

SEMI-THEORETICAL SIMULATION OF ION MIGRATION IN CONCRETE

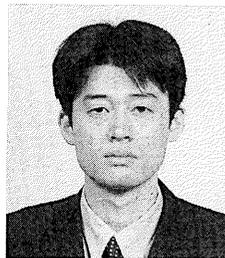
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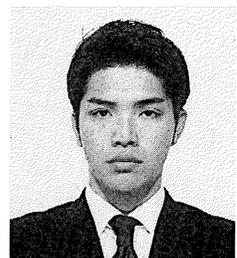
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The purpose of this research is to propose a method of estimating the long-term movement of ions in concrete under various environmental conditions. Using this method, the magnitude and direction of ion movement can be semi-theoretically simulated. Special features include considering (1) co-localized ions and (2) the electro-neutrality condition. The formula used in this method is based on the Nernst-Plank equation, Debye-Hückel theory and the electro-neutrality condition. The simulated results were confirmed by an examination of actual concrete exposed to seawater for 15.5 years. As a result, the validity of this method was confirmed.

*Keywords: Ion migration, Co-localized ions, Nernst-Plank equation, Debye-Hückel theory, Electro-neutrality condition*

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## 1. INTRODUCTION

From the viewpoint of concrete durability, the movement of ions ( $\text{Ca}^{2+}$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{OH}^-$ ,  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ , etc.) in concrete is very important. There are many previous investigations regarding these movement mechanisms, including some by the authors [1], [2], [3], [4]. However, previous studies have been half-empirical, using experimentally calculated diffusion coefficients for use in Fick's Second Law. Therefore, methods proposed in earlier research, paid attention only to the concentration gradients of ions when calculating the movement phenomena of ions. That is, ions in the surrounding solution, the type and concentration of co-localized ions, and concentration variations of the subject ion itself were not considered at all. For these reasons, such methods are unsuitable for estimating movement under various environment conditions or over the long-term.

To solve this problem, this research proposes a method of semi-theoretically estimating the movement of ions in concrete. Moreover, compatibility is shown by an example. The conditions for an appropriate method of calculation are as follows:

- 1) Concrete, on a macro scale, is a homogeneous material, and so all the pores in concrete can be thought of as continuous capillary pipes, ignoring the influence of curvature, etc.
- 2) The Nernst-Planck equation for electrochemical material movement in dilute solutions can be adopted as the basic equation for ion movement.
- 3) The influence of the concentrations of all co-localized ions can be incorporated using the Debye-Hückel theory.
- 4) The movement of ions meets the electro-neutrality condition.

However, when expressing the phenomenon of ion movement in concrete, these suppositions are to some extent inappropriate. As for 1), the influence of aggregate and the interfacial transition zones must be included. There are also many reports that deal with examinations of the relationship between pore distribution and continuous pores in concrete, but in this research the above suppositions are adopted as first approximations. In the future, the pore shape, including the influence of tortuosity [5], should be considered. On the other hand, 2), 3), and 4) are universal theories, and it is thought that they can be suitably applied to ion movement in concrete.

## 2. CONSTRUCTION OF THE SEMI-THEORETICAL SIMULATION

### 2.1 Introduction

In this section, based on the four conditions given at the end of the previous section, a simulation that describes the phenomena of ion movement in the pore solution is established. The simulation takes into account a) co-localized ions and b) the electro-neutrality condition, and based on the theories noted in suppositions 2), 3), and 4), a formula is constructed.

