

## **EFFECT OF CARBONATION ON CHLORIDE PENETRATION IN CONCRETE**

Tatsuhiko SAEKI

Dept. of Civil Engineering and Architecture, Faculty of Engineering, Niigata University,  
8050, Ikarashi 2-no-cho, Niigata 950-2181, Japan

### **Abstract**

When chloride ions ingress and carbonation take place simultaneously in concrete, chloride ions that have been fixed in cement hydrates will be unfixed and become soluble due to the deterioration of cement hydrates caused by carbonation. It has been observed that chloride ions concentrate in the region where carbonation has not occurred. Therefore, for concrete subjected to both chloride ions ingress and carbonation the corrosion of steel bars in it may take place at an early stage and the rate of corrosion may also increase.

Therefore, when chloride ions ingress and carbonation are co-existed the prediction of the distribution of chloride ions in concrete is essential to the evaluation of concrete durability.

This study is aimed to estimate the effect of carbonation on chloride penetration in concrete through an investigation into the immobilization of chloride ions in cement hydrates and the release of them when alteration of cement hydrates occurs due to carbonation. The available potential for hydrates to immobilize chloride ions and the carbonation-induced release of chloride ions is determined using artificially synthesized cement hydrates, which are immersed in an artificial pore solution. Based on these above experiments, a model characterizing the process of immobilization and release of chloride ions is established and its validity is verified by comparing calculated data with data from tests on cement paste and mortar specimens. The effect of change in micro-structure due to carbonation on chloride penetration was also evaluated in this study.

### **1. Introduction**

Chloride ions ingress and carbonation, which start from concrete surface and progress toward internal concrete, can both lead to accelerated corrosion of steel bars in concrete. When chloride ions ingress and carbonation take place simultaneously in concrete,

chloride ions that have been fixed in cement hydrates will be unfixed and become soluble due to the deterioration of cement hydrates caused by carbonation. It has been observed that chloride ions concentrate in the region where carbonation has not occurred [1]. Therefore, for concrete subjected to both chloride ions ingress and carbonation the corrosion of steel bars in it may take place at an early stage and the rate of corrosion may also increase [2].

Studies on the prediction of the deterioration of concrete due to the individual effect of chloride ions ingress or carbonation have been widely carried out [3], but as far as the compound effect of chloride ions ingress and carbonation that may greatly accelerate the corrosion of steel bar in concrete, no much attention has been paid and no detailed information can be referenced.

Therefore, when chloride ions ingress and carbonation are co-existed the prediction of the distribution of chloride ions in concrete is essential to the quantitative evaluation of concrete durability.

For the establishment of a model in consideration of both chloride ions ingress and carbonation, models for describing various reactions that are closely related to concrete deterioration have been developed at first in this study. The models used for confirmation were those for the prediction of carbonation depth and penetration depth of chloride ions in concrete. In addition, changes in micro-structure of hardened cementitious materials due to carbonation were investigated in order to clarify the effect on chloride penetration.

## **2. Mechanism of concrete deterioration due to chloride ions ingress and carbonation and models used for confirmation**

According to Kobayashi's viewpoint the mechanism of concrete degradation due to chloride ions ingress and carbonation is as follows [1]: (1) generation of Friedel's salt due to the reaction of monosulphate (AFm) with chloride ions; (2) carbonation of Friedel's salt; (3) dissolution of chloride ions into pore solution that have been immobilized in Friedel's salt and (4) increase in the concentration of chloride ions in pore solution, resulting in the further ingress of chloride ions into the internal part of concrete caused by concentrating and diffusion cycles. Hence, in the establishment of the prediction model for deterioration of concrete due to the compound effect of chloride ions ingress and carbonation following models are needed: (1) a model of cement hydration, i.e. the formation model of AFm phase; (2) a model for describing the fixation of chloride ions in AFm phase, i.e. the formation model of Friedel's salt; (3) models applied to characterize the carbonation of Friedel's salt and the release of chloride ions from carbonated Friedel's salt and (4) model for expressing the carbonation of AFm. By combining above models with the models for predicting carbonation progress in concrete [4][5] and chloride penetration in concrete [6][7] that have been developed by the authors, a model used for predicting concrete deterioration due to the compound effect of chloride ions ingress and carbonation has been made.

### 3. Models of the fixation and release of chloride ions

#### 3.1 Experimental

The main purpose of this experiment is to observe the fixation effect of AFm on chloride ions and the release of chloride ions due to carbonation occurred. AFm used in the experiment was synthesized using chemical agents.

