HALF-LIFE TIME FOR VOC EMISSION AND SORPTION OF POROUS BUILDING MATERIALS

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ABSTRACT

Most labeling or regulating systems for VOC emissions from building materials and furnishings adopts the maximum emission rate or concentration as a criterion. This criterion alone, however, may not be sufficient for solid (dry) building materials of which emissions are often characterized by low emission rates with slow decay rates. Half-life time, which is often adopted for decaying problems, can be a good supplement. For material emissions, half-life time can be defined as the time required emitting 50% of the initially contained VOC mass in the material. For sink effect, it is defined as the time to absorb 50% of the maximum VOC mass that the material can absorb for a given indoor air VOC concentration.

This study theoretically calculates the half-life time for VOC emission and sorption of porous building materials. The analytical model considers the internal diffusion and physical adsorption in the porous solid, and the convection over the upper surface of the material. The effects of air velocity (expressed as Reynolds number) and material properties on the half-life time were investigated. The theoretically calculated half-life time were compared with experimentally measured half-life time available in literature.

INTRODUCTION

Building materials are major sources of indoor air pollutants like volatile organic compounds (VOC). In order to control and reduce the VOC emissions from the building materials, several labeling or regulating systems have been introduced [Kukkonen et al., 2002;DSIC, 2000; Oppl, 1999]. The commonly adopted criterion is the maximum emission rate or concentration of TVOC and some carcinogenic compounds considering only the primary emission.

For wet surface coating materials like paint and wood stain, the emissions are characterized by the initially high VOC emission rates with fast decay rates; hence, regulating only the maximum emission rate or concentration can be sufficient. This criterion alone, however, may not be an effective measure for solid (dry) building materials. Solid materials show relatively low emission rates with slow decay rates. In terms of the primary emission source, solid materials are less significant than wet materials; however, porous solid materials also act as secondary emission sources through sorption processes, resulting in lower chamber air concentration but prolonged emissions. Therefore, VOC emissions from solid materials needs to be assessed in terms of time as well as the maximum emission rates. The labeling system used in Denmark and Norway (2000) adopted a time criterion, i.e., indoor-relevant time-value, which is defined as the time required to reach the acceptable concentration (50% of the minimum value between odour and irritation thresholds) of indoor climate under standard conditions. The indoor-relevant time-value is limited for primary emission only.

Half-life time is generally applied for decaying problems, e.g., decay of radioactive substances. In this study half-life time is adopted as a measure to characterize the VOC source (emission) and sink (sorption) effects of porous solid building materials. This study theoretically calculates the half-life time using an analytical model that considers the internal diffusion and physical adsorption/desorption within the porous material, and the boundary layer resistance due to convection over the material. A parametric study was carried out to investigate the dependence of half-life time on the material properties (diffusion coefficient, porosity, sorption property, thickness and length) and the air velocity (expressed as Reynolds number).

Meininghaus et al. (2000) measured material properties like diffusion coefficient and sorption properties of various building materials through twin chamber tests using the CLIMPAQ type chambers, and also reported half-life time obtained from the desorption-phase data. These data were compared with the theoretically calculated a half-life time.

ANALYTICAL MODEL DEVELOPMENT

Figure 1 shows the schematic diagram of the VOC source and sink problem considered. A porous solid material of length L, and thickness b, has a constant gas-phase effective diffusion coefficient $D_{e,g}$, effective adsorbed-phase or surface diffusion coefficient $D_{e,ad}$, sorption property K, porosity ε, and initial concentration C_o. There is no mass transfer along the edges of the solid. The boundary layer exists due to laminar or turbulent convection over the solid and the VOC concentration in the ambient air (C_∞) can be a function of time. The convection mass transfer coefficient (h_D) can be obtained from Sherwood number correlations.

