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SIMULATION OF CHLORIDE MOVEMENT IN HARDENED CONCRETE

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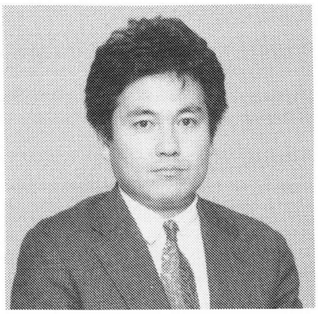

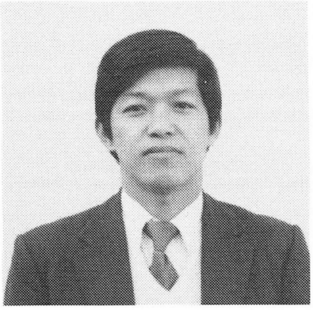

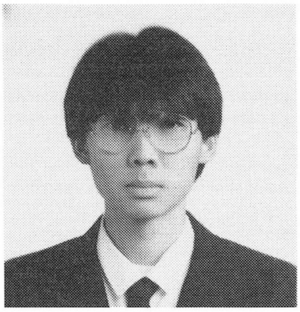

Tsuyoshi MARUYA Yasunori MATSUOKA Somnuk TANGTERMSIRIKUL

SYNOPSIS

A mathematical model for simulating chloride movement in hardened concrete was proposed. Total chloride in concrete is considered to be composed of fixed and free chlorides. Fixed chloride content is considered to be a function of total chloride content. Free chloride is the only chloride which is movable according to its concentration gradient. Models for dealing with the effect of carbonation, change of water content in concrete due to drying and wetting, and cyclic wetting and drying with salt water have been proposed. The applicability of the models was checked using our test results of and results of specimens taken from real structures. The analytical results proved to be qualitatively satisfactory.

Keywords: simulation, chloride movement, free chloride, fixed chloride, carbonation

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1. INTRODUCTION

Deterioration of reinforced concrete can be considered to be classified into two categories. The first is deterioration of concrete due to, for example, carbonation and alkaline-aggregate reaction. The second is the deterioration due to corrosion of the reinforcing steel. Due to high alkalinity in the concrete, reinforcement in the concrete will not corrode until the passivity of the reinforcement in the concrete is damaged. One of the factors damaging the passivity is chloride ion penetration into or initially incorporated in the concrete. To be able to forecast the service life of a structure deteriorated by corrosion of the reinforcement, as well as to propose a proper mix design for a durable structure, it is necessary to clarify the behavior of chloride ions in concrete.

This paper introduces a mathematical model for simulating chloride movement in hardened concrete. Chloride content in concrete, which changes with time due to movement of free chloride, can then be derived analytically.

It has been proposed that movement of chloride ions in concrete can be considered to be a diffusion process in which chloride ions move according to their concentration gradient. Fick's theory of diffusion has been generally introduced to simulate chloride penetration into hardened concrete [1]. To solve the diffusion equation, boundary conditions must be specified. Various assumptions of environmental conditions have been made, such as constant environmental conditions [1], and time-dependent environmental conditions [2,3,4,5]. For the measurement of chloride content in hardened concrete, there are various methods, such as the method proposed by the Japan Concrete Institute (JCI), which is to extract the soluble chloride using hot water and total chloride using nitric acid from a crushed sample [6]; the method for obtaining chloride concentration from pore solution [7]; and the method of calorimetry using fluorescein sodium salt and silver nitrate [8].

However, there is no computational model which is capable of dealing with the equilibrium between fixed and free chlorides, and also with all boundary and environmental conditions. Cyclic wetting and drying is one of the most complicated conditions; it requires a model for simulating water content in the concrete during the drying period. Kobayashi [9] mentions that carbonation can cause a critical chloride content in the concrete surrounding the reinforcement due to migration of free chloride from the carbonated surface concrete into the inner portion. Such problems, which could not be dealt with previously, can be solved by applying the mathematical model proposed in this paper. Also, the relationship between soluble chloride content and chloride concentration in pore solution, of which the latter is to be used in the diffusion equation, is clarified.

The proposed model was investigated for its applicability by comparing the computational results with the author's test results, other researchers' test results and the results from actual structures.

2. CHLORIDES IN CONCRETE AND THEIR QUANTIFICATION

2.1 Chlorides in Concrete

Chlorides in concrete are present in various forms. In this study, total chloride is classified into free and fixed chlorides. The chloride which is dissolved in the concrete pore solution and movable according to its concentration gradient is defined as free chloride. The remainer is then fixed chloride. It is known that Friedel's chloride is not the only type of fixed chloride when free chloride is defined by the above definition. Another form of fixed chloride is thought to be the adsorbed chloride in the solid structure of concrete [10].