##### 3.1.1 Synthesis of AFm

Analytically pure  $\text{Ca(OH)}_2$  was previously mixed with chemically active and finely ground  $\text{Al}_2\text{O}_3$  in the presence of a little water, then dried at  $105\pm 2^\circ\text{C}$  and calcined at  $1000\pm 5^\circ\text{C}$  for 6 hours. The obtained product was calcium aluminate. After grinding it was mixed with  $\text{Ca(OH)}_2$ , gypsum and water in the molar ratio of 1 : 2 : 1 : 8 and seal-cured at  $20^\circ\text{C}$ , then at  $40^\circ\text{C}$  and finally at  $20^\circ\text{C}$ . The curing time at each temperature was 2 days. The obtained hydrate was AFm identified both by XRD and TG-DTA.

##### 3.1.2 Fixation of chloride ions in AFm and carbonation of AFm and Friedel's salt

The instrument used for observing the fixation of chloride ions in cement hydrates and carbonation of cement hydrates as well is as shown in Fig.1. The experiments were all carried out at  $20^\circ\text{C}$ .

In the experiment of chloride ion fixation, the synthesized AFm was added to NaCl solution and the solution was stirred continuously. The solution was sampled after a definite time spacing and the concentration of chloride ions in it was analyzed. The amount of chloride ions that have been fixed in AFm phase was deduced from the decrease of chloride ion concentration of the solution. In the experiment the influence of  $\text{CO}_2$  should be prevented. In addition, the effects of (1) initial chloride ion concentration of solution; (2) molar ratio of AFm to chloride ions and (3) the coexistence of NaOH, KOH and  $\text{Ca(OH)}_2$  on the fixation of chloride ions have also been studied. The conditions were as follows: (1) concentrations of NaCl solution were 0.03%, 0.06%, 0.12%, 0.29%, 1.5%, 2.5%, 3.5% and 4.5%, respectively; (2) molar ratio of AFm to chloride ions were 0.5, 1.0, 2.0, 5.0, 25.9, 43.1, 60.3 and 77.6, respectively and (3) in the presence of 0.1 mol/l of KOH or NaOH or 0.02 mol/l  $\text{Ca(OH)}_2$  for the solution with NaCl concentration being 3.5%.

In investigating into the variation of the fixed amount of chloride ions in AFm phase and the release of chloride ions from Friedel's salt when carbonation occurs, carbon dioxide was introduced to the reaction container at a rate of 20 ml/min. AFm was at first added to air-free distilled water, and then the solution was stirred in the presence of  $\text{CO}_2$  bubbling. After a definite time the pH of the solution was measured and NaCl was added to it. As the decrease of the fixed amount of chloride ions could be attributed to the carbonation that happened to AFm, the carbonation ratio of AFm was therefore deduced from the difference in the amount of chloride ions fixed in AFm in the presence and without the presence of carbonation. In another test,  $\text{CO}_2$  was bubbled to solutions with the addition of AFm that has fixed chloride ions in it. After a definite time the pH and chloride ion concentration of the solution were measured. The carbonation ratio was determined based on the increase of chloride ion concentration in the solution in consideration of the

increase of chloride ion concentration being attributed to the release of chloride ions from the carbonated part of the sample. Carbonation tests have been also commenced in the presence of KOH, NaOH and Ca(OH)<sub>2</sub> addition, the added amount of them was the same as mentioned above.

### 3.2 Results and establishment of models

#### 3.2.1 Fixation of chloride ions in AFm

The variation of the amount of chloride ions fixed in AFm phase with time is shown in Fig.2. It shows that: (1) the fixing rate is somewhat varied with the existence of other ions, (2) after 0.1 day the amount of chloride ions fixed in AFm phase become stable and keep at a constant level of 5 moles of chloride ions in respect to 1 mole of AFm and (3) the fixing rate and finely fixed amount of chloride ions in AFm phase are not varied

with the initial concentration of NaCl. If the fixation of chloride ion in AFm phase is conform

to the reaction as shown in the following, the upper limit of the amount of chloride ions that can be chemically bound in 1 mole of AFm is 2 moles. In our opinions, the other 3 moles of chloride ions fixed in AFm are possibly due to the other mechanism.



In this study both adsorption mechanisms of chloride ions in AFm phase have been taken into consideration.

The above conclusions were drawn in the case when there was enough presence of chloride ions in comparison to AFm phase. When the concentration of chloride ions is much less than the upper limit of the fixing ability of AFm, the result is shown in Fig.3.