The governing equation of one-dimensional gas-phase and surface diffusions within the porous material including physical adsorption/desorption is given by,

$$\varepsilon \frac{\partial C}{\partial t} + \frac{\partial C_{ad}}{\partial t} = D_{e,g} \cdot \frac{\partial^2 C}{\partial y^2} + D_{e,ad} \cdot \frac{\partial^2 C_{ad}}{\partial y^2} \tag{1}$$

where,

ε = porosity [dimensionless];
C = the gas-phase VOC concentration [$\mathrm{mg_{voc}/m^3_{air}}$];
C_{ad} = physically adsorbed-phase VOC concentration [$\mathrm{mg_{voc}/m^3_{material}}$];
$D_{e,g}$ = effective diffusion coefficient for gas-phase diffusion [$\mathrm{m^2/s}$];
$D_{e,ad}$ = effective diffusion coefficient for adsorbed-phase or surface diffusion [$\mathrm{m^2/s}$];
y = space coordinate [m];
t = time [s]

An adsorption isotherm relates the adsorbed-phase concentration (C_{ad}) with the gas-phase concentration (C). In this model, Henry (linear) isotherm was used considering relatively low VOC concentration levels compared to the saturation VOC concentration,

$$C_{ad} = K \cdot C \tag{2}$$

where, K = sorption partition coefficient [$\mathrm{m^3_{air}/m^3_{material}}$]

Substituting this into Equation (1) gives,

$$(\varepsilon + K)\frac{\partial C}{\partial t} = (D_{e,g} + K \cdot D_{e,ad})\frac{\partial^2 C}{\partial y^2} \tag{3}$$

Let us define the overall effective diffusion coefficient of the porous material (D_s) as follows,

$$D_s = D_{e,g} + K \cdot D_{e,ad} \tag{4}$$

Applying Equation (4), Equation (3) becomes,

$$\frac{\partial C}{\partial t} = \frac{D_s}{(\varepsilon + K)} \cdot \frac{\partial^2 C}{\partial y^2} \tag{5}$$

The third boundary condition was used to describe the convection mass transfer. This is imposed at the upper surface of the solid as follows,

$$-D_s \frac{\partial C}{\partial y} = h_D\left(C_w - C_\infty(t)\right) \qquad \text{at } y = 0 \qquad (6)$$

where, h_D = the convection mass transfer coefficient [m/s];

C_w = VOC concentration at the material-air interface [mg/m^3];

C_∞ = VOC concentration in the ambient air [mg/m^3]

Since only one solid material is considered, there is no mass flux at the bottom surface of the solid.

$$\frac{\partial C}{\partial y} = 0 \qquad \text{at } y = -b \qquad (7)$$

Initially (at t=0) the solid material is assumed to have a uniform VOC concentration (C_o).

$$C = C_O \qquad \text{at } t = 0,\ -b \le y \le 0 \qquad (8)$$

The governing equation, Equation (5), can be nondimensionalized as follows,

$$\frac{\partial \theta}{\partial t^+} = \frac{1}{(\varepsilon + K)} \cdot \frac{\partial^2 \theta}{\partial {y^+}^2} \qquad (9)$$

and the nondimensional variables are taken as

$$\theta = \frac{C - C_\infty}{C_o - C_\infty};$$

$$t^+ = \frac{t}{t_d} = \frac{t}{b^2 / D_s} = Fo; \qquad (10)$$

$$y^+ = \frac{y}{b};$$

The initial and the boundary conditions in Equations (6) to (8) become,

$$\frac{\partial \theta}{\partial y^+} + Bi \cdot \theta = 0 \qquad \text{at } y = 0 \qquad (11)$$

$$\frac{\partial \theta}{\partial y^+} = 0 \qquad \text{at } y = -b \qquad (12)$$

$$\theta = 1.0 \qquad \text{at } t = 0,\ -b \le y \le 0 \qquad (13)$$

where, Bi is the Biot number ($Bi = h_D \cdot b/D_s$).

