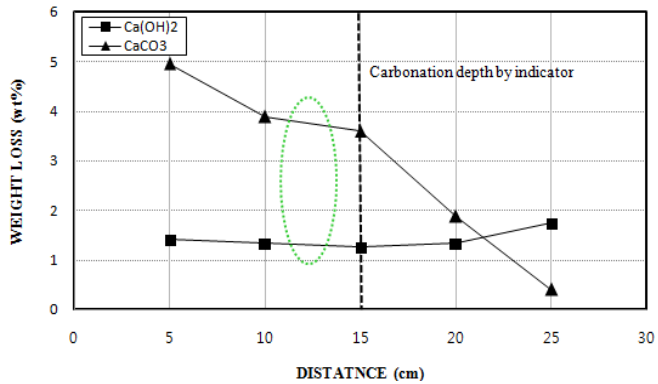


c) 8 weeks

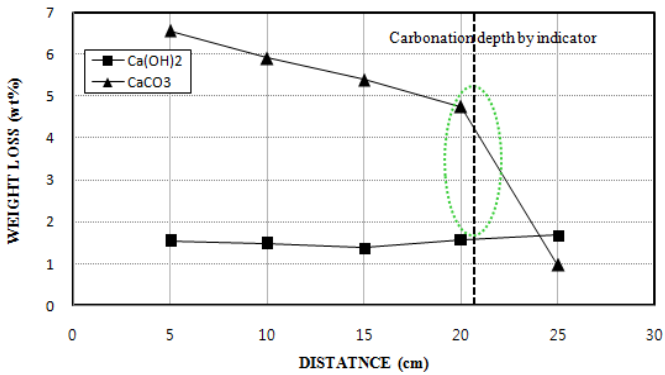
Fig. 3.22 *Weight loss of $Ca(OH)_2$ and $CaCO_3$ in mortar specimen according to accelerated carbonation time (w/c=0.55).*



a) 1 week

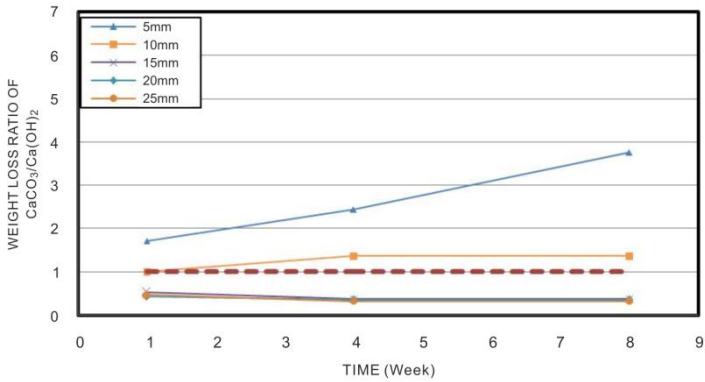


b) 4 weeks

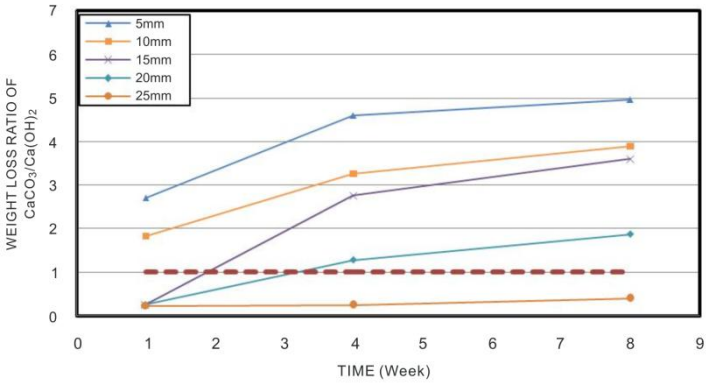


c) 8 weeks

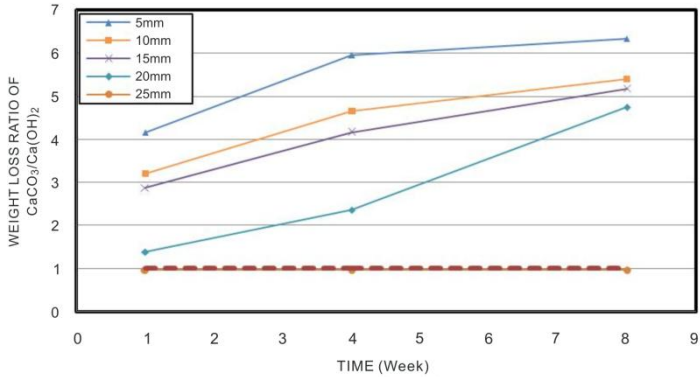
Fig. 3.23 *Weight loss of $Ca(OH)_2$ and $CaCO_3$ in mortar specimen according to accelerated carbonation time (w/c=0.65).*



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.*

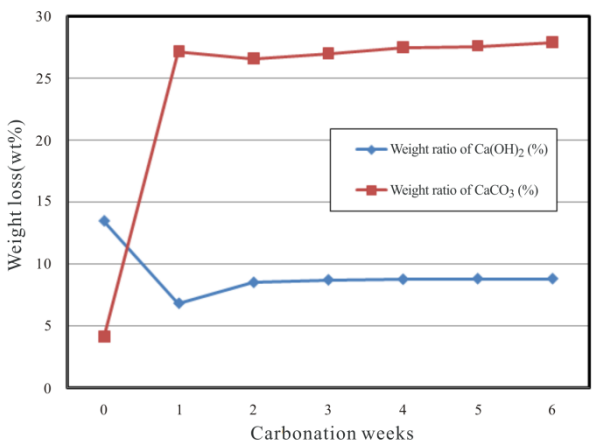


Fig. 3.26 *Weight loss of $Ca(OH)_2$ and $CaCO_3$ according to accelerated carbonation time (CO_2:100%).*

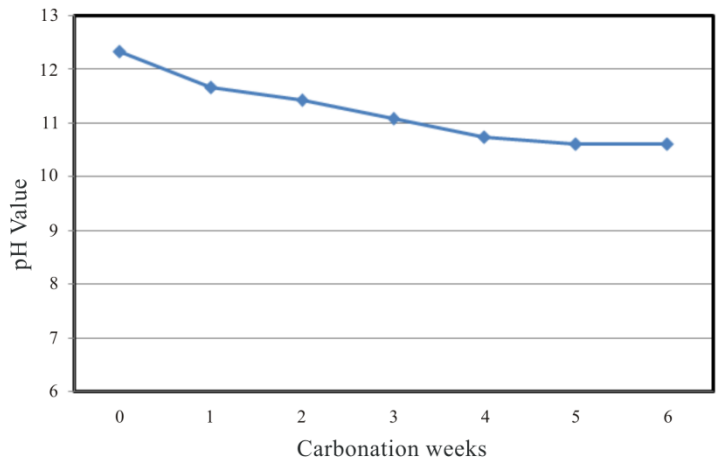


Fig. 3.27 *pH value according to accelerated carbonation time (CO_2:100%).*

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.

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

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.

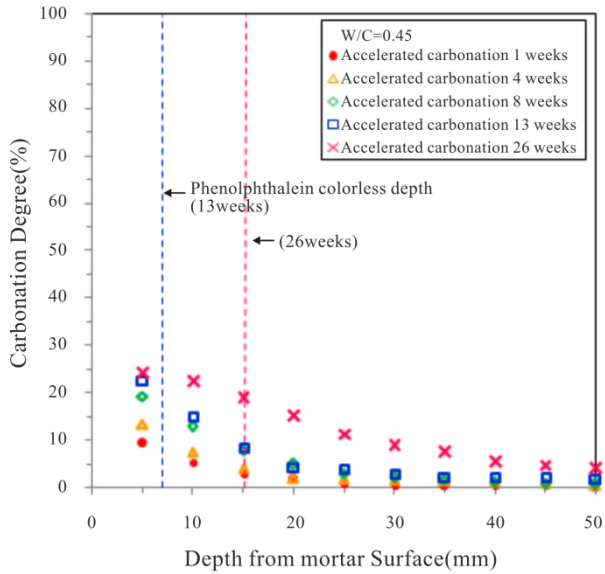


Fig. 3.28 *Relation between carbonation degree and phenolphthalein colorless depth with carbonation time (W/C=0.45).*

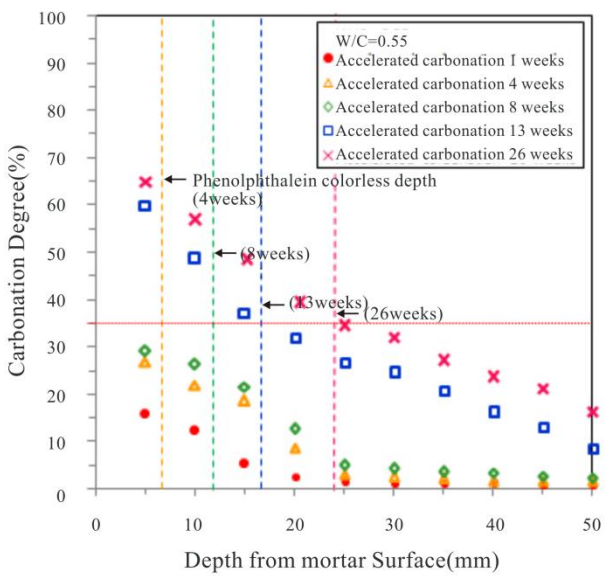


Fig. 3.29 *Relation between carbonation degree and phenolphthalein colorless depth with carbonation time (w/c=0.55).*

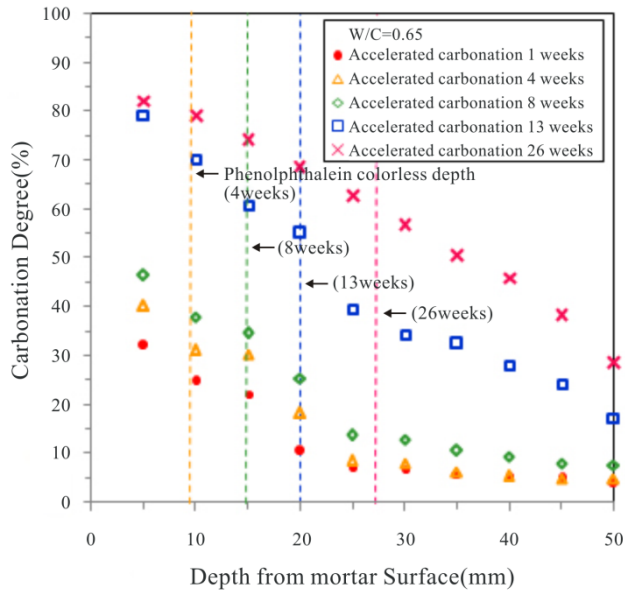


Fig. 3.30 *Relation between carbonation degree and phenolphthalein colorless depth with carbonation time (W/C=0.65).*

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 $CaCO_3$ according to weight loss ratio.*

Weight loss ratio ($Ca(OH)_2$: $CaCO_3$)	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.

Chapter 4

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 $Ca(OH)_2$ 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 $Ca(OH)_2$, 2) diffusion coefficient of CO_2 in concrete, 3) The reaction rate constant between $Ca(OH)_2$ and $CaCO_3$, and 4) CO_2 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 $Ca(OH)_2$ compared to the initial concentration of $Ca(OH)_2$ is a level of 60%.

