

2. S. E. Grechinshchev, L. V. Chistotinov, and Yu. L. Shur, *Cryogenic Physicomechanical Geological Processes and Their Prediction* [in Russian], Moscow (1980).
3. J. M. Konrad, *Can. Geotech. J.*, 21, 100-115 (1984).
4. Yu. S. Daniélyan and P. A. Yanitskii, *Inzh.-Fiz. Zh.*, 44, No. 1, 91-98 (1983).
5. I. I. Nesterov, Yu. S. Daniélyan, P. A. Yanitskii, and V. N. Galieva, *Dokl. Akad. Nauk SSSR*, 277, No. 4, 928-932 (1984).
6. Yu. S. Daniélyan, P. A. Yanitskii, V. G. Cheverev, and Yu. P. Lebedenko, *Inzh. Geol.*, No. 3, 77-83 (1983).
7. V. A. Kudryavtsev (ed.), *General Geocryology* [in Russian], Moscow (1978).
8. M. Bouls and M. Ézishék, *Teploperedacha*, 105, No. 2, 161-163 (1983).
9. T. N. Zhestkova, *The Formation of the Cryogenic Structure of Soils* [in Russian], Moscow (1982).

## THE COOLING OF A SALT SOLUTION

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UDC 532.78:536.42

Self-similar formulation is used to demonstrate the possibility of a regime involving formation of a zone with two-phase state. The boundary is found between crystallization regimes with abrupt phase transition front and with extended mixture zone.

We will consider a generalization of the classical Stefan problem (see, for example, [1, 2]) of one-dimensional passage of a planar crystallization front through a cooled liquid. We will assume that in the liquid (water) there is dissolved a small quantity of material (salt) which does not enter the solid phase upon crystallization. Since the dissolved material decreases the phase transition temperature and is retained in the liquid phase upon crystallization, it is necessary to solve a mixed thermodiffusion problem, similar to that of crystallization of a binary alloy [2, 3]. As is well known, analysis of the self-similar solution [3] has shown that it becomes physically absurd at some parameter range, since in the melt zone ahead of the phase transition front the temperature of the melt proves to be lower than the local crystallization temperature. This occurs because for a sufficiently small diffusion coefficient the concentration ahead of the front decreases very rapidly and the corresponding phase transition temperature increases with removal from the front more rapidly than the local temperature. This effect has been termed "diffusion" supercooling [3]. To construct a solution free of this shortcoming the concept and model of a two-phase zone was introduced, which on the average describes crystallization with formation of dendrites in the case of supercooling [4, 5]. This model, well known in metallurgy, has apparently not been applied to freezing processes in salt solutions, in particular, to freezing of soil moisture. Meanwhile, formation of a two-phase zone here can lead to significant quantitative and even qualitative effects. The goal of the present study is the formulation of a corresponding mathematical model and determination of the boundaries of problem parameters separating qualitatively different freezing regimes.

The fact that the classical "Stefan" regime may not be realizable is illustrated by Fig. 1, which gives an example of calculation of the self-similar solution of the problem of freezing of an aqueous solution of NaCl assuming the presence of a phase transition front. It is clear that supercooling of the solution ahead of the freezing front occurs. We will now assume that between the impurity-free ice and the liquid solution there exists an intermediate zone with a two-phase state, in which ice and the solution coexist in a state of local thermodynamic equilibrium, so that their temperatures are equal to each other and the phase transition temperature for the local value of the salt concentration in the solution. Such behavior has been observed in experiment [6], although it has been calculated only with neglect of salt diffusion.

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Mechanics Problems Institute, Academy of Sciences of the USSR, Moscow. Translated from *Inzhenerno-Fizicheskii Zhurnal*, Vol. 51, No. 5, pp. 817-821, November, 1986. Original article submitted February 5, 1985.

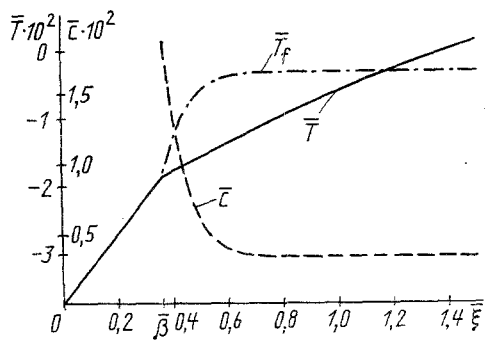


Fig. 1

Fig. 1. Dimensionless temperature  $\bar{T}$ , salt concentration  $\bar{c}$ , and local phase transition temperature  $\bar{T}_f$  vs dimensionless self-similar variable  $\bar{\xi}$  in frontal solution:  $k = -0.0149 \text{ K}^{-1}$ ;  $c_0 = 0.003$ ;  $T_0 = 276.15 \text{ K}$ ;  $T^0 = 271.15^\circ\text{K}$ .

