

# Static and dynamic phase mass transfer models of gases with a low solubility applicatable in porous media

Pavel Hron

March 19, 2017

## Dynamic Model of Oxygen Transfer

Many chemical and biological processes, e.g. dissolved iron oxidation or aerobic microbiological growth in porous medium, are dependent on the supply of oxygen to the liquid phase.

To specify the macro-scale closure relationships for the mass transfer of oxygen between gas and water phase in porous media, we follow the model discussed in [Geistlinger2005] and [Holocher2003] based on the stagnant film model for a spherical gas bubbles. Many mass transfer theories implicitly assumes that the rate of inter-phase transfer is a function of a driving force and an interfacial area between phases. If we assume that the activities can be approximated by the concentrations, the mass transfer for oxygen in water and in air is given by

$$-e_{g,O_2} = e_{l,O_2} = \beta a_{gw} (c_{l,O_2}^* - c_{l,O_2}), \quad (1)$$

where  $\beta$  is the mass transfer coefficient,  $a_{gw}$  is the effective gas-water interface,  $c_{l,O_2}^*$  is dissolved oxygen concentration at equilibrium and  $c_{l,O_2}$ ,  $c_{g,O_2}$  correspond to the dissolved oxygen concentration in water and gas phase, respectively.

Dynamic mass balance equations for oxygen in the liquid and in the gas phase can be written as

$$\frac{d(\phi s_l c_{l,O_2})}{dt} = e_{l,O_2}, \quad (2)$$

$$\frac{d(\phi s_g c_{g,O_2})}{dt} = e_{g,O_2}, \quad (3)$$

where  $\phi$  is porosity,  $s_l$  and  $s_g$  are liquid and gas saturation.

## Henry's Law

Mass transfer between liquid and gas phase occurs at the phase interface. For gases with a low solubility, like oxygen in water, the solubility of a gas in a liquid phase is

directly proportional to the partial pressure of the gas above the liquid

$$p_{g,k} k_H = c_{l,k}, \quad (4)$$

where  $p_{g,k}$  is the partial pressure of the solute in the gas phase,  $k_H$  is the Henry's law constant and  $c_{l,k}^*$  is the equilibrium molar concentration in the liquid phase. Introducing a dimensionless constant  $k_H^{cc} = k_H \cdot RT$ , Henry's law (4) is given by [Sander1999]

$$c_{l,k} = k_H^{cc} c_{g,k}. \quad (5)$$

The Henry's law constant generally depends on the solute, the solvent, the pressure and the temperature.

### Static Model of Oxygen Transfer

If the dissolution of oxygen is fast enough, we can omit the dynamic effect of the mass transfer. The dissolved oxygen concentration at equilibrium with the gas phase is expressed from Henry's law (4) as

$$c_{l,O_2}^* = k_H c_{g,O_2} RT = k_H^{cc} c_{g,O_2}. \quad (6)$$

While in the porous medium the total amount of oxygen depends on water and gas saturation, the total oxygen mass should stay constant:

$$\begin{pmatrix} s_l & s_g \\ 1 & -k_H^{cc} \end{pmatrix} \begin{pmatrix} c_{l,O_2}^* \\ c_{g,O_2} \end{pmatrix} = \begin{pmatrix} s_l & s_g \\ 0 & 0 \end{pmatrix} \begin{pmatrix} c_{l,O_2} \\ c_{g,O_2} \end{pmatrix} \quad (7)$$

From equation (7) we can express oxygen concentration for both phases in equilibrium ( $c_{l,O_2}^*, c_{g,O_2}^*$ ) as

$$\begin{pmatrix} c_{l,O_2}^* \\ c_{g,O_2}^* \end{pmatrix} = \frac{1}{s_l k_H^{cc} + s_g} \begin{pmatrix} k_H^{cc} & s_g \\ 1 & -s_l \end{pmatrix} \begin{pmatrix} s_l & s_g \\ 0 & 0 \end{pmatrix} \begin{pmatrix} c_{l,O_2} \\ c_{g,O_2} \end{pmatrix} = \frac{1}{s_l k_H^{cc} + s_g} \begin{pmatrix} k_H^{cc} s_l & k_H^{cc} s_g \\ s_l & s_g \end{pmatrix} \begin{pmatrix} c_{l,O_2} \\ c_{g,O_2} \end{pmatrix} \quad (8)$$

### Mass transfer coefficient

The mass transfer coefficient  $\beta$  for a spherical structure with the harmonic mean particle diameter  $p_d$  is given by [Clift1978]

$$\beta = \frac{D_{l,O_2}}{\delta_{eff}} = D_{l,O_2} \left( \frac{2}{p_d} + \frac{1}{\delta} \right), \quad (9)$$

where  $D_{l,O_2}$  is the oxygen diffusion coefficient in water and  $\delta$  is the thickness of the stagnant film layer.

