

論文

[1164] SIMULATION OF CHLORIDE MOVEMENT IN HARDENED CONCRETE

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ABSTRACT

This study was aimed to predict chloride content in concrete which changes with time due to migration of free chloride. It was found that quantification of fixed and free chloride contents can be made by introducing fixed chloride factor which is function of total chloride content. The chloride content in concrete can change due to various occurrences, for instance, penetration of chloride from environment, wetting and drying in salt environment and migration of chloride due to carbonation. However, this paper introduced and verified the ideas for simulating effects of carbonation as well as wetting and drying in salt environment on chloride content.

1. INTRODUCTION

Deterioration of reinforced concrete members occurs in various processes and may be categorized mainly into two namely deterioration of the concrete itself, carbonation and alkaline-aggregate reaction are the examples of this kind, and deterioration of the reinforced concrete members due to corrosion of reinforcing steel. Due to high alkalinity in the concrete, reinforcement in the concrete would not corrode until the passivity of reinforcement in the concrete is damaged by alkalinity reduction. One of the factor which causes alkalinity reduction is chloride ion which may penetrate into the concrete from the salt-rich environment. Chloride amount is one of the factor controlling corrosion of the reinforcement. The larger the amount of chloride, the higher the rate of corrosion of the reinforcement and then the higher rate of structural deterioration. To be able to forecast service life of the structure, the quantification of chloride in the vicinity of reinforcement in reinforced concrete is then important.

2. CHLORIDE IN CONCRETE

Chloride in concrete presents in various forms. In this study the amount of chloride which is dissolved in the pore solution of concrete and can migrate according to its concentration gradient in the pore solution is defined as free chloride and the rest is defined as fixed chloride. It is known that Friedel's chloride is not the only fixed chloride in concrete as far as free chloride is defined by the above definition[1]. Another form of

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fixed chloride is thought to be the adsorbed chloride in solid structure of concrete. The amount of free chloride can be measured directly by analyzing for chloride content in pore solution expressed from the concrete. However, the direct method which is to express pore solution from the hardened concrete requires large volume of concrete sample in order to obtain enough pore solution for analysis. Extraction method is a simpler method and requires less volume of sample. In extraction method, the sample is crushed into powder which is dissolved in pure water to analyze for soluble chloride content. It should be realized that the soluble chloride content derived from extraction method is not equivalent to the actual free chloride content in the pore solution of the concrete since some of the adsorbed chloride in the solid structure can be dissolved when the sample is powdered, causing the amount of soluble chloride to be greater than the amount of actual free chloride. However a good relationship between results of these two methods were obtained from results of various samples so that they can be converted to each other using the relationship shown in Fig.1 and represented by

$$C_{free} = A \cdot C_{sol} + B \quad (1)$$

where C_{sol} is soluble chloride content in weight percentage of cement by extraction method and C_{free} is free chloride content in weight percentage of cement in the pore solution by expression method. A and B were derived from regression analysis to be 1.12 and -0.255, respectively.

Quantification of free chloride is necessary since free chloride is the only chloride which is able to move according to its concentration gradient. Fig.2 reveals that a good relationship can be obtained if fixed chloride factor, the ratio of fixed chloride to total chloride contents, is plotted against the total chloride content in weight percentage 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 the following equation

$$C_{fixed} = \alpha_{fixed} \cdot C_{tot} \quad (2)$$

where C_{fixed} is the fixed chloride content and C_{tot} is the total chloride content, both have unit in weight percentage of cement. α_{fixed} is fixed chloride factor which was determined from the best fit of data in Fig.2 as

$$\alpha_{fixed} = \begin{cases} 1 & C_{tot} \leq 0.5 \\ 1 - 0.5 \cdot (C_{tot} - 0.5)^{0.39} & 0.5 \leq C_{tot} \leq 4.5 \\ 0.141 & 4.5 \leq C_{tot} \end{cases} \quad (3)$$