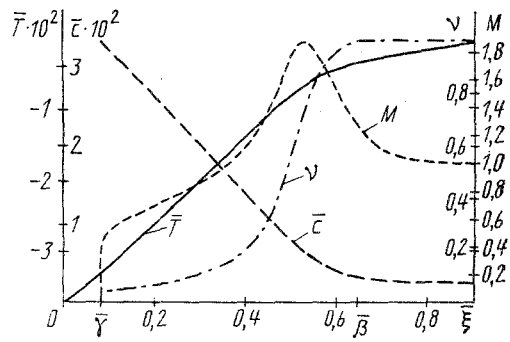


Fig. 2

Fig. 2. Dimensionless temperature  $\bar{T}$ , salt concentration  $\bar{c}$ , salt mass  $M$ , and moisture  $v$  vs dimensionless self-similar variable  $\bar{\xi}$  in solution with two-phase zone; see Fig. 1 for parameter values.

In one-dimensional formulation, corresponding to passage of a planar freezing front, this system corresponds to the problem

$$\rho_s C_s \frac{\partial T}{\partial t} = \lambda_s \frac{\partial^2 T}{\partial x^2}, \quad c = 0 \quad (0 \leq x \leq X_1(t)); \quad (1)$$

$$\frac{\partial}{\partial t} [\rho_m C_m T] = \frac{\partial}{\partial x} \left( \lambda_m \frac{\partial T}{\partial x} \right) - \rho_s q \frac{\partial v}{\partial t},$$

$$\frac{\partial (vc)}{\partial t} = D \frac{\partial}{\partial x} \left( v \frac{\partial c}{\partial x} \right), \quad T = f(c) \quad (X_1(t) \leq x \leq X_2(t)); \quad (2)$$

$$\rho_l C_l \frac{\partial T}{\partial t} = \lambda_l \frac{\partial^2 T}{\partial x^2}, \quad \frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2} \quad (X_2(t) \leq x < \infty); \quad (3)$$

$$T_- = T_+ = T_* = f(c_*), \quad c_* \frac{dX_1}{dt} = -D \left( \frac{\partial c}{\partial x} \right)_+,$$

$$\lambda_s \left( \frac{\partial T}{\partial x} \right)_- - \lambda_m (v_*) \left( \frac{\partial T}{\partial x} \right)_+ = \rho_s v_* q \frac{dX_1}{dt} \quad (x = X_1(t)); \quad (4)$$

$$v = 1, \quad c^+ = c^- = c^*, \quad T^+ = T^- = T^* = f(c^*),$$

$$\left( \frac{\partial T}{\partial x} \right)^+ = \left( \frac{\partial T}{\partial x} \right)^-, \quad \left( \frac{\partial c}{\partial x} \right)^+ = \left( \frac{\partial c}{\partial x} \right)^- \quad (x = X_2(t)); \quad (5)$$

$$T(x, 0) = T_0, \quad c(x, 0) = c_0, \quad T_0 > f(c_0), \quad T(0, t) = T^0 < f(c_0). \quad (6)$$

Equations (1)-(3) express thermal and salt concentration balance for the three zones, Eqs. (4) and (5) are integral analogs of the equations of conservation of heat and impurity, written for the boundaries of the zones with consideration of the fact that on the boundary between the mixture and solution zones the fraction of liquid phase  $v$  tends to 1. In further calculations it will be assumed that the heat capacity and transfer coefficients in the two-phase zone obey the mixture rule:

$$\rho_m C_m = v \rho_l C_l + (1-v) \rho_s C_s, \quad \lambda_m = v \lambda_l + (1-v) \lambda_s, \quad D_m = v D. \quad (7)$$

If the initial and boundary conditions  $T_0$ ,  $T^0$ , and  $c_0$  are constants, then the problem formulated has a self-similar solution of conventional form:

$$T = T(\xi), \quad c = c(\xi), \quad X_i = \xi_i \sqrt{t}, \quad \xi = x t^{-1/2}. \quad (8)$$

