Journal of Engineering Physics and Thermophysics, Vol. 75, No. 5, 2002

APPLICATION OF THE LUIKOV APPROXIMATE SOLUTIONS TO MATHEMATICAL DESCRIPTION OF THE PROCESS OF SELF-FREEZING OF MATERIALS BY DECREASING PRESSURE

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UDC 66.047.2

A mathematical model for the process of self-freezing of moist materials in a continuously increasing vacuum which is developed on the basis of the approximate solutions obtained by A. V. Luikov for drying of capillary-porous media is presented. Results of experimental investigations into the self-freezing of a moist cloth are given, from which the temperature of supercooling of the surface material layer, the temperature coefficient, and the velocity of deepening of the freezing surface are determined; all of these parameters are used in mathematical simulation of the above process.

The problems concerning freezing of moist materials are the focus of [1–3], in which the mathematical models proposed can be subdivided into two groups [4]. The first group includes the models with a generalized Stefan-type condition on the moving interface of thawed and frozen zones; in this case the existing solutions have a particular nature and satisfy specifically assigned boundary conditions [5].

The mathematical models with phase transitions in the entire volume of the massif which belong to the second group are presented by the system of Luikov differential equations [6]. Numerical solution of the latter entails certain difficulties associated with the necessity of assigning the conditions on the freezing boundary and the value of the phase-transformation criterion ε.

In the majority of cases, in the crystallization zone we have the transfer of liquid moisture ($\varepsilon_1 < 1$), while in the moist zone the liquid is partially evaporated ($\varepsilon_2 \neq 0$), i.e., ε is a continuous function of the coordinates and the time.

In technological and energy aspects, the best method of freezing a material is its self-freezing under the conditions of decrease in the pressure. In evacuation of the system, the moisture is intensely evaporated, causing a decrease in the material temperature. When the pressure in a hermetic chamber attains a value corresponding to the triple point of water (4.58 mm Hg), free moisture is frozen [7].

The intense evaporation of involatile liquids such as water is ensured at a low residual pressure in the vacuum chamber. Assuming the process to be implemented in the absence of an inert gas (air), which is removed over this period, the differential equations of change of the partial pressure and the vapor-phase temperature [8] for the case of removal of a single fluid are rearranged to the form

$$\frac{dp}{d\tau} = \frac{FR^* T}{V_{\text{fr}}\mu} j - p\left(\frac{V_{\text{v.sys}}}{V_{\text{fr}}} - \frac{1}{T}\frac{dT}{d\tau}\right), \tag{1}$$

$$\frac{dT}{d\tau} = \left[\frac{(\alpha\,(T_{\text{mt.sur}} - T) + T_{\text{mt.sur}} jc)\, FR^*}{c_\mu p} - V_{\text{v.sys}}\right]\frac{T}{V_{\text{fr}}}\,. \tag{2}$$

Kazan State Technological University, Kazan, Russia. Translated from Inzhenerno-Fizicheskii Zhurnal, Vol. 75, No. 5, pp. 34–37, September–October, 2002. Original article submitted October 3, 2001; revision submitted March 29, 2002.

1062-0125/02/7505-1048$27.00

To describe heat and mass transfer in self-freezing of moist materials, we used the Luikov approximate solutions [6] obtained for drying of capillary-porous materials.

At the initial stage of the process with a constant rate of drying the moisture is mainly evaporated on the surface of the capillary-porous body and partially in the inner layers. The approximate solution assumes the distribution of the temperature and the moisture content inside the material on condition of constancy of the pressure at all the points of the product following the parabolic law [6]

$$T_{\text{mt2}} = T_{\text{mt.cn}} - \left(\frac{x}{R_{\text{mt}}}\right)^2 (T_{\text{mt.cn}} - T_{\text{mt.sur}}) \,, \tag{3}$$

$$U_2 = U_{\text{cn}} - \left(\frac{x}{R_{\text{mt}}}\right)^2 (U_{\text{cn}} - U_{\text{sur}}) \,. \tag{4}$$