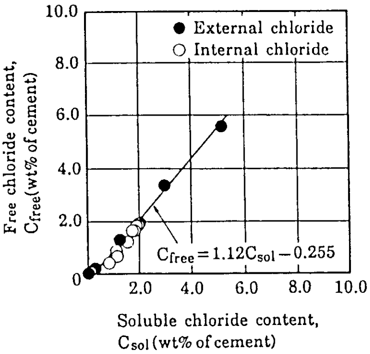

Fig.1 Relationship between soluble chloride content and free chloride content

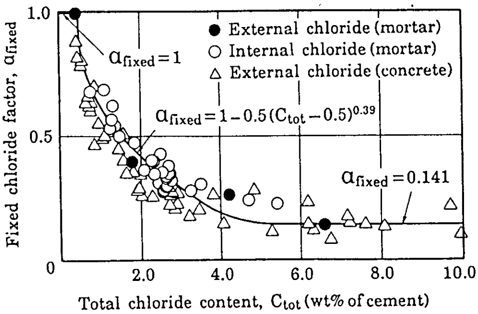

Fig.2 Relationship between total chloride content and fixed chloride factor

2.2 Quantification of Fixed and Free Chlorides

Free chloride content can be measured directly by analyzing chloride content in the pore solution expressed from the hardened concrete. However, to express the pore solution from the hardened concrete requires large amounts of concrete sample to obtain enough pore solution for ion analysis. The method of pore solution analysis was utilized to study the effect of the type of cementitious materials and the curing method on ion concentration in the pore solution [11]. The extraction method, proposed by JCI [6], is a simpler method requiring less sample volume. In this method, the sample is crushed into powder, and then dissolved in pure water to analyze for soluble chloride content. A good relationship between the results of these two methods was obtained from the results of various samples so that the results can be converted mutually using the relationship shown in Fig.1, and is represented by

$$Cfree = A \cdot Csol + B, \qquad (1)$$

where Csol is the soluble chloride content in weight percent of cement obtained by the extraction method and Cfree is the free chloride content in weight percent of cement in the pore solution by the pore solution method. The constants A and B were derived by regression analysis to be 1.12 and -0.255, respectively. All the data in this paper were derived from mortar without application of any pozzolanic materials such as slag, fly ash and silica fume. The values of A and B are expected to vary if some pozzolanic materials are added to the mixture. Nagataki et al. proposed a similar equation for cement paste [12].

Quantification of free chloride is necessary since it is the only chloride which is movable. Figure 2 reveals that a good relationship can be obtained if the fixed chloride factor, which is the ratio of fixed chloride content to total chloride content, is plotted against the total chloride content in weight percent of cement. The data were obtained from various mortar and concrete specimens. The amount of fixed chloride, which includes Friedel's chloride and adsorbed chloride, can then be derived from

$$Cfixed = \alpha\ fixed \cdot Ctot, \qquad (2)$$

where Cfixed and Ctot are fixed chloride and total chloride contents in weight percentage of cement, respectively. Coefficient α fixed is the fixed chloride factor which is derived from the best fit of data in Fig.2 as

$$\alpha\ fixed = \begin{cases} 1 & Ctot \leqq 0.5 \\ 1-0.5 \cdot (Ctot-0.5)^{0.39} & 0.5 \leqq Ctot \leqq 4.5 \\ 0.141 & 4.5 \leqq Ctot. \end{cases} \qquad (3)$$

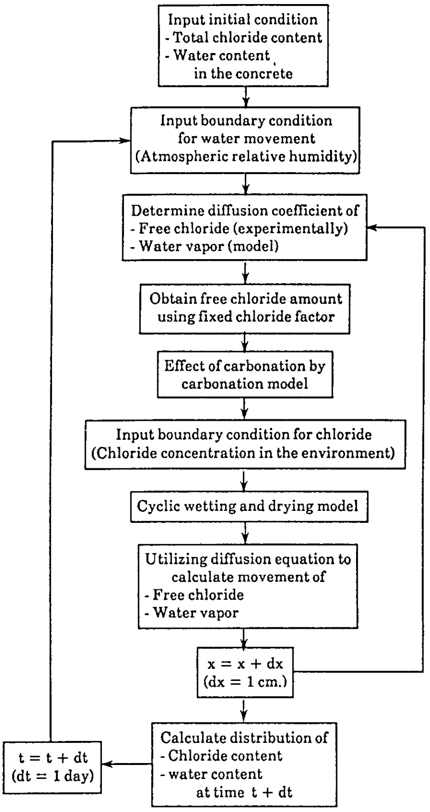

Fig.3 Flow chart demonstrating calculation process

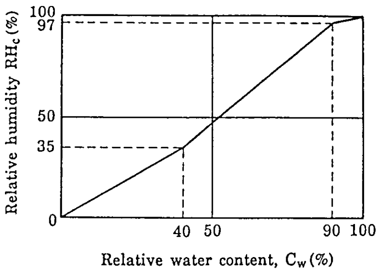

Fig.4 Relationship between relative water content and relative humidity in concrete

