

# CALCULATION OF DIFFUSION COEFFICIENT OF ION IN MULTICOMPONENT SOLUTION FOR ION MOVEMENT IN CONCRETE

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**ABSTRACT:** A method for calculating the mutual diffusion coefficients of an ion influenced by all other coexisting ions in the multicomponent solution for ion movement in concrete is presented in this paper. The method of calculation is based on the generalized form of Fick's first law suggested by Onsager, which is composed of the Onsager phenomenological coefficient and the thermodynamic force between ions that exerted by the gradient of electrochemical potential in the solution. As a result of verification by comparison with the experimental results by Saito H. et al., it is shown that by using the presented method of calculation, the calculated leaching amount of some ions exhibited close to the experimental results.

**KEYWORDS:** ion migration, multicomponent solution, mutual diffusion coefficient, generalized Fick's first law, Onsager phenomenological coefficient, thermodynamic force, electrochemical potential

## 1. INTRODUCTION

Diffusion is the most important process of the ion transport in a porous media, for example, in the fractured rocks or structural concrete. It can be considered to be the most important factor causing the deterioration of the concrete structure. In some environmental conditions for concrete structure such as in a saline environment or nuclear waste-disposal containment barriers, the durability of concrete structure must be significantly concerned. The ingress of aggressive ions such as  $\text{Cl}^-$  and  $\text{SO}_4^{2-}$ , the leaching of  $\text{Ca}^{2+}$  or some metallic ions from portlandite or calcium silicate hydrated gel in concrete pore structure are the main factors that affect the durability of concrete structures. Therefore, it is necessary to develop a calculation model for the diffusion transport, which can be used for accurate prediction of such phenomenon in the global state of concrete structure. For the diffusion of ions in concrete, the multicomponent system of the ions in concrete pore solution has to be mainly concerned. The concentrations of the co-existing ions such as  $\text{Ca}^{2+}$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{SO}_4^{2-}$ , etc. have the significant influence on the mobility of each ion [1]. The researches of ion transport in concrete concerning to the co-existing ions in the multicomponent solution have been carried out by Otsuki N. et al. [2], in which, the flux of an ion is calculated by the Nernst-Planck Equation, electro-neutrality constraint and Debye-Hückel theory.

The purpose of this research is to apply the theories of the ion transport in a multicomponent solution for calculating the matrix of diffusion coefficients of every ion existing in the pore solution in concrete. This diffusion coefficient is designated as  $D_{ij}$  or the mutual diffusion coefficient of the  $i_{\text{th}}$  species influenced by the concentration of the  $j_{\text{th}}$  species. The calculation of this model is based on a generalized form of Fick's first law that was suggested by Onsager [3]. This generalized form composed of the Onsager phenomenological coefficient [4] and the thermodynamic force between ions exerted by the gradient of electrochemical potential [1]. Consequently, from this  $D_{ij}$ , the flux and/or the concentration profile of each ion can be calculated from the generalized Fick's law. The correctness of this calculation model for  $D_{ij}$  was verified by the comparison with the experimental results of the leaching of some ions (i.e.  $\text{Na}^+$  and  $\text{K}^+$ ) from the mortar exposed to water performed by Saito H. et al. [5].

## 2. ELECTROLYTE DIFFUSION PROCESS

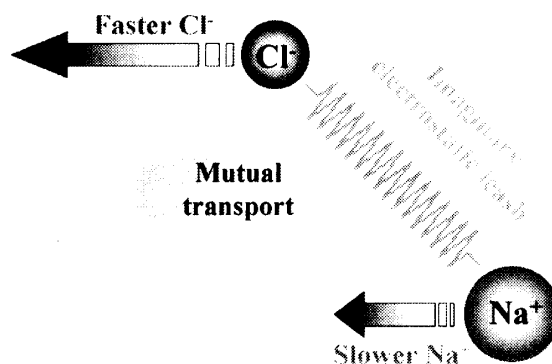
It is well known that in a electrolyte diffusion process, the movement of an aqueous species will occur by the driving forces that created from the concentration gradient of that species itself and by those

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of the other species [1,3]. Moreover, another driving force is the gradient of electrical potential created by the difference between mobility of cation and anion. The way in which the electrical potential or the electrostatic force has an influence on the electrolyte diffusion is illustrated schematically in **Fig.1**. Assuming that in a binary electrolyte solution composed of NaCl, the faster  $\text{Cl}^-$  and the slower  $\text{Na}^+$  are constrained by the electrostatic force, to move at the same rate. In addition to this, by the electro-neutrality constraint these two ions must maintain the same diffusive flux through out the transport in the solution.



