

MATHEMATICAL MODEL OF FREEZING OF ROCKS SATURATED WITH SALT SOLUTION TAKING INTO ACCOUNT THE INFLUENCE OF OSMOSIS

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Abstract: The paper presents a mathematical model of rocks freezing saturated with salt solution under impact of osmotic force. Osmosis is related to the salt concentration gradient, which is characteristic for solutions, and it is a powerful mechanism for the movement of solutions in poorly permeable porous media. A mathematical criterion for the formation of closed “pockets” with brines (cryopags) in frozen rocks has been obtained. This criterion is shown to be significantly depends on the osmosis coefficient. The model includes three layers of a porous medium saturated, respectively, with ice, ice and solution, and salt solution only. A special case was studied when there is only a second layer with a movable boundary, on which a phase transition from the second layer to the third one occurs. The investigated layer is saturated with a salt solution and ice in thermodynamic equilibrium. Other layers are replaced by boundary conditions. An approximate analytical solution of the problem is found in a self-similar formulation. The nature of the influence of osmotic force on the freezing process of rocks saturated with solution is shown. The characteristic patterns associated with the considered process are revealed. One of the features of the osmosis influence is the fact that it can cause the movement (migration) of the solution in the direction of increasing pressure, i.e. in the direction opposite to the driving force caused by the pressure gradient.

Keywords: osmosis, freezing, porous medium, salt solution, filtration, phase transition.

Citation: Ramazanov, M. M., N. S. Bulgakova, L. I. Lobkovsky (2023), Mathematical Model of Freezing of Rocks Saturated With Salt Solution Taking Into Account the Influence of Osmosis, *Russian Journal of Earth Sciences*, 23, ES5007, EDN: BYCURY, <https://doi.org/10.2205/2023es000857>

RESEARCH ARTICLE

Received: 20 March 2023

Accepted: 22 June 2023

Published: 30 December 2023



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1. Introduction

Understanding the regularities of freezing processes in rocks saturated with salt solution is important due to numerous practical applications. The problems of chemical contamination of the surface in cold regions due to the burial of various liquid radioactive waste in permafrost can be distinguished among them [Chuvilin, 1999]. In the cited work, based on the results of physical experiments, the behavior of ions of chemical elements in freezing and thawing soils and in ice is studied. The features characteristic for the interaction of frozen ground with salt solutions are described.

According to modern ideas, during the geological history permafrost in the coastal zone of the East Siberian Arctic shelf experienced alternation of freezing and thawing, as a result of which a large volume of hypersaline brines (called cryopags) were formed. At the same time, salty sea water and cryopags significantly contribute to the destruction and degradation of permafrost and, accordingly, the intensive release of methane as a result of the decomposition of metastable gas hydrates contained in frozen rocks in a self-preserved form [Lobkovskii and Ramazanov, 2018; Shakhova et al., 2017]. Methane is a powerful greenhouse gas and affects global warming [Yakushev, 2009]. Therefore, studies of the

regularities of cryopags formation during freezing of rocks saturated with a salt solution are very relevant. So, the developed mathematical model makes it possible to describe not only the freezing of porous media saturated with solution, but also to an equal extent the reverse process, i.e. the process of permafrost degradation taking into account the osmotic effect.

Modeling the processes of both freezing and thawing for rocks and soils saturated with salt solutions was carried out by some authors [Tsyppkin, 2009]. The essential difference of our proposed model is that it takes into account osmosis associated with the salt concentration gradient, which is characteristic for salt solutions and is a powerful mechanism for the movement (migration) of solutions in poorly permeable porous media [Ramazanov et al., 2019, 2022]. This, in particular, made it possible to find a criterion for the formation of cryopags, which significantly depends on the osmotic filtration coefficient.

It is generally believed that for the osmotic effect, it is necessary to have a semi-permeable membrane that passes water molecules and does not pass salt molecules. But this is an ideal case, in fact, this effect manifests itself locally in any sufficiently weakly permeable porous medium in the presence of a significant salt concentration gradient. This follows from thermodynamics, according to which the equilibrium of the solution requires the constancy of the chemical potential of both the dissolved component and the solvent [Landau and Lifshitz, 1976; Ramazanov et al., 2019]. However, the degree of osmotic effect depends on the type of rock. In particular, it is well known that clays have semi-permeable and, consequently, osmotic properties [Kemper, 1961]. It follows from this that with a sufficient salt concentration gradient, the osmotic effect should be taken into account at permeabilities of the order of one mD or less, characteristic of clays. The need to take into account osmosis, in addition to the permeability coefficient, depends on specific conditions, in particular, on pressure gradients and salt concentration. In general, this question can be answered by comparing the estimates of osmotic force with the pressure gradient in the generalized Darcy's law given below.

2. Problem Formulation

There is a horizontal permeable layer saturated with a salt solution with a constant concentration and with a given temperature. At some point in time, at the upper boundary the temperature drops below the freezing point at a given local pressure and a given solution concentration. Then two freezing fronts of the solution will spread from top to bottom. The first front is the boundary between the upper completely frozen region of the formation and the region where both the solution and the ice are in thermodynamic equilibrium. The second boundary is the boundary between the indicated equilibrium partially frozen layer and the area saturated with liquid solution (Figure 1). It is required to formulate a mathematical model of the process under consideration and to investigate the laws of evolution of such a system taking into account the osmotic force.

3. Mathematical Model

We present sets of equations in each layer and boundary conditions at the interphase boundaries. Let's point the z axis down and select the coordinate system as shown in Figure 1.

Area I. This layer contains only rocks and ice, so here we have only the equation of thermal conductivity

$$C_{mi} \frac{\partial T_i}{\partial t} = \lambda_{mi} \frac{\partial^2 T_i}{\partial z^2}, \quad C_{mi} = m\rho_i C_i + (1 - m)C_s, \quad \lambda_{mi} = m\lambda_i + (1 - m)\lambda_s.$$

Here C_{mi} is the effective heat capacity of an unit volume of a porous medium saturated with ice; T_i is the temperature; λ_{mi} is the effective thermal conductivity of the saturated porous medium; m is the porosity; ρ_i is the density of ice; C_i, C_s are the heat capacities of ice and rocks, respectively; λ_i, λ_s are the thermal conductivities of ice and rocks.

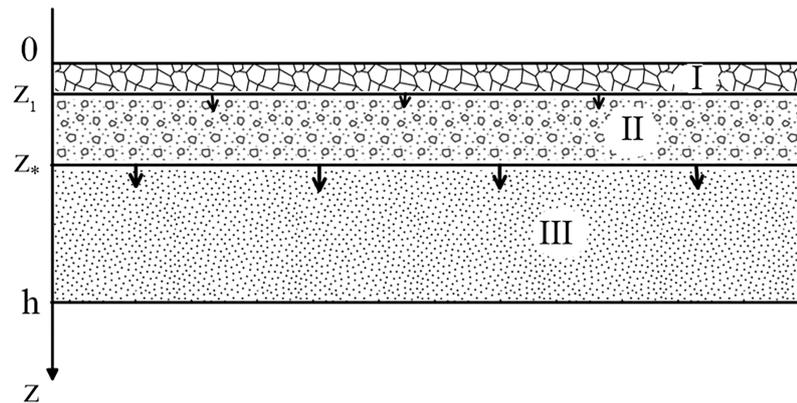


Figure 1. Diagram of the problem: I – frozen rocks containing ice; II – partially frozen layer saturated with ice and salt solution in thermodynamic equilibrium; III – unfrozen stratum saturated with salt solution; $z = z_1(t)$ is the movable boundary of the region I; $z = z_*(t)$ is the partial freezing front of the solution.

