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Time Evolution of CO₂ Diffusivity of Carbonated Concrete

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Abstract: Carbonation of cementitious materials is one of main causes of reinforcement corrosion and CO₂ diffusivity influenced by microstructural characteristics of the cementitious materials is a decisive parameter for the carbonation rate. This study focused on establishing a multifactor functional model to calculate the CO₂ diffusivity of carbonated cementitious materials. Because CO₂ gas flows through carbonated zone, it is necessary to estimate CO₂ diffusivity of carbonated concrete. Many factors on the CO₂ diffusivity, such as the diffusivity in vapor, tortuosity, microstructural characteristics of cement paste, contribution of aggregate, and reduction of porosity due to carbonation, were considered. Apparent and effective CO₂ diffusivity were calculated according to the absence or presence of moisture in the pore system of concrete, and the results were compared with previous research.

Keywords: CO₂ diffusivity; carbonation; reinforcement corrosion; moisture

1. Introduction

Concrete contains a lot of calcium hydroxide in pores because the hydration reaction of C₃S (3CaO·SiO₂) and C₂S (2CaO·SiO₂) abundantly in cement. This can help maintain a strong alkaline environment with pH 12.5 to 13.0 in pore solution and thus reinforcement embedded in the concrete can be well protected from corrosion. If CO₂ gas in the atmosphere diffuses into concrete, however, all the available calcium hydroxide is consumed due to the reaction of the carbonation. Calcium carbonate is produced from this reaction and causes a decrease in pH of pore solution to a level where the passive layer of reinforcement embedded in concrete breaks down. Carbonation may not be harmful for the concrete itself, however, reinforcement corrosion can occur immediately if the pH of the pore water drops below 11.5. As a result, carbonation can precipitate reinforcement corrosion, which ultimately reduces long-term durability performance of concrete. Thus, calculating carbonation rate is very important for predicting service life of the reinforced concrete and CO₂ diffusivity is a crucial parameter for the carbonation rate.

By the way, molecular diffusion and advection through porous media are the main driving force on the penetration of harmful substances such as chloride ions, CO₂ or O₂ gas, and so on [1–3]. For carbonation of concrete, once CO₂ gas flow through pore of the materials, CO₂ gas is dissolved in pore solution and reacts with cement hydrates. Diffusivity stands for flow rate of harmful substances and CO₂ diffusivity of cementitious material must be defined for predicting long-term durability. Most studies have obtained only chloride diffusivity of cementitious materials [4–6]. From decades of practical experience and theoretical considerations, however, it is well known that carbonation of concrete is one of main causes of deterioration of concrete [7]. Since the long-term performance of concrete structure is greatly dependent on reaction and the migration rate of CO₂ gas in concrete, the CO₂ diffusivity plays a key part in designing and estimating concrete structures under crowded urban area with high CO₂ gas.

Meanwhile, diffusivity of cementitious materials depends on time because ongoing cement hydration of cement can lead to significant densification of pore system of the cementitious materials [8]. Moreover, diffusivity of concrete is affected by various factors such as (a) pore structure system with the type of cement; (b) all mixing proportional properties of concrete; (c) interfacial transition zone between cement paste and aggregate; (d) environmental conditions such as temperature and humidity, and so on. Therefore, it is difficult to define the diffusivity of concrete systematically.

In fact, in recent decades, various methodologies for defining the diffusivity of concrete have been proposed from empirical solution to computational model [5,6]. Practical and realistic model can be realized by means of a simple formulation with affecting multi-factors. However, the relationship between each factor and the diffusivity or interference effect was not clear in previous research [9,10]. CO₂ diffusivity of concrete has a functional relationship with the pore system of cement paste during the time when the diffusion of CO₂ takes place through already carbonated concrete. It is usually assumed that carbonation front progresses after all Ca(OH)₂ has been transformed. It is important to examine knowledge about the diffusion properties of the carbonated concrete. Carbonation process is assumed to consist of a diffusion of CO₂ through carbonated zone to a front where all of the CO₂ is assumed by reaction with cement hydrates. The gradient for the diffusion process is the concentration gradient of free CO₂ from surface concrete to carbonation depth, as shown in Figure 1. According to the figure, CO₂ concentration is zero at the carbonation front, while CO₂ gas reacts with cement hydrates at carbonation zone and CO₂ gas does not exist at noncarbonated zone. This implies that CO₂ flows through the carbonation zone by carbonation rate depicted with CO₂ diffusivity, reaches the noncarbonated zone, and reacts with the cement hydrates. Therefore, CO₂ diffusivity should be estimated, based on the microstructure characteristics and changed system of microstructure due to carbonation.

