

Comprehensive Approach to Calculate Oxygen Diffusivity of Cementitious Materials Considering Carbonation

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Abstract: Oxygen diffusion would not be important for healthy concrete. Once concrete is carbonated, however, oxygen diffusion is very crucial to lead reinforcement corrosion. Therefore, oxygen is always a potential threat of reinforcement corrosion in concrete and oxygen diffusivity is a material parameter for service life determination and durability designing of the concrete. One of the simple approaches is to express the oxygen diffusivity of concrete by a multi-factor function, however, the influences of various factors on the oxygen diffusivity are still ambiguous. The purpose of this study is to establish a simple approach to calculate the oxygen diffusivity of (non)carbonated cementitious materials, which should be defined based on engineering and scientific knowledge of cement and concrete materials. A lot of parameters affecting the oxygen diffusivity, such as the diffusivity in air, tortuosity, micro-structural properties of hardened cement paste, volumetric fraction of aggregate, are taken into consideration for cementitious materials. For carbonated cementitious materials, reduced porosity due to carbonation is considered for the oxygen diffusivity.

Keywords: service life, oxygen diffusivity, carbonation, porosity, micro-structure.

1. Introduction

The durability of concrete is closely related to micro-structural properties of the cover concrete because the harmful substances penetrate through the concrete cover (RILEM 1997). The main mechanism of deterioration to concrete structures is reinforcement corrosion due to harmful substances such as oxygen, water, oxygen ions, and sulfate ions. Many researches have been focused on the chloride diffusivity of cementitious materials (Yoon 2009), however, it is very rare to examine the oxygen diffusivity of cementitious materials.

In general, gas transport through porous media mainly occurs by molecular diffusion and/or advection through the void space (Rowe 1987; Collin and Rasmussen 1990; Yanful 1993). For concrete, oxygen gas could not be a threatening of reinforcement corrosion because pH value of pore solution is around 13.5. There is a lot more calcium hydroxide in the concrete pores than can be dissolved in pore water. This can help maintain the pH at its usual level of around 12 or 13 as the carbonation reaction occurs. However, eventually all the locally available calcium hydroxide reacts, precipitating the calcium carbonated and allowing the pH to fall

to a level where passive layer breaks down at the surface of reinforcement in concrete. Once concrete is carbonated, however, reinforcement can not be protected by passive layer and reinforcement corrosion should be possible. This means that oxygen gas can be regarded as potential threatening to the concrete durability.

In addition, it is known that the oxygen diffusivity varies with time due to ongoing hydration of cement that might influence significantly the prediction of long term durability performance of concrete (Patel et al. 2016). Although oxygen diffusivity is considered as an important parameter for the determination of the concrete durability, its magnitude have been considered as a temporary constant or determined from regression analysis obtained from experimental results. However, the results are only trustful for the experiment duration and not reasonable for forecasting lont term performance. 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.

Meanwhile, a lot of models for the 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 oxygen diffusivity of concrete were ambiguous in previous studies (Xi et al. 1999; Saetta et al. 1993).

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Furthermore, the majority of these researches didn't deal with this issue in combination with carbonation of concrete, although carbonation affects the oxygen diffusivity of concrete significantly. Since most of the in situ concrete structures are carbonated, it is necessary to deal with the gaseous diffusivity of carbonated cementitious materials. The oxygen diffusivity should be based on the pore structure properties of cementitious materials.

In this paper a simple model depicting the time evolution of the oxygen diffusivity of (non)carbonated concrete is presented, based on the previous research (Yoon 2009). 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. This formulation is believed to make it possible to take into consideration durability design of concrete structures in connection with the time evolution of cementitious materials.

2. Material Modeling of Oxygen Diffusivity for Cementitious Materials

2.1 Oxygen Diffusivity

Xi et al. (1999) and Saetta et al. (1993) suggested practical and reasonable way to compute the chloride diffusivity of concrete. However, the solution 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 Arrhenius type in most of all researches.

In this study, the previous study of author (Yoon 2009) was used to depict new analytical approach with a multi-factor function as illustrated in Fig. 1. A functional multi-factors were composed of chloride diffusivity in bulk fluid, $F(D_o(S, T))$, pore structural properties, $F(St_{\text{micro}})$, tortuosity, $F(\tau_T^2)$, hindrance effect, $F(H)$. In what follows a description of these factors is given.

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

2.1.1 Oxygen Diffusivity in Air

The flow of oxygen can be ignored for full saturated concrete, however, oxygen gas flows for dried or partial saturated concrete. The flow media of oxygen can be the bulk pore as the gases can flow through air space.