Area II. The system in this region is in a state of phase equilibrium, therefore, according to the equation of state, temperature is a function of pressure and concentration of salt. It is usually assumed that the temperature depends on the concentration linearly. In other words, the equation of state can be written as

$$T = T_w(p) - \psi_0 c. \tag{1}$$

Here $T_w(p)$ is the dependence of the freezing temperature on the pressure for pure water without impurities; ψ_0 is a constant characterizing the degree of decrease in the freezing temperature of water due to the presence of dissolved salt.

The dependency (1) can be written in another way:

$$p = P_w(T + \psi_0 c). \tag{2}$$

Here $p = P_w(T)$ is the known function that is the equation of state for a pure liquid, i.e. the inverse function with respect to $T_w(p)$. Next, we will use the form (2) for the equation of state.

The set of equations in the considered layer will be written as

$$\begin{aligned} \mathbf{v} &= -\frac{k f_w(s)}{\eta} \left(\rho_w \frac{\partial \mu_1}{\partial c} \frac{\partial c}{\partial z} + \frac{dP}{dT} \left(\frac{\partial T}{\partial z} + \psi_0 \frac{\partial c}{\partial z} \right) - \rho_w g \right); \\ \frac{\partial}{\partial t} [m(s\rho_w + (1-s)\rho_i)] + \frac{\partial}{\partial z} (\rho_w \mathbf{v}) &= 0; \\ (ms + \Gamma) \frac{\partial c}{\partial t} + \mathbf{v} \frac{\partial c}{\partial z} &= m \frac{\partial}{\partial z} \left(sD \frac{\partial c}{\partial z} \right) - c_0 \frac{m\rho_i}{\rho_w} \frac{\partial s}{\partial t}, \quad \Gamma(K, c) = \frac{\partial a(K, c)}{\partial c}, \quad \lim_{Kc \rightarrow \infty} a(K, c) = a_\infty; \\ \bar{C}_m \frac{\partial T}{\partial t} + qm\rho_i \frac{\partial s}{\partial t} + \rho_w \bar{C}_w \mathbf{v} \frac{\partial T}{\partial z} &= \frac{\partial}{\partial z} \left(\lambda_m \frac{\partial T}{\partial z} \right); \\ \bar{C}_m &= C_m - ms\beta_w T \frac{dP}{dT}, \quad \rho_w \bar{C}_w = \rho_w C_w - \beta_w T \frac{dP}{dT}; \\ C_m &= m[s\rho_w C_w + (1-s)\rho_i C_i] + (1-m)C_s, \quad \lambda_m = m[s\lambda_w + (1-s)\lambda_i] + (1-m)\lambda_s, \end{aligned} \tag{3}$$

where k is the permeability; s is the water saturation; ρ is the density; \mathbf{v} is the velocity field of the solution; C is the heat capacity of the unit volume; T is the temperature; λ is the thermal conductivity; m is the porosity; μ_1 is the chemical potential of the solvent in the solution; η is the viscosity of the solution; D is the diffusion coefficient of salt in the solution; q is the specific heat of melting of ice; a is the concentration of salt in the solid

phase of a porous medium; β_w is the coefficient of thermal expansion; indices: i is ice, w is water, s is the skeleton of the rock.

Further, in this system we will assume dP_w/dT as a constant value, and for simplicity we will consider the phase permeability of the solution to be linear, i.e. we will assume $f_w(s) = s$.

In (3) the steady-state adsorption of salt is taken into account. For example, in the case of the Langmuir isotherm, the adsorption equation has the form

$$a(K, c) = a_\infty \frac{Kc}{1 + Kc},$$

where a_∞ is the value of the maximum adsorption; c is the equilibrium concentration of the adsorbent in the solution; K is the constant of the adsorption equilibrium.

Note that the first term in the Darcy's law in (3) being proportional to the concentration gradient is the osmotic force [Ramazanov et al., 2019].

In the system (3), the first equation is the generalized Darcy's law, the second equation is the mass balance of water, the third and fourth ones are the equations of the balance of salt and energy. Later, we will assume that the inequality is satisfied:

$$\frac{\rho_w g}{\gamma dP/dT} \ll 1, \quad \gamma = \frac{T_0 - T^0}{h}. \tag{4}$$

The inequality (4) means that the temperature gradient on the saturation line caused by the hydrostatic pressure drop, which is estimated to be about one degree per hundred meters, is small compared to the temperature gradient under consideration.

In accordance with the condition (4), further, in the first equation of the system (3), we will neglect gravity.

Area III. In this area, the rocks are saturated only with a liquid solution. The set of equations in this unfrozen region can be obtained from (3) if we put the saturation of water constant and equal to one. However, in the problem considered here, it is advisable to introduce simplifications. In the area, the salt concentration will be considered weakly changing and therefore the osmotic effect is neglected. For simplicity, adsorption is also neglected, although, if necessary, these effects can be painlessly taken into account. As a result, we have

$$\begin{aligned} \mathbf{v} &= -\frac{k}{\eta} \left(\frac{\partial p}{\partial z} - \rho_w g \right); \\ \frac{\partial}{\partial t} (m\rho_w) + \frac{\partial}{\partial z} (\rho_w \mathbf{v}) &= 0; \\ m \frac{\partial c}{\partial t} + \mathbf{v} \frac{\partial c}{\partial z} &= mD \frac{\partial^2 c}{\partial z^2}; \\ C_m \frac{\partial T}{\partial t} + \rho_w C_w \mathbf{v} \frac{\partial T}{\partial z} &= \lambda_m \frac{\partial^2 T}{\partial z^2}; \\ C_m &= m\rho_w C_w + (1 - m)C_s, \quad \lambda_m = m\lambda_w + (1 - m)\lambda_s. \end{aligned}$$

Boundary conditions. Considering the lower layer to be infinite for simplicity, the boundary conditions characterizing the conservation of salt, energy and mass flows of water, we write

$$\begin{aligned}
 z = 0: & \quad T_i = T_i^0; \\
 z = z_1: & \quad T_- = T_+ = T^0, \quad \lambda_{mi} \frac{\partial T_-}{\partial z} = \rho_i q m \frac{dz_1}{dt} + \lambda_m \frac{\partial T_+}{\partial z}, \\
 & \quad s_1 \left(D \frac{\partial c_+}{\partial z} + \frac{\rho_i}{\rho_w} c_+ \frac{dz_1}{dt} \right) = 0, \quad \mathbf{v}_+ = s_1 \left(1 - \frac{\rho_i}{\rho_w} \right) m \frac{dz_1}{dt} = -\frac{ks_1}{\eta} \left(\rho_w \frac{\partial \mu_1}{\partial c} \frac{\partial c_+}{\partial z} + \frac{dP}{dT} \frac{\partial T_+}{\partial z} \right); \\
 z = z_*: & \quad \rho_w \left(\mathbf{v}_- - ms_- \frac{dz_*}{dt} \right) - \rho_i m (1 - s_-) \frac{dz_*}{dt} = \rho_w \left(\mathbf{v}_+ - m \frac{dz_*}{dt} \right), \\
 & \quad T_- = T_+ = T_*, \quad -\rho_i q m (1 - s_-) \frac{dz_*}{dt} + \lambda \frac{\partial T_-}{\partial z} = \lambda_+ \frac{\partial T_+}{\partial z}, \\
 & \quad c_- = c_+ = c_*, \quad \left(\mathbf{v}_- - ms_- \frac{dz_*}{dt} \right) c_* - ms_- D \frac{\partial c_-}{\partial z} = \left(\mathbf{v}_+ - m \frac{dz_*}{dt} \right) c_* - m D \frac{\partial c_+}{\partial z}, \\
 & \quad \mathbf{v}_+ = -\frac{k}{\mu} \frac{\partial p_+}{\partial z}, \quad p_- = p_+ = p_* = P(T_*); \\
 z \rightarrow \infty: & \quad p \rightarrow p_0, \quad T \rightarrow T_0, \quad c \rightarrow c_0.
 \end{aligned}$$

Note that the water saturation at the boundaries of the phase transition can be discontinuous.

