A MODEL FOR PREDICTING THE DETERIORATION OF CONCRETE DUE TO THE COMPOUND INFLUENCE OF SALT DAMAGE AND CARBONATION

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The aim of this study is to set up a model for predicting the process of chloride ion migration in concrete under the compound influence of salt damage and carbonation. The basis of the model is an investigation into the immobilization of chloride ions in cement hydrates and their release when carbonation causes degradation of the hydrates. 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.

Key Words : chloride ion, carbonation, Friedel's salt, monosulfate

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1. INTRODUCTION

As concrete undergoes chloride ion ingress and carbonation, chloride ions that have been fixed in the cement hydrates will be released due to deterioration of the hydrates caused by carbonation. It has been found that chloride ions tend to concentrate in areas where carbonation has not occurred [1], so for concrete subjected to both chloride ion ingress and carbonation, corrosion of steel bars is possible even though the total chloride content is low and chloride levels near steel bars have not reached the critical concentration for corrosion to occur.

There have been many studies related to the prediction of concrete deterioration due to the effect of chloride ion ingress and carbonation acting independently, but as far as the compound influence of these two phenomena is concerned, little attention has been paid and no detailed information is available in the literature. This is despite the fact that they may greatly accelerate the corrosion of steels bars in the concrete.

It is clear that a quantitative evaluation of concrete durability requires prediction of the distribution of chloride ions under the combined influence of chloride ions ingress and carbonation. From another point of view, the development of improved surveying and maintenance systems for concrete also demands a more accurate method of evaluating concrete durability.

Thus, there is strong desire for a suitable prediction method. Such predictions can probably be arrived at experimentally, by implementing wet-dry cycling tests of chloride ion ingress and accelerated carbonation. But the problem is that we do not know the time-wise correspondence of this compound effect to its actual occurrence in real-life situations. Another possible and reliable way to reach the goal is to develop a model in consideration of the mechanism of concrete deterioration.

This latter approach is presented here. The establishment of a model for both chloride ion ingress and carbonation entails setting up separate models to describe the various reactions related to concrete deterioration, and this is the focus of the first part of this study. The models used for confirmation were those for the prediction of carbonation depth and penetration depth of chloride ions in concrete.

2. MECHANISM OF CONCRETE DETERIORATION DUE TO CHLORIDE IONS INGRESS AND CARBONATION AND MODELS USED FOR CONFIRMATION

According to Kobayashi [1], the mechanism of concrete degradation due to chloride ion ingress and carbonation is as follows: (1) generation of Friedel's salt due to the reaction of monosulfate (AFm) with chloride ions; (2) carbonation of Friedel's salt; (3) dissolution of chloride ions immobilized in Friedel's salt into pore solution, and (4) increase in concentration of chloride ions in pore solution, resulting in the further ingress of chloride ions deeper into the concrete through concentrating and diffusion cycles. Hence, in the establishment of a prediction model for the deterioration of concrete due to the compound influence of chloride ion ingress and carbonation, the following models are needed: (1) a model describing the fixing of chloride ions in the AFm phase, (i.e. a model for the formation of Friedel's salt); (2) models to characterize the carbonation of Friedel's salt and the release of chloride ions from carbonated Friedel's salt; and (3) a model expressing the carbonation of AFm. By combining these models with existing models for the prediction of carbonation [2,3] and chloride penetration [4,5] in concrete developed by the authors, an overall model for predicting concrete deterioration due to the compound influence of chloride ion ingress and carbonation will be set up.

3. HYDRATION MODEL OF CEMENT

(1) Formation of cement hydrates

In this study, the hydration of each mineral making up ordinary Portland cement is formulated as follows:

$$2C_3S + 6H \rightarrow C_3S_2H_3 + 3CH \quad (1)$$

$$2C_2S + 4H \rightarrow C_3S_2H_3 + CH \quad (2)$$

$$C_3A + 3C\overline{S}H_2 + 26H \rightarrow C_3A \cdot 3C\overline{S} \cdot H_{32} \quad (3)$$

$$C_4AF + 2CH + 2C\overline{S}H_2 + 18H \rightarrow C_8AF\overline{S}H_{24} \quad (4)$$

The reactions of C_3A and C_4AF after gypsum consumption are assumed to be of the following form:

$$C_3A + CH + 12H \rightarrow C_4AH_{13} \quad (5)$$

$$C_4AF + 4CH + 22H \rightarrow C_8AFH_{26} \quad (6)$$

The transition from AFt to AFm after gypsum consumption is described by the following equation:

$$2C_3A + C_3A \cdot 3C\overline{S} \cdot H_{32} + 4H \rightarrow 3(C_3A \cdot C\overline{S} \cdot H_{12}) \quad (7)$$

(2) Kinetics of cement hydration

The kinetics of cement hydration follow the model of Papadakis et al[6]. In this model, the degree of hydration of each clinker mineral is defined as below, so it is necessary to give the rate constant k and order of reaction n in order to calculate the hydration rate.

$$r_{H,i} \equiv -d[i]/dt = k_{H,i}[i]^{n_i} / [i]_0^{n_i - 1} \quad (8)$$

where, $r_{H,i}$:hydration rate (mol/m^3/sec)

$[i]$: concentration at time t(mol/m^3)
$[i]_0$: concentration at time 0 (mol/m^3)
$k_{H,i}$: rate constant (sec^{-1})
n: order of reaction

In this study, in order to decide on suitable values of k and n, the amount of combined water was calculated from the hydration rate of each clinker as given in the literature, and data agreeing with the amount of combined water as measured in this study was adopted. The kinetic equation parameters were then fixed as shown in Table 1. Data given by Brunauar and Copelamd [7] was found to agree with the experimental results for C_3S, C_3A and C_4AF, while that by Sakai et al. [8] was found to agree with the experimental results for C_2S.

