FORMATION OF A TWO-PHASE ZONE IN THE INTERACTION OF WET ROCKS WITH COOLED SALT SOLUTION

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A self-similar solution is obtained, showing the contradictions of the front model of phase transition. A mathematical model taking account of the formation of an extended frozen region is constructed.

In drilling boreholes in rock that has been frozen for many years, it is often necessary to pass through not only frozen but also thawed rock. Water-bearing thawed zones (thaws between freezing) lie at isolated intervals over the depth in regions of both insular and continuous propagation of frozen rock [1]. The existence of wet thawed rock at negative temperatures is often due to mineralization of the pore water. If the thawed rock is flooded and is weakly connected and unstable, the drilling and bracing of boreholes poses serious difficulty because of the possibility of rock collapse, absorption of flushing liquid and reduction in strength of the bracing at negative temperatures. In such rock, special methods of drilling and bracing are employed. One such method is drilling with simultaneous bracing of rock by freezing [2, 3]. The essence of the method is that, when water cooled to negative temperature is circulated in the borehole, freezing of the water in the thawed rock occurs directly in the course of drilling. The formation of a strong ice-rock crust in the borehole walls, the core, and the moving face is assumed here. Experimental investigation of the feeezing of rock when aqueous salt solutions are used as the flushing liquid indicates that sufficiently effective freezing is accompanied by breakdown of the crust which forms, on account of thawing of the ice in contact with the flushing liquid at negative temperatures [2]. In the present work, it is shown that mineralization of the pore moisture leads to significant qualitative and quantitative features of the freezing process and combined account must be taken of the influence of mineralization of the flushing liquid and the pore moisture of thawed rock in calculating the conditions of freezing when using flushing liquids based on salt solutions of with added salt.

Consider the freezing of rock saturated with an aqueous salt solution at concentration c_0 and temperature T_0 , which is in contact with a salt solution (concentration c^0) cooled to negative temperature T^0 . For simplicity, assume that, both in the pore liquid and in the flushing liquid, the same salt is dissolved (for example, NaCl). Since freezing cocurs, $T^0 < T_0$; in addition, $T < T_{ph}(c_0)$. The condition that the flushing liquid remains unfrozen must be satisfied here: $T^0 > T_{ph}(c^0)$. Under these conditions, it is natural to expect the formation of two fronts within the framework of the classical scheme of description of phase transitions (Stefan problem) [4]: a freezing front X*(t) on account of cooling of the pore liquid in contact with the flushing liquid; and a thawing front X_x(t) on account of breakdown of the ice by the mineralized flushing liquid. A mathematical model of this process is constructed in the one-dimensional case of a plane phase-transition front, allowing all the fundamental aspects of the problem to be elucidated within the framework of the self-similar solution.

Front Model

The mathematical formulaton of the problem for the thawed zones $(0 < x < X_*)$ and $(X^* < x < \infty)$ includes the heat-conduction equation

$$\frac{\partial T}{\partial t} = a_{\rm T} \frac{\partial^2 T}{\partial x^2} \tag{1}$$

and the diffusion equation of the salt

$$\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2}.$$
 (2)

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$$\frac{\partial T}{\partial t} = a_{\mathbf{F}} \frac{\partial^2 T}{\partial x^2}.$$
(3)

At the freezing front X*(t), the Stefan condition holds

$$\lambda_{\mathbf{F}} \left(\frac{\partial T}{\partial x} \right)_{+} - \lambda_{\mathrm{T}} \left(\frac{\partial T}{\partial x} \right)_{+} = \rho_{\mathbf{I}} m q \dot{X}^{*}, \tag{4}$$

as well as the condition of complete transfer of the salt to solution in the crystallization of water

$$D\left(\frac{\partial c}{\partial x}\right)_{+} + c^* \dot{X}^* = 0, \tag{5}$$

and the conditions of temperature continuity and equality of the temperature to the equilibrium temperature of phase transition

$$T_{-} = T_{+} = T^{*} = T_{\rm ph}(c^{*}) \equiv T_{\rm w} - \alpha c^{*}.$$
 (6)