The governing equation for $\theta(y^+,t^+)$, Equation (9), together with the boundary conditions given in Equations (11) and (12), and the initial condition given in Equation(13) is of the so-called diffusion type (parabolic in time and elliptic in space) and can be solved analytically using the integral transform method [Özisik, 1980]. The nondimensionalized VOC concentration, $\theta(y^+,t^+)$ in the solid is given as

$$\theta(y^+,t^+) = 2\sum_{m=1}^{\infty}\left[\frac{\mathrm{B}_m{}^2 + Bi^2}{\mathrm{B}_m{}^2 + Bi + Bi^2}\right]\cdot\cos\left\{\mathrm{B}_m\cdot\left(y^+ + 1\right)\right\}\cdot e^{-\frac{\mathrm{B}_m{}^2}{\varepsilon+K}\cdot t^+}\left[\frac{\sin\left(\mathrm{B}_m\right)}{\mathrm{B}_m}\right] \tag{14}$$

where, B_m's are the eigenvalues, which are the positive roots of the following equation,

$$\mathrm{B}\cdot\tan\left(\mathrm{B}\right) = Bi \tag{15}$$

THEORETICAL INVESTIGATION ON HALF-LIFE TIME

In the nondimensional analytical model, the independent parameters are (ε+K) and Biot number (Bi). Since Bi is the ratio of the diffusion to convection resistance of mass transfer, it is comprised of material properties (b and Ds) and the convection property (h_D), which is a function of Reynolds number and Schmidt number. The effects of these parameters on the half-life time was investigated

N-octane at the temperature of 25°C was used as VOCs of interest. Hence, the Schmidt number was set as 2.57 and the diffusion coefficient in the air (D_a) is 6.0x10-6 m^2/s. In this study, the effect of Schmidt number was not investigated since the Schmidt number for various VOC varies in a relatively small range, 0.9 – 3.1 [Sparks, et al., 1996]. (ε+K) was varied from 10 to 10^5. The porosity (ε) is within the range of 0 to 1; however, K varies significantly. Cox et al. (2001b) measured the sorption partition coefficients of various VOCs on the vinyl flooring and reported that they may vary from 810 to 4.2×10^5. Biot number (Bi) is defined as ($h_D\times b$)/D_s, which is the ratio of the diffusion to convection resistance of mass transfer. Bi was varied from 9.1×10^{-3} to 2.9×10^5, which were determined from the combination of separate ranges of D_a/D_s, b/L, and Re_L. D_a/D_s was varied in the range of 10 to 10^5. This range was decided based on the previous study, which showed the range of measured D_a/D_s for gas-phase diffusion of various building materials are from 4.42 to 1.55 $\times10^4$ [Haghighat et al., 2002]. The thickness to length ration (b/L) was varied from 10^{-4} to 10^{-2}. The Reynolds number was varied from 10^2 to 10^5, which is equivalent to the air velocity from almost stagnant to 0.34 m/s when the solid length L = 4.5m. The mass transfer coefficient (h_D) was obtained from the Sherwood number relation for the laminar forced convection over a flat plate [Holman, 1990],

$$Sh_L = 0.664\cdot \mathrm{Re}_L^{\frac{1}{2}}\cdot Sc^{\frac{1}{3}} \tag{16}$$

where

Sh_L = Sherwood number (Sh_L= $h_D\cdot L/D_a$)
Re_L = Reynolds number (Re_L= $u_\infty\cdot L/\nu$)
Sc = Schmidt number (Sc=ν/D_a)
L = material length [m]
D_a = diffusion coefficient in the air [m^2/s]
u_∞ = air velocity in the ambient air [m/s]
ν = kinematic viscosity [m^2/s]

The maximum mass of gas-phase VOC that can be emitted from or be absorbed by a porous material per unit area m_{max} is

$$m_{\max} = \left|C_o - C_\infty\right|\times b \tag{17}$$

where, m_{max} has the unit of [mg/m^2]. The half-life time($t_{0.5}$) is defined as the time required to emit/sink 50% of m_{max} from/into the material. In other words, $t_{0.5}$ is the time required emitting 50% of the initially contained VOC mass in the material for material emissions; and for sink effect, the time to absorb 50% of the maximum VOC mass that the material can absorb for a given indoor air VOC concentration. Since the nondimensional model was used, $t_{0.5}$ is normalized by the diffusion characteristic time, t_d, which is defined as b^2/D_s, and denoted as $t_{0.5}{}^+$.

