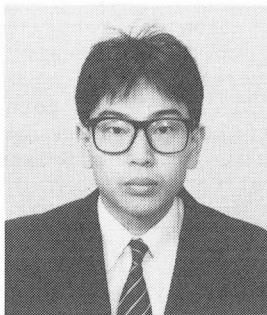


CHANGE IN MICRO-STRUCTURE OF CONCRETE DUE TO CARBONATION

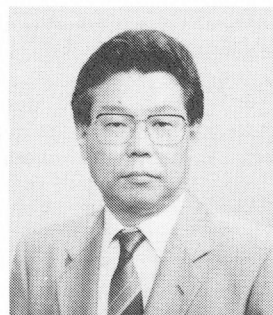
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SYNOPSIS

Micro-structure of concrete is changed due to carbonation and the change in micro-structure affects properties of concrete. An accelerated carbonation test and a wet-dry test are performed to investigate the change in micro-structure of mortar considering water-cement ratio and initial curing condition. The depth of carbonation, the amount of calcium hydroxide and calcium carbonate, pore volume, pore size distribution, and the weight of mortar are measured.

The change in pore volume and pore size distribution due to carbonation depends on water-cement ratio and initial curing period. Pore volume in the carbonated portion is decreased in the case of the continuous carbonation test. Denseness of structure induced by carbonation affects a subsequent carbonation process.

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1. INTRODUCTION

The pH value in concrete is decreased due to carbonation process. When the depth of carbonation reaches the embedded reinforcements, corrosion of the reinforcement will be occurred. It has been suggested that the rate of carbonation depends on the diffusivity of carbon dioxide in concrete [1]. Therefore, the rate of carbonation is influenced by the micro-structure of concrete. The carbonation process leads to decrease of pore volume and change in the shape of pore size distribution due to production of calcium carbonate.

The change in micro-structure of concrete due to carbonation was recognized by experimental study [2][3]. This prompts the description that diffusivity of substances in concrete and physical properties of concrete (e.g. compressive strength) are changed due to carbonation. In general, the volume of pore with hundreds Å in radius is increased due to carbonation. On the other hand, decrease of pore volume was recognized by Kroone and Crook's [4], Kondo, Daimon and Akiba's experimental results [5] under high concentration of carbon dioxide condition, and pore volume was increased due to carbonation by Tsukayama's results [6] under outdoor exposure. These researchers did not give any reason for increase or decrease in pore volume due to carbonation. As carbonation proceeds from surface into internal portion of concrete, micro-structure is changed continuously from surface into internal portion. Early researchers did not give any information for this point.

In this study, an accelerated test and wet-dry test are employed to investigate change in micro-structure of concrete due to carbonation. The relationship between micro-structure and the amount of calcium hydroxide, calcium carbonate was investigated. The effect of change in micro-structure on the rate of carbonation is also studied.

2. EXPERIMENTAL PROGRAM

2.1 Materials and mix proportion

An ordinary portland cement, which did not contain any mineral admixture such as blast-furnace slag and fly ash, was used. Chemical composition of cement is shown in Table 1. Fine aggregate used was standard sand with size ranges of 0.42-0.105mm, 0.84-0.149mm and 0.84-1.68mm. These sands were combined together in equal amounts by weight to obtain a required gradation.

Mortars with water-cement ratios of 45, 55 and 65 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 2.

2.2 Specimen

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

2.3 Initial curing condition

All specimen were cured under wet burlap for 24hours, before demolding. The

specimens were thoroughly cleaned of any grease and cured in water at a temperature of 20 °C for the subsequent 27 or 90 days (see Table 2).

Table 1 Chemical composition of cement (wt%).

lg. loss	insol.	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	HgO	SO ₃	Na ₂ O	K ₂ O
0.7	0.1	21.8	5.0	2.9	63.9	1.7	2.3	0.26	0.67

Table 2 Mix proportion of mortar.

