Transport of dissolved gases through unsaturated porous media

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Abstract. The natural porous media (e.g. soil, sand, peat etc.) usually are partially saturated by groundwater. The saturation of soil depends on hydrostatic pressure which is linearly increased with depth. Often some gases (e.g. nitrogen, oxygen, carbon dioxide, methane etc.) are dissolved into the groundwater. The solubility of gases is very small because of that two assumptions is applied: I. The concentration of gas is equal to solubility, II. Solubility depends only on pressure (for isothermal systems). In this way some part of dissolved gas transfers from the solution to the bubble phase. The gas bubbles are immovably trapped in a porous matrix by surface-tension forces and the dominant mechanism of transport of gas mass becomes the diffusion of gas molecules through the liquid. If the value of water content is small then the transport of gas becomes slow and gas accumulates into bubble phase. The presence of bubble phase additionally decreases the water content and slows down the transport. As result the significant mass of gas should be accumulated into the massif of porous media. We derive the transport equations and find the solution which is demonstrated the accumulation of gases. The influence of saturation, porosity and filtration velocity to accumulation process is investigated and discussed.

1. Introduction
The fluid flow into the unsaturated porous media is investigated during last seventy years. The interest to unsaturated media is linked to the applications because usually the media contains two phases: air and liquid. This situation is observed for any natural porous media (groundwater flow, mining etc.) and for many filtration systems. The pioneer theory of two-phase filtration is published in [1] where the idea that saturation mainly depends on phase permeabilities is proposed. After that the authors of [2] assumed that permeability of fluid depends on capillary pressure into the pores and this theory is confirmed in [3] by the analysis of experimental data. Later, the solution for direct description of the dependence of water content (saturation) on pressure is proposed in [4]. After that many particular models [5, 6, 7, 8] are published, but most of them propose the "S"–shaped curve for the dependence of saturation on pore pressure. One of simplest solution is obtained in [9] and confirmed by experimental observations. In this work the pressure is assumed as linear function of depth and the saturation becomes the power function of depth. In this way the water content is increased with depth wherein the three zones of saturation is usually distinguished: I. Dry zone - zone near ground surface where water contains only in very small pores, water content is constant and equal to residual value into this zone. II. Partially saturated zone where the water content is nonlinearly increased with depth from residual value to the porosity of media by "S"–shaped curve. III. Saturated zone where
the water content is equal to porosity of media \[3, 9\]. This structure of saturation is confirmed by many experimental data.

The diffusion of solute gases in liquids is well-studied problem see e.g. \[10, 11\]. Usually the gas-liquid interface is presented as surface and the exchange processes between gas and liquid is described by the boundary conditions. But the flow of liquid with dissolved gas through porous media is a specific process. The free gas is presented as bubbles into the massive of porous media and the interface is distributed into the volume of media. Such media is named “bubbly” media \[12, 13\]. For moderate values of pressure (the value commensurate with the atmospheric pressure) the solubility of gases is small and the concentration of dissolved gas everywhere is equal to its solubility. The solubility depends only on pressure (for isothermal problem). In the case of mechanical equilibrium the pressure linearly depends on depth it means that the gas bubbles is formed in upper layer of media where the solubility is small. The bubbles of gas are trapped in porous media by surface-tension forces. They are immovable and the main mechanism of gas transport is diffusion of gas molecules into the liquid phase. It means that the decreasing of the proportion of liquid phase slows down the diffusion transport of gases in upper layer. In result the mass of gas accumulates into the upper layer of media. This effect can be very strong for unsaturated media.

The unsaturated porous media also saturated by gas (usually it is air for natural media) and liquid. The proportion of gas is great and it is also presented by bubbles. The dry zone and the top of partially saturated zone contain weak mass of liquid because of small values of hydrostatic pressure. The gas from the solute transits here to the bubble phase and this process additionally reduces the water content. All bubbles are immovable and they occupied most part of media pores as result the diffusive transport is blocked and all significant mass of gas accumulates near the boundary of dry zone. The main purpose of paper is description of the accumulation effect especially on the example of peat bogs where the methane is emitted at decomposition of organic substances.

