

ESTABLISHMENT OF NUMERICAL ANALYSIS METHOD FOR THE PREDICTION OF LEACHING OF CALCIUM FROM CONCRETE CONSIDERING MIGRATION OF MULTIPLE IONS

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The purpose of this study is to establish and propose a numerical analysis method for predicting the long-term leaching of calcium from concrete. Using the proposed method, leaching is estimated using a model taking account of ion migration and leaching of calcium from cement paste to the pore solution. The Nernst-Plank equation, the Debye-Hückel equation, and the electro-neutrality condition are used for modeling ion migration in concrete. Also, Buil's model is used for modeling the leaching of calcium from cement paste to pore solution. In order to verify the method, predictions are compared to the results of a survey carried out on an existing structure in use for 100 years. Through this process, the new numerical analysis method for the prediction of leaching of calcium from concrete is fully established. Moreover, it is demonstrated that the leaching of calcium over a period of 1,000 years can be predicted by this method.

Keywords: leaching of calcium, hundred years, numerical analysis, prediction method, Nernst-Plank equation, Debye-Hückel equation, electro-neutrality condition

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1. INTRODUCTION

As the calcium hydrate contained in concrete dissolves into water around a concrete structure, the concrete becomes porous. This process is known as concrete deterioration caused by the leaching of calcium. Although several kinds of hydrate are present in concrete, those that contribute strength to the concrete are mainly $\text{Ca}(\text{OH})_2$ and C-S-H. Therefore, it is important to direct attention to the leaching of calcium from concrete when considering deterioration caused by hydrate leaching.

This type of deterioration progresses very slowly in comparison with other deterioration mechanisms such as the carbonation or the alkali-aggregate reaction or chemical erosion caused by acidic products. Consequently, it has not generally been considered when designing ordinary concrete structures. However, in the design of special concrete structures requiring service lives of several hundred years or more, this type of deterioration must be taken into account. For instance, in the case of a water supply facility or a dam remaining in contact with water for over 100 years, it is impossible to ignore this type of deterioration. [1]

Also, when a cement material is used for the solidification and disposal of incinerated ash containing toxic substances, the long-term stability of the material must be estimated from the viewpoint of environmental preservation. Moreover, the half-life of the radioactive elements in high-level radioactive waste material is over 100 years, so it is necessary to guarantee a service life of over 100 years for disposal facilities for radioactive waste. In order to minimize environmental effects and prevent early deterioration of the concrete by weathering or carbonation, etc, such facilities will be constructed underground according to current plans. If this is done, they will be in contact with groundwater and thus prone to deterioration caused by leaching of calcium. This means that it is necessary to estimate the durability in consideration of concrete deterioration caused by the leaching of calcium over a period of 100 years.

For the reasons outlined above, it is important to establish a prediction method for deterioration caused by the leaching of calcium. In recent years, some studies of this issue using numerical analysis have been reported. [1],[2],[3],[4] And although, diffusion was considered as a driving force of ions in these studies, electro-migration under electrostatic potential was ignored. Also, these studies did not take into account the influence of co-existing ions on the migration of Ca^{2+} and other ions, though there are several kinds of ion in pore solution.

The purpose of this study is to establish a numerical analysis method for predicting the leaching of calcium ions that takes into account both diffusion as well as electro-migration and the influence of co-existing ions.

To achieve this purpose, the Nernst-Planck equation, the electro-neutrality condition, and the Debye-Hückel equation are used together as the ion migration equation in concrete. Here, the Nernst-Planck equation, which is well known as the basic equation of ion migration, indicates the quantity of ions that migrates through a unit cross-section in unit time under the influence of the electrochemical potential gradient. Further, electro-neutrality condition restrains the migration of multiple ions in the system where the multiple ions exist together. The Debye-Hückel equation is known as the equation that represents the relationship between activity coefficient and ionic strength, and it is possible to consider the influence of co-existing ions on the diffusion of the ion in question by introducing this equation into the Nernst-Planck equation.

Combining these elements, an ion migration equation that takes into account diffusion rules and electro-migration rules as well as the influence of co-existing ions can be introduced. This equation is to

calculate the migration of multiple ions, and to estimate the ion concentration distribution.

In addition to the above, it is necessary to introduce a model for the leaching mechanism of calcium from cement paste to the pore solution, so as to predict the leaching of calcium from the concrete. In this study, the solid-liquid equilibrium model for calcium proposed by Buil, M. et al. [4] is used.

2. FLOW OF THIS STUDY

In this study, we first put together a basic theory of ion migration, by combining the Nernst-Planck equation with the electro-neutrality condition and the Debye-Hückel equation. Then, the leaching mechanism of calcium from cement paste to the pore solution is explained, and Buil's model modeling this mechanism is introduced. Next, a numerical analysis method for the prediction of calcium leaching is compounded from these basic concepts, adapting one-dimensional numerical analysis based on differential calculus.

After introducing the new method, the leaching of calcium from concrete and mortar over a period of 100 years is predicted. Then, in order to confirm its validity, the predictions are compared with the results of a survey carried out on an existing structure at a water supply facility in Shiba, Tokyo, that had been in use for 100 years. [5]

Finally, the leaching of calcium from concrete over a period of 1000 years is predicted using this method.

3. BASIC THEORY OF ION MIGRATION AND CALCIUM LEACHING MODEL

3.1 Assumptions

It is difficult to solve ion migration and calcium leaching in concrete strictly. Hence, in order to establish a prediction method for the deterioration caused by calcium leaching in this study, ion migration and calcium leaching are modeled under the following assumptions:

- (i) Concrete is a macroscopically homogeneous material.
- (ii) Ion migration in concrete follows the Nernst-Planck equation for electrochemical mass transfer. Namely, the driving force for ion motion in concrete is developed by the concentration gradient and electrostatic potential gradient.
- (iii) The influence of ionic strength on diffusion can be considered using the Debye-Hückel equation.
- (iv) The migration of multiple ions depends on the electro-neutrality condition.
- (v) All pores in concrete can be thought of as continuous capillaries filled with pore solution.
- (vi) The ions that dissolve from cement paste are Ca^{2+} and OH^- only.
- (vii) The leaching of calcium from cement paste to concrete can be represented by Buil's model, a solid-liquid equilibrium model.
- (viii) While 1 mole of Ca^{2+} dissolves from cement paste to the pore solution, 2 moles of OH^- dissolve.
- (ix) The porosity created by leaching a given quantity of calcium hydroxide is equal to the volume of the same quantity of crystalline $\text{Ca}(\text{OH})_2$.
- (x) The apparent absolute mobility, which is an index for ion migration in concrete, can be determined from the pore ratio and tortuosity factor. [6]
- (xi) It is assumed that six types of ion are contained in pore solution. That is, only Ca^{2+} , Na^+ , K^+ , OH^- , Cl^- ,



Based on these assumptions, a basic theory for ion migration and a model for calcium leaching from cement paste to the pore solution are developed into a numerical analysis method in this study.

