A multi-phase model for VOC emission from single-layer dry building materials

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Abstract−A multi-phase model for the emission of VOC from dry building materials is developed. Dry building materials are viewed as porous media. A general adsorption isotherm is used to construct the concentration equation in the porous media. The boundary conditions at the material-air interface are presented for both CFD model and one compartment model. With the use of Henry's law for the adsorption isotherm, an analytical solution is obtained and further is validated with the comparison of the experiment performed by Yang et al. [1], yielding a relatively good agreement. The effects of the model parameters on the emission are investigated in detail. Increasing the effective diffusion coefficient and the partition coefficient tends to promote the emission and increase the peak value of the concentration in the air. The effect of the porosity depends on the degree of the dependence of the effective diffusion coefficient on the porosity. When a weak dependence exists, the increase of the porosity tends to suppress the emission and decrease the peak value of the concentration in the air. However, when a strong dependence exists, the increase of the porosity tends to promote the emission and increase the peak value of the concentration in the air.

Key words: VOC Emission, Multi-phase Model, Porosity, Adsorption Isotherm

INTRODUCTION

Indoor air quality has a significant influence on human health. Many kinds of substances can lead to an indoor air quality problem, such as carbon dioxide, dust and volatile organic compounds (VOC). VOC is the most important pollutant in an indoor environment, possibly causing sick building syndrome, multiple chemical sensitivities, etc. In an attempt to reduce the concentration of VOC in an indoor environment, catalytic combustion and catalytic photo-reaction can be implemented [2,3]. The study showed that more than 60% indoor VOC was emitted from building materials. These building materials, which include carpeting, wallpaper, gypsum board, paint and glue, are categorized into wet materials and dry materials [4]. The emission of VOC from wet materials occurs mainly in the initial period and decays very fast [5,6]. However, the emission of VOC from dry building materials takes effect in a very long time [7].

Basically, dry building materials are porous, and many pores exist within dry building materials. VOCs exist in both the gas phase and the adsorbed phase. The transport of VOC within dry building materials usually concerns molecular diffusion, Knudsen diffusion and diffusion within solid matrix. These factors are so complicated that it is impractical to describe the transport process at a microscopic level. Therefore, VOC transport within dry materials is usually described at the macroscopic level. Up to now, two approaches have been widely used to study VOC emission from dry building materials. One approach views dry building materials as a virtual single-phase medium [1,7-11]. VOC is assumed to exist in this virtual single-phase medium. The model parameters are the diffusion coefficient of VOC, the initial concentration of VOC and the partition coefficient of VOC at the material-air interface. The other approach considers the porosity of dry building materials. VOC is assumed to exist in both the air phase and the adsorbed phase. Compared with the single-phase model, the multi-phase model needs an additional parameter, i.e., the porosity of dry building materials [12-16]. Both models have been widely used to study the emission of VOC from dry building materials. Haghighat et al. [17] discussed the relation of the model parameters between the single-phase model and the multi-phase model and the effect of the porosity on the emission of VOC. They concluded that VOC concentration in the air increases with the increase of the porosity of material. However, the adsorbed phase concentration in these multi-phase models was defined with respect to the volume of material instead of the volume of solid matrix. It means that the constants in the adsorption isotherm are not independent of the porosity. On the other hand, Haghighat et al. [17] only investigated the effect of the porosity on the emission of VOC from dry building materials under the case of the diffusion coefficient independent of the porosity. Note that this is the extreme case of the diffusion coefficient weakly depending on the porosity. The case of the diffusion coefficient strongly depending on the porosity has not been taken into account in the literature.

In this paper, a multi-phase model for the emission of VOC from dry building materials is presented and is validated through the experimental data obtained from literature. The effects of the model parameters are investigated in detail, especially the effect of the different dependences of the effective diffusion coefficient on the porosity.

