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MECHANISM OF CARBONATION AND PREDICTION OF CARBONATION PROCESS OF CONCRETE

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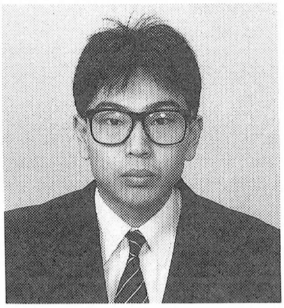
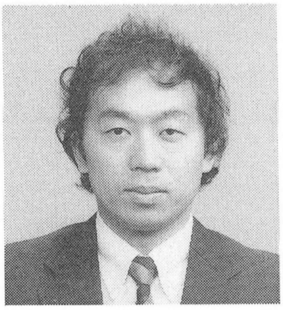

Tatsuhiko Saeki


Hiroyuki Ohga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SYNOPSIS

Accelerated carbonation test is performed to explain mechanism of carbonation of concrete. The depth of carbonation, the weight loss of mortar, the amount of calcium hydroxide and calcium carbonate, and pore volume and pore size distribution are measured. Water immersion test and air exposure test after accelerated carbonation test is also performed to evaluate the diffusion of calcium hydroxide. The depth of carbonation correlates the amount of evaporated water, and the amount of calcium hydroxide and calcium carbonate, pore volume and pore size distribution depend on exposure duration in the accelerated chamber. The depth of carbonation of mortar decreases due to the diffusion of calcium hydroxide from uncarbonated portion to carbonated portion under wetting condition. Based on these test results, the diffusion equations for water, carbon dioxide and calcium hydroxide are proposed and finite difference method is used in numerical analysis. The depth of carbonation of concrete can be predicted by analyzing these diffusion equations.

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1.INTRODUCTION

The carbonation phenomenon proposed by researchers is as follows:

1. diffusion of carbon dioxide through concrete
2. reaction between carbon dioxide (carbonic acid) and calcium hydroxide
3. decrease in pH value in concrete

Therefore, carbonation of concrete causes corrosion of the embedded reinforcement. It is very important to predict carbonation depth accurately in order to estimate of durability of reinforced concrete.

As is generally, the depth of carbonation is proportional to the square root of exposure duration:

$$x_c=b\sqrt{t} \qquad (1)$$

where Xc : depth of carbonation
t : exposure duration
b : carbonation coefficient

The carbonation coefficient is a parameter for estimating the rate of carbonation. Generally, the carbonation coefficient has been determined by experimental results, using compressive strength or water-cement ratio as parameters. However, determining carbonation coefficient requires a great deal of experiments. And in the case of outdoor and indoor exposure tests, the process of carbonation is very slow and specimen will be affected by another factors. Hence, it is very difficult to determine the carbonation coefficient experimentally.

In this study, an accelerated test is employed to investigate the carbonation mechanism of concrete. The prediction of depth of carbonation by theoretical analysis is performed.

2.EXPERIMENTAL PROGRAM

2.1 Materials and mix proportion

An ordinary portland cement, which did not contain any mineral additives such as blast-furnace slag and fly ash, was used. Fine aggregate used was standard sand with size ranges of 0.42-0.105mm, 0.840-0.149mm and 0.840-1.680mm. Three size fraction were combined together in equal amounts by weight to obtain a required gradation.

Table 1 Mix proportions of mortar.

W/C (%)	C (kg/m³)	W (kg/m³)	S (kg/m³)	S/C	Flow	Initial Curing Period in Water (days)
35	745.9	261.1	1319.4	1.77	119	28
45	648.6	291.8	1319.4	2.03	173	28, 91
55	573.6	315.5	1319.4	2.30	214	28, 91
60	542.3	325.4	1319.4	2.43	220	28
65	514.2	334.2	1319.4	2.57	241	28, 91
75	465.9	349.4	1319.4	2.83	236	28

Mortars with water-cement ratios of 35,45,55,60,65 and 75 percent were prepared. The sand-cement ratio were determined in such a way that cement paste-sand ratio by volume was equal for each mix proportion. Mix proportions of mortar are shown in Table 1.

2.2 Specimen

Specimens were 40x40x160mm prisms in accordance with JIS R5201. Immediately after initial curing, epoxy resin was coated on surfaces expect for bottom surface. Consequently, carbonation proceeded through one face.

2.3 Initial curing

All specimens were cured under wet burlap for 24hours, before demolding. The specimens were thoroughly cleaned off any grease and cured in water at a temperature of 20 C for the subsequent 27 or 90 days (see Table 1).

