

Simple approach to calculate chloride diffusivity of concrete considering carbonation

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Abstract. Chloride diffusivity of concrete is a crucial material parameter for service life determination and durability designing of marine concrete. Many research works on this issue have been conducted, varying from empirical solutions obtained experimentally to image analysis, based on multi-scale modeling. One of the simple approaches is to express the chloride diffusivity of concrete by a multi-factor function, however, the influences of various factors on the chloride diffusivity are ambiguous. Furthermore, the majority of these research works have not dealt with the carbonation process of concrete, although this process affects the chloride diffusivity of concrete significantly. The purpose of this study is to establish a simple approach to calculate the chloride diffusivity of (non)carbonated concrete. The chloride diffusivity of concrete should be defined, based on engineering and scientific knowledge of cement and concrete materials. In this paper, a lot of parameters affecting the chloride diffusivity, such as the diffusivity in pore solution, tortuosity, micro-structural properties of hardened cement paste, volumetric portion of aggregate, are taken into consideration in the calculation of the chloride diffusivity of noncarbonated concrete. For carbonated concrete, reduced porosity due to carbonation is calculated and used for calculating the chloride diffusivity. The results are compared with experimental data and previous research works.

Keywords: service life; chloride diffusivity; carbonation; porosity; tortuosity.

1. Introduction

1.1. Research background

One of the main causes of damage to concrete structures is reinforcement corrosion due to chloride penetration. This process is usually considered to begin when the chloride content at the level of reinforcement reaches a critical value. In order to predict the time to initiate corrosion, chloride diffusion models are useful. Chloride diffusivity of concrete is a key parameter for the determinations of chloride profile in the diffusion models. In addition, it is known that the chloride diffusivity varies with time due to ongoing hydration of cement that might influence significantly the prediction of long term durability performance of marine concrete. Although chloride diffusivity is considered as the most crucial parameter for the determination of the service life of concrete, its magnitude have been regarded as an arbitrary constant or determined from regression analysis

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obtained from experimental results for short-term. It is not easy to predict the diffusivity of concrete realistically because the diffusivity of concrete is influenced by many factors such as the interfacial zone property between aggregate particles and bulk cement paste as well as the micro-structural properties of the cement paste itself. Moreover, no reasonable standard test methods to measure the diffusivity of concrete have yet been established, mainly due to the diffusivities of the measurement.

Meanwhile, a lot of models for the chloride diffusivity of concrete have been developed with various approaches: from empirical solution based on the experimental results to comprehensive multi-scale model with high resolution digital analysis (Garboczi *et al.* 1998, Luciano *et al.* 1999). One of the practical and realistic solutions is to express as a simple formulation with multi-factors regarded as an individual influencing effect. However, the effects of the influencing factors on the chloride diffusivity of concrete were ambiguous in previous studies (Xi *et al.* 1999, Saetta *et al.* 1993). Furthermore, the majority of these researches didn't deal with this issue in combination with carbonation of concrete, although carbonation affects the chloride diffusivity of concrete significantly. In this paper a simple model depicting the time evolution of the chloride diffusivity of (non) carbonated concrete is presented.

1.2. Significance of research

The purpose of this study is to develop a mathematical model for the estimation of diffusivity of concrete taking into consideration various factors and carbonation process. The model is realistic but, yet simple enough for practical application in durability design.

Carbonated and non-carbonated concrete samples were used in a Rapid Chloride Migration (RCM) test to verify the proposed model. This formulation makes it possible to take into consideration the time evolution at which the concrete is exposed to the chloride laden environment.

2. Material modeling of chloride diffusivity

2.1 Chloride diffusivity

One of the practical and reasonable ways to compute the chloride diffusivity of concrete is to consider multi-factors function, Xi *et al.* (1999) and Saetta *et al.* (1993). However, the solution

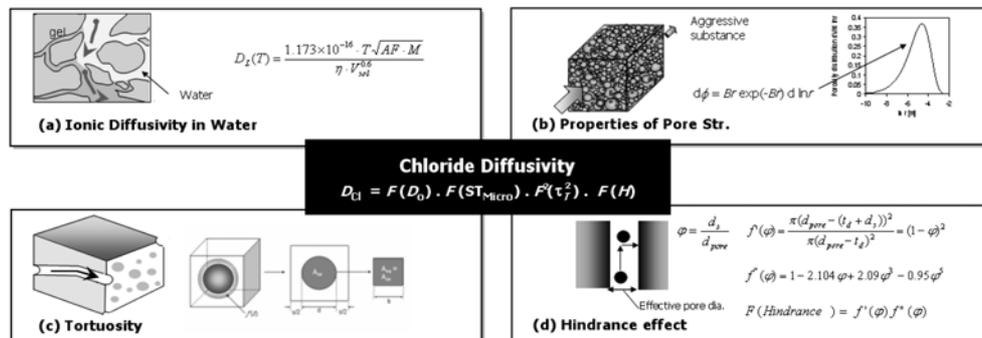


Fig. 1 Formation of chloride diffusivity to consider various affecting parameters

didn't clearly depict the effect of some important factors such as the temperature and its effect on the viscosity. These have been only depicted using the temperature equation of *Arrhnius* type in most of all researches.

