Modeling of Carbonation Reaction in Concrete Based on Pore Structure and Chemical Equilibrium

(Translation from Concrete Research and Technology of JCI Vol.13, No.3, 2002)




Hiroshi UEKI Takaharu GOTO Masaaki MURAKAMI Naoto MASHIKO

Synopsis: Over the years, we have developed a model of the carbonation reaction in concrete using pH as the evaluation criterion. The basis of the model is an assumed chemical equilibrium in the pore water. This time, we have modeled the pore structure in terms of the concrete mix proportion, handling methods, and environmental conditions. We also newly incorporated a model for predicting the diffusion coefficient of carbon dioxide in concrete. In this paper, the results of carbonation analysis using the updated model are compared with measurements of neutralization in existing reinforced concrete structures (in service for 19 to 29 years). The comparison reveals that this analytical model is capable of effectively predicting the neutralization of existing reinforced concrete structures, thus demonstrating its applicability to the performance certification and service life estimation of reinforced concrete structures.

Keywords: carbonation reaction model, pore structure, pH, function of pore volume distribution density, diffusion coefficient, chemical equilibrium

---

Hiroshi Ueki is a director of the Maintenance Department, East Tokyo Management Bureau, Metropolitan Expressway Public Corporation. His research interest is the durability of reinforced concrete structures. He is a member of JSCE and JCI.

Takaharu Goto (1950-2002) was a head of Analytic Technology Department, Taiheiyo Consultant Co., Ltd. He obtained his Ph.D. in Engineering from the University of Tokyo in 1996. He was a member of JSCE and JCI.

Masaaki Murakami is a department manager of JIP Techno Science Co., Ltd. He obtained his M.Sc. in Environmental Science from Tsukuba University in 1980. He is a specialist of FEM analysis in civil engineering applications.

Naoto Mashiko is a head of Design and Research Division, Department of Engineering, Metropolitan Expressway Public Corporation. He is a member of JSCE.

1. Introduction

In discussing the durability of reinforced concrete structures, the most important factor to be considered is possible corrosion of the steel bars arranged within the concrete. In the strong alkali environment provided by the surrounding concrete, an oxide layer known as a passive film forms over the surface of the steel bars, and this film prevents corrosion by obstructing reactions between the steel and infiltrating moisture and oxygen. However, if the concrete surrounding the steel bars is neutralized, leading to a fall in the pH of the pore water, or if the concentration of chloride ions rises beyond a certain level, the passive film will be broken down.

For this reason, in considering the durability of a given reinforced concrete structure and managing its maintenance, the proper assessment of the pH of concrete around the steel bars is crucial to forecasting the start of reinforcement corrosion. The current reality, however, is that no techniques are available for properly measuring the pH of set concrete1), so a model that allows analytical pH assessment is required. Prior studies on neutralization2) and 3) have used the pH of pore water around the steel bars as a direct indicator, but no method was available to predict this pH. Accordingly, it has been extremely difficult to anticipate the loss of cover concrete from structures due to steel corrosion accompanying a drop in pH in typical environments. At the same time, mainstream design techniques for reinforced concrete structures have been shifting from the earlier detail-specified design to performance-based methods4), and in this connection there is a keen need for the establishment of an analytical model for identifying factors that lead to deteriorated performance of reinforced concrete structures and allowing quantitative assessment of long-term performance.

In view of this need, we have proposed an analytical model using pH as the evaluation criterion based on the diffusion of carbon dioxide and the assumed chemical equilibrium in pore water5)-9). This analytical model allows the carbonation reaction to be predicted if the diffusion coefficient of carbon dioxide in the concrete is known. This leads to prediction of the pore water pH and hence the concentration of carbon dioxide and carbonation reaction products over time.

The carbon dioxide diffusion coefficient depends on the pore structure, which varies with the concrete mix proportion and handling methods as well as environmental conditions. Hence, there is also a need for a model that appropriately expresses pore structure and from which the diffusion coefficient can be derived.

This paper describes in detail a comprehensive analytical model of the carbonation reaction incorporating a pore structure model that newly reflects the concrete mix proportion, concrete handling methods, and environmental conditions. Further, the results of comparing analytical estimates of the pH of set concrete with actual measurements of neutralization depth in real structures are discussed. The definitions of the terms “carbonation” and “neutralization” in this paper follow those given in the authoritative literature1).

2. Carbonation Reaction Model for Concrete Taking Account of Chemical Equilibrium

2.1 Outline

The carbonation of concrete can be considered to take place in two stages: the physical process by which carbon dioxide (gas) from the atmosphere diffuses into the concrete and the chemical process in which the diffused carbon dioxide reacts with alkaline components including calcium hydroxide. Our model is based on the assumption that diffused carbon dioxide exists in a state of equilibrium with the various components of the gaseous phase, liquid phase, and solid phase in the fine concrete pores.

2.2 Physical Model

The analytical model is based on the supposition that carbon dioxide from the atmosphere diffuses through co-joined pores in the concrete according to Fick’s second law and that it dissolves instantaneously into pore water according to Henry’s law. Equation (1) is the unsteady-state one-dimensional diffusion equation used to calculate diffusion.

$$\partial C/\partial t = D_{CO2}' \, \partial^2 C/\partial x^2 - \Delta[C_s] \qquad (1)$$

where,

C: Concentration of carbon dioxide [mol/l]
D_{CO2}': Diffusion coefficient of carbon dioxide in concrete [cm^2/s]
t: Time [s]
x: Distance from concrete surface [cm]
$\Delta[C_s]$: Quantity of diffused carbon dioxide dissolved per Δt [mol/(l・s)]

This physical model is based on the following assumptions:

① Gaseous-phase carbon dioxide diffuses through the concrete one-dimensionally in the depth direction, and no movement of the liquid phase is taken into consideration.
② The diffusion coefficient of carbon dioxide in concrete is constant. In other words, there is no change in pore structure due to either the hydration reaction or the carbonation reaction, and the water content of the concrete remains constant, also.
③ The concentration of carbon dioxide at the surface of the concrete is constant.

