

# Model for Estimating Ion Diffusion Coefficients in Cementitious Materials Considering Hydration Reaction and Temperature Dependence

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A model is constructed for the estimation of ion diffusion coefficients in cementitious materials. The effects of temperature, humidity, degree of hydration, type of cement, amount of aggregate, and type of ion are taken into account, and the model is based on electrochemical theory and changes in porosity. Diffusion coefficients estimated using this model are compared with actual results from: immersion tests using chloride ions, sodium diffusion cell experiments, sulfate ion permeability tests, and diffusion cell experiments after calcium leaching. It is confirmed in all cases that the new model is accurate. It is also demonstrated that diffusion coefficients are affected most by temperature, humidity, and degree of hydration in that order.

**Key Words:** *diffusion coefficient, ion, hydration, porosity, temperature*

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## **1. INTRODUCTION**

While the durability of concrete structures has recently come under public scrutiny, and demand is growing for structures that are more durable, the many existing concrete structures need to be appropriately evaluated for durability and rationally maintained. Currently, the trend in concrete structure design methodology and maintenance is a move away from specification-based methods to performance-based methods. Performance- and verification-based design requires that the concrete mix proportion and the structure itself be verified to ensure

that the required performance is maintained over the design service period [1], [2]. Until now, the service life and durability of concrete have been verified by tests and experience, but advanced technology and an enormous amount of labor are necessary to satisfy verification requirements given the plethora of materials, construction methods, environments, and performance requirements in use today. As a result, there is considerable demand for new simulation techniques and event-modeling methods based on well-defined theoretical foundations.

One issue is the degradation of concrete, which typically includes corrosion of steel members owing to salt damage or carbonation, frost damage, alkali-aggregate reactions, and chemical corrosion. In all of these cases, the root cause of the degradation is mass transfer in the concrete pores. Consequently, accurate predictions of the porosity of concrete and of mass transfer through the pores are expected to play a very important role in the modeling of concrete degradation phenomena.

In view of the above, this report focuses on the movement of ions in mass transfer phenomena, and aims to construct a method of estimating diffusion coefficients, which represent ion transfer rates.

## **2. REVIEW OF LITERATURES**

The Standard Specifications for the Design and Construction of Concrete Structures [1], [2] (published by the Japan Society of Civil Engineers) give equations for predicting the apparent diffusion coefficient of chloride ions when ordinary Portland cement is used (Equation 1), and when blast furnace cement or silica fume is used (Equation 2).

$$\log D_p = -3.9 \cdot (W/C)^2 + 7.2 \cdot (W/C) - 2.5 \quad (1) \quad \log D_p = -3.0 \cdot (W/C)^2 + 5.4 \cdot (W/C) - 2.2 \quad (2)$$

Here, W/C: water-cement (cementitious materials) ratio and  $D_p$ : diffusion coefficient of concrete ( $\text{cm}^2/\text{year}$ ).

The provision of such a prediction equation in specifications for concrete structures is a rarity, and it may be considered a significant and progressive step. On the other hand, considerable research related to the prediction of diffusion coefficients has also been carried out elsewhere in the world, and many prediction equations have been proposed [3], [4]. It is already known that diffusion coefficients vary considerably with variations in materials and mix proportions, such as the type of cementitious material used and the water-cement ratio. It is also known that diffusion coefficients vary with environmental conditions, such as the concentration of reaction water, such as salt water, and drying conditions. In all studies until now, however, one or more of the effects listed below have been excluded from simultaneous consideration, and many factors still remain unknown.

- (1) Effects of environmental conditions (humidity, temperature)
- (2) Effects of hydration (time dependence, type of cement)
- (3) Effects of mix proportion (unit weight of fine aggregate, unit weight of coarse aggregate, unit water content, type of cement, etc.)

The understanding of phenomena related to pore structures and the effects of the transition zone between aggregate and paste at the microscopic level are also considered important topics. To calculate diffusion coefficients in a rational manner, or to calculate diffusion coefficients for new materials or under complex conditions, all of these phenomena need to be studied and thoroughly understood.

Accordingly, a diffusion coefficients prediction model was constructed to resolve the three types of effect listed above. Results obtained using the model were then compared with various test results, leading to verification of the model.

## **3. DIFFUSION COEFFICIENT ESTIMATION MODEL**

### **3.1 Basic model**

The diffusion and advection equation given as Equation (3) is generally used to evaluate mass transfer and concentration distribution in a porous medium. It is important to set rational boundary conditions and a valid

diffusion coefficient when using this equation.

$$\frac{\partial C_s}{\partial t} = \frac{\partial}{\partial x} \left( D_{eff} \cdot \frac{\partial C_s}{\partial x} \right) - v \cdot \frac{\partial C_s}{\partial x} - \rho_d \cdot \frac{\partial S}{\partial t} \quad (3)$$

In this equation,  $C_s$ : ion concentration per unit volume of entire porous medium;  $t$ : time;  $x$ : distance from the boundary surface;  $D_{eff}$ : effective diffusion coefficient of porous medium;  $v$ : actual flow velocity of pore solution in the micropores ( $= v_d/\theta$ , where  $\theta$ : porosity of porous medium;  $v_d$ : Darcy's velocity);  $\rho_d$ : density of porous medium;  $S$ : absorption or ion concentration generated per unit mass of porous medium.

If we ignore the second and third terms on the on the right-hand side of Equation (3), which respectively represent advection and effects such as adsorption on the structure surface and fixing or generation of ions due to reactions, then the relationship between effective diffusion coefficient  $D_{eff}$  of porous bodies such as cementitious materials and the ion diffusion coefficient  $D_0$  in dilute solution (free water) can be expressed by the equation given below.<sup>4)</sup>

$$D_{eff} = \frac{\theta}{\tau} \cdot D_0 \quad (4)$$

Here,  $\tau$  expresses the tortuosity of the micropores. In this study, the basic diffusion coefficients for each type of ion  $i$  in aqueous solution is taken to be  $D_0^i$ , and the diffusion coefficients  $D_{paste}^i$  considering the effects of tortuosity and changes in pore volume of the cement paste is given by Equations (5) and (6).

$$D_{paste}^i = f(\theta) \cdot D_0^i \quad (5)$$

$$f(\theta) = 0.001 + 0.07 \cdot \theta^2 + 1.8 \cdot (\theta - 0.18)^2 \cdot H(\theta - 0.18) \quad (6)$$

Here,  $D_0^i$ : basic diffusion coefficients of ion  $i$  in aqueous solution ( $m^2/s$ );  $f(\theta)$ : diffusion coefficient reduction function;  $H(x)$ : Heaviside function (1.0 when  $x > 0$ , and 0.0 for all other cases). Equation (6) is from the research carried out by Garboczi and Bentz [5], and has been verified by the percolation model and by experiments investigating changes in diffusion coefficients with micropore tortuosity and porosity.

Next, the ion diffusion coefficients in aqueous solution  $D_0^i$  can be calculated theoretically from electrical ion mobility based on Einstein's equation [6], [7]. Equation (7) gives the equation for calculating the theoretical diffusion coefficients in aqueous solution.

$$D_0^i = k \cdot T \cdot \frac{u^i}{Z^i \cdot e} \cdot \left( 1 + \frac{\partial \ln \gamma^i}{\partial \ln C^i} \right) \cdot 10^{-4} \quad (7)$$

Here,  $k$ : Boltzman's constant ( $1.38 \times 10^{-23}$  J/K);  $T$ : absolute temperature (K);  $u^i$ : ion mobility ( $cm^2/V/s$ )  $= \frac{\lambda^i}{F}$ ;  $\lambda^i$ : limit ionic conductivity in dilute solution ( $S \cdot cm^2/mol$ );  $F$ : Faraday's constant ( $96,485$  C/mol);  $Z^i$ : ion valence;  $e$ : elementary electric charge ( $1.6 \times 10^{-19}$  C);  $C^i$ : ion concentration (mol/l); and  $\gamma^i$ : activity coefficient (mol/l). The term within the parentheses ( ) in Equation 7 is a correction term that uses Debye-Hückel theory to take into account the effects of concentration and mutual interactions between various kinds of ion. The effect of this term is considered to be small, and it is ignored in this study.