### 2.2 Construction of formula

#### a) Nernst-Planck equation

In calculating the flux of ionic species in a dilute solution, the modified Nernst-Planck equation is suitable:

$$J_i = -k \cdot T \cdot B_i \cdot \frac{\partial C_i}{\partial x} - e \cdot Z_i \cdot B_i \cdot C_i \cdot \frac{\partial \phi}{\partial x} \quad (1)$$

- where,
- i: ionic species
  - J: flux [ $\text{mol}/\text{cm}^2/\text{sec}$ ]
  - k: Boltzman number ( $=1.38 \times 10^{-23}$  [J/K])
  - T: temperature [K]
  - B: absolute mobility [ $\text{cm}^2/\text{sec}/\text{dyne}$ ]
  - C: concentration [ $\text{mol}/\text{cm}^3$ ]
  - e: elementary electric charge ( $=1.60 \times 10^{-19}$  [C])
  - Z: ionic charge number
  - $\Phi$ : internal (static) electrical potential [V]

Therefore,  $\partial\phi/\partial x$  represents the internal electrical potential gradient.

This first term describes diffusion, in which the driving force is the concentration gradient, and it is referred to as the 'diffusion term'. On the other hand, the second term describes the electro-migration of ions, which is driven by the internal electrical potential gradient. This term is referred to as the 'electro-migration term'.

b) Debye-Hückel theory

The pore solution in concrete contains ions of many species. It is thought that the diffusion of these ions is influenced by co-localized ions. The equation given in the preceding paragraph is based on diffusion in a dilute solution, so to determine the diffusion of ions in concrete the existence of co-localized ions and their concentrations must be considered. In the case of a general solution in which the concentration of co-localized ions cannot be ignored, the Nernst-Planck equation is as follows:

$$J_i = -k \cdot T \cdot B_i \cdot \left( 1 + \frac{\partial \ln \gamma_i}{\partial \ln C_i} \right) \cdot \frac{\partial C_i}{\partial x} - e \cdot Z_i \cdot B_i \cdot C_i \cdot \frac{\partial \phi}{\partial x} \quad (2)$$

where,  $\gamma_i$  : the activity coefficient.

The activity coefficient is given by the Debye-Hückel theory as follows:

$$\log \gamma_{\pm} = - \frac{A \cdot |Z_+ \cdot Z_-| \cdot \sqrt{I}}{1 + D \cdot a \cdot \sqrt{I}} \quad (3)$$

where,  $|Z_+ \cdot Z_-|$  : the absolute value of cation and anion price number product

$a$  : ionic size parameter [cm]

$I$  : ionic strength [mol/l]

$A, D$  are constants:

$$A = 0.5115 [\text{mol}^{-1/2} \cdot \text{dm}^{3/2}]$$

$$D = 0.3291 \times 10^8 [\text{cm}^{-1} \cdot \text{mol}^{-1/2} \cdot \text{dm}^{3/2}].$$

Ion strength is defined by the following equation:

$$I = \frac{1}{2} \sum_i (Z_i^2 \cdot C_i) \quad (4)$$

Equation (3) is partially differentiated about  $C_i$  after substituting equation (4) into equation (3). As a result, the following formula is obtained:

$$\frac{\partial \ln \gamma_i}{\partial \ln C_i} = \ln 10 \times C_i \times \frac{-A |Z_+ \cdot Z_-|}{2\sqrt{I} (1 + D a \sqrt{I})^2} \quad (5)$$

Substituting equation (5) into equation (2) gives:

$$J_i = -k \cdot T \cdot B_i \cdot \left\{ \left[ \ln 10 \times C_i \times \frac{-A |Z_+ \cdot Z_-|}{2\sqrt{I} (1 + D a \sqrt{I})^2} \right] \right\} \cdot \frac{\partial C_i}{\partial x} - e \cdot Z_i \cdot B_i \cdot C_i \cdot \frac{\partial \phi}{\partial x} \quad (6)$$

c) Electro-neutrality condition

In the paragraphs above, the influence of ion concentration in the pore solution was described. This condition, however, deals with the electro-neutrality condition that governs the movement of ions. The electro-neutrality condition, meaning that cations and anions maintain electrical neutrality in passing through an arbitrary section, is given by the following equation:

$$\sum_i (Z_i \cdot J_i) = 0 \quad (7)$$

### 2.3 Assumptions Made in Simulation Calculations

#### a) Concentration of the Surrounding Solution

The composition, temperature, and pressure of the surrounding solution all remain constant.