2.3 Chemical Model

The analytical model consists of a chemical equilibrium in which it is supposed that the carbonation reaction proceeds instantaneously to equilibrium. Consequently, the progress of carbonation is determined by the diffusion rate.

Underlying the chemical equilibrium model is the assumption that the components that react with carbon dioxide are calcium oxide (CaO) and alkalis ($Na_2O + K_2O$), and these components are eluted from the hydration products and un-reacted minerals. It is presumed from the results of a basic laboratory experiment in the past$^{10)}$ that, in the pore water where the concrete is finely particled, carbon dioxide that reaches the pores (in the gaseous phase) instantaneously dissolves into the pore water, which is the reaction phase (the liquid phase), resulting in an equilibrium between the gaseous phase and the liquid phase. It is similarly assumed that calcium hydroxide and calcium carbonate in the solid phase are also have a very rapid rate of dissolution into the liquid phase (and deposition into the solid phase), so there is always equilibrium between the liquid and solid phases also.

Figure 1 illustrates how the gaseous phase, liquid phase, and solid phase equilibria in the concrete are modeled. All of these chemical equilibria are reversible reactions, as indicated by Equations (2) through (10), and the components involved all remain in full equilibrium with each other. Hydrates of calcium silicates (C-S-H) formed by the hydration of alite and belite are ignored here because of their low solubility product constants$^{1)}$. It is also supposed in this model that potassium ions (K^+) and sodium ions (Na^+) behave in the same way.

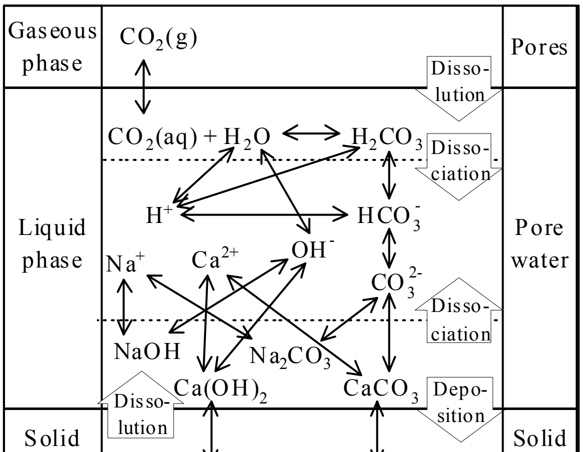


Fig. 1 Concept of chemical equilibrium model

Equation (2) represents the dissolution equilibrium of carbon dioxide between the gaseous and liquid phases. Carbon dioxide in the gaseous phase is assumed to dissolve instantaneously into the pore water according to Henry's law.

Equation (3) represents the equilibrium reaction of dissolved carbon dioxide with water. The carbonic acid that forms is dissociated into ions as indicated by Equations (4) and (5). Equations (6) through (9) represent solubility equilibria, of which the maximum value is the solubility product constant, K_{SP}. If the product of ion concentrations surpasses the solubility product constant in any of these equilibrium equations, the ions combine with one another and are deposited as solids, resulting in a shift from the liquid phase to the solid phase. Since calcium hydroxide ($Ca(OH)_2$), calcium carbonate ($CaCO_3$), sodium hydroxide ($NaOH$), and sodium carbonate (Na_2CO_3) are completely dissociated in the liquid phase, they are absent in the liquid phase as chemical species though present as ions. Equation (10) is the dissociation equilibrium equation for water, where K_w is the ion product of water.

$$CO_2(g) \overset{K_1}{\leftrightarrows} CO_2\,(aq) \quad (2)$$

$$CO_2\,(aq) + H_2O \overset{K_2}{\leftrightarrows} H_2CO_3 \quad (3)$$

$$H_2CO_3 \overset{K_{a1}}{\leftrightarrows} H^+ + HCO_3^- \quad (4)$$

$$HCO_3^- \overset{K_{a2}}{\leftrightarrows} H^+ + CO_3^{2-} \quad (5)$$

$$Ca\,(OH)_2\,(s) \overset{K_{sp1}}{\leftrightarrows} Ca^{2+} + 20H^- \quad (6)$$

$$CaCO_3\,(s) \overset{K_{sp2}}{\leftrightarrows} Ca^{2+} + CO_3^{2-} \quad (7)$$

$$NaOH\,(s) \overset{K_{sp3}}{\leftrightarrows} Na^+ + OH^- \quad (8)$$

$$Na_2\,CO_3\,(s) \overset{K_{sp4}}{\leftrightarrows} 2Na^+ + CO_3^{2-} \quad (9)$$

$$H_2O \overset{K_w}{\leftrightarrows} H^+ + OH^- \quad (10)$$

The solubility product constants, which can be calculated from these dissociation constants and solubility constants, are given in various handbooks and similar publications[11)-13)]. The equilibrium constants used in this analysis are given in Table 1. According to Equations (2) through (10), if calcium carbonate ($CaCO_3(s)$) or calcium hydroxide ($Ca(OH)_2(s)$) is present in the solid phase, the liquid phase takes on an equilibrium composition matching the concentration of carbon dioxide ($CO_2(g)$) in the gaseous phase. Carbon dioxide that has dissolved from the gaseous phase into the liquid phase ($CO_2(aq)$) reaches equilibrium in the liquid phase and, if the concentration of carbonate ions surpasses the solubility product constant of Equation (7), will immediately be deposited as calcium carbonate. This results in a decrease in calcium ions (Ca^{2+}) in the liquid phase, where the equilibrium is maintained by the dissolution and dissociation of calcium hydroxide from the solid phase. If further carbon dioxide diffuses into the gaseous phase after all of the calcium hydroxide in the solid phase has been consumed, the amount of carbon dioxide in the liquid phase ($CO_2(aq)$) will increase. As hydrogen ions (H^+) increase and as a consequence the pH drops, the number of hydrogen carbonate ions (HCO_3^-) increases while carbonate ions (CO_3^{2-}) decrease, and more calcium carbonate will be dissolved. These changes continue until the concentration of carbon dioxide in the gaseous phase equalizes with its concentration in the atmosphere.

By inputting the concentration of carbon dioxide and of alkali ions in the liquid phase, the concentrations of various ions and chemical species in the liquid phase can be calculated using Equations (2) through (10).