### 3.2 Effect of temperature

It has been observed that the limit ion mole conductivity  $\lambda^i$  mentioned above is temperature dependent. The ion transfer speed in concrete is generally said to follow the Arrhenius law for changes in temperature. Accordingly, the basic diffusion coefficient  $D_0$  is rearranged as shown in Equation (8).

$$D_0^i = a_i \cdot \exp\left(-b_i \cdot \frac{1}{T}\right) \quad (8)$$

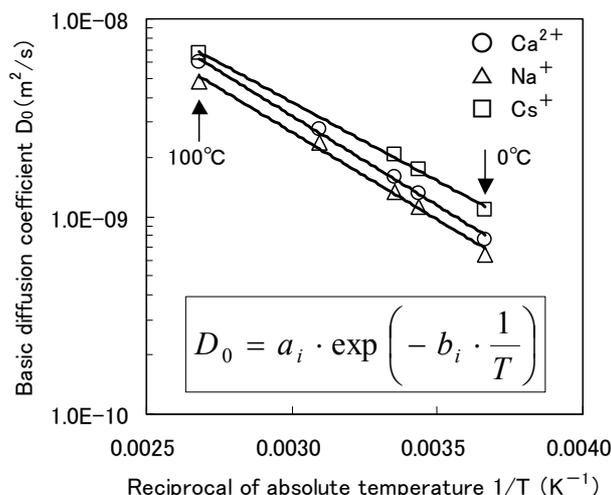
Here,  $a_i$ ,  $b_i$ : coefficients;  $T$ : absolute temperature (K).

The relationship between the reciprocal of absolute temperature and the basic diffusion coefficients of typical ions is shown in **Fig. 1** (cations) and **Fig. 2** (anions). Although the diffusion coefficients differ according to the type of ion in the figures, there is good correlation between the reciprocal of absolute temperature and the basic diffusion coefficients in the range 0°C to 100°C. It is also clear that the higher the temperature, the greater is the value of the basic diffusion coefficient  $D_0$ . The diffusion coefficients determined by this method (directly substituting the limit ion mole conductivity at 25°C given in reference [8]), the value obtained from regression Equation (8), and the coefficients  $a_i$  and  $b_i$  in Equation (8) are summarized in **Table 1**. The relative difference between the two values of diffusion coefficients is an average of 4% for the ions in the table, and a maximum of about 7%.

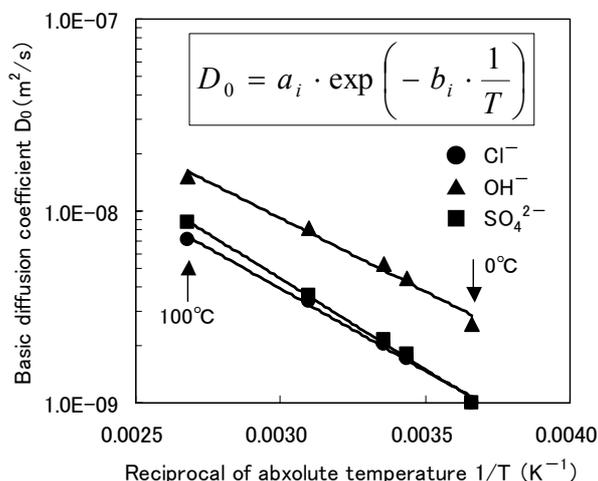
### 3.3 Effect of degree of saturation

Except in situations where concrete is permanently immersed in an aqueous solution, the distribution of moisture content within the concrete varies on account of the drying effect. As a result, the transfer speed of ions in the micropores varies. To take account of this, it was decided to use Equation (9) in reference to the test equation obtained from the relationship between water content and chloride ion diffusion coefficients in tests carried out by Saeki et al [9]. Strictly speaking, to determine the diffusion coefficients of concrete, an analysis of water content transfer should be performed, and then the water content distribution in the concrete calculated, and finally the diffusion coefficients for each depth calculated. In this study, however, the objective is to calculate the average diffusion coefficient of the concrete as a whole. Therefore, it was decided to determine the diffusion coefficients in the unsaturated condition, using the average saturation level in pores when the relative humidity of the atmosphere and the water content in the concrete (as given by Equation (10) in research conducted by Akita et al [10]) reach the equilibrium condition. **Figure 3** shows the relationship between relative humidity in this model and the ratio of the diffusion coefficients in the saturated condition to that in the unsaturated condition. It can be seen that, although the effect of water-cement ratio is not that large, the diffusion coefficient in the dry condition is significantly lower.

$$D_S^i = 0.0032 \cdot 10^{0.025 \cdot S_{avg}} \cdot D_{paste}^i \quad (9)$$



**Fig. 1** Relationship between absolute temperature and basic diffusion coefficients (cations)



**Fig. 2** Relationship between absolute temperature and basic diffusion coefficients (anions)

**Table 1** Ion mobility and regression coefficient

Ion type	$D_0 (10^{-9} \text{ m}^2/\text{s}, 25^\circ\text{C})$		Regression coefficient		
	Model Direct	Regression Equation (8)	$a_i$	$b_i$	$R^2$
$\text{Ca}^{2+}$	1.59	1.54	1.69E-06	2.09E+03	0.996
$\text{Na}^+$	1.33	1.29	1.21E-06	2.04E+03	0.994
$\text{K}^+$	1.96	1.90	1.11E-06	1.90E+03	0.995
$\text{Cs}^+$	2.06	1.97	9.20E-07	1.83E+03	0.997
$\text{Cl}^-$	2.03	1.95	1.43E-06	1.97E+03	0.996
$\text{OH}^-$	5.28	4.91	1.78E-06	1.76E+03	0.985
$\text{SO}_4^{2-}$	2.13	2.05	2.95E-06	2.17E+03	0.998

$$\begin{aligned}
S_{avg} = & 33.4 + 1.46 \cdot RH - 0.287 \cdot W/C \\
& - 1.58 \cdot 10^{-2} \cdot R^2 - 1.45 \cdot 10^{-2} \cdot RH \cdot W/C \\
& + 4.22 \cdot 10^{-4} \cdot W/C^2 + 7.73 \cdot 10^{-5} \cdot RH^3 \\
& + 1.74 \cdot 10^{-4} \cdot RH^2 \cdot W/C \\
& - 4.22 \cdot 10^{-6} \cdot RH \cdot W/C^2
\end{aligned} \quad (10)$$

Here,  $D_s^i$ : diffusion coefficient considering degree of saturation ( $m^2/s$ );  $S_{avg}$ : average saturation level (%);  $RH$ : relative humidity (%);  $W/C$ : water-cement ratio (%).

### 3.4 Effect of degree of hydration

The hydration reaction takes place in cement over a long period, and as it proceeds the structure becomes more compact. According to the literature [11], [12], strength gain continues to be observed even after several tens of years. For this reason, it was concluded that the effect of hydration could not be ignored in the calculation of diffusion coefficients.