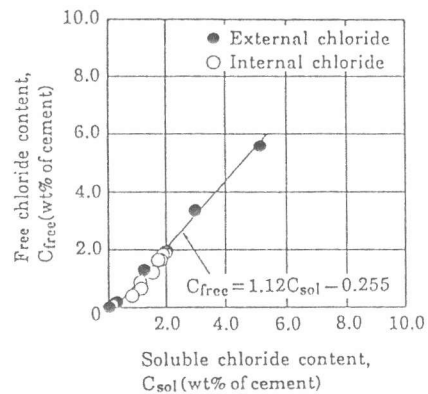


Fig.1 Relationship between soluble chloride content and free chloride content

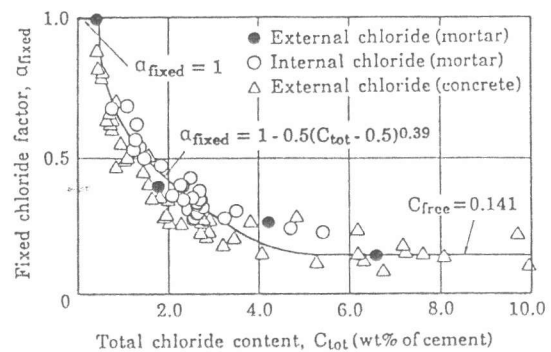


Fig.2 Relationship between total chloride content and fixed chloride factor

Free chloride content is then obtained from

$$C_{free} = C_{tot} - C_{fixed} \quad (4)$$

3. COMPUTATIONAL MODEL

3.1 MIGRATION OF WATER IN CONCRETE

The amount of water available in concrete pore is important since it is one of the important factor which controls degree of carbonation and also is necessary for calculation of free chloride concentration in the pore. It is known that degree of carbonation depends on how moist the concrete is. Free chloride concentration is the ratio of free chloride content to the available pore water content in which it is dissolved. Therefore simulation of water content distribution in the concrete is required for dealing with carbonation effect and calculating the free chloride concentration. Water in hardened concrete is believed to move according to the vapor pressure gradient and the rate of water vapor transfer is assumed to obey Fick's law of diffusion.

Based on the mentioned idea, an analytical model for deriving water content distribution of drying concrete was proposed by T. Saeki, H. Ohga and S. Nagataki[2] and was adopted to be used in this research. Details of the model is not given in this paper since it is not the purpose of this paper. Fig.3 expresses some of the test and analytical results from the model and shows that the model is satisfactory for predicting water content distribution of the tested specimens.

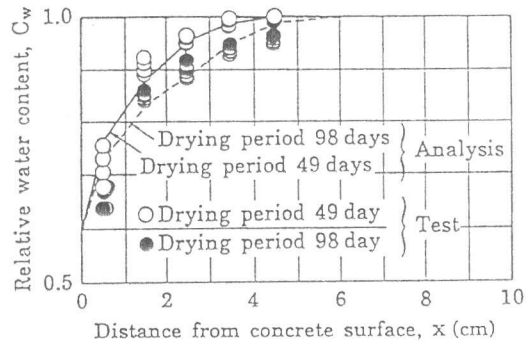


Fig.3 Test and analytical results of relative water content distribution

3.2 MOVEMENT OF FREE CHLORIDE

Free chloride in the pore of concrete moves according to its concentration gradient and the movement was assumed to obey Fick's law as

$$F_c(x, t) = -D_c \frac{\partial C_{free}(x, t)}{\partial x} \quad (5)$$

where F_c is the rate of transfer of free chloride per unit area, D_c is the diffusion coefficient of free chloride in concrete medium, C_{free} is free chloride concentration in mol/cc which can be determined when knowing free chloride and water contents in the pore of concrete in the concrete element dx , x is the distance along the diffusion direction and t is time.

3.3 EFFECT OF CARBONATION

When the concrete is carbonated, alkalinity in the carbonated area decreases and free chloride can be released from the fixed chloride resulting in higher concentration of free chloride in the carbonated area than in the non-carbonated area[3]. Therefore, free chloride moves from the carbonated area to the non-carbonated area so that higher total chloride content in non-carbonated area than in the carbonated area takes place. Degree of carbonation depends on various factors such as supply of CO_2 , rate of

carbonation reaction and moisture in the concrete pore. Fully saturated or completely dry concrete are not attacked by carbonation. On the other hand, degree of carbonation is severe when the concrete is semi-dry. This is because sufficient amount of both water and CO₂ is required for the carbonation process. The amount of free chloride released by carbonation is assumed to be direct function of degree of carbonation as

$$C_{frc} = C_{fixed} \cdot \beta_c \quad (6)$$

where C_{frc} is the amount of free chloride released by carbonation. β_c is the degree of carbonation which is actually depending on various factors such as CO₂ supply, rate of carbonation reaction and humidity in the concrete pore, however, it is simply assumed to vary with humidity in concrete pore for qualitative study as shown in Fig.4. RH_c is humidity in the pore of concrete.