Table 1 Equilibrium constants

Equation (2)	$K_1=[CO_2\,(aq)]/[p_{co2}] = 1.0 \times 10^{-1.41}$	(25°C)
Equation (3)	$K_2=[H_2CO_3]/\,[CO_2\,(aq)] = 1.0 \times 10^{-2.8}$	(25°C)
Equation (4)	$K_{a1}=[H^+][HCO_3^-]/\,[H_2CO_3] = 1.0 \times 10^{-3.50}$	(25°C)
Equation (5)	$K_{a2}=[H^+][CO_3^{2-}]/\,[HCO_3^-] = 1.0 \times 10^{-10.25}$	(25°C)
Equation (6)	$K_{sp1}=[Ca^{2+}]\,[OH^-]^2 \leqq 1.0 \times 10^{-5.26}$	(25°C)
Equation (7)	$K_{sp2}=[Ca^{2+}]\,[CO_3^{2-}] \leqq 1.0 \times 10^{-8.35}$	(25°C)
Equation (8)	$K_{sp3}=[Na^+]\,[OH^-] \leqq 1.0 \times 10^{2.23}$	(20°C)
Equation (9)	$K_{sp4}=[Na^+]^2\,[CO_3^{2-}] \leqq 1.0 \times 10^{1.29}$	(20°C)
Equation (10)	$K_w=[H^+]\,[OH^-] = 1.0 \times 10^{-14.00}$	(25°C)

3. Modeling the Pore Structure of Concrete

3.1 Outline of Textural Structure

The textural structure of concrete is formed by the gradual filling of a matrix comprising aggregate, cement particles, and water-containing pores with hydrates generated by hydration reactions. This textural structure may greatly vary with the quality of the mix and the hardening method, was well as with the type of cement (which affects the hydration reactions) and material aging (including the curing conditions. As the hydration reactions progress, hydrates of calcium silicate (C-S-H) are formed in the texture where water was originally present. These are the fine pores, or so-called gel pores. As a result, the concrete becomes a porous solid. The texture of the resultant concrete can be divided into the solid phase consisting of the aggregate and hydration products on the one hand, and the pores on the other. Depending on environmental conditions in the atmosphere, some of the water may evaporate, so pores can be classified as those saturated with water and those that are not. This concrete configuration is schematically illustrated in Fig. 2.

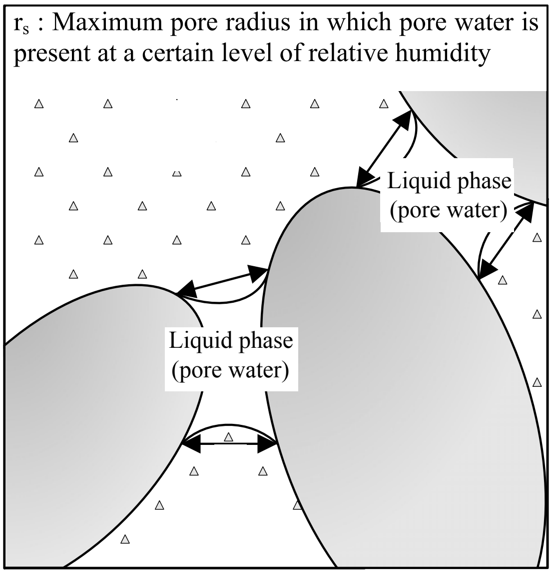


Fig. 2 Schematic of cement texture

As noted in Section 2.2, the diffusion route for carbon dioxide through concrete is assumed to consist of consecutive unsaturated pores. This means that a model able to appropriately express such a pore structure is needed, and the model must be able to quantitatively reflect characteristics that contribute to the early texture, such as the concrete mix proportion and changes in pores due to the hydration and carbonation reactions.

3.2 Form of Moisture in Pores

It is presumed that a gaseous phase (consisting of water vapor and air) coexists with a liquid phase (consisting of pore water) in the concrete pores. When these phases are in an equilibrium, and if the maximum pore radius in which a gas-liquid interface forms is represented by r_s[m], all pores smaller than r_s will be filled with pore water. From the Kelvin equation, r_s can be written as Equation (11).

$$r_s = 2\gamma \cdot M_W/R \cdot T \cdot \rho_L(\ln P_v/P_{v0})^{-1} \qquad (11)$$

where,

γ: Surface tension of pore liquid [N/m]
M_W: Molecular weight of water [kg/mol]
R: Gas constant [J/(mol・K)]
T: Absolute temperature [K]
P_v/P_{v0}: Relative humidity [-]
ρ_L: Density of pore water [kg/m^3]

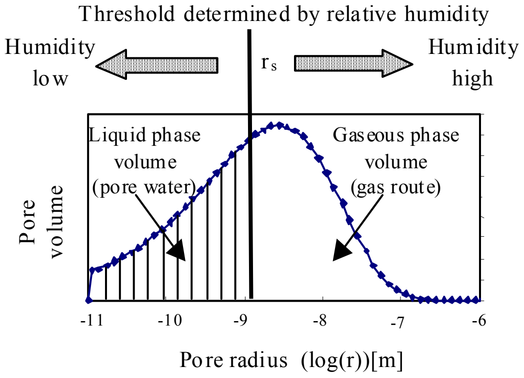


Fig. 3 Relationship between relative humidity and hydrous state

The gaseous phase can be regarded as constituting the carbon dioxide diffusion route, while the liquid phase is the field in which the carbonation reaction takes place. Figure 3 schematically illustrates the concept of threshold in this regard. The value of r_s varies with humidity; the higher the humidity, the more r_s shifts to the right, resulting in a shrinkage of the gaseous phase volume and a drop in the diffusion coefficient of carbon dioxide. This is clearly consistent with the relationship between water content and diffusion coefficient as understood in a general sense, and so can be regarded as presenting a highly rational model[14).