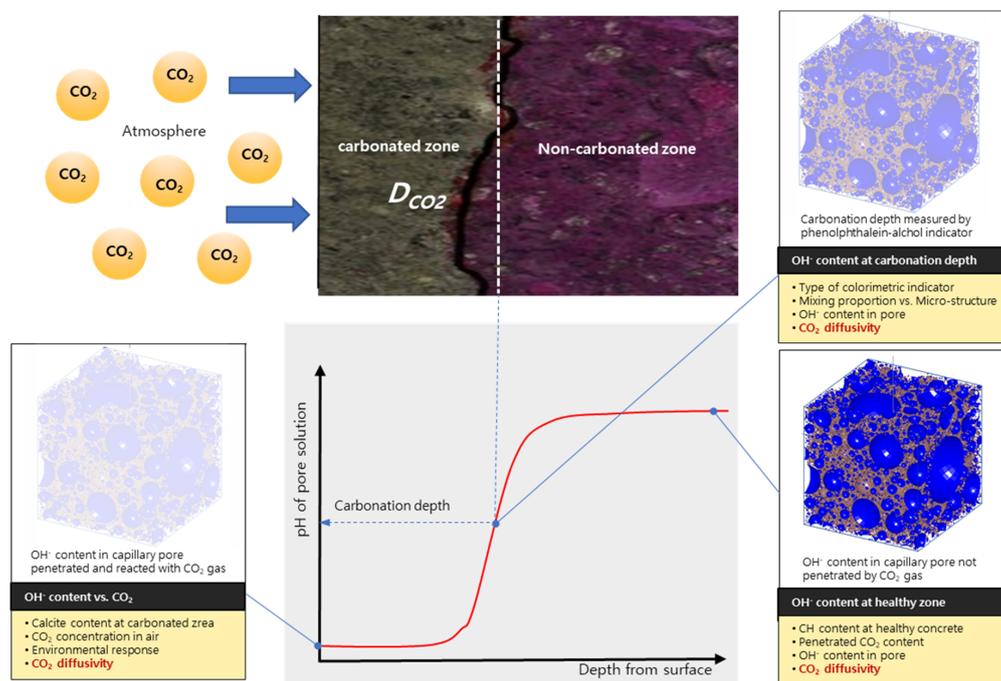


Figure 1. Importance of CO₂ diffusivity as a decisive parameter for controlling carbonation rate of concrete. In this figure, the degree of carbonation of concrete is expressed as the hydroxyl concentration of cement hydrates. In the carbonated area, the pH of the pore solution is greatly reduced, and the rate depends on CO₂ concentration in the atmosphere as an environment response. For noncarbonated area, it has an original pH value. The border between the two areas can be determined by spraying a phenolphthalein-alcohol indicator and this also can be influenced by OH⁻ content. The CO₂ diffusivity is a material parameter that can make all these decisions.

This study suggests a comprehensive model for the apparent and the effective CO₂ diffusivity of concrete, based on the previous research [4]. It was investigated how much pore solution in the concrete reduces the CO₂ diffusivity due to pore blocking at each stage of cement hydration. In particular, the difference in the CO₂ diffusivity between carbonated concrete and noncarbonated concrete was examined. The approach of this study is expected to be useful in the development of integrated carbonation model at each hydration stage of cement in the future.

2. Modeling of CO₂ Diffusivity

2.1. Formulation of CO₂ Diffusivity of Concrete

Among the models for estimating chloride diffusivity of concrete, practical multifunctional approaches have been proposed [9,10]. However, the solutions could not clearly provide the mutual interference effect between the diffusivity and affecting factors on element function. This study was conducted as an applied study essential for predicting carbonation, based on the author’s previous work [4]. Model for oxygen diffusivity was established with the approach [11].

Concrete is a random composite material composed of two phases, cement paste and aggregate. Thus, diffusivity of concrete (D_{conc}) can be expressed as a contribution function of cement paste (D_{cp}) and aggregate (D_{agg}), respectively:

$$D_{conc} = F(D_{cp}, D_{agg}) \tag{1}$$

Main functions of diffusivity of cement paste consists of diffusivity in vapor, $F(D_o(T))$, microstructure characteristics, $F(St_{micro})$, tortuosity, $F(\tau_T^2)$, disturbed diffusion, $F(H)$. The combination of these factors can be described in Equation (2) and theoretical formulation of CO₂ diffusivity was constructed with the approach as a reference [4]. The schematic diagram was elaborated in Figure 2.