Later, the pressure will be counted from the hydrostatic pressure, and the temperature from T^0 .

We can write the problem in the dimensionless form. To do this, we introduce scales:

$$\begin{aligned}
 [z] = h, \quad [v] = -\frac{k}{\eta h} \frac{dP}{dT} (T_0 - T^0), \quad [t] = \frac{h}{[v]}, \quad [T] = T_0 - T^0, \\
 [p] = -\frac{dP}{dT} (T_0 - T^0), \quad [c] = c_0.
 \end{aligned}$$

Keeping the notation, we have in dimensionless form

in the Area I

$$\frac{\partial T}{\partial t} = \frac{1}{Pe_{T_i}} \frac{\partial^2 T}{\partial z^2}, \quad Pe_{T_i} = \frac{[v] h C_{mi}}{\lambda_{mi}}, \tag{5}$$

in the Area II

$$\begin{aligned}
 \mathbf{v} &= s \left[\left(\gamma_f + \psi_0 \right) \frac{\partial c}{\partial z} + \frac{\partial T}{\partial z} \right]; \\
 \frac{1}{N_s} \frac{\partial s}{\partial t} - \frac{1}{N_p} \left(\frac{\partial T}{\partial t} + \psi_0 \frac{\partial c}{\partial t} \right) + \frac{\partial \mathbf{v}}{\partial z} &= 0; \\
 \gamma_c \frac{\partial c}{\partial t} + \mathbf{v} \frac{\partial c}{\partial z} &= \frac{s_0}{Pe_c} \frac{\partial^2 c}{\partial z^2} - \gamma_s \frac{\partial s}{\partial t}; \\
 \gamma_T \frac{\partial T}{\partial t} + \gamma_q \frac{\partial s}{\partial t} + \mathbf{v} \frac{\partial T}{\partial z} &= \frac{1}{Pe_T} \frac{\partial^2 T}{\partial z^2}.
 \end{aligned} \tag{6}$$

Here

$$\begin{aligned} \frac{1}{N_s} &= m_0 \left(1 - \frac{\rho_i}{\rho_w}\right), \quad \frac{1}{N_p} = \left[\left(s_0 + (1-s_0) \frac{\rho_i}{\rho_w} \right) \frac{\partial m}{\partial p} + \frac{m_0}{\rho_w} \left(s_0 \frac{\partial \rho_w}{\partial p} + (1-s_0) \frac{\partial \rho_i}{\partial p} \right) \right] \left(T_0 - T^0 \right) \left| \frac{dP}{dT} \right|, \\ \gamma_f &= \rho_w \left| \frac{\partial \mu_1}{\partial c} \right| c_0 \left[\left(T_0 - T^0 \right) \left| \frac{dP}{dT} \right| \right]^{-1}, \quad \gamma_c = m_0 s_0 + \Gamma, \quad \gamma_s = m_0 \frac{\rho_i}{\rho_w}, \\ \gamma_T &= \frac{C_m + m s \beta_w \bar{T} \left| \frac{dP}{dT} \right|}{\rho_w C_w + \beta_w \bar{T} \left| \frac{dP}{dT} \right|}, \quad \gamma_q = \frac{q m_0 \rho_i}{\left[\rho_w C_w + \beta_w \bar{T} \left| \frac{dP}{dT} \right| \right] \left(T_0 - T^0 \right)}, \\ P_{e_T} &= \frac{[\mathbf{v}]h \left[\rho_w C_w + \beta_w \bar{T} \left| \frac{dP}{dT} \right| \right]}{\lambda_m}, \quad P_{e_c} = \frac{[\mathbf{v}]h}{m_0 D}, \quad [\mathbf{v}] = \frac{k}{\eta h} \frac{dP}{dT} \left| T_0 - T^0 \right|. \end{aligned}$$

In the Area III

$$\begin{aligned} \mathbf{v} &= -\frac{\partial p}{\partial z}; \\ \frac{1}{N_{p_0}} \frac{\partial p}{\partial t} + \frac{\partial \mathbf{v}}{\partial z} &= 0, \quad \frac{1}{N_{p_0}} = \frac{1}{m_0} \left[\frac{\partial m}{\partial p} + \frac{m_0}{\rho_w} \frac{\partial \rho_w}{\partial p} \right] \left(T_0 - T^0 \right) \left| \frac{dP}{dT} \right|; \\ \gamma_c \frac{\partial c}{\partial t} + \mathbf{v} \frac{\partial c}{\partial z} &= \frac{1}{P_{e_c}} \frac{\partial^2 c}{\partial z^2}; \\ \gamma_T \frac{\partial T}{\partial t} + \mathbf{v} \frac{\partial T}{\partial z} &= \frac{1}{P_{e_T}} \frac{\partial^2 T}{\partial z^2}. \end{aligned} \tag{7}$$

The Boundary Conditions are

$$\begin{aligned} z = 0: \quad T &= T_i^0; \\ z = z_1: \quad T_- = T_+ = T^0, \quad \frac{1}{P_{e_{T_i}}} \frac{\partial T_-}{\partial z} &= \gamma_{qi} \frac{dz_1}{dt} + \frac{1}{P_{e_{T_i}}} \frac{\partial T_+}{\partial z}, \\ s_1 \left(\frac{1}{P_{e_{c_i}}} \frac{\partial c_+}{\partial z} + \frac{\rho_i}{\rho_w} c_+ \frac{dz_1}{dt} \right) &= 0, \quad \mathbf{v}_+ = s_1 \left(1 - \frac{\rho_i}{\rho_w} \right) \frac{dz_1}{dt} = s_1 \left[(\gamma_f + \psi_0) \frac{\partial c_+}{\partial z} + \frac{\partial T_+}{\partial z} \right]; \\ z = z_*: \quad \rho_w \left(\mathbf{v}_- - s_- \frac{dz_*}{dt} \right) - \rho_i (1 - s_-) \frac{dz_*}{dt} &= \rho_w \left(\mathbf{v}_+ - \frac{dz_*}{dt} \right), \\ T_- = T_+ = T_*, \quad -\gamma_q (1 - s_-) \frac{dz_*}{dt} + \frac{1}{P_{e_T}} \frac{\partial T_-}{\partial z} &= \frac{1}{P_{e_T}} \frac{\partial T_+}{\partial z}, \\ c_- = c_+ = c_*, \quad -\gamma_s (1 - s_-) c_* \frac{dz_*}{dt} + \frac{s_-}{P_{e_c}} \frac{\partial c_-}{\partial z} &= \frac{s_-}{P_{e_c}} \frac{\partial c_+}{\partial z}, \\ \mathbf{v}_+ &= -\frac{\partial p_+}{\partial z}, \quad p_- = p_+ = p_* = P(T_*); \\ z \rightarrow \infty: \quad p &\rightarrow p_0, \quad T \rightarrow 1, \quad c \rightarrow 1. \end{aligned} \tag{8}$$