3.3 Modeling of Pore Structure

In order to model the pore structures of concrete for the purpose of analyzing the carbonation reaction, it is necessary to differentiate between gaseous phase pores, which constitute the carbon dioxide diffusion route, and liquid phase pores, which do not pass carbon dioxide as noted in the previous section[14). In this study, the density distribution function proposed by Shimomura[15) 16) is adopted.

$$dV_{(r)}/dr = V_0 \cdot B \cdot C \cdot r^{C-1} \exp(-B \cdot r^C) \qquad (12)$$

where,

r: Pore radius [m]
$V_{(r)}$: Volume of pores of radius r [m^3/m^3]
B: Parameter determining shape of the density distribution function
C: Parameter determining shape of the density distribution function; taken to be 0.5
V_0: Total volume of pores in a unit cubic measure of concrete [m^3/m^3]

This function reveals how many pores of a certain radius are present in a unit cubic measure of the concrete being assessed, but does not go so far as to express the features of the spatial structure, such as linking of the pore texture or how the pores are twisted. A number of assumptions were made in using this density distribution function, as given below.

It is assumed that all the pores in the pore structure are ① continuous, ② isotropic, and ③ homogeneous. According to Shimomura, the density distribution function given by Equation (12) is determined by the unit water quantity and the unit cement quantity (the blending conditions), the weight ratio of combined moisture (from the type of cement and its mineral composition), and the age of the material at the start of drying (depending on work methods). Three material constants[15) are required to determine the density distribution function:V_0, B, and C. Of these, V_0 and B can be obtained using the three equations given below, while C is assumed to be 0.5.

$$V_0 = (\underline{W} - \omega \cdot \underline{C})/\rho_L \qquad (13)$$
$$\omega = (0.061 + 0.054 \cdot \ln(t_d)) \cdot (\underline{W}/\underline{C})^{0.5} \qquad (14)$$
$$B = (1880 + 2680 \cdot \ln(t_d)) \cdot (\underline{W}/\underline{C})^{-1.2} \qquad (15)$$

where,

$\underline{W}$: Unit water quantity [kg/m^3]
$\underline{C}$: Unit cement quantity [kg/m^3]
ω: Weight ratio of combined moisture of cement [-]
ρ_L: Density of pore water [kg/m^3]
t_d: Age at start of drying [d]

4. Methods of Analysis

4.1 Outline of Analysis Methods

The model predicts progress of the carbonation reaction based on the material constituents of concrete and their mix, the work methods, and environmental conditions. The specifics of the analytical model are illustrated in Fig. 4.

The input data comprise the chemical composition of cement, the unit cement quantity and water quantity in the concrete, the age at the start of drying, and the environmental carbon dioxide concentration and humidity. Based on these data, the pore structure is first presumed and the diffusion coefficient in the concrete figured out. Then the alkali concentration and the amount of calcium to react with carbonate ion in the pore water are estimated. Finally, the concentrations of various chemical species in the pore water are determined, including the amount of calcium carbonate formed, the amount of carbon dioxide involved in reaction is calculated, and the pH is estimated. It is assumed then that the pore structure and the fixed amount of alkalis does not change once drying has started. A flow chart of the analysis is given in Fig. 5, and the shape of mesh used for analysis is specified in Fig. 6. For the analysis, the finite element method was used for integration in the spatial direction and the Lax-Wendroff method for integration in the time direction. In dividing the analyzed region into elements, as shown in Fig. 6, the mesh width was set to 0.1 cm.

The assumption is that carbon dioxide would diffuse from the concrete surface (x = 0.0 cm) one-dimensionally in the X direction and that no carbon dioxide would flow in or out through any other boundary. Analysis time steps range from 5.00×10^{-5} to 1.00×10^{-4} (d). At Step 1, the initial equilibrium before the carbonation reaction starts is calculated. Steps 2 to 5 constitute a time loop, and the calculation is repeated for each point of time t. At Step 2, the diffusion of carbon dioxide is calculated using Equation (1), and at Step 3 the carbon dioxide concentration on the concrete surface is given as a boundary condition. At Step 4, convergence is sought such that all the chemical equilibria in Equations (2) through (10) hold true, and the pH and the concentrations of various chemical species at each point of time t are figured out.

4.2 Diffusion Coefficient of Carbon Dioxide in Concrete

Generally, the diffusion coefficient for a gas through concrete pores can be expressed by the following equation on the basis of a mutual diffusion coefficient.

$$D = \varepsilon/\tau^2 \cdot D_0 \qquad (16)$$

where,

D: Diffusion coefficient of gas in porous solid [m^2/s]
ε : Porosity [-]
τ: Degree of bend [-]
D_0: Mutual diffusion coefficient [m^2/s]

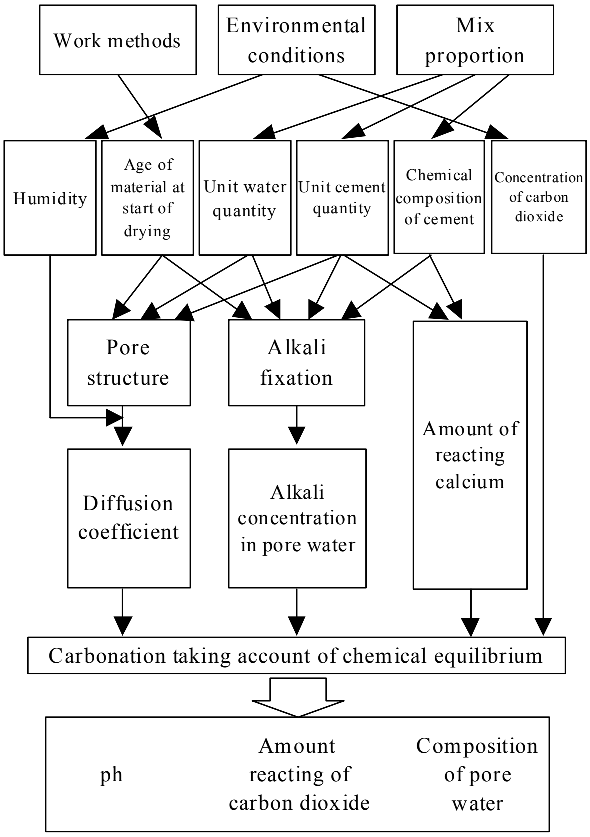
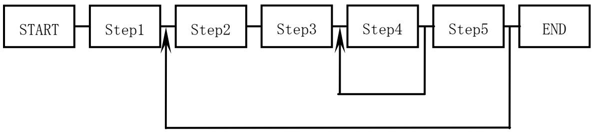