W/C (%)	C (kg/m ³)	W (kg/m ³)	S (kg/m ³)	S/C	flow
4 5	648.6	291.8	1319.4	2.03	173
5 5	573.6	315.5	1319.4	2.30	214
6 5	514.2	334.2	1319.4	2.57	241

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 a various exposure durations ranging from 1 to 10 weeks. 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 phenolphthalein in 99 percent ethyl alcohol. The specimen was transferred to the chamber again after the specimen was coated by epoxy resin. A wet-dry test was performed to estimate the carbonation process under outdoor exposure. The specimen accelerated in the chamber for 1 week was soaked in the water for 1 week at a temperature of 20 °C. The wet condition (in water) and dry condition (in acceleration chamber) were performed by turns. The test conditions are shown in Fig.1. Weight of a specimen was measured at the same duration of measuring a depth of carbonation using a specimen with the same mix proportion and the same initial curing as the specimen for carbonation test. The porosity of carbonated and uncarbonated portion of mortar was measured with a mercury porosimeter over the range 30-3500000 Å in diameter. Amount of calcium hydroxide and calcium carbonate were measured by the thermogravimetry. For accelerated test, materials for analysis were gathered from three layers, 0-5, 5-10 and 10-15mm of distance from surface (non-sealed face) of the specimen. For wet-dry test, materials were gathered from three layers, 0-carbonation front judged by phenolphthalein method,

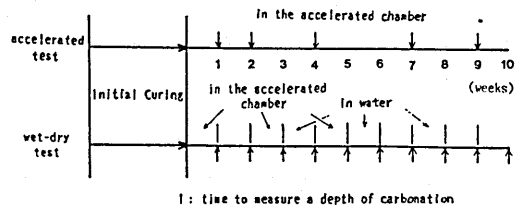


Fig. 1 Test condition.

carbonation front-carbonation front+5mm and carbonation front+5-10mm.

3.EXPERIMENTAL RESULTS AND DISCUSSIONS

3.1 Depth of carbonation under accelerated condition and wet-dry condition

Fig.2 shows the depth of carbonation under the continuous accelerated and the wet-dry conditions. In the case of the wet-dry condition, the elapsed duration do not contain the time immersed in water. The depth of carbonation under the wet-dry condition was smaller than that under the continuous accelerated condition. This result was similar to the relationship between outdoor exposure test and indoor exposure test [7]. Under the wet-dry test, low diffusivity of carbon dioxide due to presence of water in pore and diffusion of alkaline ions from uncarbonated layer to carbonated layer may restrain the process of carbonation [8].

3.2 Change in micro-structure due to accelerated test.

Fig.3 shows the change in pore volume with elapsed time under the accelerated condition. Water-cement ratio of specimen was 55 percent and initial curing period was 91 days. The pore volume of any layers was decreased due to carbonation. The lower porosity was observed for nearer layer to the surface because of production of calcium carbonate [9]. In uncarbonated layer judged by phenolphthalein method, pore volume was decreased. The fact that carbonation reaction took place in the uncarbonated layer judged by phenolphthalein method has been pointed out by observing production of calcium carbonate [10]. Although change in pore volume can be taken place through progress of hydration, pore volume may be decreased only by carbonation, because initial curing period was 91 days and low relative humidity was kept under continuous accelerated condition. This phenomenon was confirmed by Kroone and Crook, and Kondo, Daimon and Akiba.

Fig.4 shows that pore size distribution of mortar immediately after initial curing. Pore size distribution of mortar under accelerated condition is shown in Fig.5 (accelerated duration is 5 and 9 weeks). The volume of pore with small

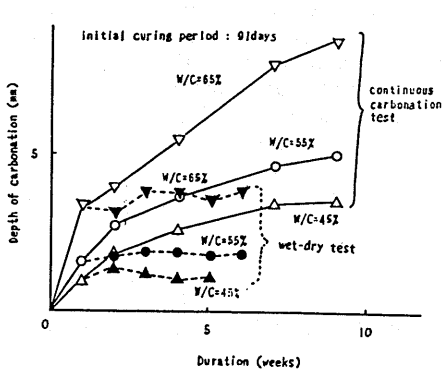


Fig. 2 Increase of carbonation depth with elapsed time under accelerated condition.