**Fig.1 Electrolyte diffusion for system of  $\text{Na}^+$  and  $\text{Cl}^-$**

Because of these electrostatic requirements, the flux of NaCl is characterized by a single diffusion coefficient, i.e. mutual diffusion coefficient, which is an average of the diffusion coefficient of  $\text{Na}^+$  and  $\text{Cl}^-$ . This mutual diffusion coefficient can be imaginatively considered as a leash tying the  $\text{Na}^+$  and  $\text{Cl}^-$  together. The faster  $\text{Cl}^-$  will be going to accelerate the slower  $\text{Na}^+$ , while at the same time, the slower  $\text{Na}^+$  will decelerate the  $\text{Cl}^-$ , keeping it from running away. All of this accelerating and decelerating effect produces a mutual diffusion coefficient.

In the similar action for a multicomponent solution system, instead of the single electrostatic leash tying one cation and one anion, imagine that there are a lot of leashes connected together by all charged species existing in the solution system. If one ion, e.g.  $\text{OH}^-$ , which is much more mobile than the others, it can accelerate the movement of ions with opposite charge, or decelerate the diffusion of ions with similar charge. In some cases, it can even cause the other ions to move against their concentration gradient.

### 3. DEVELOPMENT OF THE DIFFUSION COEFFICIENT CALCULATION MODEL

The diffusion coefficient of a species in a multicomponent solution can be calculated by considering the driving diffusive flux in the solution. The forces driving the diffusion of an aqueous species are basically originated from the thermodynamic force that can be considered as the gradient of electrochemical potential ( $\mu$ ) [1]. The electrochemical potential, which composed of the chemical part ( $\mu_{\text{chem}}$ ) and the electrical potential ( $\phi$ ) part, can be shown in the following expression.

$$\mu_j = \mu_{j(\text{chem})} + z_j F \phi \quad (1)$$

As mentioned before, according to Miller [3] the thermodynamic force on ion  $j$  ( $X_j$ ) is the gradient of electrochemical potential given by Eq. 2.

$$X_j = \frac{\partial \mu_j}{\partial x} = \frac{\partial \mu_{j(\text{chem})}}{\partial x} + z_j F \frac{\partial \phi}{\partial x} \quad (2)$$

At this point a linear relation, which relates the flux of the ion  $i$  to force exerted on the ion  $j$ , is assumed and expressed in Eq. 3.

$$J_i = - \sum_{j=1}^{n_s} l_{ij} X_j = \sum_{j=1}^{n_s} l_{ij} \left( - \frac{\partial \mu_{j(\text{chem})}}{\partial x} - z_j F \frac{\partial \phi}{\partial x} \right) \quad (3)$$

In Eq. 3,  $l_{ij}$  stands for the Onsager phenomenological transport coefficient [1,3,4] (hereafter Onsager coefficient) the significance of this coefficient on the transport in multicomponent solution will be discussed later.

The electrical potential gradient ( $\partial \phi / \partial x$ ), which is not readily measurable, can be eliminated from Eq. 3 by the electro-neutrality constraint in the solution ( $\sum_{i=1}^{n_s} z_i J_i = 0$ ).