The validity of the ion migration equation used in this study has already been confirmed in a previous study [7]. Although there are in fact hydrates including Al or Fe in concrete, the amount of these hydrates is low in comparison with calcium hydrate. Therefore, assumption (vi) can be thought of as an appropriate approximation. Also, in some previous studies of calcium leaching from $\text{Ca}(\text{OH})_2$ and C-S-H in concrete, it is supposed that $\text{Ca}(\text{OH})_2$ dissolves before C-S-H [1]. In the solid-liquid equilibrium model proposed by Buil, M. et al., this phenomenon can be considered. Hence, it is supposed that this model is reasonable for modeling the leaching of calcium from cement paste to the pore solution.

Since Ca^{2+} , Na^+ , K^+ , OH^- , Cl^- , SO_4^{2-} are the main ions in pore solution [8], these six kinds of ion are considered in this study.

3.2 Ion migration in concrete

a) Nernst-Plank equation

In this study, it is assumed that ion migration in concrete follows the Nernst-Plank equation. This, which is commonly used in solution chemistry, is formulated as follows:

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

where, i is the ionic species, J is flux ($\text{mol}/\text{cm}^2/\text{sec}$), k is the Boltzman number ($=1.38 \times 10^{-23} \text{J/K}$), T is temperature (K), B is absolute mobility ($\text{cm}/\text{sec}/\text{dyne}$), γ is the activity coefficient, C is the concentration of ions (mol/cm^3), x is the distance from the exposure surface (cm), e is the elementary electric charge ($=1.60 \times 10^{-19} \text{C}$), Z is the ionic charge number, and ϕ is electrostatic potential (V). The first term describes diffusion, in which the driving force is the concentration gradient, and it is referred to as the ‘diffusion term’. The second term describes the electro-migration, which is driven by the electrostatic potential gradient. This member is referred to as the ‘electro-migration term’. Note that equation (1) shows that the ion migration index of diffusion and electro-migration is the absolute mobility B_i only.

Incidentally, in an aqueous solution of multiple ions, such as concrete pore solution, diffusion is influenced by the co-existence of ions. The activity coefficient γ is a coefficient that account for this influence, and it is given by the Debye-Hückel equation as follows:

$$\log \gamma_i = - \frac{u \cdot Z_i^2 \cdot \sqrt{I}}{1 + v \cdot a_i \cdot \sqrt{I}} \quad (2)$$

where, a is an ion size parameter (cm), I is ionic strength (mol/l), u is a constant ($=0.5115 \text{ dm}^3/2 / \text{mol}^{1/2}$), and v is a constant ($=0.3921 \times 10^8 \text{ dm}^3/2 / \text{mol}^{1/2}$).

Ionic strength is defined by the following equation:

$$I = \frac{1}{2} \sum_i (Z_i^2 \cdot C_i) \quad (3)$$

The accuracy of the Debye-Hückel equation depends on the accuracy of the estimate of ion size parameter a_i . However, equation (2) can be simplified engineeringly as shown in equation (4), because the ion size parameters a_i of many ions are about 3 Å [9].

$$\log \gamma_i = -\frac{0.51 \cdot Z_i^2 \cdot \sqrt{I}}{1 + \sqrt{I}} \quad (4)$$

Equation (4) is partially differentiated about C_i after substituting equation (3). As a result, the following equation can be introduced:

$$\frac{\partial \ln \gamma_i}{\partial \ln C_i} = \ln 10 \times C_i \times \frac{-0.51 \cdot Z_i^2}{2 \cdot \sqrt{I} \cdot (1 + \sqrt{I})^2} \quad (5)$$

Equation (5) is part of equation (1). Therefore, by substituting equation (5) and equation (3) into equation (1), the flux shown in equation (1) can be described as a function of ion concentration and electrostatic potential.

Incidentally, it is impossible to use the absolute mobility as is when the Nernst-Planck equation is applied to concrete, because ions in concrete migrate through pores with a disorderedly distribution. Therefore, an apparent ion migration index must be used. This apparent index is defined as the engineering absolute mobility. The calculation method for it is explained in section 3.3.

b) Electro-neutrality condition

The paragraph above explains that the ion migration equation is described by ion concentration and electric potential. In this method, the ion concentration distribution is calculated from the initial ion concentration distribution. Hence, the ion concentration is the known parameter. However, the electric potential gradient can be calculated by considering the electro-neutrality condition.

The electro-neutrality condition means that cations and anions maintain electrical neutrality in passing through an arbitrary section. This condition, described by ionic charge number and flux in equation (6), shows that the multiple ions in concrete migrate while maintaining a charge balance.

$$\sum_i (Z_i \cdot J_i) = 0 \quad (6)$$

The flux of each ion shown in equation (1) is substituted into equation (6). As a result, the electrostatic potential gradient is given by the following equation:

$$\frac{\partial \phi}{\partial x} = -\frac{\sum_i \left(Z_i \cdot \left(1 + \frac{\partial \ln \gamma_i}{\partial \ln C_i} \right) \cdot B_i \cdot \frac{\partial C_i}{\partial x} \right)}{\sum_i (Z_i^2 \cdot B_i \cdot C_i)} \cdot \frac{k \cdot T}{e} \quad (7)$$

If equation (7) is used, the electric potential gradient can be described by ion concentration, also. Therefore, the flux of an ion species (*ion*) is a function of the concentrations of several kinds of ion as follows:

$$J_{ion} = -k \cdot T \cdot B_{ion} \cdot \left(1 + \ln 10 \times C_{ion} \times \frac{-0.51 \cdot Z_{ion}^2}{2 \cdot \sqrt{I} \cdot (1 + \sqrt{I})^2} \right) \cdot \frac{\partial C_{ion}}{\partial x} + k \cdot T \cdot Z_{ion} \cdot B_{ion} \cdot C_{ion} \cdot \frac{\sum_i \left(Z_i \cdot \left(1 + \frac{\partial \ln \gamma_i}{\partial \ln C_i} \right) \cdot B_i \cdot \frac{\partial C_i}{\partial x} \right)}{\sum_i (Z_i^2 \cdot B_i \cdot C_i)} \quad (8)$$