Figure 2 presents the effects of (ε+K) and Biot number on $t_{0.5}^+$. Figure 2 (a) shows that as Biot number increases, $t_{0.5}^+$ decreases. However, when Biot number is larger than 10, in other words, if the diffusion resistance is 10 times larger than the convection resistance, $t_{0.5}^+$ becomes almost constant. As (ε+K) increases, $t_{0.5}^+$ increases. As shown in Figure 2 (b), (ε+K) has linear impact on $t_{0.5}^+$.

Biot number is a nondimensional parameter that gives the ratio of diffusion resistance to convection resistance, and can be rewritten as follows:

$$Bi = \frac{h_D \cdot b}{D_s} = \frac{h_D \cdot L}{D_a} \cdot \frac{D_a}{D_s} \cdot \frac{b}{L} = Sh_L \cdot \left(D_a / D_s\right) \cdot \left(b/L\right) \tag{18}$$

Substituting the Sherwood number correlation of Equation (16) into Equation (18) gives,

$$Bi = 0.664 \cdot \mathrm{Re}_L^{\frac{1}{2}} \cdot Sc^{\frac{1}{3}} \cdot \left(D_a / D_s\right) \cdot \left(b/L\right) \tag{19}$$

Instead of lump summed effect of Biot number, the effects of separate parameters, i.e., Re_L, (D_a/D_s) and (b/L), on $t_{0.5}^+$ were investigated.

Applying all combinations of material parameters and Reynolds number, the observed trends on $t_{0.5}^+$ are presented in Figure 3, where, $t_{0.5}^+$ is plotted versus $(D_a/D_s)\times(b/L)$ and (ε+K) for various Re_L. For a given set of material properties, $t_{0.5}^+$ increases as Re_L decreases: when $(D_a/D_s)\times(b/L)$ is 0.01 and (ε+K) is 100, $t_{0.5}^+$ is 45.7 for $Re_L=10^5$, while $t_{0.5}^+$ is 785 for $Re_L=10^2$. This figure also shows that as $(D_a/D_s)\times(b/L)$ increases the effect of Re_L decreases. When $(D_a/D_s)\times(b/L)$ is 0.01, $t_{0.5}^+$ for $Re_L=10^2$ is 17 times larger than that for $Re_L=10^5$, while the same ratio drops to 1.41 when $(D_a/D_s)\times(b/L)$ is 1.0. The influence of Re_L diminishes when $(D_a/D_s)\times(b/L)$ is larger than 1.0. In other words, the assumption of negligible convection is valid for values of $(D_a/D_s)\times(b/L)$ larger than 1.0. In that region, $t_{0.5}^+/(\varepsilon+K)$ is almost constant. Hence, the dimensional half-life time, $t_{0.5}$, becomes,

$$t_{0.5} \approx A_1 \cdot \left(\varepsilon + K\right) \cdot t_d = A_2 \cdot \left(\varepsilon + K\right) \cdot \left(b/L\right)^2 \cdot \left(D_a / D_s\right) \tag{20}$$

where, A_1, A_2 are constants, i.e., $A_2 = A_1 \cdot L^2/D_a$ [s]. Equation (20) indicates that (b/L) can have more significant impact on $t_{0.5}^+$ than that of (ε+K) and (D_a/D_s).

COMPARISON WITH EXPERIMENTAL HALF-LIFE TIME

Meininghaus et al. (2000) carried out two-flow system small-scale chamber tests to study diffusion and sorption of VOCs (n-octane and ethyl acetate) in various building materials. The material specimen was placed between two identical chambers (i.e., CLIMPAQ type). Air with constant VOC concentration is introduced in one chamber, while clean air is supplied to the other chamber for sorption phase, i.e., 24 hours for n-octane and 48 hours for ethyl acetate. In desorption phase, clean air was introduced in both chambers.