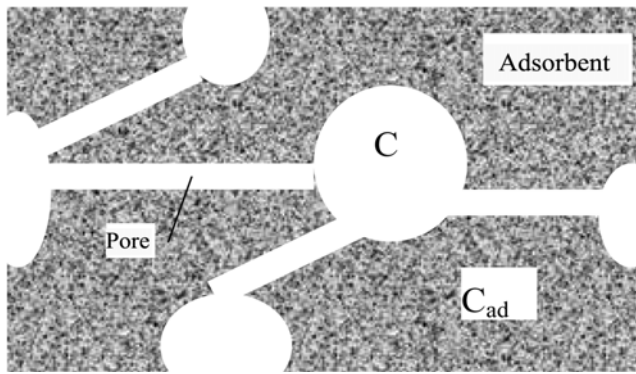†To whom correspondence should be addressed.
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Fig. 1. Adsorption and diffusion in the porous material.

DEVELOPMENT AND SOLUTION
OF THE MULTI-PHASE MODEL

Dry building materials consist of solid matrix and many pores. To describe the characteristics of solid matrix, the porosity of material ε (m^3/m^3) should be introduced. Generally, the porosity is assumed to be a constant. Corresponding to the two phases of material, there also exist the gas phase concentration and the adsorbed phase concentration. These two concentrations are functions of time and spatial coordinates. The convection in the pores can be neglected since the porosity of dry building materials is usually small. However, the diffusion occurs not only in the pores but also in solid matrix. A tiny control volume is extracted as the object, shown in Fig. 1. Thus, applying the principle of mass conservation in this tiny control volume yields,

$$\varepsilon \frac{\partial C}{\partial t} + (1-\varepsilon)\frac{\partial C_{ad}}{\partial t} = (1-\varepsilon)D_s\frac{\partial^2 C_{ad}}{\partial y^2} + \varepsilon D_g\frac{\partial^2 C}{\partial y^2} \tag{1}$$

where C is the gas phase concentration (mass per unit volume of air), C_{ad} the adsorbed phase concentration (mass per unit volume of solid matrix), D_s the diffusion coefficient of VOC within solid matrix, D_g the diffusion coefficient of VOC in the pores, which contains the effect of the Knudsen diffusion and the molecular diffusion. The two terms of the right hand side of Eq. (11) describe the diffusion through solid matrix and the pores, respectively.

However, Eq. (11) incorporates too many factors and some simplification must be introduced to solve it. It is assumed that the gas phase concentration C always keeps equilibrium with the adsorbed phase concentration C_{ad}, which reads

$$C_{ad} = f(C) \tag{2}$$

where the function f is adsorption isotherm. Note this equilibrium exists not only between the pores and the adsorbed phase but also between the adsorbed phase and the room air adjacent to materials. On the other hand, the function f doesn't contain any effect of the porosity because the definition of C_{ad}. Eq. (11) can be rewritten as

$$k_e\frac{\partial C}{\partial t} = D_{eff}\frac{\partial^2 C}{\partial y^2} \tag{3}$$

with

$$k_e = \varepsilon + (1-\varepsilon)\frac{df(C)}{dC} \tag{4}$$

and

$$D_{eff} = (1-\varepsilon)D_s\frac{df(C)}{dC} + \varepsilon D_g \tag{5}$$

df(C)/dC was called specific mass by Deng and Kim [18]. When defining the specific mass of the gas phase being unity, k_e stands for the specific mass of the porous medium. Equation shows that k_e incorporates the effect of the porosity and the adsorption isotherm. Since df(C)/dC is generally greater than unity, the existence of the porosity tends to significantly reduce the specific mass of the porous medium.

D_{eff} is the effective diffusion coefficient of VOC within dry building materials. It incorporates all factors influencing the diffusion of VOC within dry materials: the diffusion coefficient within solid matrix, the diffusion coefficient within the pores, the porosity and adsorption isotherm. Although Eq. (35) offers a way to calculate the effective diffusion coefficient, it is seldom used because of the difficulty in determining the diffusion coefficients within solid matrix and the pores. An alternative is to regard the effective diffusion coefficient as a new parameter. Thus, it can be directly evaluated from the experimental data or by some empirical correlation instead of Eq. (55). In the experiment, the diffusion flux of VOC through the material and the air-phase concentration difference of VOC between the two sides of the material were measured [15]. Then, the true diffusion coefficient was computed according to Fick's Law, denoted by $D_{eff\text{-}test}$. Note that the measured diffusion flux incorporates the effects from both the diffusion within the adsorbed phase and the diffusion in the gas phase. The influence of adsorption isotherm was also taken into account because only the air-phase concentration was of concern. Therefore, $D_{eff\text{-}test}$ includes all influencing factors. The diffusion coefficient in the governing equation should be determined as follows:

$$D_{eff} = D_{eff\text{-}test} \tag{6}$$

Another approach is to use the Bruggman correlation accounting for the effect of the porosity [19]:

$$D_{eff} = \varepsilon^n D_a \tag{7}$$

where D_a is the diffusion coefficient of VOC in the air. Eq. (7) shows that the effective diffusion coefficient increases as the porosity increases.