This study suggests a new analytical approach with a multi-factor function as illustrated in Fig. 1. A function of multi-factors might be a function of chloride diffusivity in bulk fluid, $F(D_o(S,T))$, a function of pore structural properties, $F(S_{t_{micro}})$, a function of tortuosity, $F(\tau_T^2)$, a function of hindrance effect, $F(H)$. In what follows a description of these factors is given.

$$D_{Cl(cp)} = F(D_o(S,T)) \cdot F(S_{t_{micro}}) \cdot F(\tau_T^2) \cdot F(H) \quad (1)$$

2.1.1. Chloride diffusivity in bulk fluid

For saturated concrete, the flow media of chloride ions can be the bulk pore water as the ions can flow through water-filled pores. In this respect, ion diffusivity in bulk fluid can be estimated as (Wilke *et al.* 1995):

$$D_o = \frac{1.173 \times 10^{-16} \cdot T \sqrt{AF \cdot M}}{\eta \cdot V_m^{0.6}} \quad (2)$$

where,

- D_o : ion diffusivity in liquid (m²/s),
- T : temperature (K),
- AF : association factor for the solvent (= 2.26 for water),
- M : molecular weight of the solvent (= 18.1 g/mol for water),
- η : viscosity of the solvent (Pa.s),
- V_m : molar volume of the solute at its boiling point (m³/K mol).

2.1.2. Pore structural properties in cement paste

Porosity and pore size distribution function is necessary to consider the effect of micro-structural properties of cementitious materials on chloride diffusion. Maekawa *et al.* (1999) suggested porosity distribution function as;

$$dV_p = Br \exp(-Br) d \ln r \quad (3)$$

where,

- V_p : fractional pore volume of the distribution up to pore radius, r ,
- B : sole porosity distribution parameter, which is a peak point of porosity distribution of the cement paste on a logarithmic scale.

From Eq. (3), total porosity of cement paste, ϕ , can be expressed as;

$$\phi = \int_0^{\infty} Br \exp(-Br) d \ln r \quad (4)$$

If $\ln r$ substitutes for x , r is replaced with $\exp(x)$. Then, Eq.(4) can be rewritten as;

$$\phi = B \int_0^{\infty} \exp(x) \cdot \exp\{-B \cdot \exp(x)\} dx \quad (5)$$

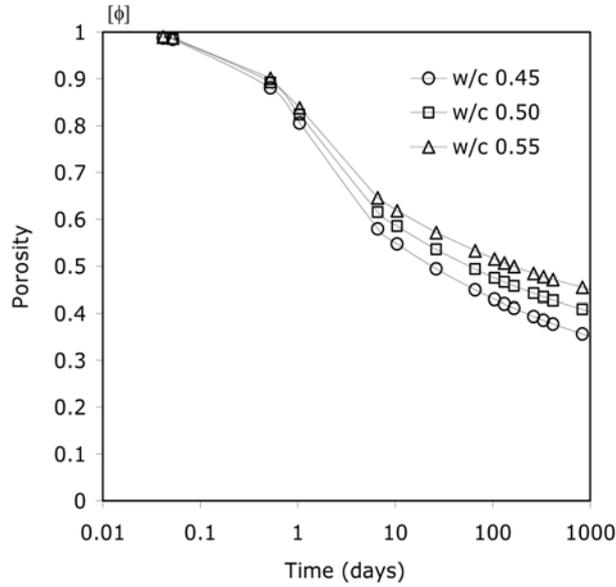


Fig. 2 Time evolution of capillary porosity in OPC cement paste for various w/c ratios

If the total porosity ϕ is known, sole porosity distribution parameter B can be calculated from Eq. (5). The total porosity ϕ can be calculated by HYMOSTRUC (Breugel 1991): a numerical simulation program for the hydration of cementitious materials. The result is shown in Fig. 2.

2.1.3. Tortuosity

Tortuosity is classically defined as a ratio l to l_e . Here l_e is effective path length in the pore and l is the shortest path distance. Unlike porosity, the tortuosity factor can't be measured directly. This tortuosity factor depends on packing arrangement, channel shape, media homogeneity and so on. It is quite difficult to define the tortuosity as a specific value, however, this study focuses on the derivation of a simple and approximate expression for tortuosity of flow path in cement paste.

Fig. 3 illustrates irregular position of cement cores at a cell, connecting with neighbored cell. On average, the middle figure of Fig. 3(b) can depict the connectivity of pores.

Fig. 4 (a) displays the possible morphology of idealized cement core and Fig. 4(b) represents

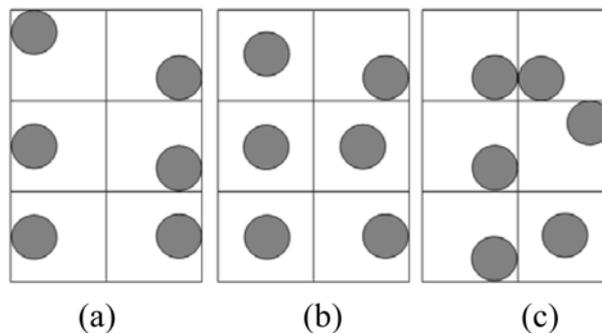


Fig. 3 Irregular position of cement cores

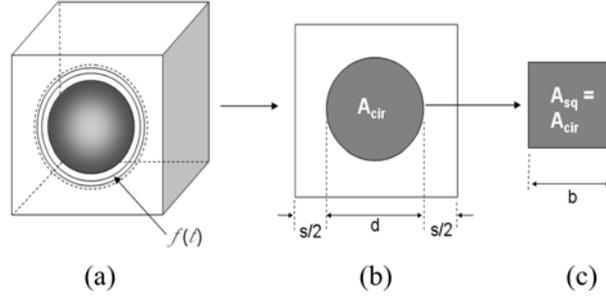


Fig. 4 Morphology of idealized cement core and transformation of circle shape into rectangle shape