2.4 Test procedure

After initial curing, the specimens were transferred to a chamber to accelerate the carbonation process. The exposure condition was maintained at a temperature of 40°C, a relative humidity of 50 percent, and 7 percent by volume of carbon dioxide. Tests were carried out at various exposure durations ranging from 0 to 10 weeks depending on the rate of carbonation. A slice with about 25mm thickness was split off from specimen at each date of testing. An indicator solution was immediately sprayed on the surface of the slice. The solution used contained 1 percent phenolphtalein in 99 percent ethyl alcohol. The specimen was transferred to a chamber again after the specimen was coated by epoxy resin. Weight of a specimen was measured at the same duration using a specimen with the same mix proportion and the same initial curing as the specimen for carbonation test. The depth of carbonation of the specimen immersed in water and exposed to air was measured after exposure in the chamber for 2 and 7 weeks. The test condition of water immersion was at a temperature 20°C and that of air exposure was at a temperature 20°C, a relative humidity of 60 percent, and 0 percent by volume of carbon dioxide. The porosity of carbonated and non-carbonated portion of mortar was measured with a mercury porosimeter over the range 75-75000 Å. Amount of calcium hydroxide and calcium carbonate was measured by X-ray diffraction method. To quantify the amount of calcium hydroxide and calcium carbonate, each peak was divided by the peak of ZnO for some of the powdered specimen. Calcium hydroxide and calcium carbonate were measured by the thermogravimetry.

3.EXPERIMENTAL RESULTS AND DISCUSSION

3.1 Relationship between the depth of carbonation and water evaporation

Fig.1 shows the depth of carbonation and weight loss of specimen under accelerated condition. Calcium hydroxide (molecular weight is 74) reacts with carbon dioxide to form calcium carbonate (molecular weight is 100). Therefore, the change in weight of specimen is not caused only by evaporation of moisture. However, the amount of calcium carbonate is negligible at the beginning of carbonation process. Consequently, weight loss of specimen can be considered to be caused by the water evaporation. Carbonation process closely correlated to moisture evaporation (see Fig.1). The relationship between the depth of carbonation and water loss of specimen (moisture evaporation) is shown in Fig.2. If the water loss from specimen was equal, the depth of

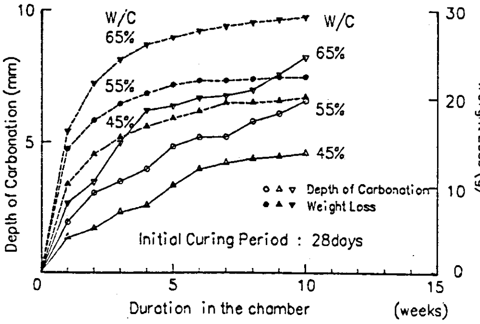

Fig.1 Depth of carbonation and weight loss.

carbonation was equal independent of water-cement ratio and initial curing period [1]. That is, rate of carbonation was determined by the diffusion characteristic of water in mortar. Because the diffusion coefficient of carbon dioxide in air (0 °C, 1 atm) and in water is 0.138 cm^2/s [2], and $1.74X10^{-5}$ cm^2/s (20°C) [3], the diffusion of carbon dioxide in water is negligible as compared with that in air. In Fig.2, the depth of carbonation of the specimen with water-cement ratio of 35 percent was larger than that with another mix proportions. This was due to that there is less space for production of calcium hydroxide because of less water-cement ratio and less calcium hydroxide produced during initial curing. Therefore little carbon dioxide can diffuse in mortar with pores saturated, and when the capillary pores of mortar are interconnected from inside to surface by water evaporation, carbon dioxide proceeds into the pores and carbonation is occurred.

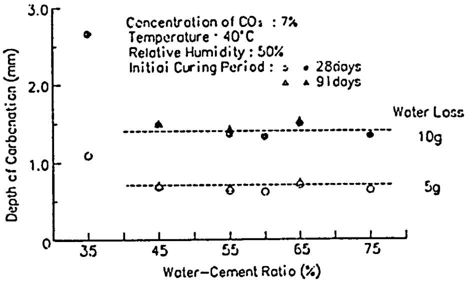

Fig. 2 Effect of evaporated water on the depth of carbonation.

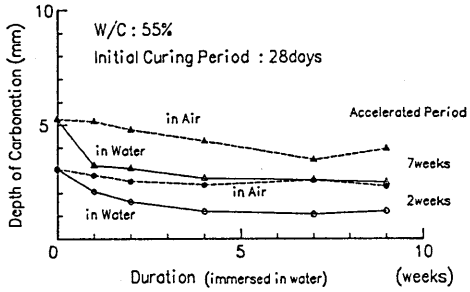

Fig. 3 Depth of carbonation of mortar immersed in water and exposed to air.

3.2 Diffusion of calcium hydroxide

Fig.3 shows changes in the depth of carbonation of mortar immersed in water or exposed to air after 2 and 7 weeks of accelerated exposure. The depth of carbonation decreased with increasing duration [1]. This was due to "counter-diffusion" of calcium hydroxide [4]. Decrease in the depth of carbonation of mortar immersed in water was larger than that exposed to air. Therefore, the counter diffusion of calcium hydroxide was accelerated by presence of water. It is reported that the rate of carbonation of concrete exposed outdoors was lower than that exposed indoors [5]. Slow rate of carbonation of concrete exposed outdoors in comparison with indoor concrete was exhibited by counter diffusion and restoration of alkaline condition. One of the reason why the retardation of carbonation was occurred in the case of mortar exposed outdoors was the restoration of alkaline content by the counter diffusion. It should be noted that other alkaline contents in pore solution, potassium hydroxide and sodium hydroxide, was neglected in this study. Calcium hydroxide represented alkaline components in pore solution.