Conventional models propose that the diffusion coefficients be handled as a function of age [3], [4], but this has the disadvantage that the diffusion coefficients become extremely small towards infinite time. On the other hand, if changes in chemical properties are excluded, the effects of hydration on the diffusion coefficients are considered to only those related to porosity accompanying hydration. Accordingly, it was concluded that the ideal method was to determine the relationship between changes in porosity with degree of hydration and the diffusion coefficients. The capillary porosity shown in Equation (11), in reference to the model proposed by T.C. Powers [13], was used to determine the porosity  $\theta$  of the paste. This equation can be used for various types of Portland cement, but if admixtures are included, either the actually measured porosity should be used, or a separate porosity model should be constructed.

$$\theta = \frac{W/C - 0.36 \cdot F_{avg}}{W/C + 0.32} \quad (11)$$

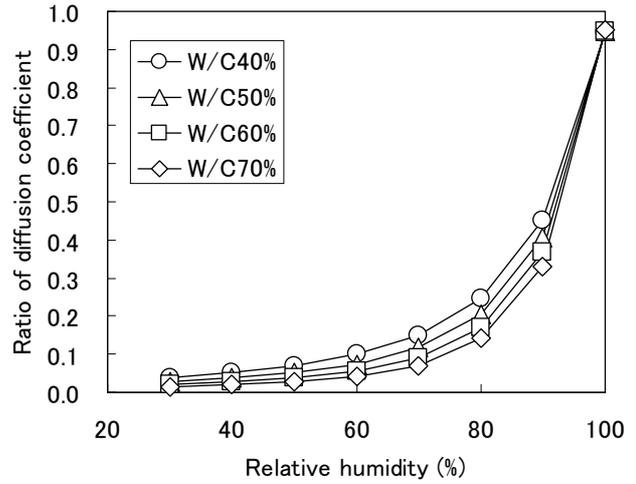
Here,  $W/C$ : water-cement ratio and  $F_{avg}$ : average degree of hydration. The average degree of hydration,  $F_{avg}$ , tends to 1.0 after a long period of hydration. However, it was decided to determine the degree of hydration during the process of hydration by referring to Equation (12) proposed by Dalziel and Gutteridge [14]. Since the effects of relative humidity are not considered in this equation, the degree of hydration needs to be appropriately corrected when the normal temperature varies.

$$F_j = 1 - \exp[-k_2(t - k_3)^{k_1}] \quad (12)$$

$$F_{avg} = \frac{\sum_{j=1}^4 (W_j \cdot F_j / 100)}{\sum_{j=1}^4 (W_j / 100)} \quad (13)$$

In the equations above,  $F_j$ : degree of hydration of each mineral (=1.0 when  $t > 1,825$  days);  $j=1$  ( $C_3S$ );  $j=2$  ( $C_2S$ );  $j=3$  ( $C_3A$ );  $j=4$  ( $C_4AF$ );  $t$ : age (days);  $k_n$ : coefficient given in **Table 2**;  $W_j$ : percentage weight of mineral  $j$  in cement clinker (%).

**Table 2** gives coefficients  $k_n$  in Equation (12) for calculating the degree of hydration of each mineral. After calculating the degree of hydration of each mineral according the elapsed time as mentioned above, the average degree of hydration of the cement as a whole can be calculated using Equation (13) according to the percentage of



**Fig. 3** Relationship between relative humidity and diffusion coefficient ratio

**Table 2** Coefficients  $k_n$  [14] for degree of hydration of each mineral

$j$	Mineral	$k_1$	$k_2$	$k_3$
1	Alite $C_3S$	0.25	0.70	0.90
2	Belite $C_2S$	0.46	0.12	0.00
3	Aluminate phase $C_3A$	0.28	0.77	0.90
4	Ferrite phase $C_4AF$	0.26	0.55	0.90

each mineral. Porosity at any arbitrary time can then be calculated using Equation (11). Consequently, the diffusion coefficients at any arbitrary time for each mineral making up a different percentage of the Portland cement can be calculated.

Typical contents of various minerals in modern Portland cement are shown in **Table 3**. When exact values are not known, the values in this table can be used. Furthermore, even in cases where the mineral composition is not known, if the chemical components present in the cement are known, then the percentage composition can be predicted using the Bogue equation [15] or by other means. **Figure 4** shows the relationship between age and degree of hydration for the mineral percentages in typical ordinary Portland cement as shown in **Table 3**. Note that the degree of hydration after about 5 years (1,825 days) reaches approximately 1.0.

### 3.5 Effect of aggregates

In mortar or concrete, there are regions with many pores at the interface between aggregate particles and paste. These are called transition zones. However, while diffusion coefficients rise, as more aggregate is added, certain opposing phenomena may occur with increasing amounts of aggregate, such as cut-off of mass transfer paths or reduction in diffusion coefficients with greater tortuosity.

Hisada et al. have clarified that as the fine aggregate volume in mortar is increased, transition zones tend to form around fine aggregate particles and apparent mobility increases. Moreover, if the coarse aggregate volume is increased, the effect of migration barriers predominates over the effect of transition zones, so mobility falls [17]. It is also clear from other work by the authors [18] on actual structures that the degradation depth accompanying leaching of calcium decreases with the increasing volume of coarse aggregate.

Accordingly, an equation for the effective diffusion coefficients of concrete is proposed as Equation (14), taking into account the effects of aggregate mixing according to the results mentioned above.

$$D_{eff}^i = \frac{1 - c \cdot G_{vol}}{1 - d \cdot S_{vol}} \cdot P_{vol} \cdot D_S^i \quad (14)$$

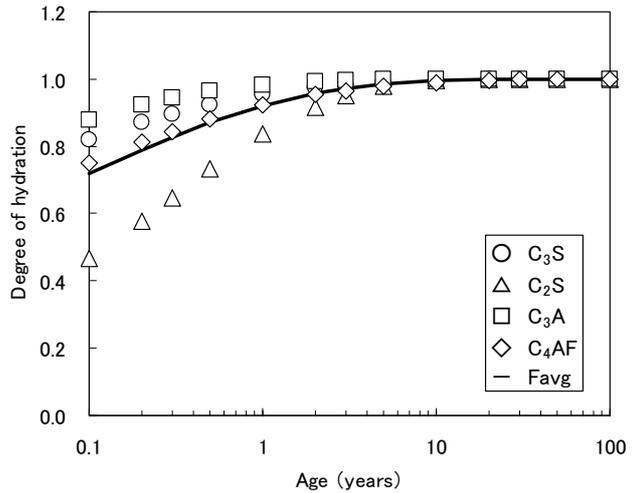
Here,  $D_{eff}^i$ : diffusion coefficient considering aggregate volume ( $m^2/s$ );  $G_{vol}$ : volume of coarse aggregate in concrete ( $m^3/m^3$ ) but with  $0 \leq G_{vol} \leq 0.6$ ;  $S_{vol}$ : volume of fine aggregate in concrete ( $m^3/m^3$ );  $P_{vol}$ : specific volume of paste in concrete  $= 1.0 - G_{vol} - S_{vol}$  ( $m^3/m^3$ );  $c, d$ : coefficients depending on aggregate (here  $c=1.5$  and  $d=0.86$  as determined by the authors referring to the results of research by Hisada [17]).