From the experimental data, they obtained the effective diffusion coefficient and sorption properties (sorption capacity and sorption partition coefficient). They also measured half-life time, which was defined as the time when the VOC concentration in chamber air has dropped down to one-fourth (due to two-flow system) of initial concentration at the beginning of desorption phase. The half-life time was reported for five building materials: carpet, aerated concrete, solid concrete, brick wall, and gypsum board.

The experimentally determined half-life time of those five materials was compared with the theoretically calculated one using the previously described analytical model. The input values of independent parameters were obtained from the reported data of material properties (i.e., diffusion coefficient, sorption partition coefficient, thickness, length and density) and experimental conditions (i.e, 0.08 m/s of air velocity at 10cm above the material surface, 24±0.5°C). Since the reported sorption partition coefficient is mass based, it was converted to volume based one using following relation.

$$K = K_m \cdot \frac{\rho_m}{\rho_a} \tag{20}$$

where,

K = volume based sorption partition coefficient [$m^3_{air}/m^3_{material}$]
K_m = mass based sorption partition coefficient [kg $_{air}$/kg $_{material}$]
ρ_m = density of the material [kg/m^3]
ρ_a =density of air [kg/m^3]

Since the porosity was not reported and it varies in small range compared to K, it was assumed that $(\varepsilon+K) \approx K$. Table 1 summarizes those input values for n-octane case.

Table 1. Summary of input values

Material	D_a/D_s	b/L	K [$m^3_{air}/m^3_{material}$]	Bi	t_d (=b^2/D_s) [s]
Carpet with SBR backing	8.56	8.46×10^{-3}	94.7	4.76	206
Aerated concrete	7.89	2.09×10^{-2}	80.9	10.8	580
Solid concrete	57.7	1.49×10^{-2}	60.0	56.6	2170
Brick wall	18.5	2.49×10^{-2}	22.6	30.2	1920
Gypsum board	7.15	$1.24 \times 10_{-2}$	68.4	5.84	186
n-octane: D_a=6.0x10^{-6} [m^2/s]; L=1.005 [m]; u_∞ =0.08 [m/s]; ρ_a=1.19 [kg/m^3]; Re_L=5211; Sc =2.57					

Figure 4 presents comparison between experimentally obtained half-life time ($t_{0.5}^+$) and theoretically calculated $t_{0.5}^+$. For small Biot number cases like carpet and gypsum board, the theoretically calculation underestimates $t_{0.5}^+$, but for larger Bi, it overestimates $t_{0.5}^+$. The error was less than 30% for low Bi cases (Bi=10.8 or less). For brick wall, the error is 84%. The maximum difference was observed for solid concrete case, which has the largest Bi: theoretically calculated $t_{0.5}^+$ is three times larger than experimental $t_{0.5}^+$. The errors may be caused not only by the difference in the boundary conditions between the analytical model and the experiment, but also by the difference in the definition of half-life time. While the theoretical calculation is based on the accumulated mass that has emitted or sorbed, the experimental half-life time is based on the VOC concentration.

Figure 5 presents the difference in half-life time due to the discrepancy in the definition: mass-based or concentration-based. $t_{0.5}^+$ of both cases were obtained using the analytical model; hence, there is no difference in boundary conditions. The mass-based $t_{0.5}^+$ is defined as the time required to emit/sink 50% of m_{max} in Equation (17) from/into the material, and the concentration-based $t_{0.5}^+$ is defined as the time required the nondimensioinalized wall concentration (θ_w) to reach 0.5. The error increases as Bi increases. For the cases of Bi = 9.1 or larger, mass-based $t_{0.5}^+$ becomes much larger than concentration-based $t_{0.5}^+$. This may explain the significant overestimation of $t_{0.5}^+$ in theoretical calculation compared to the experimental data for larger Bi cases like solid concrete. The difference between the analytical model, and the experimental set-up and procedures, can cause the additional error and be possible reasons behind the underestimation of $t_{0.5}^+$ in theoretical calculation for carpet and gypsum board cases. This, however, needs further investigations.

