Effect of Temperature Wave on the Gas Transport in Liquid-Saturated Porous Media

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We study the effect of surface temperature oscillations on gas mass transport through liquid-saturated porous media. Temperature wave induced by these oscillations and decaying deep in the massif creates the gas solubility wave along with the corresponding solute diffusion flux wave. When bubbles are immobilized by the surface tension force the only remaining mechanisms of gas mass transport are related to solute flux through liquid in pores. We evaluate analytically the generated time-average mass flux for the case of medium everywhere littered with gas bubbles and reveal the significant effect of the temperature wave on the gas release from the massif and bubble mass redistribution within the massif. Analytical theory is validated with numerical calculations.

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\section{I. INTRODUCTION}

Transport of gases, as well as of any weakly soluble substances, in liquid-saturated porous media appears to possess unique features \cite{1,2}. Specifically, for a pore diameter small enough the pore-sized bubbles are immobilized by the surface tension force. The critical pore size can be readily accessed from the balance of the surface tension and buoyancy forces, which yields the value of order of 1 mm for the air-water system. Meanwhile, the bubbles which are large compared to the pore size will experience splitting during displacement due to the fingering instability \cite{3}. As a result, the hydrodynamic transport of the gas phase through porous media becomes practically impossible for a small volumetric fraction of the gas mass transport in groundwater turns out to be of order of magnitude larger than the feasible variations of gas mass dissolved in water. Thus the principal mechanism of the gas mass transport in groundwater turns out to be the transport of gas molecules dissolved in water.

In the massif zone where the aqueous solution is saturated—i.e., porous massif is littered with bubbles of gas phase—the gas flux is solely determined by the field of solubility, which depends on pressure and temperature \cite{2,4}. In this relation it is remarkable that the temperature increase from 0°C to 20°C leads to the decrease of the solubility of the main atmospheric gases and methane by factor 1.5. This means that the annual temperature wave propagating into the porous massif (e.g., see \cite{8}) gives rise to the solubility wave of significant amplitude and associated diffusive fluxes. Hence, the annual temperature wave can significantly affect the processes of saturating groundwater with gases or methane release from wetlands and peatbogs.

The phenomenon under consideration is common and can be significant for various systems with different origins of the surface temperature oscillations, including technological systems (filters, porous bodies of nuclear and chemical reactors, etc.). However, for the sake of convenience, in this paper, we first focus on the case featured by the hydrostatic pressure gradient which is significant for geological systems, where pressure doubles on the depth of 10 meter, leading to significant change of solubility. The no pressure gradient case can be derived from the case of hydrostatic pressure.

We restrict our consideration to the case when the solution is saturated everywhere in the massif. This restriction is suggested not only by the motive of fundamental theoretical interest related to problem novelty but also by its practical relevance. It is relevant for the methane release from peatbogs, as the process of methane generation there can be intense enough to maintain the saturation \cite{4}, and for atmospheric gases. For the latter, it is important that the present time is the warm epoch against the background of the “main” cold state of 100 000-year Glacial-Interglacial cycles \cite{10}. During the cold period the groundwater is saturated with atmospheric gases under enhanced solubility conditions (low temperature), while during the warm period of diminished solubility the excessive gas mass from the solution forms gaseous bubbles in pores. For low-permeability fractureless massifs, the dominant transport mechanism is the molecular diffusion. Molecular diffusion operates with equal efficiency downwards, during the cold periods when the groundwater is being saturated with gases, and upwards, during the warm periods when the system is losing the gas mass. The longer the saturating period is, the longer duration of the release period is needed to remove the excessive amount of gases. Due to asymmetry between cold (long) and warm (short) periods groundwa-
gases from massifs under the saturation condition. Short-time temperature waves can affect the rate of this release. Thus, we can see the relevance of the problem statement assuming the solution to be everywhere saturated.

In this paper, we calculate the diffusion flux of gas in the presence of temperature wave and redistribution of the gas in non-dissolved gaseous phase. Both the cases of molecular diffusion and hydrodynamic dispersion are considered. The analytical results are validated with numerical simulation. The periods of negative temperatures with frozen groundwater are beyond the scope of this study and will be considered elsewhere.

