

REVERSIBLE SORPTION MODELING FOR MULTI-ZONE CONTAMINANT DISPERSAL ANALYSIS

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ABSTRACT

Mathematical models are presented that account for the mass transport processes associated with isothermal reversible sorption in building materials. These models account for a) the equilibrium limits of reversible sorption processes, b) boundary layer diffusion transport at the adsorbent surface, and/or c) diffusion transport within the adsorbent proper. Three distinct families of models are formulated with individual members of each family distinguished by the sorption equilibrium relation used in their formulation. The first family is based on a discrete or "lumped parameter" idealization of the zone- air/adsorbent system that enforces only the sorption equilibrium constraint. The second family is based on a more complete discrete idealization that adds to the equilibrium constraint a model of boundary layer diffusion. Finally, the third family adds a discretized continuum idealization of diffusion transport within the adsorbent using the Finite Element Method. It is argued that the first model family may be expected to provide reliable predictions of contaminant dispersal in buildings when flow transport processes and source dynamics are slow compared to boundary layer and/or intra-adsorbent transport processes; the second model family is useful for those situations where this is not the case and boundary layer diffusion transport is ratelimiting; the third family provides a means to model those cases where intra-adsorbent transport is rate-limiting.

The models are shown to be simple *assemblages* of dispersal *element equations* that may be used for general multizone analysis. A comparison the model families is made and measurable criteria are *presented to* aide in the selection of the model to use. Finally, the results of simple applications of *these* models are *presented that* provide some validation of the theory presented.

INTRODUCTION

It is a matter of common experience that sorption transport can affect the perceived quality of air in buildings – the materials of building construction and furnishings clearly adsorb and desorb certain compounds that we perceive as lingering odors – but can sorption transport significantly alter the dispersal dynamics of air pollutants in buildings? If so, how can existing multi-zone contaminant dispersal analysis theory be extended to account for this form of transport?

Some experimental studies indicate that, indeed, sorption transport can significantly alter the dispersal of indoor air pollutants (Borrazzo and Davidson 1990; Dunn 1987; Dunn and

Tichenor 1987; Matthews and others 1987; Seifert and Schmah 1987; Silberstein 1989). Attempts have been made by the investigators of these studies to model the adsorption dynamics involved using empirical or semi-empirical approaches to the problem. Other investigators tackling the closely related problem of moisture transport in building construction have approached the problem from a more fundamental basis but have not taken full advantage of the vast body of knowledge available in the adsorption science and technology literature (Cleary and Sherman 1984; Cunningham 1990; Kerestecioglu 1988; Shukuya and Saito 1990 Thomas, 1989 #319; Thomas and Burch 1990).

This paper presents sorption transport models that are formulated using *element assembly* techniques and are based on fundamental principles of adsorption science. These models provide the means to identify the conditions under which sorption transport can significantly alter contaminant dispersal in building airflow systems and can be used to extend the existing multi-zone theory to predict the quality of air in buildings. The approach taken is closely related to that of the moisture transport modeling mentioned above, although here we will limit consideration to isothermal sorption dynamics. The element assembly formulation used is expected to facilitate integration with element assembly building thermal models (Axley and Grot 1990; Axley 1988) and thereby make the generalization to nonisothermal conditions straightforward.

We will first consider some fundamental principles of adsorption science and then apply these principles to model adsorption dynamics in single rooms. From these single room (single-zone) models *element equations* for boundary layer and porous adsorbent diffusion transport will be extracted. The results of applying these equations to model formaldehyde gas and water vapor transport in gypsum wall board (gypboard) will then be reviewed.

FUNDAMENTAL PRINCIPLES

While the existing adsorption science and technology literature is relatively mature and vast it is directed toward industrial applications of sorption separation processes that involve the purposeful use of specially prepared adsorbents (e.g., activated carbon, zeolites, and synthetic resins) placed in sorption devices that are designed and controlled to achieve high rates of mass transfer (e.g., batch, flow, and fixed-bed reactors) (Jaroniec and Madey 1988; Oscik and Cooper 1982; Ponc and others 1974; Rodrigues and others 1988; Ruthven 1984; Slejko 1985; Suzuki 1990; Vermeulen and others 1984). Here, on the

other hand, we are interested in sorption phenomena that are largely unintentional involving building materials that may act as adsorbents, but are not specially prepared to do so. Consequently, we shall have to adapt ideas from the available adsorption literature and focus consideration on simpler models of sorption phenomena until additional study warrants the application and, importantly, provides the requisite data for more complete sorption models.

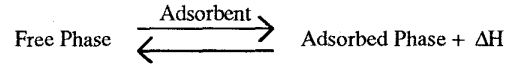
Adsorption, the separation of a substance from one phase – indoor air in the present context – and the accumulation of that substance on the surface of another phase – here, building materials – is just one step of several that together determine the nature of the *adsorption dynamics*. In the building context, adsorbate species are transported via convection and molecular and turbulent diffusion transport processes from the bulk air phase in rooms to locations near the adsorbent. At this point diffusion transport processes, alone, take over to move the adsorbate first through the boundary layer surrounding the adsorbent and then through the porous interstices of the adsorbent to near-surface locations of the solid portions of the adsorbent. Finally the actual adsorption processes come into play to bind the adsorbate to activated adsorbent surface locations. Simultaneously, desorption processes release adsorbate within the porous structure of the adsorbent that then are transported to the bulk air phase by these same processes. The rate of species transport to and from the surface-bound locations is, thus, determined by *dispersal processes* within in the building, by *boundary layer diffusion* processes near the adsorbent, by *porous diffusion* processes within the adsorbent, and by the *adsorption* process itself at the solid surface locations within the adsorbent. It is somewhat ironic that the rate of the adsorption process is, invariably, practically instantaneous and thus we shall simply ignore the kinetics of this step. The limitations placed on this step by equilibrium considerations are, however, all-important and will be central to all subsequent discussion.