It shows that even in the case the fixing process of chloride ions in AFm phase is also ended at about 0.1 day and it is yet impossible for AFm to fix all the chloride ions with some of them being retained in liquid. Based on this fact it can be said that the fixed amount of chloride ions in AFm phase bears a relation to the concentration of chloride ion in liquid. The relation between the concentration of chloride ion in liquid when the fixing reaction ends and the upper limit of the amount of chloride ions fixed in AFm phase is given in Fig.4, from which it can be found that the upper limit of fixed chloride ions in AFm phase can be expressed as a function of the concentration of chloride ions in liquid. The following models stand for the relation.

$$Cl < 2 \text{ mol/mol} \quad Fix = 2.5 \cdot Cl \quad [2-1]$$

$$Cl \geq 2 \text{ mol/mol} \quad Fix = 5.0 \quad [2-2]$$

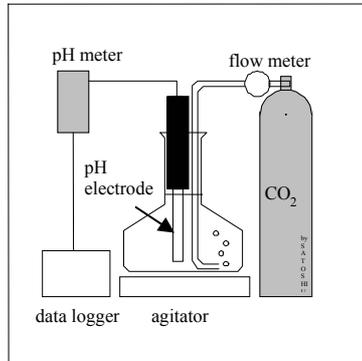


Fig.1 Reactor

where,  $Cl$  : the concentration of chloride in liquid in respect to 1 mole of AFm (mol/mol)  
Fix : the upper limit of the amount of chloride ions that can be fixed in AFm.

By using formula [2] that was made to calculate the fixed amount of chloride ions and taking the mix proportion into consideration, the amounts both of fixed and free chloride ions have been determined. From Fig.5 it can be found that the calculated results are in well consistent with the observed total amount of chloride ions and the amount of soluble chloride ions in a chloride penetration test. This indicates that the results obtained from this model have good correspondence to practical occurrence.

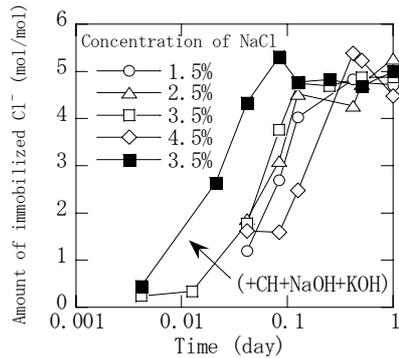


Fig.2 Effect of NaCl concentration on immobilized  $Cl^-$  (NaCl=1.5-4.5%)

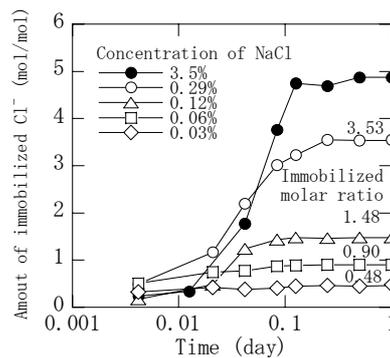


Fig.3 Effect of NaCl concentration on immobilized  $Cl^-$  (NaCl=0.03-0.29%)

### 3.2.2 Carbonation of AFm and Friedel's salt

The chloride ions fixed in Friedel's salt will dissolve into pore solution when carbonation of Friedel's salt occurs. And, when carbonation of AFm takes place previously, the originally fixed chloride ions in it will transform to free ones. Both of them are disadvantageous to the prevention of the penetration of chloride ions in concrete. Therefore, the carbonation of these two hydrates has been studied in this experiment.

The relations between the pH of liquid and carbonation ratios of AFm phase and Friedel's salt are shown in Fig.6. Carbonation started when solution pH became below 11.5 and the carbonation ratio of both AFm phase and Friedel's salt was increased with the decrease of liquid pH. In addition, at the same liquid pH the carbonation ratio of AFm phase was as same as that of Friedel's salt and, this rule also stood even in the presence of NaOH, KOH and  $Ca(OH)_2$  addition. In this study, the relation between liquid pH and carbonation ratio were modeled as follows:

$$pH < 7.5 \quad r_c = 1 \quad [3-1]$$

$$7.5 \leq pH < 9 \quad r_c = -0.4pH + 4 \quad [3-2]$$

$$9 \leq pH < 11.5 \quad r_c = -0.16pH + 1.84 \quad [3-3]$$

$$pH \geq 11.5 \quad r_c = 0 \quad [3-4]$$

where, pH : pH of liquid  
 $r_c$  : carbonation ratio of hydrates

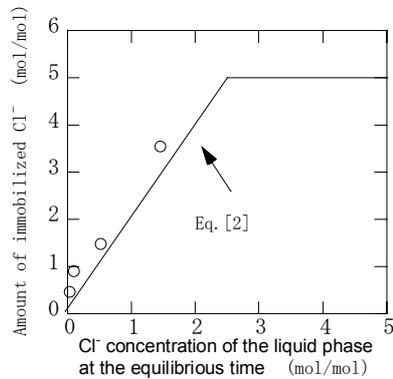


Fig.4 Relationship between  $\text{Cl}^-$  concentration in solution and immobilized  $\text{Cl}^-$