Diffusion theory for gases is based on the kinetic molecular theory of gases (Bird et al. 1960). The diffusivity D is a function of both temperature and pressure. Diffusion increases with increasing temperature (as molecules move more rapidly), and decreases with increasing pressure (which packs more molecules in a given volume, making it harder for them to move). These temperature and pressure effects are illustrated by Eq. (2), which applies to the diffusivity between any two components of a mixture (called a binary pair):

$$D_{AB_{Tpj}} = D_{AB_{TiPj}} \left(\frac{p_i}{p_j} \right) \left(\frac{T_j}{T_i} \right)^{\frac{3}{2}} \Omega_{D/T_j} \quad (2)$$

where D_{AB} : diffusivity for the binary pair at A, B,

p: pressure,

$\Omega_{D/T}$: collision integral for molecular diffusion, which is a function of kT/E_{AB} ,

k: Boltzman constant = 1.38×10^{16} ergs/ $^{\circ}$ K,

E_{AB} : energy of molecular interaction(ergs),

i,j : reference and modeled conditions, respectively.

For binary pairs of oxygen with nitrogen, carbon dioxide, and water, and in the temperature range from 0 °C to 80 °C, kT/E_{AB} ranges from about 1.3 to 3.5. Using tabulated values for kT/E_{AB} for each of the gases in the mixture, kT/E_{AB} was calculated for each binary pair according the square root rule:

$$\frac{E_{AB}}{k} = \sqrt{\frac{E_A}{k}} + \sqrt{\frac{E_B}{k}} \quad (3)$$

The collision integral Ω can be approximated from tables relating it to kT/E_{AB} . For the kT/E_{AB} values of interest Ω ranges from about 1.3 to 0.9 (decreasing as kT/E_{AB}

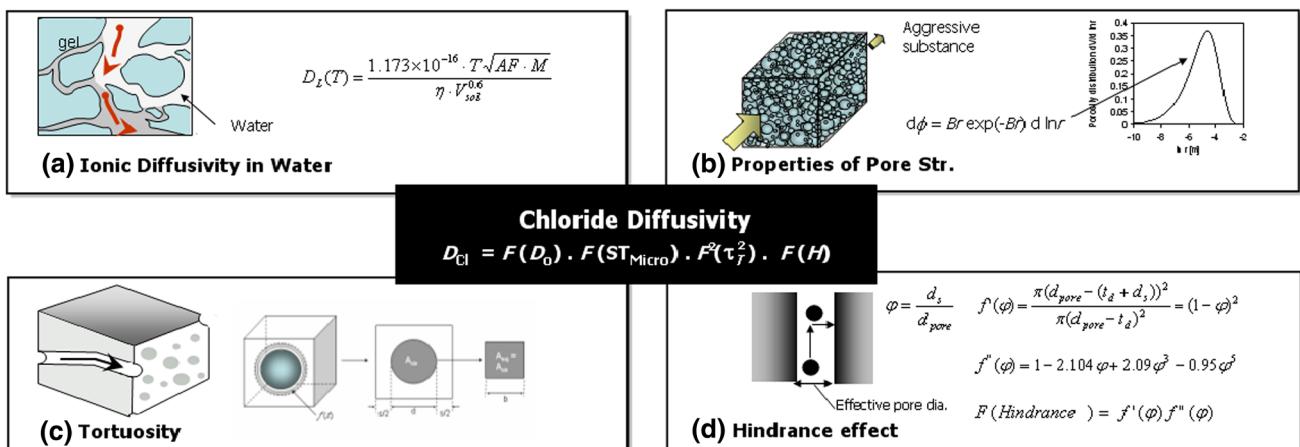


Fig. 1 Formation of chloride diffusivity to consider various affecting parameters (Yoon 2009).

increases). For this series of calculations a 5th order polynomial was fit to the $kT/E_{AB} - \Omega$. From the basis of diffusion in air, oxygen diffusivity should be equivalent to $0.176 \text{ cm}^2/\text{s}$ in the air pore of cementitious materials.

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 oxygen diffusion. Maekawa et al.(1999) suggested porosity distribution function as;

$$dV_p = Br \exp(-Br) d \ln r \quad (4)$$

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. (4), total porosity of cement paste, ϕ , can be expressed as;

$$V_p = \int_0^\infty Br \exp(-Br) d \ln r \quad (5)$$

If $\ln r$ substitutes for x , r is replaced with $\exp(x)$. Then, Eq. (5) can be rewritten as;

$$V_p = B \int_0^\infty \exp(x) \cdot \exp\{-B \cdot \exp(x)\} dx \quad (6)$$

If the total porosity V_p is known, sole porosity distribution parameter B can be calculated from Eq. (6). The total porosity V_p can be calculated by HYMOSTRUC (Van Breugel 1991), a numerical simulation program for the hydration of cementitious materials. The result is shown in Fig. 2.

