What was said above is also valid when a wetting liquid possessing a wetting hysteresis is used. In this case to obtain the sizes of the pore narrowings one must allow for the outflow factor $\cos\Theta$, while in estimating the sizes of pores at the surface one must allow for the equilibrium factor $\cos\Theta$.

To determine the total number of pores, one must draw upon additional data based on additional model considerations or microscopy data.

NOTATION

P	is the pressure;
σ	is the surface tension;
Θ	is the wetting angle;
R	is the capillary radius;
Q	is the gas flow rate through membrane;
Q_1	is the gas flow rate through wetted membrane during an increase in pressure;
Q_2	is the gas flow rate through wetted membrane during a decrease in pressure;
P'	is the capillary pressure in the narrowest part of the capillary;
P''	is the capillary pressure at the exit of the capillary at the surface.

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EVAPORATION OF SEVERAL SUBSTANCES FROM A POROUS BODY

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UDC 536.24.02

A system of equations of heat and mass transfer is derived and analyzed which describes evaporation of several volatile substances from a porous body.

Porous materials are widely heat treated in industry for the removal of volatile substances. One form of such a treatment is drying, where one substance (moisture) evaporates [1]. In some technological processes it is important to remove from a porous body not one but a group of various volatile substance (fillers) contained therein. In titanium production, e.g., the reactant mass is vacuum-heated for purification of the titanium sponge of magnesium and magnesium chloride [2]. When not one but several volatile substances are removed, there arise new patterns due to the effect which escaping of more volatile fillers has on the distribution of less volatile fillers in the porous body.

I. Mathematical Model. The system of transfer equations will be constructed on the following basic premises.

1. The condensate phase of volatile fillers is stationary relative to the "skeleton" of porous material. This is possible, e.g., when sublimation of solid fillers occurs during heat treatment. When some of the fillers are in the liquid state, however, then one assumes that they are adsorbed on the surface of the solid phase and not free to move under action of gravitational or capillary forces.

2. The fillers do not form solutions with one another or with the material of the porous body.

3. Transport of vapors through channels and pores is affected by the pressure gradient, according to Darcy's law, the role of diffusion being negligible. This also assumes a subsonic flow of vapor (Mach number smaller than unity), with vapor behaving like an incompressible fluid, and assumes the model of a continuous

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Translated from Inzhenerno-Fizicheskii Zhurnal, Vol. 37, No. 3, pp. 449-455, September, 1979. Original article submitted November 9, 1978.

0022-0841/79/3703-1052$07.50

medium to be applicable (the Knudsen number to be sufficiently small). The latter condition can always be satisfied, if the porous material does not contain very fine pores.

4. The "skeleton" of the porous material does not become deformed during heat treatment.

We consider a material containing N volatile fillers ($N \geq 1$). Let m_i^0 and ρ_i be, respectively, the mass per unit volume of porous material and the density of the i-th substance in the condensate state. The volume fraction f_i of the i-th substance is

$$f_i = m_i^0/\rho_i. \tag{1}$$

The porosity of the body is

$$v = 1 - \sum_{i=0}^{N} f_i. \tag{2}$$

Subscript i = 0 refers to the "skeleton" material and subscript i = 1 refers to the material of the most volatile filler.

Let m_i be the mass per unit pore volume of the i-th substance (i = 1, 2, . . . ,) in the vapor state and P_i be its partial pressure in pores. Then

$$m_i = vM_iP_i/RT \tag{3}$$

according to the equation of state for an ideal gas.

Let W_i be the density of internal sinks of the condensate phase resulting from evaporation of the i-th substance ($i \geq 1$), P_i^0 be the saturated-vapor pressure of the i-th substance or the equilibrium pressure of the substance adsorbed on the surface, S_i be the surface area per unit pore volume of the i-th substance in the condensate state (during evaporation) or the active surface area of pores (during condensation), and K_i be the evaporation rate coefficient [3],

$$K_i = \sqrt{M_i/2\pi RT}. \tag{4}$$

Then the equation of condensation–evaporation kinetics is

$$W_i = \begin{cases} 0; \ v = 0, \ P_i^0 < P_i; \\ 0; \ f_i = 0, \ P_i^0 > P_i; \\ K_iS_i(P_i^0 - P_i). \end{cases} \tag{5}$$

The i-th substance evaporates when $P_i^0 > P_i$ and condenses when $P_i^0 < P_i$. Expression (5) also takes into account that a condensate phase cannot evaporate when it is absent ($f_i = 0$) and that no condensation can occur in the absence of pores ($v = 0$).