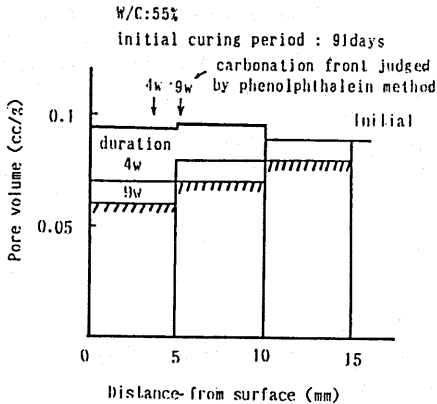
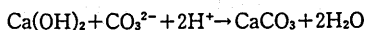
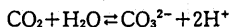


Fig. 3 Change in pore volume with elapsed time.

diameter was increased by carbonation. The volume of pore with the diameter about 100 Å was decreased in nearer layer to surface during accelerated test. On the other hand, the volume of pore with the diameter 10^5 – 10^6 Å was increased in nearer layer. These reason can be described as follows:
Carbonation reaction requires the presence of water as shown in the following reactions.



However, water evaporation takes place in carbonation process [11]. Therefore, the carbonation reaction does not take place in the dried pores. The rate of water evaporation from the pore with large diameter was higher than that with small diameter [12]. The large pore in the layer near to surface of specimen was dried up at the first stage of carbonation process. The shapes of pore size distribution depended on the distance from surface. When accelerated duration was 4 weeks, pore volume in the layer with distance from surface of 10–15mm was not changed in comparison with that of immediately after initial curing. (see Fig.3) Pore size distribution in this layer was changed with elapsed time. (see Fig.4,5) In carbonation process, micro-structure may be looser and denser simultaneously. Looser porosity was caused by dissolution of calcium hydroxide [13]. Calcium hydroxide, that is a one of main hydration product of cement, has low solubility and exists in solid phase. When the concentration of calcium ion in pore solution is dropped due to carbonation

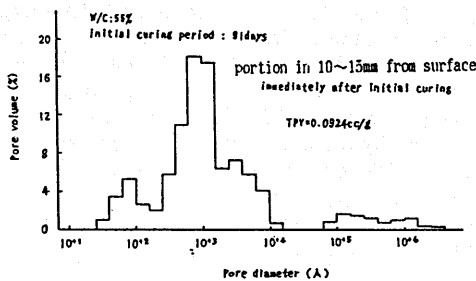


Fig. 4 Pore size distribution of mortar immediately after initial curing.

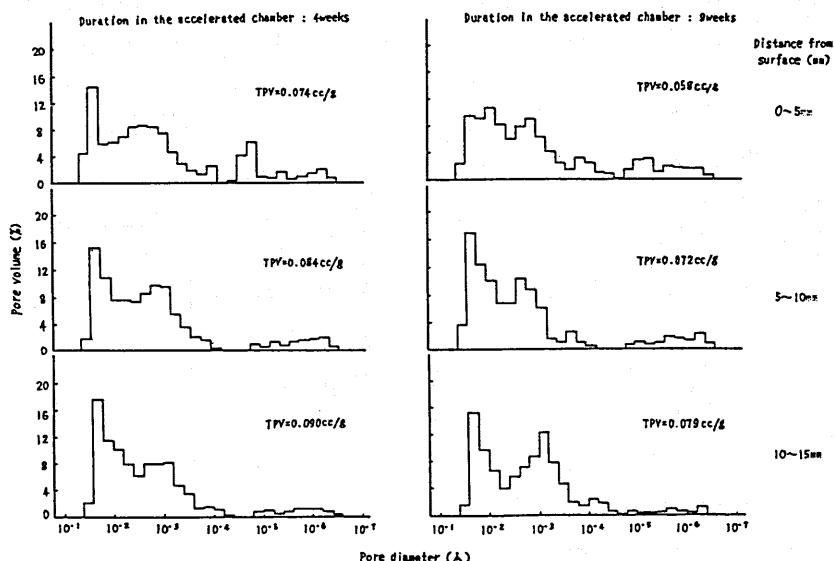


Fig. 5 Pore size distribution of mortar under the accelerated condition (initial curing period in water: 91 days).