cement core existed in one cell, as a formation of two-dimensional particle. The cement core can be expressed as a time function, $f(t)$, because of continuous hydration of cement. In principal, the morphology of cement core is similar to the shape of circle, however, the shape is transformed into a rectangular type in order to simplify the fluid flow, as shown in Fig. 4(c). The area of the rectangle (A_{sq}) should be equal to that of a circle (A_{cir}) because porosities (b) and (c) should also be equal. From this figure, total volume, V_t , in one unit cell can be drawn as;

$$V_t = (b + s)^2 \quad (6)$$

in which, b and s is the particle size and the gap size between particles, respectively. The total pore volume, V_p , in the unit cell is

$$V_p = (b + s)^2 - b^2 \quad (7)$$

Thus, the porosity is equal to

$$\phi = \frac{V_p}{V_t} = \frac{(b+s)^2 - b^2}{(b+s)^2} = 1 - \left(\frac{b}{b+s}\right)^2 \quad (8)$$

From Eq. (8), gap between particles, s , can be expressed as

$$s = b \left(\frac{1}{\sqrt{1-\phi}} - 1 \right) \quad (9)$$

Fig. 5 displays the two possible configurations for flow through porous media. In case of Fig. 5(a), the length of streamline BC can be drawn as

$$BC = b \sqrt{\left(\frac{1}{\sqrt{1-\phi}} - 1 \right)^2 + \frac{1}{4}} \quad (10)$$

Therefore, according to the definition of tortuosity, we have the tortuosity for flow through unrestrictedly overlapped particles as

$$\tau_r = \frac{BC}{BF} = \frac{\sqrt{1-\phi} \sqrt{\left(\frac{1}{\sqrt{1-\phi}} - 1 \right)^2 + \frac{1}{4}}}{1 - \sqrt{1-\phi}} \quad (11)$$

For a porous medium with unoverlapped particles, it can be assumed that another flow path follows the idealized pathway, as shown in Fig. 1(b), configuration b. Since the streamline BC is perpendicular to the horizontal direction, we take the whole length of streamline A-B-C-D to

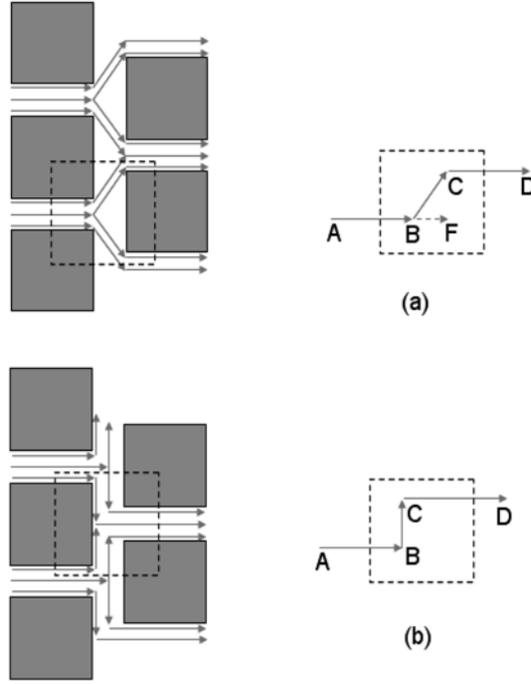


Fig. 5 Two idealized configurations of stream lines for simplicity of mass flow in cement paste (Yu *et al.* 2004)

calculate the tortuosity in the unit cell. According to the definition of tortuosity, the tortuosity for configuration b can be drawn as

$$\tau_T = \frac{BC + b + s}{b + BF} = 1 + \frac{b/2}{b + b(1/\sqrt{1-\phi} - 1)} = 1 + \frac{1}{2}\sqrt{1-\phi} \quad (12)$$

From Eq. (11) and Eq. (12), the averaged tortuosity can be given by

$$\tau_T = \frac{\sqrt{1-\phi} \sqrt{\left(\frac{1}{\sqrt{1-\phi}-1}\right)^2 + \frac{1}{4}} + \frac{1}{2}\sqrt{1-\phi} + 1}{2} \quad (13)$$

Since the shape of real cement core is similar to circle, a shape function considers differences between rectangle and circle should be introduced. That is, the amount of porosity should be same in (b) and (c) of Fig. 4. Since fluid should flow along the geometric figure of cement core, the ratio of geometric figure of rectangle to that of circle should be considered as a shape function. In order to have a same porosity, the area of rectangle should be equal to that of circle and this is equal to

$$\begin{aligned} b^2 &= \pi d^2 / 4 \\ b &= \sqrt{\pi} / 2 \cdot d \end{aligned} \quad (14)$$

Considering the shape function, averaged tortuosity can be thus defined as;

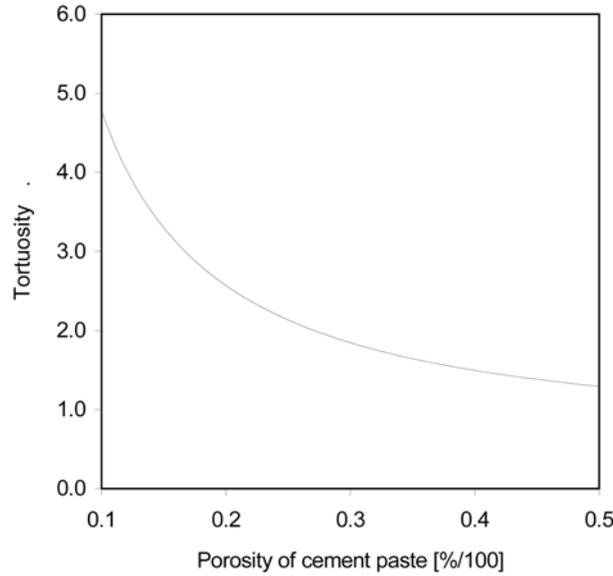


Fig. 6 Tortuosity as a function of porosity of cementitious materials

$$\tau_T = \frac{\sqrt{1-\phi} \sqrt{\left(\frac{1}{\sqrt{1-\phi}-1}\right)^2 + \frac{1}{4}} + \frac{1}{2} \sqrt{1-\phi} + 1}{4} \quad (15)$$

Since the particles in actual cement paste are randomly distributed, some particles may overlap to each other and hence it is difficult to express the tortuosity. However, the presented approach is expected to depict simplified tortuosity.