Quantity P_i^0 can be expressed as

$$P_i^0 = A_i \exp(-Q_i/RT), \tag{6}$$

where Q_i is the latent heat of evaporation per mole of the i-th substance and A_i is a constant whose value depends on the properties of this substance.

According to Dalton's law, the total vapor pressure in pores is

$$P = \sum_{i=1}^{N} P_i. \tag{7}$$

Considering the dependence of the permeability k on the porosity v

$$k = k^0 v, \tag{8}$$

Darcy's law can be expressed as

$$\langle \bar{u} \rangle = -(k^0/\eta)\, v \nabla P, \tag{9}$$

where η is the viscosity of the vapor and $\langle \bar{u} \rangle$ is its mean-mass velocity.

Flux g_i of the i-th filler in the vapor phase is determined from the relation

$$g_i = m_i \langle \bar{u} \rangle = -M_i (k^0/\eta RT)\, v^2 P_i \nabla P. \tag{10}$$

The thermal flux is

$$g = -\lambda\nabla T + \sum_{i=1}^{N} (m_i/M_i) \int_0^T c_i dT \, \langle \bar{u} \rangle . \tag{11}$$

Here c_i denotes the specific heat per mole of the i-th filler in the vapor state.

The thermal conductivity λ of a composite material can be calculated according to any of the well-known algorithms [4] from known thermal conductivities λ_i of the component substances. Here the simplest algorithm

$$\lambda = \sum_{i=0}^{N} f_i \lambda_i . \tag{12}$$

will be used.

Setting up, according to the well-known scheme [5], the equations of mass balance for each filler in the condensate state and in the vapor state, and also the heat-balance equations, will, on the basis of earlier-made assumptions and derived expressions, yield the following system of transfer equations

$$\rho_i \frac{d}{d\tau} f_i = -W_i, \; i = 1, 2, \ldots, N, \tag{13}$$

$$\begin{gathered} \frac{\partial}{\partial\tau} (vP_i/T) = (k^0/\eta) \nabla \cdot [v^2 (P_i/T) \nabla P] \\ + RW_i/M_i, \; i = 1, 2, \ldots, N, \end{gathered} \tag{14}$$

$$\begin{gathered} \left[1 + \sum_{i=1}^{N} d_i f_i + (av/RT\lambda_0 f_0) \sum_{i=1}^{N} c_i P_i\right] \frac{\partial T}{\partial\tau} \\ - (ak^0 v^2/\eta\lambda_0 f_0 RT) \sum_{i=1}^{N} c_i P_i \nabla P \cdot \nabla T = \\ = a\nabla \cdot \left[\left(1 + \sum_{i=1}^{N} e_i f_i\right) \nabla T\right] - (a/\lambda_0 f_0) \sum_{i=1}^{N} Q_i \rho_i W_i | M_i, \end{gathered} \tag{15}$$

$$a = \lambda_0 M_0/\rho_0 c_0^0; \tag{16}$$

$$d_i = \rho_i c_i^0 M_0/\rho_0 c_0^0 M_i f_0; \; e_i = \lambda_i/\lambda_0 f_0, \tag{17}$$

with c_i^0 denoting the specific heat per mole of the i-th substance (i = 0, 1, . . . , N) in the condensate state.