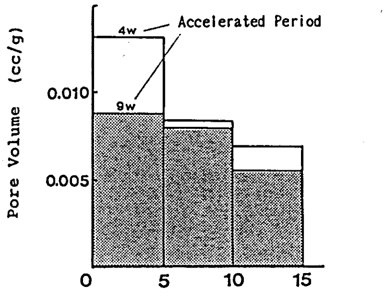

Fig. 4 Pore Volume (3 000~75 000 Å).

3.3 Change in micro-structure

Fig.4 shows the change in pore volume of mortar with radius of 3000-75000 Å under accelerated condition. Water-cement ratio of the specimen was 55 percent and initial curing period was 91 days. Pore volume was larger for the nearer layer to surface of the specimen. The carbonated mortar has low porosity because of production of calcium carbonate, and carbonation proceeds from surface to inside. Therefore, outer portion of the specimen will become denser, which is opposed to experimental results in Fig.4. This phenomenon was caused by the difference in the rate of water evaporation depending on the radius of pores. The rate of water evaporation from pore with large radius was higher than that with small radius [6]. The large pore in the layer near to surface was dried up at the first stage of accelerated test. As the carbonation reaction only took place in the presence of moisture, the carbonation reaction did not take place in the large pores (over 3000 Å) in the near layer to surface, and porosity was high as a result. In the large pores in inside layer, the carbonation reaction can be taken place. On the contrary, in the small pores near to surface, the carbonation reaction took place because of presence of more moisture under desiccating. (see Fig.5)

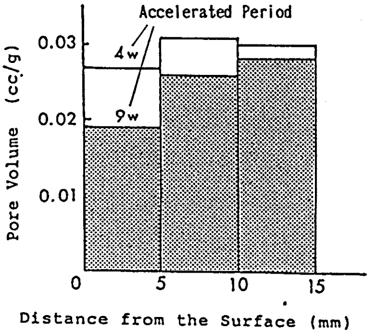

Fig.5 Pore Volume (75~750 Å).

3.4 Mechanism of carbonation

From the experimental results, the mechanism of carbonation was proposed as follows:

1. If the pores in mortar are filled with water, carbon dioxide cannot diffuse in mortar, and hence carbonation reaction do not take place.
2. When the specimen was dried, the diffusion of carbon dioxide takes place through the pores not filled with water. Carbon dioxide is dissolved into pore solution and the carbonation reaction takes place.
3. The concentration gradient formed by carbonation reaction causes the counter diffusion of calcium hydroxide from uncarbonated portion to carbonated portion of specimen.
4. The carbonation reaction do not take place when the pore solution dries out.

4.NUMERICAL ANALYSIS

4.1 Formulation of differential equations

Differential equations for diffusion were formulated in consideration of the mechanism of carbonation proposed in this study. Equations were based on diffusion of four main components in carbonation process, water, carbon dioxide, carbonic acid and calcium hydroxide.

$$\partial C_1/\partial t=\partial/\partial x(D_1\partial C_1/\partial x)+K_1C_3C_4 \quad (2)$$
$$\partial C_2/\partial t=\partial/\partial x(D_2\partial C_2/\partial x)-K_2g(C_1,\ C_2,\ C_3) \quad (3)$$
$$\partial C_3/\partial t=K_2g(C_1,\ C_2,\ C_3)-K_1C_3C_4 \quad (4)$$
$$\partial C_4/\partial t=\partial/\partial x(D_4\partial C_4/\partial x)-K_1C_3C_4 \quad (5)$$

where subscripts 1,2,3 and 4 represent water, carbon dioxide, carbonic acid and calcium carbonate.

C : concentration
D : diffusion coefficient
K_1 : the rate constant of carbonation reaction
K_2 : solubility factor of carbon dioxide
$g(C_1,C_2,C_3)$: function of C_1,C_2 and C_3

Boundary conditions are given as follows:

for x=0 (non sealed face)

$$D_1\partial C_1/\partial x=f(C_e-C_s)$$

$$C_2=C_0$$

$$\partial C_4/\partial x=0$$

where f : surface coefficient
C_e : relative humidity in atmosphere
C_s : relative humidity at surface of specimen
C_0 : concentration of carbon dioxide in atmosphere

for x=40mm (sealed face)

$$\partial C_1/\partial x=0$$

$$\partial C_2/\partial x=0$$

$$\partial C_4/\partial x=0$$

The numerical analysis used in this paper was based on following assumptions.

1. Micro-structure of mortar is uniform before exposure to the accelerated chamber.
2. The diffusion of carbonic acid is neglected.
3. The heat of carbonation reaction is neglected.
4. During the accelerated test, hydration reaction of cement was neglected.