Analogusly, at the thawing front $X_{*}(t)$, the Stefan condition holds

$$\lambda_{\mathbf{F}} \left(\frac{\partial T}{\partial x} \right)_{+} - \lambda_{\mathbf{T}} \left(\frac{\partial T}{\partial x} \right)_{-} = \rho_{\mathbf{I}} m q \dot{X}_{*}, \tag{7}$$

the mass-balance condition for the salt (taking account of the dilution of solution in the thawing of ice)

$$D\left(\frac{\partial c}{\partial x}\right)_{-} + c_* \dot{X}_* = 0 \tag{8}$$

and the conditions of temperature continuity and equality of the temperature to the equilibrium temperatures of phase transition

$$T_{-} = T_{+} = T_{*} = T_{\rm ph}(c_{*}) \equiv T_{\rm w} - \alpha c_{*}.$$
 (9)

Assuming that the rock is immersed in the solution, it follows that (disregarding the possible wetting of trhe work after thawing)

$$x = 0: T = T^{0}, c = c^{0}, T_{ph}(c^{0}) < T^{0} < T_{ph}(c_{0}).$$
 (10)

The initial distribution of the temperature and concentration of the salt are assumed to be known

$$t = 0: T = T_0, c = c_0, T_0 > T_{\rm ph}(c_0).$$
 (11)

If T_0 , c_0 , T^0 , and c^0 are constant in the initial and boundary conditions in Eqs. (10) and (11), the given problem has a self-similar solution of the form

$$T = T(\xi), \quad c = c(\xi), \quad X^* = \beta t^{1/2}, \quad X_* = \gamma t^{1/2}, \quad \xi = x t^{-1/2}.$$
 (12)

This solution is written in explicit form for the thawed zones

$$0 < \xi < \gamma: T = T^{0} + (T_{*} - T^{0}) \operatorname{erf}\left(\frac{\xi}{2a_{r}^{1/2}}\right) / \operatorname{erf}\left(\frac{\gamma}{2a_{r}^{1/2}}\right),$$

$$c = c^{0} + (c_{*} - c^{0}) \operatorname{erf}\left(\frac{\xi}{2D^{1/2}}\right) / \operatorname{erf}\left(\frac{\gamma}{2D^{1/2}}\right);$$

$$\beta < \xi < \infty: T = T_{0} + (T^{*} - T_{0}) \operatorname{erfc}\left(\frac{\xi}{2a_{r}^{1/2}}\right) / \operatorname{erfc}\left(\frac{\beta}{2a_{r}^{1/2}}\right),$$

$$c = c_{0} + (c^{*} - c_{0}) \operatorname{erfc}\left(\frac{\xi}{2D^{1/2}}\right) / \operatorname{erfc}\left(\frac{\beta}{2D^{1/2}}\right)$$
(13)
$$(13)$$

and in the frozen zone ($\gamma < \xi < \beta$)

$$T = T_* + (T^* - T_*) \frac{\operatorname{erf}(\xi/2a_{\mathbf{F}}^{1/2}) - \operatorname{erf}(\gamma/2a_{\mathbf{F}}^{1/2})}{\operatorname{erf}(\beta/2a_{\mathbf{F}}^{1/2}) - \operatorname{erf}(\gamma/2a_{\mathbf{F}}^{1/2})}.$$
(15)