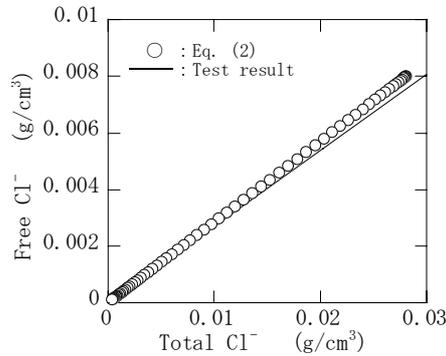


Fig.5 Relationship between total  $\text{Cl}^-$  and free  $\text{Cl}^-$

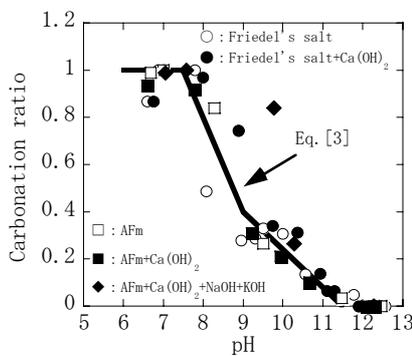


Fig.6 Relationship between pH and carbonation ratio

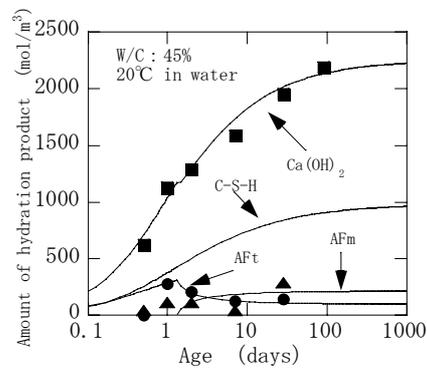


Fig.7 Prediction result of hydration process

#### 4. Prediction of the deterioration of concrete due to the compound effect of chloride ions ingress and carbonation

##### 4.1 Composing of the prediction model

The establishment of the prediction model was based on the models for the cement hydration, the prediction of carbonation [4][5] and those for chloride ion penetration in concrete [6][7]. A summary of the above models is given below.

##### 4.1.1 Model for cement hydration

The hydration model of the cement was based on the method of Papadakis et al[8]. Fig.7

shows that the calculation results and test results.

#### 4.1.2 Model for characterizing carbonation [4][5]

In the establishment of a model for characterizing the carbonation progress in concrete, the transportation of water, CO<sub>2</sub> (gaseous phase, liquid phase) and Ca(OH)<sub>2</sub> and the reaction among them have been taken into consideration. The basic equations used in the establishment of models are as following:

$$\frac{\partial C_1}{\partial t} = \frac{\partial}{\partial x} \left( D_1 \frac{\partial C_1}{\partial x} \right) + K_1 C_3 C_4 \quad [4-1]$$

$$\frac{\partial C_2}{\partial t} = \frac{\partial}{\partial x} \left( D_2 \frac{\partial C_2}{\partial x} \right) + K_2 g(C_1, C_2, C_3) \quad [4-2]$$

$$\frac{\partial C_3}{\partial t} = K_2 g(C_1, C_2, C_3) - K_1 C_3 C_4 \quad [4-3]$$

$$\frac{\partial C_4}{\partial t} = \frac{\partial}{\partial x} \left( D_4 \frac{\partial C_4}{\partial x} \right) - K_1 C_3 C_4 \quad [4-4]$$

where, C : concentration (mol/cm<sup>3</sup>)

D : diffusion coefficient (cm<sup>2</sup>/day)

K<sub>1</sub>: reaction rate constant (cm<sup>3</sup>/ mol · day)

K<sub>2</sub> : solubility of gaseous carbon dioxide in liquid phase

g (C<sub>1</sub>, C<sub>2</sub>, C<sub>3</sub>) : the function of C<sub>1</sub>, C<sub>2</sub> and C<sub>3</sub>

In the equations the footnotes 1, 2, 3 and 4 represent water, CO<sub>2</sub> (gaseous), CO<sub>2</sub> (soluble in liquid) and Ca(OH)<sub>2</sub>, respectively.

Fig.8 shows that the calculated results based on the above models are in agreement with the ones observed in accelerated carbonation tests, this indicates the models have been properly established.