#### b) Subject Ions

The system considered contains six ionic species. That is, only  $\text{Ca}^{2+}$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{OH}^-$ ,  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$  are assumed to exist.

#### c) Concrete Pores

1. The pore structure in the concrete never changes.
2. Pores are saturated with the solution.

#### d) Fixation of Chloride Ions

All chloride ions in the concrete are classified as ① free chloride ions in the liquid phase; ② chloride ions in the solid phase, as represented by Friedel's salt; or ③ absorbed chloride ions. Of these, only ① move in the pore solution. Therefore, in this research, the sum of ② and ③ is taken as the total quantity of fixed chloride ions. Chloride ion fixation within the hardened cement is calculated using Maruya's model[6], which is described by the following equations:

$$C_{\text{fixed}} = \alpha \cdot C_{\text{total}} \quad (8)$$

$$C_{\text{free}} = C_{\text{total}} - C_{\text{fixed}} \quad (9)$$

where,  $C_{\text{total}}$ : total chloride ion quantity (①+②+③)

$C_{\text{fixed}}$ : fixed chloride ion quantity (②+③)

$C_{\text{free}}$ : free chloride ion quantity (①)

(all [wt % vs cement])

$\alpha$ : fixed coefficient, described by the following equations:

$$\begin{cases} \alpha = 1 & C_{\text{total}} \leq 0.5 \\ \alpha = 1 - 0.5 \cdot (C_{\text{total}} - 0.5)^{0.39} & 0.5 \leq C_{\text{total}} \leq 4.5 \\ \alpha = 0.141 & 4.5 \leq C_{\text{total}} \end{cases}$$

In the simulations, it is assumed that only the free chloride ions as calculated by equation (7) move in the concrete.

#### e) Apparent Absolute Mobility

A schematic representation is given in Figure 1. The mortar was cast into  $\phi 10 \times 20$  cm cylinders. After curing for 28 days, the mortar specimens were cut along the transverse axis using a diamond cutter to produce a disk specimen 1 cm thick. Such disk specimens were cut only from the middle of a cylinder specimen. The disk specimens were then installed in a rubber attachment, with the boundary between mortar and rubber sealed with epoxy resin to prevent leakage of solution between the halves of the cell. This rubber plus mortar specimen configuration is known here as a disk-type specimen.

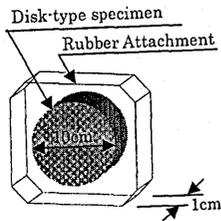


Figure 1 Disk-type specimen

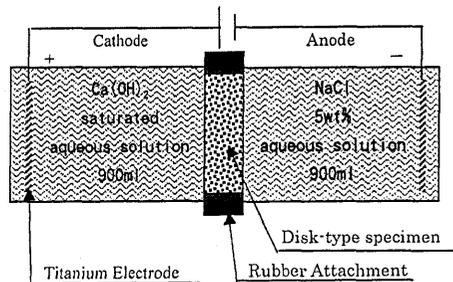


Figure 2 Electro-migration test

The electro-migration test used in this research is shown in Figure 2. A disk-type specimen was placed within an acrylic cylinder cell such that a waterproof seal was obtained. A 5 wt% NaCl solution formed the cathodic cell and a saturated Ca(OH)<sub>2</sub> solution the anodic cell. Titanium mesh was used as the electrodes. An electric current was applied across the solutions and the disk-type specimen, maintaining a current density of 1.0 A/m<sup>2</sup> over the surface area of the specimen. Time-dependent changes in chloride ion concentration in the anodic cell were measured daily using ion chromatography. Further, the voltage across the disk-type specimen was measured every time the anodic solution was extracted from the cell. In evaluating absolute mobility,  $\partial\phi/\partial x$  was calculated from this voltage. After the chloride ion concentration reached a steady state, the current was stopped. The disk-type specimens was then powdered to about 90  $\mu$  m, and then 10g of the powder was mixed with 100 g of de-ionized water. This solution was left to stand for 24 hours at 40°C. Ten milliliters of the filtered solution was then collected and subjected to ion chromatography to measure the ion concentration. Finally, a calculation was carried out to obtain the chloride ion concentration in the disk-type specimen.