Sorption Equilibria

The nature of adsorption will depend on the nature of the adsorbent, the nature of the adsorbate, and the interaction that may occur between them. After Slejko (Slejko 1985) four generic types of adsorption may be distinguished – exchange, physical, chemical, and specific adsorption. *Exchange adsorption* involves the exchange of one for another ionic species attached to the surface of an adsorbent by electrostatic forces. In *physical adsorption* the adsorbate is bound to the adsorbent by relatively weak intermolecular Van Der Waals forces. *Chemical adsorption* results from a chemical reaction between the adsorbate and adsorbent and, therefore, involves usually very strong binding forces associated with the sharing of electrons. Finally, the term *specific adsorption* is reserved for the binding of molecular groups, without chemical transformation, to specific functional groups on the adsorbent surface (e.g. polar adsorbates binding to matching polarized surface locations). These distinctions are somewhat arbitrary and each class may simply be considered to fall along a spectrum of possibilities with physical adsorption falling at the weak-force end of the spectrum and chemical adsorption at the strong-force

end. In that binding forces play a role in all cases, adsorption is an exothermic process whose reversibility is directly related to the strength of the binding forces.

Under normal conditions of temperature and pressure physical and some chemical adsorption processes may be considered to be a more or less reversible transformation between two alternative phases of the adsorbate – the *free phase* and the *adsorbed phase* – where the adsorbent may be thought to activate the transformation process not unlike a catalyst in a chemical transformation:



where ΔH is the heat of adsorption released.

In typical situations the rate of this transformation is practically instantaneous relative to dispersal and diffusion transport processes that also determine the overall rate of building sorption dynamics. Thus the kinetics of this transformation may not need to be modeled explicitly, but the equilibrium limits of this transformation must be considered. For closed systems under steady conditions the rate at which adsorbate molecules (or ions) " α " bind to adsorbate surfaces will eventually come to be equal to the rate at which they are released and the concentration of the free and adsorbed phases will remain constant at their respective equilibrium values, αC_e and αC_{se} . (Concentration for both phases will be expressed in terms of mass fraction, following one of the common conventions used in the adsorption and chemical engineering literature.)

In functional notation, we may say that the free phase equilibrium concentration of species α , αC_e , is related to the adsorbed phase concentration, αC_{se} , and the thermodynamic state of the system determined by temperature, T , and the free phase pressure, P , as:

$$\alpha C_{se} = \alpha f(\alpha C_e, T, P) \quad (1)$$

where αf is a function that is unique for each adsorbate-adsorbent system.

When reported for isothermal conditions at atmospheric pressure these equilibrium relations are identified as *adsorption isotherms*. Experimentally determined adsorption isotherms are often approximated by one of several models including the *Linear*, *Langmuir*, and *BET* models:

$$\alpha C_{se} = \alpha K_p \alpha C_e \quad \text{Linear Model (2)}$$

$$\alpha C_{se} = \frac{\alpha C_{so} \alpha K_L \alpha C_e}{1 + \alpha K_L \alpha C_e} \quad \text{Langmuir Model (3)}$$

$$\alpha C_{se} = \frac{\alpha C_{so} \alpha K_{BET} \alpha \hat{C}_e}{(1 + \alpha \hat{C}_e)(1 - \alpha \hat{C}_e + \alpha K_{BET} \alpha \hat{C}_e)}; \quad \alpha \hat{C}_e \equiv \frac{\alpha C_e}{\alpha C_{sat}} \quad \text{BET Model (4)}$$

where:

- α_{K_P} , α_{K_L} , and $\alpha_{K_{BET}}$, are the *Partition*, *Langmuir*, and *BET* "constants" that have an Arrhenius type dependency on temperature (Andelman and others 1989; Ruthven 1984; Slejko 1985);
- $\alpha_{C_{SO}}$ is the adsorbed phase concentration corresponding to complete coverage by a single layer of adsorbate (constant for a given system and independent of temperature for the Langmuir assumption of a fixed number of sites available for adsorption);
- $\alpha_{\hat{C}_e}$ is the so-called reduced concentration – a ratio of the equilibrium to the saturation free phase concentration, $\alpha_{C_{sat}}$.

Boundary Layer Diffusion

Adsorbent surfaces may be thought to be separated from the room air by a *film* or *boundary layer* over which the species concentration varies from a near-surface, air phase concentration, α_{C^*} , to the bulk air-phase concentration in the room or zone, α_C , as illustrated in Figure 1.