For advection flow regimes, the boundary layer thickness depends on the interface velocity  $\mathbf{v}_1$ . The difference between flow and interface velocity directly at the interface

is in most cases very small and therefore neglected [Niessner2011]. In this case, the thickness of the film layer can be expressed by [Holocher2003]

$$\delta = \sqrt{\frac{\pi p_d D_{l,O_2}}{\mathbf{v}_1}}.$$

Comparison of different mass transfer coefficient-velocity correlations for oxygen can be found in [Geistlinger2005].

## Gas-liquid inter-facial area

The gas-liquid interface plays a crucial role in the mass transfer in unsaturated porous media. Constitutive relationships between gas-liquid specific inter-facial area, capillary pressure and saturation have already been derived either from pore-scale network models [Cary1994, Niemet2002, Anwar2008, Gvirtzman1991, Reeves1996, Joekar-Niasar2007, Held2001], from Lattice-Boltzmann simulations [Ahrenholz2011] or from experiments [Brusseau1997, Chen2006, Culligan2004, FaisalAnwar2000, Kim1999, Schaefer2000, Porter2010].

Some proposed models are expecting the maximum degree of gas-liquid inter-facial area available for a particular porous medium occurs near to residual liquid saturation [Cary1994, Niemet2002, Gvirtzman1991, Anwar2008]. However, the network models [Reeves1996, Held2001, Joekar-Niasar2007] show that gas-liquid inter-facial area increases linearly with decreasing water saturation until a limit water saturation  $s_l^*$  is reached and then the inter-facial area rapidly decreases until the area reaches zero as the water saturation approaches zero.

The experimental techniques used to measure inter-facial area [Chen2006, FaisalAnwar2000, Kim1999, Schaefer2000], have all found monotonic increase in inter-facial area as  $s_l \rightarrow 0$  (with decreasing saturation), but results of experiments with glass beads in [Culligan2004, Porter2010] showed a good agreement with the pore network modeling [Reeves1996]. This does not indicate that any one of these experimental methods is necessarily wrong. Rather, there is a lack of understanding concerning which interfaces are being detected in any of these experimental techniques. However, in both types of studies, the gas-liquid interface is roughly proportional to the gas content  $s_g$  for  $s_l > s_l^*$ , where  $s_l^* = 0.2 - 0.3$ , which covers the main region of our interest.

As was pointed out in [Porter2010], there are differences in predicting liquid-gas inter-facial area for drainage and imbibition experiments, but the behavior of both processes is similar [Culligan2004]. A comparison between experimental total inter-facial area curves for solid surface area and water-air inter-facial area can be found in [Porter2010].

A basic model based on geometrically relationships to estimate the total surface area for any packing of spheres was presented by [Gvirtzman1991]. The total effective interstitial particle surface area per unit bulk volume is given by

$$a_{gw} = \kappa s_g \frac{6(1 - \phi)}{p_d}, \quad (10)$$

where  $\kappa$  is the fraction of air bubble surface area exposed to mobile water. This empirical factor is often approximated by the porosity [Geistlinger2005]. Similar model to (10) was used in [Geistlinger2005]:

$$a_{gw} = \kappa s_g \frac{6\phi}{p_d}, \quad (11)$$

More sophisticated approach to determine the gas-liquid inter-facial area derived from a distribution of spherical pores was proposed by [Niemet2002]. Under the assumption that the pores are discrete and symmetrical in all dimensions, following equation to determine effective gas-liquid surface area was derived

$$a_{gw} = \frac{3\phi}{2\sigma} \int_0^{s_l} p_c(S) dS, \quad (12)$$

where  $\sigma$  is the surface tension of the liquid. In contrast to model (10), that depends only on porosity  $\phi$ , model (12) takes into account the pore distribution.