3.3 Calculation of engineering absolute mobility

Using the method for evaluating an apparent transfer index from pore ratio and tortuosity factor [7], the engineering absolute mobility B_i is given by the following equation:

$$B_i = \frac{\varepsilon}{\tau^2} \cdot B_{0,i} \quad (9)$$

where, ε is pore ratio (cm^3/cm^3), τ is tortuosity factor, and B_0 is absolute mobility in dilute solution ($\text{cm}^2/\text{sec}/\text{dyne}$). The tortuosity factor is a coefficient reflecting the continuity of pores, and is about $\sqrt{2}$ for concrete [7]. Table 1 shows the absolute mobility in dilute solution used in this study.

Table 1 Absolute Mobility in Dilute Solution

Ionic species	Absolute mobility [$\text{cm}^2/\text{sec}/\text{dyne}$]
Ca^{2+}	1.66×10^{15}
Na^+	2.75×10^{15}
K^+	4.13×10^{15}
OH^-	1.11×10^{16}
Cl^-	3.94×10^{15}
SO_4^{2-}	1.84×10^{15}

3.4 Change in pore ratio due to leaching of calcium

The pore ratio of concrete increases due to the leaching of calcium. In this study, it is assumed that the porosity created by leaching a given quantity of calcium hydrate is equal to the volume of the same quantity of crystalline $\text{Ca}(\text{OH})_2$. The pore volume per unit concrete volume is given by in the following equation:

$$\varepsilon = \varepsilon_0 + \frac{M_{CH}}{d_{CH}} \cdot (1 - V_c) \cdot (C_{p0} - C_p) \quad (10)$$

where, ε is pore ratio (cm^3/cm^3), ε_0 is initial pore ratio (cm^3/cm^3), M_{CH} is the molecular weight of $\text{Ca}(\text{OH})_2$ ($=74 \text{ g/mol}$), d_{CH} is the density of $\text{Ca}(\text{OH})_2$ ($=2.23 \text{ g/cm}^3$), V_c is the volume ratio of cement ($V_c = 1/(d_c \times W/C + 1)$, d_c : density of cement), C_{p0} is the initial Ca quantity in the solid phase per unit volume of concrete (mol/l), and C_p is the quantity in the Ca concentration of solid phase per unit volume of concrete (mol/l).

3.5 Model for leaching of calcium from cement paste to pore solution

In order to calculate the ion migration associated with leaching of calcium, it is necessary to consider the equilibrium relation between Ca concentration in the cement paste and Ca^{2+} concentration in the pore solution. A model for this equilibrium relation has already been proposed by Buil, M. et al. [4], based on data in a previous study [10], as shown in Figure 1. Although this equilibrium relation may depend on temperature, details remain unresolved at present. Hence, it is assumed that the influence of temperature on this equilibrium relation can be ignored.

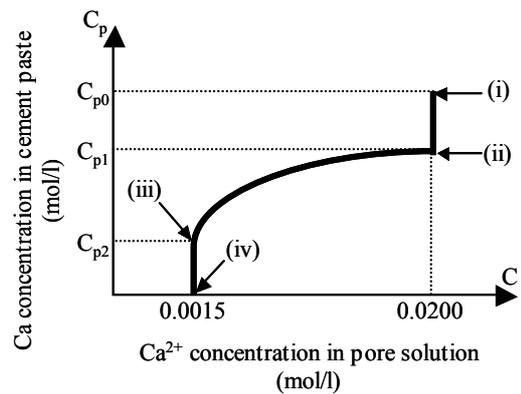


Figure 1 Buil's model

The calcium hydrates in cement paste are composed of $\text{Ca}(\text{OH})_2$ and C-S-H, and leaching of calcium from C-S-H in a particular region occurs only after all $\text{Ca}(\text{OH})_2$ dissolves there. The Ca^{2+} concentration in pore solution remains at 20 mmol/l during $\text{Ca}(\text{OH})_2$ dissolves. Section of (i) to (ii) in Figure 1 illustrates this process. C-S-H begins to dissolve once the $\text{Ca}(\text{OH})_2$ disappears due to leaching of calcium, and $\text{Ca}(\text{OH})_2$ is produced from C-S-H in the pores.



The dissolution of C-S-H progresses as shown in sections (ii) to (iii) in Figure 1. This part of the relation is described by the following equation:

$$C_p = C_{p1} \cdot (C/C_0)^{1/3} \quad (10)$$

where, C_p is Ca concentration in the cement paste (mol/l), C_{p1} is Ca concentration in the cement paste at the time of $\text{Ca}(\text{OH})_2$ disappearance, C is Ca^{2+} concentration in the pore solution (mol/l).

If the Ca concentration in the cement paste C_p falls below C_{p2} due to leaching of calcium from C-S-H, the C-S-H turns into silica gel and rapidly dissolves. During this process, the Ca^{2+} concentration in the pore solution remains at $C_1=0.0015\text{mol/l}$, as shown in the sections from (iii) to (iv) in Figure 1.

The migrations of several kinds of ions are considered in this study. Hence, it is necessary to count the amount of OH^- dissolving from the cement paste with Ca^{2+} . Hence, it is assumed that 2 moles of OH^- dissolve for every 1 mole of Ca^{2+} that dissolves.

4. FORMULATION OF NUMERICAL ANALYSIS METHOD

In this chapter, the numerical analysis method for the prediction of calcium leaching from concrete is formed using the theory of ion migration and the model of calcium leaching introduced in chapter 3.

4.1 Discreteness of time and space

In the numerical analysis method, calcium leaching is calculated numerically using the one-dimensional differential calculus. Hence, it is necessary to discretize time and space.

Improper or unsuitable discretization of time and space can have an influence on the solution obtained by one-dimensional differential calculus. Hence, in this study, a suitable discretization is determined according to the following logic.