2.1.3 Pore Blocking due to Moisture

The gaseous diffusivity depends largely on the degree of saturation of the material. According to the research of Houst and Wittmann, diffusivity had function of the relative humidity in which the porous samples of aerated concrete had been equilibrated. Since gaseous substance can not penetrate through pore filled with moisture, saturation is very important to estimate gaseous diffusivity.

The effective pore volume V_p^{eff} of the gaseous inflow is the residual pore fraction excluding the degree of saturation (S_r) in the whole pore and can be expressed as follows (FORGE 2011);

$$V_p^{eff} = V_p \cdot V_g = V_p(1 - S_r) \quad (7)$$

In this study, the pore system with saturation condition is shown in Fig. 3. The residual amount of the compounding water was calculated and reflected from the pore structure system of the cementitious material. The pore structure system of the cementitious material is composed of the vapor and the moisture volume under the blocking condition from

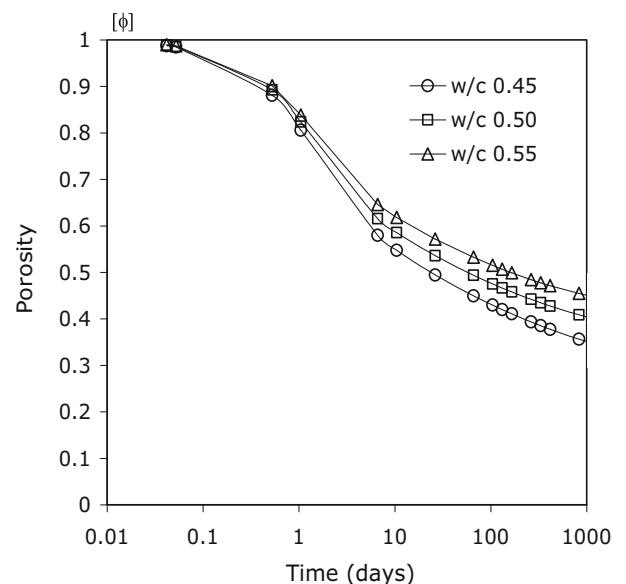


Fig. 2 Time evolution of capillary porosity in OPC cement paste for various w/c ratios.

external environment. If concrete is exposed to blocking from external environment so that moisture evaporation is prevented and the relative humidity is isolated, however, the amount of pore solution is equivalent to the amount of capillary water in pore system.

Since mixing water is ongoing consumed by hydration reaction in pore system, the amount of capillary water decreases. Thus, the volume of gas in the void per unit volume of the cement hardened body, V_g , is the amount of volume other than the capillary water content in the void existing in the volume V_{cp} of the cement paste as follows;

$$V_g(\alpha) = \frac{V_p - \frac{\rho_{ce}}{\rho_w + \rho_{ce} \cdot w/c} (w/c - 0.4 \alpha) \cdot V_{cp}}{V_p} \quad (8)$$

2.1.4 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 (Mota et al. 1998). 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

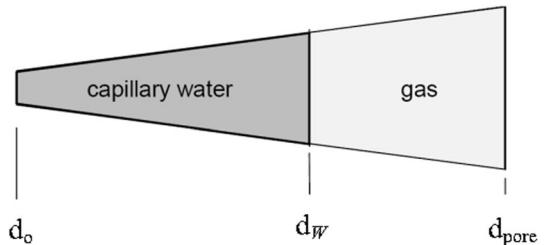


Fig. 3 Schematic representation of the border limits for the pore system with water (Van Breugel 1991).

the derivation of a simple and approximate expression for tortuosity of flow path in cement paste.

In this study, tortuosity factor was considered based on the previous study of author (Yoon 2009). 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 (Yu and Li 2004). Considering the shape function, averaged tortuosity can be thus defined as;

$$\tau_T = \sqrt{\pi} \frac{\sqrt{1 - V_p} \sqrt{\left(\frac{1}{\sqrt{1-V_p}-1}\right)^2 + \frac{1}{4}} + \frac{1}{2} \sqrt{1 - V_p} + 1}{4} \quad (9)$$

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 the study, oxygen diffusivity is assumed to be τ_T^2 .

