VOC Distribution in a Room based on CFD Simulation Coupled with Emission / Sorption Analysis

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ABSTRACT

This paper presents physical models that are used for analyzing numerically the transportation of volatile organic compounds (VOCs) from building materials in a room. The models are based on fundamental physicochemical principles of their diffusion and adsorption / desorption (hereafter simply sorption) both in building materials and in room air. The performance of the proposed physical models is examined numerically in a test room with a technique supported by computational fluid dynamics (CFD). Two building materials are used in this study. One is a VOC emission material for which the emission rate is mainly controlled by the internal diffusion of the material. The other is an adsorptive material that has no VOC source. It affects the room air concentration of VOCs with its sorption process. The floor is covered with an emission material made of SBR (polypropylene styrene-butadiene rubber). An adsorbent material made of coal-based activated carbon is spread over the sidewalls. The results of numerical prediction show that the physical models and their numerical simulations explain well the mechanism of the transportation of VOCs in a room.

KEYWORDS
CFD, VOCs, Diffusion, Adsorption, Desorption

INTRODUCTION
Indoor air quality is greatly affected by the emission and sorption of chemical compounds from building materials. In this study, physical models of emission and sorption of volatile organic compounds (VOCs) are proposed. The models are based on fundamental physicochemical principles of diffusion and sorption of VOCs within both building materials and room air. To demonstrate the validity of the models, concentration distributions of VOCs in a room are numerically analyzed by a CFD technique. Here, the floor is covered with an emission material made of SBR. The emission rate of VOCs from SBR is mainly controlled by internal diffusion in the material (Yang, X., et al, 1998). Coal-based activated carbon is spread over the sidewalls as an adsorbent material. The adsorbent material used here has no source of VOCs and affects room air concentration only through its sorption process. It is assumed that the composition ratio of VOCs does not change and a virtual VOC species (defined as simply VOCs) that represents the total property of VOCs emitted into the air is used in this study. The final goal of this study is to numerically predict the concentration of chemical pollutants in the air inhaled by the occupants of a room.

PHYSICAL MODELS OF VOC TRANSFER
Transportation in room air
VOCs emitted from building materials are transported by room air convection, diffused by molecular diffusion and turbulent diffusion, and taken out through an exhaust opening. The vapor phase concentration C [$\mathrm{kg_{VOCs}}$ / $\mathrm{kg_{air}}$] of VOCs in room air can be described by the mass conservation equation shown in Eq. (1).

$$\boldsymbol{r}_{air}\frac{\partial C}{\partial t} + \boldsymbol{r}_{air}\frac{\partial(u_j C)}{\partial x_j} = \frac{\partial}{\partial x_j}\left(\left(\boldsymbol{l}_a + \frac{\boldsymbol{r}_{air}\boldsymbol{n}_t}{\boldsymbol{s}}\right)\frac{\partial C}{\partial x_j}\right) \tag{1}$$

Here, ρ_{air} [kg/m^3] is the air density, λ_a [kg/(m·s·kg/kg)] is the molecular mass conductivity, n_t [m^2/s] is the turbulence eddy viscosity, σ is the turbulent Schmitt number (=1.0). Velocity u_j [m/s] and n_t are given by solving the flow field with the k-e turbulence model of Low Reynolds number type (Murakami, et al., 1996).

Diffusive and adsorptive transportation in materials

The transportation of VOCs in building materials (internal diffusion or permeation) is possible through the existence of fine pores within the building materials. Molecular and Knudsen diffusions in the vapor phase occur through the pores in the materials due to the concentration gradient. On the surface of the pores, vapor phase VOC is adsorbed and desorbed as shown in Figure 1.
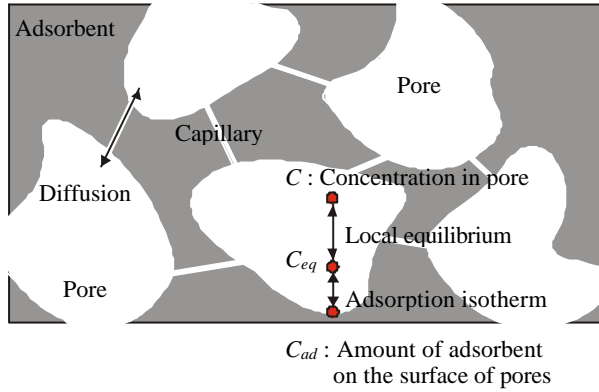