The boundary conditions on the moist material–vapor phase interface for the system of equations (1)–(4) have the following form:

the initial conditions

$$T\,(0, x) = T_{\text{mt2}}\,(0, x) = T_{\text{in}} \,, \tag{5}$$

$$U_2\,(0, x) = U_{\text{2in}} \,; \tag{6}$$

the boundary conditions ($x = R_{\text{mt}}$)

$$2a_{\text{m2}}\,\rho_0 \left(\frac{U_{\text{sur}} - U_{\text{cn}}}{R_{\text{mt}}} + \delta_{\text{tem}} \frac{T_{\text{mt.sur}} - T_{\text{mt.cn}}}{R_{\text{mt}}}\right) - j_{\text{sur}} = 0 \,, \tag{7}$$

$$-\,\lambda_2 \frac{2}{R_{\text{mt}}} (T_{\text{mt.sur}} - T_{\text{mt.cn}}) - r j_{\text{sur}} = 0 \,, \tag{8}$$

$$U_{\text{sur}} = \frac{c_{\text{mt}} + U_{\text{in}} c_{\text{liq}}}{c_{\text{liq}}} \left[\frac{r_0 + (c_{\text{vp}} - c_{\text{liq}})\,(T_{\text{mt.sur}} - 273)}{r_0 + (c_{\text{vp}} - c_{\text{liq}})\,(T_{\text{mt.in}} - 273)}\right]^{\frac{c_{\text{liq}}}{c_{\text{vp}} - c_{\text{liq}}}} - \frac{c_{\text{mt}}}{c_{\text{liq}}} \,, \tag{9}$$

$$T_{\text{mt.sur}} = \frac{B}{A - \ln p_{\text{sat}}} \,; \tag{10}$$

the symmetry conditions

$$\left.\frac{dT_{\text{mt}}}{dx}\right|_{x=0} = 0 \,, \quad \left.\frac{dU}{dx}\right|_{x=0} = 0 \,. \tag{11}$$

According to boundary condition (9), the change in the moisture content of the material surface is unambiguously determined by the rate of decrease of the pressure [9] expressed in terms of the temperature from the Antoine equation (10).

Further decrease in the pressure of the medium leads to the supercooling and freezing of moisture on the material surface [7]. The formulation of the problems on freezing of moist materials assumes that between the thawed and frozen zones there is the interface (surface of freezing), which moves into the depth of the body with a constant

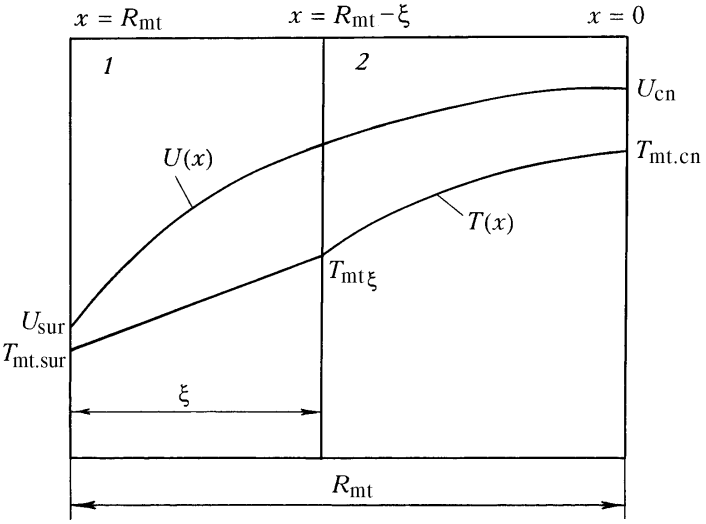

Fig. 1. Curves of distribution of the temperature and the moisture content over the material thickness in deepening of the crystallization zone during self-freezing: 1) crystallization zone; 2) moist zone.

velocity. Up to this boundary the moisture is only in the form of ice, whereas the moisture of the thawed zone is in the form of a liquid the transfer of which is absent [10].

To describe the process of freezing of moist materials, we take the linear law of distribution of the temperature in the crystallization zone and the parabolic law of distribution in the moist zone (Fig. 1). We neglect the change in the moisture content in the moist zone and take into account the moisture redistribution by introducing the mean moisture content in the region of increment of the crystallization zone [11].

In this connection, the equations for the freezing zone and for the moist zones have the following form:

the crystallization zone

$$T_{mt1} = T_{mt.sur} - \frac{x - R_{mt}}{\xi} (T_{mt\xi} - T_{mt.sur}) \, ; \tag{12}$$

the moist zone

$$T_{mt2} = T_{mt.cn} - \left(\frac{x}{R_{mt} - \xi} \right)^2 (T_{mt.cn} - T_{mt\xi}) \, . \tag{13}$$

The boundary condition determining the heat exchange between the surface of the crystallization zone and the environment ($x = R_{mt}$) is described by the expression

$$\alpha \, (T - T_{mt.sur}) - r_{sub} \, j_{sur} = - \lambda_1 \frac{T_{mt.sur} - T_{mt\xi}}{\xi} \, , \tag{14}$$

while the condition of thermal balance on the moving boundary of freezing ($x = R_{mt} - \xi$) is described by the expression

$$- \lambda_1 \left(\frac{T_{mt.sur} - T_{mt\xi}}{\xi} \right) = - 2\lambda_2 \left(\frac{T_{mt\xi} - T_{mt.cn}}{R_{mt} - \xi} \right) + r_{crys} \, \rho_0 U_{mn} \frac{d\xi}{d\tau} \, , \tag{15}$$

where U_{mn} is the mean moisture content in the region of increment of the crystallization zone.