The change in chloride ion concentration in the anodic cell is schematically shown in Figure 3. The gradient after the concentration change becomes constant is called the penetration rate. The flux can be calculated from the concentration change, because the penetration rate and flux have the following relationship:

$$J_i = \Delta Q_i \cdot \frac{V_{cell}}{F} \quad (10)$$

where,  $J_i$ : Flux [mol/cm<sup>2</sup>/sec]

$V_{cell}$ : the solution volume in the detected cell [  $\ell$  ]

$F$ : the cross sectional area of the disk-type specimen (=5×5× $\pi$  [cm<sup>2</sup>]).

$\Delta Q_i$ : the penetration rate [mol/  $\ell$ /sec]

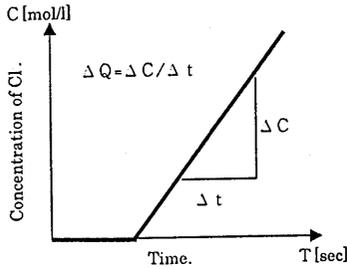


Figure 3 Concentration change of chloride ions in the anodic cell

From the results of the electro-migration test, absolute mobility was evaluated using equation (11), which is derived from the Nernst-Planck equation by ignoring the diffusion term. In this research, absolute mobilities are apparent values, because they are defined not in a pure dilute solution but in the concrete pore solution.

$$B_i = - \frac{J_i}{e \cdot Z_i \cdot C_i \cdot \frac{\partial\phi}{\partial x}} \quad (11)$$

Only the apparent absolute mobility of chloride ions was calculated from the electro-migration test; the apparent absolute mobilities of other ions were estimated from their ratio to chloride ion mobility in a pure dilute solution.

$$\frac{B_{Ca}}{B_{Cl}} \approx 0.79, \frac{B_{Na}}{B_{Cl}} \approx 0.66, \frac{B_K}{B_{Cl}} \approx 0.7, \frac{B_{OH}}{B_{Cl}} \approx 2.61, \frac{B_{SO_4}}{B_{Cl}} \approx 1.07 \quad (12)$$

## 2.4 Method of Analysis

The one-dimensional finite difference method was adopted in this research..

The concrete is divided into  $n$  separate elements and the flux of ions through neighboring elements is calculated at arbitrary time ( $t=t_m$ ). The computation is repeated along all elements that include a boundary with the surrounding solution. As a result, the movement of ions in the concrete can be comprehended.

The flux of ions is fixed by equation (2). Now, equation (2), when re-written for each individual ion species, becomes equations (13)-(18). Here, the early stage ion concentration in the concrete is known through an analysis of pore solution experiments. However, the internal electrical potential gradient is unknown. Therefore, in equations (13)-(18) the flux of the six ion species ( $J_{Ca}$ ,  $J_{Na}$ ,  $J_K$ ,  $J_{Cl}$ ,  $J_{OH}$ ,  $J_{SO_4}$ ) and the internal electrical potential gradient ( $\partial\phi/\partial x$ ) are unknown quantities.

$$J_{Ca} = -k \cdot T \cdot B_{Ca} \cdot \left\{ 1 + \left[ \ln 10 \times C_{Ca} \times \frac{-A|2 \cdot 2|}{2\sqrt{I}(1 + Da_{Ca}\sqrt{I})^2} \right] \right\} \cdot \frac{\partial C_{Ca}}{\partial x} - e \cdot Z_{Ca} \cdot B_{Ca} \cdot C_{Ca} \cdot \frac{\partial \phi}{\partial x} \quad (13)$$

$$J_{Na} = -k \cdot T \cdot B_{Na} \cdot \left\{ 1 + \left[ \ln 10 \times C_{Na} \times \frac{-A|1 \cdot 1|}{2\sqrt{I}(1 + Da_{Na}\sqrt{I})^2} \right] \right\} \cdot \frac{\partial C_{Na}}{\partial x} - e \cdot Z_{Na} \cdot B_{Na} \cdot C_{Na} \cdot \frac{\partial \phi}{\partial x} \quad (14)$$