4.2 Concrete Carbonation Model Using a FEMA

4.2.1 A Diffusion Equation of CO_2 in Concrete Based on the Chemical Reaction

A concrete carbonation is a physiochemical reaction that lowers pH in concrete because $Ca(OH)_2$, which shows a strong alkali content in concrete, is reacted with CO_2 in the atmosphere and consequently generates $CaCO_3$. 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.

$$Ca(OH)_2 + CO_2 \rightarrow Ca(CO)_3 + H_2O \qquad \text{Eq. 4.1}$$

The model for CO_2 diffusion in concrete and carbonation reaction is based on

following assumptions:

1. Concrete is a semi-infinite fixed body and CO_2 flow in concrete is considered to flow in an only one direction (X-direction).
2. The CO_2 movement in concrete diffuses by Fick's first law.
3. Reaction between $Ca(OH)_2$ and CO_2 in concrete is a one-dimensional reaction.
4. The movement of $Ca(OH)_2$ 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_2 entering by diffusion at plane X = x at time Δt is proportional to concentration gradient. So, when the concentration of CO_2, the concentration change of CO_2 during time Δt, diffusion coefficient of CO_2 in concrete is expressed in $C= C(x, t)$, Δt, D, it can be showed in Eq. 4.2.

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

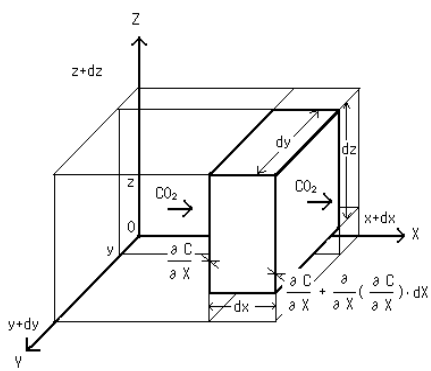


Fig. 4.1 *Migration and reaction of CO_2 in a tiny concrete section.*

The amount of CO_2 coming out from plane $X= x+\Delta x$ is expressed in Eq. 4.3.

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

Also, the amount of CO_2 being lost by reacting with $Ca(OH)_2$ in a tiny section can be expressed in Eq. 4.4 when the concentration of $Ca(OH)_2$ is $Ca = Ca\ (x, t)$ and the reaction rate constant is k.

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

The changed amount of CO_2 in the region during time, Δt can be expressed in Eq. 4.5 from Eq. 4.2, 4.3 and 4.4.

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

Eq. 4.6 is a diffusion equation of CO_2 showing one-dimension reaction between $Ca(OH)_2$ and CO_2 through dividing both sides of the above equation by dx • dy • dz.

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

4.2.2 The Progress of Carbonation Based on the Chemical Reaction

Calcium ion, Ca^{+2}, second term on the right side in Eq. 4.6, shows the concentration of $Ca(OH)_2$ and this value decreases by reaction with CO_2. Decreasing the value of Ca is a result of the reduction of the pH value in concrete and this shows concrete carbonation. Ca can be expressed as the amount of decreased CO_2 in a tiny section. Chemical reaction between CO_2 and $Ca(OH)_2$ is assumed in a one-dimension reaction and ΔC_a, the amount of concentration change of $Ca(OH)_2$ during time Δt can be expressed as follows.

$$\Delta Ca = -k \cdot C \cdot Ca \cdot \Delta t \qquad \text{Eq. 4.7}$$

Eq. 4.7 can be expressed in Eq. 4.8.

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

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

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

Eq. 4.9 shows concentration of $Ca(OH)_2$ 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 $Ca(OH)_2$ and CO_2. CO_2 diffusion in accordance with Fick's first law.

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

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]

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

[Boundary conditions]

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

where C_0 is an initial concentration at the surface of concrete. CO_2 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.

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

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

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

Substituting these expressions to Eq. 4.10, initial conditions $C(x_i, t_1) = 0$ and boundary conditions $C(x_1, t_i) = 0$ are used sequentially, the approximate solution of CO_2 concentration can be obtained.

$$C(x_i, t_{j+1}) = 1 - \frac{2D \cdot \Delta t}{\Delta x^2} - k \cdot Ca_{t=0} \cdot \Delta t \times C(x_i, t_j) \cdot$$

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

In addition, the distribution of $Ca(OH)_2$ can be obtained in Eq. 4.15 by assigning $Ca_t = 0$, the carbonation depth can be obtained at the point where $Ca(OH)_2$ concentration decreases 60% level compared to initial concentration of $Ca(OH)_2$.

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 $Ca(OH)_2$, 2) diffusion coefficient of CO_2 in concrete, 3) The reaction rate constant between $Ca(OH)_2$ and $CaCO_3$ and 4) CO_2 concentration in the air. In this chapter, required parameters to FEMA are determined through literature reviews.

4.3.2 Diffusion Coefficient of CO_2 in Concrete

Concrete carbonation is a phenomenon where CO_2 in the air penetrates into the concrete and diffuses through porosity in concrete and combines with hydration product. Diffusion coefficient of CO_2 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_2 in concrete because it is an important variable that affects speed of concrete carbonation.

Papadakis expresses diffusion coefficient of CO_2 in concrete as a function of porosity and relative humidity in concrete as in Eq. 4.17.

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

D_{e,CO_2}: diffusion coefficient of CO_2 in concrete (m^2/sec), $\in_p$: porosity in concrete (%), *RH*: relative humidity (%).

In Eq. 4.17, $\in_p$ 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_2 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_2 in concrete with hydration time and parameter change affected by relative humidity. Parameter becomes lower with increasing relative humidity from 0 to 100.

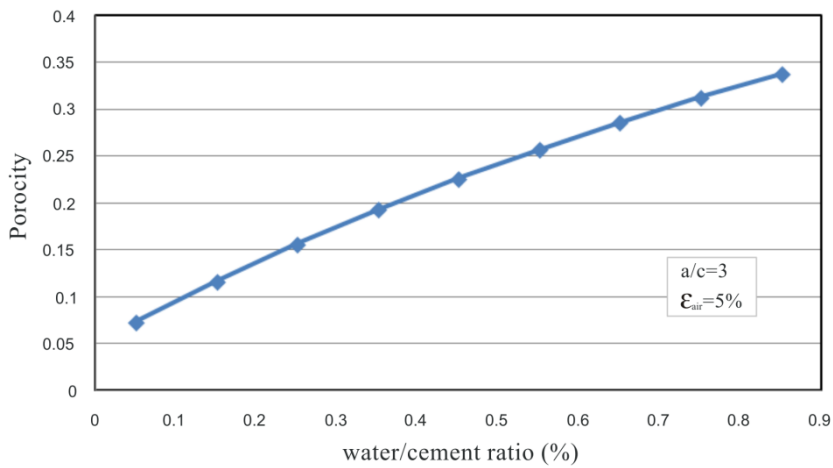


Fig. 4.2 *Porosity according to w/c ratio.*

Especially, it shows 0 in case of 100% relative humidity and CO_2 diffusion in concrete does not happen under these conditions because the porosity, that is a flow channel of CO_2 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_2 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.

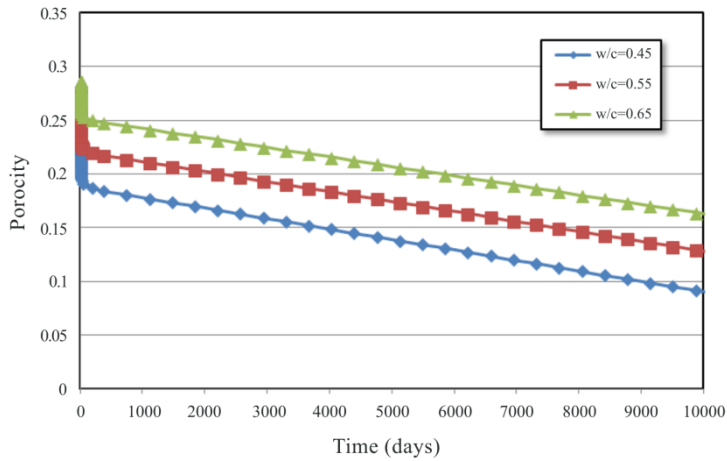


Fig. 4.3 *Porosity according to w/c ratio with time.*

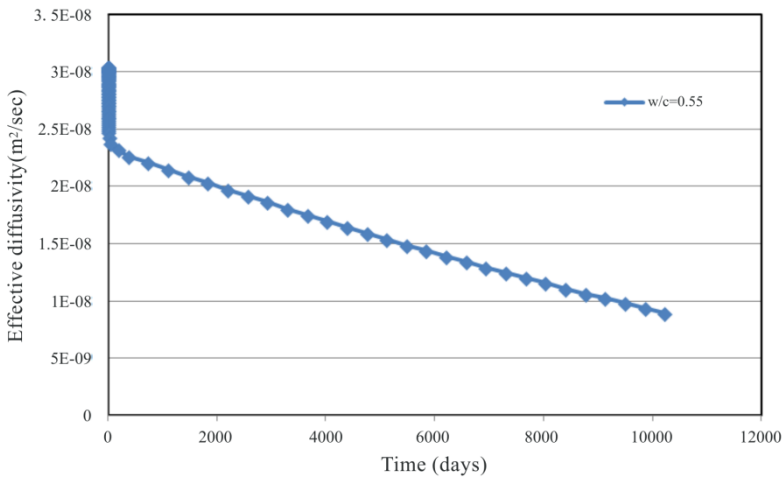


Fig. 4.4 *Effective diffusivity change with time (RH=50%).*

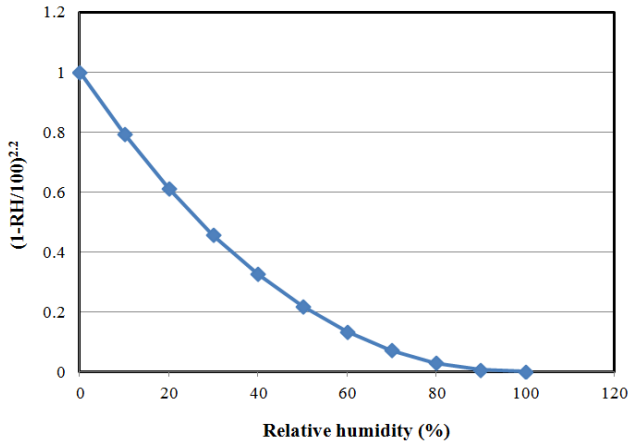


Fig. 4.5 *Effective diffusivity of CO_2 according to relative humidity.*

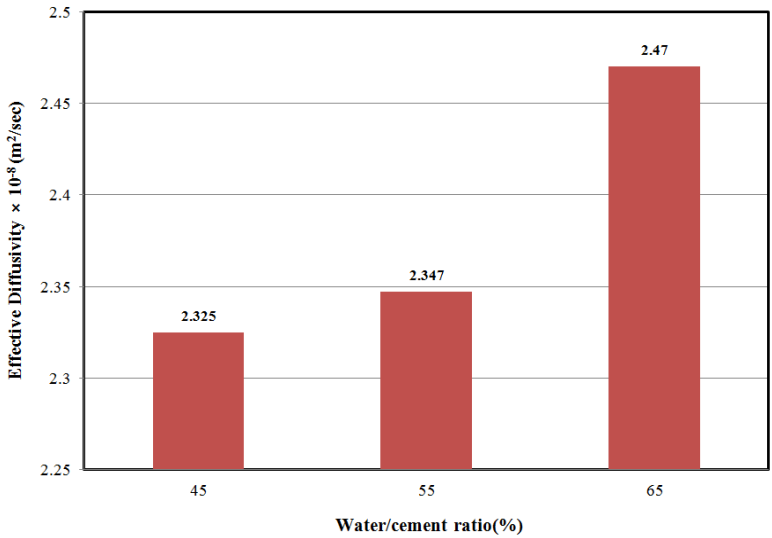


Fig. 4.6 *Effective diffusivity according to w/c ratio.*

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

4.3.3 Reaction Rate Constant Between $Ca(OH)_2$ and CO_2

Reaction rate constant between $Ca(OH)_2$ and CO_2 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)[41] proposed reaction rate constant between $Ca(OH)_2$ and CO_2 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_2 diffuses from the point of high concentration to the point of low concentration and the flow rate is proportional to concentration gradient. Therefore, CO_2 concentration change in the air affects CO_2 diffusion in concrete.

