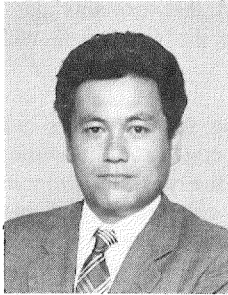
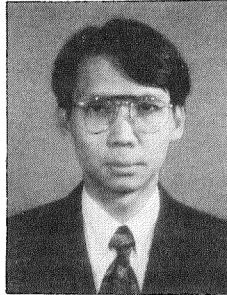


MODELING OF CHLORIDE ION MOVEMENT IN THE SURFACE LAYER
OF HARDENED CONCRETE

(Translation from proceedings of JSCE, No.585/V-38, February 1998)



Tsuyoshi MARUYA



Somnuk TANGTERMSIRIKUL



Yasunori MATSUOKA

The aim of this paper is to propose a model for simulating chloride ion movement in the surface layer of hardened concrete. The model is to be combined with an analytical method for the movement of chloride ions in hardened concrete to construct a complete model that is applicable to different environmental conditions. For chloride ion movement in the surface layer, two models are introduced. One is a surface condensation model that explains the phenomenon of higher chloride ion concentration in the surface layer than that of the submerged environment, using the concept of quasi-adsorption. The other is a cyclic wetting and drying model that explains the mechanism of chloride ion migration into concrete on the basis of capillary suction and evaporation.

Keywords :concrete, chloride ion, surface condensation, cyclic wetting and drying, simulation, fly ash, blast furnace slag

T. Maruya is a research engineer in the materials research department of the technology research center of Taisei Corporation, Yokohama, Japan. He obtained his doctor of Engineering degree from University of Tokyo in 1995. His research interests include the evaluation and protection of reinforced concrete structures subjected to corrosion, and prediction of the service life of concrete structures. He is a member of JSCE.

S. Tangtermsirikul is an associate professor in the civil engineering department of Sirindhorn International Institute of Technology, Thammasat University, Thailand. He received his Doctor of Engineering degree from the University of Tokyo in 1989. His fields of research include analytical and practical studies on the behavior of fresh and hardened concrete and new materials. He is a member of JSCE.

Y. Matsuoka is a general manager in the materials research department of the technology research center of Taisei Corporation. He received his doctor of Engineering degree from University of Tokyo in 1985. His research activities are on the chemistry of concrete, durability, development of new materials for utilization and self-compacting concrete. He is a member of JSCE.

1. INTRODUCTION

There have been many studies on the simulation of chloride movement in hardened concrete, with many those based on diffusion theory. However, none has been proved to be efficient at simulating the condition of structures in a real environment. The reason for this may be that there is still inadequate understanding of the interaction between chloride transport mechanisms and environmental conditions.

This paper aims at developing an analytical method for simulating the condensation of chlorides in both submerged and cyclic wetting and drying conditions. Beginning with a brief explanation of the previously developed analytical method for simulating overall chloride movement in hardened concrete, the focus will then move on to models for simulating chloride condensation in the cases of submerged and cyclic wetting and drying conditions. A model will be developed that explains the known phenomenon of higher chloride concentration in the surface layer than in the solution in which the concrete is submerged.

The process of developing the analytical method entailed by assembling the following quantified concepts together : a concept for the types of chloride in hardened concrete ; equations for the movement of chloride ions based on diffusion theory ; equations which are functions of the types and proportions of the concrete materials for obtaining material properties such as fixed chloride factors based on experimental results ; and concepts for computing the water content and the movement of water vapor in the pores. The resulting analytical method was then used to derive equations for apparent diffusion coefficients of chloride ions and water vapor in the hardened concrete based on the tested chloride ion distribution from a set of experiments specially designed to obtain these coefficients. The coefficients so obtained are considered to be material parameters dependent only on the mix proportion of the concrete ; they did not change with environmental conditions. It was proved that the derived equations for diffusion coefficients are applicable to every environmental condition without a need for adjustment. Finally, a method of accounting for cyclic wetting and drying environment was included to make the method suitable for actual situations. The analytical method had been verified as effective under various simulated specimens and environmental conditions.

This paper concentrates on one part of this analytical method[1] namely the characteristics of transport mechanisms of chlorides in the surface layer of hardened concrete.

2. ANALYTICAL METHOD FOR MOVEMENT OF CHLORIDE IONS IN CONCRETE

In this section, the overall structure of our analytical method for simulating chloride movement in concrete will be explained. This numerical method is applicable to various types of environment, including cyclic wetting and drying conditions. The process of assembling the various material models and theories concerning chloride movement will be explained.

2.1 Overall Structure of Analytical Method and Analytical Results

Illustrated in Fig.1 is a flow chart showing the steps involved in computation using the analytical method. Included are computations of the equilibrium between fixed and free chlorides in terms of the total-free chloride relationship, the effect of carbonation on the equilibrium, and the condensation characteristics of chlorides in the surface layer of concrete. Also used are diffusion theory, carbonation depth estimates, and computations of water content and relative humidity in the concrete needed to calculate the concentration of chlorides in the pores. Various environmental conditions can be simulated by setting the initial chloride conditions, shown on the right side of the flow chart in Fig.1, as indicated in Fig.2. For example, if we begin during a drying period of the wetting and drying cycle, the initial chloride ion concentration in the surface layer is considered to be equal to that of the environment, and there is no movement of chloride ions across the surface of concrete. When wetting begins, chloride ions move together with the wetting water into the dry portion of the concrete by capillary absorption. The movement of chloride ions in the concrete is computed at this stage using a discrete element technique to solve the differential diffusion equation. The element width is set to 1 cm and the time step is once per 1 day.