Table 1 hydration parameter of clinker

	C_3S	C_2S	C_3A	C_4AF
n	2.65	3.10	3.81	2.41
$k \times 10^5$ (sec^{-1})	1.17	0.16	1.00	2.46

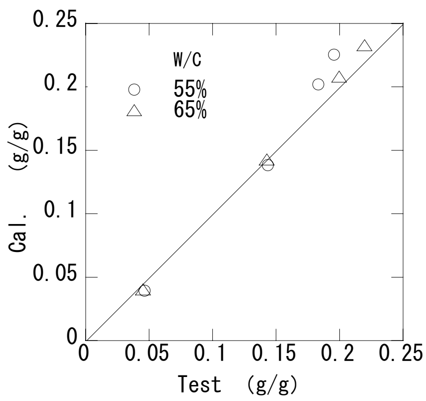


Fig.1 Prediction result of combined water

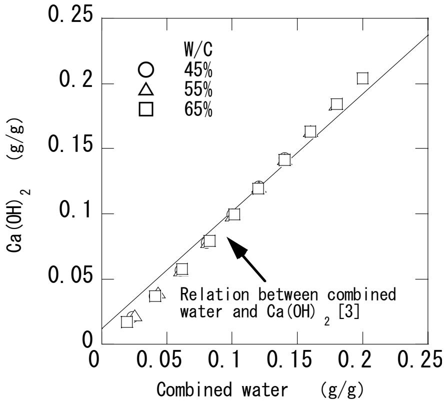


Fig.2 Relationship between combined water and $Ca(OH)_2$

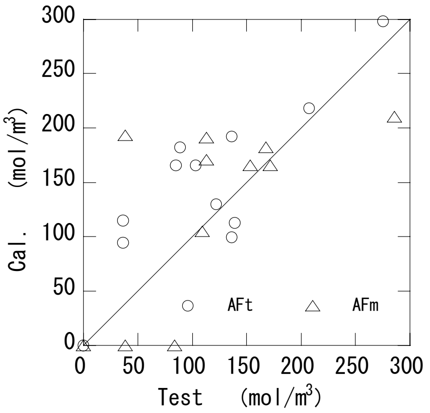


Fig.3 Prediction result of amount of AFt and AFm

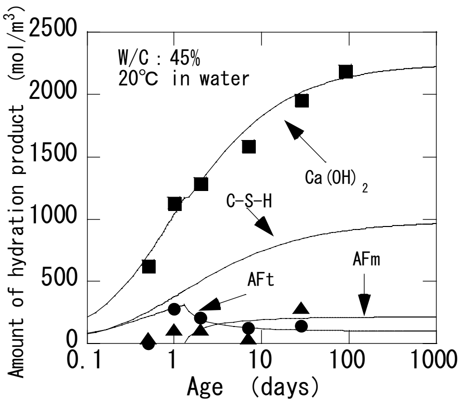


Fig.4 Prediction result of hydration process

(3) Verification of cement hydration model

Predicted quantities of combined water according to the hydration model are shown in Fig.1. These results were obtained from experiments on ordinary Portland cement unlike the result of using in order to decide the parameter of the hydration kinetics. The figure confirms that the calculated results are in good agreement with experiment. Figure 2 shows the predicted amount of calcium hydroxide. The relational expression for the amount of combined water and the amount of calcium hydroxide was obtained from the same experiment [3] as shown in Fig.1. The mineral composition of the cement used was obtained using the method described by Fujii et al. [9]. Figure 3 shows the predicted amount of AFt and AFm. In the experiment, sealed cured cement pastes with water-cement ratios of 45%, 55% and 65% were prepared, and X-ray diffraction was performed in order to quantify AFt and AFm by the internal standard method using ZnO. Although the figure, does include some experimental results that do not agree with the calculated values, it can be said that the overall trend of the behavior is predicted especially when the accuracy of the X-ray diffraction method is taken into account. Figure 4 shows the predictions for each hydration product. This demonstrates that the tendency toward variations with aging is closely matched.

As noted above, the calculated levels of AFm formation do not agree fully with the experimental results in Fig.3 and Fig.4. Accordingly, quantitative analysis using the method described by Suzuki et al. [10] was also carried out. However, this led to no improvement in the agreement between experimental and calculated results. As Suzuki et al. pointed out, it is difficult to separate AFm from AFt [10], and as a result the assay accuracy tends to be low where AFm coexists with AFt in the early stages of hydration. However, method used to predict AFm formation in this study was judged to be appropriate on the basis that the predicted amount of combined water, as calculated from the degree of hydration of each mineral, and the formation of other hydrates agree with the experimental results.

4. MODELS FOR THE FIXATION AND RELEASE OF CHLORIDE IONS

(1)Experimental

The main purposes of this experiment are to observe the effect that AFm has on the fixing of chloride ions and also the release of chloride ions due to carbonation occurred. The AFm used in the experiment was synthesized using chemical agents.

a)Synthesis of AFm

Analytically pure $Ca(OH)_2$ was mixed in advance with chemically active and finely ground Al_2O_3 in the presence of a little water, then dried at 105±2℃ and calcined at 1,000±5℃ for 6 hours. The resulting product was calcium aluminate. After grinding, this was mixed with $Ca(OH)_2$, gypsum, and

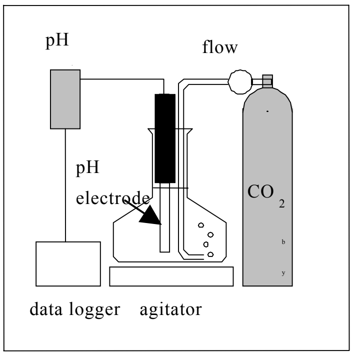


Fig.5 Schematic of reactor

water in the molar ratio of 1 : 2 : 1 : 8 and seal-cured at 20℃, then at 40℃, and finally at 20℃ again. The curing time at each temperature was 2 days. The resulting hydrate was AFm as identified both by XRD and TG-DTA.

b) Fixation of chloride ions in AFm and carbonation of AFm and Friedel's salt

The equipment used to observe the fixing of chloride ions in the cement hydrates as well as the carbonation of cement hydrates is shown in Fig.5. The experiments were all carried out at 20℃.

