

論文 Numerical Simulation on Migration of Oxygen and Carbon Dioxide in Concrete

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ABSTRACT : This research was motivated to propose a simulation model for properly reflecting the migration behavior of oxygen and carbon dioxide in concrete. By inputting mixing proportion, atmospheric conditions and integrating with the assumed porosity function, the concentration of oxygen and carbon dioxide in concrete can be calculated. Using the model to correlate the migration behavior of oxygen and carbon dioxide as well as the model to correlate them with the water vapor diffusion process, the characteristics of the migration of O₂ and CO₂ in concrete could be numerically simulated according to the model proposed in this research.

KEYWORDS : Knudsen Diffusion, Porosity, Microstructure, Moisture Diffusion, Gas Diffusion

1. INTRODUCTION

Among the researches about the durability of concrete, the problems on mass transport in concrete causing deterioration of concrete has aroused attention of many researchers. The general approach for dealing with the mechanisms of mass transport (e.g. migration of chloride, water as well as gaseous components) is to regard them as diffusion process, which can be formulated by diffusion theory. As a consequence, how to find out the reliable diffusivity of mass in concrete has been under experimental and theoretical development. Such kind of effort for the previous development can be significantly reflected on the work on the migration of chloride and water while the work on the migration of gaseous components seems to be insufficient. The reasons (ref. to. [1]) can be often enumerated as 1) the difficulty in establishing a trustworthy experiment for measuring the effective diffusivity of gaseous components, especially with the consideration of the existence of moisture or 2) the ambiguity in the theoretical approach for diffusion process of gaseous components in concrete, which is involved in the real-time quantitative description on the porosity and tortuosity, and so on. On the other hand, the researches on the gas diffusion through porous solid have been under investigation for years. Based on the relationship between the mean free path (λ) of the gas molecule and the dimension of pores (d), the gas diffusion through porous solid has been categorized into three regimes as 1) Knudsen diffusion if $\lambda > d$; 2) normal diffusion if $d \geq 10\lambda$ and 3) transition diffusion if $\lambda \leq d < 10\lambda$. It is generally believed that the effective diffusivity of gases in concrete can be a combination of the diffusivity of each regime, as expressed in Eq.(8) in [1].

In this research, the method to find out the time-dependent migration of gases in concrete was motivated from the above observation on the understanding for gas diffusion through porous solid. The proposed method belongs not to a macro-level approach (i.e. to avoid using the effective diffusivity as it is generally applied in the Fick's law), but to a micro-level approach which is to correlate the migration behavior of gases with the vapor-phase water diffusion process based on the micropores. By using this method, with the consideration on the time-dependent variation of the pore structure, the characteristics of the migration of gases in concrete such as O₂ and CO₂ could be numerically simulated.

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2. MICROSTRUCTURE RELATING MOISTURE MIGRATION IN CONCRETE

Based on the researches of Shimomura and Maekawa [2], the microstructure mechanism of moisture migration in concrete can be successfully simulated based on the integration of the models on 1) the function to describe pore structure in the representative element volume; 2) the thermodynamic equilibrium relation between liquid-phase and vapor-phase water and 3) the suction of water due to existence of capillary force. Their models make it possible that the real-time relationship between pore structure and moisture can be quantitatively calculated, which is impossible in the experimental approach. However, the algorithms of their models for deciding the shape factors of pore distribution function and the diffusivity of liquid-phase (or vapor-phase) water lack sufficient experimental verification. More efforts are expected to rationalize those parameters used in their models. In fact, up to now, there still exists little evidence to indicate if the mechanism of moisture movement in concrete is dominated by liquid-phase flow or vapor-phase flow. Nevertheless, in this research, the vapor migration is regarded as the dominant mechanism for moisture movement in concrete. For assuring the reliability of simulation of vapor migration in concrete, in this research, the verified model reported in [3], which considers the effect of water cement ratio and relative humidity on the diffusion coefficient of vapor in concrete (or mortar) as well as empirically establishes the relationship between relative humidity and water content, was utilized to simulate the vapor migration in concrete. Then, by integrating the microstructure mechanism described in [2], the real-time porosity at wet state (i.e. volume of gas-phase water per unit volume, denoted as $V_{G,Unit} : \text{cm}^3/\text{cm}^3$) and the volume of liquid-phase water per unit volume ($V_{L,Unit} : \text{cm}^3/\text{cm}^3$) can be traced according to the distribution of moisture by vapor migration simulation. For the initial condition of numerical simulation, all the elements are assumed to be saturated in the beginning of the simulation. As for the boundary conditions, the humidity in the surface element is assumed to be the same as the atmospheric humidity.