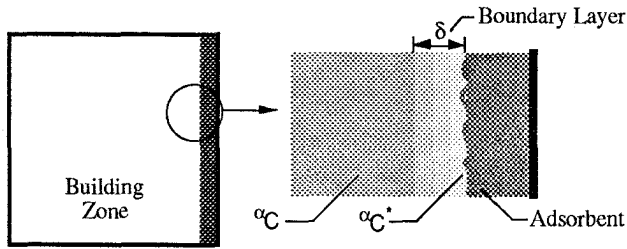


Figure 1. Boundary Layer Diffusion

If mass transport is due only to molecular and turbulent diffusion processes (i.e., there is no bulk flow of adsorbate through the boundary layer and adsorbent due to pressure gradients) then the net mass transport rate from the bulk phase to the surface, α_{w_δ} , may be approximated using steady-state mass transfer relations from boundary layer theory of the general form (White 1988):

$$\alpha_{w_\delta} = \bar{h}_m \rho A_s (\alpha_C - \alpha_{C^*}) \quad (5)$$

where \bar{h}_m is the average *film* mass transfer coefficient (length/time), ρ is the *film* density – the average of the bulk and surface densities – and A_s is the projected (i.e., exposed) surface area of the adsorbent.

The average mass transfer coefficient may be measured directly (e.g., see (Matthews and others 1987)), measured indirectly using the naphthalene sublimation technique (White 1988), estimated from published heat transfer correlations (e.g., see (Khalifa and Marshall 1990; Spitler and others 1991)) using the so-called *heat and mass transfer analogy*, or estimated from published mass transfer correlations. Mass transfer correlations, typically, relate a dimensionless form of the film coefficient – the average Sherwood number, \overline{Sh}_L , with the surface flow Reynolds number, Re_L , and the air phase Schmidt number, Sc . For flow parallel to a flat plate, a flow condition that may be

considered to be representative of air flow past interior building surfaces, White provides the following correlations:

$$\overline{Sh}_L \equiv \frac{\bar{h}_m L}{\alpha_{air} D} = 0.664 Re_L^{1/2} Sc^{1/3}; \text{ for } Re_L < 500,000 \quad (6)$$

$$\overline{Sh}_L = 0.037 Re_L^{4/5} Sc^{1/3}; \text{ for } Re_L > 500,000 \text{ \& } Sc \approx 1.0 \quad (7)$$

where:

- $Re_L = UL/\nu$ with U the mean fluid velocity (parallel to the surface) outside the boundary layer, L the length of the surface in the direction of flow, and ν the kinematic viscosity of the fluid;
- $Sc \equiv \nu/\alpha_{air} D$ with $\alpha_{air} D$ the molecular diffusivity of the binary α -air system that may be estimated using the Chapman-Enskog equation (Suzuki 1990).

(See, also, the closely related correlations for deposition velocity discussed by Nazaroff (Nazaroff and Cass 1987; Nazaroff and Cass 1989).)

Porous Diffusion in Flat Adsorbent Sheets

Transport within effective adsorbents invariably involves a complex variety of processes including:

- molecular, Knudsen, and surface diffusion within macroporous interstices (i.e., interstices that are large relative to the molecular dimensions of the adsorbate),
- diffusion processes influenced by the potential field of the adsorbent surfaces within microporous interstices that are specific to the surface characteristics of the adsorbent and the nature of the adsorbate, and
- bulk transport due to Poiseuille flow driven by pressure gradients (Ruthven 1984; Satterfield 1980; Suzuki 1990).

Macroporous diffusion and microporous diffusion, at low air phase adsorbate concentrations, in flat adsorbent sheets or panels may be modeled analogously to Fick's Law as:

$$\alpha_{w'} = -\rho A_s \alpha_{air} D(\alpha_C) \frac{\partial \alpha_C}{\partial x} \quad (8)$$

where:

- $\alpha_{w'}$ is the mass transport rate of species α relative to the bulk flow through the porous adsorbent;
- A_s is the projected surface area of the adsorbent (i.e., equal to the exposed surface area of the adsorbent);
- $\alpha_{air} D(\alpha_C)$ the effective diffusion coefficient of the adsorbate-adsorbent system that, in general, depends upon the species air phase concentration; and
- x is the coordinate direction perpendicular to the plane of the adsorbent sheet.

For diffusion in macropores the effective diffusion coefficient, $\alpha_{air} D(\alpha_C)$, may be estimated as:

$$\alpha_{air} D(\alpha_C) \approx \epsilon^2 \left(\frac{1}{\frac{1}{\alpha_{air} D} + \frac{1}{\alpha_{Dk}}} \right) \quad (9a)$$

$$\alpha D_K = \frac{2}{3} R_p \sqrt{\frac{8RT}{\pi M}} \quad (9b)$$

where: ε is the porosity of the adsorbent, αD_K is the Knudsen diffusivity, R_p is the mean pore diameter, R is the Universal gas constant, T is absolute temperature, and M is the molecular weight of the adsorbate. Other, more complex and, presumably, more accurate relations are available for estimating this effective diffusivity, but this simple relation will suffice here (Ruthven 1984; Satterfield 1980; Suzuki 1990).

With Equation 8 in hand we are in a position to analyze mass transport through a flat adsorbent panel. Consider an adsorbent panel separating two building zones, as diagrammed below in Figure 2, with diffusion transport, $\alpha w'$, superimposed upon a bulk flow, w , from zone i to zone j .