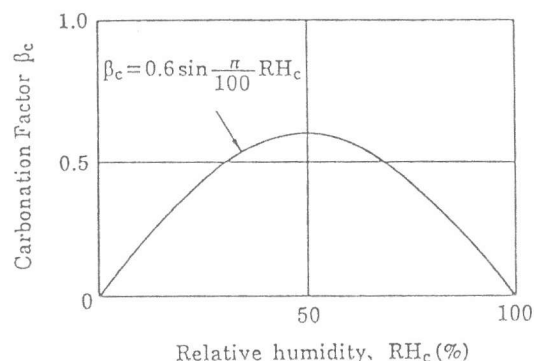


Fig.4 Relationship between relative humidity and carbonation factor

3.4 CYCLIC WETTING AND DRYING MODEL

Results tested by Masuda, Tomosawa et al., [4] in Fig.5 of both specimens subjected to cyclic wetting and drying with salt water and specimens permanently submerged in salt water indicate that chloride concentration near concrete surface increases more remarkably when the specimens undergo cyclic wetting and drying with salt water. The increase is too great to be thought that only the process of chloride diffusion can account for. It was realized that the following actual happening has to be taken into consideration. In drying stage, only

particles of water escapes from the concrete, leaving salt particles at the drying concrete then causing concentration increase due to decrease of water in the pore solution. In 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 prolonged period, salt concentration near concrete surface remarkably increases. This actual phenomena was included for simulating the effect of cyclic wetting and drying with salt water on chloride concentration in this paper.

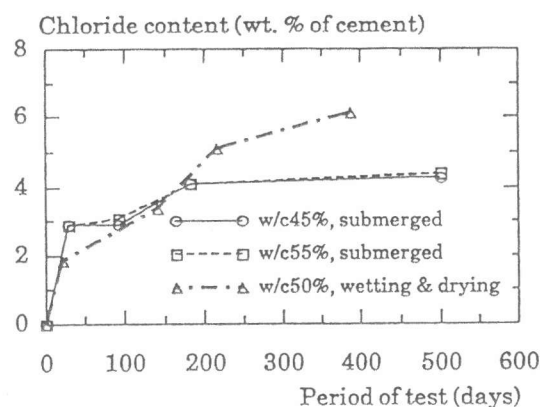


Fig.5 Test results of chloride content at surface layer (10 mm from concrete surface)

4. TEST AND ANALYTICAL RESULTS

4.1 PREPARATION OF SPECIMENS

Tests were performed in 2 series. One for determining diffusion coefficient of the tested mortar, another to clarify and establish a model for taking into account the effect of carbonation. Same mix proportion with

water to cement ratio of 50% and sand to cement ratio of 2.0, was utilized for preparing mortar specimens in both series. In first series, salt water with 5% of Cl concentration, equivalent to 2.632% of total Cl in weight percentage of cement in the specimen by calculation, was used as mixing water. Specimens were cast in $\phi 5 \times 10$ cm. prisms in which one surface of the mortar specimen was open to the atmosphere in order to yield one dimensional testing condition. Curing of the specimens was done by wrapping the specimens with vinyl sheets after casting and then storing them in a curing room with 20°C in temperature and 100% in relative humidity until the specimens were 28 days in age. In second series, all processes for preparing specimens were same as in the first series except for the concentration of Cl in mixing water. In this series, salt water with 1.82% of Cl concentration which conforms to 0.939% of total Cl in weight percentage of cement was used as mixing water.

4.2 DIFFUSION COEFFICIENT

In the first series which was conducted to determine diffusion coefficient of free chloride, specimens were submerged in fresh water so that chloride ion moves from inner part of concrete specimen to the environmental fresh water. The total chloride contents were obtained by extraction method proposed by JCI[5] and free chloride contents were derived from pore solution analysis of pore solution from expression method. Shown in Fig.6 is an example of result of chloride content distribution of specimen which was submerged for 98 days, diffusion coefficient of free chloride was derived by fitting the test results of chloride content distribution with the computational results. The derived diffusion coefficient was then utilized for all specimens throughout this study since all specimens had the same mix proportion.