The paper consists of introduction, three sections and conclusion. Into the introduction the overview of literature and our motivation is presented. The first section is devoted to the derivation of equations for gas transport description in unsaturated media. Into the second section the problem of one dimensional gas transport is formulated and the methods of solution are described. The third section presents the results of solution. The distribution of gas in bubble phase is shown and discussed the influence of governing parameters to the transport and accumulation processes. In the conclusion we summarize all results and discuss them.

2. Diffusion of gases in unsaturated porous media

In the present paper we consider the diffusion of gases in isothermal case at moderate values of pressure (less than 10 bar). In this case we assume that solubility of gas in liquid is small (e.g. it is \(10^{-4}\) for methane) and concentration of gas is equal to the solubility everywhere. In this case the diffusion of gas can be described by the following equation \[14\]:

\[
\frac{\partial}{\partial t} (Q) = \nabla (D \nabla C + UQ),
\]

where \(D\) is the effective diffusivity, \(U\) is speed of media sedimentation, \(Q = C + C_b\) is full volumic concentration of the gas while \(C\) and \(C_b\) is the parts of media volume which are occupied by the dissolved gas and the gas in the bubble phase (bubble phase consist of air and considered type of gas) respectively. The part of volume which is occupied by liquid phase in porous media is named water content and denotes by \(\theta\) whereas bubble phase occupies in the part \(\varphi - \theta\) where \(\varphi\) is porosity of media. In this case the solubility of gas and its volumic concentration in bubble phase is defined as \(X = C/\theta\) and \(X_b = C_b/(\varphi - \theta)\). For the considerable values of pressure the solubility depends linearly on pressure by the Henry law \(X = P_g/K\) where \(K\) is Henry constant.
The partial pressure of gas in bubble phase is determined by expression \( P_g = X_b P/ (\varphi - \theta) \) where \( P \) is full pressure. The substitution of all expressions for concentration to the equation (1) gives the transport equation in terms of \( X_b \), saturation and pressure:

\[
\frac{\partial}{\partial t} \left( \frac{\theta X_b P}{K (\varphi - \theta)} \right) + (\varphi - \theta) X_b = \nabla \left( D \nabla \frac{\theta X_b P}{K (\varphi - \theta)} + U \left( \frac{\theta X_b P}{K (\varphi - \theta)} + (\varphi - \theta) X_b \right) \right).
\]

For the closure of transport equation we need to use some model for media saturation. It is known [2] that for heterogeneous permeability of media the saturation depends only from capillary pressure. We use the power dependence which is proposed within the model [9].

\[
\begin{align*}
\theta &= \theta_r, \quad P < P_w, \\
\theta &= \theta_r + (\varphi - \theta_r) \left[ 1 - (1 + \alpha P^n)^{1/n} \right], \quad P_w < P < P_s, \\
\theta &= \theta_s = \varphi, \quad P > P_s,
\end{align*}
\]

where the \( \theta_r \) is the residual water content of dry porous media, \( P_w \) is characteristic pressure which needed for wetting of media, \( \theta_s = \varphi \) is water content of full saturated media and \( P_s \) is pressure of media saturation. The empiric parameters \( n \) and \( \alpha \) is described the speed of media saturation under the variation of pressure. The value of full water content of media is smaller than \( \theta \) to the volumic concentration of gas in bubble phase, because of that the full water content \( \theta_f = \theta - X_b \). We should use the \( \theta_f \) instead of \( \theta \) into the transport equations. For obtaining the close system of equation we should introduce the equation for pressure. In the present paper the quasistatic problem is considered when the moving into the media is linked only to the slow sedimentation of soil. In this case the pressure of fluid depends only on depth by the hydrostatic distribution \( P = \rho gz \) where \( \rho \) is the density of liquid, \( g \) is gravity acceleration, \( z \) is depth. Finally the system of transport equations can be written as