In the experiment to investigate chloride ion fixation, the synthesized AFm was added to NaCl solution until it reached 0.2mol AFm/l and the solution was stirred continuously. The solution was sampled after a definite time interval and the concentration of chloride ions measured. The number of chloride ions fixed in the AFm phase was deduced from the decrease in chloride ion concentration in the solution. In this experiment, it is important to prevent the influence of CO_2. Additionally, the effects of (1) initial chloride ion concentration in the solution; (2) variations in solution pH; (3) molar ratio of AFm to chloride ions, and (4) the coexistence of NaOH, KOH, and $Ca(OH)_2$ on the fixing of chloride ions were also studied. The conditions were as follows: (1) NaCl concentrations were 0.03%, 0.06%, 0.12%, 0.29%, 1.5%, 2.5%, 3.5%, and 4.5%; (2) pH-free (12-13) or with pH controlled to 11 and 12 using a buffer solution; (3) molar ratios of AFm to chloride ions were 0.5, 1.0, 2.0, 5.0, 25.9, 43.1, 60.3, and 77.6; and (4) in the presence of 0.1mol/l of KOH or NaOH or 0.02mol/l of $Ca(OH)_2$ for solutions with an NaCl concentration of 3.5%.

In investigating variations in the quantity of chloride ions fixed in the AFm phase and the release of chloride ions from Friedel's salt when carbonation occurs, carbon dioxide was introduced into the reaction container at a rate of 20ml/min. AFm was initially added to air-free distilled water until the concentration reached 0.2mol/l, and then the solution was stirred while carrying out CO_2 bubbling. After a certain time, the pH of the solution was measured and NaCl was added. Since any decrease in the quantity of fixed chloride ions could be attributed to carbonation took place in the AFm, the carbonation ratio was then deduced from the difference in the quantity of chloride ions fixed in the AFm in the presence of and without carbonation. In another test, CO_2 was bubbled through solutions containing AFm with fixed chloride ions. After a certain time, the pH and chloride ion concentration of the solution were measured. The carbonation ratio was determined based on the increase in chloride ion concentration, with any increase being attributed to the release of chloride ions from carbonated parts of the sample. Carbonation tests have also been commenced in the presence of KOH, NaOH and $Ca(OH)_2$, with the amount added the same as mentioned above.

(2)Results and establishment of models

a)Fixation of chloride ions in AFm

The changes with the time in the quantity of chloride ions fixed by the AFm phase are shown in Fig.6. This shows that: (1) the rate of fixing depends somewhat on pH and the presence of other ions and (2) after 0.1 day the quantity of chloride ions fixed in the AFm phase reaches a constant level of 5 moles of chloride ions per 1 mole of AFm. In Fig.7 it can be seen that the rate of fixing and the finely

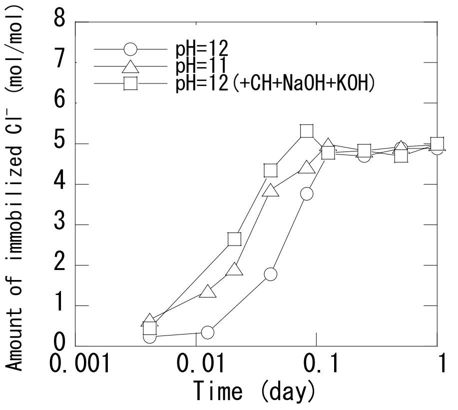


Fig.6 Amount of immobilized Cl^- (NaCl=3.5%)

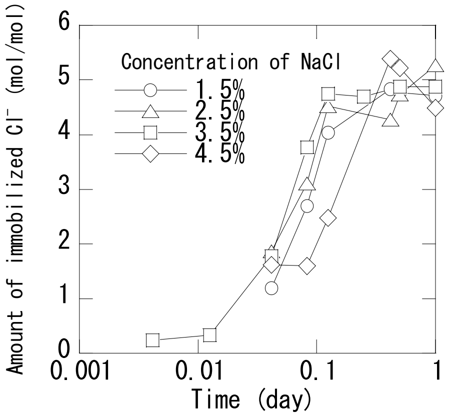


Fig.7 Effect of NaCl concentration on amount of immobilized Cl^- (NaCl=1.5-4.5%)

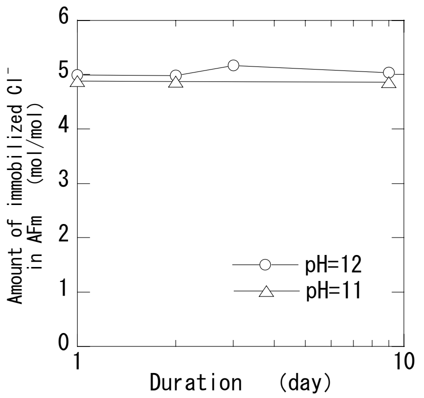


Fig.8 Change in immobilized Cl^- with time

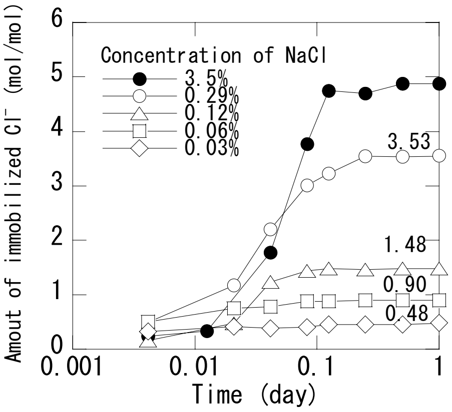


Fig.9 Effect of NaCl concentration on immobilized Cl^- (NaCl=0.03-0.29%)

equilibrium quantity of chloride ions in AFm phase does not vary with initial concentration of NaCl. If it is assumed that the fixing of chloride ions in the AFm phase obeys the reaction given below, then the upper limit of ions that can be chemically bound to 1 mole of AFm is 2 moles. In our opinion, the remaining 3 moles of chloride ions apparently fixed in AFm are taken up by another mechanism.