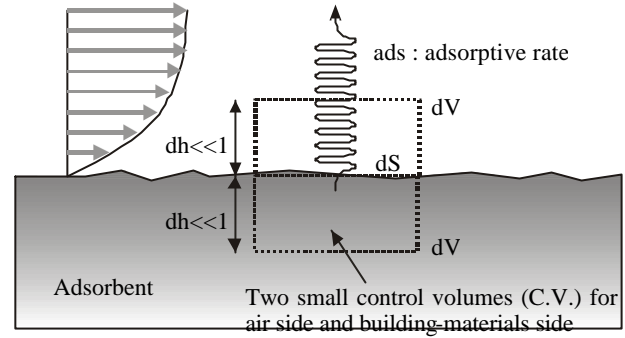Figure 1 : Modeling of VOC diffusion and adsorption in the material

Figure 2 : Modeling of adsorption and desorption of VOCs on the surface of a sorptive material

It can be assumed that VOC diffusion within the substance (the part with no pores in the material) of the material is so small that the diffusion here may be disregarded compared with that in the pores. The VOC transportation through the pores and on the surface of the pores can be described by conservation equations (2) and (3) respectively.

$$k\boldsymbol{r}_{air}\frac{\partial C}{\partial t} = \frac{\partial}{\partial x_j}\left(\boldsymbol{l}_C \frac{\partial C}{\partial x_j}\right) - adv \tag{2}$$

$$\boldsymbol{r}_{sol}\frac{\partial C_{ad}}{\partial t} = adv \tag{3}$$

Here, C [kg/kg] is the vapor phase concentration in the pores, C_{ad} [kg/kg] is the solid (adsorbed) phase concentration on the surface of a pore. $\boldsymbol{r}_{sol}$ [kg/m^3] is the net density of adsorbent of the material, $\boldsymbol{l}_C$ [kg/(ms kg/kg)] is the mass conductivity of VOCs in the air within the pores and k [m^3/m^3] is the porosity of the material. adv [kg/m^{3}s] is the mass transportation within the pores to the surface of the adsorbent.

Substituting Eq.(3) into Eq.(2), the diffusion and sorption equation in the material is obtained as Eq.(4).

$$k\boldsymbol{r}_{air}\frac{\partial C}{\partial t} = \frac{\partial}{\partial x_j}\left(\boldsymbol{l}_C \frac{\partial C}{\partial x_j}\right) - \boldsymbol{r}_{sol}\frac{\partial C_{ad}}{\partial t} \tag{4}$$

Generalized adsorption isotherm

In order to close Eq. (4), a so-called adsorption isotherm is introduced. For closed systems under steady conditions, the rate of adsorption becomes equal to the rate of desorption and thus an equilibrium state is achieved. Since this phenomenon of sorptive dynamics occurs much faster than with the molecular diffusion in gases, in a small CV (control volume) under isothermal conditions at constant pressure, an equilibrium relation between the concentration in the gas and that on the adsorbent surface is possible. The relation is expressed by the so-called general adsorption isotherm (Eq.(5)).

$$C_{ad} = f\left(C_{eq}, T\right) \tag{5}$$

Here, the function f is unique for a combination of adsorbed compound and adsorbent. T [K] is the absolute temperature. C_{eq} [kg/kg] is the vapor phase concentration in equilibrium with the solid phase concentration C_{ad} on the surface of the material. Since C in the pores becomes the same with C_{eq} (local equilibirum), C_{eq} can be substituted by C in the small CV including the adsorbent surface.

