Accumulation of gases dissolved in water saturating a nonisothermal porous massif in the presence of water freezing zones

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Abstract. A one-dimensional problem of gas transport through a bubbly medium under the effect of a temperature wave is considered, taking into account the freezing of the near-surface layer. The transport processes are described within the framework of the bubbly medium approximation. The solubility of gases in water is calculated on the basis of the scaled particle theory. It is shown that the average gas transfer to the surface increases under the action of a temperature wave, and the freezing effect leads to the slowdown of the gas transport near the surface and thus causes the accumulation of gases beneath it. Solving the heat transport equation with a phase transition we calculate the temperature field. With this time-dependent temperature field, from the solute transport equation, the distribution of the gas mass in the near-surface zone is obtained and the accumulation rate is evaluated. The effect of the parameters of the problem (the minimal annual temperature, the amplitude of the annual temperature oscillations and the intensity of gas generation) on the phenomenon of the gas accumulation is studied.

1. Introduction
The diffusion of dissolved gases in liquids is a well-studied problem (see, e.g., [1, 2]). Usually, the gas–liquid interface is presented as surface and the transport processes between gas and liquid are described by the boundary conditions. But the transport of gases through the liquid which saturates porous media is a specific process. The free gas is presented as bubbles in the porous media and the interface is distributed in the volume of media. Such media is called “bubbly” media [3, 4]. If the concentration of dissolved gas is greater than the solubility, the gas transits into bubbles. The small bubbles are trapped in porous matrix by the capillary forces. For the big enough bubbles, the buoyancy force can overcome the capillary one and the bubbles will move upwards. However, a bubble displacing in a porous medium is always unstable to splitting into smaller bubbles [5]; the splitting of bubbles occurs repetitively until they become small enough to be immobilized by the capillary force. The critical immobilisation gas volume fraction in pores varies from system to system, but remains within the range from 0.5–1% [6] to several percents [7]. The solubility depends on pressure and temperature. In the case of mechanical equilibrium, pressure linearly depends on the depth, which means that the gas bubbles are more inclined to formation in the upper layer of media where the solubility is lower. The low temperature at the boundary slows down the process of bubbles generation because the solubility increases with
the decrease of temperature. Simultaneously, the water freezing blocks the gas transport; gases accumulate in the near-surface layer and transit into the bubbles. Thus, the solving of the heat transport problem with phase transition (Stefan problem [8]) is an important part of this work.

The paper is organised as follows. Sec. 2 is devoted to the derivation of the equations for the gas transport in nonisothermal porous media. In Sec. 3, the problem of one-dimensional heat transport with phase transition is formulated and solved. Sec. 4 presents the formulation of gas transport problem with freezing and discussion of the results of numerical simulation. In the conclusion we summarize all the results and discuss them.

2. Diffusion in bubbly media with heterogeneity of thermodynamic properties

The dissolved gas transits into bubbles if the solution concentration exceeds the solubility. In porous media the small bubbles are immobilized by the capillary forces. The solubility of gases at moderate pressure depends on temperature ($T$) and pressure ($P$) as follows (see [4], which corresponds to the scaled particle theory [9]):

$$X = X_0(T_0, P_0) \frac{T}{T_0} \frac{P}{P_0} \exp \left[ q \left( \frac{1}{T} - \frac{1}{T_0} \right) \right],$$  \hspace{1cm} (1)

where $T_0$ and $P_0$ are reference values, $X_0$ is the solubility at the reference temperature and pressure, $q = G_i/k_b$, $G_i$ is the interaction energy between a solute molecule and the surrounding solvent molecules, $k_b \approx 1.38 \times 10^{-23} \text{J/K}$ is the Boltzmann constant. The equation for transport of dissolved gas with the gas generation in the porous massif can be written in the following form:

$$\frac{\partial G}{\partial t} = - \frac{\partial J}{\partial z} + A \exp(-Kz).$$  \hspace{1cm} (2)

Here $G = C + Q$ is the net molar fraction of gas in the pore matter, $Q$ is the molar fraction of the nondissolved gas, $C$ is the molar fraction of the dissolved gas; for realistic $Q \ll 1$, the difference between $C$ and the aqueous solution concentration can be neglected and one can treat $C$ as the solute concentration. The molar concentration flux $J$ of the solute is purely diffusive; $A \exp(-Kz)$ is the source function of the gas production (see, e.g., [10, 11]), where $(A/K)$ is the gas production per the ground surface area and $K$ is the attenuation coefficient. The diffusive flux in nonisothermal media with freezing zones can be written in form:

$$J = -D(T)C \left( \frac{1}{C} \frac{\partial C}{\partial z} + \frac{\alpha}{T} \frac{\partial T}{\partial z} \right);$$  \hspace{1cm} (3)