reaction, calcium hydroxide in solid phase dissolves in pore solution [11][14]. The concentration of calcium hydroxide in the layer near to surface is lower than inside layer. Hence, there is concentration gradient in the specimen and calcium ion diffuses to surface. Amount of calcium hydroxide and calcium carbonate measured by thermogravimetry is shown in Fig.6. In the layer with the distance from surface of 10-15mm, the amount of calcium carbonate was not increased, but the amount of calcium hydroxide was decreased because calcium hydroxide was diffused to carbonated layer during 4 to 9 weeks in accelerated duration. In 0-5mm from surface, pore volume with diameter of about 60 Å was decreased because of water evaporation in large pore during 4 to 9weeks. (see Fig.5) In layers of 5-10 and 10-15mm, pore size distribution was not changed because water is present in pores with all range of diameter. Same results were observed in the case of 45 and 65 percent on water-cement ratio.

Fig.7 shows the change in pore volume under accelerated condition. Water-cement ratio of specimen was 55 percent and initial curing period was 28 days. The pore volume in the layer of 0-5mm was higher than that in the layer of 10-15mm from the surface when accelerated duration was 4 weeks. At 9 weeks, the pore volume in the layer of 10-15mm was increased in comparison with that at 4 weeks. This reason was as follows. The porosity of mortar with the initial curing period of 28 days was higher than that of 91-day curing specimen. Hence, carbonation rate of specimen with the initial curing period of 28 days was higher than that of 91-day curing specimen [8]. Carbonation reaction takes place actively in 0-5mm layer. Calcium hydroxide in solid phase in 5-10mm layer dissolves in pore solution and diffuses to 0-5mm layer. During 4 to 9 weeks, carbonation reaction takes place actively in 5-10mm, so, calcium hydroxide in 10-15mm layer dissolves and diffuses. As the result, pore volume was increased. The experimental result prompts that pore volume can be increased due to carbonation.

Fig.8 shows the pore size distribution of mortar. Initial curing period of specimen was 28 days and accelerated duration was 4 and 9 weeks. Pore size distribution accelerated for 4 weeks was similar to that for 9 weeks with initial curing period of 91 days. (see Fig.5) Because the carbonation rate of the specimen with initial curing period of 28 days was higher than that of 91 days. At 4 weeks of accelerated duration, pore with the range of 10^3 - 10^5 Å was banished in the layer of 10-15mm. The presence of water in large pore caused

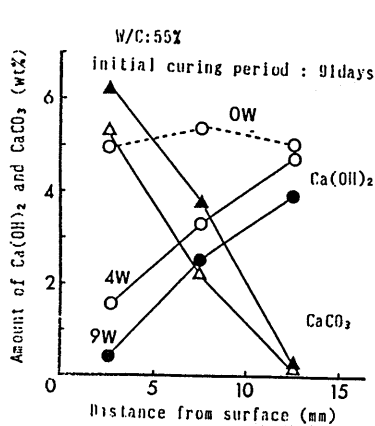


Fig. 6 Change in amount of calcium hydroxide and calcium carbonate due to carbonation.

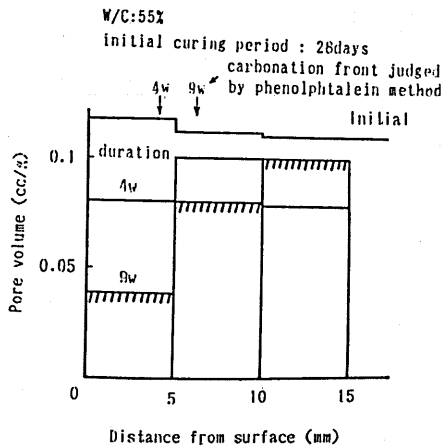


Fig. 7 Change in pore volume with elapsed time.