CONCLUSION

The half-life time for emission/sorption of porous building materials, was theoretically investigated. In this study, half-life time was defined as the time required to emit or absorb 50% of maximum transferable VOC mass. The parametric study leads to the following conclusion:

- The linear effect of $(\varepsilon+K)$ is observed for $t_{0.5}^+$. The effect of Bi, however, is nonlinear: as Bi increases, $t_{0.5}$ decreases, but for Bi larger than 10, $t_{0.5}^+$ becomes almost constant.
- When Bi is decomposed into Re_L and material properties, i.e., $(D_a/D_s)\times(b/L)$, the parametric study shows that the effect of Re_L decreases as $(D_a/D_s)\times(b/L)$ increases, and if $(D_a/D_s)\times(b/L)$ is larger than 1.0, there is little effect of Re_L on $t_{0.5}^+$.

The theoretically calculated half-life time was compared with experimentally measured one by Meininghaus et al. (2000) using the reported material properties and flow properties. For low Biot number cases, the error is less than 30%. The error becomes significant for larger Biot number cases. This may be caused by the difference in the definition of half-life time. Theoretical study uses mass-based half-life time, while experimental data was obtained from concentration-based one. It was demonstrated that as Biot number increases, the difference between mass-based half-life time and concentration-based one increases. Other factors like difference in boundary conditions, geometry, etc. can cause additional error, but this needs further investigations.

ACKNOWLEDGEMENT

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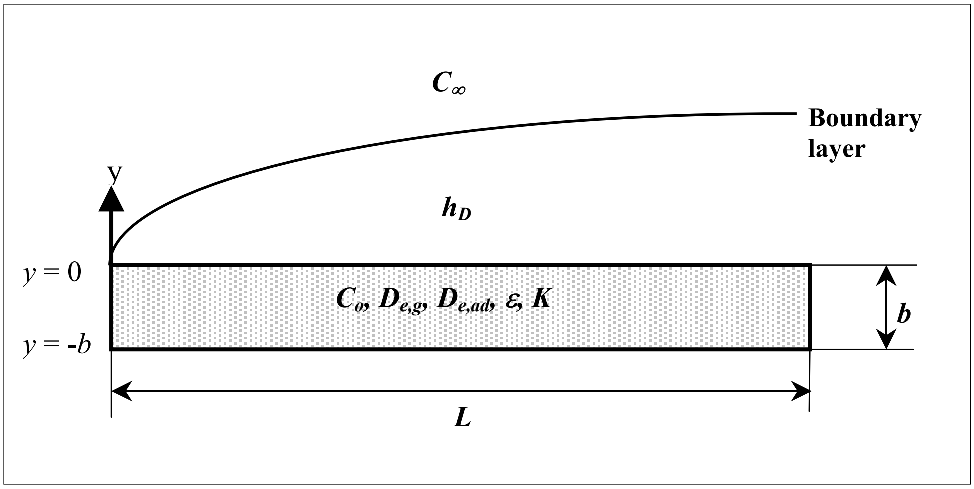