#### 4.1.3 Model for predicting the penetration of chloride ions in concrete [6][7]

The establishment of the model for predicting the penetration of chloride ions in concrete is mainly based on the following equation:

$$\frac{\partial C_5}{\partial t} + \frac{\partial (u C_5)}{\partial x} = \frac{\partial}{\partial x} \left( D_5 \frac{\partial C_5}{\partial x} \right) - \frac{\partial S}{\partial t} \quad [5]$$

where, C<sub>5</sub> : concentration of soluble chlorides (g/cm<sup>3</sup>)

D<sub>5</sub> : diffusion coefficient of chlorides (cm<sup>2</sup>/day)

S : concentration of fixed chlorides (g/cm<sup>3</sup>)

u : flow rate of water (cm/day)

From the above equation it can be seen that in the model the driving force of the penetration of chloride ions in concrete is attributed to the diffusion of ions and the penetration of

chlorides-containing water in concrete. In addition, the penetration of chloride ions should be also related to water content of concrete because it is practically a transportation process of ions in concrete. The dependence of the diffusion coefficient of chloride ions on the water content of concrete was referenced to the results obtained before [6]. The same way as did in the calculation of carbonation was carried out in calculating water transportation in concrete and  $u$  was therefore obtained. In the calculation of the fixation of chloride ions formula [2] was used. Fig.9 shows that the results calculated based on the established model are consistent with the ones observed in a wet-dry cycling test (immersion in chloride-containing solution-dried in air) of cement mortar specimens.

Diffusion coefficient of chloride ions was determined from continuous salt immersion test. Its value does not contain the effect of fixation in cement hydration products [6].

#### 4.2 Predicted results

By using the models mentioned above the prediction of the concentration of chloride ions in the concrete subjected to both carbonation and chloride ions ingress was carried out. In this method, the formed AFm and  $\text{Ca}(\text{OH})_2$  and pore concentration is deduced from the mineral composition of cement, used water to cement ratio and curing condition at first, then the transportation and reaction of various materials that take place in concrete are calculated using the model and the data obtained previously.

For testifying the established model for predicting the compound deterioration of concrete, a test with alternative impact of immersion in 3.5% NaCl solution and accelerated carbonation was conducted on mortar specimens. The temperature, R.H. and  $\text{CO}_2$  concentration in the carbonation chamber were kept at  $20^\circ\text{C}$ , 60% and 5%, respectively. Two kinds of wet-dry cycling test were adopted, i.e. 1 day in salt solution and 2 days in carbonation chamber and 2 days in salt solution and 6 days in the chamber.

The predicted results are shown in Figs.10. The calculated results clearly disclose the tendency of the concentrating effect of chloride ions caused by carbonation of hydrates.

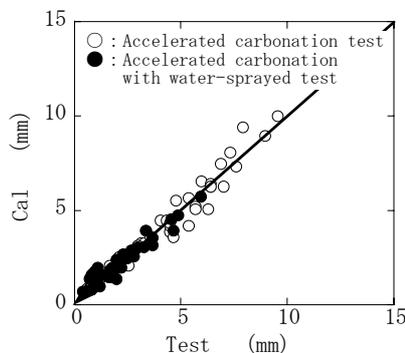


Fig.8 Prediction results of carbonation depth

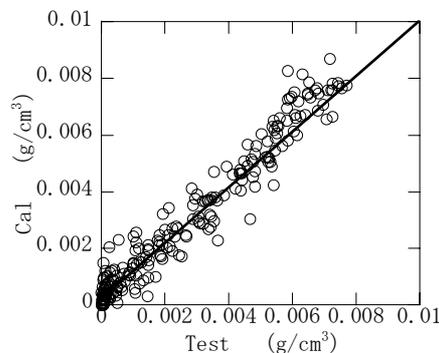


Fig.9 Prediction results of Cl concentration

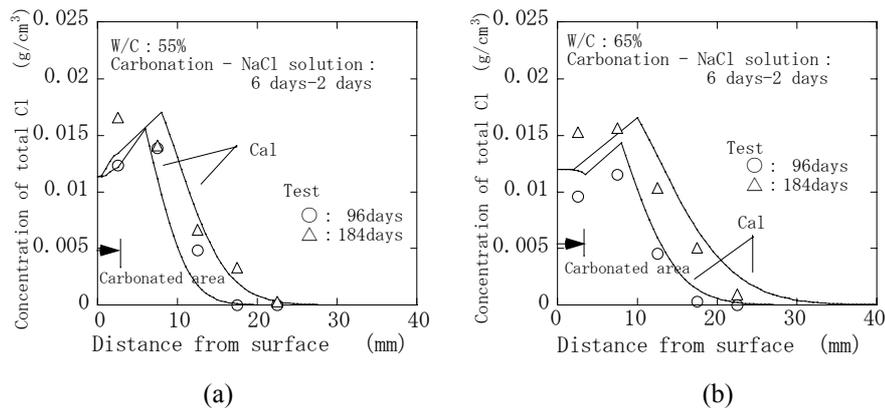


Fig.10 Prediction results of Cl<sup>-</sup> distribution under salt damage and carbonation condition

### 5. Change in micro-structure due to carbonation and its effect on chloride ions penetration

It is well known that the micro-structure of concrete is changed due to carbonation [9][10]. And the diffusivity of chloride ions in concrete depends on micro-structure. Therefore, the effect of change in micro-structure due to carbonation on chloride penetration is evaluated in this chapter.