In Fig. 6, tortuosity (τ_T) is represented as a function of porosity. For concrete with low porosity, the tortuosity tends to increase. This is because flow path is complicated due to reduced porosity. On the contrary, flow path is getting smoother for materials with high porosity. Mota *et al.* (1998) suggested 1.7 to 4.0 as a tortuosity for porous materials, and this is within the scope of Fig. 6. Carmen (1937) also proposed 2.5 for tortuosity with experimental recipe. Dkhhuizen (1989) suggested that the tortuosity equals 3.0 in homogeneous and isotropic porous media, regardless with the porosity. This value is equivalent to the tortuosity of matured cement paste, as shown in Fig. 6.

2.1.4. Effect of hindered diffusion

The forth term of Eq. (1), (d) $F(H)$, means hindrance effect due to narrow pore diameter. As the molecular diameter of the solute approaches the diameter of the pore, the diffusive transport of the solute through the solvent is hindered by the presence of the pore and the pore wall. This is known as a 'hindered diffusion'. The function of the hindered diffusion can be expressed as (Welty *et al.* 2001);

$$F(H) = f'(\phi) f''(\phi) \quad (16)$$

Two correction factors, $f'(\phi)$ and $f''(\phi)$, are theoretically bounded by 0 and 1. Furthermore, both

correction factors are function of the reduced pore diameter φ .

$$\varphi = \frac{d_s}{d_{pore}} \quad (17)$$

where,

d_s : solute molecular diameter ($\approx 4\text{\AA}$ for chloride ions).

d_{pore} : diameter of pore,

The first correlation factor, partition coefficient, is based on simple geometrical arguments, as;

$$f'(\varphi) = \frac{\pi(d_{pore} - (t_d + d_s))^2}{\pi(d_{pore} - t_d)^2} = (1 - \varphi)^2 \quad (18)$$

in which, t_d means a twice thickness of adsorbed layer. For the second correlation factor, Renkin equation, which is reasonable for $0 \leq \varphi \leq 0.6$, is used.

$$f''(\varphi) = 1 - 2.104\varphi + 2.09\varphi^3 - 0.95\varphi^5 \quad (19)$$

This expressions for the hindrance effects would be useful to depict delayed diffusion rate which is occurred in consequence of narrow pore diameter and collision of chloride ion molecules with each others.

2.1.5. Effect of aggregate

Concrete consists of cement paste and aggregate and is a random composite material in terms of media for fluid transportation. Based on the micro-structural characteristics of cement paste, an interactive behavior in compliance with the presence of aggregates should be taken into accounted in the calculation of composite diffusivity. Two possible considerations should be discussed here. First, the aggregate can reduce the whole diffusivity of concrete. The diffusivity of aggregate is generally much lower than that of hardened cement paste. This means that high volume fraction of aggregates can lead to a reduction of the whole diffusivity in the unit volume of concrete. However, it should be noticed that high volume of aggregate has the adverse effect which can induce increasing the whole diffusivity of concrete due to ITZ (interfacial transition zone) effect. As more aggregates are added, the additional, highly porous ITZ regions force the bulk matrix to be denser in order to conserve the overall w/c ratio. Thus, the existence of aggregate has advantage and disadvantage at the same time in terms of the chloride diffusivity of concrete.

In this study, EMT (effective medium theory) is used to convert the diffusivity of cement paste into that of concrete. EMT has been developed for the estimation of the overall conductivity of a multiphase material originally, however, this can be applied to variety of situations in disordered or random networks. Recently Davis (1997) and Tatlier *et al.* (2004) have extended the EMT to account for mass transfer in the presence of possible concentration gradients between the distinct phases of a composite material. Based on the EMT model, the effective diffusivity can be expressed as:

$$F(C_{comp}) = \left(\frac{D_2}{k}\right) \left(\frac{1}{1 + V(1-k)/k}\right) \left(\delta + \sqrt{\delta^2 + \frac{1}{2}k\zeta}\right) \quad (20)$$

where,

D_1, D_2 : the diffusivities in the two distinct components in the system,

V_1, V_2 : the volume fractions of the different components in the multiphase material and may be replaced by $1 - V$ and V , respectively ($V_1 = 1 - V, V_2 = V$),
 C_1, C_2 : the concentrations of the species in the different regions,
 $k = C_1/C_2$, a measure of the distribution of the diffusing species between the components in the composite material. When k is equal to 1, a uniform distribution of the diffusion species exists in the material.

$$\zeta = D_1/D_2,$$

$$\delta = (3V-1 + k\zeta(2-3V))/4.$$

A significant assumption of EMT is that the neighborhood of a certain region in a mixture can be treated as a uniform medium having a conductivity or diffusivity. That is, there should be exists no correlation between the positions of the different types of regions (Tatlier *et al.* 2004). The chloride diffusivity of aggregate is assumed to be 1×10^{-12} cm²/s (Ababneh *et al.* 2003).