$$C_4A\overline{S}H_{12} + 2Cl^- \rightarrow C_3A \cdot CaCl_2 \cdot H_{10} + 2H_2O \qquad (9)$$

Figure 8 shows the quantity of fixed chloride ions in the AFm phase beyond the end of the fixation test (Fig.6). In this experiment, agitation was continued in an N_2 atmosphere in order to prevent carbonation. This figure demonstrates that the fixed chlorides are stable against time and the mechanical action of agitation. In this study both adsorption mechanisms of chloride ions in AFm phase are taken into consideration.

The conclusions reached above are for the case when there is an abundance of chloride ions available in comparison with the AFm phase. When the concentration of chloride ions is much less than the upper limit of fixing ability of AFm, the result is as shown in Fig.9. This shows that even if the fixing of chloride ions in the AFm phase is halted at about 0.1 day, it is still impossible for the AFm to fix all the chloride ions and some of them are retained in the liquid. Based on this understanding, it can be said that the quantity of chloride ions fixed in the AFm phase bears a relation to the concentration of chloride ions in the liquid. The relationship between concentration of chloride ions in the liquid when the fixing reaction ends and the upper limit chloride ions fixed in the AFm phase is given in Fig.10. Using this figure, the upper limit of fixed chloride ions in the AFm phase can be expressed as a function of the chloride ion concentration in the liquid. The following models represent for the relationship.

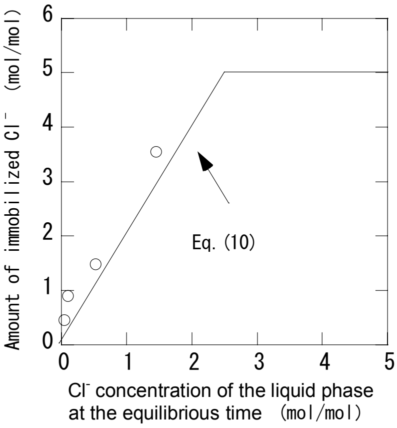


Fig.10 Relationship between Cl⁻ concentration in solution and immobilized Cl⁻

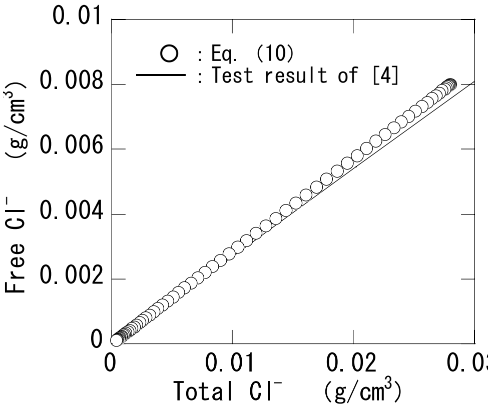


Fig.11 Relationship between total Cl⁻ and free Cl⁻

$Cl < 2\ mol/mol \qquad Fix = 2.5 \cdot Cl$ (10-1)

$Cl \geqq 2\ mol/mol \qquad Fix = 5.0$ (10-2)

where, *Cl*: the concentration of chloride ions in the liquid per mole of AFm (mol/mol)
Fix: the upper limit of chloride ions that can be fixed in the AFm. (mol/mol)

It has been reported that the hydrate C-S-H also fixes chloride ions in addition to AFm [12]. Consequently, an immobilization experiment using synthetic C-S-H was also carried out in this study. The synthesis of C-S-H was carried out using the method described by Suzuki et al. [10], and the ratio of CaO to SiO_2 was 1.5. Other experimental conditions were the same as for the AFm experiment. It was determined that the upper limit of chloride ions fixed was 0.1 mole in 1 mole of C-S-H. This is about 10% of the figure for AFm given the proportions of C-S-H and AFm. In addition, it has been reported that the amount of fixed chloride ions in C-S-H increases if many chloride ions remain unfixed in Friedel's salt [13]. However the purpose of this study is not to study the situation in which chloride ions are abundant in the concrete from the initial stage. Therefore, AFm is considered the only hydration product that fixes chloride ions in the model. However, large quantities of chloride ions may be fixed in C-S-H with the low CaO/SiO_2 ratio, because the specific surface increases as the amount of CaO/SiO_2 in C-S-H falls [12]. Further research seems also to be required regarding this fixing of chlorides in C-S-H with a low CaO/SiO_2 ratio, because low CaO/SiO_2 C-S-H results when fly ash and blast-furnace slag are used as mineral admixtures.

Using formula (10), which was set up to calculate the quantity of chloride ions fixed taking the mix proportion into consideration, the amounts both of fixed and free chloride ions can be determined. Figure 11 demonstrates that the calculated results are well consistent with the observed total quantity of chloride ions and the quantity of soluble chloride ions in a chloride penetration test. This in turn indicates that the results obtained using this model have good correspondence with real life. One point to note is that the synthesized hydrates were kept in good contact with water and the solution was continuously stirred in the experiment; as the result it is possible that the reaction observed experimentally was more rapid than will occur in actual hardened cement paste. However, taking into account that no deformity or deviation have been observed in previous studies in which a balance was assumed between chlorides in the solid phase and chlorides in the liquid phase [14][15] or in which the fixing reaction of chlorides was assumed to finish in a short time, this model is in our opinion suitable for application applied without problems.