For a van Genuchten parametrization [Genuchten1980], the integral in (12) can be computed analytically using the substitution  $z = 1 + \frac{1}{n}$ ,  $w = m - 1/n$ , where  $n, m$  are parameters in van Genuchten model (see [Niemet2002], eq. (15)). Equation (12) can be expressed as

$$a_{gw} = s_g \frac{3\phi}{2\sigma} \frac{m}{\alpha} B(w, z) (1 - I_u(w, z)), \quad (13)$$

where  $B(w, z)$  is the beta function and  $I_u(w, z)$  represents the incomplete beta function.

The comparison of different models with model based on fitting a bi-quadratic polynomial to the experimental data as in [Porter2010] are in Fig. 1.

## References

- [Ahrenholz2011] B. Ahrenholz, J. Niessner, R. Helmig, and M. Krafczyk. Pore-scale determination of parameters for macroscale modeling of evaporation processes in porous media. *Water Resources Research*, 47(7), July 2011.
- [Anwar2008] AHMF Anwar. Estimation of mass transfer coefficients using air-liquid interfacial area in porous media. *Journal of Environmental Research And Development*, 3(2):331–341, 2008.
- [Brusseau1997] ML Brusseau, Jarmila Popovicova, and Jeff A. K. Silva. Characterizing gas-water interfacial and bulk-water partitioning for gas-phase transport of organic contaminants in unsaturated porous media. *Environmental Science & Technology*, 31(6):1645–1649, 1997.
- [Cary1994] J.W. Cary. Estimating the surface area of fluid phase interfaces in porous media. *Journal of Contaminant Hydrology*, 15(4):243–248, April 1994.
- [Chen2006] Lixia Chen and TCG Kibbey. Measurement of air-water interfacial area for multiple hysteretic drainage curves in an unsaturated fine sand. *Langmuir*, 16(22):6874–80, 2006.

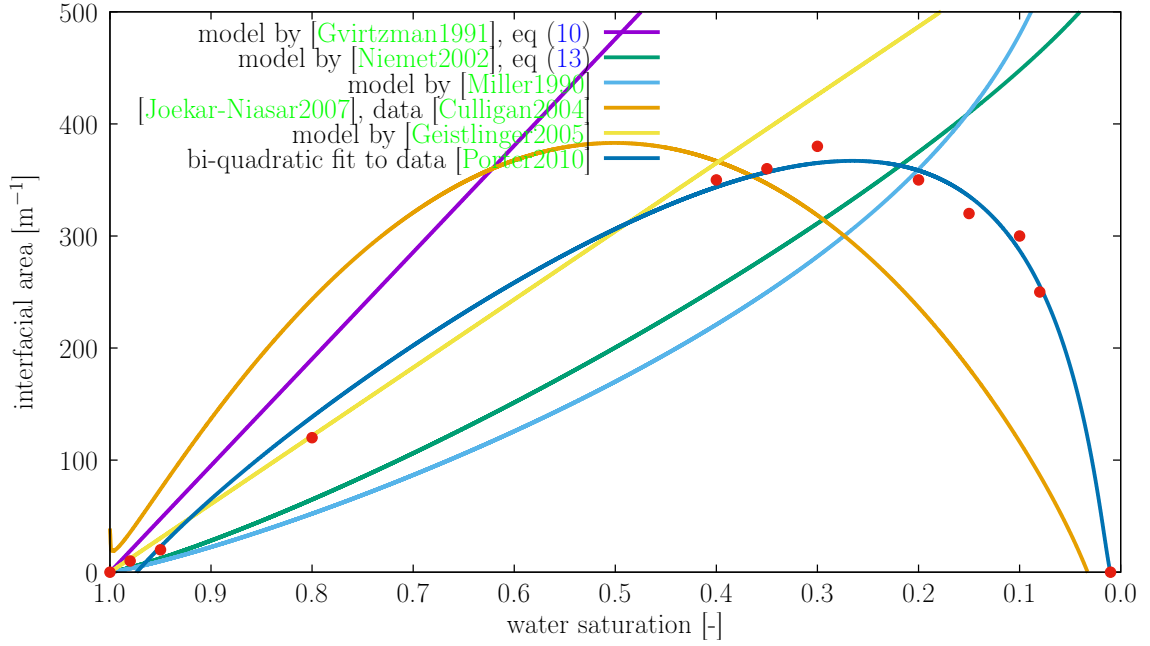


Figure 1: Water-gas inter-facial area computed with different models. Used parameters:  $\phi = 0.39$ ,  $\alpha = 0.0012$ ,  $n = 5.48$ ,  $p_d = 1.5e - 3\text{m}$ .