4. Self-Similar Formulation and Solution of the Problem

We will look for a solution in a self-similar form introducing a new coordinate

$$\xi = \frac{z}{\sqrt{t}}, \quad \mathbf{v} = \frac{\mathbf{v}(\xi)}{\sqrt{t}}, \quad T = T(\xi), c = c(\xi), \quad p = p(\xi). \tag{10}$$

Then, we have in the ice area

$$-\frac{\xi}{2} \frac{dT_i}{d\xi} = \frac{1}{P_{e_{T_i}}} \frac{d^2 T_i}{d\xi^2}. \tag{11}$$

The general solution to this problem can be written as

$$T = A_0 + A_1 \operatorname{erf}\left(\frac{\sqrt{PeT_i}}{2} \xi\right). \tag{12}$$

In the Partially Frozen Area

$$\begin{aligned} \mathbf{v} &= s \left[(\gamma_f + \psi_0) \frac{dc}{d\xi} + \frac{dT}{d\xi} \right]; \\ -\frac{\xi}{2N_s} \frac{ds}{d\xi} + \frac{\xi}{2N_p} \left(\frac{dT}{d\xi} + \psi_0 \frac{dc}{d\xi} \right) + \frac{d\mathbf{v}}{d\xi} &= 0; \\ -\left(\frac{\gamma_c \xi}{2} - \mathbf{v} \right) \frac{dc}{d\xi} &= \frac{1}{Pe_c} \frac{d^2c}{d\xi^2} + \frac{\gamma_s \xi}{2} \frac{ds}{d\xi}; \\ -\left(\frac{\gamma_T \xi}{2} - \mathbf{v} \right) \frac{dT}{d\xi} &= \frac{1}{Pe_T} \frac{d^2T}{d\xi^2} + \frac{\gamma_q \xi}{2} \frac{ds}{d\xi}. \end{aligned} \tag{13}$$

In the Unfrozen Area – the Area III

$$\begin{aligned} \mathbf{v} &= -\frac{dp}{d\xi} + \gamma_f \frac{dc}{d\xi} \\ -\frac{\xi}{2N_{p0}} \frac{dp}{d\xi} &= \frac{d^2p}{d\xi^2} - \gamma_f \frac{d^2c}{d\xi^2}, \quad \frac{1}{N_{p0}} = \frac{1}{m_0} \left[\frac{dm}{dp} + \frac{m_0}{\rho_w} \frac{d\rho_w}{dp} \right] (T_0 - T^0) \left| \frac{dP}{dT} \right| \\ -\left(\frac{\gamma_c \xi}{2} - \mathbf{v} \right) \frac{dc}{d\xi} &= \frac{1}{s_0 Pe_c} \frac{d^2c}{d\xi^2} \\ -\left(\frac{\gamma_T \xi}{2} - \mathbf{v} \right) \frac{dT}{d\xi} &= \frac{1}{Pe_T} \frac{d^2T}{d\xi^2}. \end{aligned} \tag{14}$$

Boundary Conditions in Self-Similar Coordinates

$$\begin{aligned} \xi = 0: \quad T_i &= \frac{-\delta T_i + \delta T}{\delta T}, \quad \delta T_i = T_0 - T_i^0, \quad \delta T = T_0 - T^0; \\ \xi = \xi_1: \quad T_- &= T_+ = 0, \quad \frac{1}{PeT_i} \frac{dT_-}{d\xi} = \frac{\gamma_{qi}}{2} \xi_1 + \frac{1}{Pe_T} \frac{dT_+}{d\xi}, \\ s_1 \left(\frac{1}{Pe_{c_i}} \frac{dc_+}{d\xi} + \frac{\rho_i}{\rho_w} \frac{\xi_1}{2} c_+ \right) &= 0, \quad \mathbf{v}_+ = s_1 \left(1 - \frac{\rho_i}{\rho_w} \right) \frac{\xi_1}{2} = s_1 \left(\frac{dc_+}{d\xi} + \gamma_f \frac{dT_+}{d\xi} \right), \\ \xi = \xi_*: \quad \mathbf{v}_- - \frac{m_0}{2} s_* \xi_* - \frac{\rho_i m_0}{2\rho_w} (1 - s_*) \xi_* &= \mathbf{v}_+ - \frac{m_0}{2} \xi_*, \\ T_- = T_+ = T_* &, \quad -\gamma_q (1 - s_*) \frac{1}{2} \xi_* + \frac{1}{Pe_T} \frac{dT_-}{d\xi} = \frac{1}{Pe_T} \frac{dT_+}{d\xi}, \\ c_- = c_+ = c_* &, \quad -\gamma_s (1 - s_*) \frac{1}{2} \xi_* + \frac{1}{Pe_c} s_* \frac{dc_-}{d\xi} = \frac{1}{Pe_c} \frac{dc_+}{d\xi}; \\ \xi \rightarrow \infty: \quad p &\rightarrow p_0, \quad T \rightarrow 1, \quad c \rightarrow 1. \end{aligned} \tag{15}$$

Here: $\delta T_i, \delta T$ are temperature drops at the top and bottom of the ice layer; s_1 is the water saturation at the boundary $\xi = \xi_1$ of the second (equilibrium) area with the ice layer.

Values δT_i and s_1 are given. For solving the problem, it is necessary to find: moving boundaries of phase transitions ξ_1, ξ_* , the temperature in the ice layer; the temperature, salt concentration and water saturation in the equilibrium layer II and at its boundaries; the temperature and pressure in the unfrozen area III. In particular, it is necessary to find the temperature drop δT at the boundary $\xi = \xi_1$. Note that the boundaries at the self-similar calculus simultaneously determine the speed of the corresponding fronts.

Equalities (5)–(9) and (10)–(16) at the self-similar statement, are a closed mathematical model of freezing of rocks saturated with salt solution, taking into account the osmotic driving force.

Simplifications. In the general case, the model is rather complicated, although it can be solved. For a more convex study of the influence of osmosis, we simplify the model. First of all, we obtain a condition under which the ice layer can be neglected. To do this, the first front must move much more slowly than the second, i.e.

$$\xi_1 \ll \xi_*. \tag{17}$$

We will consider the case when the filtration rate in a partially frozen layer (area II) is small, i.e.

$$v_- \ll m_0 \xi_*.$$

To do this, either the water saturation, or the Peclet number for thermal diffusivity must be small (for example, due to low permeability), i.e.

$$s \ll 1 \text{ and/or } Pe_T \ll 1. \tag{18}$$

Then from the boundary conditions (15)–(16) we obtain the estimates

$$\begin{aligned} \xi_1^2 &\sim \frac{\lambda_{mi}}{\rho_i q m_0} (T^0 - T_i^0); \\ m_0 \left(1 - \frac{\rho_i}{\rho_w}\right) (1 - s_*) \xi_* &\sim \frac{k}{\eta} \frac{p_* - p_\infty}{l_p}, \quad l_p \sim \sqrt{\frac{k}{\eta \beta_p}}; \\ T_* &\sim T^0 + \frac{\xi_*}{l_T} (T_\infty - T^0); \\ \frac{\rho_i q m_0 (1 - s_*)}{2\lambda} \xi_* &\sim \frac{T_\infty - T_*}{l_T}, \quad l_T \sim \sqrt{\frac{\lambda}{C_m}}. \end{aligned} \tag{19}$$

Here l_p, l_T are the effective thicknesses of the perturbed pressure and temperature areas, respectively, in the third layer in the self-similar representation. They are also equal to the propagation velocities of perturbations of the corresponding fields in the third layer.