2.1.5 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);

$$F(H) = f'(\varphi)f''(\varphi) \quad (10)$$

Two correction factors, $f'(\varphi)$ and $f''(\varphi)$, are theoretically bounded by 0 and 1. Furthermore, both correction factors are function of the reduced pore diameter φ .

$$\varphi = \frac{d_s}{d_{pore}} \quad (11)$$

where,

d_s : kinetic diameter (≈ 346 pm for oxygen gas).

d_{pore} : diameter of pore,

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

$$f'(\varphi) = \frac{\pi(d_p - (t_d + d_s))^2}{\pi(d_p - t_d)^2} = (1 - \varphi)^2 \quad (12)$$

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.

$$f''(\varphi) = 1 - 2.104\varphi + 2.09\varphi^3 - 0.95\varphi^5 \quad (13)$$

These 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 oxygen gas with each others.

2.1.6 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 oxygen 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:

$$F(C_{comp}) = \left(\frac{D_2}{k}\right) \left(\frac{1}{1 + V(1 - k)/k}\right) \left(\delta + \sqrt{\delta^2 + \frac{1}{2}k\varsigma}\right) \quad (14)$$

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.

$$\varsigma = D_1/D_2,$$

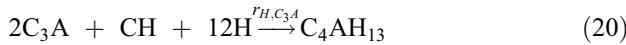
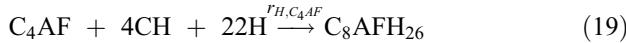
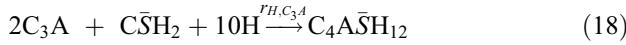
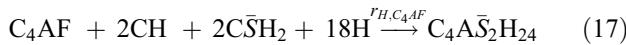
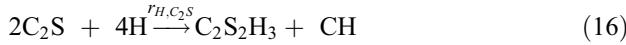
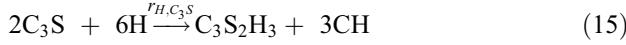
$$\delta = (3V - 1 + k\varsigma(2 - 3V))/4.$$

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 oxygen

diffusivity of aggregate is assumed to be 1×10^{-11} cm²/s, based on the research dealt with quartz (Elphick et al. 1986).

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 oxygen 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 ($i = \text{C}_3\text{S}, \text{C}_2\text{S}, \text{C}_4\text{AF}, \text{C}_3\text{A}$) is calculated based on the reaction rate with water. A reaction rate of compound i can be expressed as:

$$r_{H,i} = -\frac{d[i]}{dt} = \frac{k_{H,i}[i]^{n_i}}{[i]_o^{n_i-1}} \quad (21)$$

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. (22). The concentration of hydration product with elapsed time can be expressed by Eqs. (23)–(25).

$$F_i(t) = 1 - \frac{[i]}{[i]_o} = 1 - [1 - k_{H,i}t(1 - n_i)]^{1/(1-n_i)} \quad (22)$$

$$[\text{CSH}] = \frac{1}{2}[\text{C}_3\text{S}]_o F_{\text{C}_3\text{S}} + \frac{1}{2}[\text{C}_2\text{S}]_o F_{\text{C}_2\text{S}} \quad (23)$$

$$\begin{aligned} [\text{Ca}(\text{OH})_2] &= \frac{3}{2}[\text{C}_3\text{S}]_o F_{\text{C}_3\text{S}} + \frac{1}{2}[\text{C}_2\text{S}]_o F_{\text{C}_2\text{S}} \\ &\quad - 2[\text{C}_4\text{AF}]_o F_{\text{C}_4\text{AF}}, \end{aligned} \quad (24)$$

$0 \leq t \leq t^*$

$$\begin{aligned} [\text{Ca}(\text{OH})_2] &= \frac{3}{2}[\text{C}_3\text{S}]_o F_{\text{C}_3\text{S}} + \frac{1}{2}[\text{C}_2\text{S}]_o F_{\text{C}_2\text{S}} \\ &\quad - 4[\text{C}_4\text{AF}]_o F_{\text{C}_4\text{AF}} - [\text{C}_3\text{A}]_o F_{\text{C}_3\text{A}} \\ &\quad + [\text{C}\bar{\text{S}}\text{H}_2]_o, \quad t \geq t^* \end{aligned} \quad (25)$$

t^* can be defined as;

$$t = \frac{1}{k_{H,\text{C}_3\text{A}}(1 - n_{\text{C}_3\text{A}})} \left[1 - \left(1 - \frac{[\text{C}\bar{\text{S}}\text{H}_2]_o}{[\text{C}_3\text{A}]_o} \right)^{(1-n_{\text{C}_3\text{A}})} \right] \quad (26)$$

$$[\text{CA}]_o F_{\text{C}_3\text{A}}(t^*) + 2[\text{C}_4\text{AF}]_o F_{\text{C}_4\text{AF}}(t^*) = [\text{C}\bar{\text{S}}\text{H}_2]_o \quad (27)$$