From this step, the  $\mu_j$  will be used for representing the  $\mu_{j(\text{chem})}$  as for abbreviation. By substitution of

the flux equation in Eq. 3 into the electro-neutrality constraint, one can derive to Eq. 4.

$$\frac{\partial \phi}{\partial x} = - \frac{\sum_{k=1}^{n_s} \sum_{l=1}^{n_s} z_k l_{kl} \frac{\partial \mu_l}{\partial x}}{F \sum_{k=1}^{n_s} \sum_{l=1}^{n_s} z_k z_l l_{kl}} \quad (4)$$

By substitution of Eq. 4 into the flux equation of Eq. 3, the flux equation of  $i_{th}$  species will become as following equation.

$$J_i = \sum_{j=1}^{n_s} l_{ij} \left\{ - \frac{\partial \mu_j}{\partial x} + z_j \frac{\sum_{k=1}^{n_s} \sum_{l=1}^{n_s} z_k l_{kl} \frac{\partial \mu_l}{\partial x}}{\sum_{k=1}^{n_s} \sum_{l=1}^{n_s} z_k z_l l_{kl}} \right\} \quad (5)$$

At this step of calculation, determining the Onsager coefficient ( $l_{ij}$ ), which is the function of ion concentrations in the solution especially in relatively dilute solution [4], is necessary. However, in the system of porous media, the off-diagonal terms of this Onsager coefficient ( $l_{ij}$ ,  $i \neq j$ ) can be approximated to 0 [3]. In the other words, it can be negligible compared to its on-diagonal term of Onsager coefficient ( $l_{ij}$ ,  $i = j$ ) without significant error [3, 4].

In addition, for a relatively dilute solution, the on-diagonal Onsager coefficient can be computed from the following equation.

$$l_{ii} = \frac{D_i^0 C_i}{RT} \quad (6)$$

where  $D_i^0$  stands for the tracer diffusion coefficient in dilute solution of  $i_{th}$  species,  $R$  refers to the gas constant, equal to  $8.3145 \text{ JK}^{-1} \text{ mol}^{-1}$ ,  $T$  is the absolute temperature (K). Consequently, the gradient of the electrochemical potential is converted to the gradient of concentration by the following equation.

$$\frac{\partial \mu_j}{\partial x} = \frac{\partial \mu_j}{\partial C_j} \times \frac{\partial C_j}{\partial x} \quad (7)$$

The definition of chemical potential ( $\mu_j$ ) can be extended to the following expression [3].

$$\mu_j = \mu_j^0 + RT \ln C_j + RT \ln \gamma_j \quad (8)$$

where  $\gamma_j$  refers to the mean activity coefficient of the  $j_{th}$  species and  $\mu_j^0$  refers to the chemical potential in the standard state of the solution, which is a constant number. Therefore, the following equation can be derived.

$$\frac{\partial \mu_j}{\partial C_j} = RT \left( \frac{1}{C_j} + \frac{\partial \ln \gamma_j}{\partial \ln C_j} \right) \quad (9)$$

Consequently, the generalized form of the Fick's first law suggested by Onsager [3,4] is shown in the following expression.

$$J_i = - \sum_{j=1}^{n_s} D_{ij} \frac{\partial C_j}{\partial x} \quad (10)$$

where  $D_{ij}$  is meant for the mutual diffusion coefficient of the  $i_{th}$  species in free liquid phase influenced by the concentration gradient of the  $j_{th}$  species ( $\nabla C_j$ ). By substitution all of expressions from Eq. 6 to Eq. 9 into Eq. 5, and comparing with the similar flux term in Eq. 10, the expression of mutual diffusion coefficient can be derived as shown in Eq. 11 [3].

$$D_{ij} = \delta_{ij} D_i^0 \left( 1 + \frac{\partial \ln \gamma_i}{\partial \ln C_i} \right) - \left\{ \frac{z_i D_i^0 C_i}{\sum_{k=1}^{n_s} z_k^2 D_k^0 C_k} z_j D_j^0 \left( 1 + \frac{\partial \ln \gamma_j}{\partial \ln C_j} \right) \right\} \quad (11)$$

where  $\delta$  is designated for the Kronecker delta function which is equal to 1 if  $i = j$ , but equal to 0 if  $i \neq j$ ,  $\gamma_i$  is the mean activity coefficient of the  $i_{th}$  species and its derivative respected to the concentration

can be calculated by the Debye-Hückel theory [6] as shown in following equation.

$$\frac{\partial \ln \gamma_i}{\partial \ln C_i} = -2.302 \times C_i \times \frac{0.509 \times Z_i^2}{2\sqrt{I}(1 + 3.286\alpha_i\sqrt{I})^2} \quad (12)$$

where  $\alpha_i$  is the ion size parameter (nm) of the  $i_{th}$  species and  $I$  is the ionic strength (mol/l) of the solution.