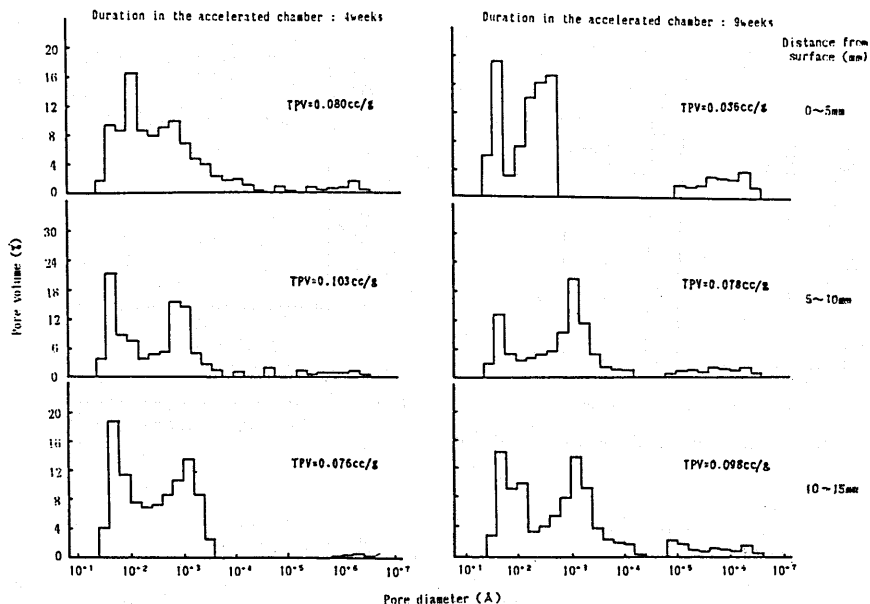


Fig. 8 Pore size distribution of mortar under the accelerated condition (initial curing period in water : 28 days).

this result due to carbonation reaction because water evaporation did not occurs in comparative large pores in internal layer. In 0-5mm layer, the ratio of pore volume with the diameter below 10^3 Å to the total pore volume was increased during 4 to 9 weeks and pore with the range of 10^3 - 10^5 Å was banished. The pore volume with the diameter over 10^5 Å was not changed, so the ratio was increased. In the pore with the diameter over 10^5 Å, carbonation reaction was occurred due to carbonation reaction. On the other hand, carbonation reaction took place under the presence of water in the pore with the diameter of below 10^5 Å. In 10-15mm layer, the pore volume with the range 5000 - 10^6 Å was increased. This result may be brought about by dissolution and diffusion of calcium hydroxide.

3.3 Change in micro-structure due to wet-dry test

The depth of carbonation had been hardly developed after 1 week of test duration under wet-dry test. (see Fig.2) The depth of carbonation was 1.6mm with the water-cement ratio of 55 percent and initial curing period of 91 days. Therefore, the layers of 0-1.6mm, 1.6-6.6mm and 6.6-11.6mm from the surface were defined as carbonated layer, uncarbonated layer 1 and uncarbonated layer 2 respectively. Similarly, the layer of 0-3.5mm, 3.5-8.5mm and 8.5-13.5mm from the surface were defined as carbonated layer, uncarbonated layer 1 and uncarbonated layer 2 in the case of water-cement ratio of 65 percent. Samples for thermogravimetry were obtained from these three layers. Fig.9 shows the pore volume of specimen under wet-dry condition at the accelerated duration of 0 and 5 weeks. In the case of water-cement ratio of 55 percent, pore volume was hardly changed for all layers. For 65 percent, pore volume of carbonated layer was increased in comparison with that immediately after initial curing and that in other layers. This result was similar to Tsukayama's study. This reason was as follows.

1. The depth of carbonation was hardly developed.
2. Calcium hydroxide diffused to water for specimen during immersion.
3. Calcium hydrogen carbonate diffused to water.

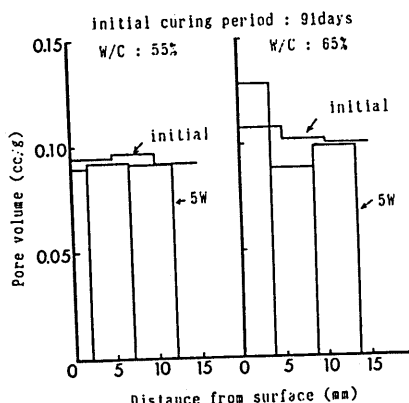


Fig. 9 Pore volume of mortar under wet-dry condition.