$$J_K = -k \cdot T \cdot B_K \cdot \left\{ 1 + \left[ \ln 10 \times C_K \times \frac{-A|1 \cdot 1|}{2\sqrt{I}(1 + Da_K\sqrt{I})^2} \right] \right\} \cdot \frac{\partial C_K}{\partial x} - e \cdot Z_K \cdot B_K \cdot C_K \cdot \frac{\partial \phi}{\partial x} \quad (15)$$

$$J_{Cl} = -k \cdot T \cdot B_{Cl} \cdot \left\{ 1 + \left[ \ln 10 \times C_{Cl} \times \frac{-A|1 \cdot 1|}{2\sqrt{I}(1 + Da_{Cl}\sqrt{I})^2} \right] \right\} \cdot \frac{\partial C_{Cl}}{\partial x} - e \cdot Z_{Cl} \cdot B_{Cl} \cdot C_{Cl} \cdot \frac{\partial \phi}{\partial x} \quad (16)$$

$$J_{OH} = -k \cdot T \cdot B_{OH} \cdot \left\{ 1 + \left[ \ln 10 \times C_{OH} \times \frac{-A|1 \cdot 1|}{2\sqrt{I}(1 + Da_{OH}\sqrt{I})^2} \right] \right\} \cdot \frac{\partial C_{OH}}{\partial x} - e \cdot Z_{OH} \cdot B_{OH} \cdot C_{OH} \cdot \frac{\partial \phi}{\partial x} \quad (17)$$

$$J_{SO_4} = -k \cdot T \cdot B_{SO_4} \cdot \left\{ 1 + \left[ \ln 10 \times C_{SO_4} \times \frac{-A|2 \cdot 2|}{2\sqrt{I}(1 + Da_{SO_4}\sqrt{I})^2} \right] \right\} \cdot \frac{\partial C_{SO_4}}{\partial x} - e \cdot Z_{SO_4} \cdot B_{SO_4} \cdot C_{SO_4} \cdot \frac{\partial \phi}{\partial x} \quad (18)$$

The ionic flux indicated by equations (13)-(18) is substituted into equation (7). As a result, the internal electrical potential gradient is given by the following equation:

$$\frac{\partial \phi}{\partial x} = - \frac{\sum_i Z_i \cdot \left( 1 + \frac{\partial \ln \gamma}{\partial \ln C_i} \right) \cdot B_i \cdot \frac{\partial C_i}{\partial x}}{\sum_i Z_i^2 \cdot B_i \cdot C_i} \cdot \frac{k \cdot T}{e} \quad (19)$$

When equation (19) is substituted once again into equations (13)-(18), the ionic flux may be calculated. On the basis of this flux, the direction and magnitude of ion movement through each of the elements at any time ( $t=t_m$ ) are found. Moreover, by totaling the ionic concentration in each element at time  $t=t_{m-1}$ , the ionic concentration at time  $t=t_m$  is calculated. This calculated ionic concentration is used to determine the flux at time  $t=t_{m+1}$ .

This simulation is then repeated, yielding the concentration distribution of ions in the concrete with the elapse of time.

### 3. CHLORIDE ION MOVEMENT IN CONCRETE BLOCKS EXPOSED TO SEAWATER FOR 15.5 YEARS

#### 3.1 Basic Overview of Concrete Blocks

The concrete blocks that were the subject of this investigation had been used as foundation consolidation blocks at Kajima Harbor, JAPAN and had been exposed into seawater for 15.5 years. The blocks were cubes of side 120cm. The cement used was ordinary Portland cement, and the maximum aggregate size was 40mm. The water to cement ration was 56%, the unit water content was 300kg/m<sup>3</sup>, and the slump was 17cm.