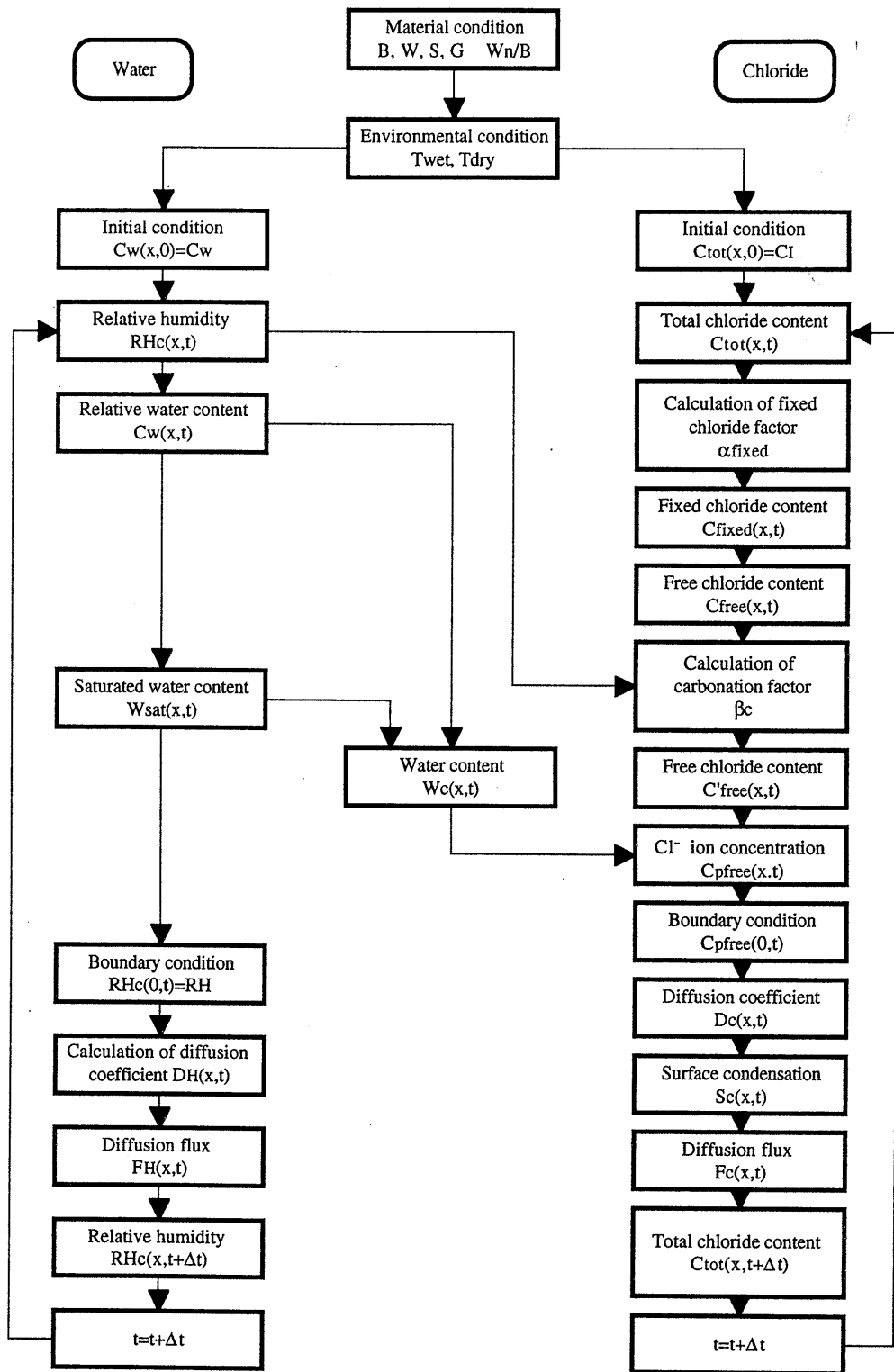


Fig.1 Flowchart of the analysis of chloride ion movement

For the material inputs, the unit binder content, B , unit water content, W , unit fine and coarse aggregate contents, S and G , and the binder reaction coefficient are essential. The binder reaction coefficient, W_n/B , is derived in terms of the ratio between nonevaporable water content, W_n , and the total binder content, B . The nonevaporable water content can be obtained by subtracting the evaporable water content, W_e , from the unit water content, W , after prolonged drying of a hardened concrete sample at 105°C to 110°C .

The three environmental conditions used in the simulation were the under-sea or submerged zone (tested by continuous submerging in salt water), the tidal and splash zones (tested by cyclic wetting and drying), and the atmospheric zone (tested by drying). T_{wet} and T_{dry} in Fig.1 represent the wetting and drying periods. Under continuously submerged conditions, only T_{wet} is input, whereas only T_{dry} is input for the continuous drying conditions. Both T_{wet} and T_{dry} are input in the case of cyclic wetting and drying conditions.

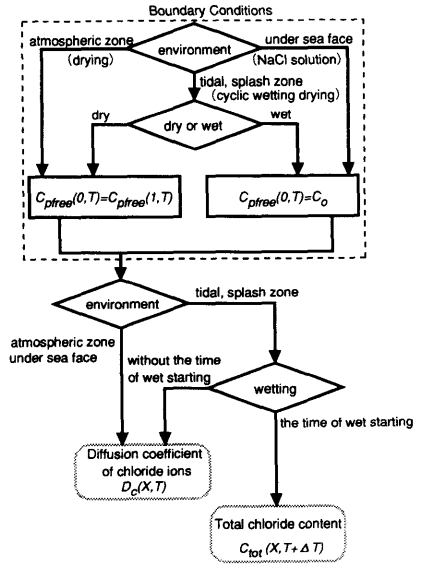


Fig.2 Flowchart of boundary conditions

2.2 Behavior and Equilibrium of Chloride Ions

From previous studies, it is known that chloride ions behave as follows. Chloride ions (Cl^-) are present in the pore solution of concrete together with other negative and positive ions such as OH^- and Na^+ , K^+ , Ca^{2+} , and an overall balance of negative and positive charge is maintained[2]. There is a unique equilibrium between fixed and free chloride ions for concrete made using the same mix proportion. The fixed chloride ions consist of Friedel's salt (solid chloride) and chlorides adsorbed between layers of the hydration products of calcium aluminate hydrate[3]. With the ingress of carbonation, which reduces the pH of the concrete, the equilibrium between fixed and free chloride changes because some Friedel's salt and adsorbed chlorides are freed into the pore solution, resulting in a higher concentration of chloride ions in the pore solution of the carbonated area[4]. All of this behavior has been considered in this analytical method.

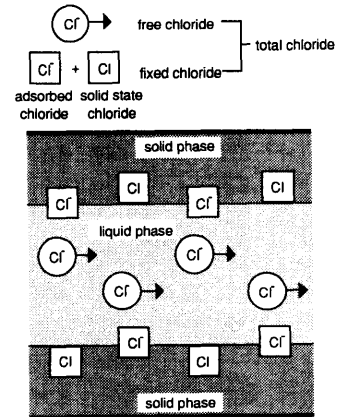


Fig.3 Classification of total chloride in concrete

Figure3 shows the classification of chlorides in the concrete. Fixed chlorides are considered to be non-moving in the concrete. Only the free chlorides, meaning the chloride ions in the pore solution, are able to move in the concrete. The fixed chlorides can be quantified made through the fixed chloride factor, α_{fixed} . Then, using the fixed chloride factor, the content of fixed and free chlorides can be derived as in Eq.(1) and Eq.(2)

$$C_{fixed}(x, t) = \alpha_{fixed}(x, t) \cdot C_{tot}(x, t) \quad (1)$$

$$C_{free}(x, t) = (1 - \alpha_{fixed}(x, t)) \cdot C_{tot}(x, t) \quad (2)$$

where $C_{fixed}(x, t)$ is the fixed chloride content (wt% of cement), $C_{free}(x, t)$ is the free chloride content (wt% of cement), $C_{tot}(x, t)$ is the total chloride content (wt% of cement), $\alpha_{fixed}(x, t)$ is the fixed chloride factor, x is the distance or element number from the exposed surface (cm), and t is time (days).

Figure4 demonstrates the effect of carbonation on the release of fixed chlorides into free chlorides. The ratio of chloride amount released by carbonation to the fixed chloride amount before carbonation is denoted as the carbonation factor, β_c . The carbonation factor is used to obtain the free and fixed chloride contents as shown in Eq.(3) and Eq.(4)

$$C'_{free}(x, t) = C_{free}(x, t) + \beta_c(x, t) \cdot C_{fixed}(x, t) \quad (3)$$

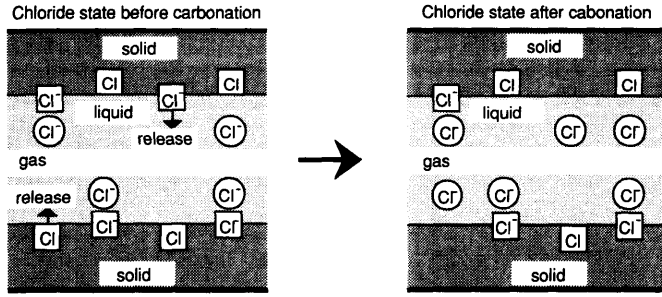


Fig.4 Chloride ion released from solid state chloride by carbonation

$$C'_{\text{fixed}}(x,t) = (1 - \beta_c(x,t)) \cdot C_{\text{fixed}}(x,t) \quad (4)$$

where $C'_{\text{free}}(x,t)$ is the free chloride content after carbonation (wt% of cement), $C_{\text{free}}(x,t)$ is the free chloride content before carbonation (wt% of cement), $C'_{\text{fixed}}(x,t)$ is the fixed chloride content after carbonation (wt% of cement), $C_{\text{fixed}}(x,t)$ is the fixed chloride content before carbonation (wt% of cement), and $\beta_c(x,t)$ is the fixed chloride factor.