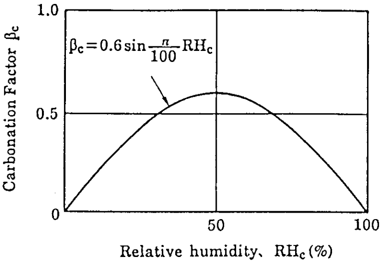

Fig.5 Relationship between relative humidity and carbonation factor

Free chloride content is then obtained from

$$Cfree = Ctot - Cfixed. \quad (4)$$

3. COMPUTATIONAL MODEL

The analytical process is shown in the flow chart in Fig. 3. Details are explained in the following sections.

3.1 Migration of Water in Concrete

The amount of water in concrete pores is an important factor controlling the degree of carbonation, and is required in the calculation of free chloride concentration in the pore. The degree of carbonation varies with moisture content of the concrete. Free chloride concentration is the ratio of free chloride content to the available pore water content in which it is dissolved. Consequently, it is necessary to introduce a model for simulating water movement in concrete.

Water in hardened concrete is considered to move through the pore structure according to the vapor pressure gradient, in other words, the relative humidity gradient. The rate of water vapor transfer is assumed to obey Fick's law of diffusion

$$Fw(x,t) = -Dw \cdot \frac{\partial RHc(x,t)}{\partial x}, \qquad (5)$$

where Fw is transfer rate of water vapor ($cm^3/cm^2/day$), Dw is diffusion coefficient of water vapor in the concrete (cm^2/day), RHc is relative humidity in the concrete (%), x is distance from the open surface (cm) and t is time (day).

This idea was utilized to derive an analytical model for computing the water content distribution in drying concrete by Saeki, Ohga and Nagataki [13]. Since the measurement of relative humidity in the concrete is difficult, the authors utilized the relative water content for evaluating the relative humidity in concrete and implemented the relationship between the relative water content and relative humidity, as shown in Fig.4. Saeki, Ohga and Nagataki proposed a similar relationship [13]. The relative water content means the ratio of the amount of evaporable water in the concrete to that in water-saturated concrete. The method for obtaining evaporable water content is given in the section on the carbonation test.

3.2 Movement of Free Chloride

Free chloride moves according to its concentration gradient and the process of movement was assumed to be diffusion obeying Fick's law

$$Fc(x,t) = -Dc \cdot \frac{\partial C_{free}(x,t)}{\partial x}, \qquad (6)$$

where Fc is the rate of transfer of free chloride through a unit area, perpendicular to the transfer direction, of concrete ($mol/cm^2/day$), Dc is diffusion coefficient of free chloride in the concrete (cm^2/day) and is considered to be a material constant, C_{free} is free chloride concentration (mol/cm^3) which can be determined if free chloride content and water content in the concrete element dx are known, x is distance along the diffusion direction (cm) and t is time (day).

3.3 Effect of Carbonation

When concrete is carbonated, alkalinity in the carbonated area decreases, causing free chloride to be released from fixed chloride. This results in a higher concentration of free chloride in the carbonated area than in the noncarbonated one [9]. Therefore, free chloride moves from the carbonated area to the noncarbonated area, resulting in higher total chloride content in the noncarbonated area than in the carbonated area. The degree of carbonation depends on various factors such as CO_2 supply, speed of carbonation reaction and moisture in the concrete. Fully saturated or completely dry concrete is virtually not attacked by carbonation. On the other hand, the degree of carbonation is severe when the concrete is semidry [13, 14]. This is because a certain amount of both water and CO_2 is required in the carbonation process. The amount of free chloride released by carbonation is assumed to be linearly proportional to the degree of carbonation, as shown in Eq.(7) and Eq.(8):

$$C'_{fixed} = C_{fixed} \cdot (1-\beta c) \qquad (7)$$

$$C'_{free} = C_{free} + \beta c \cdot C_{fixed}, \qquad (8)$$

where C'_{fixed} and C'_{free} are the fixed and free chloride contents after carbonation. The coefficient βc is the degree of carbonation which actually depends on various factors

Table 1 Properties of cement used in the study

		Chemical composition (%)													
ig. loss	insol.	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	Na_2O	K_2O	TiO_2	P_2O_5	MnO	S	Total	R_2O
1.8	0.8	20.5	5.0	3.0	63.4	2.0	2.0	0.3	0.4	0.35	0.19	0.21	0.0	100	0.56
Specific gravity				3.14			Specific surface area (cm^2/g)							3290	

such as CO_2 supply, speed of carbonation reaction and humidity in the concrete; however, it is simply assumed to vary with the humidity in concrete pores for qualitative study, as shown in Fig.5.