The heat-transfer equation (15) becomes much simpler when the specific heat of vaporization in pores is disregarded as negligible in comparison with the specific heat of condensation and when convective heat transfer by vapor is disregarded as negligible in comparison with that by condensate. It is also expedient to introduce the following set of dimensionless quantities:

$$q_i = Q_i/RT^0, \; B_i^0 = A_i \exp(-q_i), \tag{18}$$

$$\alpha_{ik} = (A_i/A_k) \exp(q_k - q_i), \tag{19}$$

$$\mathrm{Kp}_i = M_0 \rho_i Q_i/\rho_0 M_i f_0 c_0^0 \Delta T, \tag{20}$$

$$\chi_i = \rho_i R\Delta T/M_i B_i^0, \tag{21}$$

$$H_i = k^0 B_i^0/a\eta, \tag{22}$$

$$L_i = (X^0)^2 B_i^0 S_i K_i/a\rho_i, \tag{23}$$

$$t = T^0/\Delta T, \; \theta = (T - T^0)/\Delta T, \tag{24}$$

$$\mathrm{Fo} = a\tau/(X^0)^2, \tag{25}$$

$$\pi_i = P_i/B_i^0, \; \pi_i^0 = P_i^0/B_i^0, \tag{26}$$

$$b_i = \sum_{k=1}^{N} \alpha_{ki}\pi_h, \tag{27}$$

$$\omega_i = W_i\,(X^0)^2/\rho_i a. \tag{28}$$

Here X^0 is the characteristic dimension, $T^0 \neq 0$ is the reference point from which temperature is measured (°K), ΔT is the characteristic temperature difference, and B_i^0 is the characteristic pressure of the i-th filler.

With this notation and the simplifying assumptions, our system of transfer equations (13)-(15) becomes

$$\frac{d}{d\,\mathrm{Fo}} f_i = -\omega_i, \quad i = 1,\, 2,\, \ldots,\, N, \tag{29}$$

$$\frac{\partial}{\partial\,\mathrm{Fo}}\left(\frac{v\pi_i}{t+\theta}\right) = H_i \nabla\cdot\left(\frac{v^2\pi_i}{t+\theta}\,\nabla b_i\right) + \chi_i\omega_i, \quad i = 1,\, 2,\, \ldots,\, N, \tag{30}$$

$$\left(1 + \sum_{i=1}^{N} d_i f_i\right)\frac{\partial\theta}{\partial\,\mathrm{Fo}} = \nabla\cdot\left[\left(1 + \sum_{i=1}^{N} e_i f_i\right)\nabla\theta\right] - \sum_{i=1}^{N} \mathrm{Kp}_i\omega_i. \tag{31}$$

II. Algorithm and Results of Numerical Calculations. The system of equations (29)-(31) was solved by the finite-differences method according to the explicit scheme.

Let $\delta\tau$ be the time step, $E_s\Phi$ be the value of function $\Phi(\nu,\, N_{\mathrm{Fo}})$ at nodes s in the grid, and $E_s^0\Phi$ be the value of function $\Phi(\nu,\, N_{\mathrm{Fo}} + \delta\tau)$ at node s in the grid. The value $D_s\Phi$ is regarded as equal to that of function $\nabla\Phi(\nu,\, N_{\mathrm{Fo}})$ taken at the internal node s of the grid in the finite-differences approximation. With this notation, the algorithm of calculation of functions f_i, θ, and π_i ($i = 1, 2, 3, \ldots, N$) at each internal node of the grid is

$$M_s = E_s f_i - \delta\tau L_i E_s\,\{\exp\,[q_i\theta/(\theta + t)] - \pi_i\}, \tag{32}$$

$$G_i = 1 - f_0 - \sum_{k=1}^{i-1} E_s^0 f_k - \sum_{k=i+1}^{N} E_s f_k, \tag{33}$$

$$E_s^0 f_i = \begin{cases} 0, & M_s \leqslant 0; \\ G_i, & M_s \geqslant G_i; \\ M_s, & \end{cases} \tag{34}$$

$$A_s = 1 + \frac{1}{2}\sum_{i=1}^{N} d_i\,(E_s^0 f_i + E_s f_i), \tag{35}$$

$$E_s^0\theta = E_s\theta + \delta\tau\, D_s\left\{\left(1 + \sum_{i=1}^{N} e_i f_i\right) D_s\theta\right\} / A_s + \sum_{i=1}^{N} \mathrm{Kp}_i\,[E_s^0 f_i - E_s f_i]/A_s, \tag{36}$$