The free chloride content after carbonation, as obtained from Eq.(3), can be converted into a the free chloride concentration as follows.

$$C_{\text{pfree}}(x,t) = (C'_{\text{free}}(x,t)/100) \cdot \Delta A \cdot \Delta x \cdot (B/1000)/35.5/W_c(x,t) \quad (5)$$

where $C_{\text{pfree}}(x,t)$ is the concentration of free chloride ions (mol/cm^3), A is the cross-sectional area normal to the diffusion direction of the element (cm^2), x is the element width (cm), B is the unit binder content (kg/m^3), and $W_c(x,t)$ is the water content of the element under consideration (g).

Since the carbonation factor, β_c , in Eqs.(3) and (4), and the free chloride concentration, $C_{\text{free}}(x,t)$ in Eq.(5), can be derived when the relative humidity in the concrete, $RH_c(x,t)$, is known, the free chloride concentration can be obtained if the water content in the concrete is known. Therefore, the behavior of moisture in the concrete will be discussed next. At the time under consideration, t , in a no-drying condition, the saturated water content in a concrete element can be computed using Eq.(6).

$$W_{\text{sat}}(x,t) = (W - B \cdot W_n/B)/1000 \cdot \Delta A \cdot \Delta x \quad (6)$$

where $W_{\text{sat}}(x,t)$ is the saturated water content (g), W is the unit water content of the concrete (kg/m^3), B is the unit binder content (kg/m^3), W_n/B is the water-to-binder ratio, ΔA is the cross sectional area of the element (cm^2), and Δx is the element width (cm). Then the water content in each element can be derived from Eq.(7)

$$W_c(x,t) = C_w(x,t) \cdot W_{\text{sat}}(x,t)/100 \quad (7)$$

where $W_c(x,t)$ is the water content of the element under consideration (g), $C_w(x,t)$ is the relative water content of the element (%), and $W_{\text{sat}}(x,t)$ is the saturated water content of the element (g).

It is known that the water content as derived from Eq.(7) does not have a linear relationship with relative humidity in the concrete pores. And since the transport mechanism of water in pores is related to the movement of water vapor, the vapor pressure or relative humidity is necessary to simulate the movement of water in the concrete. Therefore, the relationship between water content and relative humidity in the concrete was also implemented[5].

The movement of water in the concrete pores at any time t is assumed to be diffusion-based and dependent on the vapor pressure (humidity) in the pores as

$$FH(x,t) = -DH(x,t) \cdot (RHc(x,t)/100 - RHc(x - \Delta x,t)/100) / \Delta x \quad (8)$$

where $FH(x,t)$ is the flux of vapor ($\text{cm}^3/\text{cm}^2/\text{day}$), $DH(x,t)$ is the apparent diffusion coefficient of the water vapor (cm^2/day), and $RHc(x,t)$ is the relative humidity of the concrete element (%). A higher diffusion coefficient is also assumed at the exposed surface of the concrete in this analysis.

Then the relative humidity in the pores of concrete element x at time $t+\Delta t$ can be obtained from the following equation:

$$RHc(x,t+\Delta t) = RHc(x,t) + 100 \cdot (FH(x,t) - FH(x+\Delta x,t)) \cdot \Delta t / \Delta x \quad (9)$$

where $RHc(x,t)$ is the relative humidity of concrete element x (%), Δx is the element width (cm), and Δt is the time interval (day).

2.3 Movement of Chloride Ions and Diffusion Theory

Previous research was shown that chloride ions appear to move by diffusion as a result of the ion concentration gradient[6,7], and they move together with the non-hydrated water in the pores[8]. Except in the case of cyclic wetting and drying conditions, chloride ions are assumed to move by the diffusion process in this study.

Since the diffusion process of chloride ions in concrete pores is not the same as that in water due to the complexity of the pore structure (which means the diffusion path is not straight and not always continuous) and diffusion along the path of capillary pores is not considered in the simulation, the apparent diffusion coefficient, which is smaller than the diffusion coefficient of chloride ions in water, was applied. The value of the apparent diffusion coefficient of chloride ions in hardened concrete is lower when the pore structure is more complex and less continuous. In this study, the following factors, though they have an effect on the apparent diffusion coefficient of chloride ions in hardened concrete, are not considered: temperature, degree of hydration, and the concentration of chloride ions and other ions in the pores.

Fick's First law of diffusion was adopted to simulate chloride ion movement in the concrete as[9]

$$F_c = -D_c \cdot (\partial C_{pfree} / \partial x) \quad (10)$$

where F_c is the flux of chloride ions diffusing across a unit cross-sectional area of concrete in unit time ($\text{mol}/\text{cm}^2/\text{day}$), D_c is the apparent diffusion coefficient of chloride ions in the concrete (cm^2/day), C_{pfree} is the chloride ion concentration (mol/cm^3), and x is the depth from the exposed surface of the concrete (cm).

The diffusion coefficient of the exposed surface layer of the concrete is assumed to be larger than that of the bulk of concrete because chloride ions must move along the pore path within the concrete, while they can move freely in all directions at the boundary. So,

$$D_c(1,t) > D_c(x,t) \quad x \geq 2 \quad (11)$$

It was confirmed in the laboratory that the chloride ion concentration near the surface layer may be higher than that of the solution itself when a concrete specimen is submerged continuously in it[10]. This behavior cannot be explained by diffusion theory alone. The concept of surface condensation due to ion adsorption is introduced to take this behavior into account.

$$F'_c = F_c + S_c \quad (12)$$

where F'_c is the total flux of chloride ions entering the concrete at the surface and is the sum of the fluxes due to diffusion and ion adsorption ($\text{mol}/\text{cm}^2/\text{day}$), F_c is the flux of chloride ions due to diffusion only ($\text{mol}/\text{cm}^2/\text{day}$), and S_c is the the flux of chloride ion due to ion adsorption only ($\text{mol}/\text{cm}^2/\text{day}$).

The ion adsorption mechanism arises as a result of a property of the pore walls, which are known to be electrically positive. The positive charge at the pore surface draws chloride ions from the surrounding environment into the concrete, and these condense in the surface layer[11]. When the concentration of chloride ions in the submerging solution is higher than that of the surface layer of the concrete, chloride ions move into the concrete by both diffusion and ion adsorption. On the other hand, when the chloride ion concentration of the submerging solution is lower than that in the pores of the surface layer, chloride ions move out of the concrete by diffusion but at the same time move into the concrete by ion adsorption. The ion adsorption flux falls as the chloride ion concentration in the pores increases. Therefore, the concentration of chloride ions in the surface layer gradually increases until equilibrium is reached between the diffusion and ion adsorption mechanisms. This leads to a rather constant concentration of chloride ions in the surface layer over the long term.

Thus, the diffusion equation in Eq.(10) can be modified to take the effect of ion adsorption into account as follows

$$F_c(x,t) = -D_c(x,t) \cdot (C_{pfree}(x,t) - C_{pfree}(x-\Delta x,t)) / \Delta x \quad (13)$$

$$F_c(1,t) = -D_c(1,t) \cdot (C_{pfree}(1,t) - C_0) / \Delta x + S_c(1,t) \quad (14)$$

where x is the depth from the exposed surface (cm), t is the time interval (day), $F_c(x,t)$ is the flux of chloride ions due to diffusion (mol/cm²/day), $D_c(x,t)$ is the apparent diffusion coefficient of the chloride ions (cm²/day), $C_{pfree}(x,t)$ is the concentration of chloride ions (mol/cm³), C_0 is the chloride ion concentration of the submerging solution (mol/cm³), and $S_c(1,t)$ is the flux of chloride ions due to ion adsorption (mol/cm²/day).