Fig. 4 Analytical model



Step1 ; Initial Equilibrium
Step2 ; Diffusion
Step3 ; Boundary condition
Step4 ; Equilibrium
Step5 ; Output Results

Fig. 5 Flow of Analysis

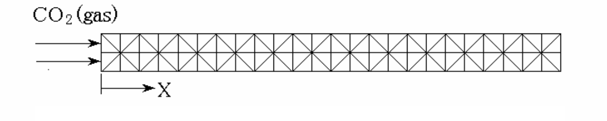


Fig. 6 Mesh (Δx = 0.1 cm)

In this study, the equation proposed by Shimomura, et al.[15) 16)] for the diffusion of water vapor was applied to carbon dioxide, and the diffusion coefficient D_{CO2}' of carbon dioxide in concrete is represented by Equation (17)[18).

$$D_{CO2}' = K \cdot V \cdot D_{CO2} \qquad (17)$$

where,

D_{CO2}: Mutual diffusion coefficient of carbon dioxide and air
K: Material coefficient representing the affect of narrowness and bends in the pore structures of concrete, wherein Equation (18)15) proposed by Shimomura is used. It can be considered synonymous with $1/\tau^2$ in Equation (16).

$$K = 1/3 \cdot 120 \cdot B^{-0.69} \qquad (18)$$

V: Material coefficient representing the porosity effective for carbon dioxide diffusion, wherein Equation (19)15) proposed by Shimomura is used. It can be considered synonymous with ε in Equation (16).

$$V = V_0 \cdot \exp(B \cdot r_s^{c}) \qquad (19)$$

By using these coefficients, the diffusion coefficient of carbon dioxide in concrete can be determined from the concrete mix and the age at the start of drying.

4.3 Quantity of Calcium Involved in Reaction

Investigators often assume that only calcium hydroxide formed by the hydration of cement is affected by the carbonation reactione.g. 14). However, others claim that almost all of the calcium oxides in the cement react with carbon dioxide19). Considering that the calcium carbonate contained in the concrete of actual structures accounts for 70% to 90% of the total calcium content20), it is improbable that calcium hydroxide resulting from hydration is the only reactant. On the other hand, since carbon dioxide and calcium hydroxide react only in the presence of moisture1), it is not necessarily true that all calcium hydroxide undergoes carbonation, because depending on the environment moisture may be in short supply.

In this model, the reactants are assumed to be only silicate compounds in the cement (unreacted alite, belite, and C-S-H) and calcium hydroxide. (These are referred to as the "quantity of calcium involved in reaction".) It is supposed that unreacted aluminate and ferrite phases, and hydrates deriving from them, do not undergo carbonation. The quantity of calcium involved in reaction can be calculated from the mineral composition, as figured out from the chemical components of the cement used, and the unit cement quantity in the concrete mix. The quantity of calcium involved in reaction is found to be about 80% of the total calcium content.

4.4 Alkali Ion Concentration in Pore Water

Although most of the alkali content of pore water results from elution out of the cement, not all of the alkali content (Table 4) makes its way into the pore water. Missing from the pore water are, presumably, alkalis remaining as solid solution in unreacting minerals and alkalis that have been fixed again after elution.

Taylor21) proposed Equation (20) for determining the concentration of alkali ions in pore water. Representing the ion concentration at a certain material age, this equation takes into account the ratio (b) of the alkali content discharged from cement (m_r) to the amount of alkalis fixed (sorbed) by cement hydrates. It accounts for the fact that, as the rate of hydration increases with advancing material age, the amount of alkali discharged from the cement (m_r) increases, while the proportion (P) of cement hydrates able to sorb alkalis (C-S-H and the AFm phase) also rises, with a resulting increase in the amount of alkalis fixed. It was decided to adopt Equation (20) in this study to determine the alkali ion concentration in the pore water, and it was assumed that alkalis not present in the pore water played no part in the chemical equilibrium of Equation (8) or Equation (9). Furthermore, since no clear knowledge of the relationship between these fixed alkalis and carbonation is available, it was assumed that the alkali ion concentration does not vary with carbonation.

$c = m_r/(A + b \cdot P)$ (20)

where,

c: Concentration of specified ionic species in pore solution [mol/l]
m_r: Quantity of alkali cations (Na^+, K^+) released from the binder [mol/m^3]
A: Amount of pore water [l/m^3]
b: Binding factor [l/m^3]
P: CRP/CRP_∞ [-]
CRP: Quantity of calcium in relevant product (C-S-H plus the AFm phase) [mol/m^3]
CRP_∞: Value of CRP for complete hydration [mol/m^3]

5. Verification of Proposed Technique using Analytical Examples

5.1 Current State of Existing Reinforced Concrete Wall Balustrades

Table 2 Mixes and ages of existing reinforced concrete balustrades

Item	Case 1	Case 2	Case 3
Water content [kg/m^3]	142	158	167
Cement content [kg/m^3]	349	316	287
Water-cement ratio [%]	41	50	58
Type of cement	Ordinary Portland Cement	Same as left	Same as left
Slump [cm]	8±2.5	Same as left	Same as left
Air quantity [%]	4±1	Same as left	Same as left
Specified design strength [kg/cm^2]	300	Same as left	Same as left
Years in service	29	19,20,21	25

The validity of the proposed analytical model was verified by comparing measurements taken from existing reinforced concrete structures with the results of analysis using the model. Reinforced concrete wall balustrades along an expressway were selected for the verification. These structures were in a state where concrete had fallen away, and cores could be readily taken. Table 2 shows the mix proportions of concrete in these balustrades and the number of years they had been in service.