Let's choose, for example, $T_i^0, p_\infty, T_\infty$ and other input parameters so that the characteristic pressure drops are of the order of 1 MPa, and the characteristic temperature drops are taken from the interval $\Delta T \sim (10^{-1} \div 10) \text{ }^\circ\text{C}$.

Using the first two equations (19), we obtain an estimate for the permeability of dry rocks, in which the condition (17) is satisfied:

$$k \gg m_0 \left(1 - \frac{\rho_i}{\rho_w}\right)^2 \frac{\lambda_{mi}}{\rho_i q} \frac{\eta}{\beta_p (p_* - p_\infty)^2} (T^0 - T_i^0) \sim 10^{-18} (10 \div 10^{-1}).$$

Thus, if the dry rock permeability is equal to or greater than 10^{-16} , this approximation is acceptable.

Using (19) from the boundary conditions for the salt concentration in (16), we can estimate the concentration difference in the second and third layers.

Continuing the simplifications, we note that in the first consideration of the problem, without compromising the qualitative properties, in a satisfactory quantitative approximation, the third layer can also be ignored by setting fixed values of temperature and concentration at the phase transition boundary, since the temperature and salt concentration in this area change relatively weakly.

Thus, we will consider only the second partially frozen layer, where ice and solution are in thermodynamic equilibrium. The equations (13) are given for this layer. We will solve the problem in two stages. First, we find the zero approximation at a zero velocity

field, and then we find the correction associated with the motion of the solution. In the absence of motion, system (13) can be written as

$$\begin{aligned}
 &-\frac{\xi}{2N_s} \frac{ds}{d\xi} + \frac{\xi}{2N_p} \left(\frac{dT}{d\xi} + \psi_0 \frac{dc}{d\xi} \right) = 0; \\
 &-\frac{\alpha_c \xi}{2} \frac{dc}{d\xi} = \frac{d^2c}{d\xi^2} - \frac{Pe_c \gamma_s \xi}{2} s_T \frac{dT}{d\xi}, \quad \alpha_c = Pe_c(\gamma_c - \gamma_s s_c), \quad s_c = -\frac{N_s}{N_p} \psi_0; \\
 &-\frac{\alpha_T \xi}{2} \frac{dT}{d\xi} = \frac{d^2T}{d\xi^2} - \frac{Pe_T \gamma_q \xi}{2} s_c \frac{dc}{d\xi}, \quad \alpha_T = Pe_T(\gamma_T - \gamma_q s_T), \quad s_T = -\frac{N_s}{N_p}.
 \end{aligned} \tag{20}$$

We integrate the first equation in (20) and obtain

$$s = s^0 + \frac{N_s}{N_p} \left[T - \psi_0 (c^0 - c) \right]. \tag{21}$$

The solution of the other equations will be sought in the form

$$\begin{aligned}
 c &= c^0 + C_1 \operatorname{erf} \left(\frac{\sqrt{\tilde{\alpha}_c}}{2} \xi \right) + C_2 \operatorname{erf} \left(\frac{\sqrt{\tilde{\alpha}_T}}{2} \xi \right); \\
 T &= C_3 \operatorname{erf} \left(\frac{\sqrt{\tilde{\alpha}_c}}{2} \xi \right) + C_4 \operatorname{erf} \left(\frac{\sqrt{\tilde{\alpha}_T}}{2} \xi \right).
 \end{aligned} \tag{22}$$

Here the parameters $\tilde{\alpha}_c, \tilde{\alpha}_T$ need to be found, and $C_i, i = 1-4$ are arbitrary constants.

Substituting (22) into (20), we obtain a linear homogeneous algebraic system of equations. The solvability condition for the system results in an identical quadratic equation for the parameters, solving which, we obtain

$$\begin{aligned}
 \tilde{\alpha}_c &= \frac{\alpha_T + \alpha_c + \sqrt{(\alpha_c - \alpha_T)^2 + 4Pe_c \gamma_s s_T Pe_T \gamma_q s_c}}{2}; \\
 \tilde{\alpha}_T &= \frac{\alpha_T + \alpha_c - \sqrt{(\alpha_c - \alpha_T)^2 + 4Pe_c \gamma_s s_T Pe_T \gamma_q s_c}}{2}.
 \end{aligned} \tag{23}$$

After eliminating the dependent coefficients, the solution has the form

$$\begin{aligned}
 c &= c^0 + C_1 \operatorname{erf} \left(\frac{\sqrt{\tilde{\alpha}_c}}{2} \xi \right) + \frac{Pe_c \gamma_s s_T}{\alpha_c - \tilde{\alpha}_T} C_3 \operatorname{erf} \left(\frac{\sqrt{\tilde{\alpha}_T}}{2} \xi \right); \\
 T &= \frac{Pe_T \gamma_q s_c}{\alpha_T - \tilde{\alpha}_c} C_1 \operatorname{erf} \left(\frac{\sqrt{\tilde{\alpha}_c}}{2} \xi \right) + C_3 \operatorname{erf} \left(\frac{\sqrt{\tilde{\alpha}_T}}{2} \xi \right).
 \end{aligned} \tag{24}$$

The remaining coefficients C_1, C_3 are determined from the boundary conditions

$$\begin{aligned}
 c_* &= c^0 + C_1 \operatorname{erf} \left(\frac{\sqrt{\tilde{\alpha}_c}}{2} \xi_* \right) + \frac{Pe_c \gamma_s s_T}{\alpha_c - \tilde{\alpha}_T} C_3 \operatorname{erf} \left(\frac{\sqrt{\tilde{\alpha}_T}}{2} \xi_* \right); \\
 T_* &= \frac{Pe_T \gamma_q s_c}{\alpha_T - \tilde{\alpha}_c} C_1 \operatorname{erf} \left(\frac{\sqrt{\tilde{\alpha}_c}}{2} \xi_* \right) + C_3 \operatorname{erf} \left(\frac{\sqrt{\tilde{\alpha}_T}}{2} \xi_* \right).
 \end{aligned} \tag{25}$$

The salt concentration at the origin c^0 is determined from the condition that the velocity at this point is zero

$$\left(\gamma_f + \psi_0 \right) \frac{dc}{d\xi} \Big|_{\xi=0} + \frac{dT}{d\xi} \Big|_{\xi=0} = 0.$$

Substituting (24), we get

$$\left[\gamma_f + \psi_0 + \frac{Pe_T \gamma_q s_c}{\alpha_T - \alpha_c} \right] \sqrt{\alpha_c} C_1 + \left[(\gamma_f + \psi_0) \frac{Pe_c \gamma_s s_T}{\alpha_c - \alpha_T} + 1 \right] \sqrt{\alpha_T} C_3 = 0.$$

4. Mathematical Criterion for the Formation of Cryopags

In this section, we assume that the water saturation at the origin is zero. In the simplest case, for cryopag formation it is necessary that in addition to the origin of coordinates, the water saturation turned to zero at one more point ξ_0 ($0 < \xi_0 \leq \xi_*$). The derivative of water saturation at this point must be negative, i.e. the conditions must be met:

$$\text{at } \xi = \xi_0 \leq \xi_* : \quad s = 0, \quad \frac{ds}{d\xi} < 0. \tag{26}$$