Then, Eq.(15) and Eq.(16) are used to compute the chloride content of element x at time $t+\Delta t$.

$$C_c(x,t+\Delta t) = C_c(x,t) + (F_c(x,t) - F_c(x+\Delta x,t)) \cdot 35.5 \cdot \Delta A \cdot \Delta t \quad (15)$$

where $C_c(x,t)$ is the total chloride content (in terms of weight) in element x at time t (g).

$$C_{tot}(x,t+\Delta t) = 100 \cdot C_c(x,t+\Delta t) / (B/1000) / \Delta A / \Delta x \quad (16)$$

where $C_{tot}(x,t)$ is the total chloride content (in terms of weight % of binder) in element x at time t and B is the unit binder content (kg/m³).

3. MODELING OF CHLORIDE CONDENSATION IN THE EXPOSED SURFACE LAYER

In this section, the reason why the model of chloride condensation in the surface layer of concrete, the modeling procedure, and the experimental methods of verifying the model are explained. The condensation does not occur by cyclic wetting and drying but does by other mechanism.

3.1 Concept of Chloride Condensation Model for the Exposed Surface Layer

Analytical methods for chloride movement in concrete based on diffusion theory have been popular for a long time. Using such methods, apparent diffusion coefficients are commonly derived from the distribution of chlorides in the concrete. In doing so, a constant chloride ion content is usually assumed at the exposed surface of the concrete as the boundary condition. Further in Japan, the free chloride content is usually obtained using the test method proposed by the Japan Concrete Institute (JCI) for the water soluble chloride content in concrete[12]. Some analytical methods have even used the total chloride content in the diffusion process. However, actual behavior is not as assumed. For example, the soluble chloride content obtained using the JCI method has been proven to be too low, with some studies on actual structures reporting results that are twice as high[13], as the free chloride ion content in the pores of the concrete. Also, the free chloride concentration in the surface layer may even become higher than that of the submerging solution as mentioned earlier. It is impossible to explain this using diffusion theory alone the concept of chloride condensation must be introduced into the analytical method.

As already explained in Section 2, the movement of chloride ions in the submerged case can be

simulated by considering both diffusion and the condensation of chloride ions by ion adsorption, as illustrated in Fig.5 and expressed by Eq.(17).

$$F'_c = F_c + S_c(C_{free}) \quad (17)$$

where F'_c is the total flux of chloride ions entering the concrete at the surface and is the sum of the fluxes due to diffusion and ion adsorption ($\text{mol}/\text{cm}^2/\text{day}$), F_c is the flux of chloride ions due to diffusion only ($\text{mol}/\text{cm}^2/\text{day}$), and S_c is the the flux of chloride ion due to ions adsorption only ($\text{mol}/\text{cm}^2/\text{day}$) and is a function of free chloride content, C_{free} is the free chloride content at the exposed surface of the concrete (wt% of cement).

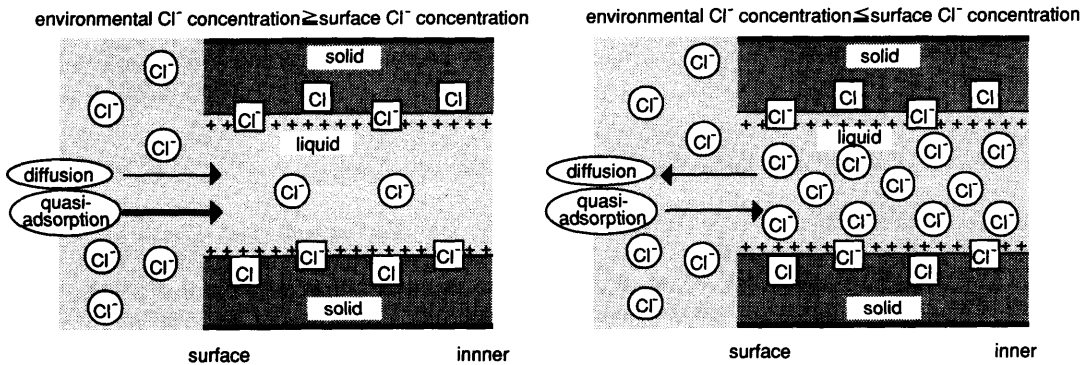


Fig.5 Condensation mechanism of chloride ions in the surface layer of concrete

3.2 Verification Experiments of Surface Condensation Model

3.2.1 Materials and Mix Proportions

The binders used in the tests were ordinary Portland cement Type I (OP), fly ash (FA), and blast furnace slag. Sand from the Ohi river (S) and crushed rock from Nishijima (G1, G2) were used as the fine and coarse aggregates, respectively. Table 1 shows the physical properties of the aggregates. Piped water supplied to the laboratory was used for mixing and curing.

Table 1 Aggregate properties

Material	Unit weight (kg/l)	Specific gravity surface dried condition	Specific gravity over dried condition	Percentage of absorption (%)	Solid content (%)	Fineness modulus
S	1.77	2.60	2.56	1.43	77.3	2.66
G1	1.55	2.67	2.85	0.70	58.5	7.14
G2	1.49	2.84	2.81	1.07	57.1	6.05

Four types of mortar specimen and one type of concrete specimen were made with the mix proportions shown in Table 2. OPM, OFM, OBM, and OFBM are the mortar specimens made from cement only, cement with fly ash, cement with blast furnace slag, and cement with fly ash and blast furnace slag, respectively. OPC is the concrete specimen with cement as the only binder. The mixture proportions of the mortar specimen is equal to that of the part of mortar in concrete.

Table 2 Mixture proportions

No.	G_{max} (mm)	W/B (%)	s/a (%)	Unit weight (kg/m ³)					
				W	B			S	G
					OP	FA	BS		
OPM	—	50	—	274	548	—	—	1355	—
OFM	—	50	—	268	431	108	—	1332	—
OBM	—	50	—	272	272	—	272	1346	—
OFBM	—	50	—	267	160	107	268	1323	—
OPC	20	50	48	175	350	—	—	866	G1:481 G2:475

3.2.2 Specimen Preparation

Mortar specimens were made using a 30-liter mortar mixer in batches of 16 liters. Mixing was according to JIS R5201. The 10x10x40cm steel formwork was divided with vinyl plates into eight 5x10x10cm specimens which were cast at the same time. The specimens were then coated with epoxy after form removal, leaving one 5x10cm face as the exposed surface for all specimens. A side face was selected for exposure in order to exclude the influence of casting direction. All specimens were cured under perfectly sealed conditions for 28 days.

Concrete specimens were made using a 100-liter pan-type mixer in batches of 50 liters. Binders and

aggregates were mixed for 30 seconds, then water was added and mixing continued for 120 seconds to obtain the fresh concrete mixture. The slump and air content of the fresh concrete were 78mm and 1.5%, respectively. The 100x100x400mm steel formwork was divided with the vinyl plates to produce two 100x100x200mm concrete specimens. Only one 100x100mm face was left exposed, with the rest coated in epoxy.

To prevent moisture exchange between specimens and the environment during curing, and to stabilize chemical reactions within the specimens, the open surfaces of the specimens were sealed with plastic sheeting, and all specimens were stored in plastic boxes. These were kept in a curing environment of 20°C and 100%RH for 28 days.