In Cases 1 and 3, the mix was estimated from core samples in accordance with Report F-18, “Report on Joint Tests on Blend Estimation of Set Concrete”, by the Special Committee for Concrete of the Japan Cement Association. In Case 2, the actual values of the mix proportion are used. Neutralization depth was determined from core samples; the circumferential face of each core was sprayed with a 1% solution of phenolphthalein in ethanol and the minimum and maximum distances from the core surface to the colored region were measured. The average neutralization depth was calculated by tracing the uncolored region onto a polyethylene sheet, measuring its area with a planimeter, and dividing that by the circumference of the core sample.

5.2 Physical Properties Required for Analysis

The physical values used to calculate the diffusion coefficient are listed in Table 3, while the alkali content and mineral composition are assumed to be those of ordinary Portland cement, as given in Table 4. Values used for calculating alkali ion concentrations are given in Table 5.

Table 6 lists the calculated values of carbon dioxide diffusion coefficient, the quantities of calcium involved in reaction, and the combined concentrations of alkali ions in the pore water (i.e., the sum of the concentrations of sodium ions and potassium ions). As environmental conditions, the concentration of carbon dioxide in the atmosphere was taken to be 0.032% with reference to *Chronological Scientific Tables*, while the relative humidity was set at 70% in view of the annual average levels of 64% and 69% in Tokyo and Yokohama, respectively.

Table 3 Values used for calculating diffusion coefficient

Variable	Definition	[unit]	Case 1	Case 2	Case 3
W/C	Water/cement ratio	[%]	41	50	58
t_d	Age of material at the start of drying	[day]	7		
P_v/P_{v0}	Relative humidity	[%]	70		
γ	Surface tension of liquid	[N/m]	0.0727		
M_w	Molecular weight of water	[kg/mol]	0.01802		
R	Gas constant	[J/(mol・K)]	8.31453		
T	Absolute temperature	[K]	293.0		
ρ_L	Density of pore water	[kg/m^3]	1000.0		
D_{CO2}	Mutual diffusion coefficient of carbon dioxide and air	[m^2/s]	0.138×10^{-4} 11)		
r_s	Maximum pore radius	[m]	3.015×10^{-9}		

Table 4 Composition of cement (assumed values) [unit: mass%]

Mineral composition				Alkali contents	
Alite C_3S	Belite C_2S	Aluminate phase C_3A	Ferrite phase C_4AF	Na_2O	K_2O
50.0	25.0	9.0	9.0	0.300	0.455

Table 5 Values used for calculating alkali ion concentrations

	Case 1		Case 2		Case 3	
	Na_2O	K_2O	Na_2O	K_2O	Na_2O	K_2O
C	0.092	0.127	0.074	0.099	0.063	0.083
M_r	12.21	14.11	11.06	12.78	10.04	11.61
A	70.09	70.79	91.91	91.91	106.4	106.4
b	108.2	69.80	97.96	63.20	88.97	57.40
P	0.585	0.585	0.585	0.585	0.585	0.585
CRP	1.616	1.616	1.463	1.463	1.329	1.329
CRP_∞	2.761	2.761	2.500	2.500	2.270	2.270

Table 6 Values of physical properties used for equilibrium calculation

	Diffusion coefficient [m^2/s]	Quantity of reacting calcium [mol/m^3]	Alkali ion concentration [mol/1]
Case 1	1.96×10^{-8}	3.30×10^{3}	0.438
Case 2	3.38×10^{-8}	2.99×10^{3}	0.346
Case 3	4.78×10^{-8}	2.72×10^{3}	0.292

5.3 Verification and Discussion

Analysis using this model yields the distribution of calcium hydroxide and calcium carbonate in the solid phase after the elapse of a certain amount of time, and the concentrations of various components represented by Equations (2) through (10), including the pH of the pore water. An example of analysis is shown in Fig. 7, where the structure has been in service for up to 30 years. It is evident that the carbonated region expands more deeply into the concrete over time, and that the pH drops as a result. The amount of calcium carbonate increases while the calcium hydroxide content falls in the vicinity of the region where carbonation is progressing. Table 7 presents the final results for all components. It is clear that the pH in the vicinity of the concrete surface is about 10.4 after 30 years. Coloring was observed in a phenolphthalein test, indicating the absence of neutralization, but there are suggestions that the relationship between pH and phenolphthalein coloration in set concrete may depend on other conditions and cannot be unequivocally defined[22].

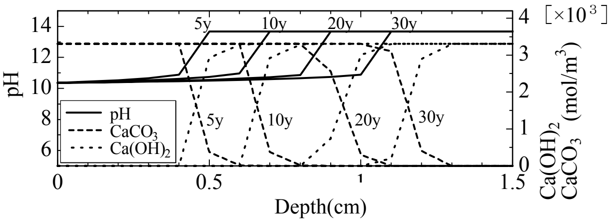


Fig. 7 pH and quantity of calcium carbonate formed at different times (Case 1)

Table 7 Concentrations of various chemical species obtained through analysis (Case 1, 30 years, in mol/l)

Depth	0.1 cm	1.0 cm	1.5 cm
pH	10.38	10.87	13.65
$CO_2(g)$	1.18×10^{-5}	1.50×10^{-6}	1.28×10^{-14}
$CO_2(aq)$	1.03×10^{-5}	1.31×10^{-6}	2.35×10^{-18}
H_2CO_3	1.63×10^{-8}	2.07×10^{-9}	3.73×10^{-21}
HCO_3^-	1.22×10^{-1}	4.83×10^{-2}	5.29×10^{-11}
CO_3^{2-}	1.63×10^{-1}	2.00×10^{-1}	1.34×10^{-7}
Na^+	4.38×10^{-1}	4.38×10^{-1}	4.38×10^{-1}
Ca^{2+}	2.74×10^{-8}	2.23×10^{-8}	2.76×10^{-5}
$Ca(OH)_2$	0.00 [mol/m^3]	0.00 [mol/m^3]	3.30×10^3 [mol/m^3]
$CaCO_3$	3.30×10^3 [mol/m^3]	3.30×10^3 [mol/m^3]	0.00 [mol/m^3]

In this paper, the carbonation depth is taken as the point below the surface at which the calcium hydroxide in the solid phase totally disappears. In Fig. 7, this is assumed to be the position at which the pH drops significantly (pH $\fallingdotseq$ 10.9). Figures 8 through 10 compare the analytical results with estimates obtained using the formula proposed by the Japan Society of Civil Engineers[23] and by Kishitani[2]. The measured values of neutralization depth were obtained from cores taken from both the inner (road) and outer sides of the balustrades, with the average, maximum, and minimum values plotted. In using the JSCE formula, the water-cement ratio in Table 2 was used, and the coefficient representing environmental effects, R, was taken to be 1.6. In calculations with Kishitani's formula, an equation representing a water-cement ratio of 60% or less was used, and a neutralization rate of R_1 = 0.4 was adopted. Equation (21) is the JSCE formula and Equation (22) is the Kishitani formula.