\[
\frac{\partial}{\partial t} \left( \frac{\theta_f \rho gz X_b}{K (\varphi - \theta_f)} \right) + (\varphi - \theta_f) X_b = \nabla \left( D \nabla \frac{\theta_f \rho gz X_b}{K (\varphi - \theta_f)} + U \left( \frac{\theta_f \rho gz X_b}{K (\varphi - \theta_f)} + (\varphi - \theta_f) X_b \right) \right),
\]

\[
\begin{align*}
\theta &= \theta_r, \quad z < z_w, \\
\theta &= \theta_r + (\varphi - \theta_r) \left[ 1 - (1 + \alpha (\rho g)^n z^n)^{1/n} \right], \quad z_w < z < z_s, \\
\theta &= \theta_s = \varphi, \quad z > z_s, \\
\theta_f &= \theta - X_b,
\end{align*}
\]

where \( z_w \) is the depth of dry zone and \( z_s \) is depth of media saturation. The system (4) describes the transport of gas into the porous media with partial saturation and the forming of gas bubbles. The solution of (4) for one dimensional problem is presented in next section.

3. Problem statement

We restrict to consider only one dimensional problem about transport of gases in vertical direction (parallel to the gravity field). In this case the massif of unsaturated porous media can be divided to three zones by the saturation: dry, partially saturated and saturated zone. The main interest is the transport in partially saturated zone, because of that we will use its depth as spatial scale \( L = z_s - z_w \). The considered porous media is a layer of depth equal to 3\( L \) where top part with depth \( L \) corresponds to dry zone, bottom part to saturated zone. Such choice of problem configuration is based on decay of perturbation outside the partially saturated zone. The configuration of problem is presented on Fig. 1.
We assume that diffusivity and sedimentation speed are constant. Under this assumption the dimensionless form of equations (4) can be written in form

\[ \frac{\partial}{\partial t} \left( \theta_f z C_0 X_b \right) + (\varphi - \theta_f) X_b \right) = \frac{\partial^2}{\partial z^2} \left( \theta_f z C_0 X_b \right) \varphi - \theta_f + (\varphi - \theta_f) X_b \right], \]

\[ \theta = \theta_r - X_b, \quad z < L, \]

\[ \theta = \theta_r + (\varphi - \theta_r) \left[ 1 - (1 + A z^n)^{1/n} - n \right] - X_b, \quad L < z < 2L, \]

\[ \theta = \theta_s = \varphi - X_b, \quad z > 3L, \]

\[ \theta_f = \theta - X_b, \]

where the units for time and depth are \( L^2/D \) and \( L \). Equations (5) contain seven parameters \( P_e = U L / D \) is the Peclet number (dimensionless speed of sedimentation), \( C_0 = \rho g L / K \) specific solubility of gas at the scale of problem, \( \varphi \) is porosity of media and \( A = C_0^n \). The meanings of parameters \( n \), \( \theta_s \) and \( \theta_r \) were explained early. The boundary conditions for (5) is chosen in following form: \( \frac{\partial}{\partial z} X_b |_{z=0} = 0 \) and \( X_b |_{z=3L} = X_0 \). The first condition corresponds to the absent of gas flux on upper boundary because the bubble of gas is immovable. The second condition means that into the deep of saturated zone the air is absent and the concentration of gas in bubble phase depends only on full concentration and pressure. The value \( X_0 \) is defined by the expression \( X_0 = Q_0 - 3C_0 \) where \( Q_0 \) is full concentration of gas and \( 3C_0 \) is the gas solubility at the depth 3L.

One of the most interesting applications of considered problem is the accumulation of methane into the peat-bogs. Because of that the considered gas is methane and the porous media is peat soil. The estimation of governing parameters for this system gives \( X_0 \sim C_0 \sim 10^{-4}, P_e \sim 0.1..10, A \sim 10^4, n \sim 5..6 \) and \( \varphi \sim 0.6..0.9 \) this values can be found in [3, 9, 16].