In solving the diffusion equation using one-dimensional differential calculus, it is generally accepted that proper solutions are obtained as long as the following equation is satisfied:

$$D_{ion} \cdot \frac{\Delta t}{\Delta x^2} \leq 0.5 \quad (13)$$

where, D is the diffusion coefficient of an ion (cm^2/sec), Δt is the discrete time step (sec), and Δx is the discrete space step (cm). In this study, it is assumed that the diffusion coefficient D in equation (13) can be obtained from the absolute mobility in solution and Einstein's equation as follows:

$$D_{ion} = k \cdot T \cdot B_{0,i} \quad (14)$$

Also, it is necessary to adopt six diffusion coefficients in equation (14) when determining the discrete step,

because six types of ion are being considered when calculating ion migration in this study. Hence, the computation equation for these time and space steps width should be obtained by solving six simultaneous inequalities introduced by substituting the diffusion coefficients of the six ions into equation (13), as follows:

$$\frac{\Delta t}{\Delta x^2} \leq 1.12 \times 10^4 \quad (15)$$

Incidentally, solutions obtained by numerical analysis using a computer include a specified computation error of ‘canceling’ or ‘rounding’. This error accumulates with the increased number of calculation iterations caused by too small a step width. In this study, predictions are made over the order of 100 or 1,000 years. Therefore, this cumulative error calculation should be minimized. In order to ensure minimization, the step width of space is set to 1cm. Moreover, the time step is set to 1×10^4 sec, which is permissible by substituting $\Delta x=1\text{cm}$ for equation (15), in order to decrease the computation error.

4.2 Calculation method for the properties of each element

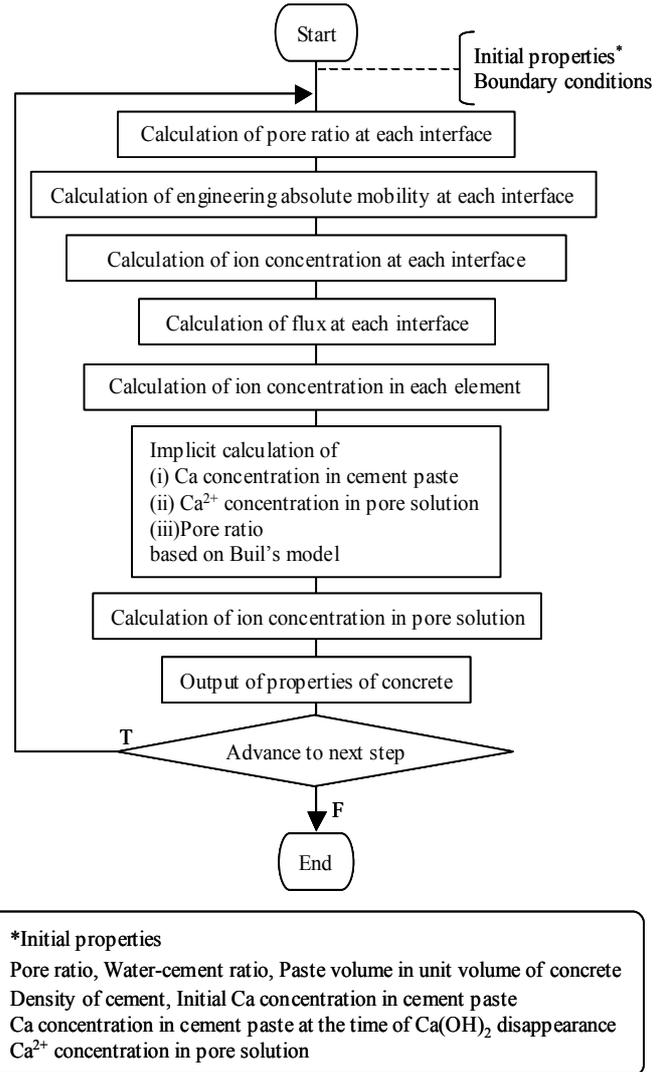


Figure 2 Calculation procedure

The calculation procedure is shown in Figure 2. First, ion migration in the concrete is calculated. Secondly, leaching of calcium from the cement paste to the pore solution is calculated using Buil’s model. Finally, the physical properties of the concrete are output.

a) Concept of ion migration calculation

Figure 3 outlines the calculation of ion migration. The concrete member under study is divided into m -elements. It is supposed that ion migration in the concrete occurs at the interface between these elements. Therefore, the flux calculated in this method is at these interfaces as shown in Figure 3. The flux of ion species n at interface l is calculated by equation (16), an approximation of equation (8), as follows:

$$J_{l,n} = -k \cdot T \cdot B'_{l,n} \cdot \left(1 + \ln 10 \times C'_{l,n} \times \frac{-0.51 \cdot Z_n^2}{2 \cdot \sqrt{I'_l} \cdot (1 + \sqrt{I'_l})} \right) \cdot \frac{S_{l+1,n} - S_{l,n} + k \cdot T \cdot Z_n \cdot B'_{l,n} \cdot C'_{l,n} \cdot \sum_i \left(Z_i \cdot \left(1 + \frac{\partial \ln \gamma'_{l,i}}{\partial \ln C'_{l,i}} \right) \cdot B'_{l,i} \cdot \frac{S_{l+1,i} - S_{l,i}}{\Delta x} \right)}{\sum_i (Z_i^2 \cdot B'_{l,i} \cdot C'_{l,i})} \quad (16)$$

where, l is the number of elements and interfaces, n is the ion species, S is the ion concentration in the element (mol/cm³), C' is the ion concentration at the interface (mol/cm³), J' is the flux at the interface (mol/cm²/sec), B' is the engineering absolute mobility at the interface (cm²/sec/dyne), I'_l is the ion strength