We consider the complete equation for water saturation, which is obtained from system (13) after eliminating the second derivatives with respect to temperature and concentration

$$\begin{aligned} & \left[\frac{1}{N_s} - \frac{2(\gamma_f + \psi_0) \frac{dc}{d\xi} + \frac{dT}{d\xi}}{\xi} + s(Pe_T \gamma_q + (\gamma_f + \psi_0) Pe_c \gamma_s) \right] \frac{ds}{d\xi} + \\ & + s \left[Pe_T \left(\gamma_T - \frac{2\mathbf{v}}{\xi} \right) \frac{dT}{d\xi} + (\gamma_f + \psi_0) Pe_c \left(\gamma_c - \frac{2\mathbf{v}}{\xi} \right) \frac{dc}{d\xi} \right] = \frac{1}{N_p} \left(\frac{dT}{d\xi} + \psi_0 \frac{dc}{d\xi} \right); \tag{27} \\ & \mathbf{v} = s \left[(\gamma_f + \psi_0) \frac{dc}{d\xi} + \frac{dT}{d\xi} \right]. \end{aligned}$$

We assume in this equation $s = 0$, then we get

$$\left[\frac{1}{N_s} - \frac{2(\gamma_f + \psi_0) \frac{dc}{d\xi} + \frac{dT}{d\xi}}{\xi} \right] \frac{ds}{d\xi} = \frac{1}{N_p} \left(\frac{dT}{d\xi} + \psi_0 \frac{dc}{d\xi} \right). \tag{28}$$

After expanding the solution in a Fourier series in powers of ξ , and taking into account the last two equations in (13), the conditions for cryopag appearance can be written as

$$\begin{aligned} & \left. \frac{ds}{d\xi} \right|_{\xi=\xi_0} = \\ & = \frac{N_s}{N_p} \frac{\frac{\gamma_f}{\gamma_f + \psi_0} \frac{dT}{d\xi} \Big|_{\xi=\xi_0} - \left[\frac{Pe_T}{2} \left(\gamma_T + \frac{\gamma_f}{\gamma_f + \psi_0} \frac{N_s}{N_p} \gamma_q \right) - \frac{Pe_c \psi_0}{2(\gamma_f + \psi_0)} \left(\gamma_c - \gamma_f \frac{N_s}{N_p} \gamma_s \right) \right] \frac{\xi_0^2}{2} \frac{dT}{d\xi} \Big|_{\xi=\xi_0}}{1 + \left[\frac{Pe_T}{2} \left(\gamma_T + \frac{\gamma_f}{\gamma_f + \psi_0} \frac{N_s}{N_p} \gamma_q \right) - \frac{Pe_c}{2} \left(\gamma_c - \gamma_f \frac{N_s}{N_p} \gamma_s \right) \right] \xi_0 \frac{dT}{d\xi} \Big|_{\xi=\xi_0}} < 0 \tag{29} \\ & s(\xi_0) = 0. \end{aligned}$$

Consider the case of low osmosis coefficients, when

$$\gamma_f \ll \psi_0. \tag{30}$$

Then from (26)–(27) we approximately obtain

$$Pe_T \gamma_T > Pe_c \gamma_c \left[1 - \frac{\gamma_f}{\psi_0} \left(1 - \frac{N_s \psi_0}{N_p \gamma_c} \gamma_s \right) - \frac{\gamma_f}{\psi_0} \frac{N_s}{N_p} \gamma_q \right], \quad \frac{\gamma_f}{\psi_0} \ll 1. \tag{31}$$

The value of ξ_0 is found from the second equation (29) or approximately from the equation

$$\begin{aligned} \frac{\gamma_f}{\psi_0} - \left[\frac{Pe_T}{2} \left(\gamma_T + \frac{\gamma_f N_s}{\psi_0 N_p} \gamma_q \right) - \frac{Pe_c}{2} \left(\gamma_c \left(1 - \frac{\gamma_f}{\psi_0} \right) - \gamma_f \frac{N_s}{N_p} \gamma_s \right) \right] \frac{\xi_0^2}{6} &= 0; \\ \frac{Pe_T}{2} \left(\gamma_T + \frac{\gamma_f N_s}{\psi_0 N_p} \gamma_q \right) - \frac{Pe_c}{2} \left(\gamma_c \left(1 - \frac{\gamma_f}{\psi_0} \right) - \gamma_f \frac{N_s}{N_p} \gamma_s \right) &> 0. \end{aligned} \tag{32}$$

As a consequence, the cryopag requires the osmosis coefficient to be non-zero. In addition, from (29) it follows that with an increase in the osmosis coefficient, the ξ_0 increases and at some critical value γ_{fc}, ξ_0 reaches the phase transition boundary ξ_* ; with further growth of γ_f the cryopag opens and the water saturation of the area under consideration at the phase boundary increases. Thus, on the one hand, small values of the osmosis coefficient are necessary for cryopag formation, and, on the other hand, if this coefficient exceeds the critical value, a closed cryopag is not formed.

The indicated critical value γ_{fc} is found from the condition $\xi_0 = \xi_*$ or

$$s(\xi_*) = 0. \tag{33}$$

Approximately γ_{fc} can be calculated assuming in (29) $\xi_0 = \xi_*$.

5. Results and Discussion

Thus, expressions (21)–(25) give the complete problem solving in the approximation of the absence of solution motion. Next we determine the approximate velocity field from the values of the temperature, concentration, and water saturation fields from the generalized Darcy law, taking into account osmosis (13)

$$\mathbf{v} = s \left[\left(\gamma_f + \psi_0 \right) \frac{dc}{d\xi} + \frac{dT}{d\xi} \right]. \tag{34}$$

Finally, the corrected water saturation field is determined from the second equation (13) using (34). After integration, it can be written as

$$s = s^0 + \frac{N_s}{N_p} \left[T + \psi_0 (c - c^0) \right] + \frac{\mathbf{v}}{\xi} + \int_0^\xi \frac{\mathbf{v}}{\xi^2} d\xi.$$

The resulting approximation is valid as long as the corrected water saturation approximation is close to the unperturbed one at zero velocity field. This is possible either when the Peclet number is small $Pe_T \ll 1$, or when the water saturation s is sufficiently small.

In the problem of freezing of water-saturated rocks, two forces act: the force that pushes the solution into the unfrozen area, and the force that draws the solution in it. The pushing force is due to the fact that the equilibrium pressure increases with decreasing temperature, as well as the difference in the densities of water and ice, and the retracting force is due to the osmotic force. Depending on the values of the parameters, one or another force prevails.

Some of the obtained results are illustrated in Figures 2–4.

Figure 2 (a–c) shows the distributions of water saturation with depth in zero and first approximations (dotted line) for two different values of pore expansion coefficients β_p (water capacity) (a, b) and two different values of the osmotic force coefficients γ_f (a, c). Curves (1–2) correspond to two different moments of time; the dotted line shows the curves corrected with the filtration velocity field. Above the water saturation curves, the distributions of the respective filtration rates are shown.