$$D_{cp} = F(D_o(T)) \cdot F(St_{micro}) \cdot F(\tau_T^2) \cdot F(H) \tag{2}$$

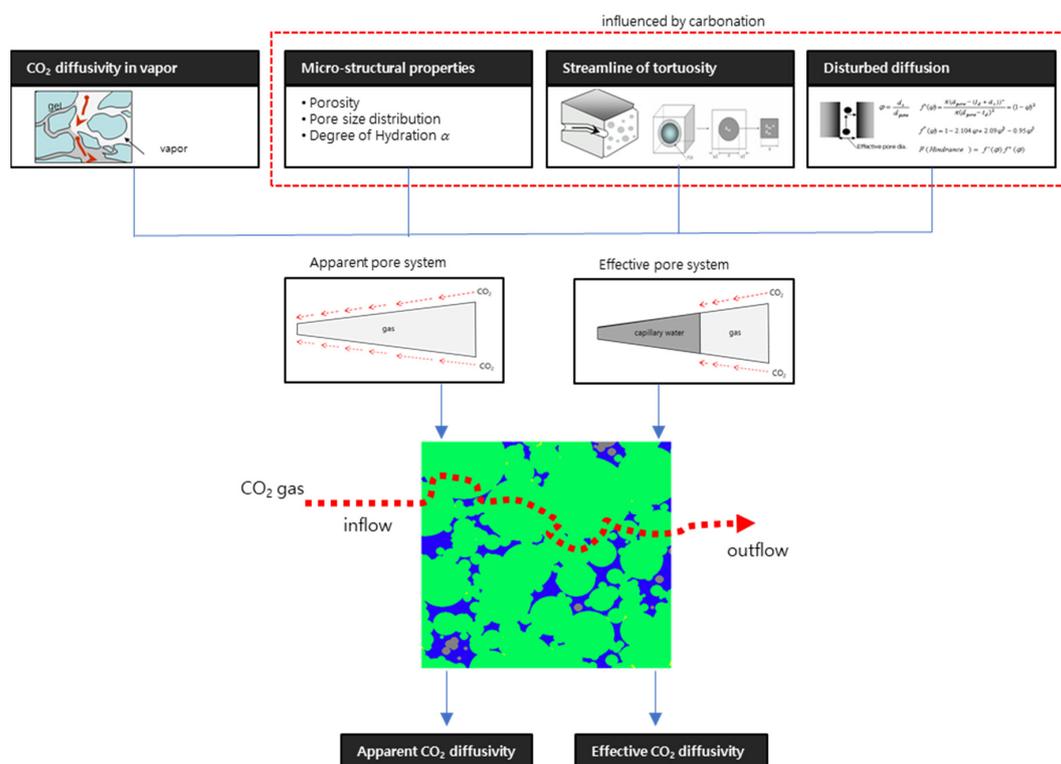


Figure 2. Model of CO₂ diffusivity with four multifunction (modified from [4]).

2.2. CO₂ Diffusivity in Vapor

The first term of Equation (2), (a) $F(D_0)$, means CO₂ diffusivity in vapor. CO₂ gas can flow through bulk pore which is not filled with solution. Diffusion theory on gases is theoretically established from kinetic molecular theory [12]. Fuller et al. suggested the diffusivity D in vapor has a function of both temperature and pressure [13]. They suggested gaseous diffusivity in vapor:

$$D^v = \frac{10^{-7} T^{1.75} \sqrt{\frac{1}{M_a} + \frac{1}{M_b}}}{P \left[(\sum_a v_i)^{\frac{1}{3}} + (\sum_b v_i)^{\frac{1}{3}} \right]^2} \tag{3}$$

in which, D^v : vapor diffusivity, T : temperature, M_a, M_b : molecular weight of components a and b , P : total pressure. According to this equation, the value of CO₂ diffusivity is approximately 0.16 cm²/s in the air pore system of concrete.

2.3. Microstructure Characterization of Cement Paste

2.3.1. Pore Structural Properties in Cement Paste

The second term of Equation (2), (a) $F(St_{micro})$, means microstructure effect of cement paste. Pore volume and the size distribution are the main factors to characterize fluid transportation through porous media in terms of microstructural characteristics. Porosity distribution function was suggested by Maekawa et al. [14]:

$$dV_p = Br \exp(-Br) d \ln r \tag{4}$$

where,

V_p : volumetric fraction of pore with distribution up to pore radius, r ,

B : a peak point of porosity distribution on a logarithmic scale.

If $\ln r$ replaces x , r is substituted for $\exp(x)$. Equation (4) is derived as:

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

With increasing degree of hydration, the pore volume decreases, mainly at the cost of the volume of the larger pores. Thus, total porosity (V_p) was calculated by HYMOSTRUC [15] for each hydration step, numerical simulation program for cement hydration. A peak point of porosity distribution B was back calculated from Equation (5).

2.3.2. Tortuosity

To account of the winding streamline of CO₂ gas, tortuosity factor was suggested in previous work of author [4]. Although it makes sense to regard the morphology of cement core as a circular shape, it is assumed to be a square to simplify the fluid streamline [16]. The difference is reflected with shape functional ratio between circle and square and thus, average streamline of tortuosity was depicted as:

$$\tau_T = \sqrt{\pi} \frac{\sqrt{1-V_p} \sqrt{\left(\frac{1}{\sqrt{1-V_p}-1}\right)^2 + \frac{1}{4}} + \frac{1}{2} \sqrt{1-V_p} + 1}{4} \tag{6}$$

For depicting flow complexity through cement paste, CO₂ diffusivity has a function with τ_T^2 , as shown in Equation (2).