2.2. Decreased porosity of concrete due to carbonation

Carbonation of concrete leads to a change of porosity and this can have significant impact on chloride diffusivity. In this study, changed porosity of concrete due to carbonation is calculated for limited mix proportion of OPC concrete. Papadakis (1991) had suggested the development of major constituents of cement paste in order to estimate the performance of concrete versus time;



Molar concentration of major ingredients ($i = C_3S, C_2S, C_4AF, C_3A$) is calculated based on the reaction rate with water. A reaction rate of compound i can be expressed as:

$$r_{H,j} = -\frac{d[i]}{dt} = \frac{k_{H,j}[i]^{n_i}}{[i]_o^{n_i-1}} \quad (27)$$

where,

$r_{H,i}$: constant of reaction rate of compound i ,

$[i]$: the current concentration of compound i ,

$[i]_o$: the concentration of compound i at initial time.

The constant of reaction rates $r_{H,i}$ can be obtained from the fraction $F_i(t)$ of compounds i . This

also can be expressed by Eq. (28). The concentration of hydration product with elapsed time can be expressed by Eq. (29) to Eq. (31).

$$F_i(t) = 1 - \frac{[i]}{[i]_o} = 1 - [1 - k_{H,i}t(1 - n_i)]^{1/(1-n_i)} \quad (28)$$

$$[CSH] = \frac{1}{2}[C_3S]_o F_{C_3S} + \frac{1}{2}[C_2S]_o F_{C_2S} \quad (29)$$

$$[Ca(OH)_2] = \frac{3}{2}[C_3S]_o F_{C_3S} + \frac{1}{2}[C_2S]_o F_{C_2S} - 2[C_2AF]_o F_{C_4AF}, \quad 0 \leq t \leq t^* \quad (30)$$

$$[Ca(OH)_2] = \frac{3}{2}[C_3S]_o F_{C_3S} + \frac{1}{2}[C_2S]_o F_{C_2S} - 4[C_4AF]_o F_{C_4AF} - [C_3A]_o F_{C_3A} + [C\bar{S}H_2]_o, \quad t \geq t^* \quad (31)$$

t^* can be defined as;

$$t = \frac{1}{k_{H,C_3A}(1 - n_{C_3A})} \left[1 - \left(1 - \frac{[C\bar{S}H_2]_o}{[C_3A]_o} \right)^{(1 - n_{C_3A})} \right] \quad (32)$$

$$[CA]_o F_{C_3A}(t^*) + 2[C_4AF]_o F_{C_4AF}(t^*) = [C\bar{S}H_2]_o \quad (33)$$

In addition, initial concentration of compound i can be obtained by:

$$[i]_o = \frac{m_i m_{ci} \rho_c (1 - V_{air})}{MW_i \left(1 + \frac{w \rho_c}{c \rho_w} + \frac{a \rho_c}{c \rho_{agg}} \right)} \quad (34)$$

where,

- m_i : the weight fraction of compound i in the clinker (kg/m³),
- m_{cl} : the weight fraction of clinker (kg/m³),
- ρ_c : density of cement (kg/m³),
- ρ_w : density of water (kg/m³),
- ρ_{agg} : density of aggregate (kg/m³).

The values of the exponents n_i and the coefficients $k_{H,i}$ are listed in Table 1.

Carbonation usually proceeds in the volume of concrete in the form of a front, separating a completely carbonated region from the rest, in which carbonation has not started yet. In this latter region, the value of decreased porosity due to carbonation ($\Delta\phi_c$) is zero, whereas in the former, $\Delta\phi_c$ is approximately equal to

$$\Delta\phi_c = [Ca(OH)_2] \Delta\bar{V}_{CH} + [CSH] \Delta\bar{V}_{CSH} \quad (35)$$

in which, the concentrations of Ca(OH)₂ and C-S-H mean those at the completion of hydration and

Table 1 Parameters of major constituents of OPC cement

Compound	C ₃ S	C ₂ S	C ₃ A	C ₄ AF
Exponent n_i	2.65	3.10	2.41	3.81
Coefficient k_H	1.17	0.16	2.46	1.00
Molar weight MW_i , g/mol	228.30	172.22	270.18	485.96

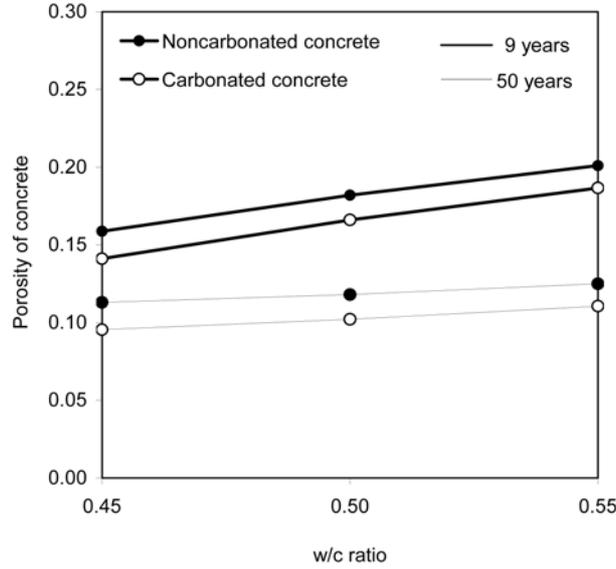


Fig. 7 Dependence of porosity of (non)carbonated concrete on time and water-cement ratio

$\Delta\bar{V}_{CH}$ and $\Delta\bar{V}_{CSH}$ equal $3.85 \times 10^{-6} \text{ m}^3/\text{mol}$, $15.39 \times 10^{-6} \text{ m}^3/\text{mol}$, respectively.