b) Carbonation of AFm and Friedel's salt

Chloride ions fixed in Friedel's salt will dissolve into the pore solution when carbonation of the Friedel's salt takes place. And when earlier carbonation of AFm has occurred, the chloride ions originally fixed in it will become free. Both of these reactions are disadvantageous with regard to preventing the penetration of chloride ions into the concrete. Therefore, the carbonation of these two

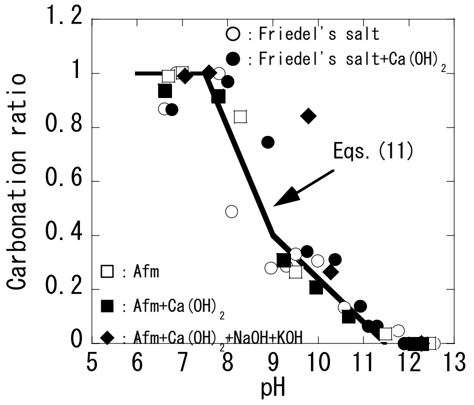


Fig.12 Relationship between pH and carbonation ratio

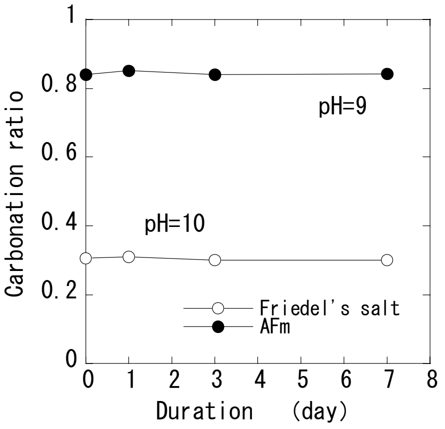


Fig.13 Change in carbonation ratio with time

hydrates is studied here.

The relationship between liquid pH and the carbonation ratios of the AFm phase and Friedel's salt are shown in Fig. 12. Carbonation begins when the pH falls below 11.5 and the carbonation ratio of both the AFm phase and Friedel's salt increases as the pH falls further. In addition, at a particular pH, the carbonation rate of the AFm phase is the same as that of Friedel's salt, and this rule stands up even in the presence of NaOH, KOH, and $Ca(OH)_2$. In this study, the relationship between liquid pH and carbonation ratio is modeled as follows:

$$pH < 7.5 \qquad r_c = 1 \qquad (11\text{-}1)$$

$$7.5 < pH < 9 \qquad r_c = -0.4pH + 4 \qquad (11\text{-}2)$$

$$9 < pH < 11.5 \qquad r_c = -0.16pH + 1.84 \qquad (11\text{-}3)$$

$$pH > 11.5 \qquad r_c = 0 \qquad (11\text{-}4)$$

where, pH: pH of solution
r_c: carbonation rate of hydrates

Figure 13 shows the carbonation ratio of hydrates when the carbonation test was interrupted (CO_2 bubbling stopped) yet agitation was continued. It was confirmed that pH did not change as time passed. From this figure, it can be seen that the carbonation ratio hardly changed over 7 days. From these results, it can be concluded that the degree of carbonation of Friedel's salt and AFm depends only on the pH of the solution.

5. PREDICTION OF CONCRETE DETERIORATION DUE TO THE COMPOUND INFLUENCE OF CHLORIDE ION INGRESS AND CARBONATION

(1)Composing the prediction model

The prediction model was established on the basis of the models for predicting carbonation [2][3] and those for chloride ion penetration in concrete [4][5].

The pore solution equilibrium model was examined once again in order to deal with the complex deterioration phenomenon that arise as a result of combining the carbonation model and the chloride penetration model. Because the degree of carbonation of the hydrates depends on the pH of the pore solution, as described in Chapter 4.

A summary of these various models is given below.

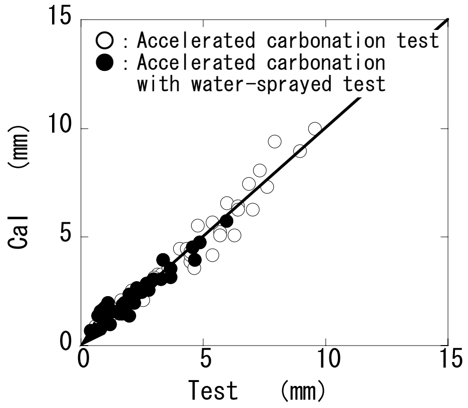


Fig.14 Prediction results of carbonation depth

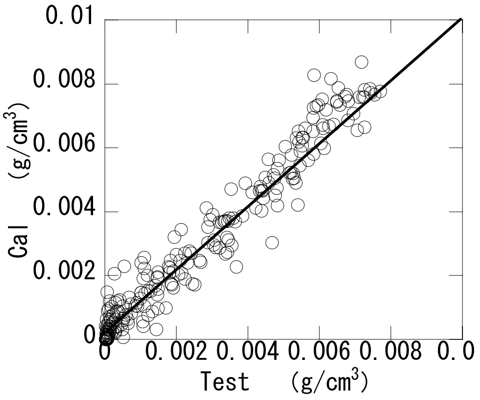


Fig.15 Prediction results of Cl^- concentration

a)Model for characterizing carbonation [2][3]