Samples were taken at the positions shown in Figure 4. Core samples were taken from a horizontal plane in four directions towards the center of the block, and the chloride ion content was measured in steps of 0, 4, 8, 12, 16, 20, 30, 40, and 50cm from the outer face.

#### 3.2 Method of Analysis

In this analysis, it is assumed that the movement of ions through fluids outside and inside the concrete occurs only at faces exposed to seawater. Furthermore, the composition of the seawater, as shown in Table 1, was assumed to be constant. Its specific gravity was taken as 1.03, and constant temperature and pressure were assumed.

It is assumed that the initial ion concentration of the samples is as shown in Table 2[7]. The sample density and porosity were assumed to be  $2.3 \times 10^{-2}$  kg/m<sup>3</sup> and 0.2[8], respectively. Further, fixed chloride ions were assumed to be absent at the beginning of exposure.

#### 3.3 Comparison of Analytical and Experimental Values of Total Chloride Ion Quantity

The weight ratio of total chloride ions (free chloride ions + fixed chloride ions) in the mortar is shown in Figure 5. This figure shows both experimental and analytical values, and it can be seen that the respective values are quantitatively equivalent. It is therefore thought possible to predict the movement of ions in concrete using the formula proposed in this research.

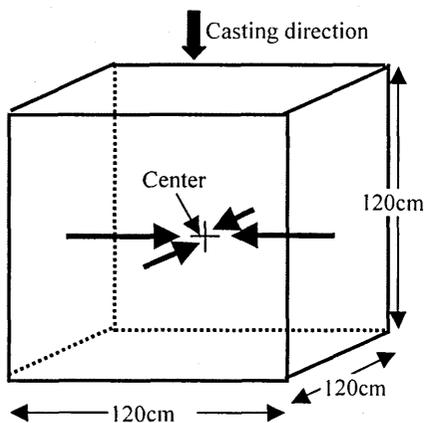


Figure 4 Sampled Concrete Block

Table 1 Ionic Concentration of Seawater

ionic species	Ca <sup>2+</sup>	Na <sup>+</sup>	K <sup>+</sup>	Cl <sup>-</sup>	OH <sup>-</sup>	SO <sub>4</sub> <sup>2-</sup>
concentration	400	1065	38	1898	0	265

Strictly, the pH of OH<sup>-</sup> is 7. Therefore, the concentration of OH<sup>-</sup> is 0.017ppm.

Table 2 Initial Ion Concentration in Pore Solution of Sampled Concrete

ionic species	Ca <sup>2+</sup>	Na <sup>+</sup>	K <sup>+</sup>	Cl <sup>-</sup>	OH <sup>-</sup>	SO <sub>4</sub> <sup>2-</sup>
concentration	144	1500	1838	7	2006	280

#### 3.4 Variation in Internal Electric Potential Gradient with Respect to Time

The internal electric potential gradient,  $\partial\phi/\partial x$ , as calculated using equation (19) is shown in Figure 6. This leads to the following observations: 1) the gradient increases in the vicinity of the exposed face; and 2) a peak appears inside the concrete, and this peak moves deeper into the concrete with increased exposure time. Namely, it is

thought that the variation in potential gradient is a result of corresponding changes in the concentration of co-localized ions. Therefore, the fact that the internal electric potential gradient, which affects the ion migration mechanism, is not constant relative to time or position has been confirmed. The effect of the internal electric potential gradient is discussed in the following paragraph.

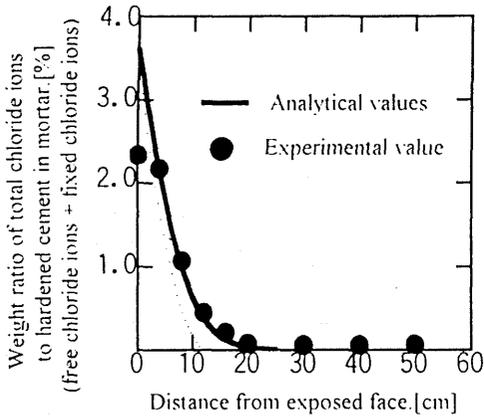


Figure 5 Weight ratio of total chloride ions (free chloride ions + fixed chloride ions) in mortar at the age of 15.5 years