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

$$[i]_o = \frac{m_i m_{\text{cl}} \rho_c (1 - V_{\text{air}})}{MW_i \left(1 + \frac{w}{c} \frac{\rho_c}{\rho_w} + \frac{a}{c} \frac{\rho_c}{\rho_{\text{agg}}} \right)} \quad (28)$$

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 (ΔV_c) is zero, whereas in the former, ΔV_c is approximately equal to

$$\Delta V_c = [\text{Ca}(\text{OH})_2] \Delta \bar{V}_{\text{CH}} + [\text{CSH}] \Delta \bar{V}_{\text{CSH}} \quad (29)$$

in which, the concentrations of $\text{Ca}(\text{OH})_2$ and C-S-H mean those at the completion of hydration and $\Delta \bar{V}_{\text{CH}}$ and $\Delta \bar{V}_{\text{CSH}}$ equal 3.85×10^{-6} m³/mol, 15.39×10^{-6} m³/mol, respectively.

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

$$V_c = V_p - \Delta V_c \quad (30)$$

where,

V_c : porosity of carbonated concrete,

V_p : 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. 4. For carbonated concrete, the changed porosity is inputted into the multi factor function of Eq. (1) again.

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

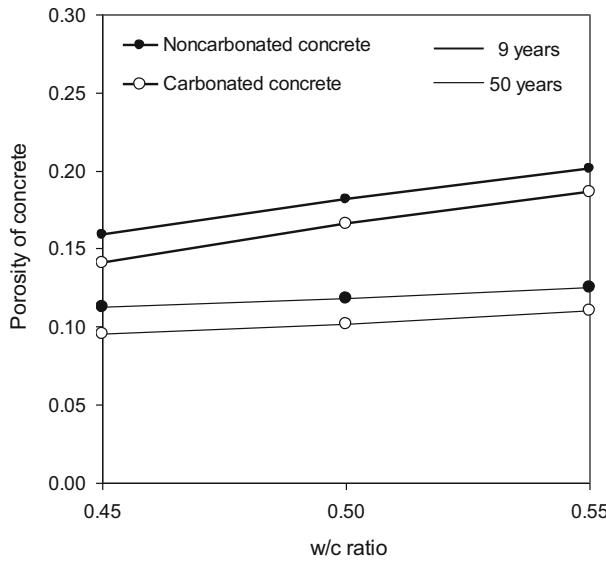


Fig. 4 Dependence of porosity of (non)carbonated concrete on time and water-cement ratio.

3. Results and Discussion

3.1 Oxygen Diffusivity of Noncarbonated Concrete

Figure 5 shows the result of calculation of apparent oxygen diffusivity of concrete for different w/c ratio. The calculation is based on assumption that total pore is available

for the flow of oxygen gas. The oxygen diffusivity decreased significantly until 28 days because the micro-structural desification of the concrete is not yet sufficiently developed. The trend of the reduction lasted even at long term because of on-going hydration of cement, however, the reduction rate was not excessive. For concrete with w/c ratio 0.50, the oxygen diffusivity of the concrete at 28 days decreased up to 4.5 times. The trend shows a noticeable decrease since then, however, this continues slightly. Therefore, it is very harmful for young concrete to be exposed to harmful substances directly and this requires very careful attention from the initial stage of construction. Meanwhile, the decrease in oxygen 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 micro-structures of concrete with high w/c ratio is more developed than that of concrete with low w/c ratio as time elapsed.

Figure 6 represents the calculation of effective oxygen diffusivity of concrete which means diffusivity with effective pore due to moisture. The calculation is based on the assumption that oxygen gas only flows through effective pore, in which the pores filled with water is excluded in total pore, to consider the effect of pore blocking due to water. Like Fig. 5, the oxygen diffusivity of concrete with effective pore tends to decrease with elapsed time. Two points should be discussed. Firstly, it can be seen that the effective oxygen diffusivity of the concrete was considerably reduced than apparent diffusivity of the concrete. This means that the pore blocking due to moisture has a very large effect on the