3.4 Cyclic Wetting and Drying Model

Cyclic wetting and drying simulates the conditions of a splash zone. It is known that chloride concentration near the concrete surface increases significantly when the concrete undergoes cyclic wetting and drying with salt water [3]. The increase is too great to be accounted for only by the process of chloride diffusion. It was realized that the following must be taken into consideration. In the drying stage, only water escapes from the concrete surface, leaving salt at the drying portion, and causing the chloride concentration to increase due to the decrease of water in the pore solution at the drying portion. In the wetting stage, salt water from the environment enters the concrete in a very short period mainly by capillary action. Therefore, when the wetting and drying process continues for a long period, chloride concentration near the concrete surface increases considerably. This actual phenomenon was included in this paper in simulating the condition of cyclic wetting and drying with salt water.

4. EXPERIMENTS

4.1 Materials and Mix Proportion

Materials used for preparing mortar specimens were ordinary portland cement, of which the chemical composition and physical properties are given in Table 1, and Toyoura standard siliceous sand. Deionized water was used as mixing water. Mortar was prepared with W/C of 0.5 and sand-to-cement weight ratio of 2.0. Sodium chloride was utilized as the source of chloride ion. The flow table values of mortar with and without incorporating sodium chloride were 210 and 175 mm, respectively. Air content was 7%.

4.2 Specimen Preparation

The size of the chlorovinyl resin cylinder mold was 51mm in diameter and 100mm in length. The specimens were cast into 2 layers, each layer being consolidated using a vibrating table. Only the cast surface was open and the boundary between mortar and mold at the open surface was sealed with latex. The purpose of preparing specimens in this manner is to create a one-dimensional condition for chloride movement in the specimens. Only the specimens in the chloride penetration test were of the size 40x40x160mm. Except for the open surface, which was 40x40mm, the other 5 surfaces were coated with epoxy resin after demolding, also to create a one-dimensional condition for chloride movement.

Before starting the test, the specimens were cured by wrapping the open surface with a plastic sheet and stored at 20℃, 100%RH in order to prevent water from evaporating from the specimens and to stabilize the chemical composition. This curing technique is called seal curing.

4.3 Chloride Penetration Test

The objective of this test is to clarify the occurrence of chloride condensation at the open surface portion of concrete when the concrete is submerged in salt water.

In this series, specimens were made with deionized water and seal-cured for 28 days. After curing, they were submerged in salt water having 8.24% of sodium chloride content (corresponding to 5.0% chloride) until the times of measurement which were 14, 28, 98 and 168 days from the beginning of submergence. At the time of measurement, specimens were cut at 5mm intervals from the open surface to the depth of 30mm and at a 10mm interval from the depth of 30mm to 40mm. The measurement of total chloride content and water soluble chloride content by the method suggested by JCI was conducted.

4.4 Chloride Dissolving Test

Generally, three techniques, namely, concentration profile, diffusion cell and electrical conductivity, may be utilized to determine the diffusion coefficient of an ion [15]. The objective of this test is to obtain the diffusion coefficient of the chloride ion by the concentration profile method. Usually, this method is applied to the data of the chloride penetration test. In this paper, the coefficient is derived from the chloride concentration profile of the chloride dissolving test in which chloride moved from the specimen into chloride-free water. The reason for selecting this test instead of the chloride penetration test is that chloride condensation at the concrete surface, the mechanism of which is still unknown, occurs in the case of the chloride penetration but not in the case of the chloride dissolving test.

In this test, chloride was initially stored in the specimens by using salt water having 8.24% of sodium chloride content (corresponding to 5.0% chloride) as mixing water to prepare the mortar for casting specimens. The specimens were seal-cured for 28 days. After curing, they were submerged in deionized water until the measuring periods of 14, 28 and 98 days after the submergence. In the test periods, measurements of total chloride content and water soluble chloride content by the JCI method and chloride ion concentration by pore solution analysis were conducted.

The measurement of total and water soluble chloride contents were conducted at 5mm intervals from the open surface to a depth of 30mm and at 10mm intervals from the depth of 30mm to 50mm. Pore solution analysis was performed every 10mm from the open surface of specimens to the depth of 50mm. In order to obtain a sufficient amount of pore solution for ion analysis, ten slices from the same depth of ten specimens with the same mix proportion and test conditions were used to express pore solution.

4.5 Carbonation Test

The objective is to verify the effect of carbonation on chloride content in the specimen. Salt water with sodium chloride content of 3.0% (corresponding to chloride content of 1.82%) was used as mixing water. The specimens were seal-cured for 28 days. After curing, they were divided for storage in 3 environments: 20℃, 60%RH, 0.06%CO_2; accelerated carbonation environment of 20℃, 60%RH, 10%CO_2; and 20℃, 100%RH. At the times of measurement, 49, 98 and 189 days from the start of storing, specimens were cut at 10mm intervals from the open surface to the depth of 50mm.