Figure 1. Schematic diagram of the model

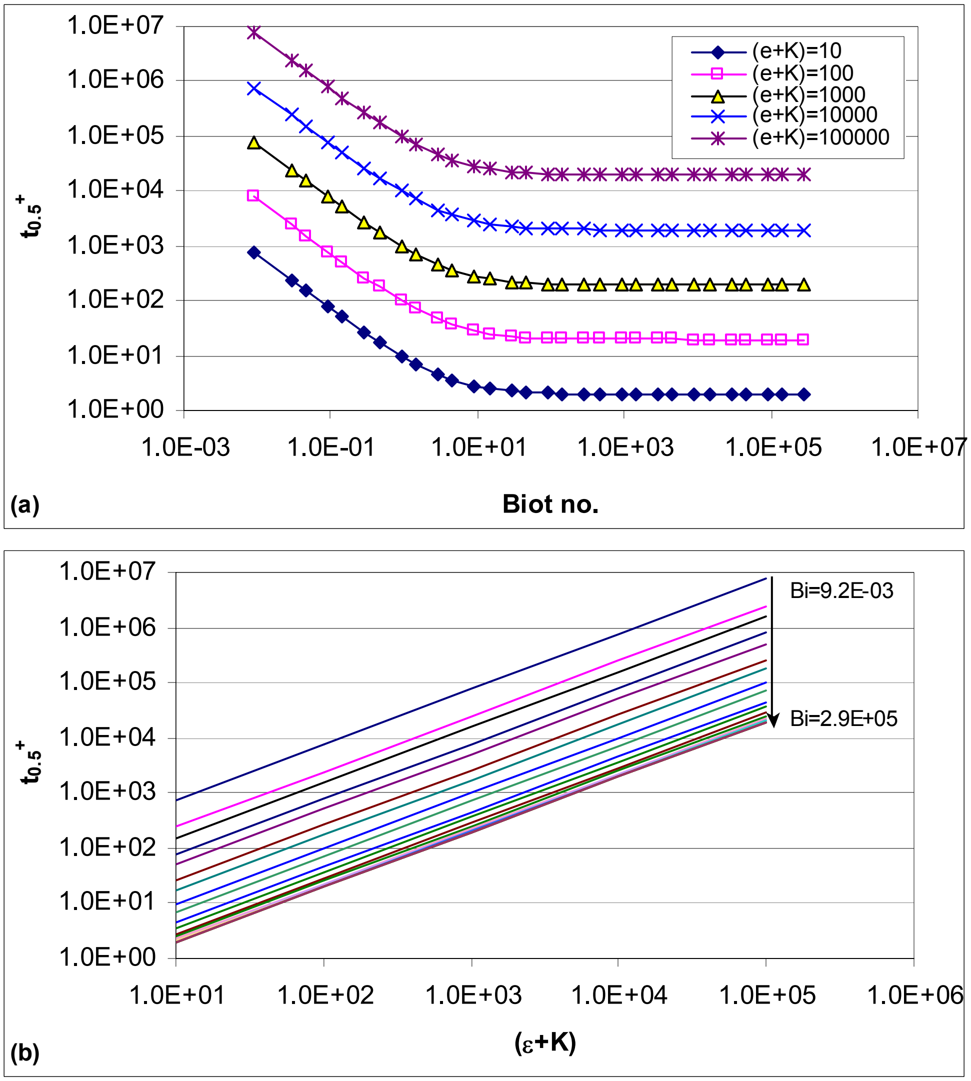

Figure 2. Effects of (ε+K) and Biot number on the half-life time, $t_{0.5}^+$

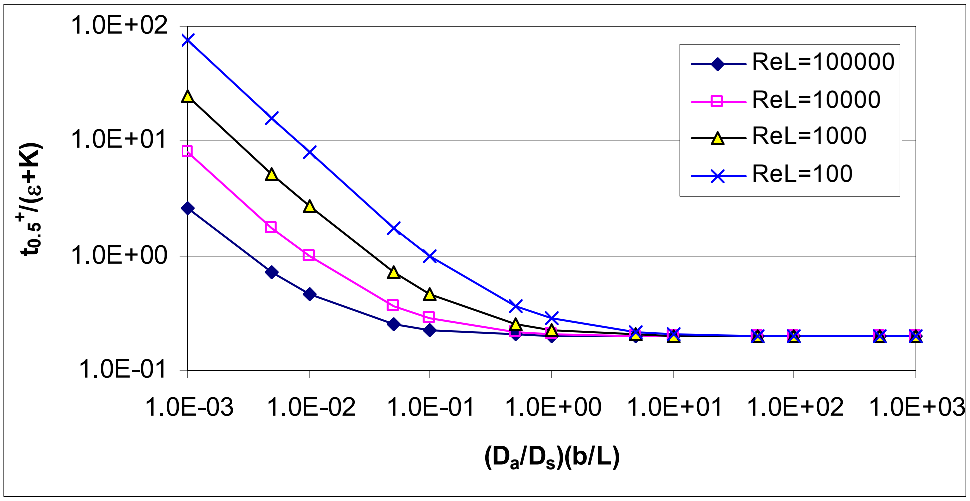

Figure 3. Effects of Reynolds number on the half-life time, $t_{0.5}^+$

