Experimental and theoretical investigations of oxygen phase transfer

H. GEISTLINGER, D. LAZIK, A. BECKMANN & G. KRAUSS
UFZ Centre for Environmental Research Leipzig-Halle, Theodor-Lieser-Straße 4,
D-06120 Halle, Germany
e-mail: geis@hdg.ufz.de

Abstract Based on the stagnant film model two different mass transfer models are discussed and estimates for the mass transfer coefficient are calculated: The diffusive film model value is $2 \times 10^{-7}$ m s$^{-1}$ and the Sherwood number value is $8.1 \times 10^{-8}$ m s$^{-1}$. These values are in good agreement with the experimental values, which lie in the range from $6 \times 10^{-7}$ to $4 \times 10^{-6}$ m s$^{-1}$.

Key words column experiments; kinetic model; mass transfer; oxygen phase transfer

INTRODUCTION

Oxygen phase transfer plays an essential role in understanding the oxygen-limiting processes of “natural attenuation” and for predicting the efficiency of in situ technologies, like biosparging and oxygen bubble walls. The accurate description of contaminant transport and fate in many subsurface multiphase systems requires good estimates of the rate constant $k_0$, i.e. the product of the specific interfacial area and the microscopic transfer coefficient $\alpha$. Since both the trapped NAPL-dissolution and the trapped gas phase dissolution are strongly controlled by the liquid-phase mass transfer, one would expect similar transport equations (Frid et al., 1999; Geistlinger, 2001a) and a similar $\alpha(Re)$-relationship ($Re =$ Reynolds number) (Miller et al., 1990). Based on the stagnant-film model an empirical Sh(Re)-relationship (Sh = Sherwood number) is used, in order to calculate estimates for $\alpha$. These values are compared with the experimental ones given by Donaldson et al. (1997); in the following we refer to their paper as DON97.

This work is of special interest, since it is the only one that provides experimental values for the microscopic transfer coefficient $\alpha$. The parameter identification algorithm is based on the constant volume approach. The authors derive a value that is two orders of magnitude larger ($\alpha \approx 10^{-6}$ m s$^{-1}$) than the stagnant-film model value ($\approx 10^{-8}$ m s$^{-1}$). The conclusion would be that the stagnant film model breaks down for velocities larger than 4 m day$^{-1}$. We re-interpret the experimental results of DON97 and obtain $\alpha \approx 10^{-8}$ m s$^{-1}$. The reason for this discrepancy is that in DON97 the wrong differential equation for the residual gas phase was used. Therefore our main conclusion is that the stagnant film model is still valid for higher velocities (up to 10 m day$^{-1}$) and gives the right order of magnitude for $\alpha$. The objective of this paper is the re-interpretation of the column experiments from DON97.
MASS TRANSFER MODELS

Stagnant-film model

Most existing models for NAPL-dissolution or gas dissolution are based on the stagnant-film model, which is shown in Fig. 1(a). The constant concentration gradient within the thin stagnant film is simply given by the ratio of the diffusion coefficient and the film thickness $\delta_w$.

$$\Delta C / \Delta t = \frac{\Delta N}{\Delta t}$$

$C_w$ is the concentration in the water phase and $C_g$ is the concentration in the gas phase.

![Fig. 1 The stagnant-film model.](image)

Diffusive-film model, Sherwood number relationship

To understand the intrinsic velocity dependence of the microscopic mass transfer coefficient $\alpha(u_w)$ it is instructive to consider the following diffusive-film model (see Fig. 1(b)). Assuming that the flow is parallel to the phase boundary, the time for traveling along the phase boundary $L$ is $t_L = L/u_w$. The important point is that a particle (black circle in Fig. 1(b)), which "jumps" into the water phase at the left 3-phase boundary (solid grain-water phase-gas phase), travels away a certain distance, $A = \delta_w$, the diffusion length, from the 2-phase boundary during this time $t_L$. This distance is just the thickness of the stagnant film $\delta_w$. Based on the stagnant film model (Schwarzenbach et al., 1993) one obtains for the velocity-dependent mass transfer coefficient:

$$\alpha(u_w) = \frac{D_w \delta_w}{H} = \frac{D_w}{H \sqrt{D_w L}} = \frac{1}{H} \left( \frac{D_w u_w}{L} \right)^{1/2} = \frac{D_w}{H d_b} \text{Re}^{1/2} \text{Sc}^{1/2}$$

(1a)

If one approximates $L$ by the bubble diameter $d_b = 1.6$ mm, the diffusive film model yields $\alpha \approx 2 \times 10^{-7}$ m s$^{-1}$. Furthermore, this simple model shows that the right definition of the Sherwood number has to include the Henry coefficient $H$:

$$\text{Sh} = \frac{\alpha H d_b}{D_w}$$

(1b)