2.3.3. Pore Blocking Due to Moisture

Diffusivity is significantly influenced by relative humidity in cementitious materials [17]. Because gas cannot penetrate through pore water, amount of capillary water should be reflected in estimating effective diffusivity. During the hydration process, capillary pores are gradually emptied until a thermodynamic equilibrium is reached. The effective pore volume (V_p^{eff}) of the gaseous inflow is equivalent to the volumetric fraction of vapor, which means the remaining air pore fraction depending on the degree of saturation (S_r) in system [18]:

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

The pore system vs. degree of saturation is illustrated in Figure 3. The remaining amount of the pore water and volume of pore system were calculated with hydration process. The pore structure system of the material is filled with vapor and pore water. If concrete is assumed to be an infinite material, moisture from outdoor environment is less easy to mobilize and moisture evaporation due to external heat should be ignored. Thus, the amount of pore water can be regarded as the amount of capillary water.

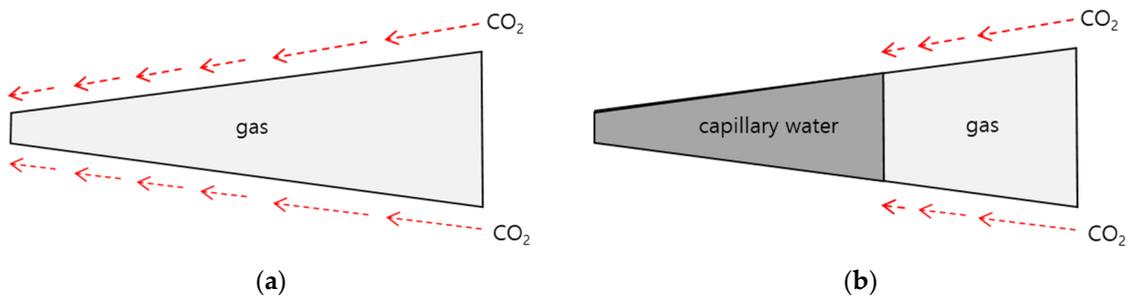


Figure 3. Comparison of CO₂ apparent diffusivity and CO₂ effective diffusivity. (a) Apparent pore system; (b) Effective pore system.

Pore system of cementitious materials consists of space filled with pore water (V_w) and remaining space with vapor (V_g):

$$V_p = V_w + V_g \tag{8}$$

Following capillary water consumed due to ongoing cement hydration [15], amount of pore water also can be expressed as:

$$V_w(\alpha) = \frac{\rho_{ce}}{\rho_w + \rho_{ce} \cdot w/c} (w/c - 0.4 \cdot \alpha) V_{cp} \tag{9}$$

in which, ρ_i : specific mass of i , α : degree of hydration.

Therefore, volumetric fraction of gas (V_g) vs. the volume of the cement paste (V_{cp}) can be expressed as:

$$V_g(\alpha) = \frac{V_p - \frac{\rho_{ce}}{\rho_w + \rho_{ce} \cdot w/c} (w/c - 0.4 \alpha) \cdot V_{cp}}{V_p} \tag{10}$$

Therefore, the CO₂ diffusivity can be divided into two diffusivities; (a) apparent diffusivity of the condition described in Figure 3a, ignoring the moisture and considering the total pores; (b) effective diffusivity of the condition described in Figure 3b, considering the effective pores through which moisture is excluded from the total pores and gas can penetrate. The calculation result was shown in Figure 4.

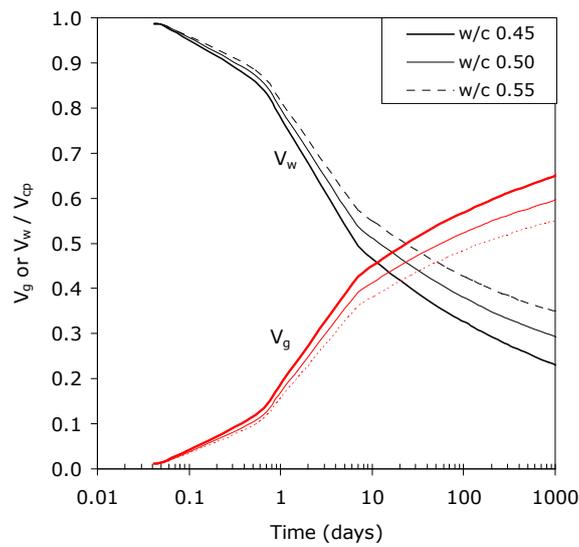


Figure 4. Volumetric fraction of gas and capillary water in pore system.