$$L_i^0 = \begin{cases} L_i, & E_s^0 f_i \neq 0; \\ 0, & E_s^0 f_i = 0, \end{cases} \tag{37}$$

$$C_s = \frac{1}{2}\,[E_s^0\,\{v/(\theta + t) + E_s\{v/(\theta + t)\}], \tag{38}$$

$$E_s^0\,\pi_i = \frac{C_s E_s\pi_i + \chi_i L_i^0\,\delta\tau E_s^0\,\{\exp q_i\theta/(\theta + t)\}}{C_s + \chi_i L_i^0\,\delta\tau - H_i\delta\tau D_s\left\{\dfrac{v^2}{\theta + t} D_s b_i\right\}}\,. \tag{39}$$

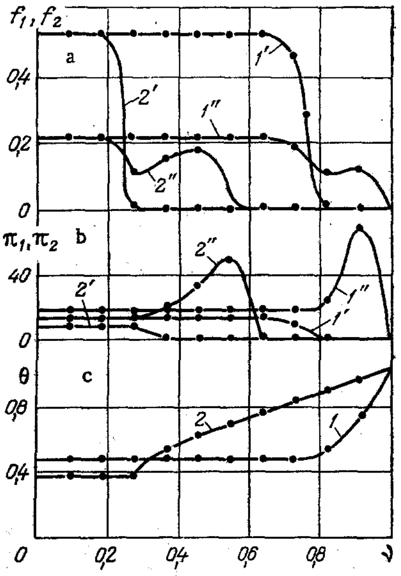

Fig. 1. Variation of (a) the volume fraction of fillers, (b) the partial pressures of their vapors, and (c) the temperature in the block of titanium sponge along the cylinder radius at the instants of time $N_{Fo} = 0.60$ (1) and $N_{Fo} = 5.50$ (2) in the course of thermovacuum purification; numerals with a single prime sign refer to magnesium, numerals with a double prime sign refer to magnesium chloride; the initial relative temperatures are $\theta = 0$, the initial partial vapor pressures of both fillers are $\pi_1 = \pi_2 = 1$; dots indicate calculated values at grid nodes.

Calculations were made for the thermovacuum process of purification of titanium sponge containing magnesium and magnesium chloride as fillers. The mathematical scheme of the problem is as follows. A porous cylinder with fillers uniformly distributed over the cross section and the height is initially at a constant temperature T^0. At the instant of time $N_{Fo} = 0$ the cylinder is subjected to heat and vacuumization, whereupon immediately a constant underpressure develops at the lateral surface and the temperature here stabilizes at $T_1 > T^0$. Both bases of the cylinder are thermally insulated and no gases escape through them. In this configuration the problem is a one-dimensional one.

Preliminary calculations had established that under conditions of thermovacuum treatment the evaporation of fillers from a sponge is characterized by degenerate kinetics. When the L_i-number characterizing the dimensionless evaporation rate with ω_i kinetics is larger than 10, then a further increase in this number will not speed up the purification process. In our case numbers L_1 and L_2 for magnesium and its salts, respectively, were of the order of 10^5-10^7. Therefore, the limiting items in the purification process were supply of heat to the porous body and removal of vapors from it.

Typical results of calculations pertaining to one particular variant of the thermovacuum purification process are shown in Fig. 1.

The zone within which the magnesium (most volatile of the two fillers) content varies substantially is narrow in the radial direction (Fig. 1a, curves 1' and 2') and, therefore, can be treated as a sort of "evaporation front" of magnesium.

Magnesium vapor carries vapor of the less volatile filler, viz., of magnesium chloride away with it from the zone of intensive magnesium evaporation. The intensity of this process, which we will tentatively call "forced entrainment," is much higher than the intensity of magnesium chloride evaporation at the same temperatures in the absence of evaporating magnesium.