Total chloride content and water soluble chloride content were measured by the JCI method. The evaporable water content at the same depth was also observed. Evaporable water content was measured by drying the cut specimens at 105℃ for 24 hours. The evaporable water content was obtained from the weight loss of the specimens.

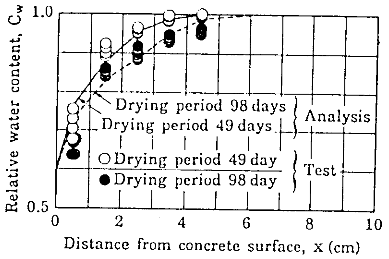

Fig.6 Test and analytical results of relative water content distribution (Data from authors)

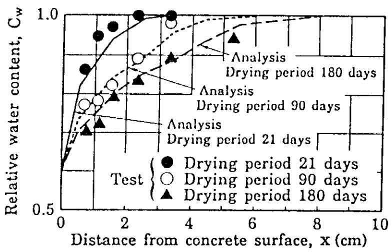

Fig.7 Test and analytical results of relative water content distribution (Data from Parrott)

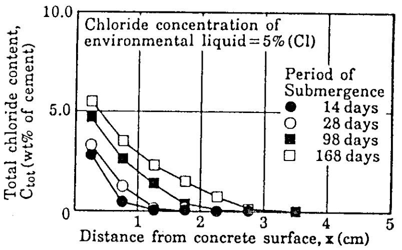

Fig.8 Test results of external chloride series (Total chloride content)

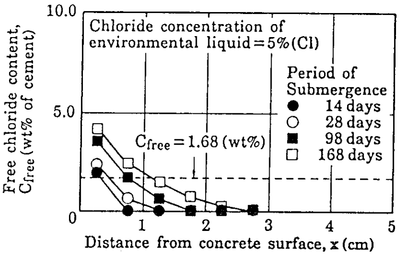

Fig.9 Test results of external chloride series (Total chloride content)

5. TEST RESULTS AND VERIFICATION

5.1 Water Movement in Hardened Concrete

The model was verified using results of relative water content from the carbonation test in Fig.6 and results obtained from Parrott [16] in Fig.7. The analytical results show satisfactory agreement with the test results shown in both figures.

5.2 Chloride Penetration Test

Figure 8 and Fig.9 show the results of total chloride content distribution and distribution of water soluble chloride content, respectively. The broken line, which is marked at 1.68wt% of cement in Fig.9, is the free chloride content calculated under the condition that the mortar is saturated with chloride solution having 5% in chloride concentration. This concentration is equivalent to that of the surrounding salt water.

Figure 9 shows that free chloride content of the surface layer (0-5mm from open surface) surpasses the value of 1.68% at the test period of 14 days. Moreover, its value exceeds twice the concentration of immersion liquid at the test period of about 100 days. Figure 10 shows the observed results of free chloride content of the surface layer at various test periods. It is obvious from the figure that chloride condensation near the open surface takes place. The test by Nagataki et al. indicates that the chloride ion concentration at the surface layer of specimens immersed in sodium chloride solution reaches twice the concentration of the surrounding solution at the test period of 91 days and has a tendency of further increase [12]. This phenomenon is called chloride condensation at the concrete surface, in this paper. Simulation has not yet been conducted for this test because mechanisms of condensation are not yet understood. It is thought that mechanisms other than diffusion must be taken into account in order to deal with the chloride condensation at the open surface.

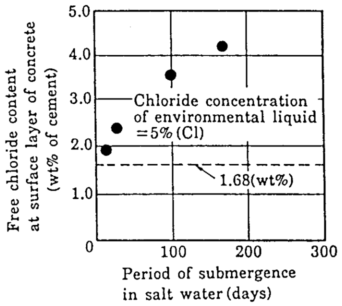

Fig.10 Variation with time of free chloride content at surface layer (5 mm from surface) of concrete

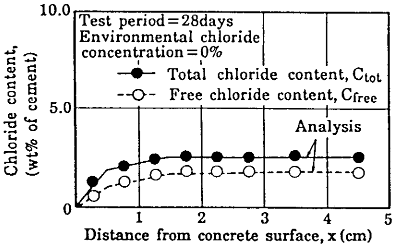

Fig.12 Test and analytical results of internal chloride series (Test period=28 days)

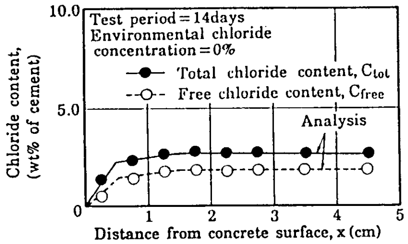

Fig.11 Test and analytical results of internal chloride series (Test period=14 days)