4.2 Diffusivity of water

The diffusion coefficient, D, and the surface coefficient, f, was determined by measuring water evaporaion from specimen at the first stage of accelerated test [7]. Fig.6 shows the relationship between water-cement ratio and diffusion coefficient at a temperature of 20 °C. The relationship between water-cement ratio and surface coefficient is shown in Fig.7. Diffusion coefficients and surface coefficients increase with increasing water-cement ratio. Fig.8 shows that the relationship between pore volume (75-75000 Å) measured immediately after initial curing and diffusion coefficient. Diffusion coefficient increased with increasing pore volume exponentially. There was poor correlation between pore volume and surface coefficient.

Temperature dependence of diffusion coefficient follows Arrhenius' low as follows [8]:

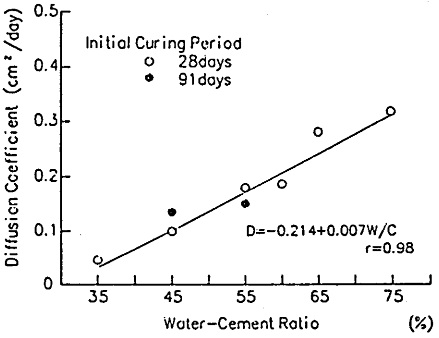

Fig.6 Effect of water-cement ratio on diffusion coefficient.

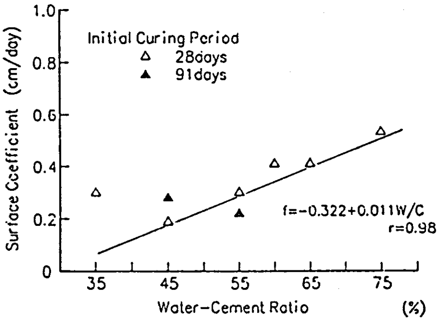

Fig.7 Effect of water-cement ratio on surface coefficient.

$$D=A\exp(-Q/RT) \qquad (6)$$

where D : diffusion coefficient
A : constant
Q : activation energy
R : gas constant
T : absolute temperature

Thus the following equation is obtained for different temperature:

$$D'=D\exp(-Q/RT'+Q/RT) \qquad (7)$$

where D' : diffusion coefficient at a temperature of T'

Q was determined by experimental results for different temperature of 20 and 40 °C. Q was 8500cal/mol·K independent of water-cement ratio. Because the above dependence of diffusion coefficient on pore volume and temperature was formulated, the diffusion coefficient of mortar under various conditions will be determined.

Diffusion of water in concrete is non linear [9][10]. The diffusion coefficient depends on concentration of water in mortar (relative humidity or rate of water content). The relationship between relative humidity and diffusion coefficient was formulated, referring to Bažant et al [10].(see Fig.9)

$90<H\le 100$	$D=D_0$
$50<H\le 90$	$D=D_0(0.002375H-1.1375)$
$H\le 50$	$D=0.05D_0$

where H : relative humidity
D_0 : diffusion coefficient for H=100

D_0 was determined by weight loss of specimen at the first stage of accelerated test.(in 4.2) The surface coefficient was assumed constant for various humidity.

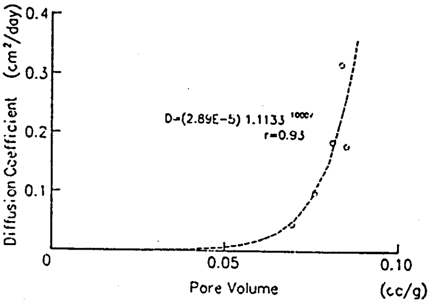

Fig. 8 Relationship between pore volume and diffusion coefficient.

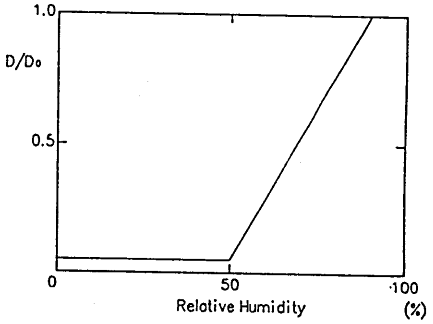

Fig. 9 Effect of relative humidity on diffusion coefficient.

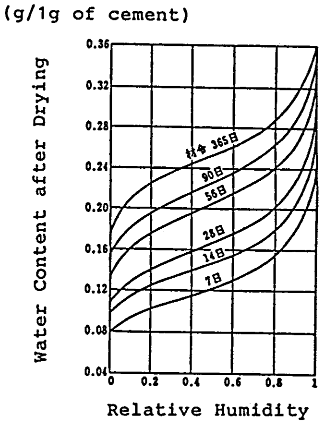

Fig. 10 Relationship between relative humidity and water content in cement paste.