Hukusima proposed CO_2 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

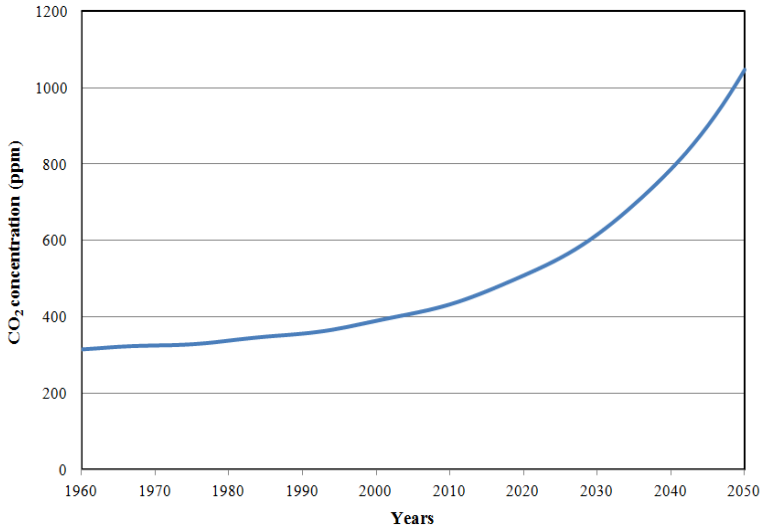


Fig. 4.7 *Expectation of CO_2 concentration change.*

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 $Ca(OH)_2$, 2) diffusion coefficient of CO_2 in concrete, 3) The reaction rate constant between $Ca(OH)_2$ and $CaCO_3$ and 4) CO_2 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 $Ca(OH)_2$ $\times 10^{-6}$(mol/cm^3)	CO_2 concentration (%)	reaction rate constant (1/day)	diffusion coefficient (cm^2/day)	$Ca(OH)_2$ 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

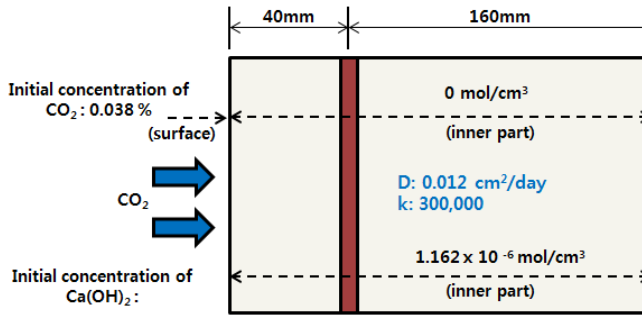


Fig. 4.8 *FEM carbonation analysis model (w/c=0.45).*

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

Figs. 4.9 - 4.11 show the results of prediction of $Ca(OH)_2$ 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 $Ca(OH)_2$ reaches 60% compared to the initial concentration of $Ca(OH)_2$ 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_2 in concrete becomes higher, as a result concentration gradient of $Ca(OH)_2$ is sweeper. On the other hand, carbonation

depth becomes shallower as water to cement ratio becomes lower because diffusion coefficient of CO_2 in concrete becomes lower, as a result concentration gradient of $Ca(OH)_2$ 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 $Ca(OH)_2$ reaches 60% compared to the initial concentration of $Ca(OH)_2$ and also mass reduction rate of $Ca(OH)_2$, $CaCO_3$ 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.

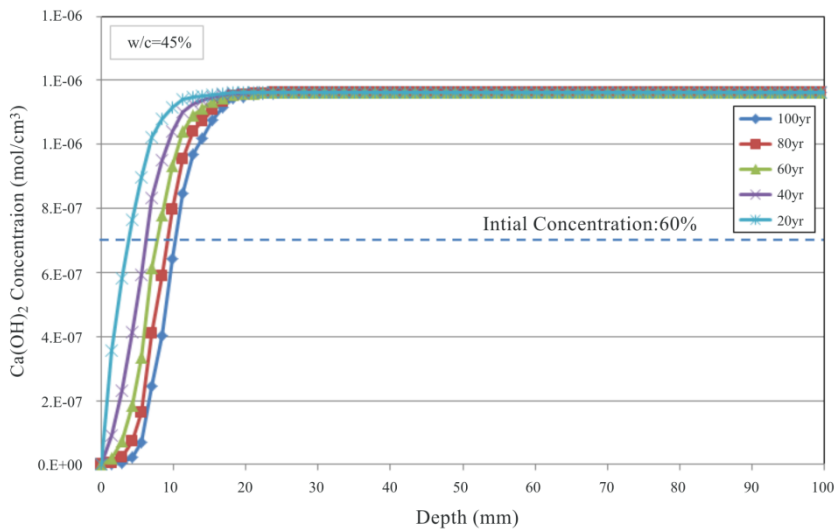


Fig. 4.9 *FEM carbonation analysis (w/c=0.45).*

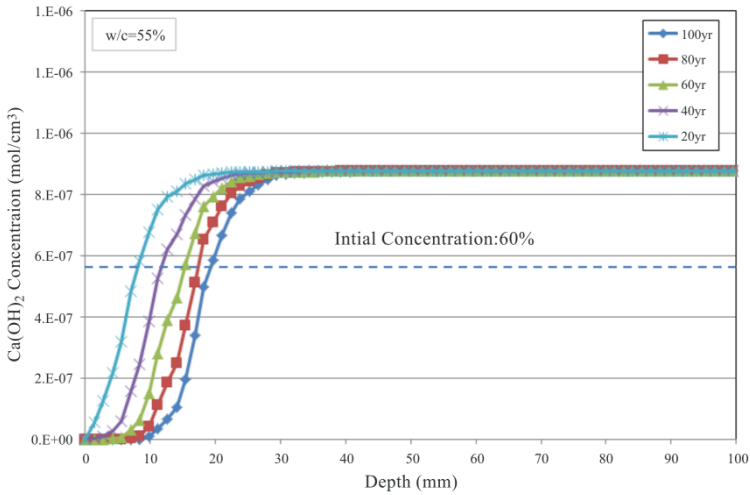


Fig. 4.10 *FEM carbonation analysis (w/c=0.55).*

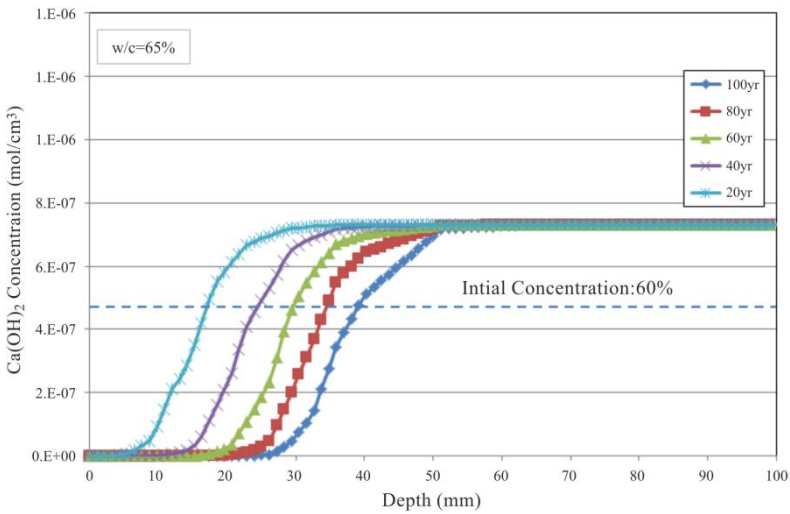


Fig. 4.11 *FEM carbonation analysis (w/c=0.65).*

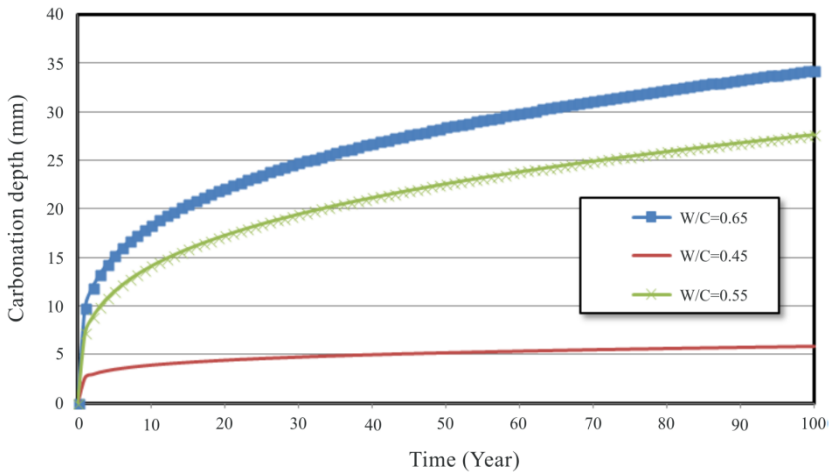


Fig. 4.12 *FEM carbonation analysis result according to w/c ratio.*

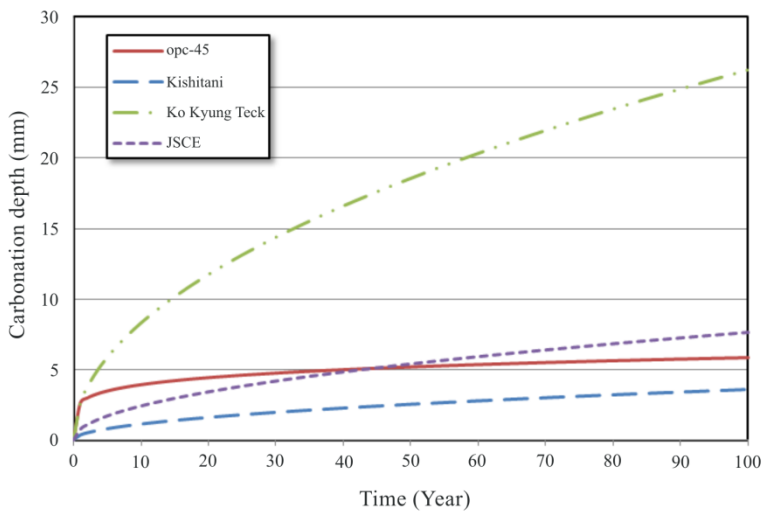


Fig. 4.13 *Comparison between other carbonation depth expectation models (w/c=0.45).*

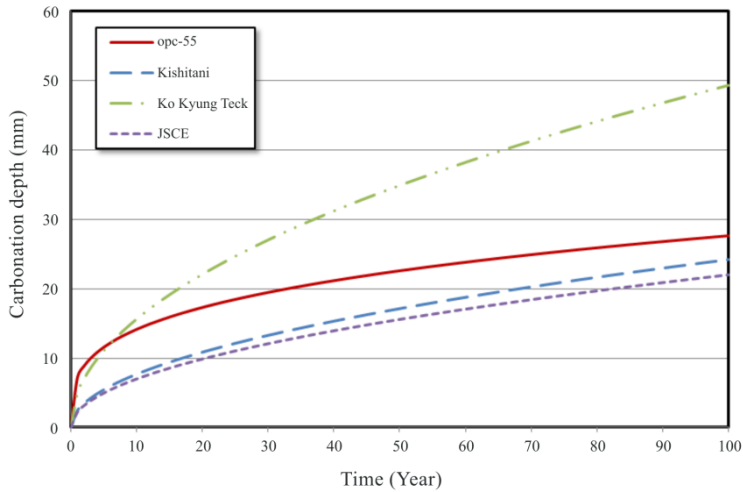


Fig. 4.14 *Comparison between other carbonation depth expectation models (w/c=0.55).*