II. TEMPERATURE WAVE IN BUBBLY MEDIA

We adopt harmonic annual oscillation of the surface temperature, \( T_0 + \Theta_0 \cos \omega t \), where \( T_0 \) is the annual-mean temperature, \( \Theta_0 \) is the oscillation amplitude, and \( \omega = 2\pi/\text{year} \). This assumption is accurate enough due to two reasons: (i) real temperature records slightly deviate from their harmonic reduction (see Fig.1 and (ii) the penetration depth of higher harmonics into massif rapidly decreases (see Eq. (1) below). With the specified surface temperature the temperature field in the half-space, which is governed by the heat diffusion equation \( \partial T/\partial t = \chi \Delta T \) with no heat flux condition at infinity, is

\[
T(z) = T_0 + \Theta_0 e^{-kz} \cos(\omega t - k z), \quad k = \sqrt{\omega/2\chi}. \tag{1}
\]

Here \( \chi \) is the heat diffusivity, the \( z \)-axis is oriented downwards and its origin is on the massif surface. The pressure field is hydrostatic

\[
P = P_0 + \rho gz, \tag{2}
\]

where \( P_0 \) is the atmospheric pressure, \( \rho \) is the liquid (mostly, water) density, and \( g \) is the gravity.

For pressure up to 10 atm and far from the solvent boiling temperature the solubility depends on temperature \( T \) and pressure \( P \) as follows \[3\]

\[
X^{(0)}(T, P) \simeq X^{(0)}(T_0, P_0) \frac{T_0}{T} \frac{P}{P_0} \exp \left[ q \left( \frac{1}{T} - \frac{1}{T_0} \right) \right], \tag{3}
\]

where molar solubility \( X^{(0)} \) is the molar amount of solute per 1 mole of solvent, \( T_0 \) and \( P_0 \) are reference values, the choice of which is guided merely by convenience reason, and \( X^{(0)}(T_0, P_0) \) is the solubility at the reference temperature and pressure; the parameter \( q \equiv -G_i/k_B \), with \( G_i \) being the interaction energy between a solute molecule and the surrounding solvent molecules, is provided in Table1.

The instantaneous flux of molar fraction \( X \) in bulk obeys

\[
\vec{J} = -DX \left( \nabla \frac{X}{T} + \alpha \frac{\nabla T}{T} \right), \tag{4}
\]

where \( \alpha \) is the thermodiffusion constant \[11\].

Generally, not only solubility but all material properties of the system depend on temperature and pressure. However, feasible amplitudes of relative variations of the absolute temperature are below 5%. Hence, one can neglect variation of those characteristics which depend on temperature polynomially and consider variation of only those characteristics which depend on temperature exponentially: solubility \[3\] and the molecular diffusion coefficient \( D \). Further, the only characteristic sensitive to pressure below hundreds of atmospheres is gas solubility.

To complete the mathematical formulation of the problem, one needs to specify the dependence of molecular diffusion on temperature \[11\]

\[
D = \frac{k_B T}{2\pi \mu R_d} \frac{\mu + \nu}{2\mu + 3\nu}, \tag{5}
\]

where \( k_B \) is the Boltzmann constant, \( \mu \) is the dynamic viscosity of the solvent, \( R_d \) is the effective radius of the solute molecules with the “coefficient of sliding friction” \( \beta \), \( \nu = R_d \beta /3 \). The dependence of dynamic viscosity on temperature can be described by a modified Frenkel formula \[12\]

\[
\mu = \mu_0 \exp \frac{a}{T + \tau}, \tag{6}
\]

For water, coefficient \( \mu_0 = 2.42 \cdot 10^{-5} \text{ Pa} \cdot s, a = W/k_B = 570 \text{ K} \) (\( W \) is activation energy), and \( \tau = -140 \text{ K} \).
III. AVERAGE GAS MASS TRANSPORT

Since the diffusion transport in liquids is by several orders of magnitude slower than the heat transfer, it can be well described in terms of average values over the temperature oscillation period. With the solubility law diffusion flux \( \vec{J} \) reads

\[
\vec{J} = -D \frac{X^{(0)}}{P} \left[ \frac{\nabla P}{P} - \left( 1 + \frac{q}{T_0} - \alpha \right) \frac{\nabla T}{T} \right].
\]