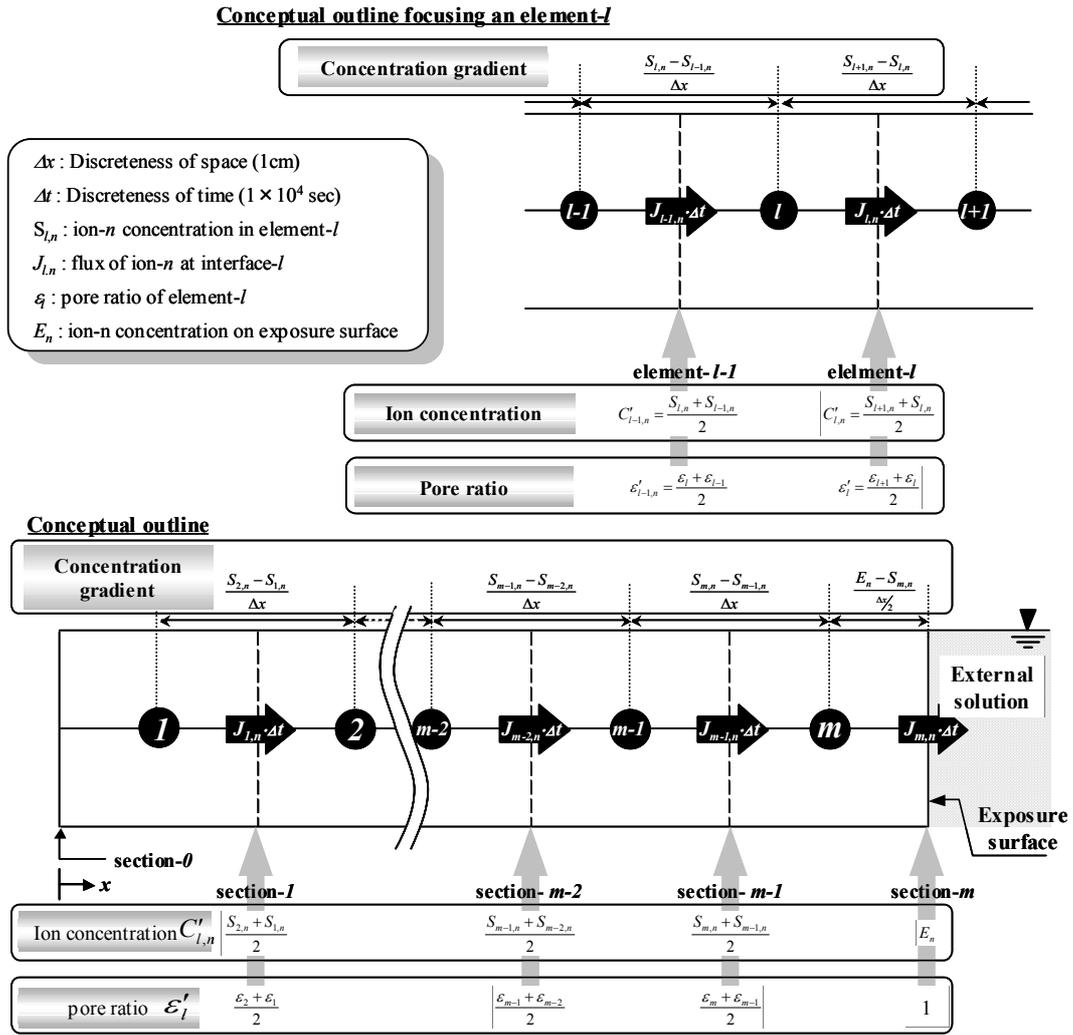


Figure 3 Concept of ion migration calculation

at the interface, and $\gamma'_{l,n}$ is the activity coefficient at the interface.

The ion concentration C' and the pore ratio at interface l is defined as the average of the ion concentrations and pore ratios in elements l and $l+1$, respectively. Furthermore, the engineering absolute mobility B' at interface l is calculated from this average pore ratio and equation (9).

b) Calculation procedure for ion migration

First, the pore ratio and the engineering absolute mobility of each interface at $t=t_j$ is calculated from the pore ratios of the elements. Second, the ion concentration at each interface is calculated from the ion concentration of the elements. Finally, the flux at each interface is calculated using equation (16), and the amount of ion migration is evaluated from the flux. From this calculation procedure, it is possible to estimate the changes in ion concentration in the concrete.

c) Calculation procedure for Ca concentration by Buil's model

The Ca concentration calculated in b) does not satisfy the equilibrium relation, as shown in Figure 1, between the cement paste and pore solution. This situation is shown as (ii) in Figure 4. Hence, the Ca

concentrations in the cement paste and pore solution have to be re-calculated in order to fit them into the equilibrium relation. As shown in Figure 4, the Ca^{2+} concentration in the pore solution decreases due to the migration of Ca^{2+} , while the Ca concentration in the cement paste decreases through leaching of calcium from the cement paste. Hence, the Ca^{2+} concentration in the pore solution increases. At the same time, the pore ratio of the concrete increases with leaching of calcium. This increase in pore ratio influences the calculation of Ca concentration in the cement paste and pore solution. As a result, computation error can occur when calculating the pore ratio and Ca concentration in the cement paste and pore solution to match Buil's model using an explicit method. From the reason above, these properties at $t=t_{j+1}$ are calculated using an implicit method as shown by the calculation procedure from (ii) to (iii) in Figure 4.

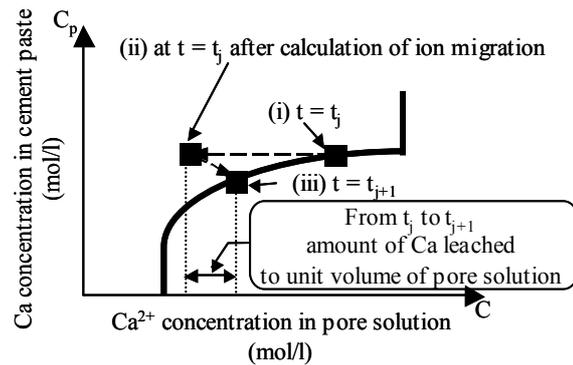


Figure 4 Path of ion concentration at steps of time

Finally, the amount of OH^- that dissolves from the cement paste between $t=t_j$ and $t=t_{j+1}$ and the ion concentrations in the pore solution at $t=t_{j+1}$ are calculated.

Repeating these calculation procedures, the quantity of ions leaching from the concrete can be calculated.

4.3 Boundary conditions

The boundaries of this method are interface- m , which is the exposure surface, and interface- 0 , which is the deepest part of the concrete.

The ion concentration at interface- m is assumed to be equal to the external solution. Also, the engineering absolute mobility at interface- m is assumed to be equal to that of absolute mobility in the dilute solution. In other words, at interface- m , the pore ratio ε and the tortuosity factor τ are assumed to equal 1. Incidentally, the ion concentration gradient, required when calculating the flux at interface- m , is defined as shown in Figure 3. Also, ion migration does not occur at the interface- 0 .

5. VALIDITY OF THE NUMERICAL ANALYSIS METHOD

The purpose of chapter 5 is to confirm the validity of the numerical analysis method explained above. To achieve this, predictions obtained using the method are compared with survey results obtained from existing concrete members that had been in contact with water for about 100 years [3], [5].