Fig.11 shows that relationship between the total amount of Ca(OH)<sub>2</sub> and CaCO<sub>3</sub>, and the pore volume of ordinary portland cement mortar (OPC mortar) under carbonation condition. Amount of Ca(OH)<sub>2</sub> is an index of the degree of hydration, and amount of CaCO<sub>3</sub> is an index of the degree of carbonation. The relation was formulated as follows.

$$C_T < 5.0 \quad P = -0.0750C_T + 0.505 \quad [6-1]$$

$$C_T \geq 5.0 \quad P = -0.236C_T + 0.248 \quad [6-2]$$

where,  $C_T$  : amount of Ca(OH)<sub>2</sub> and CaCO<sub>3</sub>  
(wt%)

$P$  : pore volume with the range of  
0.015 ~ 15 μm in diameter

The pore volume of carbonated mortar was corrected by Eqs.[6] and these equations were also used for the prediction in chapter 4.

Figs.12 show that chloride distributions in the OPC mortar under cycling complex deterioration test (2 days in salt solution and 6 days in carbonation chamber). And for the comparison, the cycling CO<sub>2</sub> free wet-dry test was performed. The specimens were exposed in the air at the

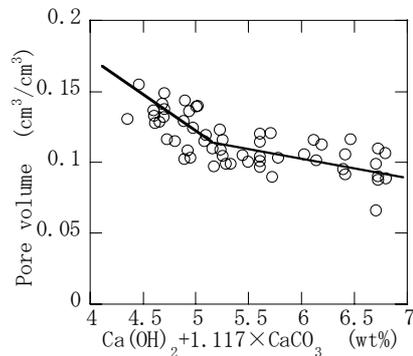


Fig.11 Relationship between Ca(OH)<sub>2</sub> and CaCO<sub>3</sub>, and pore volume

same temperature and relative humidity with accelerated carbonation test, i.e. 2 day in salt solution and 6 days in the CO<sub>2</sub> free air. These test results are also shown in Figs.12. From these figures, it can be seen that the carbonation controls the chloride ingress. This reason seems to be a decrease in the pore volume, as it can be seen in Fig.11.

Figs.13 show that carbonation depth and chloride penetration depth judged by AgNO<sub>3</sub> solution under cycling complex deterioration test and cycling CO<sub>2</sub> free wet-dry test. In these test, OPC mortar and blast-furnace slag cement mortar (BFS mortar) were used. The water-binder ratio of mortars was 55% and the content of blast-furnace slag powder was 50% (B50) or 70% (B70). It can be seen that the chloride penetration depth of BFS mortar is less than that of OPC mortar in the case of non-carbonation condition. For the OPC mortar, chloride penetration was suppressed due to carbonation. On the other hand, chloride penetration of BFS mortar was accelerated due to carbonation. Especially in the case of B70, the effect of carbonation on chloride penetration is remarkable.

From the above fact, it was confirmed that the chloride penetration was accelerated carbonation when the blast-furnace slag cement is used. Then, the micro-structures were examined in order to clarify the cause of this phenomenon. It is observed that pore size distributions of mortars at the immediately after initial curing and at 4 weeks of continuous accelerated carbonation test in Figs.14. From these figures, the pore volume with the diameter 0.02-1 μm was increased, though the total pore volume was decreased due to carbonation. And when the blast-furnace slag was used, the increase of pore volume with the range of 0.02-1 μm was large.