As Eq.(2) is for relative humidity in order to know the amount of water in mortar, relative humidity must be translated into water content. Water content was defined as the ratio of amount of water in mortar at specified time to amount of water in saturated mortar. The relationship between relative humidity and water content was expressed as Fig.10 [11]. This relationship was explained by capillary-condensation [12]:

$$\log_{10}(P/P_s)=-2\sigma V/rRT \qquad (8)$$

where P : vapor pressure in pore

P_s : saturated vapor pressure
(P/P_s): relative humidity
σ : surface tension of water
V : molecular volume
r : pore radius
R : gas constant
T : absolute temperature

Eq.(8) means that air phase is in equilibrium with liquid phase at (P/P_s), relative humidity in pore with radius of r. Because rate of water evaporation from pores with large radius was higher than that with small radius as pointed out above. Relative humidity decreases with decreasing water content of mortar. The schematic diagram of water in pores can be seen in Fig.11. Fig.12 shows the relationship between relative humidity and water content used for numerical analysis.

for 20°C
$W \le 0.4$ $H=75W$
$0.4 < W \le 0.8$ $H=150W-30$
$0.8 < W \le 1.0$ $H=50W+50$
for 40°C
$W \le 0.4$ $H=87.5W$
$0.4 < W \le 0.75$ $H=(1100W-195)/7$
$0.75 < W \le 1.0$ $H=40W+60$

where H : relative humidity
W : water content

This relationship depends on temperature, because the pore radius which is in equilibrium with the humidity becomes smaller at higher temperature. This relationship depends also on pore size distribution, but pore size distribution measured in this study were almost same. Therefore the same relationships were used for all mix proportions.

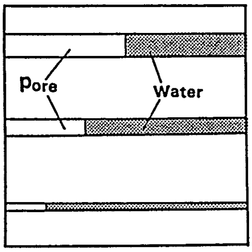

Fig. 11 Schematic diagram of water in pore.

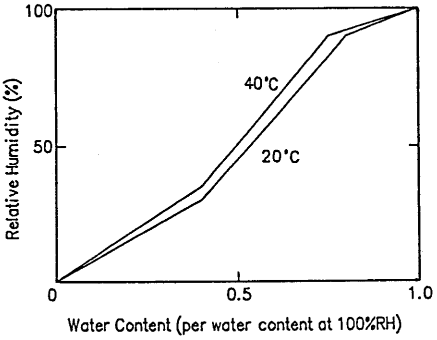

Fig. 12 Relationship between water content and relative humidity.

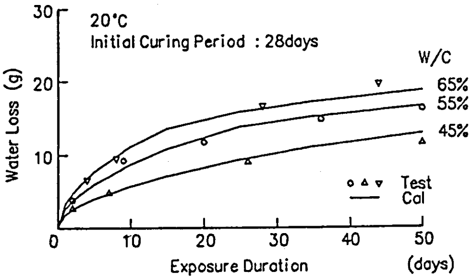

Fig. 13 Prediction of water loss.

Diffusion coefficient, surface coefficient and the relationship between relative humidity and water content determined by these above methods were used in the numerical analysis. Water loss of mortar was calculated using diffusion equation (2) by the implicit-type finite difference method because this equation was non linear. It can be observed that the calculation fitted to experimental results in Fig.13. Calculations were accurate enough to predict water loss of mortar.

4.3 Diffusivity of carbon dioxide

Kobayashi et al [13]-[15] reported that diffusion coefficient of oxygen through mortar and concrete was related exponentially to pore volume with over 10 μm in radius, and that diffusion coefficient decreased with increasing water content. As carbonation depends on extent of desiccation for mortar, the influence of water content on diffusion of carbon dioxide, should be investigated. Fig.14 shows the relationship between diffusion coefficient of oxygen and pore volume within the range 75-75000 Å of radius. The effective pore volume is defined as total pore volume subtracted by volume of water in pores. By regression analysis, this relationship could be expressed as below.

$$D=0.43(3.62\times10^{12})^V \qquad (9)$$

where D : diffusion coefficient of oxygen in mortar (cm^2/day)
V : effective pore volume (cc/cc)

As the diffusion coefficient of gases depends only on molecular weight if chemical reaction do not take place, the diffusion coefficient of oxygen is 1.3 times higher than that of carbon dioxide. Therefore, Eq.(10) was obtained.

$$D=0.33(3.62\times10^{12})^V-0.33 \qquad (10)$$

where D : diffusion coefficient of carbon dioxide
V : effective pore volume

The second term in Eq.(10) was obtained in according to the assumption that diffusion of carbon dioxide in mortar was neglected when water content was 1.0 (effective pore volume : V=0).

The dependence of diffusion coefficient of carbon dioxide on temperature is shown in Eq.(11) [3].

$$D=D_i(T/T_i)^2 \qquad (11)$$

where D : diffusion coefficient at a temperature of T
D_i : diffusion coefficient at a temperature of T_i

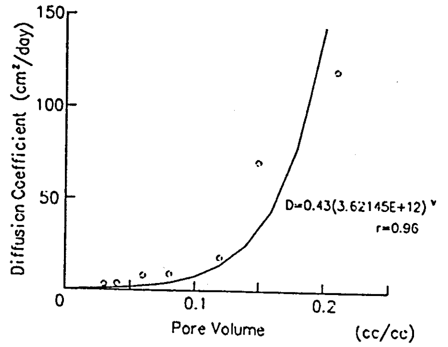

Fig. 14 Effect of pore volume on diffusion coefficient.