As mentioned before, the definition of  $D_{ij}$  is based on the assumption that the mutual movement of separated ions is caused by not only the electro-neutrality constraint, but also the electrochemical potential gradient occurred by the difference between each ion mobility. Therefore, the movement of ions can be considered similar to that of uncharged species. In general, the matrix of mutual diffusion coefficients is not symmetric, i.e.  $D_{ij} \neq D_{ji}$ . The diagonal terms ( $D_{ii}$ ) are generally large compared to the off-diagonal terms ( $D_{ij}$ ,  $i \neq j$ ). By using the initial value quoted in the next section as the input parameters, the matrix of  $D_{ij}$  in the unit  $m^2/s$  at particular concentrations in a multicomponent solution composed of 7 ions is shown in **Table 1**.

From the value shown in **Table 1**, the positive value represents the pulling effect between mutual movements of ions, while the negative value represents the pushing effect of that. In addition, we can see that the diagonal term is higher than the off-diagonal terms for every ion.

$[D]_{i,j} =$

**Table 1. Example of calculated mutual diffusion coefficients at particular concentrations ( $D_{ij}$ ,  $\times 10^{-9} m^2/s$ )**

$i \backslash j$	$Ca^{2+}$	$Mg^{2+}$	$Na^+$	$K^+$	$SO_4^{2-}$	$Cl^-$	$OH^-$
$Ca^{2+}$	0.791	-0.0009	-0.0008	-0.0012	0.0013	0.0013	0.0030
$Mg^{2+}$	0	0.706	0	0	0	0	0
$Na^+$	-0.170	-0.152	1.12	-0.198	0.223	0.219	0.511
$K^+$	-0.231	-0.206	-0.184	1.57	0.303	0.297	0.694
$SO_4^{2-}$	0.0419	0.0374	0.0333	0.0486	0.981	-0.0537	-0.126
$Cl^-$	0	0	0	0	0	2.03	0.0
$OH^-$	1.10	0.977	0.872	1.27	-1.43	-1.41	1.46

Therefore, at each particular concentrations and time the matrix of diffusion coefficients ( $D_{ij}$ ) can be calculated. In the simulation of ion transport in concrete materials by applying these diffusion coefficients and the equation of continuity, the general form of Fick's second law can be written as following equation.

$$\frac{\partial C_i}{\partial t} = \sum_{j=1}^{n_i} D_{ij,l} \frac{\partial^2 C_j}{\partial x^2} \quad (13)$$

where  $D_{ij,l}$  designates the intrinsic mutual diffusion coefficient in the pore solution of concrete.

For a general porous media, it is easier to determine the term of diffusion coefficient in the terms of the average flux per unit area of the medium (rather than the liquid) leading the definition of intrinsic diffusion coefficient. The intrinsic mutual diffusion coefficient of concrete porosity  $\varepsilon$  and tortuosity  $\tau$  can be formulated by the following expression [7].

$$D_{ij,l} = \frac{\varepsilon}{\tau^2} D_{ij} \quad (14)$$

#### 4. VERIFICATION OF THE CALCULATION MODEL

In the present research, the correctness of the calculation model for the  $D_{ij}$  of the ions in multicomponent solution for prediction the transport of ions in concrete is verified by comparing with the experimental results performed by Saito H. et al. [5]. In this experiment, the mortar specimen of 65% W/C with 5 cm diameter and 3 cm thickness disk

**Table 2. The parameters for calculation of  $D_{ij}$  matrix**

Ion	$C_i$ , Concentration in pore solution (mol/l)	$\alpha_i$ , Ion size parameter (nm)	$D_i^0$ , Tracer diffusion coefficient ( $m^2/s$ )
$Ca^{2+}$	0.001 <sup>*</sup>	0.60	$7.92 \times 10^{-10}$
$Mg^{2+}$	0.0	0.80	$7.06 \times 10^{-10}$
$Na^+$	0.203 <sup>§</sup> (55 mg)	0.40	$1.33 \times 10^{-9}$
$K^+$	0.187 <sup>§</sup> (86 mg)	0.30	$1.96 \times 10^{-9}$
$SO_4^{2-}$	0.033 <sup>*</sup>	0.40	$1.07 \times 10^{-9}$
$Cl^-$	0.0	0.30	$2.03 \times 10^{-9}$
$OH^-$	0.326	0.35	$5.26 \times 10^{-9}$

<sup>\*</sup>The number is referred from C. L. Page et al. [8].