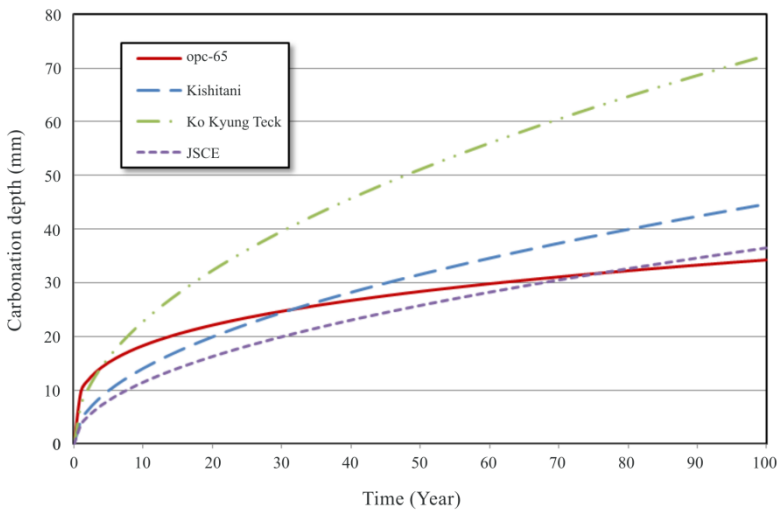


Fig. 4.15 *Comparison between other carbonation depth expectation models (w/c=0.65).*

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 $Ca(OH)_2$ reaches 60% compared to the initial concentration of $Ca(OH)_2$ and also mass reduction rate of $Ca(OH)_2$, $CaCO_3$ 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 $Ca(OH)_2$ reaches 60% compared to the initial concentration of $Ca(OH)_2$ and it becomes deeper with carbonation times.

Chapter 5

$LCCO_2$ Assessment of RC Structures Considering Concrete Carbonation Degree

5.1 Outline

Concrete carbonation is a phenomenon where concrete absorbs CO_2 from the air. In this chapter, the amount of CO_2 absorption in concrete through carbonation is calculated quantitatively during service life of RC structure that is predicted in chapter 4. Also, CO_2 emission is calculated when concrete of unit volume is produced and CO_2 balance and $LCCO_2$ are defined and evaluated during service life to an apartment building.

5.2 Definition and Evaluation of CO_2 Balance of Concrete

The CO_2 balance of concrete is defined as the difference between the quantity of CO_2 emitted from the production of 1 m^3 concrete and the quantity of CO_2 absorption through carbonation during the service life of the concrete. It can be calculated by using Eq. 5.1. It is used to design and select material such concrete as an eco-friendly one.

$$CO_2 \text{ balance of concrete (kg-}CO_2\text{/m}^3\text{)} = CO_2 \text{ emission} - CO_2 \text{ absorption} \qquad \text{Eq. 5.1}$$

5.3 Calculation of CO_2 Emissions and Absorption of Concrete

5.3.1 Estimation Outline of CO_2 Emissions Arising from the Manufacture of Concrete

The CO_2 emissions of concrete can be calculated by summing the CO_2 emission of each component used in concrete based on Table 5.1.[41)] Researches

and data[42-46] about CO_2 emission is in Korea, but it is limited in some material in concrete so in this study data on Table 5.1 is used. The CO_2 emissions include the mining of raw materials and energy production but exclude transportation of the material. The emission of total concrete used in the process of constructing a building is calculated considering total volume of used concrete based on CO_2 emission of 1 m^3 concrete by concrete strength.

Table 5.1 *CO_2 emission of component material in concrete (unit: kg-CO_2/Kg)*[41].

	Water	Cement	Fly ash	Fine aggregates	Coarse aggregates	AE reducing water agent
kg-CO_2/kg	-	0.7466	0.0196	0.0037	0.0028	0.25

5.3.2 CO_2 Absorption Calculation by Concrete Carbonation

(A) Outline of CO_2 Absorption Calculation of Concrete

Process of concrete carbonation produces a $CaCO_3$ from combining $Ca(OH)_2$ in concrete with CO_2 absorbed in the air as in Eq. 5.2. There are other reactants such as CSH($3CaO.SiO_2.3H_2O$), C_3S($3CaO.SiO_2$), C_2S($2CaO.SiO_2$) in the concrete that can combine with CO_2 as in Eqs. 5.3 - 5.6 except for $Ca(OH)_2$.

$$\mathrm{Ca}(OH)_2 + CO_2 \xrightarrow{r_{CH}} CaCO_3 + H_2O \qquad \text{Eq. 5.2}$$

$$3\mathrm{CaO} \cdot 2\mathrm{Si}O_2 \cdot 3H_2O + 3\mathrm{C}O_2 \xrightarrow{r_{CSH}} 3CaCO_3 + H_2O \qquad \text{Eq. 5.3}$$

$$2\mathrm{CaO} \cdot \mathrm{Si}O_2 + 2\mathrm{C}O_2 + rH_2O \xrightarrow{r_{C_2S}} \mathrm{Si}O_2 \cdot rH_2O + 2CaCO_3 \qquad \text{Eq. 5.4}$$

$$3\mathrm{CaO} \cdot \mathrm{Si}O_2 + 3\mathrm{C}O_2 + rH_2O \xrightarrow{r_{C_3S}} \mathrm{Si}O_2 \cdot rH_2O + 3CaCO_3 \qquad \text{Eq. 5.5}$$

The molar concentration of $Ca(OH)_2$ that combines with CO_2 through carbonation is equal to one of CO_2 at left side in Eq. 5.1. Noting this, the molar concentration of CO_2 that concrete can absorb is assumed to be equal to total molar concentration of each reactant that can combine with CO_2 in concrete.

From this assumption, the amount of CO_2 that concrete absorbs in the air through carbonation is predicted by calculating molar concentration of substances ($Ca(OH)_2$, CSH, C_3S, C_2S) in concrete that can react with CO_2. The process for predicting molar concentration of carbonatable substances in concrete is shown in Fig. 5.1.

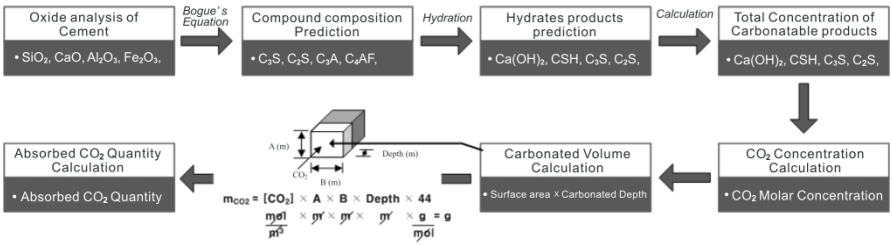


Fig. 5.1 *Absorbed CO_2 molar concentration calculation process of carbonated concrete.*

The molar concentration of carbonatable substances at an arbitrary time can be calculated by predicting hydration product of carbonatabele substances quantitatively by time after predicting cement compounds using Bogue's equation from analysis of cement oxide composition.[37] CO_2 absorption in concrete during service life can be calculated quantitatively by 1) multiplying using surface area of concrete exposed to the air, 2) carbonation depth with using time, and 3) the molar concentration of carbonatable substances in concrete under the assumption that the molar concentration of CO_2 that concrete absorbs is equal to one of carbonatable substances in concrete.

(B) Prediction of the Molar Concentration of the Cabonatable Hydration Products

Hydration model can predict the molar concentration of hydration products and this process is explained in chapter 3. Hydration products with time is

shown in Fig. 5.2

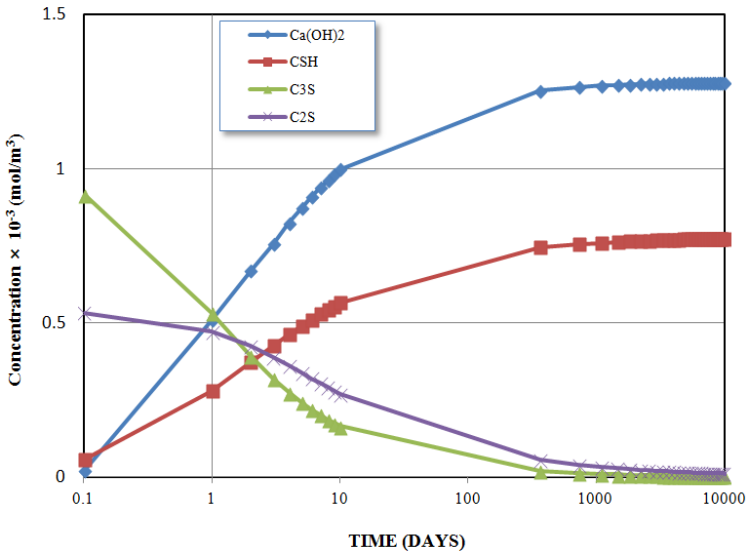


Fig. 5.2 *Hydration products process with time.*

(C) Calculation Method of CO_2 Uptake of Concrete[43)]

Fig. 5.3 shows carbonated concrete volume. CO_2 penetrate from the surface area A(m)×B(m) of concrete into the depth D in concrete. CO_2 absorption in concrete can be calculated quantitatively by multiplying the values: 1) the molar concentration of carbonatable substances in concrete, 2) the carbonated volume of concrete, 3) the molecular weight of CO_2 (44g/mol).

3-1) Calculation the molar concentration of carbonatable substances:

Under the assumption that the molar concentration of CO_2 that concrete absorbs is equal to summarized one of carbonatable substances in concrete ($[Ca(OH)_2]+3[CSH]+3[C_3S]+2[C_2S]$: $[CO_2]$), the molar concentration of CO_2 that concrete can absorb is calculated in 40, 60, 80 years and the results is

shown in Table 5.2 and Fig. 5.4.

Hydration of ordinary Portland cement proceeds rapidly. Hydration degree reaches 90% in 3 months and it is almost done in one year. So, the molar concentration of carbonatable substances is almost same in 20, 40, 60 years. As a result, when 1 m^3 concrete is fully carbonated in 80 years, the amount of CO_2 absorption in concrete is approximately 3,575 mol.

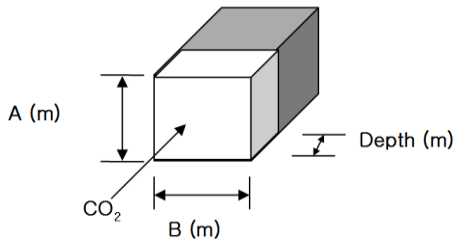


Fig. 5.3 *Concept for volume calculation of carbonated concrete.*

$$m_{co_2} = [CO_2] \times \mathrm{A} \times \mathrm{B} \times \mathrm{Depth} \times 44 = \frac{mol}{m^3} \times \mathrm{m} \times \mathrm{m} \times \mathrm{m} \times \frac{g}{mol} = g \quad \text{Eq. 5.6}$$

where:

CO_2: the concentration of materials that can react with CO_2 in the concrete,

A ×B: the surface area of the concrete exposed to air,

Depth: the carbonated depth of concrete

44: the molecular weight of CO_2 (g/mol)

3-2) In order to calculate carbonated concrete volume, carbonated depth with time and surface area exposed to the air is required. As an example, carbonated depth is predicted in 40, 60 and 80 years of service life with water to cement ratio of concrete and the results are shown in Fig. 5.5. Carbonated depth prediction with water to cement ratio uses carbonation model using FEMA in chapter 4.