3. MODEL RELATING VAPOR DIFFUSION TO GAS DIFFUSION IN CONCRETE

It is well known that, the researches on gas diffusion through porous solid have been developed for decades and the achievements of these researches have also been highly evaluated. However, how about the possible application of these theories on the problem of gas diffusion in concrete? According to the understanding of this problem, the answer may be very disappointing due to the existence of the moisture. Generally speaking, porosity and tortuosity of pore structure in the porous solid at dry state can be reasonably represented by the appropriate modeling based on the characteristics of the pore structure. Then, by the gas diffusion theory developed for porous solid, the problem of gas diffusion through porous solid can be solved. However, in concrete, due to the existence of moisture, the transport process of which may include diffusion, evaporation or condensation, will influence the free space for the transport of gaseous component. Therefore, the model to describe the pore structure at dry state is obviously inappropriate for representing the pore structure of concrete at wet state. Fortunately, as introduced in the preceding section, the microstructure mechanism of moisture migration in concrete developed as in [2] is thought to be sufficient for this task to simulate the real-time variation of pore structure even with the existence of moisture.

Besides, by observing the drying process of concrete, it is generally recognized that 1) there is no air in the concrete due to the initial saturation; 2) along with the drying process, the air will enter the concrete from the surface being-dried and 3) the more the moisture releases through the surface, the more air enters through the surface. Such phenomena is generally regarded to occur at constant pressure and should be considered as the dominant mechanism of gas diffusion in concrete. By this observation and assuming air and vapor as ideal gases, the gas diffusion in concrete can be simply stated as "the influx of air (J_{Air} , Unit : $\text{cm}^3/(\text{cm}^2 \cdot \text{day})$) in the free space of pore is equal to the outflux of vapor (J_{Vapor}) in the free space of pore". As schematized in **Fig.1**, the vapor gain due to evaporation and loss due to condensation is also needed to be considered, which is implicitly included in the calculated outflux of vapor according to the method used for simulation of vapor migration in concrete. In order to correctly obtain the influx of air in the free space of pore, the following equation

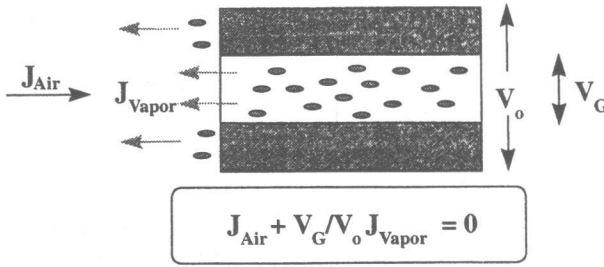


Fig.1 Model on Gas Diffusion in Concrete due to Water Vapor Diffusion

process for gas diffusion through porous solid, the effective diffusivity of the bulk porous material may be written as follows [1] :

$$D_e = \epsilon_1 D_k + \epsilon_2 D_t + \epsilon_3 D_n \quad (2)$$

where $D_k = 2/3 \langle V \rangle r$: Knudsen Diffusivity; $D_n = 1/3 \langle V \rangle \lambda$: Normal Diffusivity; $D_t = D_n / (1 + \lambda / 2r)$: Transition Diffusivity; ϵ_1, ϵ_2 and ϵ_3 are the volume fraction of the three regimes; r : the radius of the pore; $\langle V \rangle = (8RT / \pi M)^{0.5}$: the average molecular speed of the gas molecule; $\lambda = RT / (\pi N d^2 P)$: the mean free path of the gas molecule; R : ideal gas constant; T : absolute temperature ; M : molar mass of gas; N : Avogadro number and P : pressure. To find out the flux of each gaseous component in this research, the expression of effective diffusivity in Eq.(2) stimulated us to propose one model, considering the gas diffusion process, by assuming that the flux of each gaseous component should be the same as the summation of the fluxes occurring in different regime, which can be formulated as

$$\langle J_{Air} \rangle_i = C_{k,i} \langle V_{k,i} \rangle + C_{t,i} \langle V_{t,i} \rangle + C_{n,i} \langle V_{n,i} \rangle \quad (3)$$