2.4. Disturbed Diffusion

The fourth term of Equation (2), (d) $F(H)$, can express hindered diffusion due to interaction of substance and narrow path between pore walls. As the molecular diameter of the harmful substances approaches the pore wall, the transport of the harmful substances through the pore should be disturbed by the narrow pore wall. The function of the disturbed diffusion is described as [19]:

$$F(H) = f'(\phi)f''(\phi) \tag{11}$$

Two correction factors, $f'(\phi)$ and $f''(\phi)$, are related to the reduced pore diameter ϕ :

$$\phi = \frac{d_s}{d_{pore}} \tag{12}$$

where,

d_s : kinetic diameter ($\approx 3.34 \times 10^{-8}$ cm for CO_2 gas).

d_{pore} : diameter of pore,

The first correlation factor, based on geometrical arguments, can be expressed as:

$$f'(\phi) = \frac{\pi(d_p - (t_d + d_s))^2}{\pi(d_p - t_d)^2} = (1 - \phi)^2 \tag{13}$$

in which, t_d means a twice thickness of adsorbed layer. The second correlation factor can be expressed as Renkin equation:

$$f''(\phi) = 1 - 2.104\phi + 2.09\phi^3 - 0.95\phi^5 \tag{14}$$

The effect is effective to depict disturbed diffusion rate due to consequence of narrow pore diameter and collision of CO_2 gaseous molecules to each other.

2.5. Effect of Aggregate

The above methods are influencing factors for obtaining the CO_2 diffusivity of the cement paste. Concrete consists of cement paste and aggregate. Effective medium theory (EMT) is used to change diffusivity of composite materials with two phases [20,21]. EMT pertains to analytical modeling that describes the macroscopic properties of composite materials and can be a solution on concentration

gradients between phases of the materials. The diffusivity of composite material with two phases can be expressed as:

$$F(C_{comp}) = \left(\frac{D_2}{k}\right) \left(\frac{1}{1 + V(1-k)/k}\right) \left(\delta + \sqrt{\delta^2 + \frac{1}{2}k\zeta}\right) \quad (15)$$

where,

D_1, D_2 : the diffusivities in two phases,

V_1, V_2 : the volumetric fractions of the two phases,

$V_1 = 1 - V, V_2 = V,$

C_1, C_2 : the mass concentrations in the different zones,

$k = C_1/C_2$, the distribution of substances between the phases,

$\zeta = D_1/D_2$,

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

In EMT theory, the neighborhood region in the multiphase materials is assumed to be a uniform medium. This means that there should exist no correlation between different regions [21]. Diffusivity of cement paste was calculated from multifunctional model described in Sections 2.3 and 2.4, depending hydration stage of cement. The CO₂ diffusivity of aggregate was regarded as a constant to be 1×10^{-11} cm²/s [22].

2.6. Porosity Reduction Due to Carbonation

Carbonation of concrete greatly affects changes of pore structure system, which is inevitably connected to the rate of CO₂ diffusion through carbonated concrete. The change of pore structure system in concrete due to carbonation was limited to OPC concrete, in this study. Papadakis et al. proposed the following equation, based on the ratio of the volume of Ca(OH)₂ and CSH in concrete before carbonation to calcium carbonate after carbonation [23]:

$$V_c = V_p - \Delta V_c \quad (16)$$

where,

V_c : porosity of concrete after carbonation,

V_p : porosity of concrete before carbonation.

Decreased porosity due to carbonation (ΔV_c) is approximately equal to:

$$\Delta V_c = [\text{Ca(OH)}_2] \Delta \bar{V}_{CH} + [\text{CSH}] \Delta \bar{V}_{CSH} \quad (17)$$

in which, $\Delta \bar{V}_{CH}$ and $\Delta \bar{V}_{CSH}$ are equivalent to 3.85×10^{-6} m³/mol, 15.39×10^{-6} m³/mol, respectively. Although the concrete is carbonated, the pores of the aggregate remain the same and the pores of the cement paste change. Therefore, changed pores, calculated by Equation (16), was reinputted into Equation (5) to characterize the pore system of carbonated cement paste.

Based on the above analysis, the CO₂ diffusivity of concrete before and after carbonation was calculated, and the mixing conditions of concrete used in the calculation are shown in Table 1.

Table 1. Mixing condition of concrete used for calculation.

w/c	Unit Weight (kg/m ³)			
	Water	Cement	Sand	Gravel
0.45	185	411	706	1001
0.50	185	370	720	1021
0.55	185	336	732	1038

3. Results and Discussion

3.1. CO₂ Diffusivity of Concrete before Carbonation

Figure 5 represents apparent and effective CO₂ diffusivity of noncarbonated concrete with time and the difference means the effect of moisture content on CO₂ diffusivity. Three points should be discussed. Firstly, for concrete with a high w/c ratio, the diffusivity was high, and the difference between apparent diffusivity and effective diffusivity was also large. This is coincided with experiment study of Nokken et al. [24]. This would be because high degree of cement hydration and high densification due to microstructure development with elapsed time for cement paste with a high w/c ratio. Secondly, all concrete showed that the CO₂ diffusivity decreased significantly until 28 days because the microstructural densification of the concrete is greatly developed until 28 days. The trend continued because of the ongoing reaction of cement hydration. The trend of the reduction lasted even at long term; however, the reduction rate has become modest. Thirdly, the effective CO₂ diffusivity was considerably smaller than the apparent diffusivity. It can be seen that pore closing due to moisture has great influence on the CO₂ diffusivity. The work has good agreement with Yoon’s work that carbonation rate of concrete exposed to the outdoor environment was greatly decreased due to raining [25].