Accordingly, the porosity of carbonated concrete can be written as;

$$\phi_c = \phi - \Delta\phi_c \quad (36)$$

where,

ϕ_c : porosity of carbonated concrete,

ϕ : porosity of non-carbonated concrete, which can be calculated by HYMOSTRUC, as shown in Fig. 2.

As a result, the porosity of carbonated concrete is calculated and presented as shown in Fig. 7. For carbonated concrete, the changed porosity is inputted into the multi factor function of Eq. (1) again.

3. Experimental program

3.1 Carbonation of concrete

To validate the analytical formulation presented in this study, experimental measurement for the chloride diffusivity of (non)carbonated concrete is carried out. An ordinary Portland cement (OPC) is used in the experiment. The natural sand has a specific gravity of 2.63, and a unit weight of $1,830 \text{ kg/m}^3$. The fineness modulus and water absorption of the sand are 2.80 and 0.9%, respectively. The coarse aggregate (crushed stone) has a specific gravity of 2.70, a unit weight of $1,660 \text{ kg/m}^3$, a maximum aggregate size of 16 mm, and water absorption of 0.78%.

The mix proportion of concrete is presented in Table 2. All samples has a diameter of 100 mm and a thickness of 50 mm. Water curing of the specimens is carried out at 20°C for 28 days. The

Table 2 Mixing proportion of concrete

Air (%)	Slump (cm)	W/C	Unit weight (kg/m ³)			
			Water	Cement	Sand	Gravel
4.5±1.5	15±1	0.45	185	411	706	1001
4.5±1.5	15±1	0.50	185	370	720	1021
4.5±1.5	15±1	0.55	185	336	732	1038

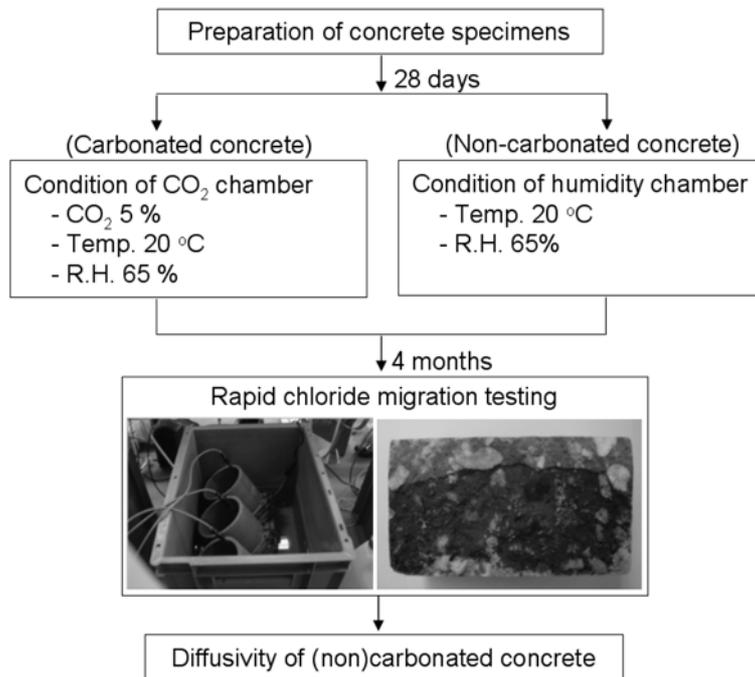


Fig. 8 Experimental procedure for acquisition of chloride diffusion coefficient of (non)carbonated concrete

surface of the concrete specimens is coated by gas-tight paint, leaving one end free to be exposed to CO₂ gas. Three samples were taken from each mixture. After four months, Phenolphthalein indicator was applied on the fresh fractured surfaces of the specimens to make sure of the creation of fully carbonated concrete. Fig. 8 expresses the outline of the experimental procedure.

3.2. Rapid chloride migration testing

In the last decade, the Rapid Chloride Migration (RCM) test, standardized in NordTest NT-Build 492, has been used more and more to investigate penetration of chloride into concrete. The test is considered as a non-steady state migration test. One side of the sample is exposed to a salt solution, while the other side of the sample is exposed to 0.3 N NaOH solution. Using stainless steel plate electrodes on both sides of the sample, a DC voltage is applied to force the negatively charged chloride ions through the sample. After conducting the test, the samples are split and sprayed with 0.01 N AgNO₃ solution to visualize the ingress of chloride into the sample. For more details on the test see NT Build 492. Based on the chloride penetration depth, chloride diffusion coefficients

(chloride migration coefficients) could be calculated by

$$D = \frac{RT x_d - \alpha \sqrt{x_d}}{zFE t} \quad (37)$$

where,

$$E = \frac{U-2}{L},$$

$$\alpha = 2 \sqrt{\frac{RT}{zFE}} \cdot \operatorname{erf}^{-1} \left(1 - \frac{2C_d}{C_o} \right),$$

- z : absolute value of ion valence (= 1 for chloride),
- F : Faraday constant (= 9.648×10^4 J/(V·Mol)),
- U : applied voltage (V),
- R : gas constant (= 8.314 J/(K·Mol)),
- T : average value of the initial and final temperatures in the acolyte solution (K),
- L : thickness of the specimens (m),
- x_d : chloride penetration depth (m),
- t : test duration (sec),
- erf^{-1} : inverse of error function,
- C_d : chloride concentration at which the color changes (= 0.07 N),
- C_o : chloride concentration in the catholyte solution (= 2 N).