We note that a more rigorous model, which combines laminar flow with diffusion from a stagnant phase into the mobile water phase, is treated by the Graetz-Nusselt model (Cussler, 1997).
In DON97 the following empirical Sherwood number relationship:

\[ Sh = \frac{\alpha d_h}{D_w} = 2 + 0.6 \frac{Re^{1/2}}{Sc^{1/3}} \]  

(2)

(see equation (D17), equations from DON97 are given a prefix D) is used to support their experimental values, where Re denotes the Reynolds number and Sc the Schmidt number. With the following parameters: kinematic viscosity = $10^{-6} \text{ m}^2 \text{ s}^{-1}$, aqueous diffusion constant $D_w = 10^{-9} \text{ m}^2 \text{ s}^{-1}$, velocity $\mu = 4.6 \times 10^{-5} \text{ m} \text{ s}^{-1}$, diameter $d_h = 1.6 \text{ mm}$, one obtains: Sc = 1000, Re = 0.074, Sh = 3.62, and $\alpha = 2.27 \times 10^{-6} \text{ m} \text{ s}^{-1}$. The conclusion in DON97 was that the experimental values have the right order of magnitude $\sim 10^{-6} \text{ m} \text{ s}^{-1}$. However, according to equation (1b) the right definition of the Sherwood number has to include the Henry coefficient ($= 28$). This leads to an $\alpha = 8.1 \times 10^{-8} \text{ m} \text{ s}^{-1}$, which is consistent with the estimated value of the diffusive film model.

**RE-INTERPRETATION OF THE COLUMN EXPERIMENTS**

**Constant volume model**

Before we re-calculate Table 2 in DON97, especially the values for the microscopic transfer coefficient, we have to verify the differential equations (D13) and (D14). Using dimensionless variables and the transformation (D12a) and (D12b):

\[ C_w = \frac{c_w - c_w^{in}}{c_w^{out} - c_w^{in}} \quad C_g = \frac{c_g - c_g^{in}}{H(c_w^{out} - c_w^{in})} \]

(3)

the differential equations for the constant volume approach (see Geistlinger et al. 2001a,b) become:

\[ \frac{\partial C_w}{\partial T} + (R-1) \frac{\partial C_g}{\partial T} = \frac{1}{P} \frac{\partial^2 C_w}{\partial X^2} - \frac{\partial C_w}{\partial X}, \quad (R-1) \frac{\partial C_g}{\partial T} = \omega_d \cdot H (C_w - C_g) \]

(4)

(subscript $w$ = water phase and $g$ = gas phase, $c^{in}$ = initial concentration, $c^0$ = concentration at $x = 0$, $P$ = Peclet number, $\omega_d = \alpha_d A_g/Q$, $A_g$ = gas–water phase boundary area, $Q$ = water flux, $R = 1 + H \cdot Sg/Sw$, $S$ = saturation, $T = u \times t/L_x$, $X = x/L_x$). Comparing equation (4) with the corresponding equation in DON97 (equation (D13)), it is obvious that a factor $(R - 1)$ on the l.h.s. and a factor $H (= 28)$ on the r.h.s. are missing in equation (D13). It seems that the first error may be a misprint, however the second one seems to be a serious one, since the dimensionless transfer coefficient $\omega_d (= 2.36$ for experiment 2) was used, in order to derive the microscopic transfer coefficient $\omega_d (= 1.57 \times 10^{-6} \text{ m} \text{ s}^{-1}$, see Table 1). We calculate the breakthrough curve once again using the same initial- and boundary conditions as in DON97. The theoretical curve is shown in Fig. 2 (dashed line denoted by “constant volume”), where $\omega = \omega_d \cdot H = 2.36$ was used instead of $\omega_d = 2.36$. The good agreement with the experimental data is remarkable. Furthermore, the breakthrough curve was calculated with the variable volume approach (for details see Geistlinger et al., 2001b), which also shows an excellent agreement with the experimental data.

It is important to note that for $\omega_d = 2.36$ our kinetic model yields the equilibrium curve (thin solid line in Fig. 2). It is evident that an equilibrium model is not able to describe the experiments.
Parameter identification

First we must correct the inconsistent data for column- and gas bubble geometry given in DON97. Since an inside diameter of $d_c = 5.8 \text{ cm}$ and a column length of 25 cm (p.273 in DON97) does not yield the total column volume of 608 cm$^3$ (p.277 in DON97), we had to correct these values according to Table 2 (p.274 in DON97).

Multiplying the Peclet number with the dispersivity gives the corrected column length: $L_c = 30 \text{ cm}$. Then one verifies the total column volume by calculating the aqueous velocity ($= 0.0046 \text{ cm s}^{-1}$ for experiment 2, porosity $\phi = 0.38$) from the given flow rate, $Q = 2 \text{ ml min}^{-1}$. This yields a corrected inside diameter $d_c = 5.08 \text{ cm}$.