TABLE 1. Dependence of the Time for Complete Purification of Titanium Sponge on the Initial Ratio of Filler Volume Fractions

Item No.	f_1	f_2	$(f_1/f_2)^{-1}$	Fo^0
1	0,73	0	0	7,516
2	0,63	0,10	0,159	7,192
3	0,56	0,17	0,303	7,518
4	0,52	0,21	0,404	7,845

The velocity of the vapor stream increases along the path between the zone of forced entrainment and the surface of the cylinder. The partial pressure of magnesium chloride vapor rises along this path (Fig. 1b, curves 1" and 2") on the other hand, and can exceed the equilibrium pressure. In this case there occurs condensation of magnesium chloride vapor, a process which we will tentatively call intermediate condensation.

The zone of forced entrainment and the zone of intermediate condensation appear, respectively, as an intermediate minimum and an intermediate maximum along the curve of f_2 (volume fraction of magnesium chloride) as a function of the radial coordinate v (Fig. 1a, curves 1" and 2").

The temperature inside the region where evaporation of magnesium has not yet begun decreases with time, as it does inside the evaporation zone too, even though the temperature of the outside cylinder surface remains constant (Fig. 1c, curves 1 and 2).

The length of time N_{Fo}^0 required for complete purification of titanium sponge by removal of fillers depends on the initial ratio f_2/f_1 of filler volume fractions. Results of calculations regarding this dependence are given in Table 1. The initial sum of both magnesium and magnesium chloride volume fractions in our block of titanium sponge was held constant at 0.73 and the volume fraction of titanium in the sponge was assumed to be 0.26.

The data in Table 1 indicate the existence of an optimum initial f_2/f_1 ratio, close to 0.16, which will ensure the shortest time for complete removal of fillers from titanium sponge.

NOTATION

N	is the number of volatile fillers;
i	is the consecutive number of a substance (i = 0 refers to the "skeleton," i > 0 refers to fillers);
m_i^0	is the mass of condensate per unit volume of the medium;
m_i	is the mass of vapor per unit volume of pores;
ρ	is the density;
f_i	is the volume fraction;
v	is the porosity;
M_i	is the molecular mass;
R	is the universal gas constant;
T	is the absolute temperature;
ΔT	is the characteristic temperature difference;
W_i	is the density of internal sinks;
P_i	is the partial pressure;
P_i^0	is the saturated-vapor pressure or the equilibrium vapor pressure of an adsorbed substance;
P	is the total pressure;
S_i	is the surface area per unit volume of pores;
K_i	is the evaporation rate coefficient;
Q_j	is the latent heat of evaporation;
k^0	is the permeability;
$\langle u \rangle$	is the mean-mass velocity of vapor in pores;
η	is the viscosity of vapor;
g_i	is the mass flux density of a substance;
g	is the thermal flux density;

c_i^0	is the specific heat of condensate;
c_i	is the specific heat of vapor;
λ	is the thermal conductivity of the composite material;
λ_i	is the thermal conductivity of the material components;
a	is the thermal diffusivity;
d_i	is the relative heat capacity;
e_i	is the relative thermal conductivity;
q_i	is the dimensionless thermal effect of evaporation;
B_i^0	is the characteristic pressure;
α_{ik}	is the ratio of the characteristic pressures of substances i and k;
Kp_i	is the phase transformation number;
χ_i	is the vapor tension number;
H_i	is the permeability number;
L_i	is the evaporation intensity;
T^0	is the reference temperature (°K)
τ	is the time;
x_k	is the space coordinate;
X^0	is the characteristic dimension;
ν_k	is the referred radial coordinate;
N_{Fo}	is the dimensionless time;
θ	is the dimensionless temperature;
π_i and π_i^0	are the dimensionless partial pressure and saturated-vapor pressure of the i-th substance;
b_i	is the total pressure referred to the characteristic vapor pressure of the i-th substance;
ω_i	is the dimensionless density of internal sinks;
$\delta\tau$	is the time step;
$E_s\Phi$ and $E_s^0\Phi$	are the values of functions $\Phi(\nu, N_{Fo})$ and $\Phi(\nu, N_{Fo} + \delta\tau)$, respectively, at node s of the grid;
$D_s\Phi$	is the difference analog of function $\nabla\Phi(\nu, N_{Fo})$ at an internal node s of the grid;
T_1	is the temperature at the boundary;
N_{Fo}^0	is the dimensionless time for complete purification of a porous material.

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