3.2.3 Measurements and Methods

After sealed curing, the one surface of each specimen was exposed and all specimens were submerged in a 3% NaCl solution under a control 20°C environment. This will be referred to as the chloride penetration test here after. After submerging for 28, 91, 180, and 365 days, the mortar specimens were cut into layers at intervals of 5mm down to a depth of 20mm from the exposed surface and at intervals of 20mm to a depth of 50mm. The concrete specimens were cut at intervals of 10mm down to 50. A hand diamond cutter was used for cutting. The total chloride and soluble chloride content of each cut layer was analyzed using the JCI method[12].

3.3 Modeling of Surface Chloride Condensation

A model for surface chloride condensation has been proposed by the authors on the basis of the chloride penetration test results[1]. The condensation effect not explainable by the diffusion process was modeled by the concept of ion adsorption.

It is necessary to establish the relationship between fixed and total chloride, in this case in terms of the ratio between fixed and total chlorides (α_{fixed}), in order to compute the free chloride concentration for use in chloride movement analysis. The apparent diffusion coefficient of free chloride ions in the concrete is also necessary. Methods for deriving these two coefficients have been given in a previous study by the authors[1]. The values of α_{fixed} and diffusion coefficients for the different types of binder tested are given in Fig.6 to Fig.9 and Table 3, respectively.

Based on the analysis of the chloride penetration test results, S_c in Eq.(17) was derived for each type of binder as in Eqs.(18), (19), (20), and (21) for cement only, cement + fly ash, cement + blast furnace slag, and cement + fly ash + blast furnace slag, respectively.

$$S_c = 1.4 \cdot 1.0 \cdot 10^{-5} \cdot \exp(-1.15 \cdot C_{free}(1,t)) \quad (18)$$

$$S_c = 1.4 \cdot 0.6 \cdot 10^{-5} \cdot \exp(-1.15 \cdot C_{free}(1,t)) \quad (19)$$

$$S_c = 1.4 \cdot 0.3 \cdot 10^{-5} \cdot \exp(-1.15 \cdot C_{free}(1,t)) \quad (20)$$

$$S_c = 1.4 \cdot 0.2 \cdot 10^{-5} \cdot \exp(-1.15 \cdot C_{free}(1,t)) \quad (21)$$

3.4 Verification of Surface Condensation Model

Figure10 shows the relationship between the flux due to ion adsorption and the free chloride content of the surface layer. The flux due to ion adsorption is largest for cement only and is lower for cement + fly ash, cement + blast furnace slag and cement + fly ash + blast furnace slag, in that order. This can be explained by the lower positive charge at the pore surface in the blended binders, especially when the pozzolan ratio is higher or the cement ratio is smaller.

Table 3 Diffusion coefficient of chloride ions in analysis

Specimen	Apparent diffusion coefficient of Cl ⁻ (cm ² /day)	
	surface $D_c(X,T)$;X=1	inner $D_c(X,T)$;X>1
OPM	3.20×10^3	2.67×10^3
OPC	2.06×10^3	1.72×10^3
OFM	1.37×10^3	1.14×10^3
OBM	4.58×10^4	3.82×10^4
OFBM	3.82×10^4	1.91×10^4

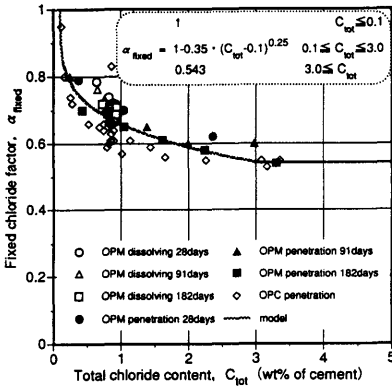


Fig.6 Fixed chloride factor and total chloride content (OPM,OPC)

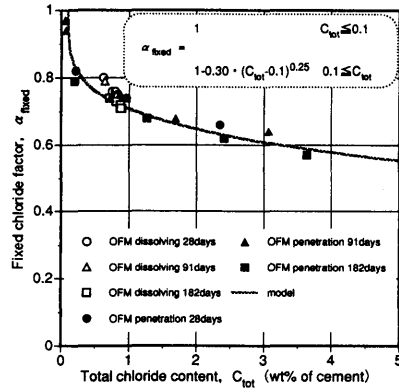


Fig.7 Fixed chloride factor and total chloride content (OFM)

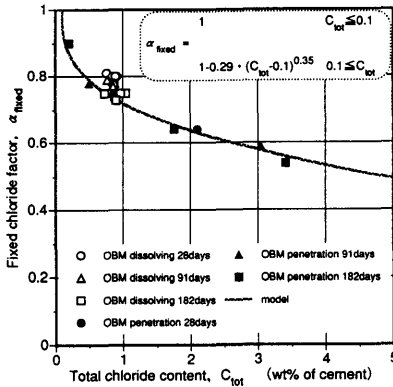


Fig.8 Fixed chloride factor and total chloride content (OBM)

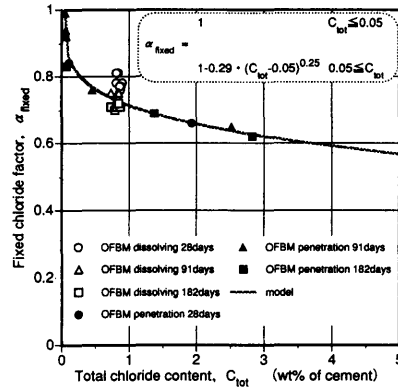


Fig.9 Fixed chloride factor and total chloride content (OFBM)

Figure 11 to Fig. 15 show the test and analytical results for free and total chloride contents the surface layer versus submerging time for OPM, OPC, OFM, OBM and OFBM specimens, respectively. Here, the surface layer is the layer from the exposed surface to a depth of 10mm. Free chloride contents are converted from the test results of soluble chloride content [1]. As shown in Fig. 11 and Fig. 12, the contents of free and total chlorides increase until approximately 182 days. After that, the chloride contents remain almost constant at a value higher than the chloride concentration of the solution in which the specimens were submerged. For the specimens with fly ash (OFM and OFBM) in Fig. 13 and Fig. 15, the free chloride contents increase until 182 days, but are lower at 365 days and nearer the value of the solution. This is because the chloride ion flux due to ion adsorption is lower over the long term due to the pozzolanic reaction of the fly ash. This pozzolanic reaction is considered to be very active from 28 to 91 days. As the reaction proceeds, SiO_2 in the fly ash reacts with the Ca(OH)_2 produced by the hydration of cement [14]. The Ca(OH)_2 content is thus reduced by the pozzolanic reaction. This reduces the ion adsorption effect in specimens with fly ash, so diffusion of chloride ions back into the solution takes place over the long term. On the other hand, specimens with OBM do not exhibit a tendency to reduced free chloride ions after 182 days because the pozzolanic reaction of blast furnace slag is not as reactive as that of fly ash. This indicates that the effect of reduced ion adsorption in fly ash blended binder has to be taken into account in the future.