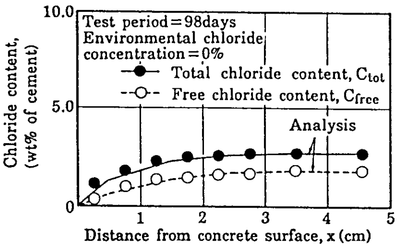

Fig.13 Test and analytical results of internal chloride series (Test period=98 days)

5.3 Chloride Dissolving Test

Figure 11 to Fig.13 show the test and analytical results of distribution of total and free chloride contents of the specimens after being submerged in deionized water for 14 days, 28 days and 98 days, respectively. Applying the analytical model to the test results, the best-fit results yield a free chloride diffusion coefficient of 4.20x10^{-3}cm^{2}/day for the surface layer and 1.19x10^{-3}cm^{2}/day for the others. The greater diffusion coefficient of the surface layer is thought to be due to the effect of discontinuity at the boundary (open surface). Due to irregularity of the pores in concrete, the chloride ion moved slower in the concrete than in the water medium at the surface. The derived values of the diffusion coefficient were utilized in all simulations in this paper since all specimens were made of the same materials and mix proportion. It should be noted that since the diffusion coefficient is a material constant, it changes according to the materials and mix proportions. A quantitative model for deriving the chloride diffusion coefficient in concrete is required for quantitative simulation without conducting tests to determine the coefficient for all different mix proportions.

5.4 Carbonation Tests

Figure 14 to Fig.16 show chloride content distributions at test periods of 49 days, 98 days and 189 days, respectively, of the specimens stored under the conditions of 20℃, 60%RH and 10%CO$_2$. Solid and broken lines in the figures show analytical results of total chloride content and water soluble chloride content, respectively. The analysis was carried out based on the derived diffusion coefficient of 1.19x10^{-3}cm^{2}/day without considering the larger diffusion coefficient at the surface layer since the condition of analysis was assumed to be that without migration of the chloride across the open surface of the specimen. Figure 17 shows the distribution of chloride content at the test period of 49 days of the specimen stored at 20℃, 60%RH and 0.06%CO$_2$. The results of test periods of 98 and 189 days are illustrated in Fig.18 and Fig.19, respectively.

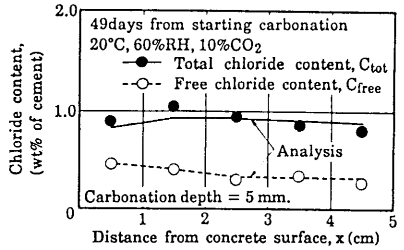

Fig.14 Chloride condensation by carbonation (result of accelerated carbonation test)

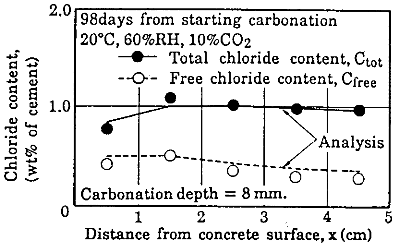

Fig.15 Chloride condensation by carbonation (result of accelerated carbonation test)

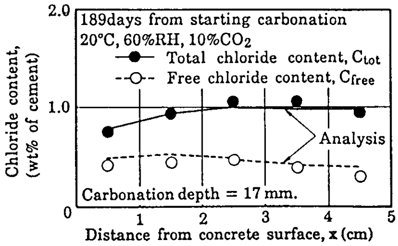

Fig.16 Chloride condensation by carbonation (result of accelerated carbonation test)

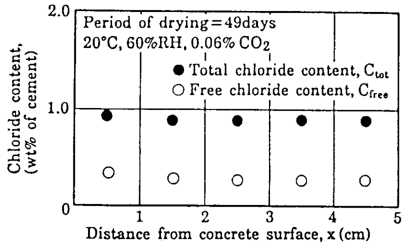

Fig.17 Results of carbonated specimen (Normal CO_2 level)

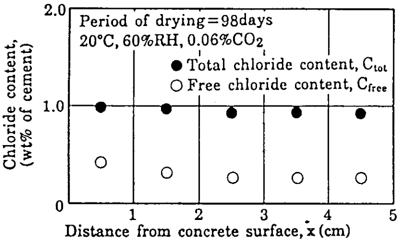

Fig.18 Results of carbonated specimen (Normal CO_2 level)

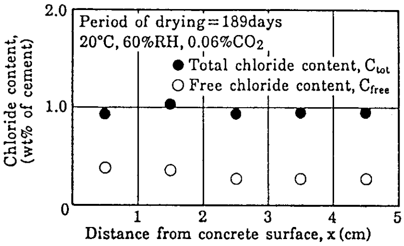

Fig.19 Results of carbonated specimen (Normal CO_2 level)

There is an increase of total chloride content at the distance of 10mm to 20mm from the open surface at test periods of 49 and 98 days in Fig.14 and Fig.15, respectively. The increase of total chloride cannot be observed in Fig.17 or Fig.18. Chloride moves further into the inner portion of the specimen when the period of carbonation is longer, as seen in Fig.16. There is also condensation of total chloride at the location 10mm to 20mm from the open surface in the specimen stored at 20℃, 60%RH and 0.06%CO2 for the test period 189 days in Fig.19. This shows that condensation of total chloride also takes place in the case of low CO2 concentration over a long term. It can be observed from Fig.14 to Fig.16 that near the open surface, the fixed chloride contents, derived from the difference between total chloride and free chloride contents, are less than those of the inner region. This indicates that decomposition of fixed chloride has taken place.