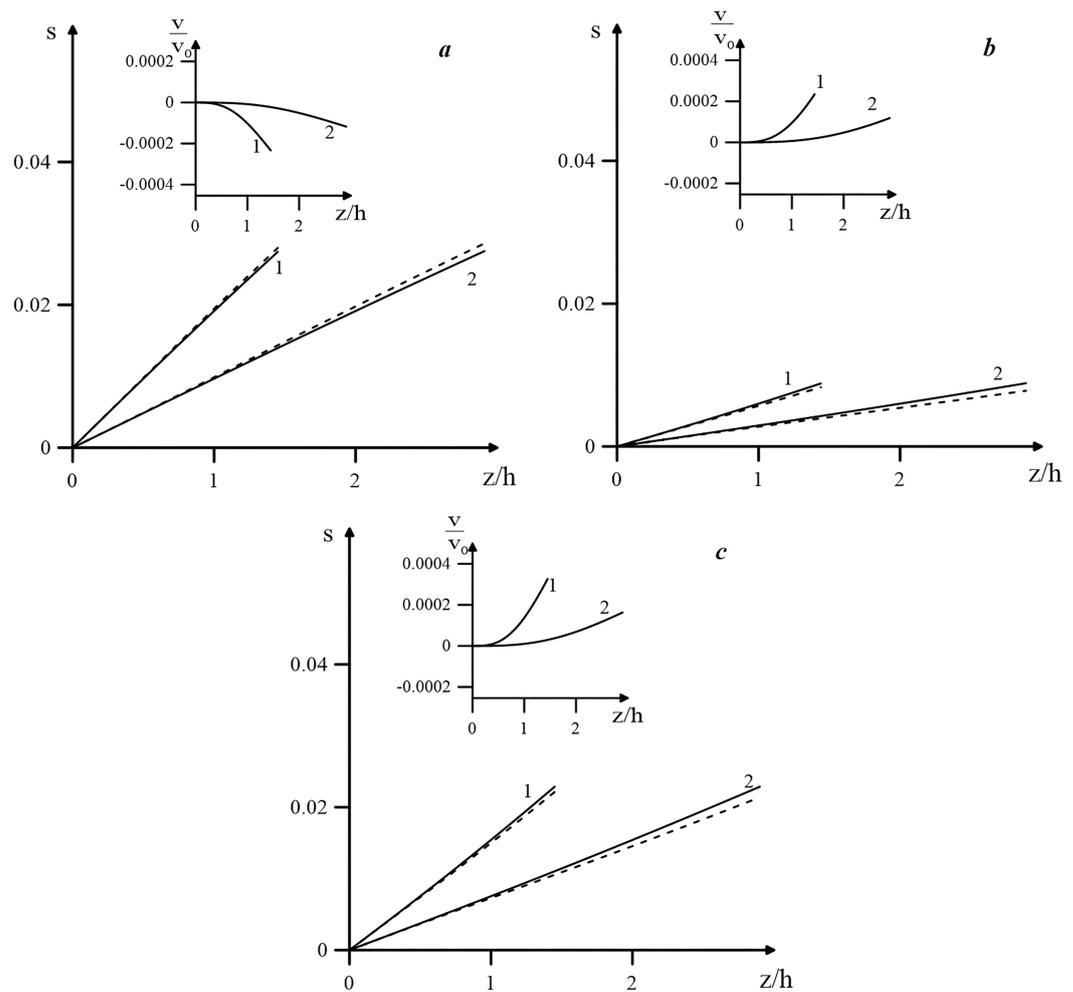


Figure 2. Water saturation distribution in the zero and first approximations (dashed line) for two points in time (the distributions of the filtration rate are shown above) for $Pe_c = 10, Pe_T = 10^{-2}, c_* = 2.8\%, T_0 = -1.88\text{ }^\circ\text{C}, \psi_0 = 1.7, t = 1$; 4 (1-2), where $(\gamma_f, \frac{1}{N_p}) = (2, 0.01)$ a); $(2, 0.003)$ b); $(1, 0.01)$ c).

First of all, it follows from [Figure 2](#) that, with time, the water saturation behind the phase transition front decreases monotonically due to freezing. In this case, the velocity field is negative, i.e. the solution is pulling into the partially frozen area from the thawed area by osmosis ([Figure 2a](#)). Accordingly, water saturation increased after correction for velocity (the dotted line is higher than the solid line). Comparing the solid and dotted lines, we see that the obtained solution has a very good accuracy with $Pe_T = 10^{-2}$.

If the water capacity β_p is reduced with unchanged other parameters, the pushing force prevails ([Figure 2b](#)). In this case, the corrected water saturation decreased. In [Figure 2c](#), in comparison with [Figure 2a](#), the osmotic force coefficient is reduced. As can be seen from the comparison, a decrease in the osmotic force also resulted in predominance of the pushing force and so leads to decrease in water saturation.

These results are quite consistent with the results of physical experiments presented in [[Chuvilin, 1999](#)], where it is shown that clays under the considered freezing conditions draw the salt solution from the thawed area, but sands are pushed it out on the contrary. At the same time, as already noted, it is known that clays have semi-permeable and, consequently, osmotic properties [[Kemper, 1961](#)].

It should be emphasized that the patterns shown in [Figure 2](#) associated with water saturation are valid, strictly speaking, only for the considered approximation of sufficiently low filtration rates. In the general case, an increase or decrease in water saturation depends not only on the inflow or outflow of the solution, but also on additional freezing of the

solution or melting of ice caused by a disturbance of the velocity field. As a result, at not too low speeds and certain values of the parameters, the dotted curve in Figure 2a can be below the solid line or cross it. This also applies to Figure 2b, c. As for the laws associated with osmosis and its influence on the direction of movement of the salt solution, in the case of “normal” osmosis it is also true for not low filtration rates.

Figure 3a–d shows the distributions of salt concentration in solution, temperature, pressure and filtration velocity fields for two different values of pore expansion coefficients β_p (water capacity) and two different values of osmotic force coefficients. We take curves 1 as the base curves for comparison. Figure 3a (curve 2) showed that a decrease in the water capacity resulted in a decrease in the salt concentration.