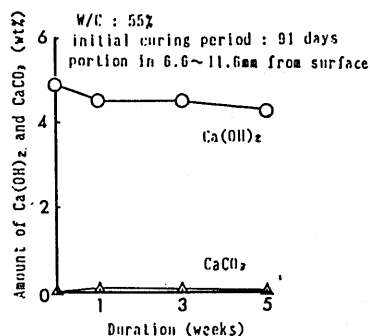


Fig. 11 Change in the amount of calcium hydroxide and calcium carbonate under wet-dry condition.

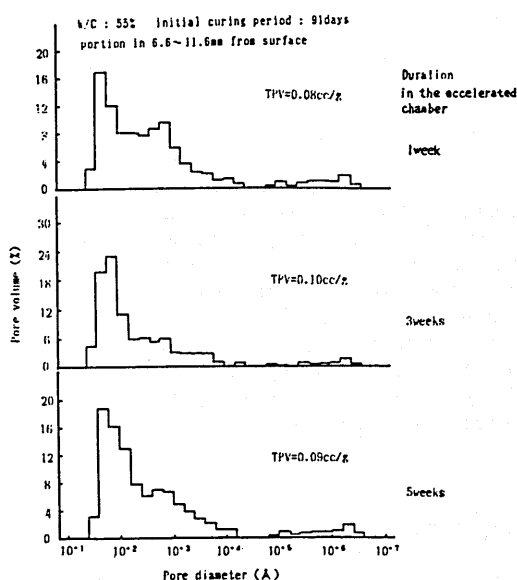


Fig. 10 Pore size distribution of mortar under wet-dry condition.

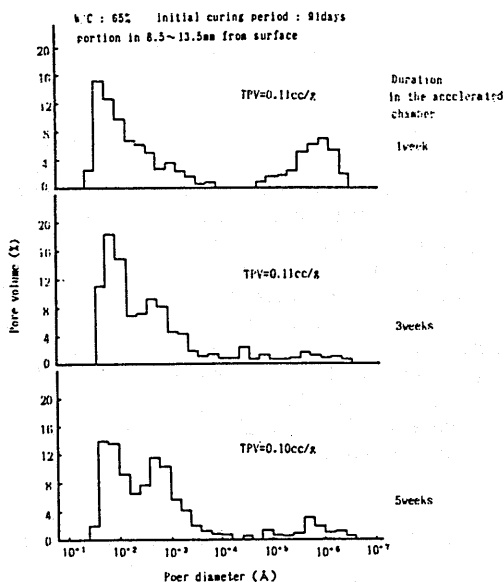


Fig. 12 Pore size distribution of mortar under wet-dry condition.

Calcium carbonate and carbonic acid reacts to be calcium hydrogen carbonate and calcium hydrogen carbonate possesses high solubility. Therefore, calcium hydrogen carbonate dissolves to pore solution [15] and diffuses to water for specimen immersed. Decrease in calcium carbonate during immersing in water was measured by thermogravimetry. Fig.10 shows the pore size distribution in uncarbonated layer 2 (6.6-11.6mm from surface) under wet-dry condition. Water-cement ratio of specimen was 55 percent and initial curing period was 91 days. Pore volume was hardly changed. On the contrary, pore size distribution was changed in comparison with that immediately after initial curing (see Fig.4) and shape of pore size distribution was typical shape of carbonated specimen, that is, pore volume with the diameter of about 1000 Å was decreased and of about 100.