### 3.6 Summary of diffusion coefficients estimation model

**Figure 5** is a flow chart of the calculation procedure for the diffusion coefficients of concrete based on the models described above. First, the ion type to be studied is selected, and the average temperature conditions are set. The basic diffusion coefficient in water  $D_0^i$  is then calculated. Next, the degree of hydration is determined from the chemical composition of the cement or from the percentage composition of the mineral or simply from the age of the concrete. The porosity  $\theta$  can then be calculated, together with the water-cement ratio. This allows the effective

**Table 3** Composition of minerals in cement clinker [15], [16]

Type of cement	Mineral composition $W_i$ (%)			
	$W_1$	$W_2$	$W_3$	$W_4$
	$C_3S$	$C_2S$	$C_3A$	$C_4AF$
Ordinary PC	50	25	9	9
High-early-strength PC	65	11	8	8
Moderate heat PC	42	36	3	12
Sulfate-resistant PC	63	15	1	15



**Fig. 4** Relationship between age and degree of hydration

diffusion coefficient of the paste  $D_0^i$  to be calculated using the equation for  $D_{paste}^i$  as determined earlier. Furthermore, the diffusion coefficient under unsaturated conditions  $D_s^i$  can be calculated by considering the water-cement ratio and the relative humidity. This finally leads to the effective diffusion coefficient of concrete  $D_{eff}^i$ , in which the aggregate volume of the concrete is taken into account. Thus, if the concrete mix proportion and temperature/relative humidity are known, the diffusion coefficients of any arbitrary ion at any arbitrary age can be calculated. The aggregate volume is also included in the model; therefore, the diffusion coefficients of paste or mortar can also be predicted.

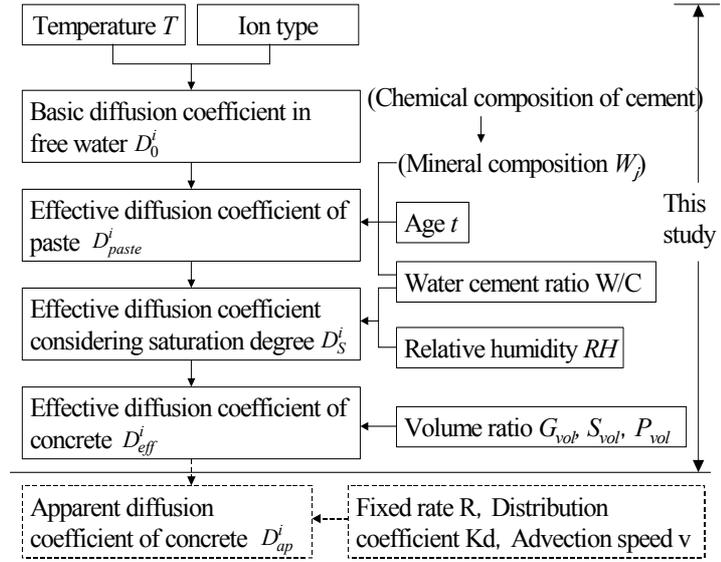


Fig. 5 Calculation of diffusion coefficients

In this investigation, it was decided not to consider the effects of reaction and advection, but if the fixed rate or distribution coefficient, advection speed, and so on, are already known, an apparent diffusion coefficient  $D_{ap}^i$  can be estimated.

Table 4 Materials used

Type	Quality
Water (W)	Ion exchange water
Cement (C)	Ordinary Portland cement; density: 3.15 g/cm <sup>3</sup> ; specific surface area: 3,350 cm <sup>2</sup> /g
Fine aggregate (S)	Sand; density: 2.61 g/cm <sup>3</sup> ; percentage of absolute volume: 68.7%; FM: 2.69
Coarse aggregate (G)	Crushed hard sandstone; density: 2.65 g/cm <sup>3</sup> ; percentage of absolute volume: 60.0%; FM: 6.76
AE water-reducing agent (Ad.)	Lignin sulfonic acid based agent

#### 4. VERIFICATION OF MODEL

##### 4.1 Verification by chloride ion immersion tests

###### a) Test method

Chloride ion immersion tests were carried out to confirm the effects of temperature dependence, water-cement ratio, and hydration. Table 4 shows the materials used and their quality, while Table 5 gives the mix proportion of the concrete. The concrete was

Table 5 Mix proportions used

W/C (%)	s/a (%)	Weight per unit volume (kg/m <sup>3</sup> )					Slump (cm)	Air content (%)
		W	C	S	G	Ad.		
40	41	168	420	699	1,022	C × 0.25%	13.5	4.6
50	44		336	781	1,010		12.0	4.5
70	47		240	872	998		12.5	4.4

mixed for 90 seconds in a forced dual-axis mixer, and placed in a 10 x 10 x 10 cm formwork. After placement of the concrete, one day curing took place in the formwork at a constant 20°C and 90% humidity. Next, it was cured under water at 20°C until the age of 4 days and 25 days, five faces were sealed in epoxy resin. Then, at the age of 7 days and 28 days, the concrete was immersed in simulated seawater at a constant temperature of 10, 30, or 50°C. Once the specified test age was reached, the concrete was sliced at a 5-mm pitch along the direction of chloride penetration, and the total chloride ion content and total soluble chloride ion content were measured according to the JCI SC4 [19] method.

Figure 6 summarizes the results of these measurements. Soluble chloride ions made up 72% of the total chloride ion content, irrespective of concentration. This means that the concentration of adsorbed chloride ions per unit volume of concrete,  $\rho_d S$ , can be expressed in the Freundlich adsorption form, as shown in Equation (15), on the basis of the relationship in Fig. 6.

$$\rho_d \cdot S = R \cdot C_S^{Cl} = (1 - 0.72) \cdot C_S^{Cl} = 0.28 \cdot C_S^{Cl} \quad (15)$$

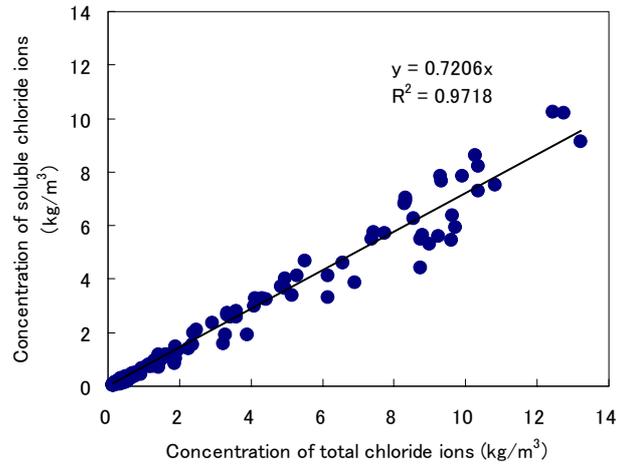
Here,  $R$  is the binding rate of chloride ions. If, as in these tests, there are no effects of hydraulic gradient or dryness/wetness, then mass transfer resulting from advection can be ignored. Then Equation (16) can be written using Equations (3) and (15) [20].

$$\begin{aligned}
 \frac{\partial C_S}{\partial t} &= \frac{\partial}{\partial x} \left( D_{eff}^{Cl} \cdot \frac{\partial C_S}{\partial x} \right) - \rho_d \cdot \frac{\partial S}{\partial t} \\
 &= \frac{\partial}{\partial x} \left( D_{eff}^{Cl} \cdot \frac{\partial C_S}{\partial x} \right) - R \cdot \frac{\partial C_S}{\partial t} \\
 &= \frac{\partial}{\partial x} \left( \frac{D_{eff}^{Cl}}{1+R} \cdot \frac{\partial C_S}{\partial x} \right) \quad (16) \\
 &= \frac{\partial}{\partial x} \left( \frac{D_{eff}^{Cl}}{1.28} \cdot \frac{\partial C_S}{\partial x} \right) \\
 &= \frac{\partial}{\partial x} \left( D_{ap}^{Cl} \cdot \frac{\partial C_S}{\partial x} \right)
 \end{aligned}$$