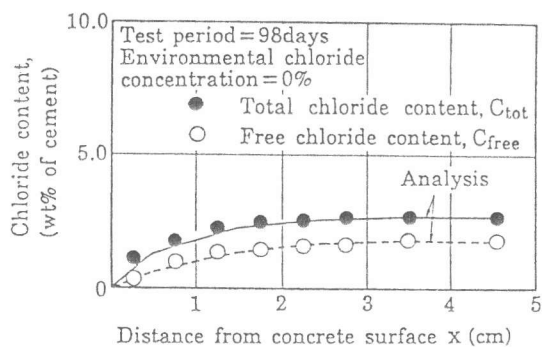


Fig.6 Test results for deriving coefficient of diffusion

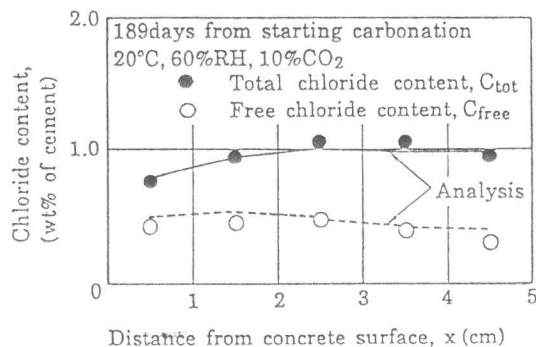


Fig.7 Chloride condensation by carbonation (Test and analytical results)

4.3 CARBONATION EFFECT

Shown in Fig.7 is an example of test and analytical results of second test series in which specimens were stored in a room with temperature 20°C, 60% RH and 10% of CO₂ concentration until the time of measurement. The distributions of total and free chloride contents were obtained in the same way as in the first series. With the use of carbonation model explained previously, the test results in second series were simulated as shown in the figure. Both the test and analytical results indicate that after carbonation, the total amount of chloride in the concrete does not change from that before carbonation, however, free chloride content near concrete surface increases causing the free chloride to move toward the non-carbonated portion because carbonation results in increase of free chloride in the carbonated area. It can be seen that the results were nearly quantitatively satisfied.

4.4 EFFECT OF CYCLIC WETTING AND DRYING WITH SALT WATER

Fig.8 shows the analytical results of chloride content distributions for both cases of permanently submerged in salt water and cyclic wetting and drying with salt water. It can be seen that chloride contents near concrete surface of cyclic wetting and drying specimens increase more rapidly than those of the permanently submerged specimens of which the results of the latter were calculated based on diffusion of free chloride only. It can be seen that the simulated results were qualitatively in accordance with the test results in Fig.5.

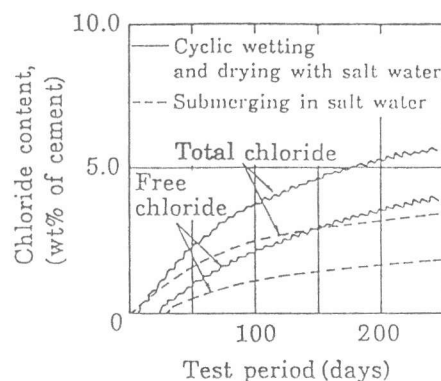


Fig.8 Variation with time of chloride content at surface layer (10 mm from concrete surface)

5. CONCLUSIONS

The following conclusions are made based on the content of this paper.

- 1) A mathematical model for simulating chloride content in hardened concrete was proposed.
- 2) Chlorides in hardened concrete were thought to be categorized into 2 types namely free and fixed chlorides and only the free chloride is movable.
- 3) Movement of free chloride was simulated based on diffusion theory.
- 4) Effect of carbonation was considered to be the dissolving of fixed chloride which increases amount and concentration of free chloride in the carbonated portion. Free chloride then migrates to the low chloride concentration portion of the non-carbonated portion.
- 5) The effect of cyclic wetting and drying with salt water was modeled by regarding that only water escapes from the surface portion of concrete in drying period, however, salt water enters the concrete by capillary action in wetting period.
- 6) The model was utilized to simulate the effect of carbonation and effect of wetting and drying with salt water where the results were nearly quantitatively satisfactory and qualitatively satisfactory, respectively.

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