With expansion

\[
D = D_0 + D_1(T - T_0) + \frac{1}{2} D_2(T - T_0)^2 + \ldots,
\]

where \( D_0, D_1, \) and \( D_2 \) can be plainly evaluated from Eqs. (5) and (6), straightforward but laborious analytical calculations yield mean flux

\[
\langle J \rangle = -D_0 X^{(0)}(T_0, P_0) \left[ \frac{\rho g}{P_0} \left( 1 + A_1 \frac{Q_0^2 e^{-2kz}}{2T_0^2} \right) \right. \\
- \left( 1 + \frac{\rho g z}{T_0} \right) A_2 k \Theta_0^2 e^{-2kz} + O \left( \frac{\Theta_0^4}{T_0^4} \right)
\]

where

\[
A_1 = 1 + 2 \frac{q}{T_0} + \frac{q^2}{2T_0^2} - \frac{D_1 T_0}{D_0} \left( 1 + \frac{q}{T_0} \right) + \frac{D_2 T_0^2}{2 D_0},
\]

\[
A_2 = \frac{q}{T_0} + \left( 2 + \frac{q}{T_0} - \frac{D_1 T_0}{D_0} \right) \left( 1 + \frac{q}{T_0} - \alpha \right).
\]

Beyond the penetration zone of the decaying temperature wave, i.e., for \( k z \gtrsim 2 \), the diffusion flux is homogeneous, no gas mass accumulation or substraction is created by the flux divergence. Meantime, in the near-surface zone where the temperature wave is non-small, the flux divergence is non-zero and one observes the growth (or dissolution) of the gaseous phase;

\[
\frac{\partial \langle X_b \rangle}{\partial t} = - \frac{\partial \langle J \rangle}{\partial z}.
\]

Here \( X_b \) is the molar amount of matter in the gaseous phase per 1 mole of all the matter in pores. The latter equation is valid for small volumetric fraction of bubbles in pores, which well corresponds to the systems we consider.

In Fig. 2 one can see that analytical results involving the expansion match well the results of numerical calculations even for surface temperature oscillation amplitude \( \Theta_0 \) as large as 15 K. Henceforth, our treatment relies entirely on these analytical results.

IV. MOLECULAR DIFFUSION AND HYDRODYNAMIC DISPERSION

Up to this point our results are derived for the molecular diffusion mechanism. With molecular diffusion, terms \( (D_1 T_0^2 / D_0) \) and \( (D_2 T_0^4 / D_0) \) are of the order of magnitude of 10\(^{-17} \); they make principal contribution to constants \( A_1 \) and \( A_2 \), and play a decisive role in the systems evolution. Noticeably, calculations reveal the effect of thermodiffusion (\( \alpha \)) to be practically unobservable against the background of other contributions to the diffusion flux. Hence, the uncertainty of the value of \( \alpha \) for aqueous gas solutions is not a significant issue for the results provided in this paper.

However, along with the molecular-diffusion dominated systems, there are systems where horizontal filtration flux of groundwater is present. This flux is treated as horizontal because it is parallel to the surface and natural systems are typically much more uniform in the horizontal directions than in the vertical one. Due to the microscopic irregularity of pore geometry the filtration flux does fluid mixing which operates like an additional diffusion mechanism, the “hydrodynamic dispersion” \( \theta_1 \). Although hydrodynamic dispersion was previously studied in the relation to the evolution of atmosphere gases bubbles in aquifers, the effect of temperature waves was not addressed.

When hydrodynamic dispersion is present, it is typically by several orders of magnitude stronger than molecular diffusion (\( \theta_1 \), cf. in Fig. 3), and the latter can be neglected. There is no analog of thermodiffusion for hydrodynamic dispersion and \( \alpha = 0 \) for this case. Furthermore, hydrodynamic dispersion depends on the flux strength and pore geometry but not temperature, and the correlations between instantaneous flux oscillations and temperature are not obvious; therefore, \( D = D_0 \) and \( D_1 = D_2 = 0 \). Finally, for hydrodynamic-dispersion dominated system, Eqs. (9) and (10) yield

\[
\frac{\partial \langle X_b \rangle}{\partial t} = D_0 X^{(0)}(T_0, P_0) \left( 1 + \frac{2q}{T_0} + \frac{q^2}{2T_0^2} \right) \Theta_0^2 \frac{T_0^2}{2 T_0^2} \]

\[
\times \left[ 1 + \frac{\rho g z}{P_0} e^{-2kz} \right] + O \left( \frac{\Theta_0^4}{T_0^4} \right).
\]
Ken by the competition between terms and multipliers. With exponential and linear in hydrodynamic dispersion $D$ from gas to gas. Analytical expression (8) contains both parameters ($\alpha$, $\Theta_0$) and bubble growth for higher mean temperatures (Fig. 3a) and bubble growth for lower mean temperatures (Fig. 3b). This is dominantly controlled by hydrostatic pressure gradient and annual-mean temperature oscillations. Meanwhile, for natural systems the penetration depth of the annual temperature wave never reaches 10 m \cite{3}, the latter case, with bubble depletion above $z_*$ and growth below $z_*$, is not feasible and can be relevant only for longer climate cycles.