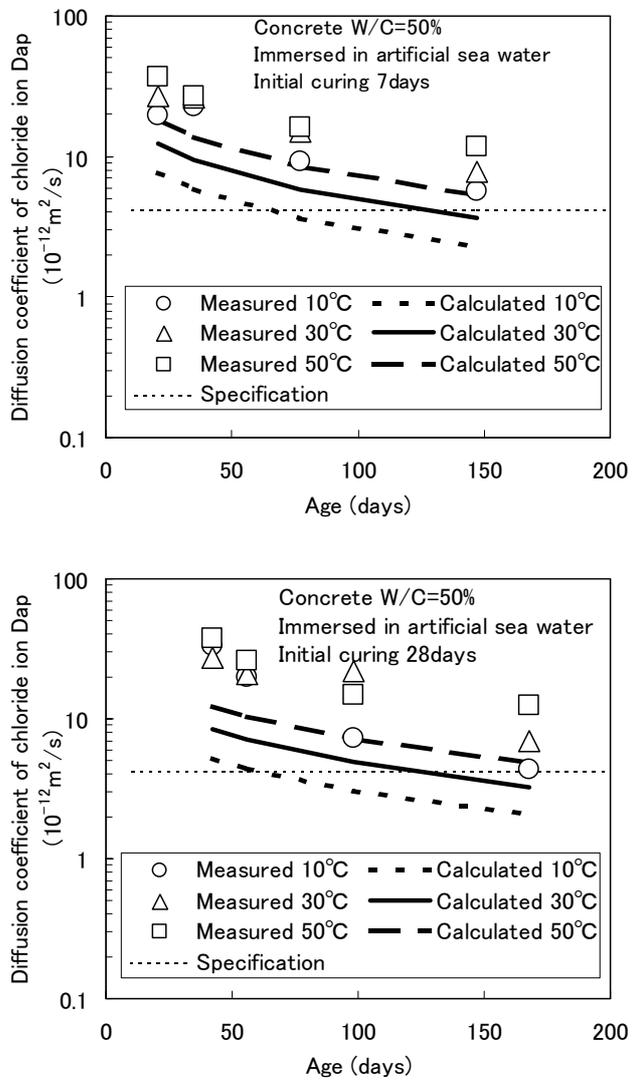
That is, the apparent diffusion coefficient excluding adsorption effects,  $D_{ap}^{Cl}$ , becomes 1/1.28 times the effective diffusion coefficient,  $D_{eff}^{Cl}$ . Accordingly, the concentration distribution of soluble chlorides in this test was fitted to Fick's diffusion law, the effective diffusion coefficient was calculated using the method of least squares, and the apparent diffusion coefficient excluding the effects of adsorption,  $D_{ap}^{Cl}$ , was calculated. This value is then used in the verification described below. The actual quantity of chloride ions in the micropore solution can be measured by high-pressure extraction of the micropore solution at room temperature; this is called the amount of free chloride. The soluble chloride mentioned in JCI SC4 is measured in hot water at 50°C for powdered cement hydrates, and it differs from the free chloride. According to previous research, however, the concentration of soluble chloride ions is directly proportional to the concentration of free chloride ions. Therefore, the diffusion coefficients of both types of ions calculated from the concentration distribution are the same. Consequently, it was concluded that the soluble chloride ions could be used in the calculation of diffusion coefficients.

#### b) Effects of hydration

The mineral composition of ordinary Portland cement as given in **Table 3** was used, and the degree of hydration  $F_{avg}$  at any arbitrary time was calculated using Equations (12) and (13). This value and the water-cement ratio (50%) were



**Fig. 6** Relationship between total chloride and soluble chloride



**Fig. 7** Change with time of chloride ion diffusion coefficients

substituted in Equation (11) to calculate the porosity  $\theta$ . Next, the basic diffusion coefficient,  $D_0^{Cl}$ , was determined from Equation (8) for temperatures 10, 30, and 50°C. Next, the  $D_0^{Cl}$  values and porosity  $\theta$  as obtained from Equation (11) were substituted into Equation (5), and the effective diffusion coefficient of the paste,  $D_{paste}^{Cl}$ , was calculated. Since the concrete was under saturated conditions, Equation (5) and the volume percentages of the aggregates were substituted into Equation (14). Finally, the apparent diffusion coefficient of chloride ions in concrete,  $D_{ap}^{Cl}$ , was predicted using Equation (16).

**Figure 7** compares the measured and predicted values of diffusion coefficients. Overall, the actually measured values are higher than the predicted ones, but the general trend of falling diffusion coefficients with age can be distinctly observed in both sets of results.

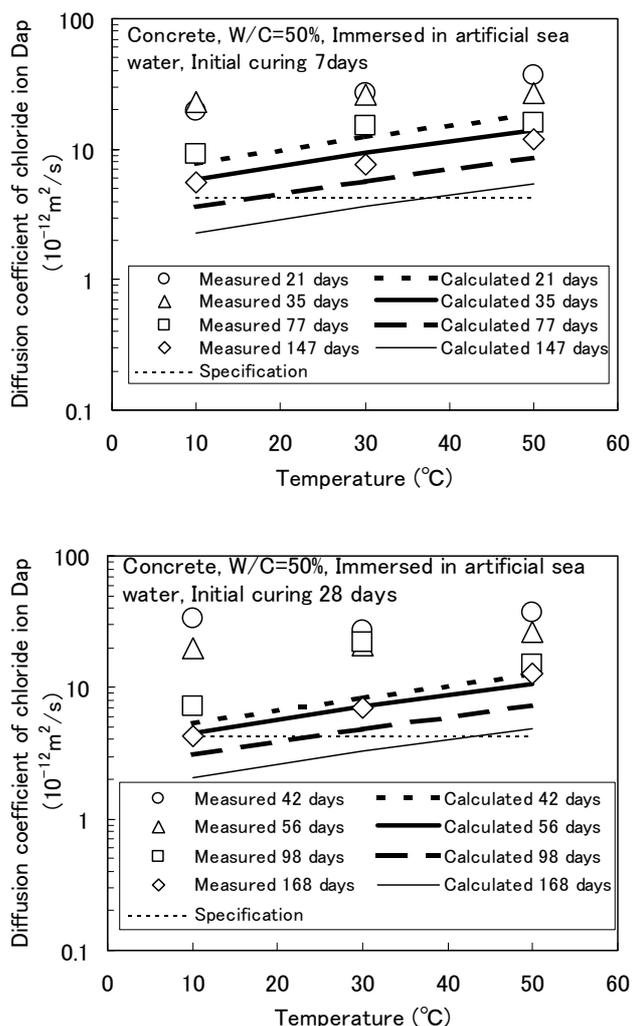
With aging, the diffusion coefficient is seen to fall to about one-fourth or even one-half of its initial value. This means that age (or degree of hydration) is an important consideration when evaluating diffusion coefficients. Also, if detailed analysis of a structure is to be performed, it is considered necessary to solve non-steady diffusion equations to take into account changes with time in the diffusion coefficients. The values predicted using the equation given in the Standard Specifications for Concrete Structures—2002 (Japan Society of Civil Engineers) are given together with Equation (1) in the figure; from these, it can be concluded that the equation given in the Standard Specifications gives diffusion coefficients at a comparatively advanced age of more than half a year at a temperature of 10-30°C.