Simple transportation model governed by effective diffusion

Eq. (4) of the diffusion and sorption equations in porous materials is re-expressed as Eq. (6) using the relation of the adsorption isotherm of Eq. (5).

$$\left(k\mathbf{r}_{air} + \mathbf{r}_{sol}\frac{\partial f}{\partial C}\right)\frac{\partial C}{\partial t} = \frac{\partial}{\partial x_j}\left(\mathbf{l}_C\frac{\partial C}{\partial x_j}\right) - \mathbf{r}_{sol}\frac{\partial f}{\partial T}\frac{\partial T}{\partial t} \tag{6}$$

In Eq. (6), local equilibrium in a pore ($C_{eq}=C$) is assumed. When it is isothermal, $\partial T/\partial t$ can be omitted and Eq. (6) can be rewritten as simple diffusion equations in Eqs. (7) and (8).

$$\mathbf{r}_{air}\frac{\partial C}{\partial t} = \frac{\partial}{\partial x_j}\left(\mathbf{r}_{air}D_C\frac{\partial C}{\partial x_j}\right) \tag{7}$$

$$D_C = \mathbf{l}_C \Big/ \left(k\mathbf{r}_{air} + \mathbf{r}_{sol}\frac{\partial f}{\partial C}\right) \tag{8}$$

Here, D_C [m²/s] is the effective diffusion coefficient of VOCs in the material. Dc includes the adsorption isotherm f. Eq. (7) is closed when isotherm models such as Eqs. (13), (15) and (17) are introduced as described later. Vapor phase concentration C is related to the solid (adsorbed) phase concentration C_{ad} in the adsorbent with the adsorption isotherm in Eq. (5) through the assumption of $C=C_{eq}$. In this context, C represents the total VOC concentration in the material. In this study, C is used as the equivalent vapor phase concentration to express the concentration in the material, instead of C_{ad}.

The boundary condition at the air-material interface for analyzing the concentration in room air

Since the transportation of C in the material and in the room air are solved simultaneously, a boundary condition should be set at the air-material interface. The VOC emission rate at the air-material interface should be identical with the transportation rate by internal diffusion from the inside. This condition is expressed as a conservation law at the surface of the material, as shown in Eq. (9).

$$-\mathbf{r}_{air}D_C\frac{\partial C}{\partial x}\bigg|_{B+} = -\mathbf{l}_a\frac{\partial C}{\partial x}\bigg|_{B-} \tag{9}$$

Here, $B+$ is the air-material surface in the material-side region, and $B-$ is the air material surface in the air-side region. Eq. (9) is used as the boundary condition with coupled simulation in the material and in the room air.

SIMPLE TRANSPORTATION MODEL ON SORPTIVE SURFACE

In general, the diffusion and sorption process in the material can be described using the effective diffusion coefficient D_C that includes implicitly the effect of sorption. If the material has no VOC source and it contributes to the room air concentration only with its sorptive process, we can simplify the modeling of the sorption process compared to the modeling stated above. For simple modeling, it is assumed that the adsorption occurs only on the surface (Figure 2). VOC transfer near building materials is also governed by Eqs. (2) and (3), as well as the phenomenon within the pores of the material. Here, two CVs (dV[m³]) are set at the interface for simply modeling the transportation on adsorbent material as shown in Figure 2. The thickness dh [m] normal to the surface element dS [m²] is very thin. This surface element dS is sandwiched by the CVs; i.e. the CV in the material and the CV in the air. Here, dh is assumed so small that the sorption process reaches equilibrium immediately in the CV. When volume integration is performed for Eqs.(2) and (3) in each CV neglecting the time differential term of the vapor phase concentration in air, following Eqs. are given.

$$0 = \mathbf{l}_a\frac{\partial C}{\partial x}\bigg|_{B-}dS - adv \cdot dV \qquad \text{(CV in the air)} \tag{10}$$

$$\mathbf{r}_{sol}\frac{\partial C_{ad}}{\partial t}dV = adv \cdot dV \qquad \text{(CV in the material)} \tag{11}$$