An outline of the existing concrete members is given first. Next, the results of the comparison are shown.

5.1 Outline of existing members

This section outlines the existing concrete members that had suffered deterioration through leaching of calcium. Two types of structural member were studied; one a concrete member and the other a mortar

Table 2 Mix Proportions of Surveyed Members

	W/C (%)	Unit content (kg/m ³)			
		Water	Cement	Fine aggregate	Coarse aggregate
Concrete member	72	109	152	688	1427
Mortar member	72	253	352	1595	-

member.

The concrete structure chosen for study was the floor system of an impounding facility at a water supply facility in Shiba, Tokyo [5]. The mortar member was part of the wall of a water channel at the same water supply facility. [3] Excavations for this structure were begun in 1893, and it was completed in 1896; the members investigated in this study were constructed between 1894 and 1895.

The survey results suggested that these members had been exposed to water contact for long time. Also, quantitative measurements of hydrates demonstrated that they had deteriorated through the leaching of calcium. This deterioration explained up to 70mm and 100 mm from the exposure surface in case of the concrete member and the mortar member, respectively. The mix proportions of these old members were estimated by following the Concrete Expert Committee report F-18, published by the Cement Assoc. of Japan, as shown in Table 2.

5.2 Prediction of calcium leaching over 100 years and confirmation of validity

In this section, the validity of this method is confirmed by comparing (i) results of a survey of existing members in contact with water for 100 years with (ii) predictions of leaching after 100 years obtained by this method after applying the estimated initial physical properties and pore solution ion concentration of the members surveyed.

In carrying out the predictions, it is necessary to use the initial physical properties and pore solution ion concentration of the surveyed members as the initial values. So, first, these initial values have to be estimated correctly.

Values estimated using the method of Y. Yokozeki et al. [5] are adopted as the initial physical properties of the members. The initial Ca concentration in the cement paste C_{p0} was estimated by analysis of the mix proportions of the members and the components of cement used at the time. The Ca concentration in the cement paste after consumption of Ca(OH)_2 , C_{pl} , was dealt with as a parameter in a previous study [3], because it proves difficult to estimate this value from the mix proportion or theoretical values. In this study, $C_{pl}=8.48$ mol/l is adopted, because the correlation between survey results and predictions was best when using this value in a previous study [3].

Next, the initial Ca^{2+} concentration in the pore solution is defined as 0.02 mol/l according to Bui's model. The initial Na^+ , K^+ , Cl^- , and SO_4^{2-} concentrations in the pore solution are determined by taking samples from a specimen whose mix proportions are the same as the surveyed members, following JCI-SC4. Also, for OH^- , this concentration is determined by keeping the sum of the ion electric charge in pore solution equal to 0.

Table 3 shows the estimated initial values of the surveyed members as used in this study.

Table 3 Estimated Initial Values and Ion Concentration in Pore Solution of Surveyed members

Estimated Initial Values and Ion Concentration in Pore Solution	Concrete member	Mortar member
Pore ratio (cm ³ /cm ³)	0.11	0.25
Water-cement ratio (%)	71.7	71.7
Paste volume in unit volume of concrete (m ³ /m ³)	0.049	0.115
Density of cement (g/cm ³)	3.15	3.15
Initial Ca concentration in cement paste (mol/l)	10.6	10.6
Ca concentration in cement paste at the time of calcium hydrate disappearance (mol/l)	8.48	8.48
Initial Ca ²⁺ concentration in pore solution (mol/l)	0.0200	0.0200
Initial Na ⁺ concentration in pore solution (mol/l)	0.0342	0.0342
Initial K ⁺ concentration in pore solution (mol/l)	0.0381	0.0381
Initial Cl ⁻ concentration in pore solution (mol/l)	0.0004	0.0004
Initial OH ⁻ concentration in pore solution (mol/l)	0.1060	0.1060
Initial SO ₄ ²⁻ concentration in pore solution (mol/l)	0.0030	0.0030

The length of the concrete and mortar members to which the method was applied is defined as 15 cm and 40 cm, respectively, referring to previous studies [3], [5]. Incidentally, the chemical composition of the water around the existing members was obscure. Hence, the OH⁻ concentration and other ion concentrations in the external solution are defined as 1×10^{-7} mol/l and 0 mol/l, respectively.

The prediction made by calculation and the surveyed data used for confirmation of its validity is the calcium leaching ratio in the cement paste, as shown in equation (17):

$$L.R.(t) = \frac{C_{p0} - C_{pt}}{C_{p0}} \times 100(\%) \quad (17)$$

where, $L.R.(t)$ is the calcium leaching ratio in cement paste at time t (%), C_{p0} is the initial Ca concentration in cement paste (mol/l), and C_{pt} is the Ca concentration in cement paste at time t (mol/l). It is assumed that C_{pt} of the surveyed members can be calculated from the Ca/Si mole ratio in cement paste as given in equation (18).

$$C_{pt} = \frac{M_t}{M_0} \cdot C_{p0} \quad (18)$$

where, M_0 is initial Ca/Si mole ratio in cement paste, and M_t is Ca/Si mole ratio in cement paste at time t .

The Ca/Si mole ratio is evaluated by energy-dispersion X-ray (JSM-5310 LV by JEOL Ltd.). Also, it is assumed that the initial Ca/Si mole ratio in the cement paste is equal to the Ca/Si mole ratio in areas judged non-deteriorated from the viewpoint of Ca/Si distribution in the surveyed members.