The next necessary correction follows from the finding that a gas bubble diameter of 0.8 mm (p.277 in DON97) yields a single bubble volume of $2.7 \times 10^{-4} \text{ cm}^3$ and not the given value of $2.1 \times 10^{-3} \text{ cm}^3$ (p.277 in DON97). If one uses a corrected gas bubble diameter of 1.6 mm ($= 2d_0$), one obtains both the given value for the bubble volume and the bubble surface ($8.0 \times 10^{-2} \text{ cm}^2$).

For the purpose of clarity we give the procedure for calculating the microscopic transfer coefficient: Starting with the measured quantities (geometric parameters, gas saturation, total flux $Q$) the velocity (column 4, Table 1) and the theoretical retardation coefficient (column 6) are derived. From curve fitting the parameters ($R_{exp}$, $\delta_l$, $\omega_D$) are obtained, where the longitudinal dispersivity $\delta_l$ ($= L_c/P$) was determined by a conservative Bromide tracer, independently (see DON97). Using the single bubble model (bubble diameter $= 1.6 \text{ mm}$), the interface $A_g$ and the microscopic transfer coefficient $\alpha$ can be calculated.

Based on the corrected geometric values and using $\omega$ instead of $\omega_D$, the re-calculated mass transfer coefficients $\alpha$ are given in column 10 of Table 1. The wrong mass transfer coefficients from DON97 are shown in column 9. We emphasize that the re-calculated mass transfer coefficients $\alpha$ ($= 5 \times 10^{-8} \ldots 4 \times 10^{-7} \text{ m s}^{-1}$) have the same order of magnitude as the estimated values obtained from the stagnant film model. In the following we only discuss some of the physical dependencies of Table 1, which are of special interest for our oxygen wall model (discussed in Geistlinger et al., 2001b).
Table 1 Oxygen-phase-transfer experiments with different trapped gases from DON97. Re-calculated mass transfer coefficients: $\alpha_D = \text{old value, } \alpha = \text{new value} (\alpha_D = Ha)$.

<table>
<thead>
<tr>
<th>Exp.</th>
<th>Gas</th>
<th>$S_e$ (%)</th>
<th>$n \times 10^5$ (m s$^{-1}$)</th>
<th>$\delta_i$ (cm)</th>
<th>$R_{\text{theor}}$</th>
<th>$R_{\text{exp}}$</th>
<th>$a_0$</th>
<th>$\alpha_D \times 10^8$</th>
<th>$\alpha \times 10^8$</th>
<th>$k_0 \times 10^5$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Air</td>
<td>0.7</td>
<td>4.33</td>
<td>5.07</td>
<td>1.20</td>
<td>1.20</td>
<td>0.58</td>
<td>314.6</td>
<td>11.2</td>
<td>1.1</td>
</tr>
<tr>
<td>2</td>
<td>Air</td>
<td>5.8</td>
<td>4.59</td>
<td>1.20</td>
<td>2.72</td>
<td>3.28</td>
<td>2.36</td>
<td>156.8</td>
<td>5.6</td>
<td>4.6</td>
</tr>
<tr>
<td>3</td>
<td>Air</td>
<td>12.4</td>
<td>4.94</td>
<td>0.63</td>
<td>4.95</td>
<td>5.16</td>
<td>5.68</td>
<td>176.7</td>
<td>6.3</td>
<td>11.1</td>
</tr>
<tr>
<td>4</td>
<td>Air</td>
<td>1.0</td>
<td>21.86</td>
<td>0.47</td>
<td>1.29</td>
<td>1.29</td>
<td>0.25</td>
<td>468.5</td>
<td>16.7</td>
<td>2.4</td>
</tr>
<tr>
<td>5</td>
<td>Air</td>
<td>10.0</td>
<td>24.04</td>
<td>0.32</td>
<td>4.11</td>
<td>4.29</td>
<td>3.62</td>
<td>696.3</td>
<td>24.9</td>
<td>35.4</td>
</tr>
<tr>
<td>6</td>
<td>Air</td>
<td>20.5</td>
<td>27.23</td>
<td>0.20</td>
<td>8.23</td>
<td>13.60</td>
<td>12.10</td>
<td>1134.0</td>
<td>40.5</td>
<td>118.5</td>
</tr>
<tr>
<td>7</td>
<td>N2</td>
<td>1.1</td>
<td>21.87</td>
<td>0.65</td>
<td>1.30</td>
<td>1.22</td>
<td>0.30</td>
<td>548.2</td>
<td>19.6</td>
<td>2.9</td>
</tr>
<tr>
<td>8</td>
<td>N2</td>
<td>6.6</td>
<td>23.16</td>
<td>0.43</td>
<td>2.97</td>
<td>3.14</td>
<td>3.34</td>
<td>976.5</td>
<td>34.9</td>
<td>32.7</td>
</tr>
<tr>
<td>9</td>
<td>N2</td>
<td>21.1</td>
<td>27.41</td>
<td>0.17</td>
<td>8.47</td>
<td>8.75</td>
<td>11.00</td>
<td>1005.0</td>
<td>35.9</td>
<td>107.7</td>
</tr>
<tr>
<td>10</td>
<td>He</td>
<td>1.1</td>
<td>21.87</td>
<td>0.58</td>
<td>1.30</td>
<td>1.11</td>
<td>0.55</td>
<td>1005.0</td>
<td>35.9</td>
<td>5.4</td>
</tr>
<tr>
<td>11</td>
<td>He</td>
<td>6.6</td>
<td>23.16</td>
<td>0.58</td>
<td>2.97</td>
<td>5.95</td>
<td>2.30</td>
<td>672.5</td>
<td>24.0</td>
<td>22.5</td>
</tr>
<tr>
<td>12</td>
<td>He</td>
<td>17.4</td>
<td>26.19</td>
<td>0.57</td>
<td>6.89</td>
<td>10.30</td>
<td>5.76</td>
<td>637.9</td>
<td>22.8</td>
<td>56.4</td>
</tr>
</tbody>
</table>