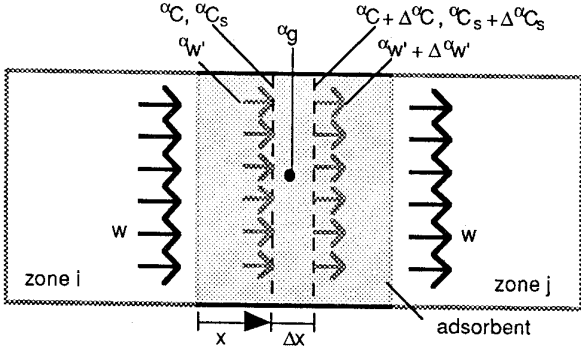


Figure 2. Convection-Diffusion with Adsorption in a Flat Adsorbent

At position "x" in the adsorbent the air phase and adsorbed phase concentrations are αC and αC_s , respectively. Accounting for a change of these values over a small distance Δx and the possibility of species generation in the adsorbent αg we may directly write a species mass balance for the Δx slice:

$$w(\alpha C - (\alpha C + \Delta \alpha C)) + (\alpha w' - (\alpha w' + \Delta \alpha w')) + \alpha g \Delta x = \rho A_s \varepsilon \Delta x \frac{\partial \alpha C}{\partial t} + \rho_s A_s \Delta x \frac{\partial \alpha C_s}{\partial t} \quad (10)$$

where ρ_s is the bulk density of the adsorbent. In the limit, as $\Delta x \rightarrow 0$ Equation 10 becomes:

$$-w \frac{\partial \alpha C}{\partial x} - \frac{\partial \alpha w'}{\partial x} + \alpha g = \rho A_s \varepsilon \frac{\partial \alpha C}{\partial t} + \rho_s A_s \frac{\partial \alpha C_s}{\partial t} \quad (11)$$

This is a differential species mass balance relation that is quite general, but not yet in a form that is useful. We shall modify this expression by first assuming that adsorption is practically instantaneous so that αC and αC_s are related by the equilibrium relation defined by Equation 1 (i.e., $\alpha C_s = \alpha f(\alpha C)$) and then introducing the porous diffusion relation defined by Equation 8. After some simplification we obtain:

$$\rho A_s \alpha_{\text{air}} D \frac{\partial^2 \alpha C}{\partial x^2} + \alpha g = \left(\rho A_s \varepsilon + \rho_s A_s \frac{\partial \alpha f}{\partial \alpha C} \right) \frac{\partial \alpha C}{\partial t} + w \frac{\partial \alpha C}{\partial x} \quad (12)$$

an equation that has the form of the one-dimensional convection-diffusion equation – although here with possibly nonlinear coefficients due to the terms $\alpha_{\text{air}} D$ and $\partial \alpha f / \partial \alpha C$ – that we shall identify as the *one-dimensional convection-diffusion-adsorption equation*. This equation is similar to those used to model the dynamics of adsorption in packed columns or chromatographic columns (Greenkorn 1983; Suzuki 1990).

BUILDING SORPTION DYNAMICS

The forgoing principles may be directly applied to the problem of modeling adsorption dynamics in buildings. We will focus consideration on the single-zone case moving from simple models to more complete models and from these results extract element equations that can be used for general multi-zone contaminant dispersal analysis. The single zone models presented differ, in essence, by the number of control volumes used to model the system's behavior. In the first model a single control volume will be employed for the zone air and adsorbent together. In the second model the zone air and the adsorbent will occupy individual control volumes linked by boundary layer mass transport. Finally in the third model the adsorbent will be sliced up into multiple control volumes to enable the modeling of porous diffusion transport. In all cases the zone air will be assumed to be well-mixed.

EA: Equilibrium Adsorption Model

Consider a single well-mixed zone containing a volume of air of mass m and a quantity of adsorbent of mass m_s with air flowing into and, by continuity, out of the zone at a mass flow rate w , as illustrated in Figure 3.

Given the species concentration in the zone αC and that of the air flowing into the zone αC_{in} , the species mass flow rates into and out of the zone are as shown on the figure and, thus, the species mass balance may be written as:

$$w \alpha C + m \frac{d \alpha C}{dt} + m_s \frac{d \alpha C_s}{dt} = \alpha G + \alpha G_s + w \alpha C_{in} \quad (13)$$

where we have admitted the possibility of species generation in the zone air, αG , and in the adsorbent, αG_s .

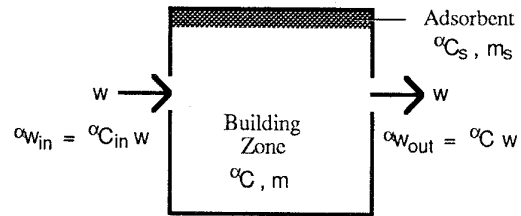


Figure 3. Single-Zone Equilibrium Adsorption Model

If now we make the simplifying assumption that the adsorbate concentration within the adsorbent is uniform and the zone air remains, at all times, in equilibrium with the adsorbent (i.e., $\alpha C_s = \alpha f(\alpha C)$) then the mass balance assumes a form that is similar to that defining the dilution dynamics alone:

$$w\alpha C + m_{\text{eff}} \frac{d\alpha C}{dt} = \alpha E \quad (14a)$$

$$m_{\text{eff}} = \left(m + m_s \frac{d\alpha f}{d\alpha C} \right) \quad (14b)$$

where the terms on the right hand side of Equation 13 have been collected into a single term – the system *excitation* αE – and an *effective participating mass* of the system, m_{eff} , appears as the sum of the zone air mass plus the adsorbent mass scaled by the slope of the adsorption isotherm. For example, for the Linear adsorption isotherm the effective mass is simply $m_{\text{eff}} = (m + m_s \alpha K_p)$.