where $\alpha$ is the thermodiffusion constant, $D_\ast$ is the effective diffusivity coefficient in the liquid-saturated porous medium, $T_\ast$ is the freezing point. The gas molecules transport is solely due to the solution flux through the solvent phase [12, 13]. The gas in ice and in bubbles is immobilized. The net molar fraction $G$ is $G = C$ for $G < X$ and $G = X + Q$ for $G > X$ (the gas excess over the solubility transits into the bubbles). Pressure is hydrostatic, $P = P_0 + \rho gz$, where $g$ is the gravity acceleration and $\rho$ is the pore fluid density. The transport problem (2)–(3) significantly depends on the temperature profile $T(z,t)$. The temporal evolution of this profile is to be determined from the heat conductivity problem with the account for the phase transition (freezing of water)—Stefan problem. The next section is devoted to the solution of this problem.

3. Temperature wave with phase transition

The main reason of a possible accumulation of gas bubbles is a nonlinear dependence of the diffusive flux and the solubility on temperature. The temperature profile in the massif with
the account for the phase transition is given by the solution of a one-dimensional Stefan problem (see Figure 2). At the upper boundary of the massif, temperature depends on time as $T_m + T_a(1 + \cos \omega t)$, where $T_m$ is the minimal annual temperature, $T_a$ and $\omega$ are the amplitude and the frequency of the annual temperature oscillation, respectively.

For solving the Stefan problem it is convenient to introduce the fraction of frozen water in pores, $h(z, t)$. In what follows, we neglect the frost heaving of soils, since it is small for regions, where the air temperature becomes negative for some part of the year. Then, the governing equations for the heat transfer read

$$
(\rho c_P)_{p.m.} \frac{\partial T}{\partial t} = \frac{\partial}{\partial z} \left( k_{p.m.} \frac{\partial T}{\partial z} \right) + Q(z, t); \\
Q(z, t) = -\rho_l \lambda \phi \frac{\partial h}{\partial t}; \\
\frac{\partial h}{\partial t} = \begin{cases} 
  r_\lambda (T_s - T), & \text{for } T > T_s, \ h > 0; \\
  r_\lambda (T - T_s), & \text{for } T < T_s, \ h < 1; \\
  0, & \text{otherwise};
\end{cases} \\
T|_{z=0} = T_m + T_a(1 + \cos \omega t), \quad \frac{\partial T}{\partial z} \bigg|_{z=L} = 0.
$$

Here the first equation describes the temperature field evolution, $(\rho c_P)_{p.m.}$ and $k_{p.m.}$ are the volumetric specific heat and the heat conductivity of the saturated porous medium (generally, these parameters depend on $h$), $Q(z, t)$ is the heat release (consumption) rate due to water phase change, $\rho_l$ is the liquid density, $\lambda$ is the specific latent heat of phase transition, $\phi$ is the porosity. The third equation of system (4) describes the ice melting, where it is present ($h > 0$) and temperature is high ($T > T_s$), and water freezing, where liquid water is present ($h < 1$) and temperature is low ($T > T_s$). The phase transition rate $r_\lambda$ is practically so high that one can consider the transition to the thermodynamic equilibrium between ice and liquid water as instant. Accordingly, for numerical simulation the specific value of this parameter is also not important if it is large enough. In the last line of (4), the boundary conditions are specified.

For a real porous massif, one can assume $L = \infty$; for numerical simulations, the value of $L$ was chosen large enough to have no effect of its doubling on the results of calculations.
Figure 2. The temperature profile at time moment \( t = 475 \) months, the position of the ice–water interface \( z = \zeta \) is indicated with dots (left panel). The position of interface \( \zeta \) versus time is plotted in right panel. Parameters: \( T_a = 15 \) K, \( T_m = 260 \) K.

The problem (4) was solved numerically by the implicit finite differences scheme of the second order of accuracy in space and the first order of accuracy in time. Here we describe the annual oscillations of temperature; therefore, the convenient unit of time is month and all distances are measured in meters. The parameters are chosen for the system of water in a peat bog: the temperature diffusivity of the saturated massif is nearly the same for liquid water and ice and was adopted \( \chi_{p.m} = 1.82 \text{m}^2/\text{month}, k_{p.m} = 1.5 \text{W/(m K)} \), other parameters were \( \lambda = 3.3 \cdot 10^5 \text{J/kg}, \phi = 0.6, \omega = 2\pi/12 \text{month}^{-1} \) and \( T_* = 273.15 \) K [4, 12, 13].