4. Results and discussion

4.1. Chloride diffusivity of non-carbonated concrete

Fig. 9 shows the result of calculation of the chloride diffusivity of concrete for different w/c ratio. The chloride diffusivity decreases significantly after 28 days. For concrete with w/c ratio of 0.50, the chloride diffusivity of the concrete at 28 days decreased up to 4.7 times. The trend shows a noticeable decrease since then, however, this continues slightly. This leads to fact that it is very harmful for young concrete to be exposed to sea water directly and this requires very careful attention. Meanwhile, the decrease in chloride diffusivity is clear for concrete with high w/c ratio and this is identical to the experimental result of Nokken *et al.* (2006). This would be because microstructures of concrete with high w/c ratio is more developed than that of concrete with low w/c ratio as time elapsed.

Fig. 10 represents the comparison of chloride diffusivity of this study and experimental data of RCM testing. From the regression equation with 0.9572 of R^2 , it is found that experimental data is higher than computation result around 5.6%. It is thought that the reason is because the effect of ITZ between cement paste and aggregate on chloride diffusivity is not considered. For more accurate computation, it is necessary to consider the effect of ITZ in this analysis for future research.

Fig. 11 provides the comparison of chloride diffusivity of this analytical formulation and experimental data of RCM (rapid chloride migration) testing of Van Dalen (2005). The analytical formulation as

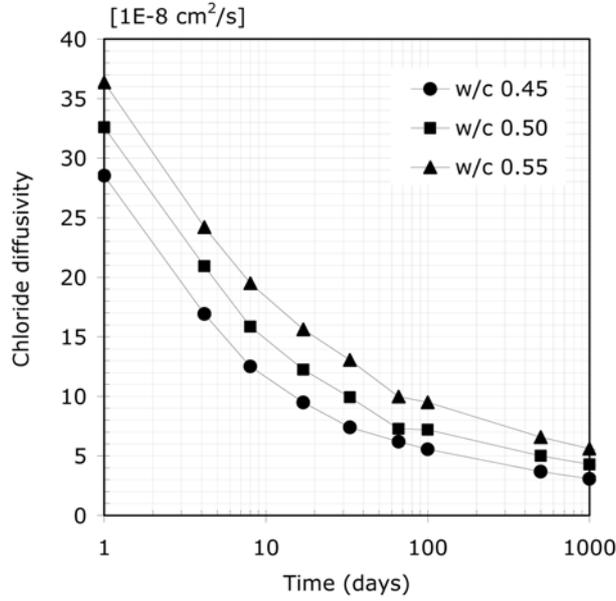


Fig. 9 Chloride diffusion coefficient for three different w/c ratios, based on the effect of the time evolution of the micro-structure on chloride diffusion

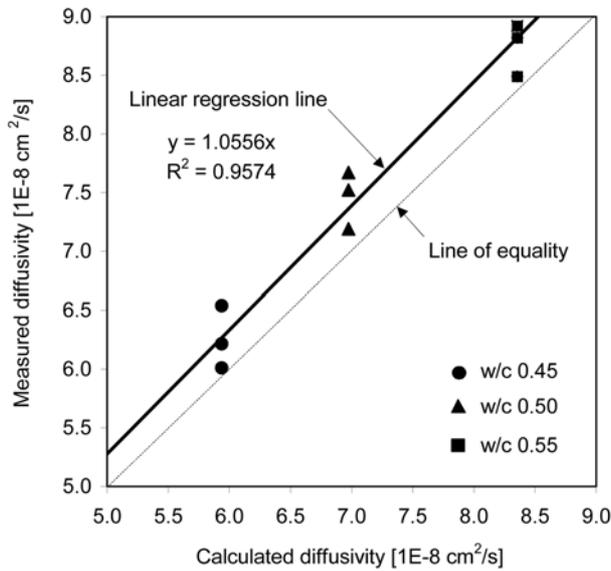


Fig. 10 Comparison of chloride diffusivity of this numerical study & experimental data of RCM testing for three different w/c ratios

proposed in this paper shows good agreement with experimental data approximately and the method is also turn out to be suitable for practice. In this figure, it is clear that the densification of the microstructure of concrete due to ongoing hydration of cement should lead to a significant reduction of the chloride diffusivity of concrete.

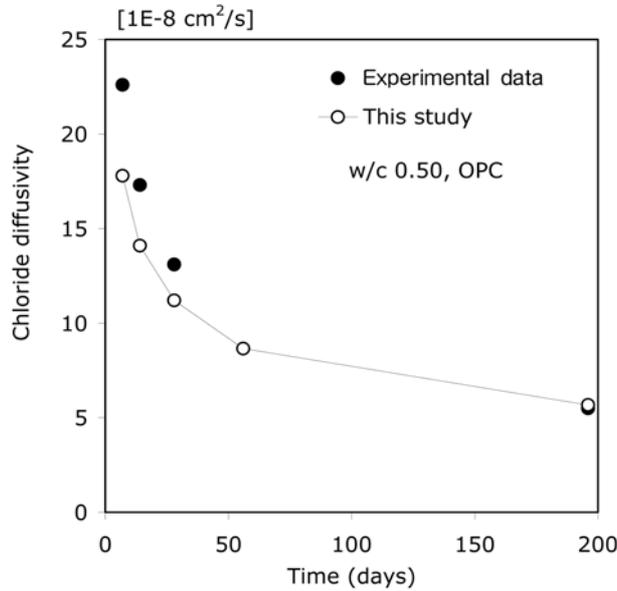


Fig. 11 Comparison of chloride diffusivity of this numerical study & published experimental data of RCM testing with elapsed time