With Eqs. (10) and (11), the VOC adsorption rate on the surface of the material is related to the molecular diffusion of VOCs close to the surface of the adsorbent as shown in Eq. (12).

$$-\mathbf{l}_a\frac{\partial C}{\partial x}\bigg|_{B-} = -adv \cdot \frac{dV}{dS} = -ads = -\left(\mathbf{r}_{sol}\frac{\partial C_{ad}}{\partial t}\right)\frac{dV}{dS} = -\mathbf{r}'_{sol}\frac{\partial C_{ad}}{\partial t} \tag{12}$$

Here, ads [kg/m²s] is the sorption rate (positive/ negative of ads corresponds to the adsorption/ desorption rates respectively). $\mathbf{r}'_{sol}(=\rho_{sol}\ dV/dS)$ [kg/m²] is the plane density of a sorptive material.

Typical isotherm models

<u>Henry model</u>

For the adsorption under low concentrations of VOCs in the air, the Henry model (linear model) is utilized.

$$C_{ad} = k_h \cdot C_{eq} = k_h \cdot C \tag{13}$$

Here, k_h [-] is the Henry's coefficient. The adsorption term in Eq. (12) is rewritten as Eq. (14).

$$l_a \left. \partial C \middle/ \partial x \right|_{B-} = ads = r'_{sol} \left. \partial C_{ad} \middle/ \partial t \right. = r'_{sol} \cdot k_h \left. \partial C \middle|_{B-} \middle/ \partial t \right. \qquad (14)$$

In the numerical simulation, the VOC concentration in the air-side CV adjacent to the material $C|_{B-}$ is assumed to be the same as the concentration in the equilibrium state; i.e, $C|_{B-} = C_{eq}$. Eq. (14) is used as the boundary condition for the sorptive surface when solving Eq. (1).

Langmuir model

When the VOC concentration in room air becomes high, the concentration of adsorbed VOCs, C_{ad} on the adsorbent saturates at a certain level of room air concentration. In this situation, the Henry model overestimates the amount of adsorbed VOCs. The Langmuir model is based on the model of monolayer adsorption that takes into account the concept of saturated concentration of C_{ad0}. The Langmuir model, which can be applied to higher VOC concentration fields, is more sophisticated than the Henry model.

$$C_{ad} = C_{ad0} \cdot k_l \cdot C \middle/ \left(1 + k_l \cdot C\right) \qquad (15)$$

Here, k_l [1/(kg/kg)] is the Langmuir's coefficient and C_{ad0} [kg/kg] is the concentration of the saturated adsorption by monolayer adsorption. The adsorption term in Eq. (12) is rewritten as Eq. (16) in the same manner as Eq. (14). Eq.(16) is used as the boundary condition for the sorptive surface when solving Eq. (1).

$$l_a \left. \partial C \middle/ \partial x \right|_{B-} = ads = r'_{sol} \left. \partial C_{ad} \middle/ \partial t \right. = r'_{sol} \cdot C_{ad0} \cdot k_l \middle/ \left(1 + k_l \cdot C|_{B-}\right)^2 \cdot \left. \partial C \middle|_{B-} \middle/ \partial t \right. \qquad (16)$$

Polanyi DR model

The Polanyi DR approach may be used to describe sorption equilibrium for whole classes of compounds on a particular adsorbent and the variation of the equilibrium with temperature. This relation is most often presented as a so-called characteristic curve of the form shown in Eq. (17).

$$C_{ad} = C_{ad0} \cdot exp\left(-k_p \left(T \middle/ V_m\right)^2 \cdot ln\left(C_{sat} \middle/ C\right)^2\right) \qquad (17)$$

Here, k_p [(cm^3/mol K)^2] is the Polanyi's coefficient, C_{sat} [kg/kg] is the saturated concentration, V_M [cm^3/mol] is the molecular volume. The adsorption rate 'ads' at this time serves as Eq. (18).