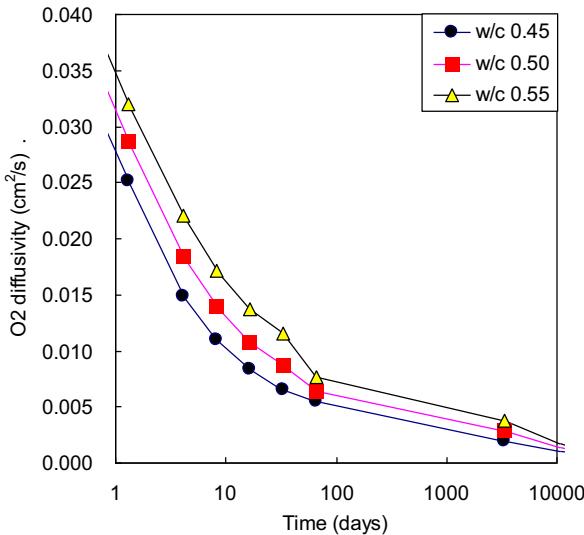


Fig. 5 Apparent oxygen diffusivity of noncarbonated concrete calculated with apparent pore.

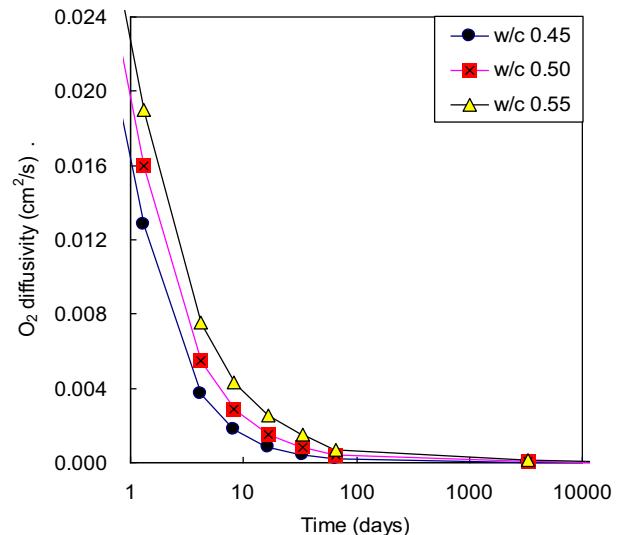


Fig. 6 Effective oxygen diffusivity of noncarbonated concrete.

oxygen diffusivity of concrete. Secondly, the value of the oxygen diffusivity was extremely reduced after 100 days. This implies that the effect of reducing oxygen diffusivity due to moisture was obvious in long-term age.

Figure 7 presents the effect of pore blocking due to moisture on the oxygen diffusivity of concrete. The influence of moisture was not significant in the early age of concrete, however, the effective diffusivity of concrete decreased remarkably with elapsed time and the trend was evident depending on w/c ratio of concrete. The effective diffusivity has decreased to less than 1/10 of the apparent diffusivity, as 1,000 days have passed. It is confirmed, therefore, that the effect of moisture is very important for calculating the gaseous diffusivity of cementitious materials accurately.

3.2 Oxygen Diffusivity of Carbonated Concrete

For carbonated concrete, (a) oxygen diffusivity in bulk fluid is constant, however, (b) the function of pore structural properties, (c) tortuosity and (d) hindrance effect are changed. That is, the carbonation of concrete leads to reduce porosity and to more complicated and narrow path. Figure 8 represents calculation result of oxygen diffusivity of carbonated concrete with apparent pore. The oxygen diffusivity of concrete was also greatly reduced by carbonation, compared with Fig. 7.

The oxygen diffusivity of carbonated concrete is computed and compared with that of non-carbonated concrete in Fig. 9. It is clear that the oxygen diffusivity of carbonated concrete decreases. 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

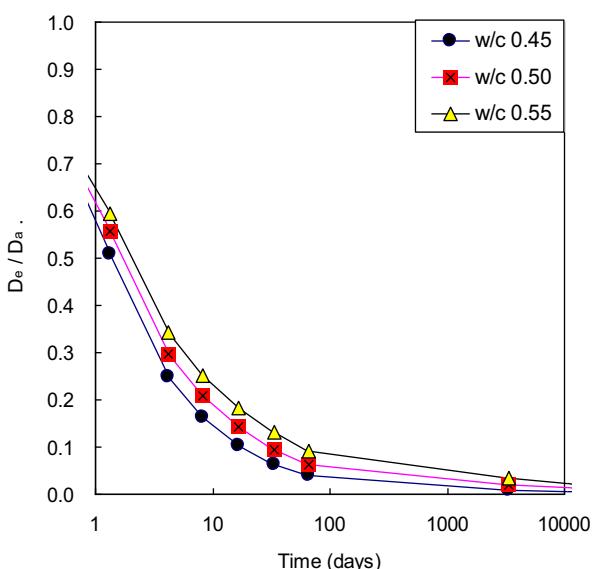


Fig. 7 Comparison of effective oxygen diffusivity of concrete (D_e) and apparent oxygen diffusivity (D_a) of concrete.