It is obvious from comparing the test results with the analytical results that the computational model is effective for analyzing the condensation of chloride due to carbonation.

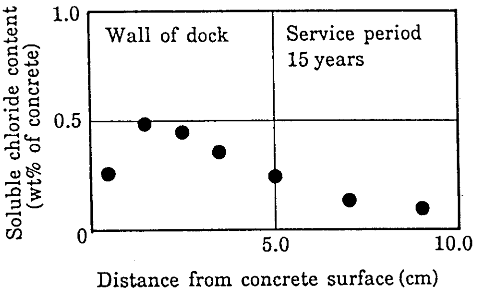

Fig.20 An example of soluble chloride distribution of real structure in marine atmospheric environment

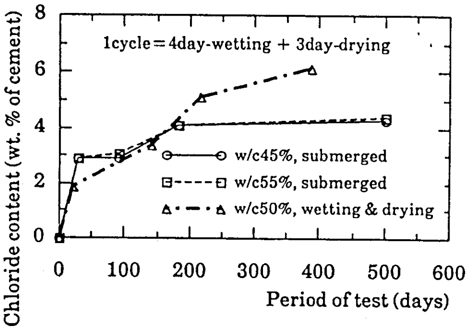

Fig.22 Test results of chloride content at surface layer (10 mm from concrete surface)

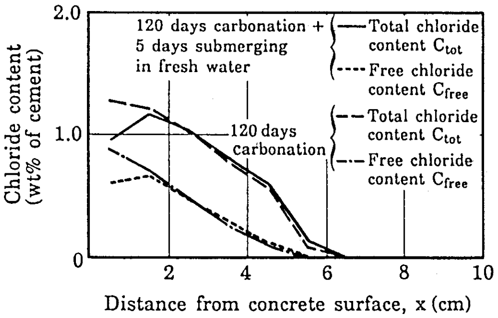

Fig.21 Simulated results of concrete in marine atmospheric environment

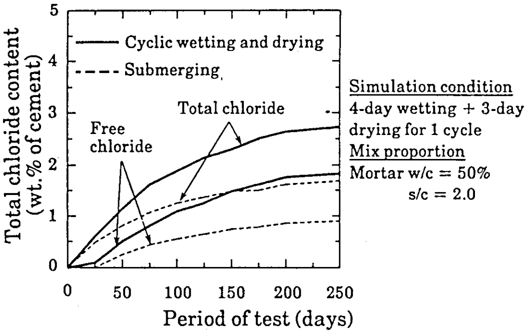

Fig.23 Variation with time of total and free chloride contents at surface layer (10 mm from surface)

6. APPLICATION TO COMPLICATED BOUNDARY CONDITIONS

6.1 Atmospheric Zone

Figure 20 shows the result obtained by analyzing core samples taken from the wall of a dock located in the atmospheric zone of a sea environment and which contained no initial chloride. The distribution of total chloride content does not show a maximum at the exposed surface, but at a certain distance from the surface, then decreases forwards the inner region. This is due to the effect of rain and carbonation. Chloride at the surface can be washed away by rain. Also, carbonation causes free chloride to move into the inner portion. In the analysis, the carbonation model explained earlier was utilized and the condition of submerging in fresh water was assumed for the rainy period.

The analysis was conducted for two cases. The first was external chloride with carbonation and the second was external chloride with carbonation and rain. The latter analysis showed maximum total and free chloride at the distance of 1~2 cm from the surface. This tendency corresponds to the result in Fig.21 and indicates that both carbonation and rain should be included in the simulation of structures in the atmospheric zone.

6.2 Splash Zone

Results of tests by Masuda, Tomosawa et al.[3] in Fig.22 on specimens subjected to cyclic wetting and drying with salt water and specimens permanently submerged in salt water indicate that chloride ion content near the concrete surface increases more markedly when the specimens undergo cyclic wetting and drying with salt water. Applying the idea for dealing with the effect of wetting and drying proposed earlier, the analytical results shown in Fig.23 can be obtained. The movement of free chloride was assumed to be only diffusion in the case of permanent submergence in salt water in the analysis. Both the total and free chloride contents near the concrete surface of cyclic wetting and drying specimens increased more rapidly than those of the permanently submerged specimens in the analysis.