The boundary condition at the material-air interface depends on the model solving the concentration in the air. When the CFD model is used to solve the concentration field in the air, Eq. (33) is subject to the following boundary condition at the material-air interface:

$$-D_a\frac{\partial C}{\partial y}\Big|_{y=\delta_+} = -D_{eff}\frac{\partial C}{\partial y}\Big|_{y=\delta_-} \tag{8}$$

$$C\big|_{y=\delta_+} = C\big|_{y=\delta_-} \tag{9}$$

When the one-compartment model is used to solve the concentration in the air, Eq. (33) is subject to the following boundary condition at the material-air interface:

$$-D_{eff}\frac{\partial C}{\partial y}\Big|_{y=\delta} = h(C\big|_{y=\delta} - C_a) \tag{10}$$

where h is the mass transfer coefficient through the air boundary layer, C_a the concentration of VOC in the chamber air, δ the thick-

ness of the material.

Given that the total mass of VOC within the dry building material and the volume of the material are m and V, respectively, the initial concentration of VOC should be calculated as follows:

$$(1-\varepsilon)f(C_0)+\varepsilon C_0 = \frac{m}{V} \tag{11}$$

Compared with the governing equations of the single-phase model [8], the following correlations can be concluded:

$$k_e = K_{ma} \tag{12}$$

$$D_{eff} = k_e D_m \tag{13}$$

$$C_0 = C_{m0}/k_e \tag{14}$$

VALIDATION OF THE MULTI-PHASE MODEL

The multi-phase model must be solved coupled with the transport of VOC in the air. Either the CFD model or one-compartment model can be used. For simplicity, the one compartment model is used, which assumes that the concentration in the air is uniform, i.e., total mixing. It means the mass balance of VOC in the chamber.

$$\frac{\partial C_a}{\partial y} = -LD_{eff}\frac{\partial C}{\partial y}\bigg|_{y=\delta} - NC_a \tag{15}$$

where L is loading factor of the material, N the air exchange rate.

Taking into account that the material is placed on the stainless steel, no mass flux goes through the bottom of the material:

$$\frac{\partial C}{\partial y}\bigg|_{y=0} = 0 \tag{16}$$

K_e in Eq. (33) should be determined by Eqs. (44) and (22). Henry's law is selected as the adsorption isotherm

$$C_{ad} = K_m C \tag{17}$$

where K_m is the partition coefficient.

Then, K_e is calculated as follows:

$$k_e = \varepsilon + (1-\varepsilon)K_m \tag{18}$$

The system of Eqs. (33), (10), (15) and (16) can be solved by Laplace transform. The solution process can be referred to Deng and Kim [20]. The solution is directly written here as follows:

$$C_a(t) = 2C_0 k_e \beta \sum_{n=1}^{\infty} \frac{q_n \sin q_n}{A_n} e^{-D_{eff}k_e^{-1}\delta^{-2}q_n^2 t} \tag{19}$$

with

$$A_n = [k_e\beta + (\alpha - q_n^2)k_e Bi_m^{-1} + 2]q_n^2 \cos q_n$$
$$+ q_n \sin q_n [k_e\beta + (\alpha - 3q_n^2)k_e Bi_m^{-1} + \alpha - q_n^2] \tag{20}$$