The equations (5) with boundary conditions is solved numerically [17] by the semi-implicit finite difference scheme of second order accuracy in space and first order in time. The results of solution and the influence of governing parameters to accumulation are discussed in following section.
4. Results

The profiles of concentration of gas in bubble phase are presented into this section. All profiles demonstrate the effect of gas accumulation into partially saturated zone. The parameters of saturation and the concentration of gas in bubble phase at the depth 3L for all calculations are $A = 10^4$, $n = 6$ and $X_0 = 10^{-3}$. The concentration of accumulated gas reached the value $X_b = 0.09 \sim 100X_0$. The effect is strong into the unsaturated media because the small saturation of media and transition of gas into the bubble phase both slow down the diffusive transport. The sedimentation process speeds up the transportation and the mass of accumulated gas decreases with increasing of Peclet number. This effect is demonstrated in figure Fig. 2.

![Figure 2](image_url)

**Figure 2.** The profiles of gas concentration in bubble phase. The effect of Peclet number variation. The values residual water content and porosity are $\theta_r = 0.05$ and $\varphi = 0.9$.

![Figure 3](image_url)

**Figure 3.** The profiles of gas concentration in bubble phase. The effect of porosity variation. The values of residual water content and Peclet number are $\Theta_r = 0.05$, $Pe = 1$.

The figure Fig. 3 demonstrates the influence of porosity variation. The decreasing of porosity leads to increasing the proportion of gas into the pores because the volumic concentration is the same. In result the concentration of gas in bubble phase increases. The effect of residual concentration variation is shown in Fig. 4. It is seen that the increasing of residual water content produced the increasing of mass of accumulated gas and the maximum value of concentration is moved to the upper boundary. This effect can be explained by the expansion of zone where
gas can be transferred by the diffusion. This expansion can be illustrated by the Fig. 5. The profile of gas concentration Fig. 5 is obtained for the full saturated porous media. The diffusion does not block because the concentration of gas in bubble phase is not reach the critical value. The profile corresponds the problem of porous media saturation and we obtain the well known 
\[3, 4, 2, 9, 16\] "S"–shaped curve for full water content \(\theta_f = \varphi - X_b\).

\[\begin{align*}
0 &\quad 0.2 &\quad 0.4 &\quad 0.6 &\quad 0.8 &\quad 1
\end{align*}\]
\[\begin{align*}
0 &\quad 0.2 &\quad 0.4 &\quad 0.6 &\quad 0.8 &\quad 1
\end{align*}\]

Figure 4. The profiles of gas concentration in bubble phase. The effect of residual water content \(\theta_r\) variation. The values of porosity and Peclet number are \(\varphi = 0.9\), \(Pe = 0.5\).

\[\begin{align*}
0 &\quad 0.2 &\quad 0.4 &\quad 0.6 &\quad 0.8 &\quad 1
\end{align*}\]
\[\begin{align*}
0 &\quad 0.1 &\quad 0.2 &\quad 0.3 &\quad 0.4
\end{align*}\]

Figure 5. The concentration of gas in bubble phase under the constant water content \(\theta = 0.9 = \varphi\). The value of Peclet number is \(Pe = 0.5\).

5. Conclusion
The transport of dissolved in liquid gas into the unsaturated porous media is investigated. The gas concentration into the solute is equal to solubility which is dependent only on pressure. When the value of pressure is low the part of gas transits from the solute to the bubble phase. The main mechanism of gas transport is diffusion of gas molecules into the liquid. The bubbles are immovable because of that the transport slows by the bubbles generation. It is shown that the presence of air in unsaturated porous media additionally slows down the diffusion in upper zone of media. The diffusion is blocked and gas accumulates in thin layer. It is obtained that the concentration of accumulated gas may exceed the concentration in the deep layers of media to the
hundred times. The equations for gas transport description are derived and the one dimensional problem is solved numerically. It is shown that the increasing of sedimentation speed leads to the reducing of accumulated gas mass due to speed up of transport. The variation of porosity weakly affects to the accumulation. The increasing of water content leads to expansion of zone where diffusive transport of gas is not blocked. Finally it is show that for full saturated media the one dimensional problem of gas transport becomes the problem of media saturation. The resulted profile of gas concentration has the well known "S"–shaped form.

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