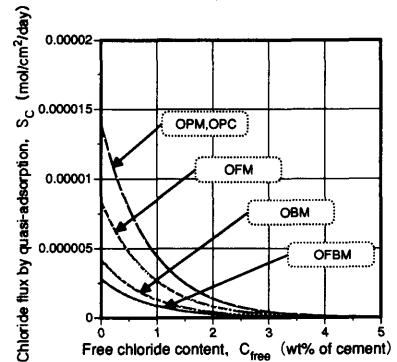


Fig.10 Chloride ion flux by quasi-adsorption in the surface

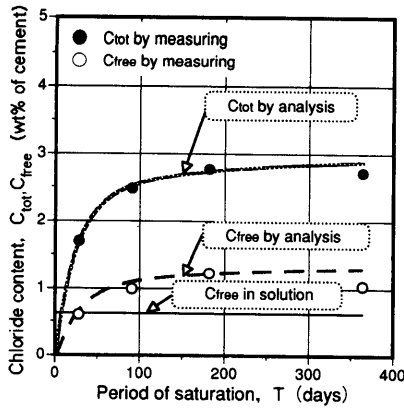


Fig.11 Variation of chloride content in the surface layer (OPM)

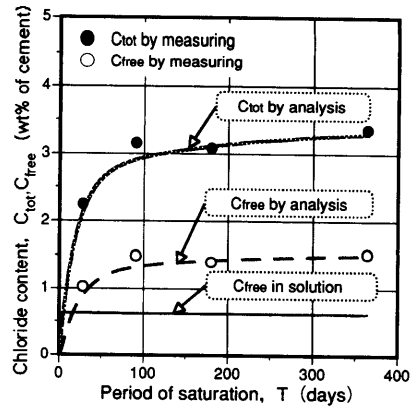


Fig.12 Variation of chloride content in the surface layer (OPC)

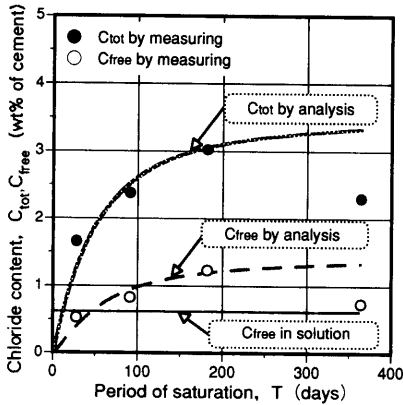


Fig.13 Variation of chloride content in the surface layer (OFM)

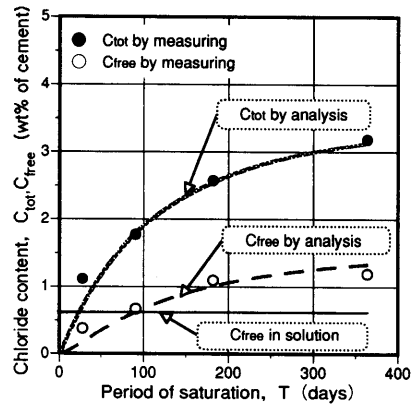


Fig.14 Variation of chloride content in the surface layer (OBM)

4. ANALYSIS OF CHLORIDE ION MOVEMENT IN CYCLIC WETTING AND DRYING

The analysis in this section is proposed for investigation of the splash zone, which is the most critical zone as regards steel corrosion, and of the marine tidal zone. These two zones can be reasonably simulated as an alternating wet and dry condition.

4.1 Concept of Model for Wetting and Drying Environment

In the first drying period, water evaporates from the exposed surface of the concrete into the environment, causing a reduction in the relative water content in the concrete near the exposed surface. When wetting occurs, salt water enters the dried portion of the concrete from the environment, saturating or nearly saturating the concrete within a relatively short time period. During the next drying cycle, the water evaporates out of the concrete, leaving salt in the dried portion. This process is illustrated in Fig.16. So, when alternating from drying to wetting, the total chloride content in the surface layer and near the surface layer increases suddenly. Therefore, in the wetting and drying model, Eq.(22) and Eq.(23) are applied for the chlorides and Eq.(24) is applied for water.

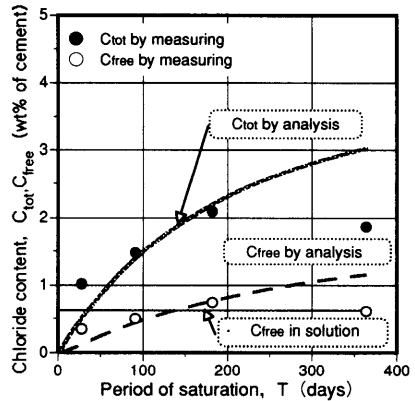


Fig.15 Variation of chloride content in the surface layer (OFBM)

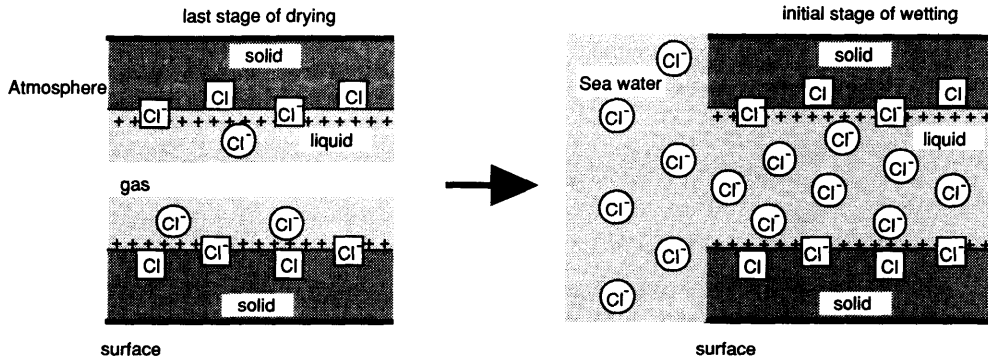


Fig.16 Mechanism of chloride penetration into concrete by cyclic wetting and drying

$$C_{tot}(x,t+\Delta t) = C'_{tot}(x,t) + C''_{tot}(x,t) \quad (22)$$

where t is the last time step of the drying period (day), $C_{tot}(x,t+\Delta t)$ is the total chloride content at the beginning of the wetting period (wt% of cement), $C'_{tot}(x,t)$ is the total chloride content at the end of the drying period (wt% of cement), and $C''_{tot}(x,t)$ is the total chloride content of the salt water that saturates the dried portion of concrete at the beginning of the wetting period (wt% of cement).

$$C''_{tot}(x,t) = C_0 \cdot (1 - C'_w(x,t)) \cdot C_{wsat} \cdot 35.5/B \cdot 100 \quad (23)$$

where C_0 is the chloride ion concentration of the sea water (the solution in which the concrete is submerged) (mol/cm^3), $C'_w(x,t)$ is the relative water content at the end of the drying period, C_{wsat} is the unit saturated water content ($= W - W_n$, kg/m^3), and B is the unit binder content (kg/m^3)

$$C_w(x,t+\Delta t) = 1 \quad (24)$$

where $t+\Delta t$ is the beginning of the wetting time (day).

4.2 Verification Experiments of Wetting and Drying Model

To verify the wetting and drying model, concrete specimens with the OPC mix proportion as shown in Table 2 were made. After sealed curing for 28 days, the specimens were subjected to cyclic wetting and drying conditions. One cycle consisted of 14 days, with 7 days of drying and 7 days of wetting. The measurements of total and free chlorides were made after the 2nd, 7th, 13th, and 42nd cycle, which is consistent with 28, 98, 182, 378 and 588 days after curing. The drying environment was 20°C , 60%RH, and 0.06 CO_2 concentration. Wetting was in 20°C salt water. The procedure for measuring total and free chlorides was the same as in the verification tests for surface condensation.

Figure 17 shows the test and analytical results for total and free chloride contents in the exposed surface layer of the concrete specimens subjected to wetting and drying. The surface layer was defined to have a thickness of 10 mm from the exposed surface. The analysis showed that at the beginning of wetting, the chloride content in the surface layer increased suddenly, while it gradually fell during drying as the chloride ions moved deeper into the concrete. For comparison, the increase in chloride content in the cyclic wetting and drying test was slower than the chloride penetration (Fig.12) early on at the beginning period, but the chloride content did not reach a constant value, as in the case of the chloride penetration test, but kept on rising with time.