This ordinary differential equation may be solved to determine the time variation of zone-air concentration, αC , and from this solution the adsorbent concentration response may be recovered using the assumed equilibrium relation $\alpha C_s = \alpha f(\alpha C)$.

The assumption of equilibrium adsorption is reasonable when boundary layer diffusion, porous diffusion, and adsorption transport rates are rapid relative to flow transport dynamics. This is likely to be the case when the adsorbent is well distributed in the zone and when zone air concentrations are changing slowly. We shall identify this model as the *Equilibrium Adsorption* or *EA* model.

BLDC: Boundary Layer Diffusion Controlled Model

Consider the same zone where, now, we isolate the adsorbent and the zone in separate control volumes linked by boundary layer mass transport αw_δ :

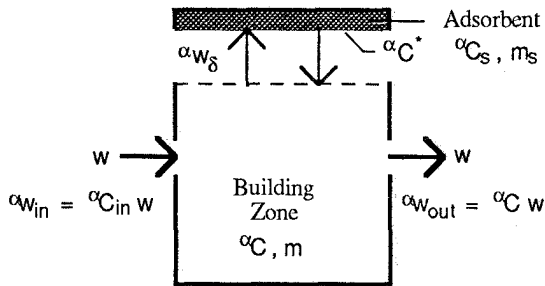


Figure 4. Single-Zone Boundary Layer Diffusion Controlled Model

Two mass balance relations may be written for this system idealization, one for the zone air and one for the adsorbent:

$$w\alpha C + \bar{h}_m \rho A_s (\alpha C - \alpha C^*) + m \frac{d\alpha C}{dt} = \alpha G + w\alpha C_{\text{in}} \quad (15a)$$

$$-\bar{h}_m \rho A_s (\alpha C - \alpha C^*) + m_s \frac{d\alpha C_s}{dt} = \alpha G_s \quad (15b)$$

If now we make the simplifying assumption that the species concentration within the adsorbent is uniform and the air at the surface of the adsorbent remains, at all times, in equilibrium with the adsorbent (i.e., $\alpha C_s = \alpha f(\alpha C^*)$) then we obtain two equations in two unknown variables, αC and αC^* , the zone and near-surface air phase concentrations:

$$\begin{bmatrix} w + \bar{h}_m \rho A_s & -\bar{h}_m \rho A_s \\ -\bar{h}_m \rho A_s & \bar{h}_m \rho A_s \end{bmatrix} \begin{Bmatrix} \alpha C \\ \alpha C^* \end{Bmatrix} + \begin{bmatrix} m & 0 \\ 0 & m_{\text{seff}} \end{bmatrix} \begin{Bmatrix} \frac{d\alpha C}{dt} \\ \frac{d\alpha C^*}{dt} \end{Bmatrix} = \begin{Bmatrix} \alpha E \\ \alpha E_s \end{Bmatrix} \quad (16a)$$

$$m_{\text{seff}} = m_s \frac{d\alpha f}{d\alpha C^*} \quad (16b)$$

where the terms on the right hand side of Equations 15a and 15b have been collected in a single system *excitation vector* $\{\alpha E\}$. For this model, then, an effective participating mass of the adsorbent appears that is simply equal to the second term of the total effective mass, Equation 14b, obtained for the EA model. For example, for the Linear adsorption isotherm this effective mass is simply $m_{\text{seff}} = m_s \alpha K_p$.

Note that the first array of Equation 16a can be written as the sum of a symmetric and an asymmetric array:

$$\begin{bmatrix} w + \bar{h}_m \rho A_s & -\bar{h}_m \rho A_s \\ -\bar{h}_m \rho A_s & \bar{h}_m \rho A_s \end{bmatrix} = \begin{bmatrix} w & 0 \\ 0 & 0 \end{bmatrix} + \bar{h}_m \rho A_s \begin{bmatrix} 1 & -1 \\ -1 & 1 \end{bmatrix} \quad (16c)$$

The first array on the right hand side is due to flow transport and the second array is due to boundary layer transport and is, in fact, the transport matrix for a *boundary layer transport element*.

This system of two ordinary differential equations may be solved to determine the time variations of the zone and the near-surface air-phase concentrations, αC and αC^* , and from this solution the adsorbent concentration response may be recovered using the assumed equilibrium relation $\alpha C_s = \alpha f(\alpha C^*)$.

An analysis of this system of equations may be found in an earlier publication (Axley 1990) where it is shown that for a Linear adsorption isotherm this model simplifies to the EA model when the rate of diffusion transport is large relative to the air flow rate (i.e. when $\bar{h}_m \rho A_s \gg w$).

The assumptions underlying this model are justified when boundary layer diffusion is slow relative to porous diffusion – a criterion similar to the Biot criterion used in heat transfer (see (Thomas and Burch 1990)). For this reason we will identify this model as the *Boundary Layer Diffusion Controlled* or *BLDC* model.

BLPD: Boundary Layer and Porous Diffusion Model

Reconsider the same zone again where, now, we isolate the zone in a one control volume and spatially discretize the adsorbent in to n slices linking it, by boundary layer mass transport αw_δ , to the zone control volume, as illustrated below in Figure 5.