We discussed our analytical results in relation to geological systems featured by the hydrostatic pressure gradient and annual temperature oscillations. Meanwhile, Eqs. (8) and (10) hold valid for the systems where the hydrostatic pressure gradient is either absent or insignificant. The latter case may be, for example, daily temperature oscillation, the penetration depth of which is 0 K and can be relevant only for longer climate cycles.

V. RESULTS AND DISCUSSION

In Fig. 3 one can see the results of calculations of the methane bubble growth rate in molecular-diffusion and hydrodynamic-dispersion dominated systems. These plots demonstrate several unique features of these cases. Let us discuss these features and their origins in detail.

Noteworthy, with molecular diffusion of methane, one can observe both bubble dissolution for lower mean temperatures (Fig. 3a) and bubble growth for higher mean temperatures (Fig. 3b). This is dominantly controlled by parameters ($D_1T_0/D_0$) and ($D_2T_0^2/D_0$) and may vary from gas to gas. Analytical expression (8) contains both exponential and linear in $z$ terms and multipliers. With purely exponential terms, the shape of the bubble growth rate profile would be determined only by $k$ [see Eq. (8)]. Owing to the linear in $z$ multiplier in Eq. (8), this tolerance of the profile shape to parameters $A_1$ and $A_2$ is broken by the competition between terms $e^{-2kz}$ and $z e^{-2kz}$.

In particular, Figs. 3a and 3b demonstrate that the penetration depth of the bubble depletion zone is nearly twice bigger than the penetration depth of the growth zone.

On the contrary, for hydrodynamic-dispersion dominated systems, only growth of bubbles is possible. According to Eq. (10), the shape of the bubble growth rate profile is determined by the second $z$-derivative term. This derivative profile depends on $k = \sqrt{\omega/2\chi}$. The second $z$-derivative is everywhere positive for $k > \rho g/P_0 = 0.1 \text{ m}^{-1}$, i.e., for temperature wave penetration depth below 10 m, while for $k < \rho g/P_0$ it turns negative in the upper zone above $z_* = k^{-1} - P_0/\rho g$. Since for natural systems the penetration depth of the annual temperature wave never reaches 10 m \cite{3}, the latter case, with bubble depletion above $z_*$ and growth below $z_*$, is not feasible and can be relevant only for longer climate cycles.
for soils—a depth on which the hydrostatic pressure increase is negligible. The case of no pressure gradient can be derived from Eq. (8) by eliminating the gravity; one finds

\[
\langle J \rangle = D_0 X^{(0)}(T_0, P_0) A_2 \frac{k \Theta_5^2 e^{-2kz}}{2T_0^2} + \mathcal{O} \left( \frac{\Theta_5^4}{T_0^4} \right) .
\] (11)

Here we can see a non-trivial temperature wave effect on gas release for various technological and natural systems as well.

VI. CONCLUSION

We have addressed the problem of influence of the surface temperature oscillation (and consequent temperature wave) on the gas transport through liquid-saturated porous media. Specifically, we have considered the problem for the case of saturated gas solution, i.e., when bubbles are spread everywhere in the medium. Strong exponential dependence of the solubility and the molecular diffusion coefficient on temperature has been found to lead to non-negligible instantaneous diffusion fluxes although the amplitude of the relative variation of absolute temperature does not exceed 5%. Due to nonlinearity these fluxes are not averaged-out to zero but create the mean mass flux.

Our main findings are expressed by Eq. (8) and its reductions for hydrodynamic-dispersion dominated systems [Eq. (10)] and no pressure gradient systems [Eq. (11)]. These analytical equations have been shown to fairly match the results of numerical calculations (see Fig. 2). We have revealed that the temperature wave can either enhance or deplete the near-surface bubbly zone in molecular-diffusion dominated systems and only enhance this zone for hydrodynamic-dispersion dominated systems (for instance, see Fig. 3).

The phenomenon we have addressed is expected to be of significance not only for gases but also for any weakly soluble substance, given its solubility is sensitive to temperature.

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[17] For instance, \((D_1T_0/D_0)\) and \((D_2T_0^2/D_0)\) are within the range 20–30 for methane as can be calculated with Eqs. (3), (5), (6) and data from Table I.

[18] Up to authors’ knowledge, neither experimental data nor reliable theoretical calculation of thermodiffusion constant \(\alpha\) for weakly solvable gases in liquid water can be found in the literature.