Table 5.2 *Molar concentration of each carbonatable constituents and absorbable CO_2 in concrete (Unit: x 1,000 mol/m^3).*

	$Ca(OH)_2$	CSH	C_3S	C_2S	CO_2
40 years	1.261	0.763	0.002	0.009	3.576
60 years	1.262	0.764	0.001	0.007	3.575
80 years	1.262	0.765	0.001	0.007	3.575

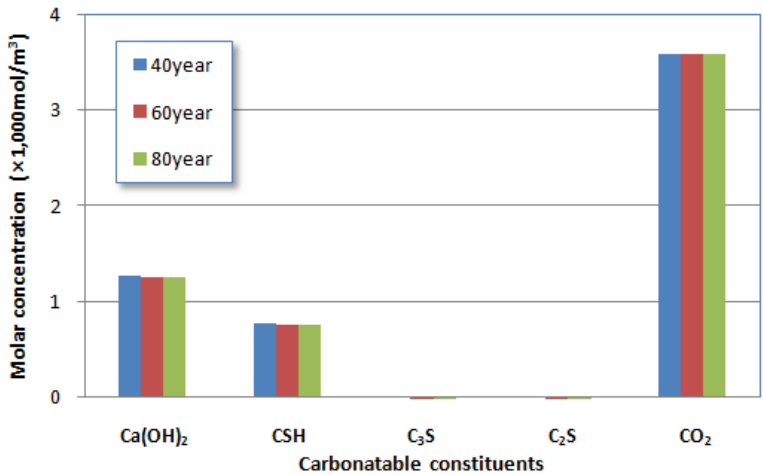


Fig. 5.4 *Molar concentration of each carbonatable constituents and absorbable CO_2 in concrete according to time.*

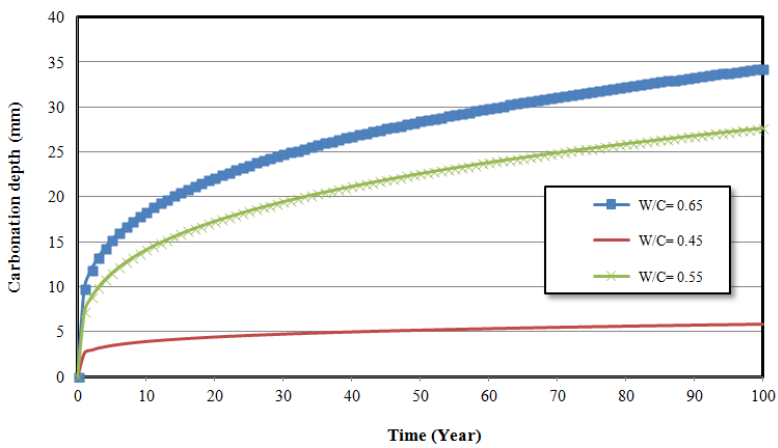


Fig. 5.5 *Carbonated depths according to w/c ratio with time.*

5.3.3 CO_2 Emissions-Absorption Evaluation Methodology Considering Concrete Production and the Use Period of Concrete

Evaluating method for CO_2 balance of concrete is the difference between the quantity of CO_2 emitted from the production of 1 m^3 concrete and the quantity of CO_2 absorption through carbonation during the service life of the concrete. CO_2 emission from concrete production can be calculated quantitatively by summarizing values that multiplied CO_2 emission of each material that are used in concrete with used quantities in concrete. CO_2 absorption in concrete in an arbitrary time during service life is calculated quantitatively using surface area of concrete exposed to the air, carbonation depth with using time, the molar concentration of carbonatable substances in concrete.

Table 5.3 shows CO_2 emission of 1 m^3 concrete production and this is a result of calculation using mix proportion as shown in Table 5.3 with water to cement ratio of 0.45, 0.55 and 0.65 and CO_2 emission of each material.

Table 5.3 *CO_2 emission of concrete and its component material (unit: kg-CO_2/kg).*

No.	Index	W/C	Mix proportion (kg/m^3)					CO_2 emission quantity
			W	C	S	G	AE reducing water agent	CO_2 emission quantity
1	C-OPC-45	0.45	216	480	751	866	0	364
2	C-OPC-55	0.55	206	375	863	866	0	286
3	C-OPC-65	0.65	202	311	944	850	0	238
CO_2 emission quantity of concrete and its component material			-	0.7466	0.0037	0.0028	0.25	kg-CO_2/m^3

Table 5.4 shows the calculation results of CO_2 absorption in 1 m^3 concrete with water to cement ratio in 30 and 60 years during service life. The molar concentration of carbonatable substances with water to cement ratio is

calculated by a hydration model in chapter 3. The molar concentration and quantity of CO_2 that concrete absorption is calculated quantitatively and the result is shown in Fig. 5.6.

Table 5.4 *Molar concentration of each carbonatable constituents and absorbable CO_2 in concrete (Unit: x 1,000 mol/m^3).*

service life	**W/C**	**$Ca(OH)_2$**	**CSH**	**C_3S**	**C_2S**	**Fully carbonated concrete**	
service life	**W/C**	**$Ca(OH)_2$**	**CSH**	**C_3S**	**C_2S**	**absorbable CO_2**	**absorbed CO_2 quantity (kg/m^3)**
30 year	0.45	1.281	0.774	0.002	0.01	3.634	159.90
30 year	0.55	1.008	0.609	0.002	0.008	2.859	125.82
30 year	0.65	0.841	0.508	0.001	0.007	2.385	104.98
60 year	0.45	1.282	0.776	0.001	0.007	3.632	159.82
60 year	0.55	1.008	0.611	0.001	0.006	2.858	125.76
60 year	0.65	0.841	0.509	0.001	0.005	2.384	104.93

CO_2 emission increases in a low water to cement ratio because the amount of used cement in concrete increases. Also, CO_2 absorption increases in a low water to cement ratio because carbonatable substances such as $Ca(OH)_2$, CSH in concrete increase from using more cement. As a result, the ratio of absorption over emission of CO_2 is almost same to approximately 44% regardless of water to cement ratio when concrete is fully carbonated.

But in real condition, it is difficult for concrete to be fully carbonated in the air. Therefore, CO_2 absorption capacity through carbonation in the air is proportional to carbonated depth of concrete. Carbonated concrete depth with water to cement ratio is predicted in chapter 4 and the result are shown in Fig. 5.6. Carbonated concrete depth is affected by water to cement ratio and it decreases sharply in case of water to cement ratio of 0.45. Table 5.5 shows calculation results of carbonated concrete depth and CO_2 absorption with water to cement ratio in 30 and 60 years.

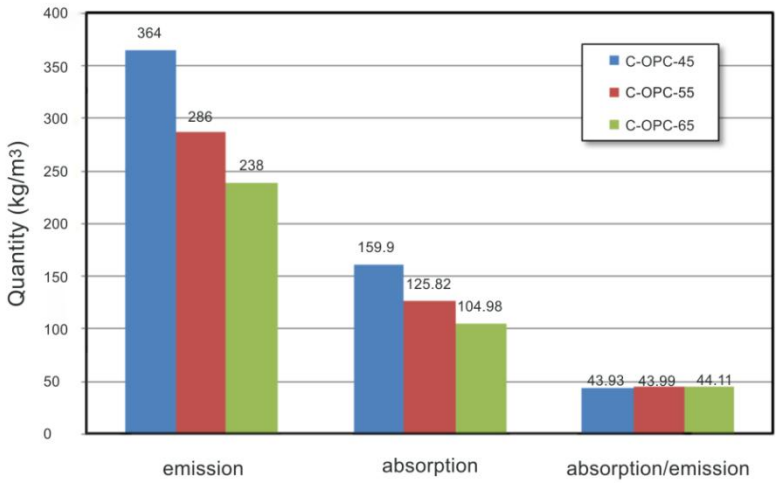


Fig. 5.6 *Calculation of emission, absorption and absorption/emission according to w/c ratio.*

Table 5.5 *Calculation amount of CO_2 absorption according to W/C in 30 and 60 years.*

		absorbable CO_2 (Unit: ×1,000 mol/m^3)	**Carbonated depth (mm)**	**absorbed CO_2 quantity (g/m^3)**
30 year	w/c=0.45	3.634	4.75	4.55
30 year	w/c=0.55	2.859	19.44	14.67
30 year	w/c=0.65	2.385	24.77	15.59
60 year	w/c=0.45	3.632	5.35	5.12
60 year	w/c=0.l55	2.858	23.80	17.95
60 year	w/c=0.65	2.384	29.88	18.8

Concrete carbonation does not progress fast in a real condition of exposure to the air. As a result, CO_2 absorption of concrete through carbonation is tiny. Fig. 5.7 shows carbonated depth and CO_2 absorption of concrete with water to cement ratio according to service life. The increase of CO_2 absorption is proportional to carbonated depth of concrete. So, in case of water to cement ratio of 0.65, carbonated depth and CO_2 absorption of concrete is evaluated as the most significant.

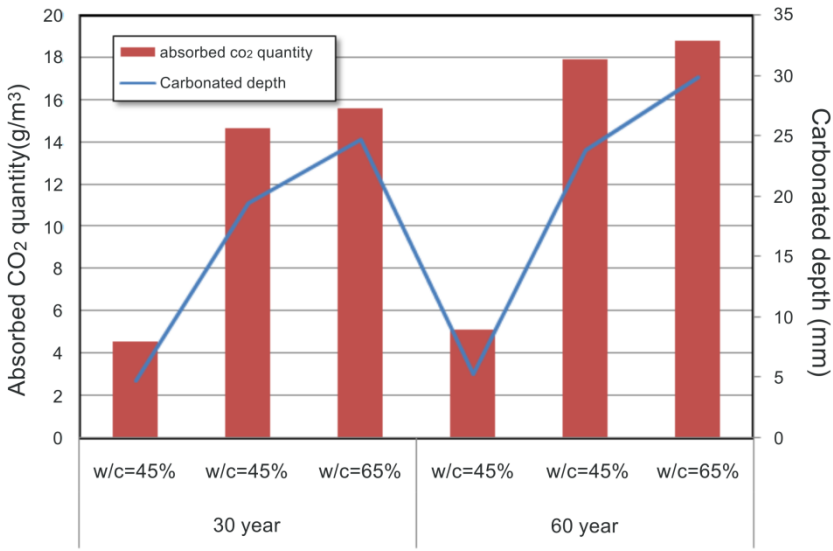


Fig. 5.7 *Calculation of the amount of CO_2 absorption and carbonated depth according to W/C in 30, 60 years.*

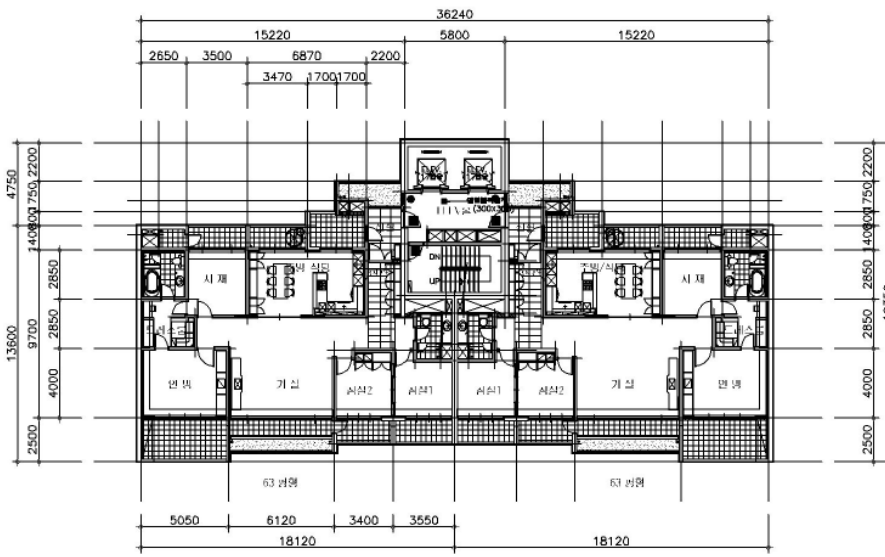
5.4 Case Study: Evaluation of the CO_2 Balance of an Apartment Building in South Korea During Its Service Life