In this idealization the primary dependent variables are again air phase concentrations but now we will attempt to determine the spatial variation of air phase concentration within the adsorbent pore structure with the discrete variables $\alpha C_1, \alpha C_2, \dots, \alpha C_n$. Following the strategies employed above, we will assume that the pore air phase concentrations remain in equilibrium with the adsorbed phase concentrations or:

$$\alpha C_{si} = \alpha f(\alpha C_i) ; i = 1, 2, \dots, n.$$

The mass balance relation for the zone air may be formed directly – it will be similar to Equation 15a above – but the formation of the mass balance for the adsorbent slices is a bit more challenging. Two approaches are available. In the first approach we may simply treat each slice as a control volume and formulate mass balances using average concentrations for the slice. This approach is sometimes called a *finite difference control volume* approach (e.g., see (Cunningham 1990; Shukuya and Saito 1990)) although it might be better identified as a finite or *discrete control volume* approach. The second approach, which will be taken here, is the Finite Element Approach wherein a) the form of the spatial variation of the concentration (*shape function*) is assumed for each slice and is related to the discrete concentration variables, b) a governing differential equation is identified – in our case it is the one-dimensional convection-diffusion-adsorption equation presented above, Equation 12 – and the assumed shape functions are substituted, c) a minimization principle (e.g., the Galerkin Method) is applied to formulate *element equations*, and d) the element equations are *assembled* to form the system equations.

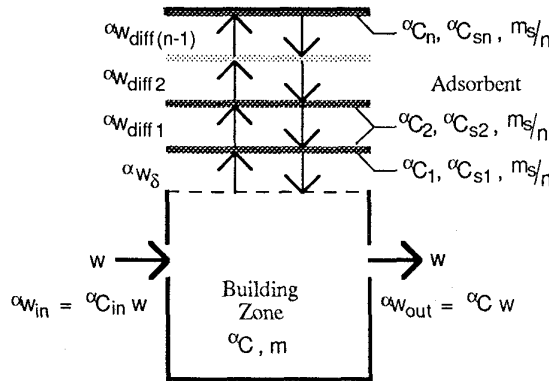


Figure 5. Single-Zone Boundary Layer Porous Diffusion Model

The application of the Finite Element Method to the one dimensional convection-diffusion equation and element assembly techniques are discussed elsewhere (Axley 1989; Huebner and Thornton 1982). Here we shall assume no Poiseuille-type flow

in the adsorbent and, therefore, need only consider the slightly simpler problem of one-dimensional diffusion with equilibrium adsorption. For linear shape functions, lumped mass, and no generation within the adsorbent, the resulting *element equations*, or, equivalently, mass balance equations for transport from node i to j are:

$$\frac{\rho A_s^{\alpha\text{-air}} D}{\delta x^e} \begin{bmatrix} 1 & -1 \\ -1 & 1 \end{bmatrix} \begin{Bmatrix} \alpha C_i \\ \alpha C_j \end{Bmatrix} + m_{\text{seff}}^e \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix} \begin{Bmatrix} \frac{d\alpha C_i}{dt} \\ \frac{d\alpha C_j}{dt} \end{Bmatrix} = \{0\} \quad (17a)$$

$$m_{\text{seff}}^e = \frac{A_s L^e}{2} \left(\rho \epsilon + \rho_s \frac{\partial \alpha f}{\partial \alpha C} \right) \quad (17b)$$

where δx^e is the *element thickness* (i.e., the thickness of each slice). For this lumped mass formulation an *element effective mass*, m_{seff}^e , appears – completely analogous to the EA and BLDC effective mass contributions – that is equal to the mass of adsorbent within one-half of the slice scaled by the slope of the adsorption isotherm plus the mass of the air within the pores of this half-slice. The transport term of this element equation (i.e., the first array of Equation 17a) is also similar to the boundary layer transport term discussed above.

The complete system of equations for this third model will not be presented due to space limitations. Suffice it to say it is simply a slight modification and extension of Equation 16 with $n-1$ additional equations. This system of equations may be solved to determine the $n+1$ air phase concentrations and then the adsorbent concentrations may be recovered using the equilibrium relation $\alpha C_{si} = \alpha f(\alpha C_i)$.

The assumptions underlying this model are not very restrictive therefore we should expect this model to provide the best estimate of system response, although at the cost of extra complexity and computation.

Discussion

Model Variants: The models developed above are each based on the general functional expression for sorption isotherms, Equation 1. The substitution of a specific isotherm relation yields a specific *member* of each *family* of models. With the three commonly-used isotherm relations defined above, Equations 2, 3, and 4, we obtain the Linear, Langmuir, and BET members of the EA, BLDC, and BLPD families. Other adsorption isotherms can also be used directly.

In all cases the slope of the isotherm (i.e., $\partial \alpha f / \partial \alpha C$) for the current state of free phase/adsorbed phase concentration is required. In many situations it is likely that the free phase/adsorbed phase concentration response will fall within a range over which this slope may be relatively constant and thus a linearized approximation to the isotherm (e.g., using a truncated Taylor's expansion) may be used to avoid this source of nonlinearity.

Model Selection: The BLPD model family provides the

most complete idealization of the zone-adsorbent system but requires an estimation of the effective diffusion coefficient and, possibly, the porosity, mean pore radius, and other physical characteristics of the adsorbent – data that may be hard to come by. It is also rather complex and, therefore, somewhat more difficult to implement. The question arises, then, when can the simpler EA or BLDC models be expected to be accurate? Following the basic strategy of the Biot criteria used in the related boundary layer/ conduction heat transfer problem we may establish model selection criterion based on a three-part ratio:

$$w : \bar{h}_m \rho A_s : \rho A_s^{\alpha\text{-air}} \mathcal{D} / \delta x \quad (18)$$

where δx is the total thickness of the flat adsorbent sheet or panel.