$$l_a \left. \frac{\partial C}{\partial x} \right|_{B-} = ads = 2 \cdot r'_{sol} \cdot k_p \cdot (T/V_m)^2 \cdot C_{ad0} \middle/ C|_{B-} \cdot ln\left(C_{sat} \middle/ C|_{B-}\right) \cdot exp\left(-k_p \left(T \middle/ V_m\right)^2 ln\left(C_{sat} \middle/ C|_{B-}\right)^2\right) \cdot \left. \partial C|_{B-} \middle/ \partial t \right. \qquad (18)$$

It is convenient to analyze the indoor air quality with this Polanyi model since it explicitly includes the temperature dependence of the sorption effect in the formulation.

ROOM MODEL AND BUILDING MATERIALS USED

The room model (2D) used for simulation is shown in Figure 3. The room model has the dimensions (x) × (z) = 75 L_0 × 50 L_0 (= 4.5m × 3.0m, L_0 = 0.06m = width of supply inlet). As the VOC source, SBR plate was selected and used to cover the floor. The emission rate from the material is strongly related to both the initial concentration distribution C_0 and the effective diffusion coefficient D_C within the SBR. In this study, the initial VOC concentration distribution in SBR is assumed to be uniform, C_0 =0.16 [kg/kg]. Here it is assumed that a new carpet of young age is furnished. D_C is assumed to be 1.1×10^{-14} [m^2/s] (at 23°C), following Yang, X. et al. The thickness of SBR is 0.025L_0 (1.5×10^{-3}m). The diffusion of VOCs at the side face and bottom is assumed to be cut off. As the adsorptive surface, coal-based activated carbon was spread over the sidewalls. The capacity of adsorption depends on the surface area of the adsorbent. The activated carbon has a wide surface area of more than 10^6 [m^2] per 1 [kg]. In this study, the plane density r'_{sol} is set to be 1×10^{-6} [kg/m^2]; i.e. the surface area of the adsorbent is the same as that of the building materials. This value is quite small from the viewpoint of practical cases. However, one of the objects of this study is to examine the difference in various models of adsorption isotherm and such a difference will be clear in the condition where C_{ad} becomes close to its saturated concentration. Therefore the amount of the adsorbent material was decreased in this study. The parameters in the sorption isotherm are estimated by an experiment in which toluene is adsorbed on coal-based activated carbon (Yu, 1987). Here, we assumed that Henry's k_h [-], Langmuir's k_l [1/(kg/kg)] and Polanyi's k_p [(cm^3/mol·K)^2] coefficients are 3.0×10^5, 1.5× 10^6 and 1.3 ×10^{-3} respectively. Other estimated values are shown in Table 1.
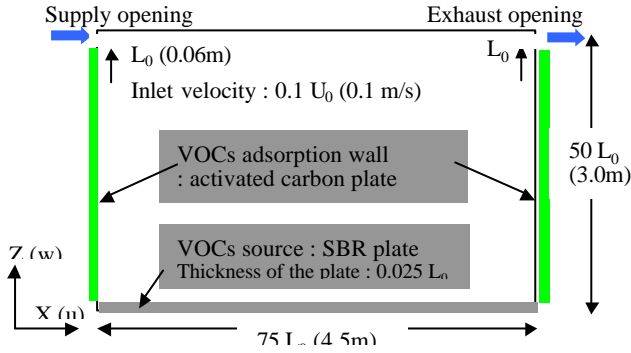
Figure 3 : Room model (2D)

TABLE 1 : Cases Analyzed

Case No.	Isotherm model	Applied Parameter
Case1	Carpet only	-
Case2	Henry model	k_h [-]= 3.0 ×10^5
Case3	Langmuir model	k_l [1/(kg/kg)]= 1.5 ×10^6 C_{ad0} [kg/kg]= 0.25
Case4	Polanyi model	k_p [(cm^3/mol·K)^2]= 1.3 ×10^{-3} C_{ad0} [kg/kg]= 0.43 C_{sat} [kg/kg]= 0.13 V_M [cm^3/mol]= 106