c) Effect of temperature

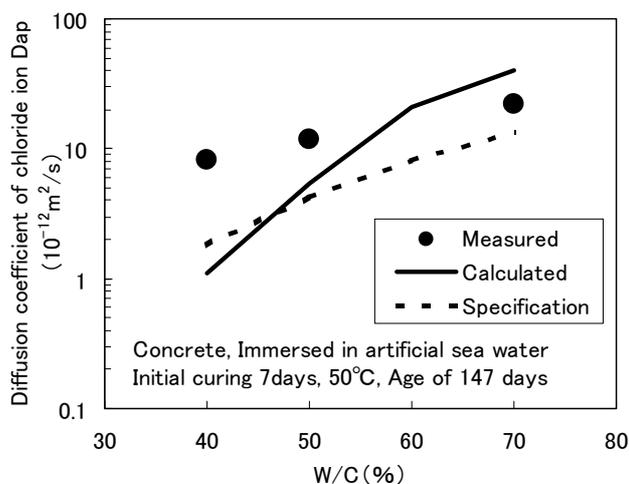
**Figure 8** shows the temperature dependence of chloride ion diffusion coefficients using the same data as in **Fig. 7**. This indicates that the temperature dependence of the prediction model is valid. It was also observed that the diffusion coefficients vary by a maximum of a factor of three in the range 10-50°C in the tests.

d) Effect of water-cement ratio

**Figure 9** shows the relationship between water-cement ratio W/C and the diffusion coefficients of chloride ions. Although the prediction accuracy is fairly good at a W/C of 50%, when W/C is greater than 50%, the predictions are high compared with the actually measured values; also,



**Fig. 8** Relationship between temperature and diffusion coefficients of chloride ions



**Fig. 9** Relationship between W/C and diffusion coefficients of chloride ions

when W/C is less than 50%, the predicted values are slightly lower than the actually measured values.

On the other hand, the W/C dependence of diffusion coefficients as determined from Equation (1) in the Standard Specifications tends to be close to the actually measured values, but the effects of temperature cannot be taken into account. For this reason, it is concluded that these predicted values are actually lower in general than the actually measured values.

Whereas the hydration reaction proceeded quickly in the 50°C environment used during some of these tests, the hydration reaction model used does not take into account the temperature. For this reason, it is concluded that differences arose in the actually measured and predicted values for large values of W/C. Further investigations are considered necessary in future to resolve this issue.

The reasons for the appreciable differences at low values of W/C include the possibility of discrepancies between the change in degree of hydration indicated by Equations (11) or (12) for calculating porosity and actual change, or the effects of transition zones. These issues will be investigated in the future.

The diffusion coefficients for chloride ions varied between several times and several tens of times over the range of W/C from 40% to 70% as investigated in these tests.

#### 4.2 Effect of relative humidity

Concrete with a water-cement ratio W/C=55% [22], [23], as shown in **Table 6**, and using ordinary Portland cement was exposed for a period of 8.5 years in an actual marine environment on the Pacific coast (undersea water conditions: annual average sea water temperature = 18°C; degree of saturation assumed as 100%; tidal zone with average annual temperature of 12.9°C; average annual relative humidity assumed to be 86.5% referenced with the Science Chronology).

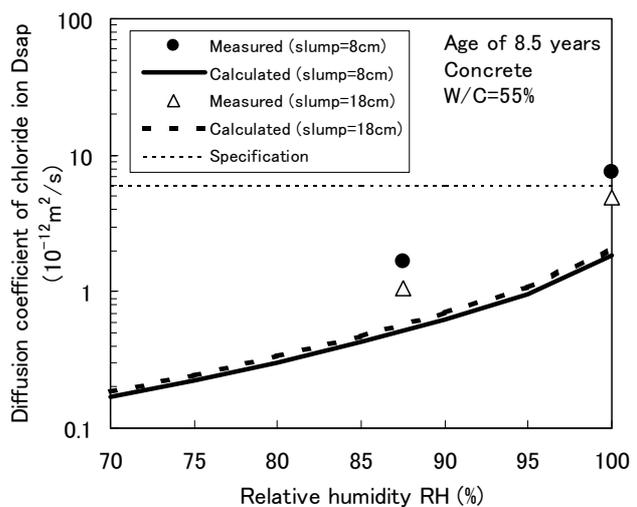
As with the tests in (1) above, the porosity  $\theta$  at W/C=55% and age 8.5 years was calculated using Equations (11) to (13). Using this porosity value, the effective diffusion coefficient of the paste  $D_{paste}^{Cl}$  at a temperature of 12.9°C in the tidal zone and in the sea at a temperature of 18°C was calculated using Equations (5) to (8). The diffusion coefficient  $D_S^{Cl}$  at relative humidity RH=100% and 86.5% was calculated using Equations (9) and (11). Finally, Equation (9) was substituted into Equations (14) and (16), and the apparent diffusion coefficient of chloride ions in concrete  $D_{ap}^{Cl}$  was estimated.

**Figure 10** compares the measured values of effective diffusion coefficients of chloride ions and the values predicted by this model. The reduction in diffusion coefficients with reduced humidity represents the actually measured values very well. Here, the relative humidity in the vicinity of the test specimens might have been higher than the values actually indicated. Because the average annual relative humidity (86.5%) was taken as 73% on land and the average value of undersea relative humidity was taken as 100%, considering the effects of tides in the tidal zone. If the relative humidity can set up highly, the actual measurement and the prediction values fit better.

**Table 6** Mix proportion used in exposure tests

W/C (%)	s/a (%)	Weight per unit volume (kg/m <sup>3</sup> )					Slump (cm)	Air content (%)
		W	C	S	G	Ad.		
55	48	158	287	881	965	C×	8.5	5.2
		175	318	847	928	0.25%	18.5	5.1

Density: C=3.15, S=2.60, G=2.65



**Fig. 10** Change in diffusion coefficients due to differences in relative humidity

When predicting the mobility of chloride ions in the unsaturated condition, if the aqueous solution permeates after the drying process, then the effects of advection in the material need to be considered, together with the absorption of the aqueous solution into the micropores. That is, in addition to the diffusion coefficients indicated here, it is necessary to quantitatively evaluate the advection rate  $v$  in the diffusion and advection relation given as Equation (3), and to calculate the changes in concentration together with the advection term.

Studies (1) and (2) above show that, the diffusion coefficients vary by a factor of about ten according to the difference in degree of hydration, as shown in Fig. 7. Over the temperature range 0 to 40°C, which is the normal maximum range of environmental temperature, the diffusion coefficients vary by several tens of times, as shown in Fig. 8. Similarly, the diffusion coefficients vary by several times over the water-cement ratio range (40% to 70%) in general use (Fig. 9). It is also found to vary by about ten times in the normal environmental range of humidity of 60% to 100% (Fig. 10). That is, when ranked by degree of influence, hydration, humidity, water-cement ratio, and temperature affect the chloride ion diffusion coefficients in that order.

#### 4.3 Effect of ion type

The adaptability of this model to ions other than chloride ions can be verified from the results of previous research, as explained below.

##### a) Sodium ions

Table 7 shows the conditions used to determine the diffusion coefficients for sodium ions in ordinary Portland cement paste in NaOH diffusion cell tests experimented by Uchikawa et al [24], [25]. Porosity  $\theta$  at W/C = 30%, 40%, and 60% was calculated at the age of 64 days using Equations (11) to (13). This porosity value was used in Equations (5) to (8) to calculate the effective diffusion coefficient of the paste  $D_{paste}^{Na}$  at a temperature of 20°C.