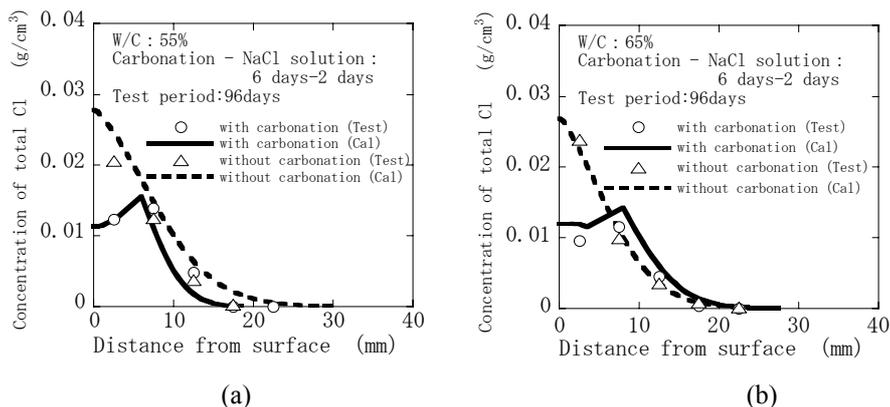


Fig.12 Chloride distribution under the cycling complex deterioration test and the cycling CO<sub>2</sub> free wet-dry test

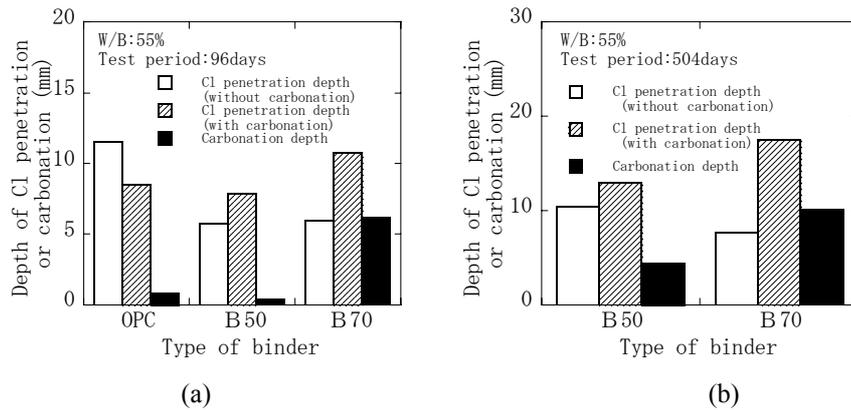


Fig.13 Carbonation depth and chloride penetration depth of OPC mortar and BFS mortar

It has already been confirmed that the pore volume of BFS mortar became porous after carbonation in the past research [11]. This reason was explained that large amount of water were released from C-S-H with lower molar ratio of  $\text{CaO}/\text{SiO}_2$  due to carbonation. The C-S-H with low ratio of  $\text{CaO}/\text{SiO}_2$  is produced by slag hydration. Generally, the carbonation process leads to decrease in pore volume due to production of  $\text{CaCO}_3$ , because the mole volume increases about 11.7% when  $\text{CaCO}_3$  is formed from  $\text{Ca}(\text{OH})_2$ . However, the micro-structure may become porous, when C-S-H is carbonated. Fig.15 shows that the pore size distribution of B70 under the complex deterioration accelerated test. It can be recognized that the pore volume at the surface layer was increased.

From these experimental results, the estimation method of change in pore volume due to carbonation was proposed. It was assumed that the amount of  $\text{CaCO}_3$  formed from  $\text{Ca}(\text{OH})_2$  was an index of denseness of micro-structure and the amount of  $\text{CaCO}_3$  formed from other hydration products was an index of porous. The amount of  $\text{CaCO}_3$  formed from  $\text{Ca}(\text{OH})_2$  was calculated from the difference between the amount of  $\text{Ca}(\text{OH})_2$  immediately after initial curing and the amount of  $\text{Ca}(\text{OH})_2$  after accelerated carbonation test. The remaining  $\text{CaCO}_3$  was assumed as that formed from C-S-H. Considering the volume difference between hydration products ( $\text{Ca}(\text{OH})_2$  and C-S-H) and carbonation products ( $\text{CaCO}_3$  and  $\text{SiO}_2$  gel), index CP was defined as follow.

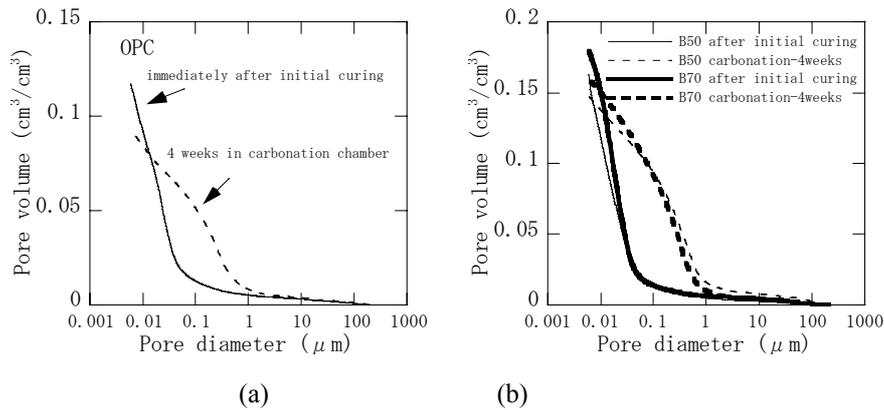


Fig.14 Change in pore size distribution due to carbonation under continuous carbonation condition