NUMERICAL METHODS AND BOUNDARY CONDITIONS

Table 2 shows the numerical conditions. Flow fields were analyzed with a low Reynolds number k- model (MKC model (Murakami, et al., 1996)) with an inflow velocity of 0.1 U_0 (= 0.1 [m/s]; air change rate = 1.6 [h^{-1}]) A centered difference scheme is used for the convection term in air. Using the results of flow field simulations, the behaviors of VOC transportation were analyzed. Table 1 shows the cases analyzed. Four cases were examined in total, under the different adsorption isotherm models. The time history of the room air concentration was obtained over a duration of 1.4 ×10^6 T_0 (24 hours, $T_0 = L_0/U_0$).

TABLE 2 : Numerical Conditions

Number of grid points (2D)		
Air region	:	68(x) × 64(z) (= 4.5m (x) × 3.0m(z))
Material region dominated by internal diffusion	:	68(x) × 41(z) (= 4.5m(x) × 1.5×10^{-3}m(z))
Width of the mesh adjacent to the surface	:	0.6 × 10^{-9} [mm]
Region of adsorptive surface for side walls	:	55(z) (= 2.94m(z))
Reynolds number	$U_0 L_0 / \nu$	= 4.2×10^3
Molecular diffusion coefficient of VOCs in air	l_a / r_{air}	= 5.9×10^{-6} [m^2/s] (23)
Effective diffusion coefficient of VOCs in the material (Yang et. al.)	D_C	= 1.1×10^{-14} [m^2/s] (23)
Inflow velocity	0.1 U_0	= 0.1 [m/s]

RESULTS AND DISCUSSION

For the flow field of the model room, we have conducted precise model experiments with identical Reynolds numbers. The velocity distribution given from the prediction with the low Reynolds number k-ε model and the results obtained in the model experiment are in very good agreement (Murakami, et al., 1999).
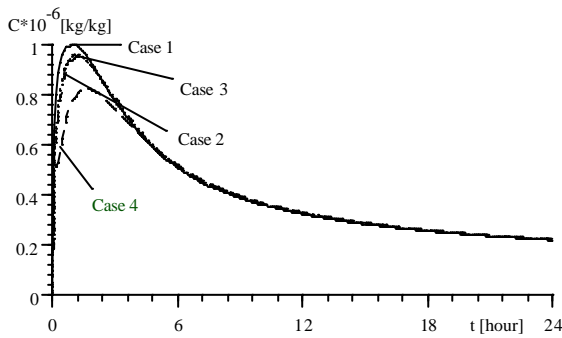

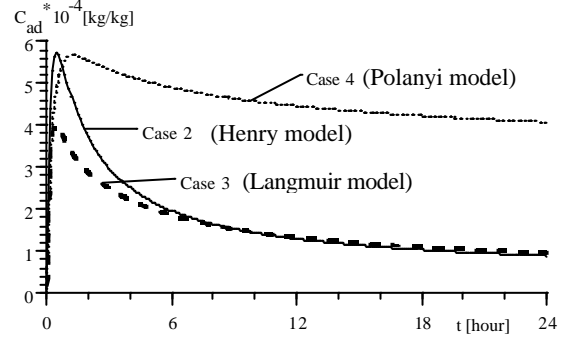Figure 4 : Time history of room-averaged Concentration