In the establishment of a model for characterizing the carbonation progress in concrete, the transportation of water, CO_2 (gaseous phase, liquid phase) and $Ca(OH)_2$ and the reaction among them have been taken into consideration. The basic equations used in the establishment of models are as following:

$$\frac{\partial \boldsymbol{C}_1}{\partial \boldsymbol{t}} = \frac{\partial}{\partial \boldsymbol{x}}\left(\boldsymbol{D}_1 \frac{\partial \boldsymbol{C}_1}{\partial \boldsymbol{x}}\right) + \boldsymbol{K}_1 \boldsymbol{C}_3 \boldsymbol{C}_4 \tag{12-1}$$

$$\frac{\partial \boldsymbol{C}_2}{\partial \boldsymbol{t}} = \frac{\partial}{\partial \boldsymbol{x}}\left(\boldsymbol{D}_2 \frac{\partial \boldsymbol{C}_2}{\partial \boldsymbol{x}}\right) + \boldsymbol{K}_2 \boldsymbol{g}(\boldsymbol{C}_1, \boldsymbol{C}_2, \boldsymbol{C}_3) \tag{12-2}$$

$$\frac{\partial \boldsymbol{C}_3}{\partial \boldsymbol{t}} = \boldsymbol{K}_2 \boldsymbol{g}(\boldsymbol{C}_1, \boldsymbol{C}_2, \boldsymbol{C}_3) - \boldsymbol{K}_1 \boldsymbol{C}_3 \boldsymbol{C}_4 \tag{12-3}$$

$$\frac{\partial \boldsymbol{C}_4}{\partial \boldsymbol{t}} = \frac{\partial}{\partial \boldsymbol{x}}\left(\boldsymbol{D}_4 \frac{\partial \boldsymbol{C}_4}{\partial \boldsymbol{x}}\right) - \boldsymbol{K}_1 \boldsymbol{C}_3 \boldsymbol{C}_4 \tag{12-4}$$

where, C: concentration (mol/cm^3)
D: diffusion coefficient (cm^2/day)
K_1: reaction rate constant ($cm^3/ mol \cdot day$)
K_2: solubility of gaseous carbon dioxide in the liquid phase
g (C_1, C_2, C_3) : a function of C_1, C_2 and C_3

In the equations, subscripts 1, 2, 3, and 4 represent water, CO_2 (gaseous), CO_2 (soluble in liquid), and $Ca(OH)_2$, respectively.

Figure 14 shows that the calculated results based on the above models are in agreement with the observations made during accelerated carbonation tests, and this indicates that the models are properly formulated.

b)Model for predicting the penetration of chloride ions in concrete [4][5]

The model for predicting the penetration of chloride ions in concrete is established on the basis of the following equation:

$$\frac{\partial \boldsymbol{C}_5}{\partial \boldsymbol{t}} + \frac{\partial (\boldsymbol{u}\boldsymbol{C}_5)}{\partial \boldsymbol{x}} = \frac{\partial}{\partial \boldsymbol{x}}\left(\boldsymbol{D}_5 \frac{\partial \boldsymbol{C}_5}{\partial \boldsymbol{x}}\right) - \frac{\partial \boldsymbol{S}}{\partial \boldsymbol{t}} \tag{13}$$

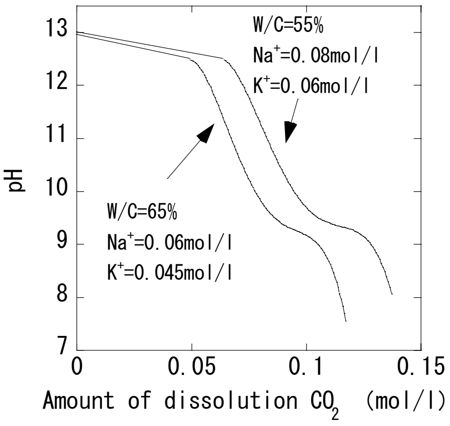


Fig.16 Relationship between the amount of dissolution carbon dioxide and pH

where, C_5: concentration of soluble chlorides (g/cm^3)
D_5: diffusion coefficient of chlorides (cm^2/day)
S: concentration of fixed chlorides (g/cm^3)
u: flow rate of water (cm/day).

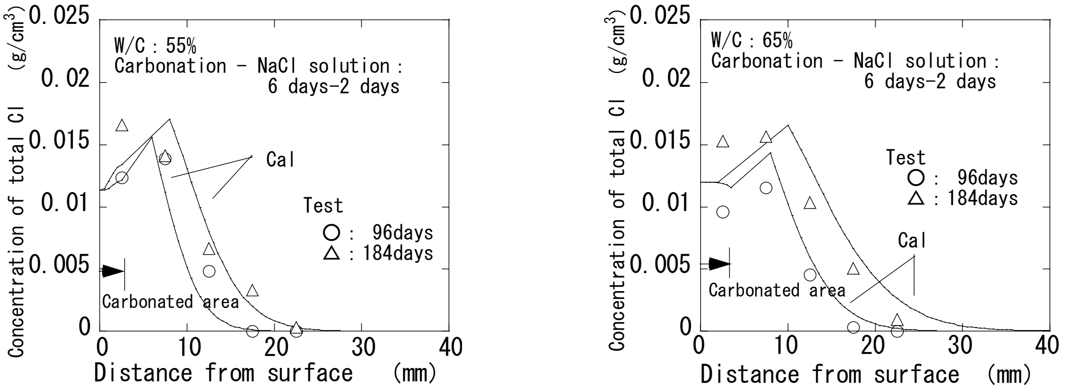
The above equation means that the driving force for penetration of chloride ions in concrete in the model is the diffusion of ions resulting from a concentration difference and the penetration of chloride-containing water through the concrete. The penetration of chloride ions should also be related to the water content of the concrete, because it is in essence a transportation process of ions in concrete. The dependence of the chloride ion diffusion coefficient on concrete water content can be referenced in results obtained previously [4]. Just as carbonation was calculated earlier, so water transportation in the concrete is calculated similarly here and u is obtained. In calculating the fixing of chloride ions, formula (10) was used. Figure 15 shows that the results calculated using this newly established model are consistent with the ones observed in a wet-dry cycling test (immersion in chloride-containing solution; then dried in air) on cement mortar specimens.

c) Ionic equilibriums in pore solution

As equilibrium model for ions in the pore solution is established in order to predict changes in pore solution pH due to the dissolution of CO_2. The ions and ion pairs considered in this study are H^+, OH^-, H_2CO_3, HCO_3^-, CO_3^{2-}, Ca^{2+}, $Ca(OH)_2^0$, $CaCO_3^0$, $CaHCO_3^+$, $Ca(HCO_3)_2^0$, Na^+, $NaCO_3^-$, $NaHCO_3^0$, $Na_2CO_3^0$, K^+, KCO_3^-, $KHCO_3^0$ and $K_2CO_3^0$. Equilibrium constants for each ion were obtained from enthalpy and the entropy of generation [17]. Ionic equilibriums in the pore solution were calculated by combining the law of conservation of mass, the law of mass action, and the electroneutrality principle. Rather than concentration, the activity of ions and ion pairs was adopted as the variable, because the pore solution was very concentrated. Activity coefficients were calculated using Debey-Huckel theory [17].