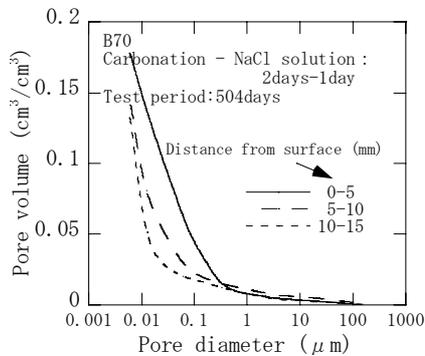


Fig.15 Change in pore size distribution of BSF mortar under the complex deterioration accelerated test

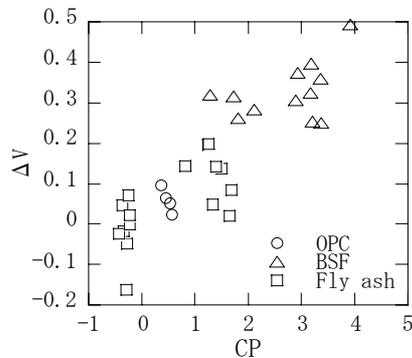


Fig.16 Relationship between CP and change ratio of pore volume

$$CP = \alpha CC_{CH} + \beta CC_{CSH} \quad [7]$$

where,  $CC_{CH}$  : Amount of  $CaCO_3$  formed from  $Ca(OH)_2$

$CC_{CSH}$  : Amount of  $CaCO_3$  formed from C-S-H

$\alpha, \beta$  : Constant

The volume of the released water from C-S-H due to carbonation seemed to cause the increase of pore volume, the coefficient  $\alpha$  and  $\beta$  in Eq.[7] were decided for each cement. Generally,  $\alpha$  has negative value and  $\beta$  has positive value. Compositions of C-S-H were assumed as  $C_{1.7}SH_{2.5}$  for OPC [12] and as  $C_{0.39}SH_{1.3}$  for BFS [13]. The density of each hydration and carbonation products was based on literatures [12], and the density of the C-S-H with the ratio of  $CaO/SiO_2$  below 1.0 was assumed as  $2.0g/cm^3$ .

The relationship between index CP and change ratio of pore volume is shown in Fig.16. The change ratio of pore volume " $\Delta V$ " was defined as the ratio of volume change due to carbonation to pore volume of non-carbonated mortar. The positive value of  $\Delta V$  means loosened micro-structure and the negative value means dense micro-structure. The pore for estimation was within  $0.015 \sim 15 \mu\text{m}$  in diameter, because there was high correlation between the pore volume with this range and mass transfer [4]. In the case of BFS, almost of  $\text{Ca}(\text{OH})_2$  was consumed by the hydration of slag. Therefore  $CC_{\text{CSH}}$  was larger than  $CC_{\text{CH}}$ , and CP and  $\Delta V$  are also large. From this figure, there is the correlation at CP and  $\Delta V$  regardless of the type of cement. Therefore, there seems to be the validity in the carbonation of C-S-H regarding as a cause of pore volume increase. From these results, it seems to be able to formulate the change of the micro-structure due to carbonation.

From the studies for micro-structure, it is indicated that the acceleration of chloride penetration due to carbonation is caused by loosened micro-structure in the case of BFS mortar.

It is necessary that composition and density of C-S-H with low  $\text{CaO}/\text{SiO}_2$  is clarified and quantitative estimation method for micro-structure is developed in order to establish the chloride penetration prediction method for any materials.

## 6. Conclusions

- (1) The amount of chloride ions fixed in AFm phase is dependent on the concentration of chloride ions in liquid phase; their relations can be expressed by formula [2].
- (2) The carbonation ratio either of AFm or Friedel's salt is correlated with pH of liquid phase, the relations between them can be expressed as in [13].
- (3) By combining the models of characterizing the fixation of chloride ions in AFm phase and the carbonation of AFm and Friedel's salt into the models for predicting carbonation progress and chloride penetration in concrete, it is able to predict the distribution of chloride ion in concrete when it is simultaneously subjected to carbonation and chloride ions ingress.
- (4) When blast-furnace slag cement is used, the micro-structure is loosened due to carbonation. Therefore, carbonation may promote chloride penetration in that case.

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