After substitut5ing Eqs. (12)-(15) into Eas. (4)-(9), the problem reduces to a system of two transcendental equations in γ and β , which is easily solved numerically. The following parameter values are used in the calculations: $\alpha_{\rm T} = 0.59 \cdot 10^{-6} \ {\rm m}^2/{\rm sec}$, $\alpha_{\rm F} = 1.14 \cdot 10^{-6} \ {\rm m}^2/{\rm sec}$, $\lambda_{\rm T} = 1.56 \ {\rm W/m\cdot K}$, $\lambda_{\rm F} = 2.14 \ {\rm W/m\cdot K}$, $\rho_{\rm W} = 1000 \ {\rm kg/m^3}$, $\rho_{\rm I} = 910 \ {\rm kg/m^3}$, $\rho_{\rm S} = 2000 \ {\rm kg/m^3}$, $C_{\rm W} = 4.19 \ {\rm kJ/kg\cdot K}$, $C_{\rm I} = 2.09 \ {\rm kJ/kg\cdot K}$, $C_{\rm S} = 0.92 \ {\rm kJ/kg\cdot K}$, $\lambda_{\rm W} = 0.58 \ {\rm W/m\cdot K}$, $\lambda_{\rm I} = 2.33 \ {\rm W/m\cdot K}$, $\lambda_{\rm S} = 2.09 \ {\rm W/m\cdot K}$, $D = 1.45 \cdot 10^{-9} \ {\rm m}^2/{\rm sec}$, m = 0.35, $q = 333.7 \ {\rm kJ/kg}$, $T_{\rm W} = 0^{\circ}$ C, $\alpha = 66.7^{\circ}$ C.

The results of the calculations are shown in Fig. 1. Here (and below)

$$\overline{T} = (T - T_{\mathbf{w}})/\tau, \quad \overline{c} = \alpha c/\tau, \quad \overline{T}_{\mathbf{ph}} = -\alpha c/\tau,$$

$$\tau = mq/C_{\mathbf{w}}, \quad \overline{\xi} = \xi (\lambda_{\mathbf{w}}/\rho_{\mathbf{w}}C_{\mathbf{w}})^{-1/2}.$$
(16)

The solution corresponding to the case of the freezing of rock saturated with weakly mineralized liquid is shown in Fig. 1a. It is evident that, in the thawed zone in front of the freezing zone, supercooling is seen, since the temperature curve lies below the temperature curve of phase transition uniquely corresponding to the salt concentration according to the relation $T_{ph} = T_w - \alpha c$.

The case when the front solution indicates an absence of phase transitions, or $X^* = X_*$ is also of interest. This situation arises when all of the ice formed immediately melts, on account of the insufficiently strong cooling and the high mineralization of the pore and flushing liquids. An example of the calculation of such a solution is shown in Fig. 1b. However, in this case, supercooling is again observed, which reveals an internal contradiction of the front model.

Supercooling was first observed in the crystallization of metallic alloys [5]. In [6, 7], a model of a two-phase zone between the zones of single-phase states was developed to construct a solution not admitting of supercooling. In the two-phase zone, the liquid and solid phases coexist in conditions of thermodynamic equilibrium or in conditions determined by the crystallization kinetics. In fact, the introduction of the two-phase zone entails rejection of the idea that phase transition is localized at a front, and the adoption of the concept that phase transition occurs in a temperature spectrum in the volume of the two-phase zone. This is in qualitative agreement with a physical experiment indicating dendrite growth in the case of supercooling [10]. In [8, 9], this approach was extended to the description of the freezing of aqueous salt solutions in a porous medium.

Model with Two-Phase Zone

A consistent theoretical description eliminating supercooling is now constructed. This entails introducing the model of the two-phase zone: a zone in which there is a mixture of unfrozen water and ice; the volumes of water and ice present are determined in solving the problem. In the particular case when the boudnary of thawing coincides with the near boundary of the two-phase zone, the mathematical formulation takes the form in Eqs. (1) and (2) in the thawed zones ($0 < x < X_*$) and ($X^* < x < \infty$); in the two-phase zone, the formulation includes an energy equation which takes into account that phase transition occurs in the whole volume of the zone

$$(\rho C)_{t} \frac{\partial T}{\partial t} = \frac{\partial}{\partial x} \lambda_{t} \frac{\partial T}{\partial x} - mq \rho_{I} \frac{\partial v}{\partial t}, \qquad (17)$$

the mass-conservation law for the salt in the solution

$$\frac{\partial}{\partial t} (vc) = D \frac{\partial}{\partial x} v \frac{\partial c}{\partial x}$$
(18)

and the condition of thermodynamic equilibrium: the local temperature of the mixture of ice and solution is equal to the temperature of phase transition corresponding to the local salt concentration in solution