A typical calculation result is shown in Fig.16. The carbon dioxide amount, as plotted on the horizontal axis, corresponds to the amount of dissolved carbon dioxide after all the $Ca(OH)_2$ has been carbonated. Concentrations of Na^+ and K^+ for the calculation were obtained by measuring the pore solution of mortar with a water-cement ratio of 55% and 65%. It can be seen that the pH of the solution falls, as the dissolution of carbon dioxide (H_2CO_3+HCO_3^-+CO_3^{2-}) increases. However, the reduction in pH is not proportional to the amount of carbon dioxide dissolution. This behavior has been confirmed experimentally [18].

In this model, other ions in the pore solution (such as SO_4^{2-}) and the effect of cement hydration are not taken into account. And the carbonation acceleration mechanism caused by NaCl [1] is not also taken into consideration. These effects are problems for the future.



(a) (b)

Fig.17 Prediction results of Cl⁻ distribution under salt damage and carbonation condition

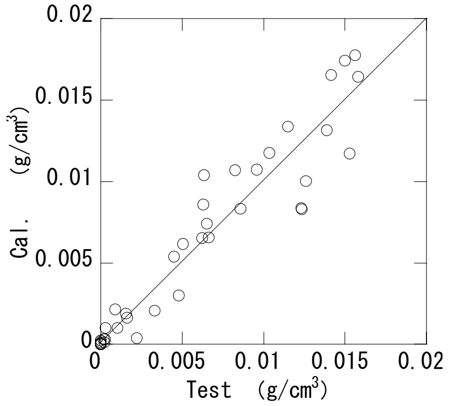


Fig.18 Relationship between test results and prediction results

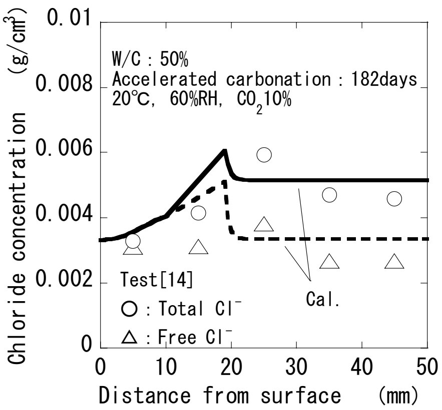


Fig.19 Prediction result in the case which the chloride ions was mixed at the concrete mixing

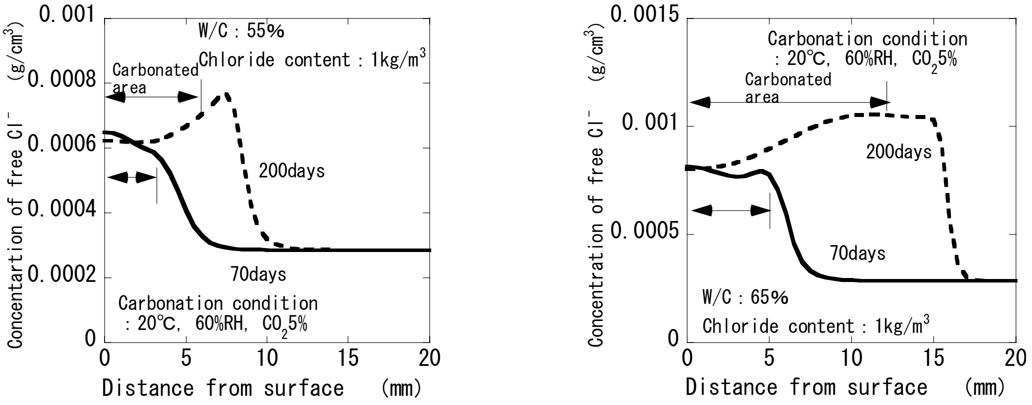
(2)Predicted results

By putting together all of the models described, it was made possible to predict the concentration of chloride ions in the concrete under the influence of both carbonation and chloride ion ingress. The method adopted was to first deduce the amount of AFm and $Ca(OH)_2$ formed and the pore concentration from the mineral composition of the cement, the water-cement ratio, and curing conditions. Then the transport and reactions of various components in the concrete were calculated using the model, bringing in data obtained previously.

To verify that the newly established model is able to predict compound deterioration in concrete, a test in which mortar specimens were alternately exposed to immersion in 3.5% NaCl solution and then accelerated carbonation was conducted. The temperature, R.H., and CO_2 concentration in the carbonation chamber were kept at 20℃, 60%, and 5%, respectively. Two patterns of wet-dry cycling were adopted: 1 day in salt solution and 2 days in the carbonation chamber; and 2 days in salt solution and 6 days in the chamber.