When boundary layer transport and pore diffusion transport are rapid relative to flow transport:

$$w \ll \bar{h}_m \rho A_s \ll \rho A_s^{\alpha\text{-air}} \mathcal{D} / \delta x \quad (19)$$

then we should expect the EA model to provide accurate predictions. When boundary layer transport and flow transport are of similar magnitude but pore diffusion transport is large:

$$w \approx \bar{h}_m \rho A_s \ll \rho A_s^{\alpha\text{-air}} \mathcal{D} / \delta x \quad (20)$$

we should expect the BLDC model to provide accurate results. Finally, if all transport process are of similar magnitude or the first two are greater than the porous diffusion rate:

$$w \approx \bar{h}_m \rho A_s \approx \rho A_s^{\alpha\text{-air}} \mathcal{D} / \delta x \quad (21)$$

we should use the complete BLPD model.

Multi-Zone Analysis: The models developed above presumed that adsorption was local to the single zone being considered. It was also shown that these models can be assembled from boundary layer transport element equations, Equation 16c, pore diffusion transport elements, Equation 17a, and/or adsorption capacitance terms, Equations 14b, 16b, or 17b. For multi-zone modeling of adsorption that is local to a given zone it is theoretically and physically consistent to expect that these same elements may be used directly to model either EA, BLDC, or BLPD dynamics local to each zone in question. Indeed, one may directly consider a mixed model wherein some zones include EA assemblages (e.g., due to curtain fabric adsorption), others include BLDC adsorption (e.g., due to carpet adsorption), while yet others include BLPD adsorption dynamics (e.g., moisture adsorption in wood construction). (See (Axley 1989) regarding the *element assembly* approach for multi-zone analysis.)

For multi-zone adsorption that is not local to single zone – for example, due to bulk flow through the adsorbent from one zone to another or equivalently due to bulk flow through an adsorbent filter system – then the complete one-dimensional convection-diffusion equation, Equation 12, and the element equations derived from it (see (Axley 1989; Huebner and Thornton 1982)) hold promise.

APPLICATION & VALIDATION

In this section we will briefly review the results of

comparisons of measured data with model predictions using results of two studies conducted at the National Institute of Standards and Technology. Both studies examine gyboard adsorption but the first study considered the adsorption of formaldehyde gas (HCHO) while the second study considered water vapor adsorption.

NIST Formaldehyde Sorption Study

Silberstein studied the HCHO adsorption and desorption dynamics of a 1.2 m x 2.4 m specimen of 0.013 m thick gyboard that was attached to one wall of a 1.22 m x 2.44 m x 0.61 m test chamber (Silberstein 1989). The test chamber was placed in a closed environment maintained at 23 °C and 50% RH, a constant fresh air flow rate through the chamber of approximately 1 air change per hour was maintained, and formaldehyde gas was introduced into the chamber at a constant rate for eleven days. This test was modeled with the EA, BLDC, and BLPD models using the Linear adsorption isotherm with a partition coefficient of 5.5 g-air/g-gyboard. The average mass transfer coefficient was determined using the correlation given above, Equation 6, with the boundary layer Reynolds number estimated to be $Re_L = 287$ by assuming a velocity profile within the chamber similar to that which would occur in a duct with the same volumetric flow rate. The comparison of measured response to predicted response is shown below in Figure 6 for $Re_L = 287$ and in Figure 7 for a Reynolds number ten times this value.

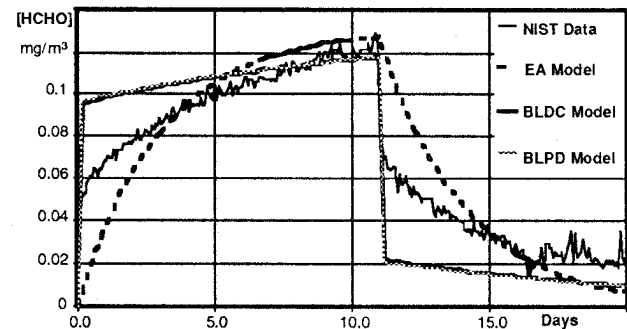


Figure 6. HCHO Sorption on Gyboard: $Re_L = 287$

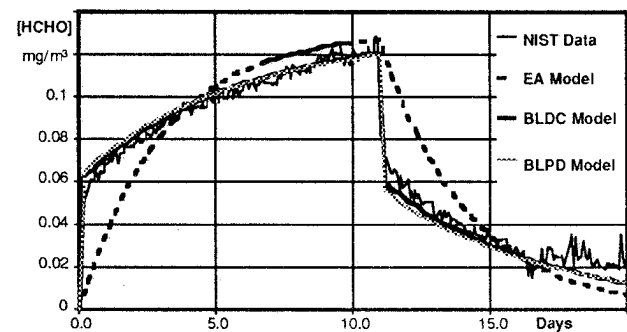


Figure 7. HCHO Sorption on Gyboard: $Re_L = 2870$

The measured and predicted responses are seen to be of exponential nature with time constants on the order of days while the nominal time constant of the test chamber, based on the air

flow rate of one air change per hour, was just one hour. Thus, in this case adsorption transport has indeed a significant impact. The EA model, being a single-degree-of-freedom model, approximates the response with a single exponential and provides a reasonable estimate of the overall response but does not capture the early rapid rise of the adsorption and rapid fall of the desorption phases.