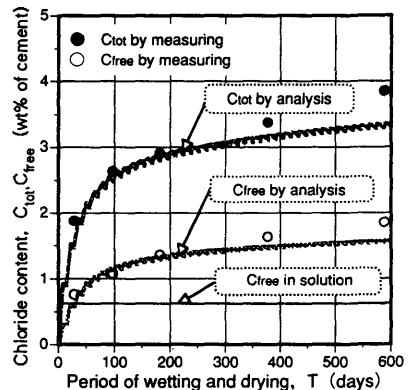


Fig.17 Variation of chloride content in the surface layer

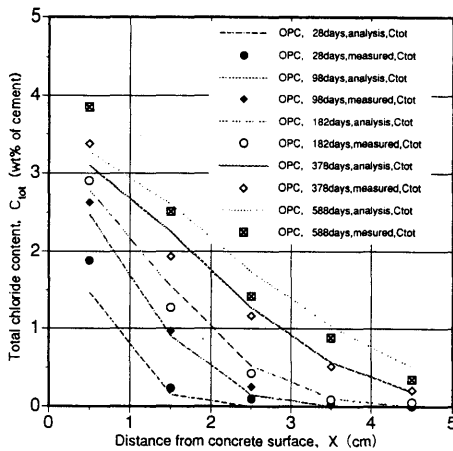


Fig.18 Total chloride content distribution in wetting and drying test

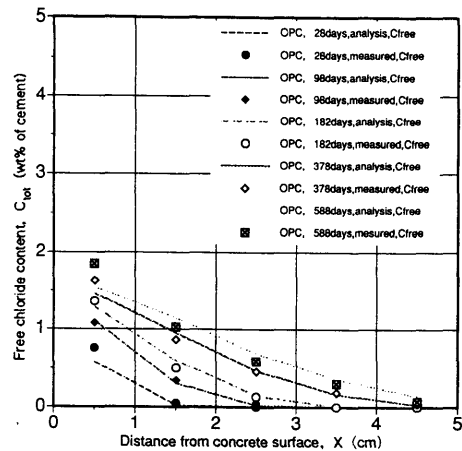


Fig.19 Free chloride content distribution in wetting and drying test

Fig.18 and Fig.19 show the test and analytical results for total and free chloride distributions, respectively, below the exposed surface of the tested concrete specimens at 28 days (4 cycles), 98 days (7 cycles), 182 days (13 cycles), 378 days (27 cycles), and 588 days (42 cycles). Figure 20 shows the analyzed distribution of chloride ion concentration. It should be noted here that all analysis of the cyclic wetting and drying condition considered the effect of carbonation in the drying period (20°C, 60%RH, 0.06 CO₂) and also the ion adsorption effect in the wetting period.

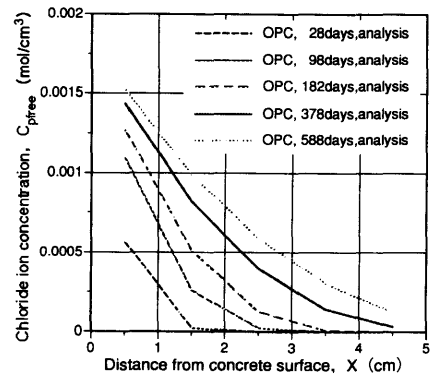


Fig.20 Cl⁻ concentration distribution in wetting and drying test

4.3 Application of Analysis to Cyclic Wetting and Drying Environment

In the actual environment, the periods of wetting and drying of the concrete surface are complicated. The moisture and ambient temperature also vary greatly in the real environment. The process of chloride penetration into the concrete is also different for different types of structure and different parts of structures. To be able to predict steel corrosion in reinforced concrete structures, it is necessary to analyze the movement of chloride ions in the concrete under these complicated conditions. In this study, the classification of marine environments into submerged, tidal, and splash zones is illustrated in Fig.21. This classification is different from the classification made by the Japan Concrete Institute [15].

In the submerged zone (under the sea surface), the concrete is always saturated. The mechanisms of chloride movement in the surface layer are assumed to be ion adsorption and diffusion, whereas only diffusion is considered for the inner bulk concrete. This is the same assumption as made in the submerging (chloride penetration) simulation.

In the tidal zone, concrete structures are subjected to wetting and drying, normally at a frequency of 2 cycles/day. Since the time step in the analytical computer program was fixed at 1 day, it is assumed that the 1-day wetting + 1-day drying cycle simulates the conditions of the tidal zone closely enough. Nevertheless, it is possible to modify the time step so that 2 cycles/day of wetting and drying can be simulated.

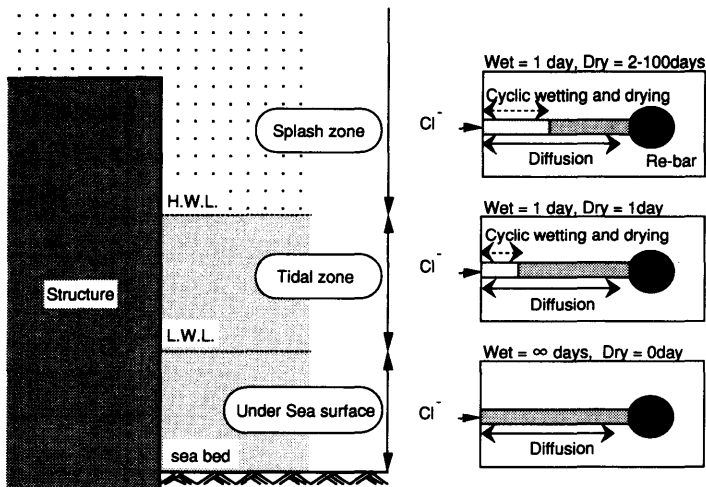


Fig.21 Classification of marine environment and mechanism of chloride ion movement

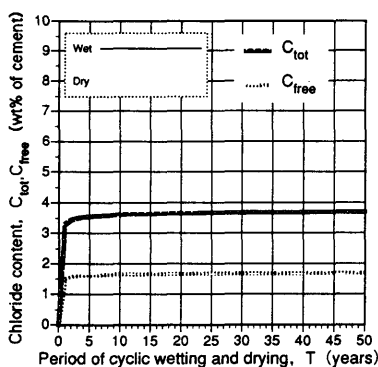


Fig.22 Variation of total chloride content in the surface layer (under sea surface)

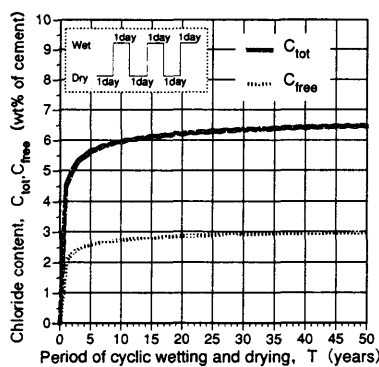


Fig.23 Variation of total chloride content in the surface layer (tidal zone)

In the splash zone, wetting and drying conditions may apply too. However, the drying period is usually longer in this case than that considered for the tidal zone. Even when in similar splash zones, structures may experience different microscopic environmental conditions. In this analysis, it is assumed that the cycles of wetting and drying in the splash zone can be simulated as 1 day of wetting and x days of drying, where x ranges from 2 to 100 days depending on the details of the environment at the structure surface.

Figure22 to Fig.24 show examples of simulated results for concrete structures in the various zones i.e. submerged, tidal, and splash zones, using the assumed behavior mentioned earlier in this section. The wetting and drying cycles for the splash zone in Fig.24 were assumed to be 1-day wetting + 5-day drying. From the simulated results in the figures, it can be seen that chloride penetration is more serious in the tidal and splash zones than in the submerged zone, and is particularly serious in the splash zone. The chloride content of the surface layer of the concrete in the submerged zone reaches a constant value at some time, whereas it tends to increase gradually in the splash zone even up to 50 years.