With time the boundary of phase transitions moves into the depth of the material during which the crystallization zone of thickness [6]

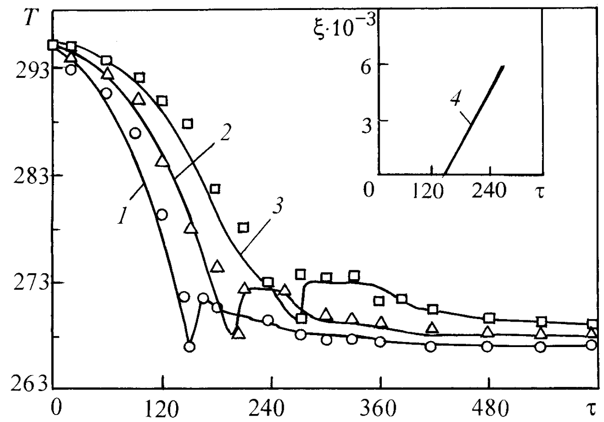

Fig. 2. Temperature curves for the process of self-freezing of moist cloth for different coordinates of the body [1) x = 6 mm; 2) 3; 3) 0] and the thickness of the crystallization zone (4).

$$\xi = b\,(\tau - \tau_0) \tag{16}$$

is formed; here b is the velocity of deepening of the freezing surface determined from the experimental data.

The supercooling temperature of the body at any point corresponding to the onset of the crystallization process is determined from the expression [7]

$$T_{\text{spc}} = T\,(R_{\text{mt}}) + A'\,(x - R_{\text{mt}})\,. \tag{17}$$

The mathematical model of the process of self-freezing of moist capillary-porous materials presented by the system of equations (1)–(17) was solved using the numerical method of finite differences [12] according to the following algorithm:

1) based on the starting and initial data, we determined the vapor-phase parameters p and T causing changes in $T_{\text{mt.sur}}$ and U_{sur};

2) when $T_{\text{mt.sur}} > T_{\text{spc}}$, we calculated the distributions $T_{\text{mt}}(x)$ and $U(x)$ for the stage of evaporation of free moisture from the material (ξ = 0);

3) for $\xi \neq 0$ we simulated the process of self-freezing, i.e., we determined the boundary parameters $T_{\text{mt.sur}}$, $T_{\text{mt}\xi}$, and $T_{\text{mt.cn}}$, and the temperature distribution over the zones $T_{\text{mt1}}(\xi)$ and $T_{\text{mt2}}(R_{\text{mt}} - \xi)$;

4) the process of self-freezing was considered to be completed when the phase interfaces converged at the center of the material ($\xi = R_{\text{mt}}$).

To check the adequacy of the developed mathematical description to the process studied and to determine its parameters (the supercooling temperature of the material surface, the travel velocity of the crystallization zone, and the constant coefficient in Eq. (17)), we carried out experimental investigations into the self-freezing of a moist cloth on the installation which contains the hermetic chamber with a built-in balance and the vacuum pump. The material temperature was monitored using a Chromel–Copel thermocouple and was recorded by a potentiometer. The degree of rarefaction was monitored using a vacuum gauge.

The parameters of the process of self-freezing by means of decreasing the pressure were varied within the following limits: the residual pressure in the vacuum chamber was relieved from atmospheric pressure (100 kPa) to 1.0–0.5 kPa; the volumetric capacity of the vacuum pump was maintained at a level of $1.38 \cdot 10^{-5}$ m^3/sec.

Based on the analysis of the temperature curves carried out according to the procedure proposed by A. V. Luikov [6], we determined the parameters of the process. Figure 2 presents the kinetics of self-freezing of the moist cloth under the conditions of decrease in the pressure. The solid curves correspond to the data obtained by calculations; the points correspond to the experimental results. In the calculations, the numerical values of the thermodynamic coefficients for the cloth varied within the following limits: $a_{\text{m}} = 2.3 \cdot 10^{-8}$–$2.5 \cdot 10^{-8}$ m^2/sec, λ_1 = 0.927–0.950

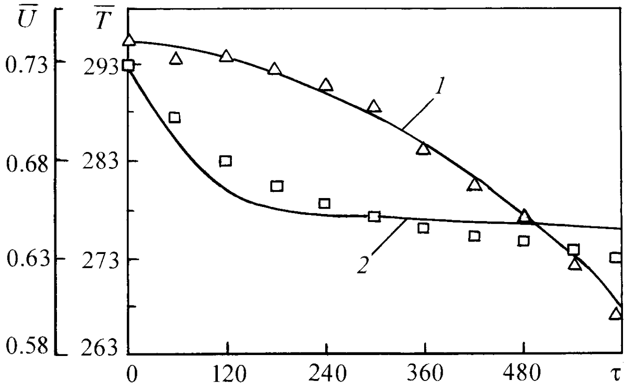

Fig. 3. Curves of change in the integral temperature (1) and moisture content (2) of moist cloth in the course of self-freezing.