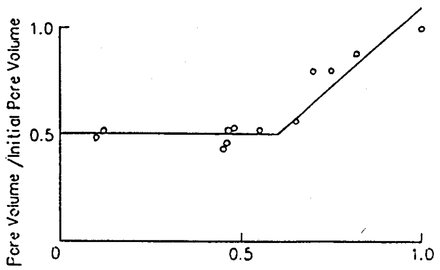

Fig. 15 Relationship between calcium hydroxide and calcium carbonate.

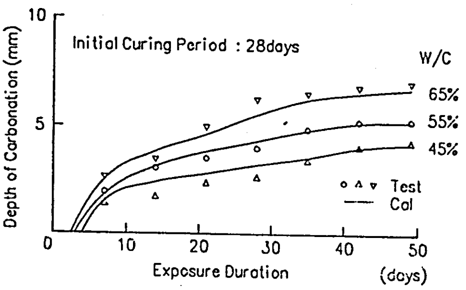

Fig. 16 Prediction of carbonation depth of mortar.

The carbonation process leads to decrease in pore volume due to the production of calcium carbonate. Therefore, the effective pore volume depends on the production of calcium carbonate. Fig.15 shows the relationship between the amount of calcium hydroxide and pore volume. Decease in calcium hydroxide is synchronized with the formation of calcium carbonate by carbonation reaction.

The relationship between calcium hydroxide and pore volume was formulated as follows by the least square method.

$$0.6 < C_4' < 1.0 \qquad V' = (C_4' - 0.1)V$$
$$C_4' <= 0.6 \qquad V' = 0.5V$$

where V : pore volume immediately after initial curing (cc/cc)
V' : pore volume after carbonation (cc/cc)
C_4' : the ratio of concentration of calcium hydroxide at specified time to the concentration immediately after initial curing.

It is important to know the amount of carbon dioxide dissolved to pore solution as carbonic acid. Henry's law was used for this problem [16].

$$P_B = KX_B \qquad (12)$$

where P_B : partial pressure of B
X_B : mole fraction of B
K : Henry's constant

In the case of carbon dioxide, K is 150 (at 20 °C 1 atm). Concentration of carbonic acid can be determined by Eq.(12) because P_B is C_2 in Eq.(3). But, in practice, Henry's law can not be applied to high pH value solution like pore solution. Henry's law is for equibrium condition. For high pH value solution, the solution can not be achieved to equibrium condition with maintaining pH value. But it is required for the analysis to determine concentration of carbonic acid. To be exact, rate equation for adsorption which is proportional to difference between partial pressure in liquid phase and in air phase must be solved. The rate of absorption is influenced by rate constant of reaction, the diffusion coefficient and fluidity of solution. Therefore, it is scarcely possible to determine the rate of absorption. In this study, it was assumed that dependence of rate of absorption on the partial pressure followed Henry's law, because rate of dissolution became larger with higher partial pressure of carbon dioxide. On the implicit-type finite difference method, dependent variable (concentration in this case) changes abruptly just after t and maintains constant value until $t+\Delta t$. Therefore, concentration of carbon dioxide in air phase will maintain a value during Δt . If the requisite time for carbon dioxide to be absorbed in pore solution is negligible in comparison with Δt, concentration of carbonic acid in liquid phase will maintain a constant value. That is, consumption of carbonic acid is compensated by carbon dioxide in air phase during Δt. Therefore, carbonation reaction is regarded as the first-order reaction depending only on concentration of calcium hydroxide in spite of the assumption in Eq.(4) and (5), which carbonation reaction is the second-order reaction. The absorption of carbon dioxide into pore solution is influenced by contact area between air phase and liquid phase. Parameter K_2 is therefore regarded as function of water content (see Fig.11). Supposed that water content is in inverse proportion to the contact area, the following equation is proposed.

$$K_2 = K_0(1-W) \qquad (13)$$

where W : water content
K_0 : solubility parameter when W=1.0.