- [Clift1978] R Clift, J R Grace, and M E Weber. *Bubbles, drops, and particles*. Academic Press Inc., New York, 1978.
- [Culligan2004] Katherine A. Culligan, Dorte Wildenschild, Britt S. B. Christensen, William G. Gray, Mark L. Rivers, and Andrew F. B. Tompson. Interfacial area measurements for unsaturated flow through a porous medium. *Water Resources Research*, 40(12):W12413/1–W12413/12, December 2004.
- [FaisalAnwar2000] A.H.M. Faisal Anwar, Mehdi Bettahar, and Uichiro Matsubayashi. A method for determining air–water interfacial area in variably saturated porous media. *Journal of Contaminant Hydrology*, 43(2):129–146, April 2000.
- [Geistlinger2005] Helmut Geistlinger, Annika Beckmann, and Detlef Lazik. Mass transfer between a multicomponent trapped gas phase and a mobile water phase: Experiment and theory. *Water Resources Research*, 41(11), 2005.
- [Genuchten1980] MT Van Genuchten. A closed-form equation for predicting the hydraulic conductivity of unsaturated soils. *Soil Science Society of America Journal*, 44:892–8, 1980.
- [Gvirtzman1991] H Gvirtzman and PV V Roberts. Pore scale spatial analysis of two immiscible fluids in porous media. *Water Resources Research*, 27(6):1165–1176, 1991.

- [Held2001] Rudolf J. Held and Michael a. Celia. Modeling support of functional relationships between capillary pressure, saturation, interfacial area and common lines. *Advances in Water Resources*, 24(3-4):325–343, February 2001.
- [Holocher2003] J. Holocher, F. Peeters, W. Aeschbach-Hertig, W. Kinzelbach, and R. Kipfer. Kinetic Model of Gas Bubble Dissolution in Groundwater and Its Implications for the Dissolved Gas Composition. *Environmental Science & Technology*, 37(7):1337–1343, April 2003.
- [Joekar-Niasar2007] V. Joekar-Niasar, S. M. Hassanizadeh, and A. Leijnse. Insights into the Relationships Among Capillary Pressure, Saturation, Interfacial Area and Relative Permeability Using Pore-Network Modeling. *Transport in Porous Media*, 74(2):201–219, December 2007.
- [Kim1999] Heonki Kim, PSC S C Rao, and MD D Annable. Gaseous tracer technique for estimating air–water interfacial areas and interface mobility. *Soil Science Society of America journal*, 63:1554–1560, 1999.
- [Miller1990] Cass T. Miller, Michele M. Poirier-McNeil, and Alex S. Mayer. Dissolution of trapped nonaqueous phase liquids: Mass transfer characteristics. *Water Resources Research*, 26(11):2783–2796, 1990.
- [Niemet2002] Michael R. Niemet, Mark L. Rockhold, Noam Weisbrod, and John S. Selker. Relationships between gas-liquid interfacial surface area, liquid saturation, and light transmission in variably saturated porous media. *Water Resources Research*, 38(8):10–1–10–12, August 2002.
- [Niessner2011] J. Niessner. *The role of interfacial area in two-phase flow in porous media: bridging scales and coupling models*. Südwestdeutscher Verlag für Hochschulschriften, 2011.
- [Porter2010] Mark L. Porter, Dorte Wildenschild, Gavin Grant, and Jason I. Gerhard. Measurement and prediction of the relationship between capillary pressure, saturation, and interfacial area in a napl-water-glass bead system. *Water Resources Research*, 46(8), 2010.
- [Reeves1996] Paul C. Reeves and Michael a. Celia. A Functional Relationship Between Capillary Pressure, Saturation, and Interfacial Area as Revealed by a Pore-Scale Network Model. *Water Resources Research*, 32(8):2345–2358, August 1996.
- [Sander1999] Rolf Sander. Modeling atmospheric chemistry: Interactions between gas-phase species and liquid cloud/aerosol particles. *Surveys in Geophysics*, 20(1):1–31, 1999.
- [Schaefer2000] C. E. Schaefer, D. A. DiCarlo, and M. J. Blunt. Experimental measurement of air-water interfacial area during gravity drainage and secondary imbibition in porous media. *Water Resources Research*, 36(4):885–890, 2000.