[Japan Society of Civil Engineers formula]

$$y = R(-3.57 + 9.0W/B)\sqrt{t} \qquad (21)$$

where,

W/B: Effective water-binding material ratio = $W/(C_p + k \cdot Ad)$
W: Mass of water per unit volume
B: Mass of effective binding material per unit volume
C_p: Mass of Portland cement per unit volume
Ad: Mass of admixture per unit volume
R: Coefficient representing environmental effects
k: Coefficient representing admixture effects

[Kishitani's formula]

$$t = [7.2/R_1^2(4.6x - 1.76^2)]\, C^2 \qquad (22)$$

where,

t: Time taken for neutralization to reach depth C [years]
X: Water-cement ratio in terms of strength [%]
C: Neutralization depth [cm]
R_1: Neutralization rate [－]

Estimates of neutralization depth obtained using the JSCE and Kishitani formulas are substantially the same where the water-cement ratio is low, and they correspond closely to the minimum values of measured neutralization depth. However, as the water-cement ratio rises, estimates by the JSCE formula tend toward the average of the measured values, while the Kishitani formula gives results close to the minimum value.

On the other hand, values of neutralization depth obtained with the proposed model are closer to the maximum measured values, and at higher water-cement ratios they somewhat exceed the maximum measured value. This indicates that the model yields results that fall on the safe side as regards danger to the public. Incidentally, the designed concrete cover for these wall balustrades was 3.0 cm, and the maximum predicted neutralization depth is about 2.0 cm after 30 years of use, suggesting that carbonation will not reach the steel reinforcement.

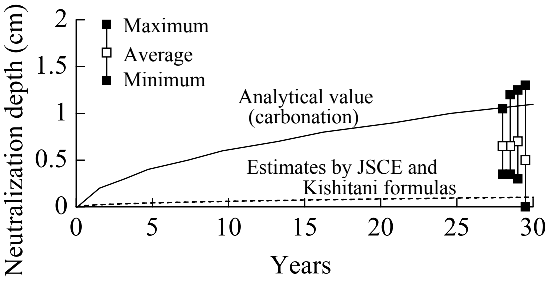


Fig. 8 Variation in neutralization depth over time (Case 1)

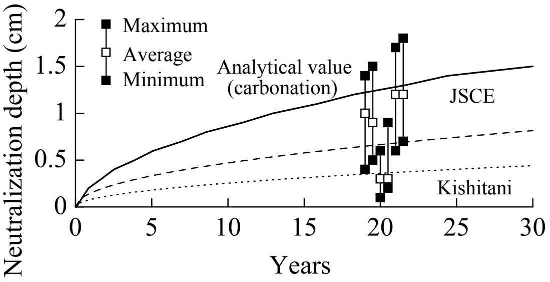


Fig. 9 Variation in neutralization depth over time (Case 2)

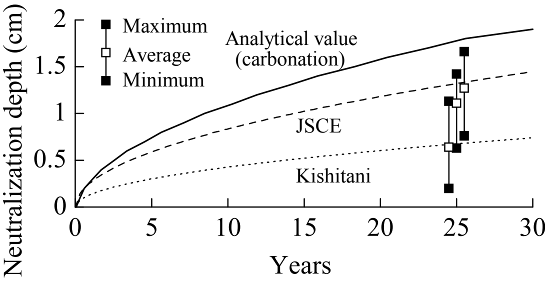


Fig. 10 Variation in neutralization depth over time (Case 3)

As differences are found between the analytical values obtained with the proposed model and measurements, their causes will be considered. The major factors affecting carbonation depth are the diffusion coefficient and the quantity of calcium involved in reaction.

Regarding the diffusion coefficient, it was taken as constant throughout the service life once drying began (after seven days), and no changes in pore structure with hydration or carbonation reaction were taken into account. However, analysis with the proposed model tends to overestimate the diffusion coefficient, and therefore carbonation depth, at higher water-cement ratios. This is because the increase in finer pore structure accompanying the hydration reaction is ignored. This point calls for further amplification.

The balustrades tested in this investigation were exposed to motor vehicle emissions (NOx and SOx), so it is conceivable that these substances also diffused into the concrete and dissolved into the pore water. This would have caused a drop in pH. While the impact of this could be introduced into the proposed model by adding equilibrium equations for these components to the chemical equilibrium model, this has been left for the next step in our research.

6. Conclusion

In this study of neutralization in reinforced concrete structures, a carbonation reaction model is developed in which the pH of pore water is the evaluation index. The carbon dioxide diffusion coefficient is obtained by modeling the pore structure of a particular concrete structure from the mix proportion, curing method, and environmental conditions. This is used in conjunction with a model of ionic equilibrium in the pore water.

Unlike many other studies that have focused on the diffusion of carbon dioxide using neutralization depth as the indicator, this newly proposed model succeeds not only in quantitatively estimating the extent of carbonation in terms of pH, but also in basing the estimation on the concentration of various chemical species present in the pores. In the future, it is expected to prove a very versatile technique for the quantitative estimation of the impact of car emissions on concrete.

The proposed model was verified by measuring the neutralization depth in actual structures. While measured neutralization depths in actual structures are subject to wide fluctuations, it was demonstrated that the analytical values obtained make it possible to approximately track neutralization depth while obtaining results on the safe side.