where, i : i^{th} gaseous component; $C_{k,i}, C_{t,i}$ and $C_{n,i}$: volume fraction of i^{th} gaseous component in the three regimes, which should satisfy $C_{k,i} + C_{t,i} + C_{n,i} = C_i$ (i.e. the concentration of i^{th} gaseous component) while $\langle V_{k,i} \rangle, \langle V_{t,i} \rangle$ and $\langle V_{n,i} \rangle$ are the average molecular speed of i^{th} gaseous component in the three regime. The ratio for $\langle V_{k,i} \rangle, \langle V_{t,i} \rangle$ and $\langle V_{n,i} \rangle$ can be calculated by the known diffusivity for three regimes as

$$\langle V_{k,i} \rangle : \langle V_{t,i} \rangle : \langle V_{n,i} \rangle = 1 : \lambda / (\lambda + 2r) : \lambda / 2r \quad (4)$$

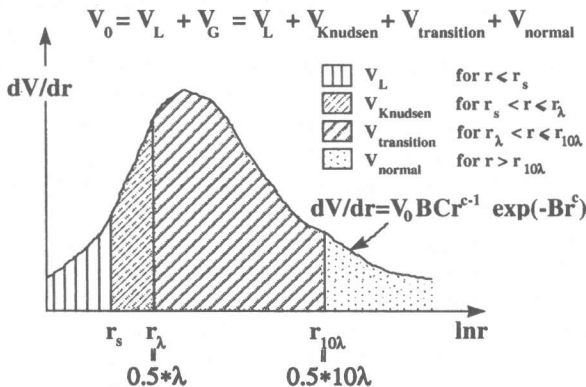


Fig.2 Tridispersed Model of Gas Diffusion in Concrete

And $\langle V_k \rangle$ is considered to be the same as $\langle V \rangle$. In order to decide the value of $C_{k,i}, C_{t,i}$ and $C_{n,i}$, the assumed density distribution function of pore size used in [2] was applied. As illustrated in Fig.2, the value of $C_{k,i}, C_{t,i}$ and $C_{n,i}$ are defined respectively as

$$C_{k,i} = V_{knudsen} / V_G \quad (5.a)$$

$$C_{n,i} = V_{normal} / V_G \quad (5.b)$$

$$C_{t,i} = V_{transition} / V_G \quad (5.c)$$

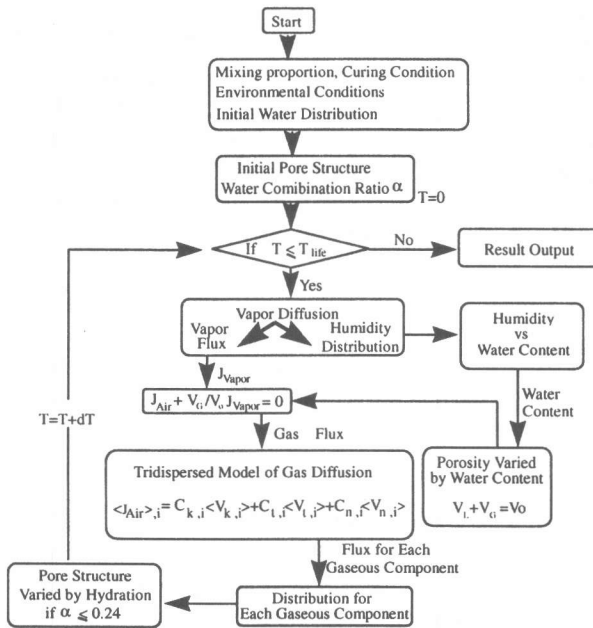


Fig.3 Computational Flow for Gas Diffusion in Concrete

In addition, with the assumption that the movement of each gaseous components is independent to one another, the summation of the influx of all the gaseous components is equal to the influx of the air, i.e.

$$\langle J_{Air} \rangle = \text{Sum of } \langle J_{Air} \rangle_i \text{ for } i=1..n \quad (6)$$

where n : number of gaseous components. By substituting Eq.(3)~(5) into Eq.(6), the influx of each gaseous component can be calculated explicitly. Then, as shown in Fig.3, after the influx of each gaseous component is available, the distribution of each gaseous component in concrete can be further calculated. Besides the features of this method explained in the preceding section, the variation of pore structure due to the simultaneous hydration reaction is also considered in this method. Because the relationship between hydration rate and the shape factor on the density distribution function of pore size has been given in [2], no detailed description is given here. However, as indicated by Mindess

and Young [4], the maximum combined water due to hydration is generally not be greater than 0.24g/per gram cement. Thus, if the water combination ratio is greater than 0.24, there will be no need to vary the shape factors and pore volume. Then, the above algorithm of this method will be carried out in an iterative way until the service period is reached.