Table 1. Physical property of VOC

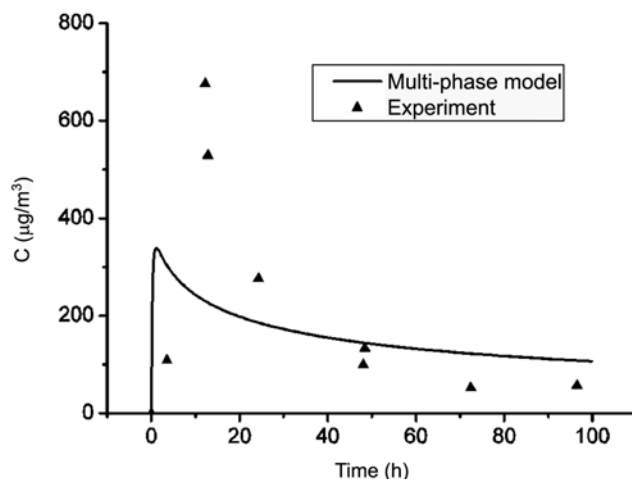|	D_{eff} (m^2 s^{-1})	C_0 (μg·m^{-3})	k_e
TVOC	2.52e-7	1.6e+4	3289
Hexanal	2.52e-7	3.5e+3	3289
α-pinene	6.72e-7	1.76e+3	5602

Fig. 2. Chamber concentration of α-pinene emitted from particle board with time.
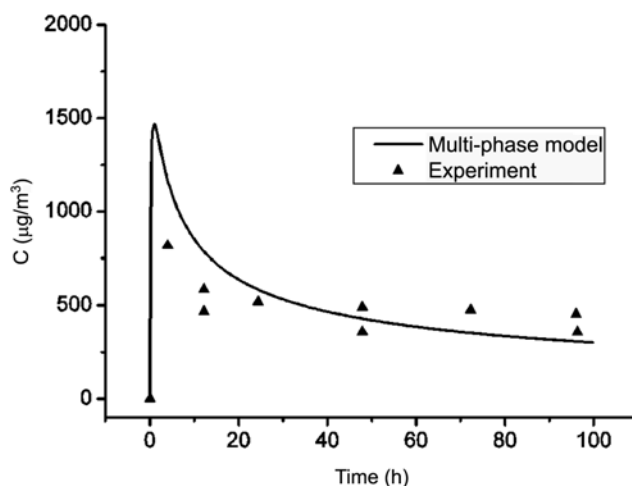

Fig. 3. Chamber concentration of hexanal emitted from particle board with time.
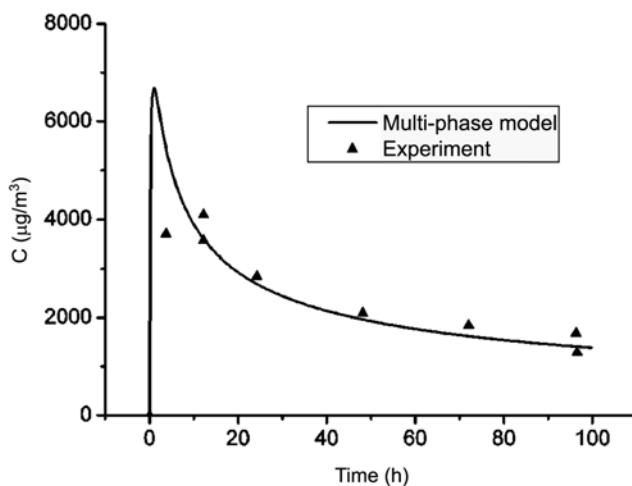

Fig. 4. Chamber concentration of TVOC emitted from particle board with time.

$$Bi_m = h\delta k_e / D_{eff} \quad \alpha = N\delta^2 k_e / D_{eff} \quad \beta = L\delta \tag{21}$$

$$q_n \tan q_n = \frac{\alpha - q_n^2}{k_e \beta + (\alpha - q_n^2) k_e Bi_m^{-1}} \tag{22}$$

The physical properties are listed in Table 1. Note that all these values are transformed from the data of Yang et al. [1] based on Eqs. (12)-(14). The computed concentrations of TVOC, hexanal and a-pinene in the air with the experimental data from Yang et al. [1] are depicted in Figs. 2-4. The computed results agree well with the experimental results except the initial data in Fig. 2. The same discrepancy was also observed by Yang et al. [1].

INFLUENCES OF THE MODEL PARAMETERS

In the following section, all environmental parameters, the surface area of the material and the thickness of the material are held.