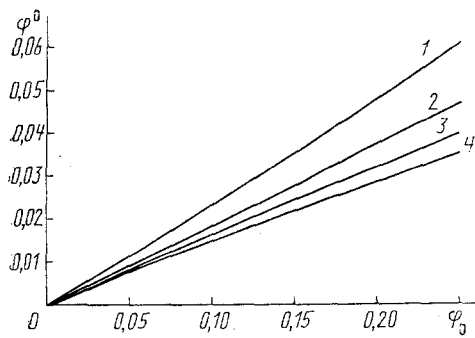


Fig. 3. Boundary between crystallization regimes in plane  $(\phi_0, \phi^0)$  for fixed value of  $D/\kappa_l = 0.02$  and various values of  $\psi$ : 1)  $\psi = 0.0025$ ; 2)  $0.0046$ ; 3)  $0.4169$ ; 4)  $0.0292$  ( $\psi^* = 0.0292$ ; classical regime with abrupt phase transition front corresponds to region below curves).

Its determination reduces to solution of the boundary problem for a system of ordinary differential equations which can be written in explicit form for regions of a one-phase state:

$$T = T^0 + (T_* - T^0) \operatorname{erf}(\xi/2\sqrt{\kappa_s})/\operatorname{erf}(\gamma/2\sqrt{\kappa_s}) \quad (0 \leq \xi \leq \gamma);$$

$$T = T_0 + (T^* - T_0) \operatorname{erfc}\left(\frac{\xi}{2\sqrt{\kappa_l}}\right)/\operatorname{erfc}\left(\frac{\beta}{2\sqrt{\kappa_l}}\right), \quad \beta \leq \xi < \infty; \quad (9)$$

$$c = c_0 + (c^* - c_0) \operatorname{erfc}\left(\frac{\xi}{2\sqrt{D}}\right)/\operatorname{erfc}\left(\frac{\beta}{2\sqrt{D}}\right), \quad \beta \leq \xi < \infty;$$

$$T^* = f(c^*).$$

The constants  $\gamma$ ,  $\beta$ ,  $c^*$ ,  $T^*$  must be determined from the condition of consistency of the solutions through the mixture zone, in which after substitution of Eqs. (8), (2), (4), and (5) we have

$$\lambda_m T'' + T'v'(\lambda_l - \lambda_s) + T'\rho_m C_m \xi/2 + v'T(\rho_l C_l - \rho_s C_s)\xi/2 + \rho_s qv'\xi/2 = 0,$$

$$Dvc'' + Dv'c' + vc'\xi/2 + cv'\xi/2 = 0. \quad (10)$$

We will assume the quantity  $k = (f')^{-1}$  constant. Then  $c = k(T - T_w)$  and Eq. (10) becomes a system for determination of the quantities  $T$  and  $v$  with the supplementary conditions:

$$T = T_*, \quad c = c_* = k(T_* - T_w), \quad c_*\gamma/2 = -Dc'_+,$$

$$\lambda_s T'_- - \lambda_m(v_*)T'_+ = \rho_s v_* q\gamma/2 \quad (\xi = \gamma),$$

$$T = T^*, \quad c = c^* = k(T^* - T_w), \quad v^* = 1, \quad (11)$$

$$T'_- = T'_+, \quad c'_- = c'_+ \quad (\xi = \beta).$$

The nonlinear boundary problem of Eqs. (10), (11) can be solved numerically. To do this we first specify an arbitrary value of  $\beta$ , then solve the Cauchy problem for system (10) and select a value of  $\gamma(\beta)$ , which satisfies the boundary condition

$$c_*\gamma/2 = -Dc'_+ \quad (\xi = \gamma) \quad (12)$$

on the boundary between the solid phase and the mixture. The thermal balance condition

$$\lambda_s T'_- - \lambda_m(v_*)T'_+ = \rho_s v_* q\gamma/2 \quad (\xi = \gamma), \quad (13)$$

is not then, generally speaking, satisfied. Therefore iterations are performed for the initial  $\beta$  value until both Eqs. (12) and (13) are satisfied to the specified accuracies. Calculation results are shown in Fig. 2. Qualitatively they reflect the expected features of the solution. It is interesting that under the influence of a concentration gradient directed toward the surface ( $x = 0$ ) an oppositely directed flow of salt develops, with its mass per unit volume of the medium increasing with removal from ice-mixture boundary in the direction of increasing temperature, reaching a maximum near the mixture-solution boundary, and then decreasing to its initial unperturbed value.