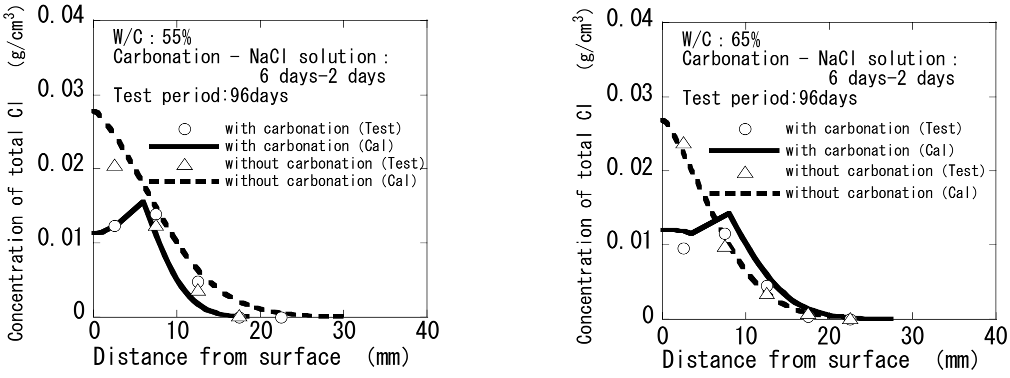
One of the predictions obtained with the model is shown in Fig.17. The calculated results clearly demonstrate the tendency of chloride ions to concentrate through the carbonation of hydrates. At the same time, Fig.18 shows that the calculated results agree well with the observations, indicating that the model has been appropriately established

Figure 19 shows a prediction for a case in which chloride ions were added at the concrete mixing stage. The experimental values given in the figure are from earlier research [14]. Again, it can be seen that



(a) (b)

Fig.20 Prediction result for the low chloride contaminated concrete



(a) (b)

Fig.21 Chloride distribution under the cycling complex deterioration test and the cycling CO_2-free wet-dry test

the calculated values agree with the experimental ones in overall tendency. However, chloride peak in the calculated curve is closer to the surface than in the experiments. The cause of this discrepancy seems to be that the carbonation acceleration mechanism due to NaCl is not taken into account in the model. The amount of NaCl added to the concrete mixed in this case was 8.48kg/m^3[14]. Adding such a large quantity of NaCl at the initial stage causes the carbonation rate to increase by either about 3 times [1] or about 1.5 times [19] (depending on the source) in comparison with concrete containing no NaCl. Therefore, it is apparent that the increase in carbonation rate will have to be taken into account for cases where a large amount of NaCl is present in the concrete. The predictions made by this model are suitable for concrete with low levels of chloride contamination, as in such cases the effect of the NaCl on carbonation rate is small. Results are given in Fig.20 for a low- contamination case: 1kg/m^3 NaCl. It can be seen that the concentration of soluble chloride ions is relatively low in the non-carbonated area due to immobilization, but is high in the carbonated area. In particular, the concentration of soluble chloride ions in the carbonated area is 3 times greater than in the non-carbonated area when the water-cement ratio of the mortar is 65%. These results suggest that complex deterioration mechanisms have a significant effect on concrete durability when the water-cement ratio is high or chloride ions are present from the initial stage.

(3)Future research

Figure 21 shows the chloride distribution in mortar during cyclic complex deterioration testing (2 days in salt solution and 6 days in the carbonation chamber). For the comparison, a cyclic CO_2-free wet-dry test was carried out. The specimens were exposed in air at the same temperature and relative humidity

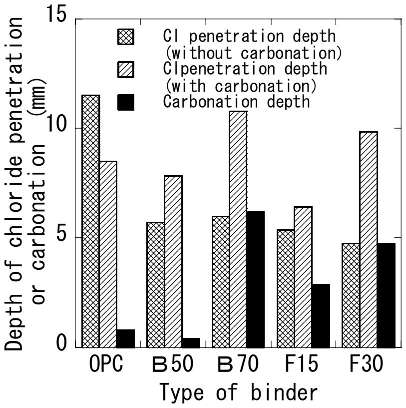


Fig.22 Effect of mineral admixture on carbonation and chloride penetration

as in the accelerated carbonation test (2 days in salt solution and 6 days in CO_2-free air). The results of this test are also shown in Fig.21. It is clear from the figures that carbonation controls chloride ingress. Generally, the chloride penetration rate is enhanced when the concrete is wet. On the contrary, the carbonation rate is higher when the concrete is dry. Consequently, the possibility of rapid degradation through a combination of salt damage and carbonation seems low. However, the cycling of accelerated carbonation (or air exposure) and salt water immersion in the experiment may not correspond will with actual environmental conditions. Future research is necessary to investigate actual environmental conditions.

Figure 22 shows carbonation depth and chloride penetration depth, as judged by $AgNO_3$ solution, under cyclic complex deterioration testing and cyclic CO_2-free wet-dry testing (1 day in salt solution and 6 days in carbonation chamber/CO_2-free air). In these tests, OPC mortar, blast-furnace slag cement mortar (BFS mortar), and fly-ash cement mortar (FA mortar) were used. The water-binder ratio of the mortars was 55% and the content of blast-furnace slag was 50% (B50) or 70% (B70), and the content of fly ash was 15% (F15) or 30% (F30). The initial curing period was 28 days at 20℃ in water. It can be seen that the chloride penetration depth of BFS mortar and FA mortar is less than that of OPC mortar in the absence of carbonation. In the OPC mortar, chloride penetration was suppressed when carbonation took place. On the other hand, the chloride penetration in BFS mortar and FA mortar accelerated when carbonation took place. The enhancing effect of carbonation on chloride penetration is particularly remarkable in cases B70 and F30. It has already been confirmed in past research that the pore volume of BFS mortar increases after carbonation [20]. Given this situation, further research is needed to look into the effect of mineral admixtures, as it is not considered in the prediction method described here.

6. CONCLUSIONS

(1) The quantity of chloride ions fixed by reaction in the AFm phase depends on the concentration of chloride ions in the liquid phase. The relationship is expressed by formula (10).
(2) The carbonation ratio of both AFm and Friedel's salt correlates with the pH of the liquid phase. The relation between them is expressed by formula (13).
(3) By combining models that characterize the fixing of chloride ions in the AFm phase and the carbonation of AFm and Friedel's salt into a single model for predicting carbonation and chloride penetration in concrete, it is possible to predict the distribution of chloride ions in concrete subject to simultaneous carbonation and chloride ion ingress.

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