4.4 Diffusivity of calcium hydroxide

Diffusion coefficient of calcium hydroxide was determined from water immersion test (3.2).

$$\partial C_4/\partial t = D_4 \partial^2 C_4/\partial x^2 \qquad (14)$$

Pertinent value were substituted into D_4 in Eq.(14) to fit with the test results. Eq.(14) is a linear equation because specimen is saturated and little carbon dioxide is present in water. In the analysis, carbonation front measured by phenolphtalein method was judged by concentration of calcium hydroxide, 0.00052 mol/cm^3 or peak ratio by the X-ray diffraction method, 0.6. Most of calcium hydroxide is present in mortar in solid phase and calcium hydroxide which diffuses and reacts that dissolves is in liquid phase. Exactly, D_4 is diffusion coefficient of calcium hydroxide in liquid phase. But it is very difficult to determine the solubility of calcium hydroxide to pore solution which do not contain constant component during the accelerated duration. In this study, apparent diffusion coefficient was obtained by Eq.(5) and (14) using total concentration of calcium hydroxide in mortar. D_4 value was 0.002(cm^2/day). D_4 depends on water content, W, of specimen. Therefore, D_4 was given as follows:

$$D_4 = 0.002W \qquad (15)$$

4.5 Rate of carbonation reaction

It is very difficult to determine the rate of carbonation reaction in pore solution which contains many kinds of ions. Therefore, the rate constant, K_1, was determined by substituting pertinent value for K_1 to fit with carbonation depth of accelerated specimen with a water-cement ratio 55 percent and initial curing period 28 days. As calculated condition was, $\Delta t = 0.1$ days and $\Delta x = 0.5$mm in Eq.(2)-(5). K_1 determined was 115.7cm^3/mol·s. Calculated value fitted with test results in the case of another water-cement ratio in Fig.16. Fig.17 shows calculated concentration of calcium hydroxide and calcium carbonate. Concentration of calcium hydroxide at the surface of specimen was higher than inside. This was because water required for carbonation reaction was evaporated at the surface. This phenomenon was recognized in test results of concrete [17].

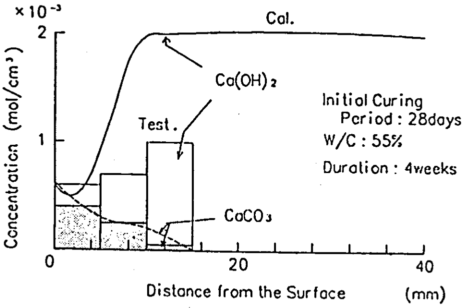

Fig.17 Calculated concentration of calcium hydroxide and calcium carbonate.

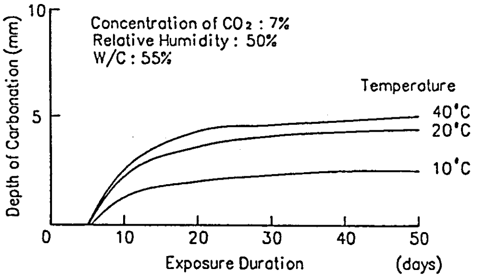

Fig.18 Effect of temperature on depth of carbonation under the condition of high concentration of carbon dioxide.

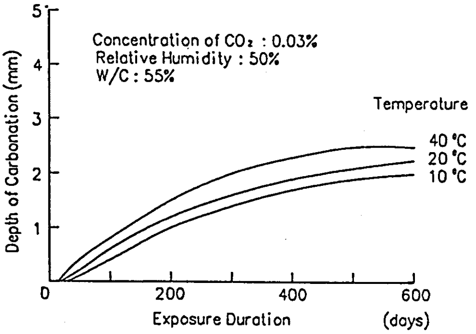

Fig.19 Effect of temperature on depth of carbonation exposed outdoors.

4.6 Simulation

Fig.18 and 19 show the influence of temperature on the rate of carbonation.

Concentration of carbon dioxide was 7 and 0.03 percent in Fig.18 and 19. Rate of carbonation was higher at higher temperature. As the degree of dependence of the rate constant on temperature was unknown, analyzed values were calculated using the same K_1 value at 40 °C. In practice, the temperature influence will be more remarkable.

Fig.20 shows the influence of concentration of carbon dioxide on the rate of carbonation. Larger depth of carbonation was observed in the case of higher content of carbon dioxide.

Fig.21 and 22 show the influence of relative humidity of environment on the depth of carbonation. Concentration of carbon dioxide was 7 and 0.03 percent in Fig.21 and 22. In Fig.22, depth of carbonation was the largest at relative humidity of 50 percent and was smaller at more or less than 50 percent of relative humidity. This phenomenon was recognized in test results [18]. Low humidity allows evaporation of most water and then halts chemical reaction. High humidity retards the diffusion of carbon dioxide through the pore network in mortar. However, the critical humidity for depth of carbonation to show maximum was about 20 percent in Fig.21. Under accelerated condition, carbonation will proceed before the specimen will dry out. Test results of accelerated test do not always show the same trend of natural exposure test. Under the "distorted" condition such as accelerated test, exact result can not be attained when the environment influence on carbonation was estimated experimentally.

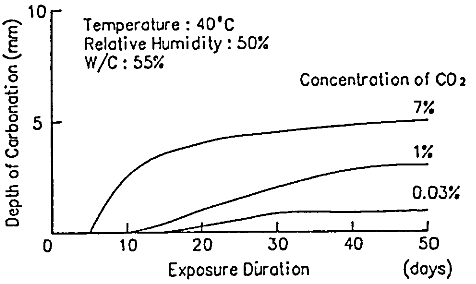

Fig. 20 Effect of concentration of carbon dioxide on depth of carbonation.