4.2. Chloride diffusivity of carbonated concrete

The chloride diffusivity of carbonated concrete is computed and compared with that of non-carbonated concrete in Fig. 12. It is obvious that the chloride diffusivity of carbonated concrete decreases. For carbonated concrete, (a) chloride diffusivity in bulk fluid is constant, however, (b) the

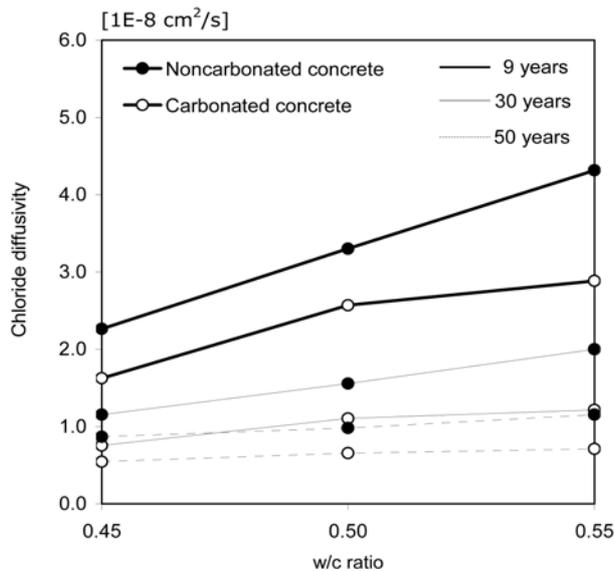


Fig. 12 Comparison of chloride diffusivity of noncarbonated concrete and that of carbonated concrete

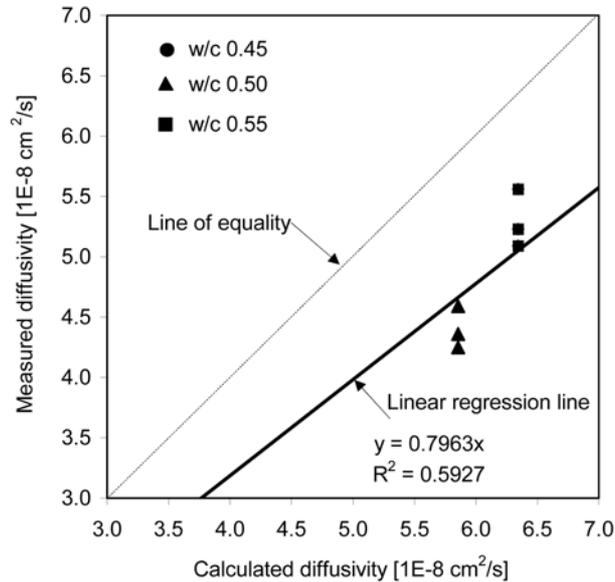


Fig. 13 Comparison of chloride diffusivity of this numerical study & experimental data of RCM testing for carbonated concrete

function of pore structural properties, (c) tortuosity and (d) hindrance effect are changed. That is, the carbonation of concrete leads to reduction of porosity and to more complicated and narrow path. According to experimental result of Saeki *et al.* (2006), chloride diffusivity of OPC carbonated concrete decreased, while that of blended concrete with flyash increased or decreased, depending the replacement ratio. For blended concrete with granulated blast furnace slag, the chloride diffusivity increased. The reason is because concrete become more porous if concrete with granulated blast slag is carbonated (Ngala *et al.* 1997). It is necessary to construct the theoretical formulation of chloride diffusivity for blended concrete.

Fig. 13 depicts the comparison of chloride diffusivity of carbonated concrete and non-carbonated concrete. Because concrete with w/c ratio of 0.45 is not fully carbonated after four months of accelerating carbonation testing, the concrete is excluded in the figure. Computation result is lower than experimental data for the diffusivity of non-carbonated concrete, however, the trend for carbonated concrete is in the contrary. According to regression equation, experimental data represents around 80% of the theoretical calculation.

For the characteristics of the microstructure of paste, it should be observed that specific properties of concrete like ITZ (Interfacial Transition Zone) might also affect the diffusion of chlorides through the path. The ITZ effect on chloride diffusivity is very ambiguous in carbonated concrete. It is necessary to investigate the effect of chemical decomposition and changed ITZ of concrete due to carbonation on the chloride diffusivity and to calculate changed porosity due to carbonation exactly.

5. Conclusions

The chloride diffusivity is of particular important material parameter for calculating the service

life of marine concrete. The purpose of this study is to establish the chloride diffusivities of carbonated and non-carbonated concrete. To this end, a comprehensive approach for formulation with the multi-factor function is constructed, considering many affecting factors. The calculation is compared with experimental result for its validation.

For non-carbonated concrete, the chloride diffusivity decreased significantly from initial casting time to 28 days and continued to decrease slightly. The experimental result was around 5.6% higher than the calculation because the effect of ITZ between cement paste and aggregate on chloride diffusivity was not considered in the calculation.

For carbonated concrete, the changed porosity due to carbonation was computed and considered in the calculation of the chloride diffusivity. The porosity of OPC concrete due to carbonation decreased and this led to the reduction of the chloride diffusivity. The computed chloride diffusivity of carbonated concrete was around 20.4% higher than that of the experimental result.

The proposed formulation is simple, yet realistic which can be used for reasonable durability design of concrete structures.

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