W/(m·K), λ_2 = 0.052–0.054 W/(m·K), and r_{crys} = 333.33 J/kg. The values of the parameters are obtained by calculation according to the procedure described in [13] and are taken from the references [14].

The analysis of the curves shows that in different layers of the material the temperature at the initial instant of time obeys the parabolic law. When the surface temperature attains 267 K, the curve increases sharply by several degrees. The increase in the temperature indicates the onset of the process of freezing of water at this point, which is accompanied by the release of the crystallization heat. To freeze the moisture, the solid body–liquid system must be changed from the stable state to an unstable one, which can be achieved, according to the Gibbs law, by supercooling the moisture. The energy expended is released in the form of heat in phase transition of the substance from one state to another (crystallization), bringing the system back to the equilibrium state. The quantity of heat released over this period is determined by the thickness of the crystallization zone and by its mean moisture content (by the mass of the liquid contained in the volume of the crystallizing layer). The completion of the process of freezing of the moisture is characterized by a further decrease in the temperature of the material caused by the sublimation of ice, which follows from boundary condition (14). This situation is observed in all layers of the material; the magnitude of the supercooling of the liquid decreases from the surface into the depth of the body. The bend points of the temperature curves over the cross section of the material indicate the extension of the crystallization zone, whose deepening occurs following the linear law (curve 4, Fig. 2).

The supercooling temperature at any point of the body was determined from the experimental data according to dependence (17) with the constant coefficient A' = 333.33 K/m. After 150 sec from the beginning of decrease in the pressure, the appearance of the crystallization process was noted; the rate of freezing of the material was 0.000045 m/sec.

In the course of self-freezing, the integral moisture content of the material changed from the initial $\bar{U}$ = 73% to final $\bar{U}$ = 63%, while the integral temperature decreased from 295 to 268 K (Fig. 3).

By checking the mathematical model for adequacy to the actual process it has been found that the maximum discrepancy between the calculated and experimental data on the moisture content is 17%. This is explained by the partial transfer of moisture in the moist and frozen zones not taken into consideration in the mathematical model.

Thus, the mathematical model developed on the basis of the approximate solutions proposed by A. V. Luikov can be used to simulate the self-freezing process on a computer and to investigate the influence of different factors on the kinetics of the process with the aim of revealing the fields of practical implementation of this method.

NOTATION

p, partial pressure of the vapor, Pa; τ, time, sec; F, surface of heat and mass exchange, m^2; R^*, universal gas constant, J/(kmole·K); T and $\bar{T}$, local and integral temperatures, K; j, mass flux, kg/(m^2·sec); $V_{\text{v.sys}}$, volumetric capacity of the vapor-removal system, m^3/sec; V_{fr}, free volume of the apparatus, m^3; μ, molecular weight, kg/kmole; c, mass heat capacity, J/(kg·K); c_μ, molar heat capacity, J/(kmole·K); α, heat-transfer coefficient, W/(m^2·K); x, running coordinate, m; U and $\bar{U}$, local and integral moisture contents, kg/kg; R_{mt}, characteristic dimension of the body, m; a_{m}, mass-transfer coefficient, m^2/sec; ρ_0, density of the absolutely dry material, kg/m^3; δ_{tem}, relative coefficient of thermal diffusion, 1/K; λ, thermal-conductivity coefficient, W/(m·K); r and r_0, latent heat of vaporization at running temperature and at 0^oC, respectively, J/kg; A and B, empirical coefficients in the Antoine equation; r_{sub}, specific heat of sublimation, J/kg; r_{crys}, specific heat of crystallization, J/kg; ξ, thickness of the crystallization zone, m; b, velocity of deepening of the freezing surface, m/sec; A', constant coefficient, K/m. Subscripts: mt, material; liq, liquid; vp, vapor; sur, surface; cn, center; in, initial; sat, saturated; ξ, crystallization surface; fr, free; v.sys, vapor system; tem, temperature; crys, crystallization; μ, molar; spc, supercooled; sub, sublimation; mn, mean; 0, dry material and zero temperature according to the terms; 1, crystallization zone; 2, moist zone.

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