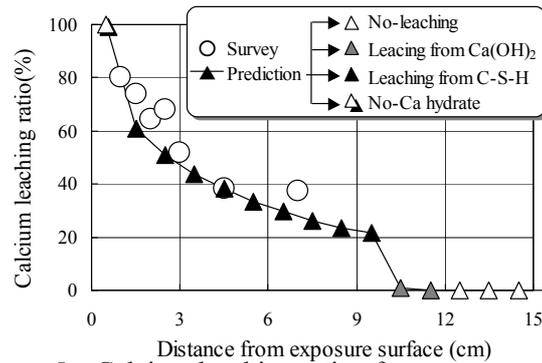


Figure 5 Calcium leaching ratio of concrete member

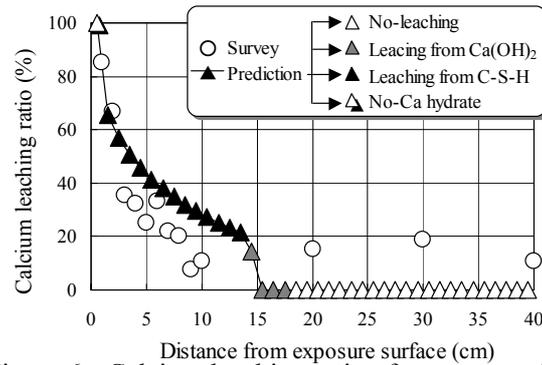


Figure 6 Calcium leaching ratio of mortar member

Figures 5 and 6 show the calcium leaching ratio obtained by prediction and survey for the concrete member and the mortar member, respectively. These figures show that leaching of calcium occurs from the exposure surface; and that deterioration caused by leaching of calcium expands inwards gradually.

Further, from the distribution of calcium leaching ratio obtained by this method, it can be determined that these are three regions of deterioration by calcium leaching: (i) areas where calcium dissolves from $\text{Ca}(\text{OH})_2$ only, (ii) areas where calcium dissolves from C-S-H and $\text{Ca}(\text{OH})_2$ has been already been consumed completely, and (iii) areas where there is no calcium in the cement paste. This is because it is assumed that calcium in the cement paste dissolves from $\text{Ca}(\text{OH})_2$ before the C-S-H dissolves in Buil's model.

It can be seen that the predictions correspond with the survey results. Therefore, it can be said that the proposed method is able to predict the leaching of calcium from concrete. Incidentally, since initial values and boundary conditions set in this study may differ slightly from the true initial values and boundary conditions, some errors may be present in the predictions.

Next, the influence of expected errors in initial values on the predictions is examined. Here, the initial value examined is the Ca concentration in the cement paste after consumption of $\text{Ca}(\text{OH})_2$, C_{pl} . This is because it may be anticipated that this value, as it was not determined from the mix proportion or a theoretical value, would have greater estimation error in comparison with the other initial conditions. The value of C_{pl} used for the sensitivity analysis is from 7.2 mol/l to 9.0 mol/l. This range was estimated from the chemical composition of the cement used at the time of construction with the assumption that the Ca/Si mole ratio in C-S-H was from 1.6 to 2.0.

The results of sensitivity analysis for C_{pl} are shown in Figures 7 and 8. From these results, the predictions for the concrete member can be seen to correspond with the survey result regardless of C_{pl} . On the other hand, the predictions for the mortar member tend to diverge as C_{pl} becomes smaller. However, for both members, the predictions correspond broadly with the survey results. It can be concluded that the influence of estimation errors in C_{pl} on the reliability of the predictions is small.