The CO₂ diffusivity is a material parameter that directly reflects the carbonation rate. If concrete is exposed to high CO₂ concentrations at early ages, carbonation can threaten concrete significantly. Therefore, extending the curing period could be a good solution in controlling the carbonation rate effectively.

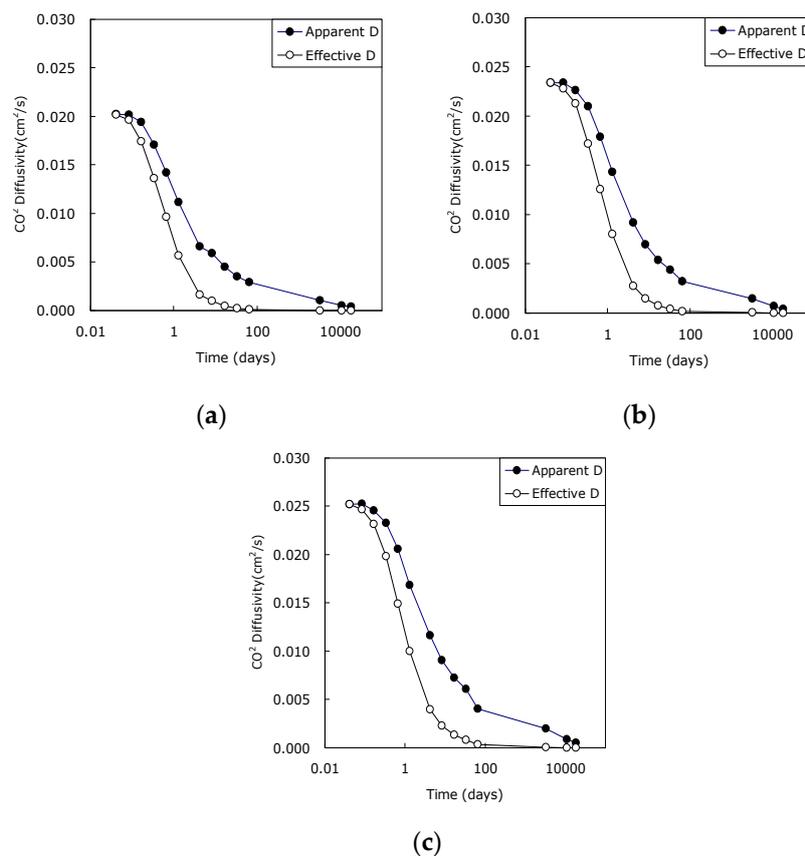


Figure 5. Apparent and effective CO₂ diffusivity of noncarbonated concrete. (a) w/c 0.45; (b) w/c 0.50; (c) w/c 0.55.

Figure 6 illustrates the ratio of the effective diffusivity and the apparent diffusivity of concrete with w/c ratio. The apparent diffusivity decreases with time because of only development of microstructure of cement paste, while the effective diffusivity decreases with time because of remained amount of pore water after consumption due to cement hydration as well as the microstructural development. For this reason, the difference between two diffusivities was not significant at the beginning of age; however, the difference was obvious with elapsed time. The ratio had decreased significantly to the level of 0.1 to 0.2 after 28 days. At early ages, the difference between two diffusivities was not high because cement was not sufficiently unhydrated and pore was highly filled with water. However, the difference between two diffusivities was clearly noticed with elapsed time because water was continuously consumed by the hydration reaction of cement as it became hydrated. Therefore, it is very important to consider water content in estimating gaseous diffusivity of cementitious materials.

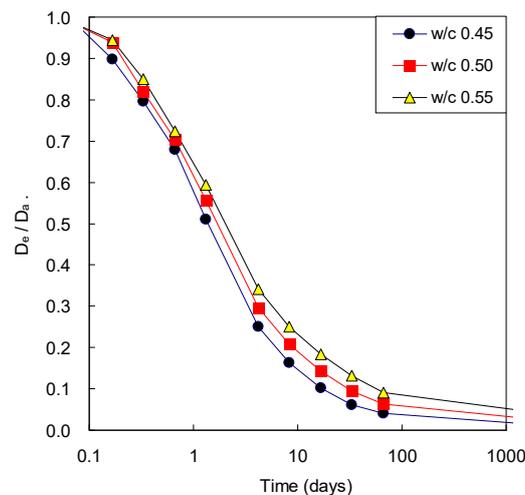


Figure 6. Comparison of effective CO₂ diffusivity of concrete (D_e) and apparent CO₂ diffusivity (D_a) before carbonation.