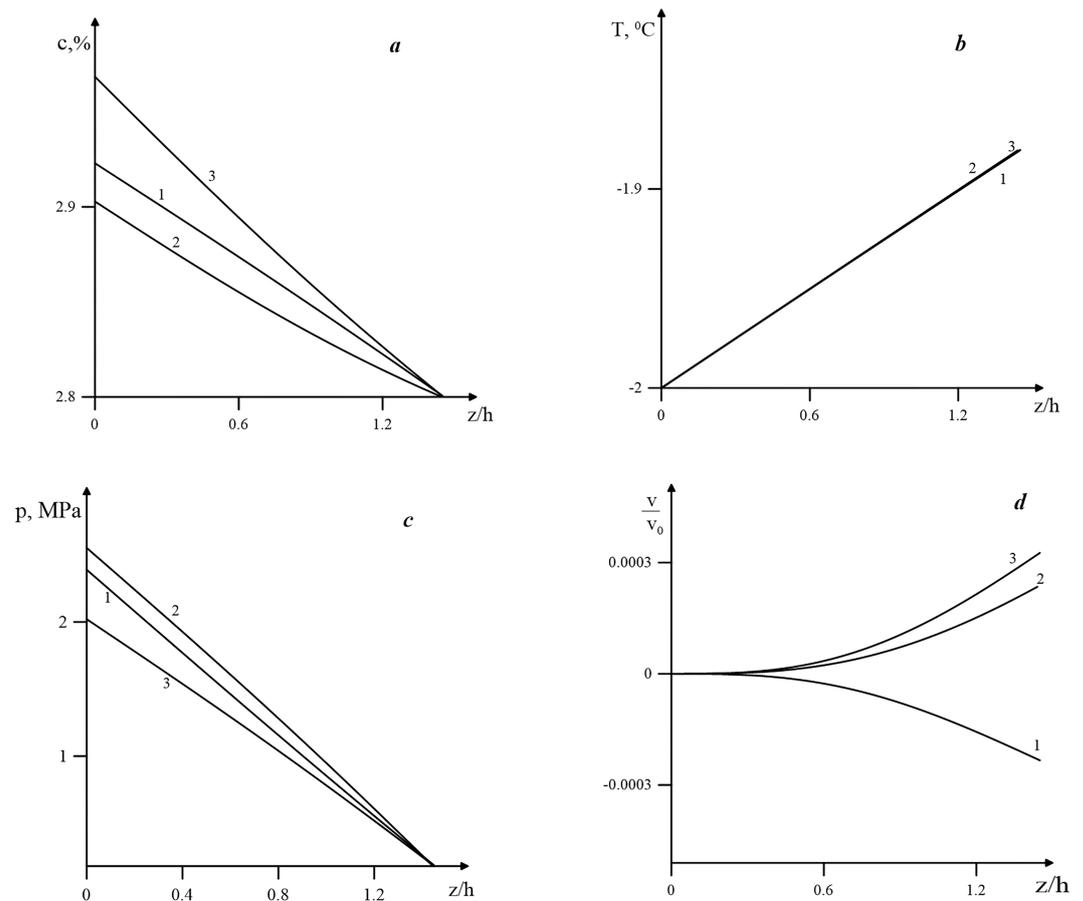


Figure 3. Distribution of salt concentration (a); temperature (b), pressure (c) and filtration rate (d) at $Pe_c = 10, Pe_T = 10^{-2}, c_* = 2.8\%, T_0 = -2\text{ }^\circ\text{C}, \psi_0 = 1.7$, where: $(\gamma_f, \beta_p = \frac{1}{N_p}) = (2, 0.01) 1); (2, 0.003) 2); (1, 0.01) 3).$

The curve 3 in Figure 3a shows that a decrease in the osmotic force coefficient leads to an increase in solution concentration. To explain these properties, first of all, we note that, as follows from Figure 3b, the temperature distributions for the three considered cases almost coincide. Such a low sensitivity of temperature to the considered changes in parameters is due to the fact that, in contrast to the concentration, the temperature is fixed at both boundaries and the curves are almost linear at the considered small Peclet numbers. The concentration at the origin is not specified, but it is found from the solution of the problem of freezing.

At a constant temperature, it follows from the condition of thermodynamic equilibrium (1)–(2) that with increasing pressure, the concentration of the solution decreases and vice versa. At the same time, a decrease in water capacity (compressibility of the skeleton) leads to an increase in pressure, and a decrease in the osmosis coefficient results in a decrease in pressure (see Figure 3c), which explains the patterns in Figure 3a–c.

Finally, from Figure 3c (curve 1), we can see that for these parameters the salt solution is drawn into the considered area. The curves 2 and 3 showed that both a decrease in water capacity and a decrease in osmotic force resulted in a predominance of the pushing force.

Thus, under certain conditions of freezing of rocks saturated with salt solution, cryopags (closed “pockets with brine”) can form in the permafrost. The mathematical criterion for the formation of a cryopag in the framework of this problem is given by formulas (26)–(33). However, the authors do not deny the possibility of other mechanisms of cryopag formation.

Some of the properties associated with cryopags are illustrated in Figure 4a, b. As calculations show, cryopags under the given conditions are formed in the presence of an osmosis coefficient γ_f , but it should be sufficiently small. Figure 4a shows that with an increase in the osmosis coefficient, the cryopag grows and expands (curve 2). With further increase in γ_f , the cryopag opens (curve 3). Figure 4b shows the evolution of the cryopag over time. The top corner shows the velocity field. We can see that the cryopag expands as the freezing front advances. In addition, we note that the solution inside the cryopag is practically immobile.

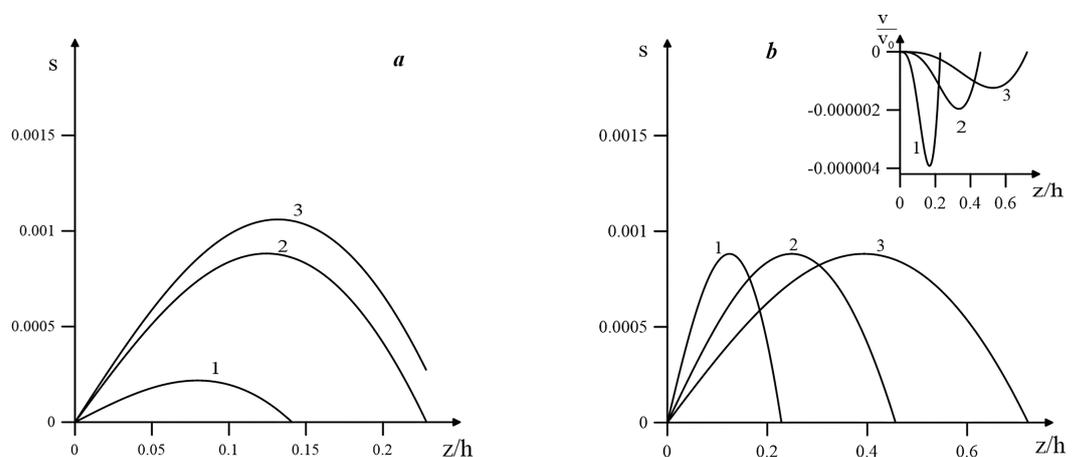


Figure 4. a) Distribution of water saturation with depth for different values of the osmosis coefficient: $\gamma_f/\gamma_{f0} = 0, 3; 0.79; 0.9$ (1–3); b) Distribution of water saturation with depth for $\gamma_f/\gamma_{f0} = 0.79$ for different time values: $t = 1; 4; 10$ (1–3); General values of parameters: $Pe_c = 10, Pe_T = 1.55, \frac{1}{N_p} = 0.1, \psi_0 = 1.7, c_* = 2.8\%, T_0 = -2 \text{ }^\circ\text{C}, T_* = -1.88 \text{ }^\circ\text{C}$.

6. Conclusion

A mathematical model of freezing for rocks saturated with salt solution is proposed. An approximate analytical solution of the problem in a self-similar formulation has been obtained, and the properties of the solution have been studied. A mathematical criterion for the formation of closed “pockets” with brines (cryopags) in frozen rocks is derived. The regularities of the osmosis effect on the process of freezing of rocks are shown, as well as the criterion for the formation of cryopags.

At high values of the osmotic coefficient, the solution is shown to be drawn into the freezing zone from the thawing zone, and at low values, on the contrary, it is pushed out. The pushing force is due to the fact that the equilibrium pressure increases with decreasing temperature, as well as to the difference in the densities of water and ice. This is quite consistent with the results of physical experiments on freezing clay and sand, where clay, in which osmotic properties are strongly pronounced, retract the salt solution, but sands, on the contrary, push it out [Chuvilin, 1999].

The proposed mathematical model makes it possible to describe not only the freezing of saturated porous media, but also the reverse process of permafrost degradation, taking into account the osmotic effect.

Note that when the phase boundary approaches the lower boundary of the reservoir, the self-similar approximation will be violated, but this does not apply to the resulting model itself. On a finite time, interval, the solution will be essentially non-stationary and, in the limit, will pass into a stationary solution.

Acknowledgments. This research, in general, was funded by the Russian Science Foundation, grant No. 22-67-00025.

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