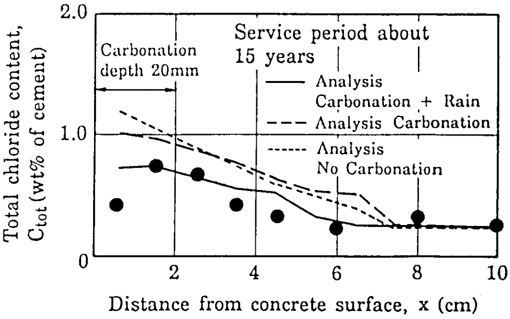

Fig.24 Test and analytical results of real structure

It can then be concluded by comparing the test and analytical results that the simulated results are qualitatively in accordance with the test results. Quantitative verification is to be conducted following this study.

7. APPLICATION TO AN ACTUAL STRUCTURE CASE

Figure 24 shows the distribution of total chloride content in a concrete core sample taken from a structure located about 500m from the sea.

Chloride seemed to mix into the concrete from the beginning of construction due to the use of sea sand. The sampling positions were usually in atmospheric zone but occasionally in the rainy or typhoon zone.

The characteristic of the distribution of total chloride content is that the maximum content occurs at a depth of 10-20mm from the surface and is about three times the content of the inner position. Assuming that chloride content in the inner portion of the concrete structure is not affected by the movement of free chloride near the concrete surface, it can be considered the initial chloride content. It was, therefore, inferred that chloride penetrated into the structure from the environment, because measured results show an increase of total chloride content in the sample relative to the initial total chloride content. Carbonation depth was measured to be 20mm, which is considered rapid for the structure which was estimated to be in use for only 15 years.

The computational model was applied to derive total chloride content distribution. Initial conditions were uniform chloride content equal to that at the deepest position and humidity of 100%RH. Chloride supply was assumed to be a constant flux entering the concrete during the no rain period. Conversely, chloride migrates from the concrete to the environment in the rainy period. The boundary condition for environmental humidity was the average relative humidity of the area where the structure was located [17] for the non rainy period and 100%RH for the rainy period. The rainy period was assumed to continue for 3 months in summer. Using the analytical condition set up above, three cases of environmental conditions, namely, carbonation with rain, carbonation without rain and neither carbonation nor rain were investigated. The analysis of carbonation with rain, which is the condition closest to the actual state, is the most similar to the measured results in Fig.24. From the result of this analysis, the analytical model was found to be applicable for complicated environmental conditions and effective to simulate the results of existing structures.

8. CONCLUSIONS

A mathematical model for simulating chloride movement in hardened concrete was proposed. The model is capable of dealing with many boundary and environmental conditions. Various tests were conducted to confirm the model, and the versatility of the model was checked using results from tests and actual structures. The following conclusions can be drawn based on this study.

1) Chlorides in hardened concrete are categorized into 2 types, namely, free and fixed chlorides. Equilibrium between fixed and free chlorides can be quantified by implementing a relationship between the ratio of fixed to total chloride and total chloride content.

2) Only free chloride is movable and the movement of free chloride is based on the diffusion theory in which free chloride concentration in concrete pores is necessary. The derivation of free chloride concentration from tests is inconvenient, but it can be calculated using the relationship between free chloride and soluble chloride contents, of which the latter is derived from the JCI method for extracting soluble chloride.

3) Water content in concrete is important for converting free chloride content into concentration; also, it controls the degree of carbonation. The rate of water movement in concrete is simulated based on the gradient of vapor pressure.

4) The effect of carbonation was regarded to be the dissolving of fixed chloride which caused an increase in the amount and concentration of free chloride in the carbonated portion. Free chloride migrates to the low-chloride-concentration portion in the noncarbonated area. The degree of dissolving is considered to be a function of relative humidity in the concrete pore. With this idea, the model was utilized to simulate the results of accelerated carbonation tested by the authors and satisfactory results were obtained.

5) For the case of chloride penetration, the concentration of free chloride at the surface layer was found to be greater than that in the environment. Further intensive studies must be conducted to clarify this chloride condensation phenomenon.

6) The proposed model was utilized to simulate the condition of chloride moving from the initially chloride-incorporated specimens into chloride-free water. The diffusion coefficient of free chloride was derived using the concentration profile method. The coefficient derived under this condition is more reliable than that of chloride penetration from the environment since the latter encounters chloride condensation at the exposed surface.

7) The distribution of chloride content in structures in the atmospheric zone shows a maximum at a certain distance from the exposed surface. This can be simulated by incorporating the effects of both carbonation and rain.

8) In the splash zone, the effect of cyclic wetting and drying with salt water was modeled by assuming that only water escapes from the surface portion of concrete in the drying period, but that salt water enters the concrete by capillary action in the wetting period.

9) According to the results of simulation of a case study, the model is considered to be effective for simulating chloride movement in actual structures.

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