3.2. CO₂ Diffusivity of Concrete after Carbonation

Figure 7 shows the result of estimating CO₂ diffusivity of carbonated concrete with w/c ratio. The result reflected the reduction of pore due to carbonation. Among the four main functions of Equation (2), (a) CO₂ diffusivity in bulk fluid is constant because it has nothing to do with cementitious material. However, (b) pore structural characterization; (c) tortuosity of streamline, and (d) disturbed effect are influenced by carbonation. That is, the carbonation of concrete can make the flow characteristics of the fluid more complicated by reducing the pore system of the concrete. In particular, the CO₂ diffusivity of early carbonated concrete decreased significantly. However, carbonation led to the reduction of CO₂ diffusivity of concrete regardless of age, and this tendency was obvious for all concrete.

Saeki et al. suggested that chloride diffusivity of OPC concrete was significantly decreased after carbonation, while blended concrete showed different results depended on admixture type or the replacement ratio [26]. That is, chloride diffusivity of concrete with fly ash decreased, while that of concrete with granulated blast furnace slag increased. As Ca(OH)₂ is transferred to CaCO₃ due to carbonation, the microstructure characteristics of the concrete is bound to change because of the difference in molar volumetric expansion of the two materials [27]. However, this is not the case for all concrete and pore of carbonated concrete with blast furnace slag rather increased [28].

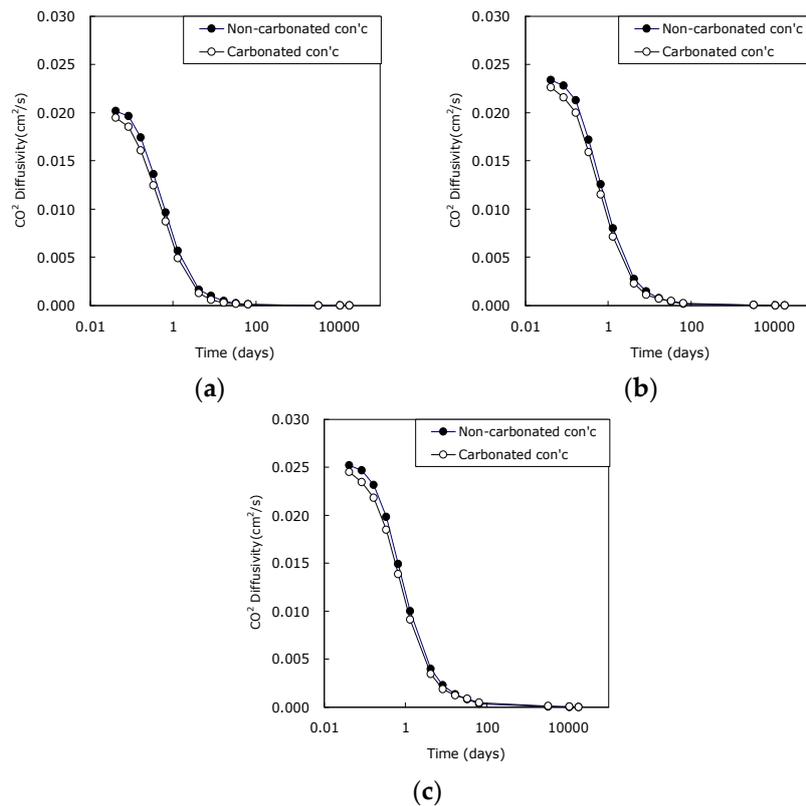


Figure 7. Effect of carbonation on CO₂ effective diffusivity. (a) w/c 0.45; (b) w/c 0.50; (c) w/c 0.55.

Figure 8 illustrates the difference between effective CO₂ diffusivity and apparent diffusivity of concrete after carbonation. Like the comparative ratio in Figure 5, the ratio of carbonated concrete showed a similar trend.

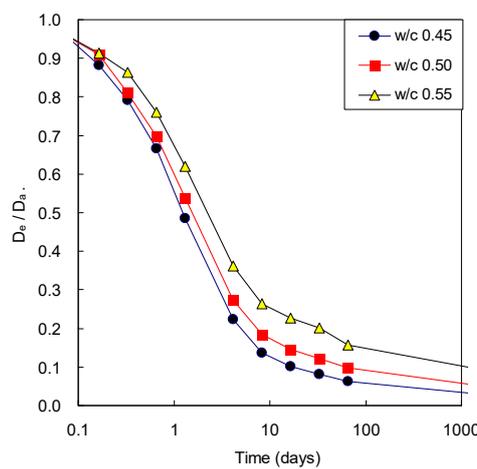


Figure 8. Comparison of effective CO₂ diffusivity of concrete (D_e) and apparent CO₂ diffusivity (D_a) after carbonation.

Figure 9 shows the result of comparing the diffusivity concrete before and after carbonation. The ratio of the two diffusivities decreased as time passed. and the width of the w/c ratio decreased with elapsed time. In concrete with a high w/c ratio, the trend of decreasing the diffusivity due to carbonation with time was pronounced. Carbonation led to reducing the effective diffusivity of concrete to the level of 47~69%. This reduction ratio tended to decrease as w/c ratio of concrete was low and time elapsed.