The depth of saturated layer in peat bogs varies from 20 to 150 m, but the characteristic depth of thermal wave penetration can be estimated as \( d = \sqrt{2\chi/\omega} \sim 2.5 \) m. The size of the calculation domain for temperature was \( L = 50 \text{m} = 20 \cdot d \). The example of the results for the temperature profile evolution problem are presented in Figure 2.

4. Diffusion in bubbly media under action of temperature wave with freezing

For a given temperature profile \( T(z,t) \), Eqs. (1)–(3) yield the full gas transport problem:

\[
\frac{\partial G}{\partial t} = \frac{\partial}{\partial z} \left[ D(T) \left( \frac{\partial C}{\partial z} + \frac{\alpha C T}{T} \frac{\partial T}{\partial z} \right) \right] + A \exp(-Kz);
\]

\[
D(T) = \begin{cases} D_*, & T > T_*; \\ 0, & T \leq T_*; \end{cases}
\]

\[
C = \begin{cases} G, & G \leq X; \\ X, & G > X; \end{cases}
\]

\[
X = X_0 \frac{T_0}{T} \left( 1 + \frac{\rho gz}{P_0} \right) \exp \left[ q \left( \frac{1}{T} - \frac{1}{T_0} \right) \right];
\]

\[
C|_{z=0} = 0, \quad \frac{\partial C}{\partial z}|_{z=L} = 0.
\]

Here the condition at the atmosphere–porous-media interface corresponds to the release of the emitted gas into the atmosphere; the condition at \( z = L \) means no gas flux from beneath. The problem (5) is solved numerically with an implicit finite differences scheme of the second
Figure 3. The profiles of the dissolved gas concentration $C$, the net molar fraction $G$ and solubility of gas $X$ for time moment $t = 475$ months (left panel). The dependence of net molar fraction on time at $z = 1.5$ m (right panel). The results are presented for the temperature profile shown in Figure 2; parameters: $T_a = 15$ K, $T_m = 260$ K.

order of accuracy in space and the first order of accuracy in time. The most noticeable implication here is the accumulation of methane in a bogged soil. Hence, all reference values of parameters are chosen for methane and water; specifically, $q = 1138$ K, $D_s = 2.8 \cdot 10^{-3}$ m$^2$/month, $X_0 = 2.6 \cdot 10^{-5}$, $\alpha = 0.3$, $P_0 = 1$ atm and $T_0 = 293$ K (see [14, 15, 16, 17, 18]).

The example of spatial distribution of gas (total amount and dissolved) is presented in Figure 3 (left panel). It can be seen that the zone of methane accumulation is located just below the zone of soil freezing (see Figure 2) and beneath $\approx 1$ m, which is consistent with experimental data [19]. In our model, the accumulated methane has no ways for emission into the atmosphere. However, in nature, if the volumetric fraction of gas bubbles exceeds some threshold value the gas seepage occurs and an excessive amount of gas is released from the soil [6]. These events are recognized as emission of methane from peat bogs, and natural observations show that these events are periodic [20]. In our model, the amount of gas in the bubbly layer increases linearly with time (see Figure 3, right panel) and the gas seepage is not included in the model. In this case the most interesting characteristic is the rate of accumulation ($\gamma = \tan \beta$) because it allows to calculate the periods of emission for any specific soil and peat bog.

The dependencies of the accumulation rate $\gamma$ on the minimal temperature ($T_m$) and the annual temperature amplitude ($T_a$) are presented in Figure 4. One can seen that the accumulation rate is fixed if the near-surface soil is frozen all over the year and becomes lower with the increase of temperature. The dependencies of $\gamma$ on the parameters of gas generation ($A$ and $K$) are plotted in Figure 5. Figure 5 shows that the accumulation rate decreases with the decrease of the intensity of gas generation.

5. Conclusion
The gas transport through a bubbly medium under the effect of a temperature wave has been investigated with the account for the freezing of the near-surface layer. The gas transport and accumulation have been described within the framework of the bubbly medium approximation. It has been shown that the average gas transfer to the surface increases under the action of a temperature wave, and the freezing effect leads to the blockage of the gas transport—the
accumulation of gas immediately beneath the surface. We have obtained numerically the solution for the heat transport problem with a phase transition (Stefan problem) in form of temperature distribution. For this time-dependent distribution, from the transport equations, the distribution of the gas amount in the near-surface layer has been obtained numerically. The effect of gas accumulation has been revealed and the rate of the accumulation has been calculated. The effect of the parameters of the problem on the phenomenon of the gas accumulation has been analysed. The rate of accumulation has been shown to be constant if the surface of the massif is frozen all over the year and to decrease with the increase of the mean surface temperature. The
rate of accumulation has been found to increase with the intensification of the gas generation in the porous massif.

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