5.4.1 Overview of the Apartment Building

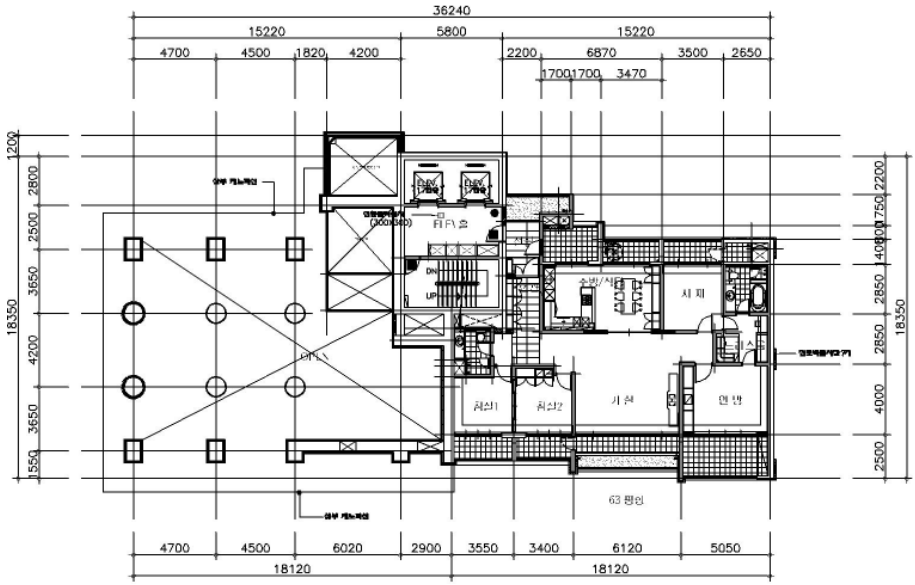
Table 5.6 outlines an apartment building with 34 floors above ground and one floor below ground. The height of each story is 2.9 m, and the total height of the building is 104.8 m. The compressive strength of concrete used for the vertical members of the building is 35 MPa from the first basement to the ninth floor, 30 MPa from the 10th floor to the 19th floor, 27 MPa from the 20th floor to the 26th floor, and 24 MPa from the 27th floor to the roof. The planes of the apartment are as shown in Fig. 5.8.

Table 5.6 *Used concrete volume by story.*

Story (floor)	Used concrete volume (m^3)					Strength (MPa)	W/C
Story (floor)	**Column + Wall**	**Slab**	**Sum (Wall+Slab)**	**Story**	**Total**	**Strength (MPa)**	**W/C**
Basement 1st	185	0	185	1	185	35	0.39
1st	220	84	304	1	304	35	0.39
2nd	248	79	327	1	327	35	0.39
3rd	181	47	229	1	229	35	0.39
4th	180	468	649	1	649	35	0.39
5th–9th	178	155	334	5	1,670	35	0.39
10th–19th	178	155	334	10	3,341	30	43
20th–26th	178	155	334	7	2,338	27	46
27th–31st	178	155	334	5	1,670	24	0.50
32nd	406	155	561	1	561	24	0.50
Roof Floor	152	58	211	1	211	24	0.50
Penthouse 1st	191	33	224	1	224	24	0.50
Penthouse 2nd	25	9	34	1	34	24	0.50



(a) Normal plane (5th~31st)



(b) 1st floor plane

Fig. 5.8 *Normal plane (5th~31st).*

5.4.2 Calculating CO_2 Emission from the Concrete Used in the Apartment Construction

The volume and CO_2 emission according to the types of concrete used were needed to calculate the total CO_2 emissions of all concrete used in constructing the apartment. The used concrete volume by floor was roughly divided into the volumes of vertical and floor members. The concrete volume of the vertical members was calculated by summing the volume of the columns and wall area multiplied by the story height (2.9 m) for each floor plan. The concrete volume of the floor member was calculated by summing the volume of the slab area multiplied by the slab thickness (0.2 m) for each floor plan. Table 5.6 shows the volume of each concrete depending on the type of concrete used in the apartment. Table 5.7 shows the CO_2 emissions from the production of 1 m^3

concrete according to the type of concrete used in the apartment. The total CO_2 emissions can be calculated by summing the total volumes multiplied by the CO_2 emissions per unit of each type of concrete used in the apartment. The results of the calculations are listed in Table 5.8.

Table 5.7 *Concrete mixture and calculated CO_2 emission of 1 m^3 concrete by strength.*

MPa	W/C	Unit weight (kg/m^3)						Total CO_2 emission (kg-CO_2/m^3)
MPa	W/C	Water	Cement	Fly ash	Sand	Gravel	AE Water Reduction Agent	Total CO_2 emission (kg-CO_2/m^3)
24	0.49	174	304	45	848	944	2.09	234
27	0.46	175	328	49	832	934	2.64	252
30	0.43	178	348	61	797	935	3.07	267
35	0.39	179	394	69	759	926	3.70	301

Table 5.8 *CO_2 emission of concrete by strength.*

Design strength	CO_2 emission (kg-CO_2)	
	by strength	Total
35 MPa	1,013,261	3,123,729
30 MPa	890,721	3,123,729
27 MPa	588,327	3,123,729
24 MPa	631,420	3,123,729

5.4.3 Calculating CO_2 Absorption of Concrete Used in the Apartment During Its 20-years' Service Life

As mentioned in 5.3.2, the surface area of concrete exposed to air, carbonated depth of concrete, and molar concentration of materials that can react with CO_2 are needed to calculate the CO_2 absorption of concrete during an arbitrary service life. The surface areas of concrete exposed to air in the apartment structure for each plane are shown in Table 5.9. The total surface area of concrete exposed to air according to the types of concrete is listed in Table 5.10.

Table 5.9 *Surface area of concrete exposed to the air by strength and ground plan.*

Story	Surface area (m^2)						Design Strength (MPa)
Story	**Left wall**	**Rear wall**	**Right wall**	**Front wall**	**Slab**	**Inner wall + column**	**Design Strength (MPa)**
Basement 1st	0	0	0	0	596	947	35
1st	0	0	0	0	596	549	35
2nd	53	60	53	76	596	631	35
3rd	54	62	54	77	596	642	35
4th	53	105	53	105	596	1,123	35
5th-9th	53	105	53	105	596	1,116	35
10th-19th	53	105	53	105	596	1,116	30
20th-26th	53	105	53	105	596	1,116	27
27th-31st	53	105	53	105	596	1,116	24
32nd	60	119	60	119	596	1,355	24
Penthouse 1st	50	98	61	98	596	484	24
Penthouse 2nd	50	73	50	73	596	292	24

Table 5.10 *Total surface areas of concrete exposed to air by concrete strength.*

Design strength (MPa)	24	27	30	35
Total surface area (m^2)	14,386	14,204	20,292	17,830

Eq. 5.7 [25] estimates the carbonated depth of concrete from the water to cement ratio (W/C) and the exposure time. It considers W/C, the South Korean climate, and CO_2 concentration in air. The calculated values of the carbonated depth for each concrete over 20 years using the corresponding Eq. 5.7 are listed in Table 5.11.

$$C = (2.823 - 0.548 \log CO_2)\times(0.0303\ W/C - 1.0187)\times(CO_2 \cdot t)^{0.5} \qquad \text{Eq. 5.7}$$

Where C is the concrete carbonated depth (mm); CO_2, the CO_2 concentration in the air (=0.035); W/C, the water to cement ratio; and t, the exposure time (years).

Table 5.11 *Carbonated depth by concrete strength in 20 years.*

Design strength (MPa)	24	27	30	35
Carbonated depth (mm)	16.88	12.76	9.66	5.54

Table 5.12 lists the molar concentration of materials that can react with CO_2 according to the type of concrete. Finally, the total CO_2 absorption of concrete used in the apartment was calculated during its 20-years' service life by using Eq. 5.6. The results are listed in Table 5.13.

Table 5.12 *CO_2 molar concentration that could be carbonated in concrete by strength.*

Design strength	Molar concentration of CO_2	Unit
35 MPa	3,575	mol/m^3
30 MPa	2,821	
27 MPa	2,789	
24 MPa	2,749	

Table 5.13 *CO_2 absorption of concrete based on types of concrete after 20 years.*

Design strength	CO_2 absorption of concrete	Unit
35 MPa	15,538	kg-CO_2
30 MPa	24,331	
27 MPa	22,242	
24 MPa	29,373	
Total Quantity	91,484	

5.4.4 Evaluation of CO_2 Balance of Concrete

CO_2 emissions were calculated based on the concrete used and the CO_2 absorption of the concrete used in the apartment building during its 20-years' service life. Based on these values, the CO_2 balance of the apartment building and the CO_2 ratio of emission to absorption were calculated using Eq. 5.1 and 5.8. The results are shown in Table 5.14.

The CO_2 ratio of emission to absorption (%) = (CO_2 absorption/CO_2 emission) ×100 Eq. 5.8

Table 5.14 *Assessment result of CO_2 ratio of emission to absorption.*

	Value	Unit
CO_2 emission quantity	3,123.73	
CO_2 absorption quantity	91.48	ton-CO_2
CO_2 balance	3,032.25	
CO_2 ratio of emission to absorption	2.92	%

5.5 Review of the Method to Improve the CO_2 Balance of Concrete Considering Service Life of RC Structure During Century

The CO_2 balance of concrete for the apartment building during its 20-years' service life was 3,032 tons. The CO_2 ratio of emission to absorption was approximately 2.92%, which is very low. One method for improving the CO_2 balance of concrete is to reduce CO_2 emissions and increase CO_2 absorption. This concept is shown in Fig. 5.9.

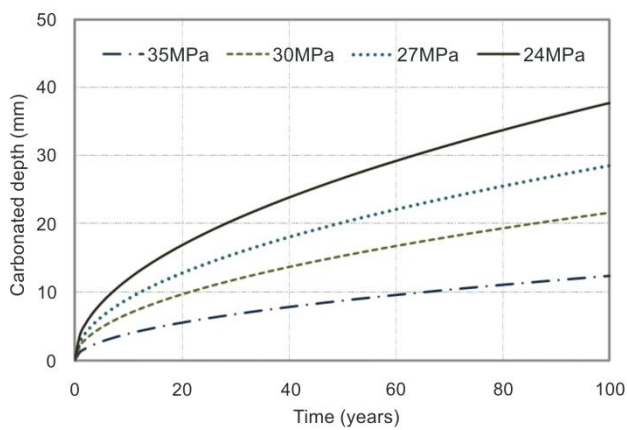


Fig. 5.9 *Carbonated depths by concrete strength by exposure time.*

Methods for reducing CO_2 emissions for the CO_2 balance of concrete are as follows:

1. Reduce the raw materials and cement used in a new construction by extending the service life of the structure.

2. Replace some of the cement in concrete with blended cement, such as fly ash or blast furnace slag.

Methods for increasing CO_2 absorption for the CO_2 balance of concrete are as follows:

1. Extend the service life of RC structures; this increases the carbonated depth of concrete.

2. Recycle waste concrete as sub-base materials or aggregate after deconstruction to increase the carbonated volume of concrete by increasing the surface area of concrete exposed to air.