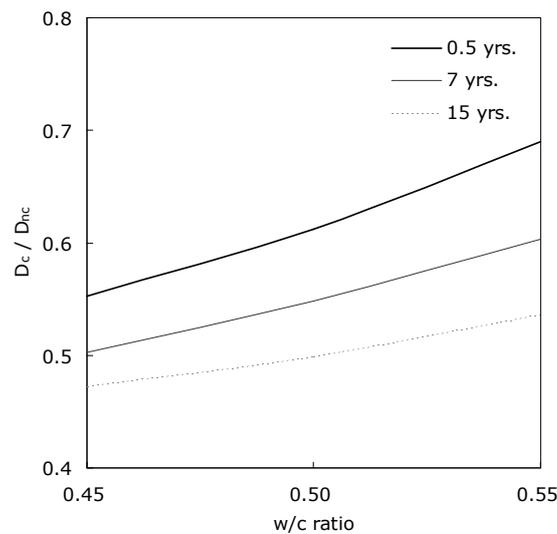


Figure 9. Effective CO₂ diffusivity (D_c) of carbonated concrete vs. effective CO₂ diffusivity (D_{nc}) before carbonation.

Based on all results above, this study is believed to be useful in expressing the CO₂ diffusivity as a function of the mixing conditions of concrete and degree of cement hydration. As a material parameter plays a decisive role in the accuracy of durability design system for concrete structures, CO₂ diffusivity with time is very important to calculate the service life of the concrete in detail. This work will be combined with the system in the future.

3.3. Comparison with Previous Research

The rate of gas penetration depends largely on the saturation of concrete. The rate of gas penetration decreased if concrete is more than 50% RH [17]. The diffusivity was constant if concrete is exposed to condition with less than 60% RH. That is, the diffusivity decreased significantly when RH exceeded 60% [16]. The result was similar to the experiment of Martin et al. [29]. They studied the CO₂ diffusivity of porous media, not concrete, and the diffusivity greatly decreased as RH exceeded around 55%. The apparent and the effective CO₂ diffusivity of concrete cured for 28 days was calculated to be in the range of 3.5×10^{-3} to 6.1×10^{-3} cm²/s, 2.1×10^{-4} to 8.3×10^{-4} cm²/s, respectively. In particular, the effective diffusivity of carbonated concrete matched with the limit suggested by CEB 1990 Model Code [30].

In this study, the diffusivity of concrete was estimated from the individual diffusivities of cement and aggregate. The effect of Interfacial Transition Zone (ITZ) at aggregate surface on gas diffusion was not considered. Although the effect of ITZ on the durability of concrete is well known, research on the effect of the CO₂ diffusivity is rare. In the future, it is necessary to study the CO₂ diffusivity of concrete with three phases, cement paste, aggregate, and ITZ and the influence of carbonation on the porosity of ITZ.

4. Conclusions

CO₂ diffusivity is a decisive material parameter for estimating a carbonation rate of concrete and quantifying durability performance of infrastructure. A comprehensive model with multifunctional factors such as diffusivity bulk fluid, pore structural characteristics, streamline of tortuosity in the pore system, hindrance effect, and volumetric contribution of cement paste and aggregate, was modified to estimate the diffusivity. Apparent and effective CO₂ diffusivities were suggested in terms of the effect of pore water on diffusivity. Because CO₂ diffusivity is a material parameter in the area from surface concrete to carbonation depth, the CO₂ diffusivity of concrete was calculated after carbonation.

(1) For concrete before carbonation, CO₂ diffusivity did not have a constant value, and it continuously decreased with the degree of cement hydration. The trend also maintained a clear trend depending on w/c ratio of concrete. Above all, the trend of decreasing CO₂ diffusivity was more pronounced until 28 days. The reduction rate gradually became more modest over time. The decreasing trend of the diffusivity of concrete with w/c ratio over time also showed the same. The difference between apparent and effective diffusivity was not significant at beginning of age, however, the difference was obvious with elapsed time.

(2) As a result of comparing the CO₂ diffusivity of carbonated concrete and noncarbonated concrete, carbonation significantly reduced CO₂ diffusivity at the early age. Since carbonation of concrete greatly reduced the pore structural system, it resulted in a significant reduction in the CO₂ diffusivity to the level of 47~69% compared to that of noncarbonated concrete. However, this reduction ratio showed a trend of decreasing over time as well.

Author Contributions: I.-S.Y. conceived and designed outline of this study; I.-S.Y. performed modeling; I.-S.Y. and C.-H.C. analyzed the outcome; I.-S.Y. and C.-H.C. wrote the paper. All authors have read and agreed to the published version of the manuscript.

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Conflicts of Interest: The authors declare no conflict of interest.

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