From the applications viewpoint the question of the conditions under which transition from the "discontinuous" (classical Stefan) crystallization regime to the mixture zone regime considered above occurs is of importance. Limiting ourselves to the case of linear

dependence of the phase transition temperature  $T_f$  on impurity concentration  $c$ , we can easily show by dimensional analysis that the problem has four independent dimensionless parameters:

$$\varphi_0 = (T_0 - T_f(c_0))/\theta, \quad \varphi^0 = (T_f(c_0) - T^0)/\theta, \quad (14)$$

$$\psi = |c_0/k\theta|, \quad D/\kappa_l.$$

Here the characteristic temperature  $\theta = q\kappa_l/\lambda_l$  is the "temperature equivalent of the heat of phase transition of the pure liquid." Thus, the boundary between the regimes is a three-dimensional surface in the four-dimensional space of the process parameters, Eq. (14). For a fixed solvent-dissolved material system, the last of the four parameters is fixed. Figure 2 shows the boundary between the regimes in the plane of the parameters  $(\phi_0, \phi^0)$  for various values of the dimensionless initial concentration  $\psi$ . It is clear that low values of the cooling  $\phi^0$  and low salt concentrations correspond to the classical regime with abrupt phase transition front. In the plane  $(\phi_0, \phi^0)$  such a regime corresponds to the area below the curves separating the regimes. Increase in the dimensionless initial salt concentration  $\psi = |c_0/k\theta|$  naturally leads to reduction in size of the zone corresponding to the classical regime. However, it proves to be the case that beginning at some dimensionless concentration value  $\psi = \psi^*$  the converse is observed: the region of existence of the classical regime expands with increase in  $\psi$ . Thus, for a fixed value of the parameter  $D/\kappa_l$  there is an area in the plane  $(\phi_0, \phi^0)$  in which the classical crystallization regime is always realized for any initial concentration (of course, while the linear dependence of phase transition temperature on concentration is preserved and local precipitation of salt does not occur).

In the mixture zone the phase distribution is significantly non-one-dimensional; formation of such structures has been observed repeatedly in rapid crystallization of binary systems (see, for example, [7]). However, it is significant that on the whole, such a non-one-dimensional pattern can be described one-dimensionally.

#### NOTATION

$t$ , time;  $x$ , coordinate;  $\rho$ , density;  $C$ , specific heat;  $\lambda$ , thermal conductivity coefficient;  $\kappa$ , thermal diffusivity;  $D$ , diffusion coefficient;  $q$ , specific heat phase transition of water;  $f$ , liquidus curve;  $T$ , temperature;  $c$ , salt concentration;  $v$ , moisture (volume fraction of liquid per unit volume of medium);  $x_{1,2}$ , coordinates of zone boundaries;  $\xi$ , self-similar variable;  $\gamma, \beta$ , self-similar coordinates of zone boundaries;  $T_w$ , crystallization temperature of water. Dimensionless variables and parameters:  $\bar{T} = (T - T_w)/\theta$ , temperature;  $\bar{T}_f = (f(c) - T_w)/\theta$ , phase transition temperature;  $\bar{c} = -c/k\theta$ , salt concentration;  $\bar{\xi} = \xi/\sqrt{\kappa_l}$ , self-similar variable;  $\bar{\gamma} = \gamma/\sqrt{\kappa_l}$ ,  $\bar{\beta} = \beta/\sqrt{\kappa_l}$ , self-similar coordinates of zone boundaries;  $M = vc/c_0$ , mass of salt;  $\phi, \psi$ , parameters introduced in Eq. (14). Subscripts:  $s$ , pure ice zone;  $l$ , liquid solution zone;  $m$ , mixture zone (two-phase zone);  $-$ , to left of zone boundary;  $+$ , to right of zone boundary;  $*$ , value on zone boundary.

#### LITERATURE CITED

1. A. N. Tikhonov and A. A. Samarskii, Equations of Mathematical Physics [in Russian], Moscow (1966).
2. L. I. Rubinshtein, The Stefan Problem [in Russian], Riga (1967).
3. G. P. Ivantsov, Dokl. Akad. Nauk SSSR, 81, No. 2, 179-181 (1951).
4. V. T. Borisov, Dokl. Akad. Nauk SSSR, 136, No. 3, 583-586 (1961).
5. V. T. Borisov, V. V. Vinogradov, and I. L. Tyazhel'nikova, Izv. Vyssh. Uchebn. Zaved., Chern. Metall., No. 5, 127-134 (1977).
6. L. Y. Fang, F. B. Cheung, J. H. Linehan, and D. R. Pedersen, Trans. ASME: J. Heat Transf., 106, 385-393 (1984).
7. C. Korber, M. Scheiwe, and K. Wollhover, Int. J. Heat Mass Transf., 26, 1241-1253 (1983).