Fig. 1. Dependence of the dimensionless temperature, salt concentration and phase-transition temperature on the dimensionless self-similar variable in the front solution: a) $T_0 = 2^{\circ}C$, $T^0 = -2^{\circ}C$, $c_0 = 0.003$, $c^0 = 0.05$; b) $T_0 = 1^{\circ}C$, $T^0 = -3^{\circ}C$, $c_0 = 0.03$, $c^0 = 0.05$.

$$T = T_{\rm ph}(c) = T_{\rm w} - \alpha c. \tag{19}$$

Here $(\rho C)_t = \rho_s C_s (1 - m) + \rho_w C_w m v + \rho_I C_I m (1 - v), \lambda_t = \lambda_s (1 - m) + \lambda_w m v + \lambda_I m (1 - v).$

At the rear boundary of the two-phase zone, the conditions of heat and mass balance of the salt hold, taking account of the desired value of the moisture content v_x at this boundary $x = X_x(t)$

$$\lambda_{t} \left(\frac{\partial T}{\partial x}\right)_{+} - \lambda_{T} \left(\frac{\partial T}{\partial x}\right)_{-} = \rho_{I} \eta q (1 - v_{*}) \dot{X}_{*},$$

$$D \left(\frac{\partial c}{\partial x}\right)_{-} - D v_{*} \left(\frac{\partial c}{\partial x}\right)_{+} + (1 - v_{*}) \dot{X}_{*} = 0,$$

$$T_{-} = T_{+} = T_{*} = T_{ph}(c_{*}) \equiv T_{w} - \alpha c_{*}, \quad c_{-} = c_{+} = c_{*}.$$
(20)

At the forward boundary of the two-phase zone X*, the moisture content v^* is unity. Here the continuity condtiions for the temperature, the salt concentration, and the heat and mass fluxes of salt $x = X^*(t)$ are satisfied

$$\left(\frac{\partial T}{\partial x}\right)_{-} = \left(\frac{\partial T}{\partial x}\right)_{+}, \quad \left(\frac{\partial c}{\partial x}\right)_{-} = \left(\frac{\partial c}{\partial x}\right)_{+},$$

$$\mathbf{v}^{*} = 1, \quad T_{-} = T_{+} = T^{*} = T_{\mathbf{ph}}(c^{*}) \equiv T_{\mathbf{w}} - \alpha c^{*}, \quad c_{-} = c_{+} = c^{*}.$$
 (21)

The boundary conditions at the motionless boundary and the initial conditions take the form in Eqs. (10) and (11), respectively.

If T_0 , c_0 , T^0 , and c^0 are constant in the initial and boundary conditions, the given problem has a self-similar solution of the form in Eq. (12); here again, $v = v(\xi)$. This solution is written in the explicit form in Eq. (13) in the thawed zone ($0 < \xi < \gamma$) and in Eq. (14) in the thawed zone ($\beta < \xi < \infty$). In the two-phase zone ($\gamma < \xi < \beta$), a system of ordinary differential equations is obtained

$$\lambda_{t} T'' + T' v' m (\lambda_{w} - \lambda_{1}) + m \rho_{1} \gamma v' \xi/2 + T' (\rho C)_{t} \xi/2 = 0,$$

$$Dvc'' + Dvc' + vc' \xi/2 + cv' \xi/2 = 0,$$
(22)

and the temperature and salt concentration are related at each point by the condition of thermodynamic equilibrium in Eq. (19).

Thus, finding the solution reduces to solving the boundary problem for the system in Eqs. (19) and (22) with the boundary conditions at the desired boundaries of the two-phase zone in Eqs. (20) and (21).

The results of the calculations are shown in Fig. 2. Here the two-phase zone ($\gamma < \xi < \beta$) is a zone of partial freezing, where phase transition occurs in a temperature spectrum in the volume occupied by a mixture of mineralized water and ice, and the boundary of the



Fig. 2. Dependence of the dimensionless temperature, salt concentration, and moisture content on the dimensionless self-similar variable in the solution with a two-phase zone: a, b) as in Fig. 1.