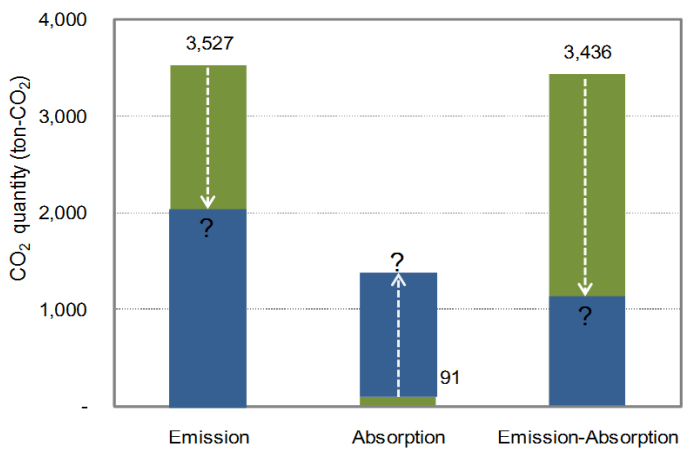


Fig. 5.10 *Concept for improving the CO_2 balance.*

5.5.1 Reduction of CO_2 Emission of Concrete by Extending the Service Life of the Apartment Building

The concept of $LCCO_2$ was used to select the appropriate service life of an apartment over a century. The service life of an apartment was assumed to be 20, 40, 60, 80, or 100 years. Fig. 5.10 shows the calculated $LCCO_2$ according to each service life of the apartment over a century considering reconstruction times after each service life. For the 20-years' service life, the $LCCO_2$ was 17,178 tons over a century; this was five times more than that of the 100-years' service life. One can infer that the number of reconstructions is a crucial factor that affects the increase in $LCCO_2$ because every reconstruction produces a large amount of CO_2. Therefore, extending the service life of an apartment building is very important for reducing CO_2 emissions over a century. The 100-years' service life had an $LCCO_2$ of 3,323 tons, which was the lowest value.

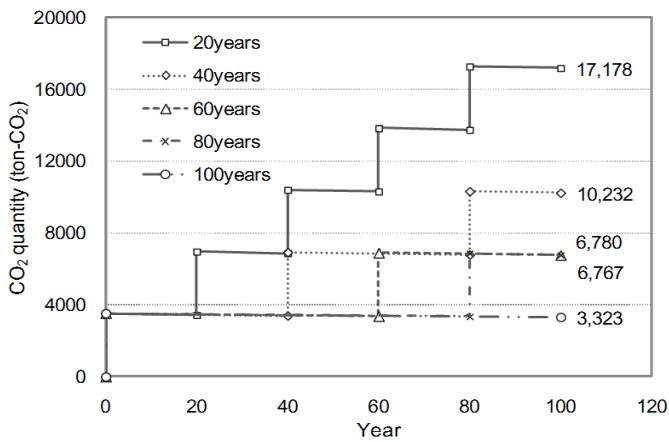


Fig. 5.11 *CO_2 balance analysis according to each service life.*

Fig. 5.11 shows the service life of apartment buildings by countries[26]. However, in the case of apartments in South Korea, the life cycle spans mostly 20 to 30 years. There are no cases in which the life cycle of an apartment buildings

house exceeds 100 years due to changes in social demands and building safety codes concerning natural disasters or unanticipated accidents[27)].

The appropriate service life for an apartment building to improve its $LCCO_2$ seems to be 60 years with one reconstruction in terms of $LCCO_2$ during a century. The $LCCO_2$ was better for the 60-years' service life of an apartment building than that for the 80-years' service life. This is because the growth of the carbonated depth of concrete attributed to carbonation slows down with time as shown in Fig. 5.6.

5.5.2 Reduction in CO_2 Emission of Concrete by Using Blended Cement in Concrete

Blast furnace slag cement is an industrial by product that can be used as a mineral admixture for cement. Its CO_2 emissions are approximately 28 times lower (0.0265 kg-CO_2/kg) than that of ordinary cement (0.7466 kg-CO_2/kg)[15)]. Therefore, the CO_2 emissions of concrete can be reduced if some of the cement (348 kg cement used for 30 MPa concrete) used in concrete is replaced by blast furnace slag. In this study, the CO_2 emissions of concrete were calculated in terms of increasing the slag-to-cement replacement ratio in 1 m^3 concrete from 0% to 60% in 20% increments.

Table 5.15 lists the mixing proportion of concrete and CO_2 emissions according to slag-to-cement replacement ratios in 1 m^3 of 30 MPa concrete[28)]. The CO_2 emission from 1 m^3 concrete is 267 kg without blast furnace slag. However, this value decreases as more blast furnace slag is used to replace cement.

Table 5.15 *CO_2 emission by replacement ratios of blast furnace slag to the cement.*

MPa	Replacement ratio (%)	Total CO_2 emission (kg-CO_2/m^3)	Unit weight (kg/m^3)						
MPa	**Replacement ratio (%)**	**Total CO_2 emission (kg-CO_2/m^3)**	**W**	**C**	**BS**	**FA**	**S**	**G**	**AE reduction water agent**
30	0	267	178	348	0	61	797	935	3.07
30	20	216	178	278	70	61	797	935	3.07
30	40	166	178	209	139	61	797	935	3.07
30	60	116	178	139	209	61	797	935	3.07
	CO_2 emission(kg-CO_2/m^3)		-	0.7466	0.0265	0.196	0.0037	0.0028	0.25

The CO_2 emissions are 116 kg when the slag-to-cement replacement ratio is 60%; thus, this method can reduce CO_2 emissions by 56% compared to concrete without blast furnace slag. Therefore, CO_2 emissions can be reduced by using blast furnace slag in the concrete. If a 60% slag-to-cement replacement ratio becomes obligatory, then the CO_2 emissions from the apartment building in the case study would be reduced to 1,362 tons, which is a reduction in CO_2 emissions of 56% compared to concrete without blast furnace slag (Table 5.16). If the CO_2 absorption of concrete during a 20-years' service life is assumed to be the same as that of the existing building, then a total of 91.48 tons of CO_2 will be absorbed. In this case, the CO_2 ratio of emission to absorption would be 5.6%, which results in an approximately 3% improvement compared to the existing mixture proportion.

Table 5.16 *Total CO_2 emission of the apartment by replacement ratio of the blast furnace slag to the cement.*

Blast furnace slag replacement ratio (%)	CO_2 emission	Unit
0	3,123,730	kg-CO_2
20	2,536,380	kg-CO_2
40	1,949,030	kg-CO_2
60	1,361,680	kg-CO_2

5.5.3 Increase in CO_2 Absorption of Concrete by Extending the Service Life of the Apartment Building

One method for increasing the CO_2 absorption of concrete is to extend the service life of an apartment building. The CO_2 absorption of the subject apartment building was calculated quantitatively and evaluated according to the service life of the apartment building described in Section 4: 20, 40, 60, 80, and 100 years. The longer service life of the RC structure led to a deeper carbonated depth of the concrete and more carbonated volume, as shown in Fig. 5.6. As a result, the CO_2 absorption increased by approximately 2.2 times, from approximately 91 tons of CO_2 for a 20-years' service life to 204 tons of CO_2 for a 100-years' service life, as shown in Fig. 5.12. Thus, a longer service life for the RC structure increases CO_2 absorption, but the increment is quite small compared to the CO_2 emissions from construction, as shown in Fig. 5.13. Therefore, extending the service life of apartment buildings is very important for reducing CO_2 emissions by preventing unnecessarily early deconstruction.

5.5.4 Increase in CO_2 Absorption of Concrete by Recycling Waste Concrete After Deconstruction of RC Structure

Another method for increasing CO_2 absorption is to recycle waste concrete after deconstruction of an RC structure. If waste concrete is crushed into small pieces, the uncarbonated lump of concrete in the structure is exposed to air and can absorb more CO_2 because the total surface of small-volume.

Concrete would be increased. Fig. 5.15 shows the relation between the surface area and CO_2 absorption of 1 m^3 concrete exposed to air with side lengths ranging from 1 cm to 100 cm. When a side length of 1 m^3 concrete was

reduced from 100 cm to 1 cm, the surface area increased 100 times from 6 m^2 to 600 m^2. This means that CO_2 absorption increased 100 times, from 14.64 kg to 1,464 kg for 24 MPa concrete.

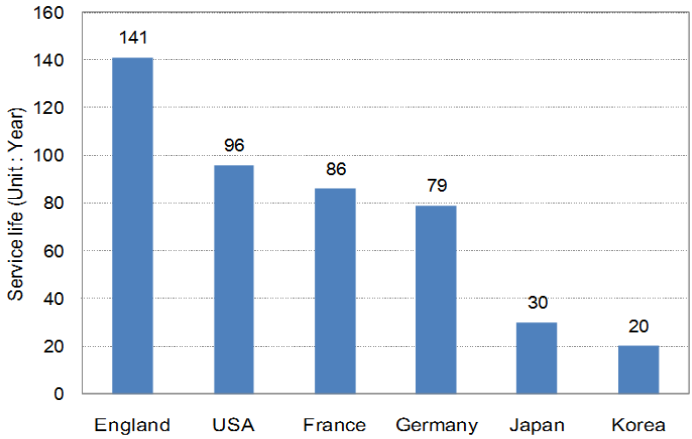


Fig. 5.12 *Service life of apartment house by countries.*

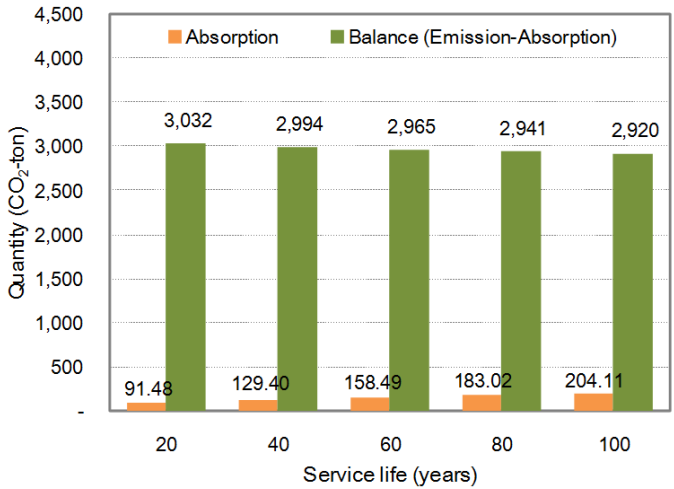


Fig. 5.13 *CO_2 absorption and its balance according to service life.*

Generally, the surface area of concrete in the RC structure that is exposed to air is very limited. This is why the surface area and volume of carbonated

concrete in the RC structure is only a small portion of the entire concrete volume. For example, the wall thickness of RC structure such as an apartment in South Korea is typically 20 cm. However, the carbonated depth would only be about 37 mm for 24 MPa concrete after a 100-year service life (Fig. 5.6). In this case, the carbonated ratio to the full thickness would only be approximately 37% even if both sides (inside and outside) of the wall were considered to be carbonated over 100 years.

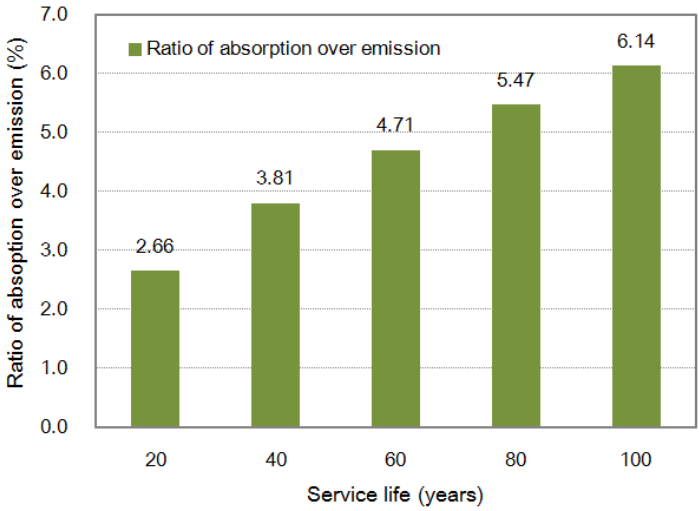


Fig. 5.14 *CO_2 ratio of absorption over emission.*

However, when concrete is crushed into small lumps, the surface area exposed to air is increased 100 times compared to that of uncrushed concrete, as shown in Fig. 5.14. This increases the carbonated volume of concrete in the RC structure to be proportional to the volume of used concrete. A study in Denmark showed that the recycling rate of waste concrete from a building as an aggregate reached 90% and that the CO_2 absorption by recycling waste concrete was approximately 2.4 times more than that of the carbonated concrete volume during the service life of a building[3)].