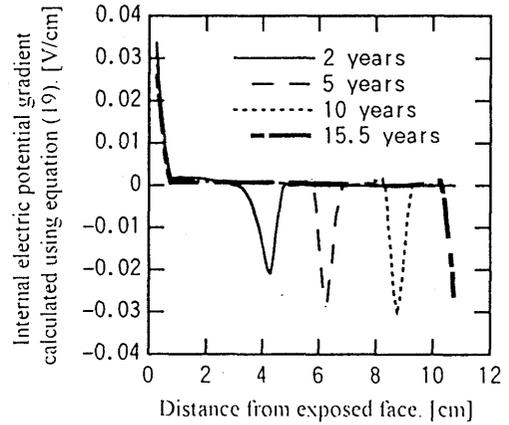


Figure 6 Internal electrical potential gradient  $\partial\phi/\partial x$  calculated using equation (19)

Table 3 Comparison of diffusion and electrophoresis terms (terms 1 and 2, respectively) of equations (13) ~ (18) at the age of 15.5 years

(a) Ion movement flux 1cm from the exposed face

(b) Ion movement flux at a location 10cm from the exposed face

Ionic species	[10 <sup>-8</sup> × mol/cm <sup>2</sup> /sec]		Ionic species	[10 <sup>-8</sup> × mol/cm <sup>2</sup> /sec]	
	Diffusion term	Electrophoresis term		Diffusion term	Electrophoresis term
Ca <sup>2+</sup>	7.28	6.16	Ca <sup>2+</sup>	6.12	-1.07
Na <sup>+</sup>	344	95.5	Na <sup>+</sup>	142	-10.2
K <sup>+</sup>	-0.14	2.26	K <sup>+</sup>	1.71	-1.34
Cl <sup>-</sup>	584	-118	Cl <sup>-</sup>	148	4.09
OH <sup>-</sup>	-31.1	-0.445	OH <sup>-</sup>	-29.2	5.22
SO <sub>4</sub> <sup>2-</sup>	28.2	-11.2	SO <sub>4</sub> <sup>2-</sup>	5.97	1.05

Note: The plus sign represents movement from the exposed face into the concrete.

### 3.5 Effect of Concentration Gradient and Internal Electric Potential Gradient

In this section the effects of concentration gradient and internal electric potential gradient are compared. Table 3 compares the diffusion and electrophoresis terms (terms 1 and 2, respectively) from equations (13) ~ (18). Table 3 (a) represents the ion movement flux 1cm from the exposed face, while (b) represents that of a location 10cm from the exposed face. From these tables, the following points can be noted: 1) the order of the diffusion and electrophoresis terms is generally equivalent; and 2) for certain ionic species, the plus and minus signs reverse. Regarding this second point, regarding point 2), the direction of ion migration caused by the concentration gradient, and the direction of that caused by the internal electrical potential gradient, are different. On the basis of these results, it can be said that there is a need to consider both the effect of concentration gradient and the effect of internal electric potential gradient when studying the migration of ions in concrete. Namely, it is not possible to ignore the electro-neutrality condition (electrophoresis term).

### 3.6 Apparent Diffusion Coefficient of Chloride Ions

Fick's Diffusion Equation, which considers only the effect of the concentration gradient, is written as follows:

$$J = -D' \cdot \frac{\partial C}{\partial x} \quad (20)$$

where  $D'$  : apparent diffusion coefficient of chloride ions [ $\text{cm}^2/\text{sec}$ ]

The apparent diffusion coefficient was calculated by substituting the ion migration flux and concentration gradient, as obtained using the simulation technique proposed in this paper, into equation (20). The variation in this apparent diffusion coefficient of chloride ions with time is shown in Figure 7. Clearly, this apparent diffusion coefficient varies considerably with exposure time and position within the concrete. This is thought to be due to the variance in internal electrical potential gradient with respect to time and position, as mentioned in the previous section. Furthermore, comparing equation (1) and equation (20), the part of equation (20) corresponding to the diffusion coefficient is seen to be a function of concentration in equation (1), so this result is logical.