Å was increased. Therefore, carbonation reaction was taken place in this layer. Fig.11 shows the amount of calcium hydroxide and calcium carbonate in uncarbonated layer 2 under wet-dry condition. The amount of calcium carbonate was small and was hardly changed during wet-dry test. The amount of calcium hydroxide was decreased with elapsed time. Calcium hydroxide may diffuse to carbonated layer. Fig.12 shows the pore size distribution in uncarbonated layer 2 (8.5-13.5mm from surface) under wet-dry condition. Water-cement ratio of specimen was 65 percent and initial curing period was 91 days. Pore volume with the diameter of about 10^0 Å was remained due to water evaporation in the pore with this range when the test duration was 1 week. After that, these pore was decreased due to water supply under wet condition. The pore volume with the diameter of about 1000 Å was increased during 1 to 5 weeks. During 1 to 3 weeks, this results may be explained by the fact that the pore with diameter of about 10^0 Å shifted to about 10^3 Å. During 3 to 5 weeks, that was not explained by this reason. Therefore, calcium hydroxide in solid phase dissolves to pore solution and micro-structure became porous. Fig.13 shows the amount of calcium hydroxide and calcium carbonate in uncarbonated layer 2 under wet-dry condition. The amount of calcium hydroxide was decreased with elapsed time. The amount of calcium carbonate was hardly increased; decrease in calcium carbonate was caused by diffusion to carbonated layer. This result was not observed under continuous accelerated test. Therefore, diffusion of calcium hydroxide requires presence of water.

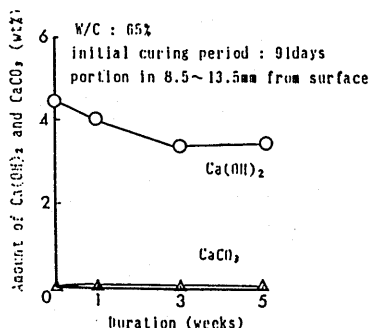


Fig. 13 Change in the amount of calcium hydroxide and calcium carbonate under wet-dry condition.

3.4 Weight of specimen under wet-dry condition

In this study, weight of specimen at the end of a dry period and a wet period was measured. Weight change was defined as water loss and water gain. In carbonation process, weight of specimen can be increased due to production of calcium carbonate. But, the amount of calcium carbonate was small in wet-dry test, so influence of calcium carbonate was negligible. (see Fig.6,11,13) Fig.14 shows the weight loss of specimen (that is the amount of water evaporation) under a dry condition. For the specimen with the water-cement ratios of 45 and 55 percent, weight loss was decreased gradually. On the other hand, in the case of water-cement ratio of 65 percent, weight loss was increased until 5 cycles. Fig.15 shows the weight gain (that is the amount of water absorption) under a wet condition. For water-cement ratios of 45 and 55 percent, weight gain was hardly changed. For 65 percent, weight gain was increased. This difference was attributed to the difference of pore size distribution. The rate of water evaporation of large pore is higher than that of small pore in porous medium [12]. And the rate of water absorption shows same trend [16]. Pore size distribution was shifted to small size due to carbonation for water-cement ratios of 45 and 55 percent. (see Fig.10) For water-cement ratio of 65 percent, pore volume with the diameter of about 1000 Å was increased and that with the diameter about 100 Å was decreased during wet-dry test. (see Fig.12)

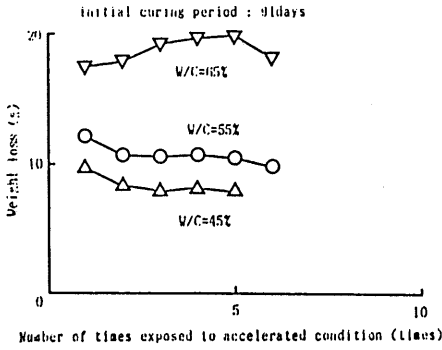


Fig. 14 Weight loss of mortar under accelerated condition.

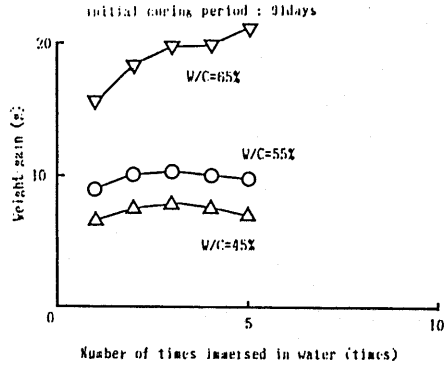


Fig. 15 Weight gain of mortar under wetting condition.