The effect of the effective diffusion coefficient on the VOC emission is shown in Fig. 5. The emission of VOC is promoted as the effective diffusion coefficient increases. The peak value of the con-
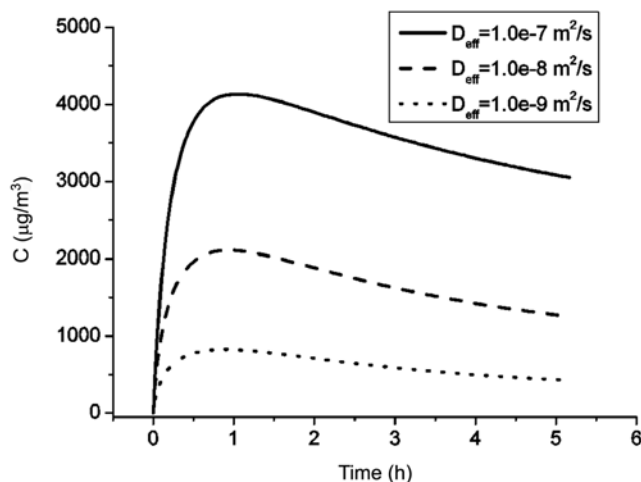
centration in the air tends to increase. This is because the diffusive flux through the material-air interface is proportional to the effective diffusion coefficient.

The effect of the partition coefficient on the VOC emission is shown in Fig. 6. The emission of VOC is promoted also as the partition coefficient increases. The peak value of the concentration in the air increases with the increase of the partition coefficient. The increase of the partition coefficient tends to increase the specific mass. The increase of the specific mass is two-fold: increasing the mass contained within the material and increasing the ability of the material to keep VOC. The former one tends to promote the emission, while the latter tends to suppress the emission. The increase of the peak value shows that the former dominates when the specific mass increases.

The effect of the porosity is very complicated. It not only affects the value of k_e but also has an influence on the effective diffusion coefficient. The effect of the porosity on the specific mass is determined by Eq. and the specific mass k_e decreases with the increase of the porosity. Since the initial concentration within the dry building material is kept a constant, the mass contained in the material decreases with the increase of the porosity. The effect of the porosity on the effective diffusion coefficient can be categorized into two classes: the weak dependence of D_{eff} on the porosity and the strong dependence of D_{eff} on the porosity. The former case implies that D_{eff} varies little when the porosity varies. The latter case means that D_{eff} increases much when the porosity increases. Two cases are selected as representative:

$$D_{eff} = 1.0 \times 10^{-7} \, m^2/s \tag{23}$$

$$D_{eff} = \varepsilon^{1.5} D_a \tag{24}$$

Note that Eq. (23) is an extreme case of the weak dependence.

The concentrations in the air for the case of weak dependence are shown in Figs. 7-9. The peak values of the concentration in the air increase as the porosity decreases. It also proves that the increase of the specific mass tends to increase the peak values. Note this conclusion is in accordance with the effect of the partition coefficient. Both the decrease of the porosity and the increase of the partition coefficient tend to increase the specific mass. Then, the peak value

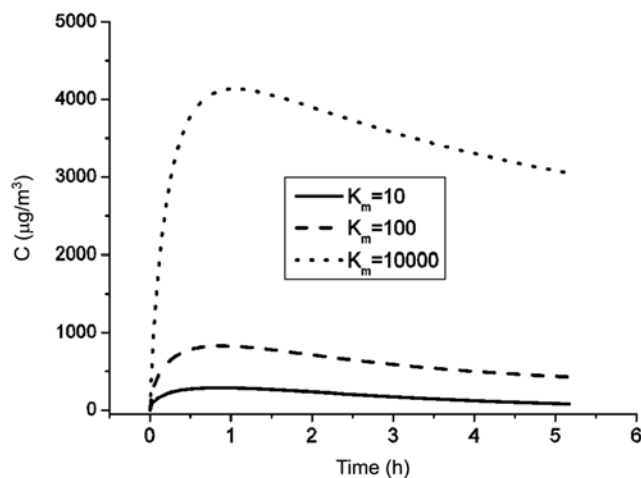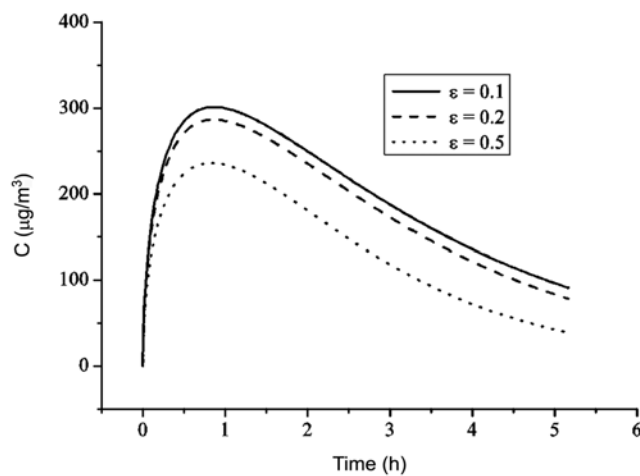**Fig. 5. Concentrations in the air with different effective diffusion coefficients (ε=0.2, K_m=10,000).**