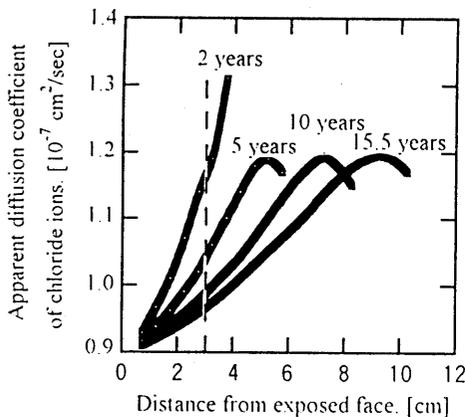


Figure 7 Variation in apparent diffusion coefficient of chloride ions with time

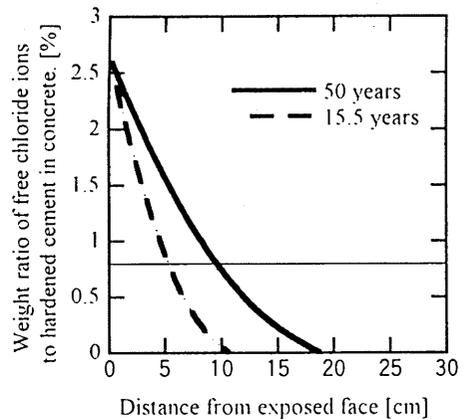


Figure 8 Chloride ion ratio in concrete blocks predicted on the assumption that exposure to seawater is continued for 50 years.

Moreover, the apparent diffusion coefficients of chloride ions at a point 3cm from the exposed face are compared. According to Figure 7, the diffusion coefficient decreases with increasing exposure time. This means, it is difficult to predict long-term migration phenomena based on relatively short-term general diffusion coefficients, such as those for 2 or 5 years.

### 3.7 Prediction of Chloride Ion Migration in Concrete Blocks Exposed to Seawater for 50 Years

In Figure 8, the ratio of chloride ions in the concrete blocks is predicted on the assumption that the seawater exposure continued for 50 years. From this, it can be seen that the quantity of chloride ions is higher in the concrete block exposed for 50 years than that for the 15.5 years. According to the author's research [9], if the weight ratio of chloride ions in hardened cement exceeds 0.8%, the passivity of the steel reinforcement has a 50% chance of being lost. This suggests that the possibility of corrosion occurring in the reinforcement under even 10cm of concrete is very high.

## 4. CONCLUSIONS

The results of this research are summarized as follows:

(1) A semi-theoretical simulation method is proposed for ion migration in concrete, in which co-localized ions and the electro-neutrality condition are considered. This simulation method is developed from the Nernst-Planck equation, Debye-Hückel theory, and the electro-neutrality condition.

(2) Analysis is conducted for concrete blocks exposed to seawater for 15.5 years. The experimental and analytical values of total chloride ion content are generally equivalent. Therefore, the simulation method proposed in this research can be considered valid for the prediction of ion migration phenomena in concrete.

(3) In the case of concretes with water to cement ratios around 50% that are exposed to marine conditions for 50 years, there is concern about corrosion of the steel reinforcement even at a depth of 10cm.

(4) There is a need to consider the effect of both concentration gradient and internal electric potential gradient when studying the migration mechanisms of ions in concrete. For example, chloride ions can migrate from the surrounding seawater into the concrete due to the concentration gradient. On the other hand, due to the internal electric potential gradient, it is possible for chloride ions to migrate from within the concrete to the surrounding seawater.

(5) The apparent diffusion coefficient of chloride ions varies with two factors: a) position in concrete and b) exposure time. Therefore, it is extremely difficult to predict the long-term migration of ions if these factors are disregarded and a steady diffusion coefficient is used in Fick's diffusion equation.

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