3.5 Influence of change in micro-structure due to carbonation on the rate of carbonation

In this study, numerical analysis was performed to investigate the influence of change in micro-structure due to carbonation on the rate of carbonation. Differential equations for diffusion were formulated in consideration of the mechanism of carbonation. Equations were based on diffusion of four main components, water, carbon dioxide, carbonic acid and calcium hydroxide in carbonation process [17].

$$\frac{\partial C_1}{\partial t} = \frac{\partial}{\partial x} (D_1 \frac{\partial C_1}{\partial x}) + K_1 C_3 C_4 \dots\dots\dots (1)$$

$$\frac{\partial C_2}{\partial t} = \frac{\partial}{\partial x} (D_2 \frac{\partial C_2}{\partial x}) - K_2 g(C_1, C_2, C_3) \dots\dots\dots (2)$$

$$\frac{\partial C_3}{\partial t} = K_2 g(C_1, C_2, C_3) - K_1 C_3 C_4 \dots\dots\dots (3)$$

$$\frac{\partial C_4}{\partial t} = \frac{\partial}{\partial x} (D_4 \frac{\partial C_4}{\partial x}) - K_1 C_3 C_4 \dots\dots\dots (4)$$

where subscripts 1, 2, 3 and 4 represented water, carbon dioxide, carbonic acid and calcium hydroxide.

- 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

Diffusion coefficient of carbon dioxide D_2 in Eq(2) depended on pore volume. Therefore, D_2 was changed due to production of calcium carbonate.

$$D_2 = 0.33(3.62 \times 10^{12})^V - 0.33$$

where V : pore volume

Fig.16 shows the relationship between the amount of calcium hydroxide and pore volume. Decrease in calcium hydroxide was synchronized with the formation of calcium carbonate under continuous accelerated condition. The relationship between the amount of calcium hydroxide and pore volume was formulated as follows.

$$\begin{aligned} 0.6 < C_4' &\leq 1.0 & V' &= (C_4' - 0.1)V \\ C_4' &\leq 0.6 & V' &= 0.5V \end{aligned}$$

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

Fig.17 shows the depth of carbonation with elapsed time under continuous accelerated condition. A continuous line indicates real carbonation process, that is the phenomenon that micro-structure is changed due to carbonation. A dotted line indicates the case supposing that micro-structure is not changed due to carbonation. The change in micro-structure due to carbonation controls the subsequent progress of carbonation.

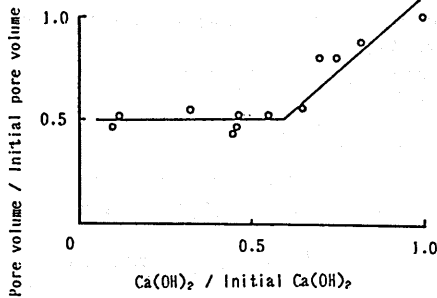


Fig. 16 Relationship between calcium hydroxide and pore volume.

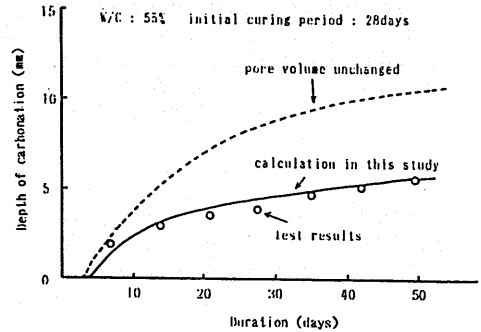


Fig. 17 Effect of pore volume change on depth of carbonation.

4.CONCLUSION

The following conclusions can be obtained from this study:

1. Micro-structure, such as pore volume and pore size distribution, of mortar is changed due to carbonation.
2. Pore volume of mortar is decreased under continuous carbonation test. Pore size distribution is shifted to small size and pore volume with the diameter of about 100 Å pore increased.
3. Pore volume of mortar is hardly changed or increased under wet-dry carbonation condition. This reasons are as follows: Depth of carbonation is hardly developed. Calcium hydroxide in solid phase dissolves to pore solution. Calcium hydrogen carbonate is produced and dissolves.
4. In the case of high water-cement ratio, pore volume with the diameter of about 1000 Å is increased under wet-dry carbonation test.
5. The rate of water evaporation and water absorption is decreased due to change in pore size distribution for low water-cement ratio and is increased for high water-cement ratio.
6. Change in micro-structure due to carbonation controls the subsequent progress of carbonation.

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