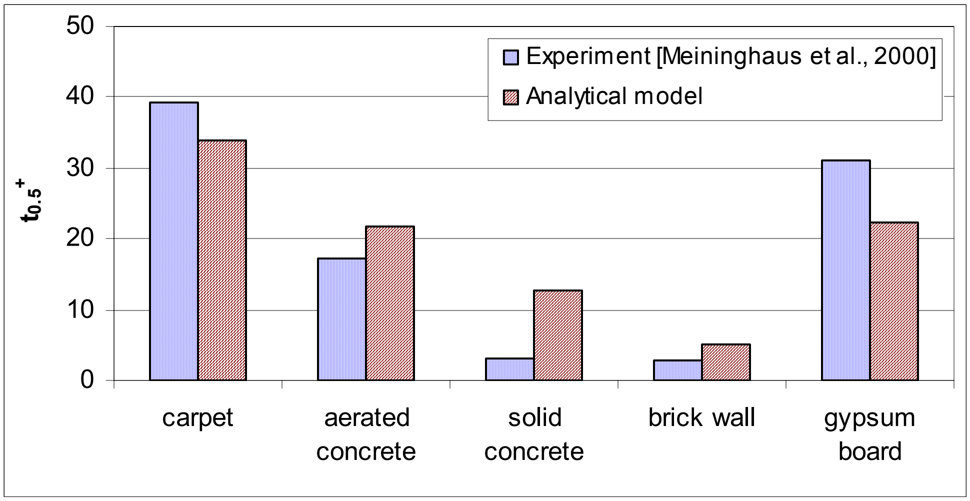

Figure 4. Theoretical versus experimental half-life time

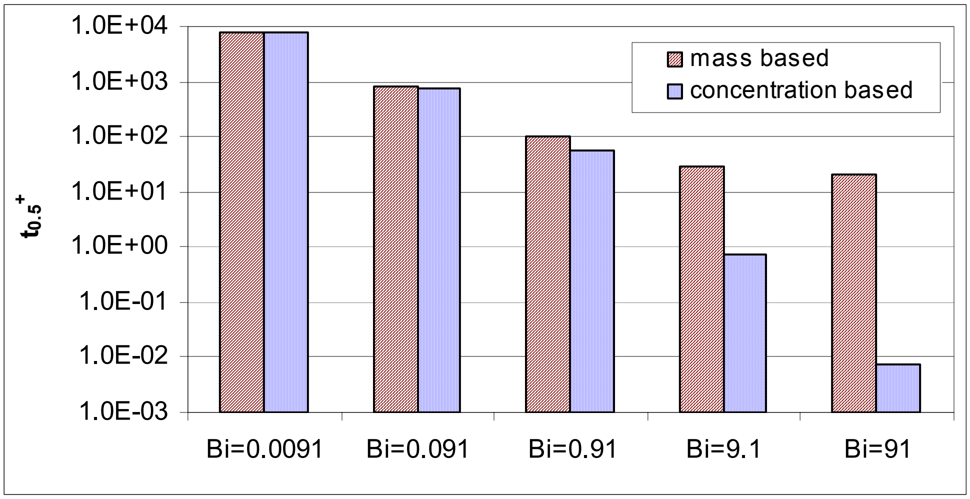

Figure 5. Mass-based half-life time vs. concentration-based half-life time