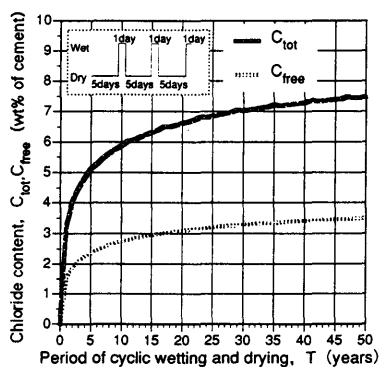


Fig.24 Variation of total chloride content in the surface layer (splash zone)

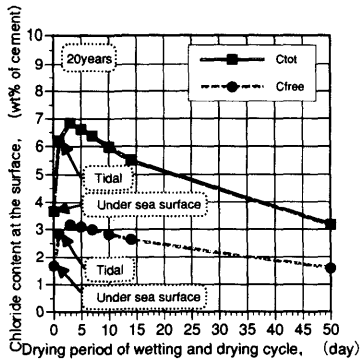


Fig.25 Chloride content in the surface layer and drying period (20years)

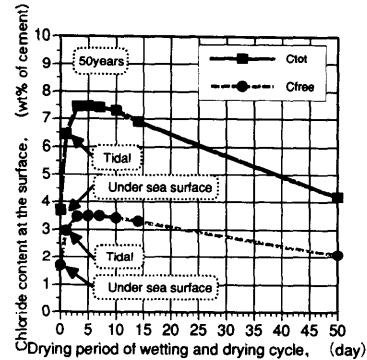


Fig.26 Chloride content in the surface layer and drying period (50years)

Figure 25 and Fig. 26 illustrate the simulated results of total and free chloride contents in the concrete surface layer when subjected to cyclic wetting and drying for 20 years and 50 years, respectively. The parameter on the horizontal axis is the length of the drying period with a fixed wetting period of 1 day. It is clear from the figures that a drying period of 5 days results in the greatest chloride content in the surface layer of the concrete.

5. CONCLUSIONS

(1) It was confirmed that the chloride ion concentration in the surface layer of concrete continuously submerged in salt water can exceed that of the salt water in which it is submerged. This is considered to have an effect on the chloride content of the inner concrete, so modeling of this surface chloride condensation is important. The condensation effect is caused by an ion adsorption mechanism driven by the properties of the pore walls, which are known to be electrically positive. The positive charge at the pore surface draws chloride ions into the concrete from the solution and causes condensation in the surface layer. Thus, movement of chloride ions in the submerged condition is due to both diffusion and ion adsorption.

(2) Based on the relationship between fixed and total chloride content derived from chloride dissolving and chloride penetration tests, together with the apparent diffusion coefficient derived from the chloride dissolving tests, the flux due to ion adsorption was derived as a function of the free chloride content of the concrete surface layer. The ion adsorption effect was smaller in blended binders than in a cement-only mixture. Among the blended binders, the effect of ion adsorption was smallest in the cement + fly ash + blast furnace slag binder, followed by the cement + blast furnace slag binder, and the cement + fly ash binder, respectively. However, the flux due to ion adsorption in fly ash blended binders had a tendency to fall over the long term due to the pozzolanic reaction.

(3) Cyclic wetting and drying conditions were simulated by assuming that when the change from drying to wetting conditions took place, salt water from the environment immediately moved into the dried portion of the concrete, suddenly saturating the dried portion. In simulating chloride movement under cyclic wetting and drying conditions, a number of results were applied: the relationship between fixed and total chloride content derived from the chloride dissolving and chloride penetration tests; the apparent diffusion coefficient derived from the chloride dissolving test; the surface condensation model derived from the chloride penetration test; the carbonation model derived from the carbonation test; and the apparent diffusion coefficient for the diffusion of water vapor. The simulated results were found to be satisfactory.

(4) The analytical method can be applied to the simulation of chloride movement in various actual marine environments, i.e. the submerged, tidal and splash zones, by varying the length of the wetting and/or drying periods. It was clear from the analysis that with a constant wetting period of 1 day, the peak chloride content was obtained when the drying period was 5 days.

Acknowledgment

We would like to thank Professor Taketo Uomoto, Professor Hjime Okamura, Professor Itaru Yasui, Professor Isaomi Mushiake, and Professor Kohichi Maekawa for their teachings of the theme of this thesis. The first author is especially thankful to them for advises when he wrote the doctor thesis.

References

- [1] Maruya, T., Tangtermsirikul, S., and Matsuoka, Y., "Simulation of Chloride Movement in Hardened Concrete," Concrete Library of Japan Society of Civil Engineering, No.20, 1992, pp.57-70
- [2] Matsuoka, Y., and Naitoh, T., "Characteristics of Pore Solution of Concrete under Various Salt Environment", Proceedings of the Japan Concrete Institute, Vol. 14, No.1, 1987, pp.75-78 (in Japanese)
- [3] Page, C.L., and Vennesland, Ø., "Pore Solution Composition and Chloride Binding Capacity of Silica Fume Cement Pastes", Material and Construction, Vol.16, No.91, 1983, pp.19-25
- [4] Kobayashi, K., Shiraki, R., Uno, Y., and Kawai, K., "Condensation due to Carbonation of Concrete Added with Chloride (I)", Research Report of the Institute of Industrial Science, University of Tokyo, Vol.40, No.11, 1988, pp.33-36 (in Japanese)
- [5] Saeki, T., Ohga, H., and Nagataki, S., "Mechanism and Prediction of Carbonation Intrusion in Hardened Concrete", Proceedings of JSCE, No.414, Vol.12, 1990, pp.99-108 (in Japanese)
- [6] Zdenek, P Bazant, "Physical Model for Steel Corrosion in Concrete Sea Structures-Theory", Journal of Structure Division, ASCE, Vol.105, No.ST6, 1979, pp.1137
- [7] Browne, R.D., "Design Prediction of the Life for Reinforced Concrete in Marine and Other Chloride Environments", Durability of Building Materials, Vol.1, 1982, pp.113-125
- [8] Maekawa, K., Ozawa, K., and Kunishima, M., "Prediction of Time Dependent Deterioration System Considering Multi Parameters", Proceedings of the Symposium on Life time Prediction and Durability Design of Concrete Structures, 1988, pp.39-46 (in Japanese)
- [9] Crank, J., The Mathematics of Diffusion [Second Edition], Oxford University Press, 1975
- [10] Nagataki, S., Otsuki, N., and Wee, T., "Condensation and Binding of Intruded Chloride ion in Hardened Cement Matrix Materials", Proceedings of JSCE, No.414, Vol.12, 1990, pp.205-215
- [11] Gotoh, S., Shige, K., J., Takagi, T., and Daimon, M., "Diffusion of Ion and Pore Size Distribution of Hardened Cement Paste", Annual Report on Cement Technology, Vol.36, 1982, pp.49-52 (in Japanese)
- [12] Japan Concrete Institute, Corrosion of Concrete Structures , Standards and Test Methods for Corrosion Protection (Guide), 1987 (in Japanese)
- [13] Maruya, T., Tangtermsirikul, S., and Matsuoka, Y., "Simulation of Chloride Penetration in Hardened Concrete", Proceedings of the 3rd CANMET/ACI International Conference on Durability of Concrete, 21-26 May 1994, Nice, France, pp.519-538
- [14] Maruya, T. and Matsuoka, Y., "Evaluation of Durability of Binding Materials based on Analysis of Liquid and Solid Phases", Proceedings of JSCE, No.478, Vol.21, 1993, pp.41-50 (in Japanese)
- [15] Japan Concrete Institute , Recommendation on Corrosion Protection of Concrete Structures in Marine Environment (Guide), Revised Version, 1990 (in Japanese)