Figure 5 : Time history of the amount of VOCs adsorbed by sorptive material
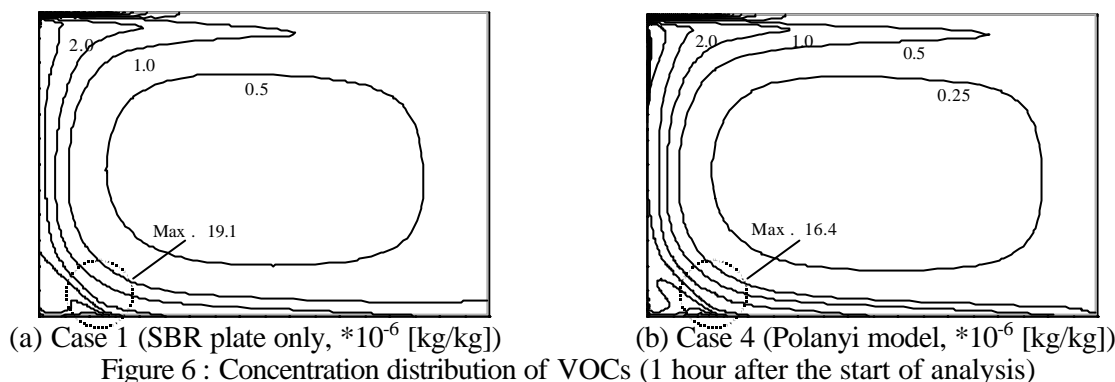
VOC concentration in room air

The history of the room-averaged concentration for 24 hours is shown in Figure 4. The concentration C is normalized by the initial concentration of the source material C_0. Almost none of the influences of sorption are seen in this analysis especially after about 6 hours. However, it is noted that there is very little quantity of the adsorbent material installed in the sidewalls in this analysis. The room-averaged concentration after 24 hours decreases to 4.22×10^{-5} [g/m^3], and reaches steady state. The maximum room-averaged concentration in te early stages is evaluated as low in Case 2 and Case 3, which installed additional adsorption material compared with Case 1, and it turns out that the

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adsorbent materials have controlled the rise in the room-averaged VOC concentration. In Case 2 and Case 3, since VOC concentrations near the adsorption walls are very low, there are little differences between the results for the Henry and Langmuir models. The maximum room average concentration is evaluated as low in Case 4 using the Polanyi model that evaluates the amount of adsorption greatly in a low concentration region.

Amount of adsorption on Adsorbent

In this analysis, since VOCs generated from the floor are mainly conveyed in the direction of the left wall by the room airflow, the amount of adsorption in the left wall side becomes large. The history of the average amount of adsorption (C_{ad}) by the left wall over 24 hours is shown in Figure 5. In Case 2 (Henry model), the amount of adsorption is evaluated as higher than that in Case 3 (Langmuir model) at the early stage of analysis. In Case 4 (Polanyi model), the amount of adsorption is continuously estimated as large.

(a) Case 1 (SBR plate only, $*10^{-6}$ [kg/kg])   (b) Case 4 (Polanyi model, $*10^{-6}$ [kg/kg])

Figure 6 : Concentration distribution of VOCs (1 hour after the start of analysis)

VOC concentration distribution in room

The concentration distributions of VOCs in Case 1 and Case 4 1 hour from the start of the analysis are shown in Figure 6. By preparing adsorbent material in the sidewalls, high-concentration VOCs will not spread in the room. The VOCs concentration near the left wall is about 4 times higher than that near the right wall due to the influence of the airflow pattern. The VOC concentration distribution in the room is influenced by the position of the source and sink materials. The influence of the adsorbent material on the room concentration becomes small when the sorption material is limited and the concentration reaches a steady state. The concentration is not uniform in the space, and rapidly changes near the floor of the VOC source. The VOC concentrations near the floor (4.67×10^{-4} [g/m^3]) are about 11 times higher than the average room concentration.

CONCLUDING REMARKS

A physical model of VOC emission where the emission rate is controlled by internal diffusion was deduced and applied to the VOC emission from SBR plate in a room. The adsorption effect of building materials was simply modeled and was included in the prediction model of the VOC concentration in room air. The model was applied to adsorption by coal-based activated carbon that was thinly spread on the walls.

(1) The room-averaged VOC concentration decays gradually during the duration of the analysis. The adsorption effect on the room air concentration becomes clear when the room air concentration changes rapidly.

(2) Since the concentration distribution in the room is not uniform, the amount of adsorption materials and their positions are important for the concentration.

(3) The differences between 3 types of adsorption isotherm models were clear under the conditions of a small amount of adsorbent material.

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