Figure 11 compares the actual test results with the values estimated using this model. In the immersion tests for chloride ions shown in Fig. 9, the actually measured values of chloride ion diffusion coefficients were less sensitive to changes in W/C than the estimated values, but in these tests, the effect of W/C on the diffusion coefficients was several tens of times greater. The experimental results generally correspond to the predicted results. The cause of the difference in diffusion between chloride ions and sodium ions is attributed to the effect of ion adsorption in the cementitious hydrates. The porous wall of the cementitious hydrate is generally thought to have a positive electric charge. Chloride ions, which are anions, are adsorbed, but sodium cations are not. As mentioned earlier, chloride ions are also chemically adsorbed, but practically no sodium ions are adsorbed in this way. Considering that these chemical and electrical adsorption effects vary with the quantity and type of cement, the differences between the chloride ions and sodium ions could be explained.

##### b) Sulfate ions

Table 8 shows the conditions used to estimate the diffusion coefficients for sulfate ions as determined from sodium sulfate immersion tests [26], [27]. Where conditions were not known, they were assumed as shown in the table. In tests with paste, W/C was as low as 35% and sulfate-

Table 7 Conditions for estimating diffusion coefficients of sodium ions

Item	References [24], [25]
Target ion	Na <sup>+</sup>
Category	Paste
W/C (%)	30, 40, 60
Cement	OPC
C <sub>3</sub> S	Not known (Table 3 used)
C <sub>2</sub> S	
C <sub>3</sub> A	
C <sub>4</sub> AF	
Degree of saturation	1.0
Temperature (°C)	20
Age (days)	64

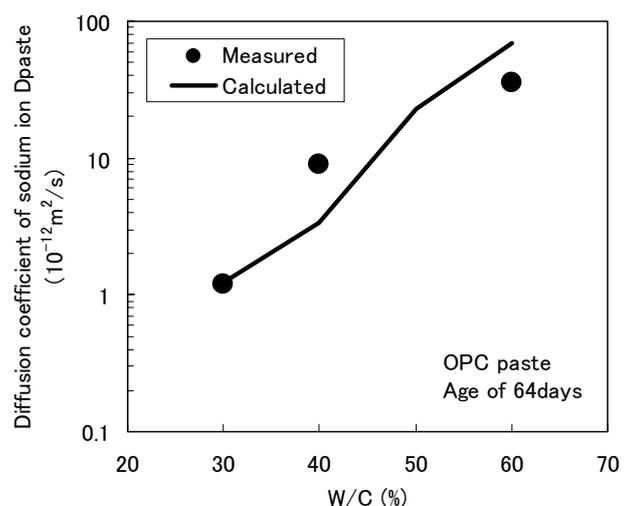


Fig. 11 Relationship between W/C and diffusion coefficients of sodium ions

resistant Portland cement (SRPC) was used. In tests with concrete, ordinary Portland cement (OPC) was used with a standard mix proportion of W/C=55%.

Porosity  $\theta$  at W/C = 35% and 55% was calculated for an arbitrary age using Equations (11) to (13). This porosity value was used in Equations (5) to (8) to calculate the effective diffusion coefficient of the paste  $D_{paste}^{SO_4}$  at a temperature of 25°C and 20°C. Furthermore, Equation (5) was substituted into Equation (14) in the case of reference [27], and the effective diffusion coefficient of sulfate ions in concrete  $D_{eff}^{SO_4}$  was estimated.

Figures 12 and 13 compare the actually measured values with the predicted effective diffusion coefficients for sulfate ions. It can be seen from the paste tests in Fig. 12 that the actually measured values and predicted values agree well.

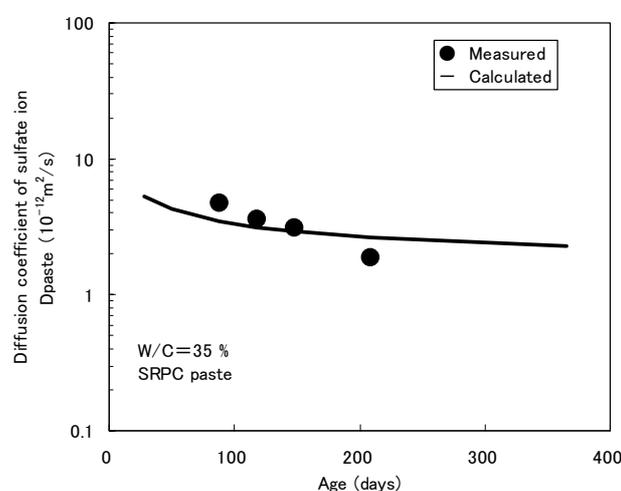
On the other hand, in case of concrete as shown in Fig. 13, an interpolation of the experimental results into the initial stage of curing might indicate that predictions are fairly reliable for an early age, but the actually measured values fall below the predicted values as aging proceeds. This difference arises is because SRPC was used in the paste (shown in Fig. 12), so the  $C_3A$  content was low and the amount of ettringite generated was also low. In contrast, OPC was used in the concrete (shown in Fig. 13), so a large amount of ettringite was generated, and the structure compacted temporarily. As a result, the diffusion coefficients decreased with aging. However, as aging progresses further, gypsum is formed and expansion failure occurs, leading to a later increase in the value of the apparent diffusion coefficients. Hence, studies extending over a longer period are necessary, and the need to incorporate reaction-induced changes in porosity into the model is also suggested.

Thus, although it is possible to predict the diffusion coefficients to a certain extent, it is deemed necessary to modify the porosity prediction relation given by Equation (11) according to the type of cement used so as to take into account changes in porosity caused by chemical reaction. This modification is given in Equation (17) below. It is also necessary to improve the model using reaction terms considering chemical reactions with the hydrates and sulfate ions, as given in Equations (3) and (15).

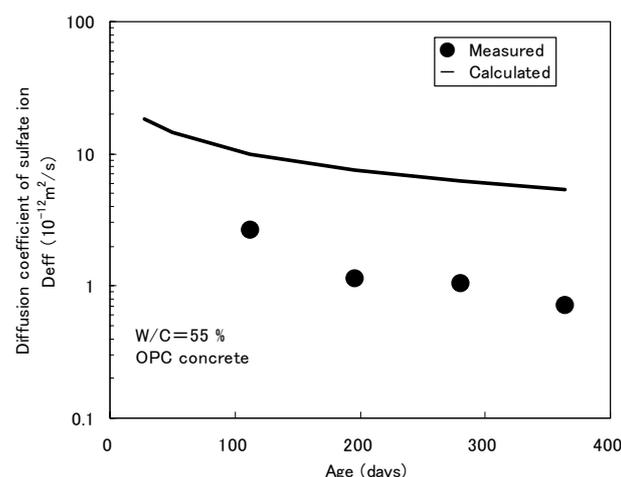
#### 4.4 Effect of leaching

**Table 8** Conditions for estimating diffusion coefficients of sulfate ions

Item	Reference [26]	Reference [27]
Target ion	$SO_4^{2-}$	
Category	Paste	Concrete
W/C (%)	35	55
Cement	SRPC	OPC
$C_3S$	42.83	Not known (Table 3 used)
$C_2S$	27.75	
$C_3A$	2.81	
$C_4AF$	16.29	
Svol (%)	—	31.7
Gvol (%)	—	37.2
Degree of saturation	1.0	1.0
Temperature (°C)	Unknown (assumed to be 25)	20



**Fig. 12** Diffusion coefficients of sulfate ions (SRPC)



**Fig. 13** Diffusion coefficients of sulfate ions (OPC)

Environmental conditions may cause an increase in porosity, in contrast with the reduction caused by the hydration reaction. Although cement hydrates do not dissolve easily, they do go into solution. It is well known [18] that hydrates dissolve under the effects of water or other chemicals, and the resulting solution moves through the pore solution by diffusion and leaching, thereby increasing porosity.