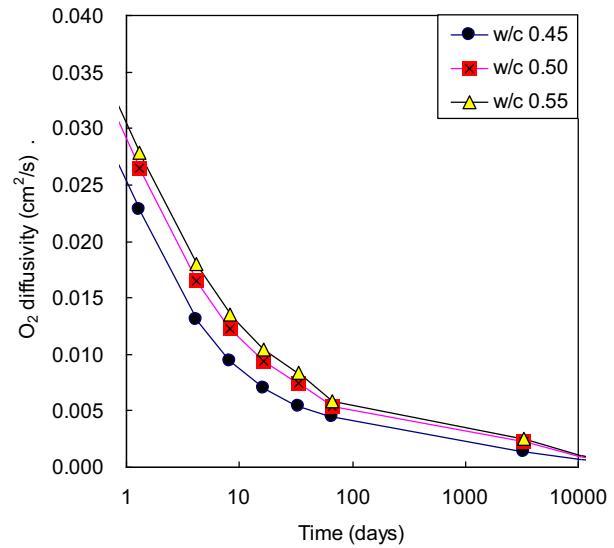


Fig. 8 Apparent oxygen diffusivity of carbonated concrete with apparent pore.

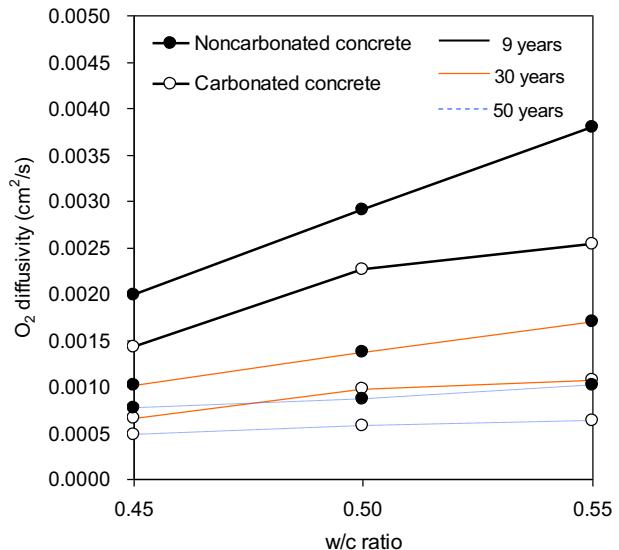


Fig. 9 Comparison of oxygen diffusivity of non-carbonated concrete and that of carbonated concrete.

granulated blast slag is carbonated (Ngala et al. 1997). It is necessary to construct the theoretical formulation of oxygen diffusivity for blended concrete.

Figure 10 illustrates effective oxygen diffusivity of carbonated concrete. The combined effect of carbonation and moisture influences oxygen diffusivity, compared with Fig. 8. The effective oxygen diffusivity of carbonated concrete was around 25 ~ 38% lower than that of noncarbonated concrete.

Figure 11 presents the effect of pore blocking due to moisture on the oxygen diffusivity of carbonated concrete. The influence of carbonation was significant from initial time and that is similar to Fig. 7. The effect of moisture was not significant in the early age of concrete and the effective diffusivity of concrete decreased remarkably with elapsed time. However, the trend was not severe, compared with

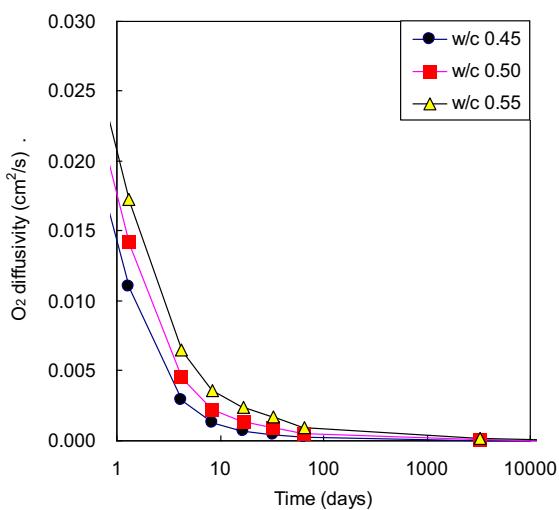


Fig. 10 Effective oxygen diffusivity of carbonated concrete.