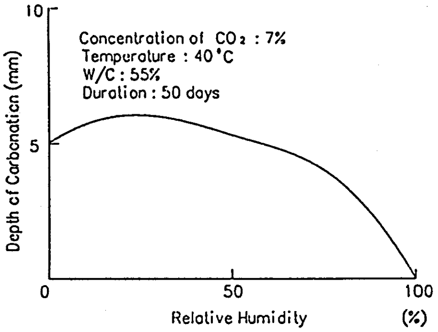

Fig. 21 Relationship between relative humidity and depth of carbonation under the condition of high concentration of carbon dioxide.

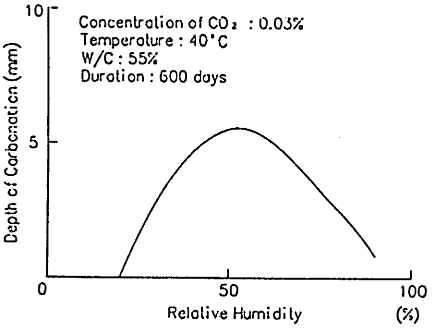

Fig. 22 Relationship between relative humidity and depth of carbonation exposed outdoors.

5.CONCLUSION

The following conclusions can be obtained from this study:

1. The rate of carbonation increases with increasing water evaporation from specimen. If the amounts of water evaporation is equal, the depths of carbonation show the same independent of water-cement ratio and initial curing period.

2. The carbonation reaction takes place only in the presence of moisture. The change in pore volume takes place due to change in volume of pores in specific range of pore radius because the rate of water evaporation from pores with large radius is higher than that from small pores.

3. The diffusion of calcium hydroxide takes place in the presence of water, and then restoration of alkaline condition is shown in carbonated portion.

4. The depth of carbonation can be predicted in consideration of diffusion of water, carbon dioxide and calcium hydroxide. The influence of environmental conditions on the rate of carbonation can be estimated by the numerical analysis proposed.

5. The test results of accelerated test do not always show the same trend of natural exposure test.

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Reference

[1] T.Saeki, H.Ohga, S.Nagataki, "Mechanism of carbonation of concrete", Proceeding of the Japan Concrete Institute, Vol.11, June. 1989
[2] National Astronomical Observatory, "Rika nenpyo (Chronological scientific tables)", Maruzen Co.,Ltd., 1971
[3] K.Sato, "Inference method of physical properties constants", Maruzen Co.,Ltd., 1982
[4] T.Fukushima, "Predictive method on the progress neutralization (carbonation) of concrete by unsteady state dynamic analysis", Review of the 42nd General Meeting, Tokyo, May. 1988
[5] S.Nagataki, H.Ohga, "Study on the carbonation of concrete with fly ash and the corrosion of reinforcement in long-term test (part 3)", Technical report No.38, Department of Civil Engineering Tokyo Institute of Technology, Dec. 1987
[6] A.Yonekura, "Study on the properties and mechanism of drying shrinkage and creep of high strength concrete", Doctoral thesis of Tokyo Institute of Technology, 1980
[7] K.Okada, M.kawamura, "Some considerations on drying shrinkage stress of soil-cement", Proceedings of JSCE, No.142, June. 1967
[8] P.G.Shewmon, "Diffusion in solid", Corona Co.,Ltd., 1980
[9] K.Sakata, O.Kuramoto, "A study on the water diffusion and shrinkage in concrete by drying", Proceedings of JSCE, No.316, Dec. 1981
[10] Z.P.Bažant, L.J.Najjer, "Nonlinear water diffusion in nonsaturated concrete", Materiaux et Costructions, No.25, Vol.5, 1972
[11] K.Iwasaki, "Properties of concrete", Kyoritu Shuppan Co.,Ltd., 1979
[12] Editors' of committee of ENCYCLOPAEDIA CHIMICA, "ENCYCLOPAEDIA CHIMICA", Kyoritu shuppan Co.,Ltd., 1967
[13] K.Kobayashi, K.Shutto, K.Tsuji, K.Ogawa, "Diffusivity of oxygen ion and chlorine ion through cementious materials", JCI 8th Conference, June. 1986
[14] K.Kobayashi, K.Shutto, "Study on the diffusivity of oxygen gas through various cementious materials", Concrete Journal, No.12, Vol.24, 1986
[15] K.Shutto, "Study on the diffusivity of oxygen gas through cementious materials", Special report of the technical research institute of Maeda Construction Co.,Ltd., No.29-1, 1988

[16] W.J. Moore, "New physical chemistry", Tokyo Kagaku Dojin Co.,Ltd., 1970
[17] E.K.Kim, "Study on the carbonation of concrete with fly ash", Master's thesis of Tokyo Institute of Technology, 1986
[18] H.J.Wierig, "Long-time studies on the carbonation of concrete under normal exposure", RILEM Seminar Durability of Concrete Structure under Normal Outdoor Exposure, 1984