The BLDC model is a two-degree-of-freedom model and as such the response is represented by the sum of two exponentials. Here, these two exponentials have very different time constants and as a result the BLDC captures the early rapid rise of the adsorption and fall of the desorption phases.

For this case the mass transport ratios are, for $Re_L = 287$:

$$w : \bar{h}_m \rho A_s : \rho A_s \alpha_{\text{air}} D / \delta x = 2200 : 817 : 5320$$

and for $Re_L = 2870$

$$w : \bar{h}_m \rho A_s : \rho A_s \alpha_{\text{air}} D / \delta x = 2200 : 2580 : 5320$$

so we should expect the BLDC and BLPD models to yield similar results – the results bear this out. It is seen that the results are sensitive, however, to the boundary layer mass transfer. With a ten fold increase in Reynolds number (i.e., a $\sqrt{10}$ increase in mass transfer) we move from poor to a very good prediction of response.

NIST Water Vapor Sorption Study

Thomas and Burch studied the desorption of water from a small circular specimen of gypboard, 0.18 m in diameter and 0.013 m thick, with edges and one surface sealed with wax and the remaining surface exposed to a test chamber maintained at constant conditions of relative humidity (Thomas and Burch 1990). An initial moisture content corresponding to a mass fraction of 0.0133 g-water/g-gypboard was established by placing the specimen in the test chamber maintained at 73.6 % RH, 23.6 °C for forty days. The specimen was then quickly removed and placed in a chamber maintained at 25.7 % RH, 23.6 °C until equilibrium was established. This test was modeled with the BLDC, and BLPD models using an adsorption isotherm, an average mass transfer coefficient, and an effective diffusivity determined experimentally by the investigators:

$$C_{se} = \frac{1.37 C_e}{1.37 C_e + (1 + 504 C_e)(1 - 52 C_e)}$$

$$\bar{h}_m = 1.57 \text{ m/h} ; \text{H}_2\text{O-air } D = 0.022 \text{ m}^2/\text{h}$$

(This air-phase diffusivity is equivalent to the adsorbed-phase diffusivity actually reported by Thomas and Burch.) For this limiting case, with no air mass flow through the chamber (zone), the EA model may not be applied.

The comparison of measured response to predicted response is shown in Figure 8 for the BLDC model and the BLPD model using using 5- and 10-element meshes. From these results it is clear that the adsorption dynamics in this case are porous-diffusion controlled demanding a relatively fine element mesh to capture the response. The nominal mass transport ratios

support this conclusion:

$$\bar{h}_m \rho A_s : \rho A_s \alpha_{\text{air}} D / \delta x = 471 : 49$$

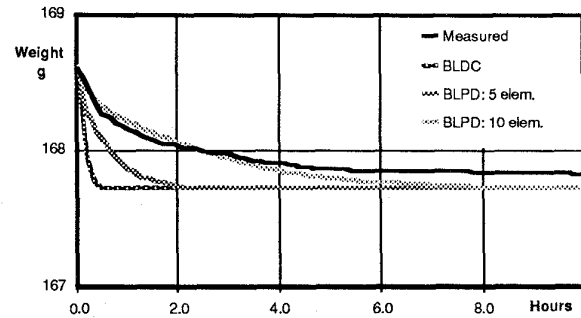


Figure 8. H₂O Desorption From Gypboard

CONCLUSION

Three families of adsorption dynamics models, based upon fundamental principles of adsorption science, have been presented. These models account for a) the equilibrium limits of reversible sorption processes, b) boundary layer diffusion transport at the adsorbent surface, and/or c) diffusion transport within the adsorbent proper. Individual members of the model families are distinguished by the sorption equilibrium model used in the model formulation. Importantly, the parameters of these models – the equilibrium adsorption characteristics of the adsorbate-adsorbent system being considered, the mass transfer coefficient associated with boundary layer transport, and the effective diffusivity of the adsorbate within the adsorbent – may be measured directly, using standard test procedures, or may be estimated using available theory. That is to say, the models presented are fundamentally based and not empirically determined.

Criteria are presented, analogous to the Biot criteria used in heat transfer, that provide a basis for model selection. First comparisons with experimental results have been promising showing that accurate predictions of response may be realized if the appropriate model is employed as indicated by the criteria. In the cases studied, it was apparent that dynamic predictions were sensitive to a) the value of the boundary layer mass transfer coefficient for boundary layer limited diffusion and b) the mesh refinement for porous diffusion limited dynamics. This sensitivity reflects the physical sensitivity of the systems and is not a numerical artifact.

The models presented apply to adsorption processes that are local to a zone, therefore, it is argued, these models may be directly integrated with existing multi-zone contaminant dispersal analysis methods to model local sorption dynamics. *Element equations* to do this are presented. The fundamental theory presented may, however, be applied to the more general cases of adsorption transport between zones due to bulk transfer through adsorbents (e.g., transport through building construction and through filtration devices). Future studies should be directed toward these potential applications.

ACKNOWLEDGEMENT

The first phase of the research reported here was supported by the Indoor Air Quality and Ventilation Group of the U. S. National Institute of Standards and Technology through funding provided by the U. S. Department of Energy.

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