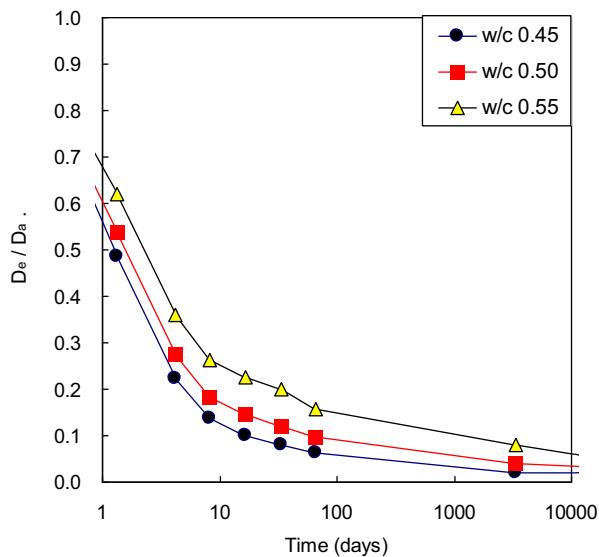


Fig. 11 Comparison of effective oxygen diffusivity of concrete (D_e) and apparent oxygen diffusivity (D_a) of carbonated concrete.

Fig. 10. It is confirmed, therefore, that the moisture and carbonation are significantly related to oxygen diffusivity and it is very important to calculate the diffusivity of cementitious materials.

3.3 Comparison with Previous Researches

For cementitious materials, a lot of studies have been accomplished on chloride diffusivity, however, study on oxygen diffusivity is rare. It is worth mentioning that the CEB 1990 Model Code states that the effective diffusivity of CO_2 and oxygen in concrete is in the range of 0.5×10^{-4} to $6 \times 10^{-4} \text{ cm}^2/\text{s}$. Gaseous penetration is highly dependent on the degree of saturation of cementitious materials rather than liquid penetration. Gaseous penetration decreased rapidly at the degree of saturation of more than 50% (FORGE 2011).

Houst and Wittmann examined that CO_2 diffusivity was 10 times higher than oxygen diffusivity in the same concrete. According to their study, the diffusivity was constant when the relative humidity was less than 60%, however, the values were reduced if the relative humidity exceeds 60%. The results coincided with experiment work accomplished by Martin et al. (2006), who measured oxygen diffusivity with mine.

In the calculation of this study, the apparent oxygen diffusivity of matured concrete at 28 days was in the range of 3×10^{-3} to $6.5 \times 10^{-3} \text{ cm}^2/\text{s}$, which is similar to the results of Houston and Wittmann. On the other hand, the effective oxygen diffusivity of the same cured concrete was calculated to be in the range of 3×10^{-4} to $8 \times 10^{-4} \text{ cm}^2/\text{s}$, which was within the limits of the CEB 1990 Model Code. It has been shown, however, that a 9 year elapsed period has to be elapsed for the reduction to the limit of $0.5 \times 10^{-4} \text{ cm}^2/\text{s}$, which is the limit range of CEB 1990 Model Code. Therefore, the calculation results of this study are approximately consistent with the ranges presented in the previous literatures.

For the microstructural characteristics of paste, it should be observed that specific properties of concrete like ITZ (Interfacial Transition Zone) might also affect the diffusion of oxygens through the path. The ITZ effect on oxygen 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 oxygen diffusivity and to calculate changed porosity due to carbonation exactly.

4. Conclusions

The oxygen diffusivity is of particular quantitative parameter for estimating durability performance quantitatively and for taking into account the effect of oxygen on calculation of service life of concrete. The purpose of this study is to establish the oxygen diffusivity for carbonated as well as noncarbonated concrete. A comprehensive approach for formulation with the multi-factor function is constructed, considering many affecting factors. In this study, apparent/effective oxygen diffusivity of concrete and reduction of oxygen diffusivity of carbonated concrete were calculated.

For noncarbonated concrete, the oxygen diffusivity decreased significantly from initial casting time to 28 days and continued to decrease slightly. For carbonated concrete, the changed porosity due to carbonation was computed and considered in the calculation of the oxygen diffusivity. The porosity of OPC concrete due to carbonation decreased and this led to the reduction of the oxygen diffusivity. The effective oxygen diffusivity of carbonated concrete was around 25 ~ 38% lower than that of non-carbonated concrete.

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

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