Therefore, increasing CO_2 absorption by recycling waste concrete should be strongly considered by the construction industry of South Korea. If the CO_2 absorption by recycling waste concrete increased by 2.4 times in South Korea, then the CO_2 absorption for a building during a 20-years' service life would increase from 91.48 tons to 219.55 tons. The CO_2 rate of emission to absorption would increase by approximately 3.48%, from 2.66% to 6.14% (Fig. 5.15).

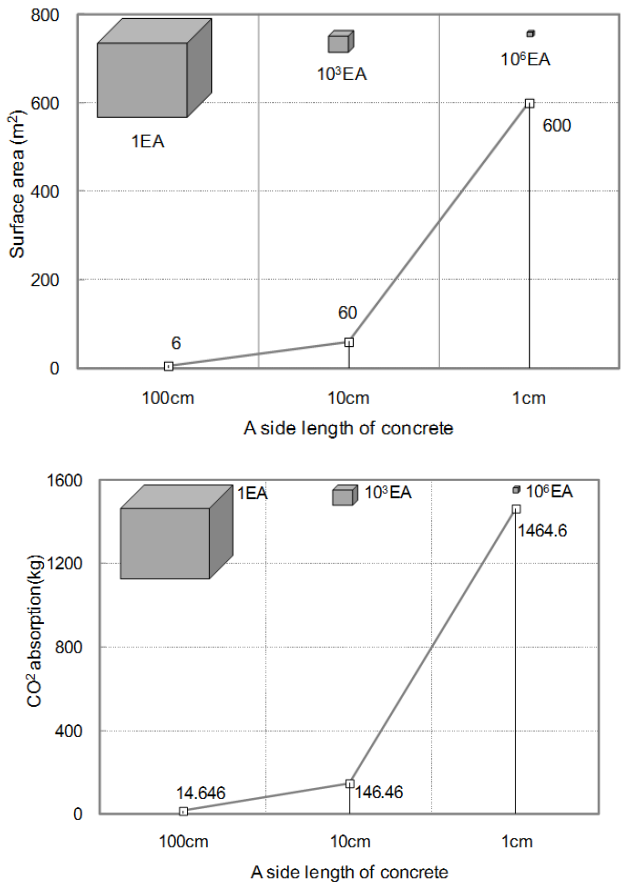


Fig. 5.15 *Changes in surface area and CO_2 absorption by the side-length of $1m^3$ concrete.*

5.6 Review Summary: Improving Effect of $LCCO_2$ with Proposed Methods

Based on the above results, the following sustainable development method based on the life cycle CO_2 balance of concrete is proposed for the construction industry in South Korea:

1. Use of blended cement in concrete is made obligatory to reduce CO_2 emissions.

2. Apartment service life should be at least 60 years to reduce CO_2 emissions from building reconstruction due to early deconstruction.

3. Waste concrete from RC structures should be recycled and reused as aggregates or sub-base materials to increase CO_2 absorption of the waste concrete through carbonation.

The method were applied to actual apartment buildings to review and compare the CO_2 balance for two cases: (1) the concrete of an apartment building razed after 20 years of service life and (2) the concrete of an apartment whose service life is 60 years with 60% of the cement replaced by blast furnace slag and a 90% recycling ratio of waste concrete after demolition. The CO_2 ratio of emission to absorption based on the service life increased by approximately six times more from 2.59% to 19.07%, as shown in Fig. 5.16; case (2) resulted in a CO_2 emission reduction of 702 tons compared to case (1). In addition, the $LCCO_2$ efficiency over a century of a 60-years' service life increased eightfold from 2.59% to 21.25% compared to that of a 20-years' service life, as shown in Fig. 5.17, in terms of the number of reconstructions. The $LCCO_2$ of concrete with a 60-years' service life was reduced by approximately 11,975 tons

compared to that of a 20-year service life over a century.

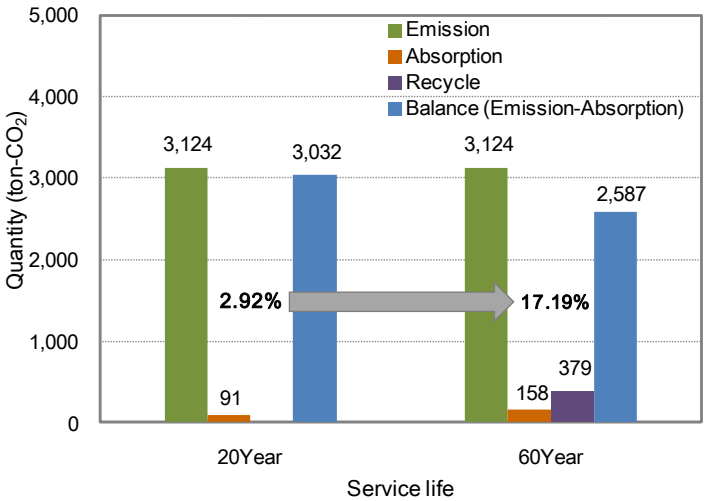


Fig. 5.16 *Calculating CO_2 balance according to service life.*

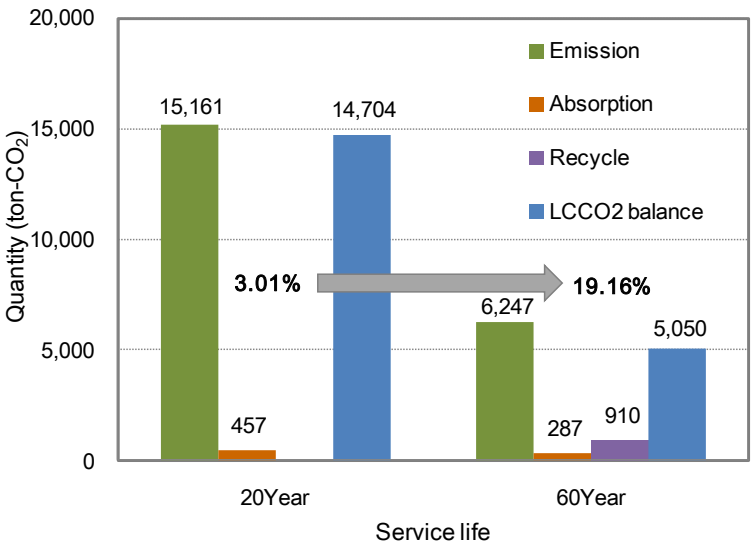


Fig. 5.17 *$LCCO_2$ balance and its efficiency over 100 years according to service life.*

5.7 Summary

In this chapter, CO_2 emission from production of concrete, CO_2 absorption during service life considering carbonation degree and $LCCO_2$ are calculated quantitatively. As a result, conclusions are as follows:

1. CO_2 emission from concrete production can be calculated quantitatively by summarizing values that multiplied CO_2 emission of each material that are used in concrete with used quantities in concrete.

2. CO_2 absorption in concrete during service life is calculated quantitatively using surface area of concrete exposed to the air, carbonation depth with using time, the molar concentration of carbonatable substances in concrete and molecular weight of CO_2.

3. Evaluation method for CO_2 balance and $LCCO_2$ that is studied in this chapter can be used to select optimal material design and service life.

5.8 Conclusions

Evaluation method by indicator has a qualitative assessment limit that instability color change may happen in the carbonation depth anytime. In addition, carbonation depth measurement method by the indicator has a problem that concrete color does not discolored in early progress of carbonation. Above all, carbonation depth measurement method using an indicator may cause prediction error of service life of RC structure when measurement error by measurers has happened because of ambiguous boundary. Therefore, a quantitative evaluation methods and standards for carbonation are required to overcome this problem.

So, this study proposed a quantitative evaluating method that overcomes the limitation of qualitative evaluation, which is carried out using the naked eye with respect to the color change boundary by spraying indicator. Carbonation depth becomes the basic data for estimating the residual life and durability of RC structures.

To achieve this objective, correlation between pH value and quantities of $Ca(OH)_2$, $CaCO_3$ is analyzed experimentally by carbonation weeks, concrete depths through accelerated carbonation experiment in order to propose a quantitative evaluating basis. Quantity of $Ca(OH)_2$ is important to predict service life of concrete against carbonation and cement hydration model can predict it quantitatively to any concrete mix. Therefore, validation for cement hydration model is verified by comparing prediction values and measured values of $Ca(OH)_2$. And then prediction model for carbonation based on FEM is used to predict the service life of RC structure.

Required input parameters such as initial concentration of $Ca(OH)_2$, diffusion coefficient of CO_2, reaction velocity constant, CO_2 concentration in the air for FEMA are decided through literature review. The proposed quantitative evaluation basis in chapter 3 is used to evaluate and predict service life. As a final step, CO_2 emission of concrete considering concrete mix and CO_2 absorption through carbonation during service life for unit volume concrete is calculated quantitatively. And then, CO_2 balance (emission-absorption of CO_2) and $LCCO_2$ is evaluated quantitatively to a real building. The results of this study can be summarized as follows:

1. Proposal of a quantitative evaluation basis for carbonation depth

   a) Carbonation depth is determined. Approximately 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.

b) Mass loss rate of $CO_2(C_0)$ is 1.0% after hydration and pH value is 10.6 and mass loss rate of $CO_2(C_{max})$ is 27.15% when concrete carbonated fully.

c) Proposed quantitative method for carbonation can evaluate in 1 week carbonation time even though method by indicator cannot evaluate because of uncolored concrete.

2. Prediction of service life to all mixtures of concrete using carbonation degree

a) Hydration model is valid to estimate the amount of $Ca(OH)_2$ after comparing experimental value and predicted value.

b) Predicted value using a point where the concentration of $Ca(OH)_2$ is 60% value shows similar existing result after comparing exiting predicted model.

c) Prediction of service life for carbonation to all mixtures of concrete is possible by the result of FEMA using a hydration model and carbonation degree

3. Proposing of evaluation method for concrete $LCCO_2$ by carbonation degree

a) In terms of CO_2 reduction, evaluation method of $LCCO_2$ and CO_2 balance for concrete with proposed carbonation can be used for determining the mix proportion of concrete and service life of structure

This study has limitations and as such it cannot be used as a method for quantitative evaluation of concrete carbonation, because it is based on only the experimental result for water to cement ratio of 0.45, 0.55 and 0.65 with ordinary Portland cement. In future, an additional investigation for the concrete with fly ash and blast furnace slag will be needed.

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Brief Introduction to the Book

Concrete carbonation decreases durability of concrete. Therefore, quantitative evaluating method for the amount of CO_2 absorption through carbonation should be considered under the condition that carbonation does not affect durability of RC structure. This study proposed a quantitative evaluating method that overcomes the limitation of the traditional qualitative evaluation, which is carried out using the naked eye with respect to the color change boundary by spraying indicator. Carbonation depth becomes the basic data for estimating the residual life and durability of RC structures. To achieve this objective, the quantitative change of $Ca(OH)_2$ and $CaCO_3$ for each depth in concrete according to the carbonation process is measured using TG/DTA in order to propose a quantitative method and an evaluation basis. Another goal is to propose evaluating method of CO_2 absorption in the air through carbonation and how to evaluate $LCCO_2$ (emission – absorption of CO_2).

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