<sup>§</sup>The value calculated by leaching amount which shown in parenthesis. [5]

was prepared for predicting the deterioration due to dissolution of extremely amount of cement hydrate. In some parts of this experimental work, the amount of  $\text{Na}^+$  and  $\text{K}^+$  that leached from the pore solution of mortar exposed to water was investigated with the exposure time.

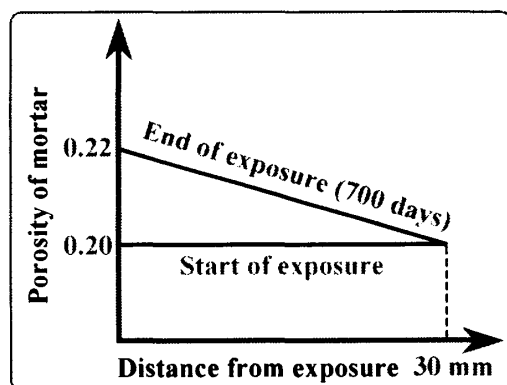


Fig.2 Porosity change of mortar specimen due to dissolved  $\text{Ca(OH)}_2$

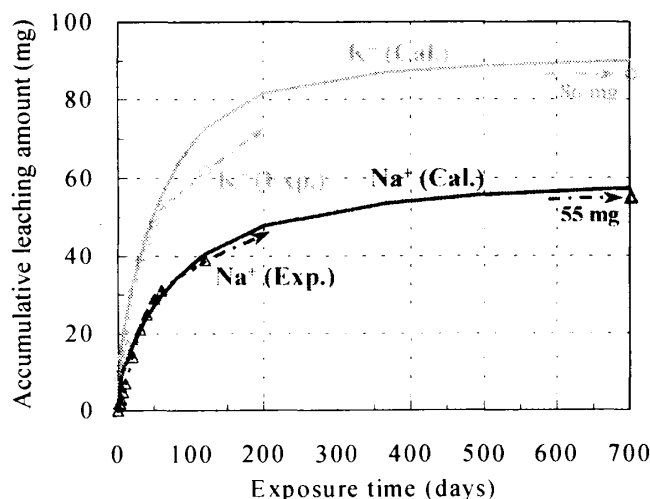


Fig.3 Calculated and experimental results for leaching amount of ions from mortar exposed to water

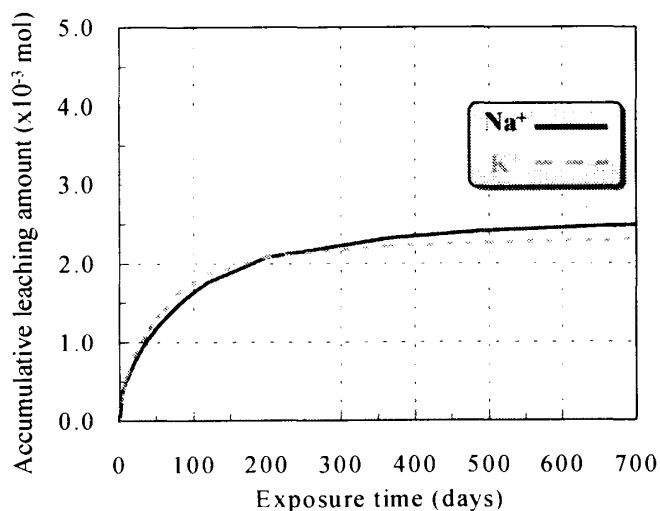


Fig.4 Calculated leaching amount in mol unit

As shown in **Table 2**, the initial concentrations of  $\text{Na}^+$  and  $\text{K}^+$  in the pore solution are determined from the total accumulative amount of leaching ions from the experiment [5], though those of  $\text{Ca}^{2+}$  and  $\text{SO}_4^{2-}$  are quoted from C.L.Page et al. [8], and that of  $\text{OH}^-$  is determined by the electro-neutrality constraint. In addition, the other necessary parameters such as ion size parameter ( $\alpha_i$ ) and the tracer diffusion coefficient ( $D_i^0$ ) for the calculation of  $D_{ij}$  are also shown in this table.