5. RESULTS FOR SIMULATION ON NATURALLY EXPOSED CONCRETE

After the features of this proposed method are briefly explained, the applicability of this method for simulating the gas diffusion process in concrete is necessary to be verified. For this purpose, one most common example is the problem of gas diffusion in naturally exposed concrete. As known, there are many types of gaseous components in atmosphere. However, by investigating the volume fraction of those gaseous components, it is well understood that about 99% per unit volume of atmospheric gases is occupied by nitrogen (N_2 , about 78.084%) and oxygen (O_2 , about 20.946%) while less than 1% is occupied by the other gaseous components. Among those gaseous components occupying less than 1% per unit volume of atmospheric gases, the volume fraction of carbon dioxide (CO_2), the existence of which is directly related to the problem of carbonation of concrete, only takes around 0.034%. Due to the assumption that all the elements are initially saturated, the initial concentration for all the gaseous components is taken as 0 (cm^3/cm^3). The gas concentration in surface element during calculation is assumed to be the product of the concentration of the atmospheric gases and the wet-state porosity (V_G) of the surface element. Though carbonation often happens during CO_2 diffusion in concrete, the simulation of carbonation is not considered in the algorithm of this proposed method for simplicity. The dimension of the specimen for simulation is 10 x 10 x 100 mm with 5 sealed surface and 1 unsealed exposed surface. The temperature for the exposure remains at 20°C while the relative humidity of atmosphere is selected to be 40, 50 and 60% to understand the influence of the relative humidity on diffusion of O_2 and CO_2 in concrete. The time interval for calculation is taken as 1 day.

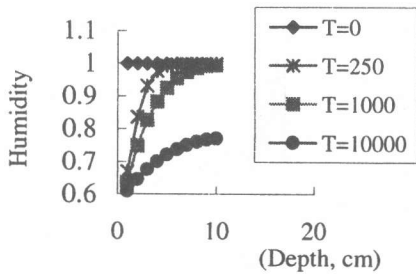


Fig.4 Humidity along specimen depth

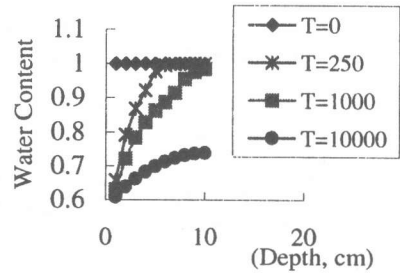


Fig.5 Water content along specimen depth

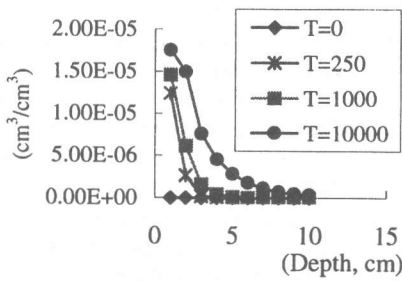


Fig.6 Distribution of O₂ along specimen depth (RH=60%)

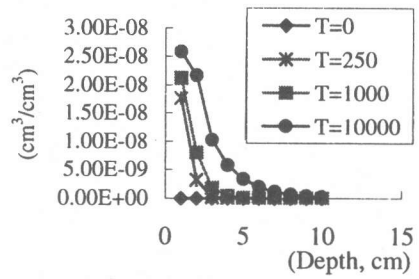


Fig.7 Distribution of CO₂ along specimen depth (RH=60%)