The relations between the different transfer coefficients are: $\alpha_D = Ha$, $\alpha = \phi \alpha_D$. The total flux $Q$ is 2 ml min$^{-1}$ for experiments 1, 2, and 3 and 10 ml min$^{-1}$ for the others.

$S_e = \text{gas saturation.}$

$R_{\text{theor}} = 1 + H \times S_e(1 - S_e)^{1} = \text{theoretical retardation coefficient.}$

$k_0 = 3\phi \times S_e \times (0.5d_h)^{1} \times \alpha = \text{rate constant, } \phi = 0.38 = \text{porosity, } d_h = 1.6 \text{ mm.}$

For a comprehensive discussion we refer to DON97. First we discuss the retardation factors $R_{\text{theor}}$ and $R_{\text{exp}}$ (columns 6 and 7). The experiments start with an initial gas saturation of a certain trapped gas (column 3), which is in equilibrium with the adjacent water phase (10 mg l$^{-1}$ for trapped air; =0 mg l$^{-1}$ for trapped nitrogen and helium). Switching the inlet concentration to oxygen-saturated water (48 mg l$^{-1}$) an oxygen phase transfer from the water to the gas phase will occur and hence the average gas saturation during the experiment will be higher than the initial value.

Therefore one would expect that the experimental retardation coefficient $R_{\text{exp}}$, which represents some averaged trapped gas volume, will be higher than the theoretical ones. This picture is established by Table 1. For increasing initial gas saturation the deviation increases too. For small deviations the constant volume approach should be an adequate physical model. However, in the case of large deviations the changed volume approach with a time-dependent retardation coefficient should be applied. For instance, the gas saturation during experiments 11 and 12 changes from 6.6% to 15%, and from 17.4% to 25%, respectively.

The key parameter for further use both in oxygen wall modelling and air sparging modelling is the transfer rate constant $k_0$ and its dependence on gas saturation $S_e$. Since $k_0$ has a process specific factor (the microscopic mass transfer coefficient) and a geometry- or structure specific factor (the specific phase boundary: $A_g/V$) one would expect that the main $S_e$-dependence is caused by $A_g(S_e)$. Therefore we can assume that $\alpha$ is nearly $S_e$-independent. In Fig. 3 the velocity dependence of the mass transfer coefficient is shown. Two nonlinear best fits (Leveberg-Marquardt algorithm, origin 6.1) based on the diffusive film model (dashed line) and on the empirical Sherwood number relationship (solid line) are shown.
CONCLUSIONS

Our main conclusion is that the re-calculated mass transfer coefficients \( \alpha (= 6 \times 10^{-8} \ldots 4 \times 10^{-7} \text{ m s}^{-1}) \) have the same order of magnitude as the estimated values obtained from the stagnant film model. Both the constant-volume model and the variable-volume model yield an excellent agreement between the theoretical and the experimental breakthrough curves from DON97. It can be concluded that for small changes of the trapped gas phase due to dissolution or exsolution, the constant-volume approach is justified. The inconsistency of the constant-volume model is that the averaged retardation coefficient, that is used as a fitting parameter, deviates significantly from the theoretical retardation coefficient. The re-calculated mass transfer coefficients exhibit a distinct velocity-dependence that is parameterized by an empirical Sherwood number relationship, which is used for oxygen wall modelling (Geistlinger et al., 2001b).

REFERENCES