The passive film covering steel reinforcing bars is thought to begin degrading around pH = 11, eventually leading to corrosion24). Since this model uses pH as an evaluation index, steel corrosion due to falling pH can be predicted. Accordingly, the model can serve as an effective tool in the preventive conservation of concrete covering against exfoliation. Future work will include continued efforts at verification with data derived from actual structures with a view to further improvement of analytical accuracy. The eventual aim is to establish the model as a tool for diagnosing deterioration as part of a systematic effort to maintain the existing social infrastructure.

[Acknowledgments]
Special appreciation is due to Dr. Takumi Shimomura, assistant professor at Nagaoka University of Technology, for his generous guidance in introducing the function of pore volume distribution density. We are also indebted to Dr. Yasuhiko Furusawa, Kajima Corporation, and Mr. Yukinori Yamazaki, A&A Material Corporation, for their kind advice regarding the model architecture. Further gratitude is due to Dr. Ryuji Kawamura, Work Box, Inc., for his helpful guidance and support.

[Obituary]
The authors are sad to report that one of their co-authors, Dr. Takaharu Goto, passed away on July 6, 2002.

References

1) Japan Concrete Institute, Report by the Carbonation Research Committee, p. 1, March 1993
2) Koichi Kishitani, *Durability of Reinforced Concrete,* Kajima Corporation Technical Institute Press, p. 165, 1963
3) Shigeyoshi Nagataki, Hiroyuki Ooga, and Tatsuhiko Saeki, “Prediction of neutralization depth of concrete,” *Annual Report of Cement Technology*, No. 41, pp. 343-346, 1987
4) Japan Society of Civil Engineers, *Standard Specifications for Concrete Structures: Durability Certification Type (Execution)*, pp. 9-10, January 2000
5) Toru Makino, Hiroshi Ueki, Ryuji Kawamura, Yukinori Yamazaki, and Masaaki Murakami, “Reaction analysis of carbonation of concrete by using coupled geochemical code and finite element method,” *Proceedings of JCI Symposium on Chemical Reaction and Process Analysis of Cement Concrete*, pp. 59-64, May 1996

6) Akitaka Momose, Hiroshi Ueki, Yukinori Yamazaki, and Masaaki Murakami, "The simulation analysis of carbonation of RC members," *Proceedings of the JCI,* Vol. 18, No. 1, pp. 729-734, 1996
7) Mitsumasa Osada, Hiroshi Ueki, Yukinori Yamazaki, and Masaaki Murakami, "Simulation analysis of carbonation reaction of concrete members taking alkali elements into consideration," *Proceedings of the JCI ,* Vol. 19, No. 1, pp. 793-798, 1997
8) Yoichi Matsumoto, Hiroshi Ueki, Yukinori Yamazaki, and Masaaki Murakami, "Model analysis of carbonation reaction with redissolution of $CaCO_3$," *Proceedings of the JCI,* Vol. 20, No. 2, pp. 961-966, 1998
9) Yoshito Konishi, Hiroshi Ueki, Takaharu Goto, and Kazuhiro Kawaguchi, "Model of carbonation of concrete considering ionic equilibrium in pore solution," *Proceedings of the JCI,* Vol. 22, No. 2, pp. 763-768, 2000
10) Yoshito Konishi, Hiroshi Ueki, Takaharu Goto, and Yoichi Ishikawa, "Basic experimentation for modeling of carbonation reaction of concrete," *Proceedings of the JCI,* Vol. 21, No. 2, pp. 1087-1092, 1999
11) National Astronomical Observatory of Japan, ed., *Chronological Scientific Tables,* 2001, Maruzen, p. 97, November 2000
12) The Chemical Society of Japan, ed., *Chemistry Handbook*, *Fourth Revised Edition, Basic Section*, Maruzen
13) The Society of Chemical Engineers, Japan, ed., *Handbook of Chemical Industry, Sixth Revised Edition*, Maruzen
14) Tetsuya Ishida and Koichi Maekawa, "Modeling of pH profile in pore water based on mass transport and chemical equilibrium theory," *Proceedings of JSCE,* No. 648/V. 47, pp. 203-215, May 2000
15) Takumi Shimomura, "Dry contraction model of concrete based on the function of pore volume density distribution function," diploma thesis presented to the University of Tokyo, 1993
16) Takumi Shimomura and Koichi Maekawa, "Drying shrinkage model of concrete based on micromechanisms in concrete," *Proceedings of JSCE ,* No. 520/V. 28, pp. 35-45, August 1995
17) Gordon R. Youngquist, "Diffusion and Flow of Gases in Porous Solids, *Flow through Porous Media Symposium*, Vol. 62, No. 8, pp. 52-63, August 1970
18) Hiroshi Ueki, Naoto Masiko, and Takaharu Goto, "Formulation of gaseous diffusion coefficient of concrete," *The 24th Japan Road Conference Collection of General Papers (B)*, pp. 232-233, 2001
19) Yukinori Yamazaki, Michio Funato, and Hiroaki Matsusato, "Carbonation and compositional change of concrete bridge piers," *Collection of Papers Presented at the Symposium Regarding Carbonation of Concrete,* pp. 15-22, April 1993
20) Hiroshi Ueki, Naoto Masiko, Takaharu Goto, and Kazuhiro Kawaguchi, "Analysis of carbonation in practical concrete members and discussion," *Proceedings of the JCI ,* Vol. 23, No. 2, pp. 487-492, 2001
21) H. F. W. Taylor, "A method for predicting alkali ion concentrations in cement pore solutions," *Advances in Cement Research*, Vol. 1, No. 1, pp. 5-17, October 1987
22) Toshio Fukushima, Kiyotaka Kawase, Fuminori Tomozawa, and Hiroshi Akaishi, "Relevance between neutralization and carbonation of outer and inner wall concrete of existing RC buildings (influences of finish materials, water content, and phenolphthalein solution used)," *Summarized Scholarly Lectures at the Architectural Institute of Japan Convention (Tohoku Region)*, pp. 253-254, October 1982
23) Japan Society of Civil Engineers, *Standard Specifications for Concrete Structures (Maintenance)*, pp. 81-85, January 2001
24) *Chemistry of Cement Concrete and Its Applications*, Japan Cement Association, pp. 47-52, 1994

(Draft received: September 10, 2001)