Fig. 6. Concentrations in the air with different partition coefficients (ε=0.2, D_{eff}=1.0e-7 m²/s).

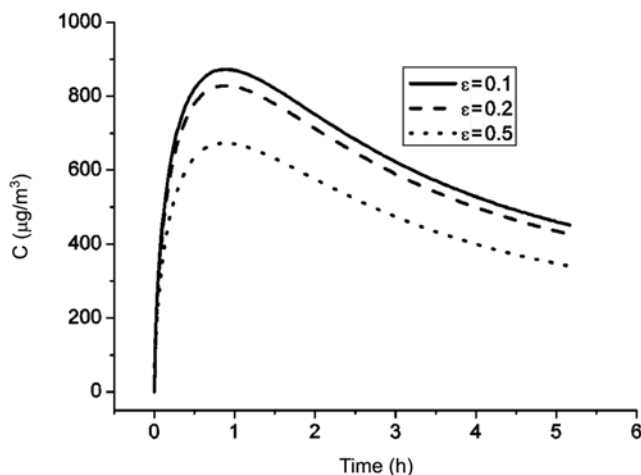**Fig. 7. Concentrations in the air with the effective diffusion coefficient being a constant (K_m=10).**

Fig. 8. Concentrations in the air with the effective diffusion coefficient being a constant (K_m=100).
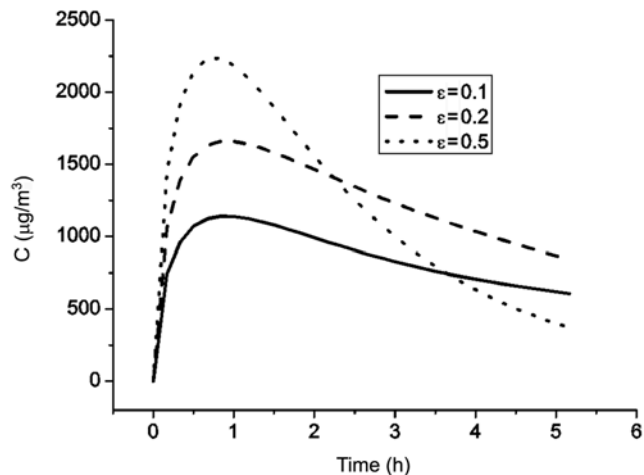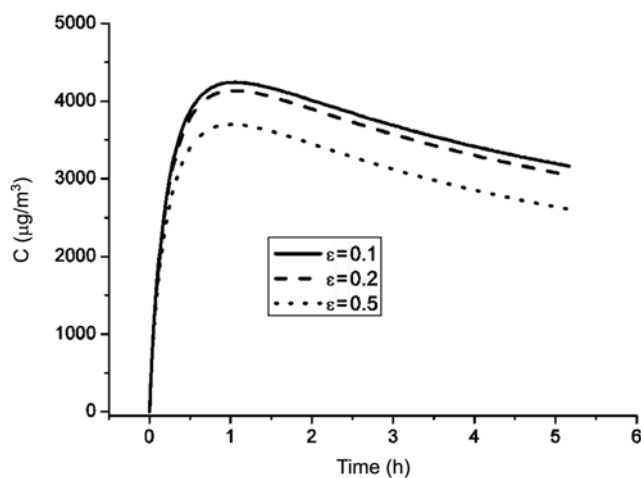

Fig. 9. Concentrations in the air with the effective diffusion coefficient being a constant (K_m=10,000).