Diffusion cell tests using cesium ions ( $\text{Cs}^+$ ) and tritium (HTO) were carried out on samples in which calcium leached out from ordinary Portland cement paste, and the diffusion coefficients were determined from the literature<sup>28)</sup>. These values of diffusion coefficients were compared with values predicted using this model. **Table 9** shows the conditions used to make the estimates.

The increase in porosity corresponding to calcium leaching was evaluated using Equation (17), based on earlier research carried out by the authors [18].

$$\theta = \theta_0 + \alpha \cdot \frac{M_{CH}}{d_{CH}} \cdot (C_{P0} - C_P) \quad (17)$$

Here,  $\theta_0$ : initial porosity of paste ( $\text{m}^3/\text{m}^3$ );  $M_{CH}$ : molecular weight of  $\text{Ca}(\text{OH})_2$ ;  $d_{CH}$ : density of  $\text{Ca}(\text{OH})_2$  (2,230 g/L);  $C_P$ : solid-phase calcium concentration in paste (mol/L);  $C_{P0}$ : initial solid-phase calcium concentration in paste (mol/L); and  $\alpha$ : correction factor for change in porosity owing to leaching of components other than calcium (taken as 1.0 here).

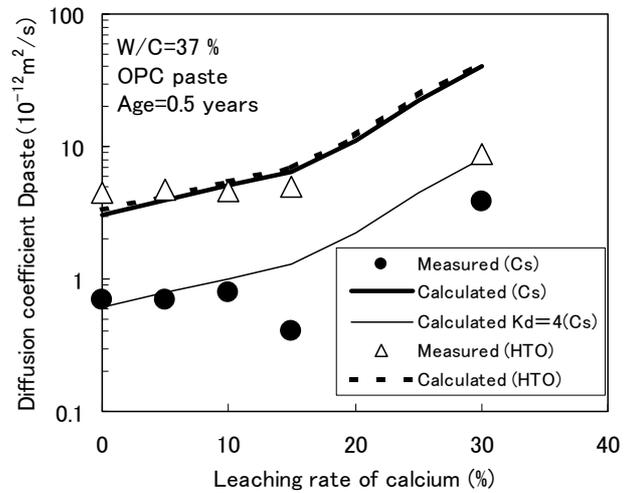
The initial porosity  $\theta_0$  at W/C = 37% and at age 6 months was calculated using Equations (11) to (13), and the calculated value was substituted into Equation (17). This was used in Equations (5) to (8) to calculate the effective diffusion coefficient of calcium in paste  $D_{paste}^{Cs}$  at a temperature of 25°C. For tritium, the self-diffusion coefficient of water ( $2.14 \times 10^{-9} \text{ m}^2/\text{s}$  at 25°C) was taken as the basic diffusion coefficient  $D_0$ , and the change in this coefficient with the changes in porosity was estimated using Equations (5) and (17).

**Figure 14** shows both the actually measured results and the estimated values. Compared to the diffusion coefficients of cesium ions in published research documents, the values predicted by this model are several times higher. However, the shape of the two curves is clearly similar, and the increase in diffusion coefficients with calcium leaching is found to be dependent on the increase in porosity. On the other hand, the predicted values agreed closely with the actually measured results of diffusion coefficients for tritium, which was not adsorbed. This demonstrates the need to use diffusion coefficients that take adsorption into account in the case of adsorbable ions such as cesium. Accordingly, R in Equation (16) was taken as the distribution coefficient Kd, and the diffusion coefficients of cesium ions were predicted taking  $Kd = 4.0$ . The predicted results are shown in **Fig. 14**. In this case, the actually measured and predicted values agreed well. It is concluded that if differences in ion characteristics, such as variations in adsorption, are taken into account in the model, then better accuracy results.

Moreover, if the calcium-leaching rate increases by 30%, the difference between predicted and actually measured values increases appreciably. This is shown in Equation (17). It is concluded that the equations for the change in porosity with leaching, and especially the term with coefficient  $\alpha$ , need to be modified according to the density of the hydrates that leach out.

**Table 9** Estimation conditions for change in diffusion coefficients with leaching

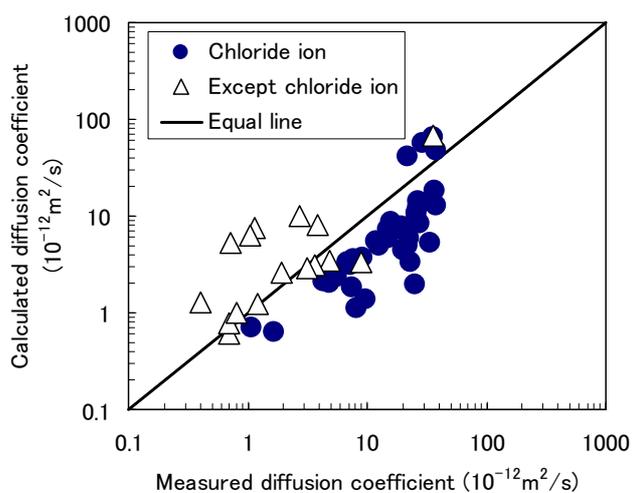
Item	Reference [28]
Target Ions	$\text{Cs}^+$ , Tritium HTO
Category	Paste
W/C (%)	37
Cement	OPC
$\text{C}_3\text{S}$	Not known (Table 3 used)
$\text{C}_2\text{S}$	
$\text{C}_3\text{A}$	
$\text{C}_4\text{AF}$	
Degree of saturation	1.0
Temperature (°C)	Unknown (assumed to be 25)
Age	3 to 9 months (assumed to be 6 months)



**Fig. 14** Change in diffusion coefficients with calcium leaching

#### 4.5 Overall evaluation

**Figure 15** summarizes all the measured and predicted values described in (1) to (4) above. This figure confirms that experimental and estimated values agree well over a wide range of diffusion coefficients values, thus verifying the reliability of the present model. Accordingly, this model is considered reliable for use in performance evaluations related to ion movement in cementitious materials. Measured values for chloride ions, however, generally tend to be higher than those predicted by the model. Therefore, it is considered necessary to carry out further studies to determine the concentration correction term, which was ignored this time, in the Debye-Hückel theory. In evaluating the life of structures, a modified diffusion coefficient should be used in the model. This should take into account the chemical reactions of the cement hydrates, as described earlier, as well as physical and chemical adsorption phenomena. Moreover, when a hydraulic gradient or dryness/wetness affects the structure, the use of diffusion and advection equations that take into account the advection term and apparent diffusion coefficients will likely lead to more accurate predictions. As of this time, the effects of temperature cannot be considered in the hydration reaction model used. This is a topic to be studied henceforth.



**Fig. 15** Comparison between actually measured and predicted values of diffusion coefficients

## 5. CONCLUSION

A model for estimating the diffusion coefficients of various ions was proposed. The model takes into account the effects of temperature, relative humidity, mix proportion, and hydration reactions. A comparison of estimates made with the model against chloride ion immersion tests and against data obtained in tests in the literature led to the conclusions given below.

- (1) Good correlation between test values and estimated values was obtained when studying the effects of temperature dependence and time dependence after the onset of hydration.
- (2) The effects of water-cement ratio could be predicted to a certain extent, but since they depend on the type of ions, further improvements are necessary.
- (3) As relative humidity falls, the chloride ion diffusion coefficients decrease. This effect was modeled satisfactorily.
- (4) The factors having most effect on the diffusion coefficients, ranked in order of magnitude, were degree of hydration, humidity, and temperature.
- (5) The diffusion coefficients of various ions, such as sodium ions, sulfate ions, and cesium ions, could be estimated using this common method.
- (6) The model captured changes in diffusion coefficients resulting from degradation caused by calcium leaching.

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