Fig. 3. Regions of realization of different freezing conditions $(\omega = 0.227 \ 10^{-2}, \varphi^{0} = 0.1191)$: 1) $\varphi_{0} = 0.48 \cdot 10^{-4}$; 2) $0.95 \cdot 10^{-4}$; 3) $1.43 \cdot 10^{-4}$; 4) $1.91 \cdot 10^{-4}$.

zone and the distribution of the desired functions are completely determined by the set of initial and boundary conditions.

Regions of Realization of Freezing Conditions

In the space of dimensionless parameters of the problem, the boundaries of the regions of realization of front conditions and conditions with the formation of a two-phase zone are now found. The following dimensionless parameters are introduced

$$\omega = D/a_{\tau}, \quad \theta_0 = (T_0 - T_{\rm ph}(c_0))/\tau, \\ \theta^0 = (T^0 - T_{\rm ph}(c_0))/\tau, \quad \phi_0 = \alpha c_0/\tau, \quad \phi^0 = \alpha c^0/\tau.$$
(23)

The front model becomes inapplicable in two cases: first, when supercooling appears in front of the crystallization front; and second, when the solution indicates the absence of phase transitions in the supercooling of pore water. In these cases, the solution of the problem is constructed taking account of the formation of a two-phase zone. Thus, analysis of the front model allows the boundaries of the different regions to be constructed.

The boundaries on the plane (θ_0, θ°) are shown in Fig. 3 with various values of φ_0 and fixed φ^0 and ω . Here the regions above the curves correspond to front conditions of crystallization, and increase in the initial salt concentration φ_0 leads to reduction in their region of realization and correspondingly to increase in the region of realization of conditions with the formation of a two-phase zone (the regions under the curves). With any φ_0 , an interval of initial temperatures θ_0 for which front conditions of phase transitions do not appear at all (the case of no phase transformations) may be isolated.

As follows from this analysis of the applicability of the front model to the description of the freezing of thawed rocks by cooled salt solution, there is a parameter range in which this model leads to contradiction (supercooling) and does not permit adequate description of the physical process. On account of the dependence of the phase-transition temperature on the salt concentration, freezing of the solution occurs not at a localized front but in the volume of the zone of coexistence of unfrozen water and ice. The use of the model of the two-phase zone allows the contradiction of the front scheme to be eliminated; in fact, this model is a formalization of the well-known principle of dynamic equilibrium of water and ice in frozen rock formulated in [11] on the basis of numerous experimental data. For the given process of the freezing of thawed rock by a cooled salt solution, there is a range of parameters in which no formation of a continuous ice-rock crust occurs, since only partial freezing occurs on account of the mineralization of pore water, and mineralization of flushing liquid leads to thawing of the ice which forms. This conclusion agrees with the observable formation of a "slush" zone in the experiment [2]. However, reduction in temperature of the flushing liquid results in decrease in content of unfrozen water in the partialfreezing zone, which leads to improvement in the strength properties and decrease in permeability of the frozen rock.

NOTATION

c, mass concentration of salt; T, temperature; T_{ph} , phase-transition temperature; T_w , phase-transition temperature of pure water; X, coordinate of the zone boundary; v, moisture content (volume of liquid per unit pore volume); m, porosity; a, thermal diffusivity; D, diffusion coefficient of salt; λ , thermal conductivity; C, specific heat; ρ , density; q, heat of phase transition; α , coefficient of reduction in phase-transition temperature; ξ , self-similar variable; γ , β , self-similar coordinates of the zone boundaries; ω , θ_0 , θ^0 , Ψ_0 , and Ψ^0 , dimensionless parameters introduced in Eq. (23). Indices: I, ice; w, water; s, skeletal frame of porous medium; *, value at zone boundary; O, initial and boundary conditions; T, thawed zone; F, frozen zone; t, two-phase zone.

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