Fig. 10. Concentrations in the air with the effective diffusion coefficient strongly depending on the porosity (K_m=10).
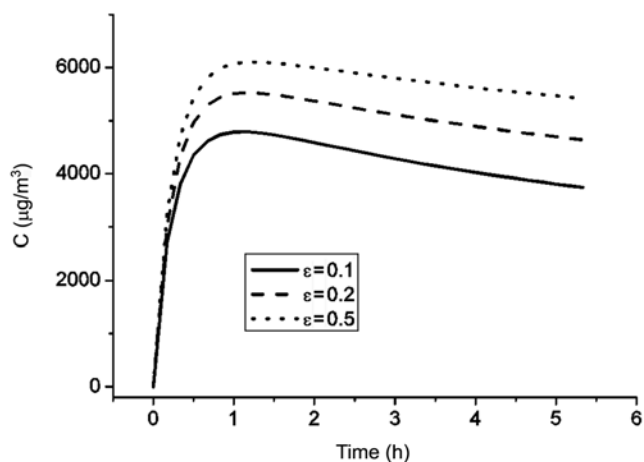

Fig. 11. Concentrations in the air with the effective diffusion coefficient strongly depending on the porosity (K_m=100).
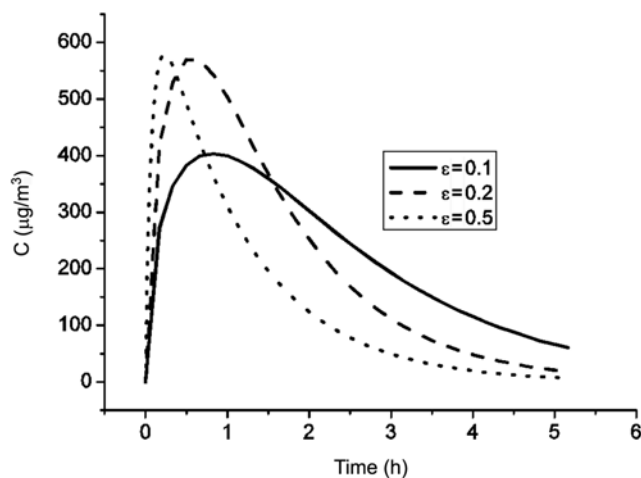

Fig. 12. Concentrations in the air with the effective diffusion coefficient strongly depending on the porosity (K_m=10,000).

must increase as the porosity decreases. On the other hand, the differences between the peak values increase with the increase of the partition coefficient. It shows that the effect of the porosity on the emission becomes stronger when the partition coefficient becomes much bigger. Since Eq. (23) is an extreme case of the weak dependence, it can be concluded that the above conclusion also applies to other weak dependences.

The concentrations in the air for the case of strong dependence are shown in Figs. 10-12. The peak values of the concentration in the air increase as the porosity increases. The bigger the partition coefficient is, the higher the peak value is. This situation is totally different from the case of weak dependence. Thus, it is necessary to determine the dependence of the effective diffusion coefficient on the porosity. In general, the effect of the porosity on the concentration in the air becomes stronger when the partition coefficient becomes much bigger.

CONCLUSIONS

In this multi-phase model, VOC emission from dry building ma-

terials is studied by taking into account the existence of VOC both in the adsorbed phase and in the air phase. Based on the developed analytical solution of the concentration equation, the effects of the model parameters are investigated in detail. Both the effective diffusion coefficient and the partition coefficient have a positive effect on the emission of VOC from dry building materials. A high peak value of the concentration in the air appears with the increase of these two parameters. The porosity takes effect by influencing the effective diffusion coefficient. When the porosity has a weak effect on the effective diffusion coefficient, the emission of VOC can be suppressed with the increase of the porosity. For the cases of strong effect existing, the emission of VOC can be suppressed with the decrease of the porosity. It means that these two cases must be treated correctly when changing the porosity to improve the mission of VOC from building materials.

ACKNOWLEDGMENTS

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