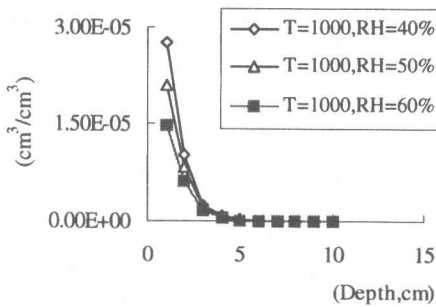


Fig.8 Influence of humidity on distribution of O₂

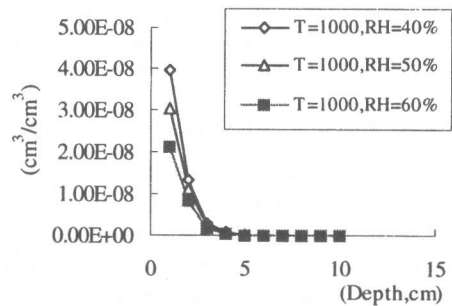


Fig.9 Influence of humidity on distribution of CO₂

Before showing the simulation result of gas diffusion, the simulation result on the variation of humidity and water content along specimen at RH = 60% , with different exposure time T, are given in **Fig.4** and **5** individually. Both of them depict the release of migration from concrete along specimen depth reasonably. Besides, by observing the variation of humidity (or water content) at the surface layer of the specimen (i.e. X (depth) = 1cm), the amount of release tends to decrease as the exposure time increases, which can be understood as the equilibrium state between external and internal moisture exchange is gradually achieved. Then, under the same environmental conditions, **Fig.6** illustrates the distribution of O₂ along with the specimen depth while **Fig.7** gives the case on CO₂. As can be observed at X = 1, the amount of O₂ (or CO₂) increases with the time. Yet, the amount of increase is gradually close to zero when the exposure time increases. Next , the influence of humidity

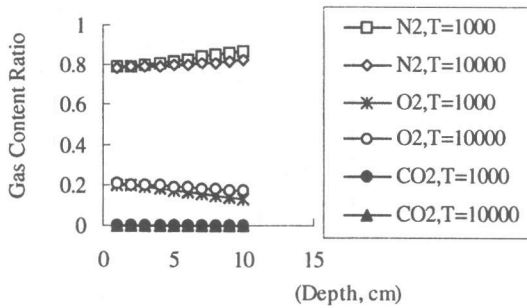


Fig. 10 Gas content ratio distribution

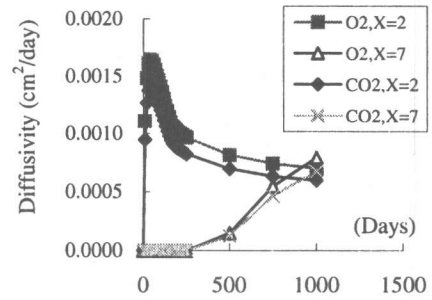


Fig. 11 Comparison on diffusivity of O_2 and CO_2 at different depth

on distribution of O_2 and CO_2 along specimen depth (at $T = 1000$ days) are shown in **Fig.8** and **9** respectively. It is obviously observed that the diffusion of O_2 (or CO_2) will gradually decrease if the atmospheric humidity increases. This numerical result corresponds to the observation on the case of the actual exposed concrete. In addition, with the increase of time, the gas content ratio distribution along specimen depth should be close to the constant ratio as in the atmosphere. This feature is also correctly simulated by this method, as indicated in **Fig.10**. By defining the diffusivity of the element as the product of the flux of the element and the reciprocal of the concentration gradient of the element, the variation of diffusivity of O_2 and CO_2 are given in **Fig.11** at $X=2$ and 7 . The reason for the diffusivity of O_2 and CO_2 variation with the exposure time can be explained as 1) at the initial stage of drying, the outflux of moisture at the surface layer of concrete is large while that of the inner part of concrete is close to zero due to saturation. As a result, the influx of atmospheric gas at the surface layer of concrete is large at the initial stage of drying and close to zero in the inner part of concrete; 2) with the gradual achievement of equilibrium state between external and internal moisture exchange, the outflux of moisture tends to be zero. Thus, the influx of gas is also close to zero. That is to say, the distribution of gas also has the tendency to achieve the state of equilibrium with the increase of time. These tendencies can be obviously observed in **Fig.11**.

6. CONCLUDING REMARKS

By the above discussion and the examples illustrated in this research, the characteristics of this method can be concluded as follows : 1) By introducing the model of gas diffusion in concrete suggested in this research, there seems an alternative to simulate the gas diffusion in concrete without the need to obtain effective diffusivity of gas in concrete and 2) Through the illustrated examples, not only the applicability of this model in simulating the gas diffusion in concrete was verified, but also the influence of relative humidity on the gas distribution as well as the influence due to the variation of microstructure in concrete on the diffusivity could be qualitatively verified in this research.

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