Therefore, the matrix of diffusion coefficient ( $D_{ij}$ ) of every ion can be established according to the concentration at each time step and position. In the calculation of the concentration profile or the leaching amount of ions, the dissolution of  $\text{Ca}^{2+}$  from pore structure of mortar did not taken into account for present study. However, from the experimental result, the dissolution of  $\text{Ca(OH)}_2$  can approximately account for the increased porosity by 10% in period of 2 years. The change of porosity for this calculation, which based on the experimental result, is shown in **Fig.2**. The porosity of exposure surface increased linearly from 0.20 to 0.22 after 700 days of exposure, with a constant at 3 cm depth. The tortuosity ( $\tau$ ) of mortar for the calculation of present research was assumed to be constant and equal to 3.0 [9].

In this way it is assumed that the effect of dissolving  $\text{Ca(OH)}_2$  is of great significance with respect to the change of the physical characteristics but little to the electrochemical characteristics for the particular test.

The comparisons of the calculated results with the experimental ones are shown in **Fig.3**. The experimental results in this figure are the accumulative leaching amount of  $\text{Na}^+$  and  $\text{K}^+$  collected from the exposure solution (water). At the 120 days of exposure, the leached ion could be collected to the amount of 39 mg and 62 mg for  $\text{Na}^+$  and  $\text{K}^+$ , respectively. This number would gradually increase with the exposure time and could be estimated to the possible maximum value of 55 mg and 86 mg, respectively [5]. From the same figure, the calculated results exhibited preferable conformity with the experimental results for  $\text{Na}^+$  and with slightly higher estimation for  $\text{K}^+$  at 120 days of exposure. Nevertheless, it

can be concluded that the model for calculation of  $D_{ij}$  can provide the appropriate calculation of the ion transport in cement-based material.

The rate of diffusion can be seen from **Fig.4**, which shows the calculated accumulative leaching amount of  $\text{Na}^+$  and  $\text{K}^+$  in mol unit. From this figure, we can see that in the beginning, the diffusion rate of  $\text{K}^+$  is higher than that of  $\text{Na}^+$  because of the higher tracer diffusion coefficient of  $\text{K}^+$  that contributes to higher mutual diffusion coefficient of it. However, after the exposure time being passed, as a result of rapid decreasing in the concentration of  $\text{K}^+$ , its mutual diffusion coefficients also decrease. Therefore, in the later part of exposure time, the rate of diffusion of  $\text{Na}^+$  is slightly higher than that of  $\text{K}^+$ . In other words, even though  $D_{ij}$  of  $\text{Na}^+$  is lower than that of  $\text{K}^+$ ,  $\text{Na}^+$  with higher concentration than that of  $\text{K}^+$  shows higher rate of diffusion. Consequently, we can state that not only the tracer diffusion coefficient, but also the concentration of the ion itself has an influence on the rate of diffusion of these ions.

## 5. CONCLUSIONS

From the model for calculating the mutual diffusion coefficients of ions in the multicomponent solution, the ion movement in concrete can be simulated. By comparison the calculated results with some experimental results we can conclude that;

1. A new calculation model is proposed for simulating the ion transport in cement-based materials. The model is established by the generalized form of Fick's first law, which composed of the Onsager phenomenological coefficient and the thermodynamic force between ions exerted by the gradient of electrochemical potential.
2. By verification of the model with the experimental results, it can predict well the accumulative leaching amount of  $\text{Na}^+$  and  $\text{K}^+$  from the mortar specimen exposed to water. However, the model of chemical equilibrium such as the dissolution of  $\text{Ca}^{2+}$  or the other metallic ions that occurs inside the pore solution of a cement-based material has also to be included to the model for further study.

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