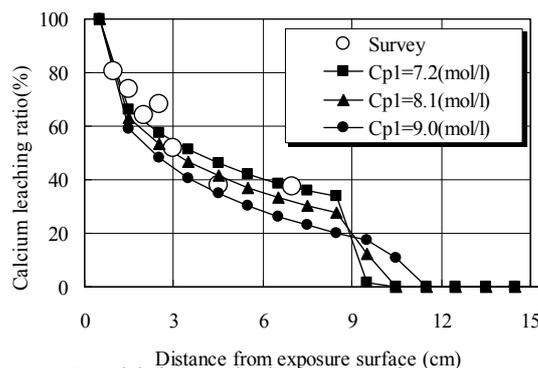


Figure 7 Sensitivity analysis for C_{pl} of concrete member

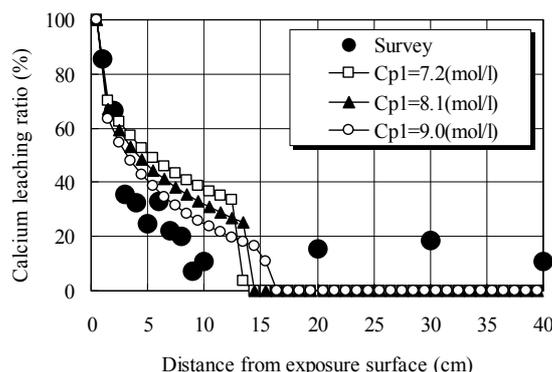


Figure 8 Sensitivity analysis for C_{pl} of mortar member

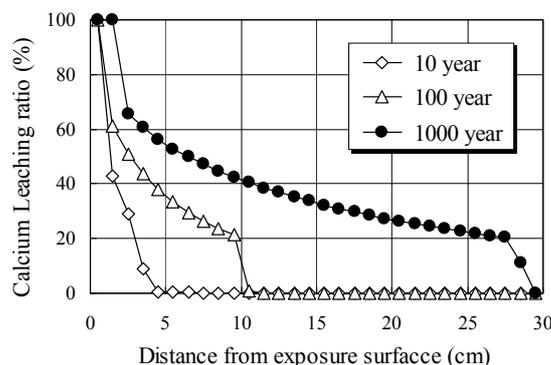


Figure 9 Predictions for concrete member after 1,000 years

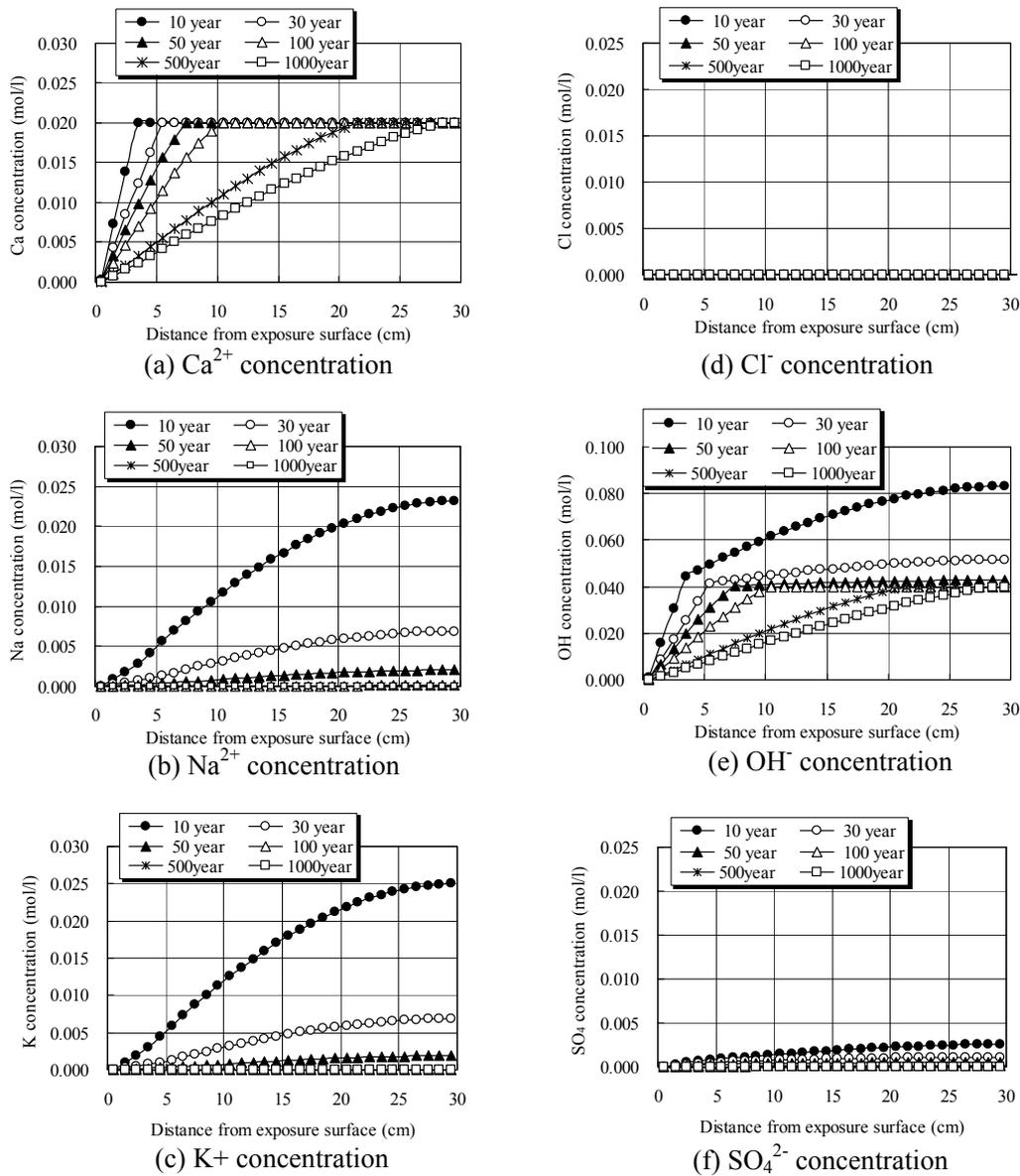


Figure 10 Changes in ion concentrations in pore solution

6. PREDICTION OF CALCIUM LEACHING AND ION CONCENTRATION DISTRIBUTION IN CONCRETE OVER 1000 YEARS

In chapter 6, the leaching of calcium from concrete over a period of 1000 years is predicted using the numerical analysis method established in this study. The concrete for which the prediction is made is the same concrete member used to confirm the validity of this method in chapter 5. However, the length in this case is set to 30 cm. The predictions are shown in Figure 9.

It is clear from this figure that the deterioration caused by calcium leaching expands inwards. Furthermore, it is predicted that calcium leaching will be taking place at a depth of 30 cm from the exposure surface after 1000 years. Also, in the region within 27 cm of the exposure surface, the calcium leaching ratio will be over 20%, and it is clear that $\text{Ca}(\text{OH})_2$ in the cement paste will have already dissolved. Incidentally, in a previous study [12], it was indicated that there is no $\text{Ca}(\text{OH})_2$ in regions where a decrease in compressive strength due

to calcium leaching is confirmed. Using this finding, the region in which $\text{Ca}(\text{OH})_2$ dissolves completely is defined as the physical deterioration region, and for the concrete exposed for 1000 years it is the region within 27 cm of exposure surface. In other words, areas deeper than 27 cm from the exposure surface will still have no deterioration.

A further merit of this method is that the behavior of coexisting ions can be predicted. Figure 10 (a)-(f) shows the change in ion concentrations in the pore solution considered in this method.

From these figures, it is clear that Na^+ , K^+ , Cl^- , and SO_4^{2-} are completely dissolved within 100 years from all regions of the concrete member. On the other hand, it is clear that a remarkable decrease in Ca^{2+} and OH^- takes place in the region within 10 cm of the exposure surface. This is because Ca^{2+} and OH^- are supplied from the cement paste to the pore solution. However, after 1000 years, the decrease of Ca^{2+} and OH^- concentration can be seen in all regions of the member.

From these predictions, the decreasing ion concentration of the pore solution is shown analytically to differ quantitatively by the type of ion.

7. CONCLUSIONS

This study establishes a numerical analysis method for the prediction of calcium leaching from concrete using one-dimensional differential calculus. The leaching of calcium from concrete and mortar over a period of 100 years can be predicted using the new method. In order to confirm the validity of the method, predictions are compared with the results of surveys on old concrete and mortar members of a water supply facility in Shiba, Tokyo, that had been in contact with water for 100 years. Finally, the leaching of calcium in the case of a concrete member 1000 years old is predicted. The conclusions of this study are summarized as follows:

- (1) A numerical analysis method for the prediction of calcium leaching from concrete was established using one-dimensional differential calculus. By using (i) the Nernst-Planck equation, the electro-neutrality condition, and the Debye-Hückel equation for ion migration, and (ii) Buil's model for the equilibrium relation between Ca concentration in cement paste and Ca^{2+} concentration in pore solution to take into account leaching of calcium from cement paste to pore solution, it is possible to calculate the distribution of ion concentration and to predict leaching of calcium from concrete.
- (2) The leaching of calcium from concrete and mortar members over 100 years was predicted using the new method. The prediction results were then compared with the actual results of surveys carried out on old members that had been in contact with water for 100 years. From this comparison, it is clear that the predictions correspond with the surveys; hence, the validity of this method is confirmed.
- (3) Using the new method, the leaching of calcium from concrete over 1000 years was predicted. Leaching of calcium was found to reach the region 30 cm below the exposure surface. Also, if the region where $\text{Ca}(\text{OH})_2$ dissolves completely is defined as the physical deterioration region, physical deterioration of the 1,000-years-old concrete can be expected to reach within 27 cm below the exposure surface.

This new method still leaves some issues to be resolved from the viewpoint of detail. However, it is possible to calculate multiple ion migrations simultaneously using this method, so it is expected to have good extendability.

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