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KINETICS OF THE REMOVAL OF LIQUID FROM CAPILLARY-POROUS BODIES IN A FLUIDIZED BED UNDER NONISOTHERMAL CONDITIONS

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A theory of mass transfer in capillary-porous bodies is proposed which allows for thermogradient transfer of a bound substance in liquid form. The results obtained are used to calculate the process of drying of ceramic articles in a fluidized bed.

Existing methods of calculating processes of drying of capillary-porous bodies under isothermal and nonisothermal conditions are based mainly on analytical solutions of the system of differential equations of heat and mass transfer known from the phenomenological theory of irreversible processes [1, 2]. The main obstacle to the wide use of these equations is the considerable nonlinearity of the problem—the dependence of the kinetic coefficients appearing in them on the concentration of the bound substance and the temperature [3-5]. Under isothermal drying conditions (in the case of bodies of small size), calculations with allowance for the dependence $a_m = f(\bar{u}, t)$ are made by zonal methods [4]. In the presence of a temperature gradient within the material being dried, the number of criteria determining the kinetics of the process grows considerably [6], and it becomes impossible to use the zonal method of calculation. In such cases one artificially separates the heat- and mass-exchange processes and allows for the influence of the temperature field on the kinetics of the mass transfer using functions obtained from experiment for the relation between the volumetric-mean concentration and temperature [7], which are subsequently used in calculations of transfer processes in systems having a solid phase under quasi-isothermal conditions. However, numerous experimental data give evidence of temperature gradients which exert considerable influence on the kinetics of the drying process [8-10].

Moreover, it should be noted that a phenomenological examination of the stated problem does not allow one to characterize the fluxes of the bound substance in a porous body.

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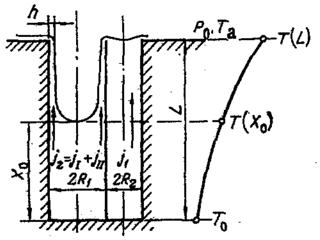

Fig. 1. Model of capillary-porous body and calculating diagram for first stage of the process.

In contrast to the well-known reports [1, 2], we will seek solutions on the basis of an investigation of the flow of a bound substance in the form of a liquid in the pores of a model capillary-porous system with allowance for film transfer. In doing this we will be confined to consideration of the case when transfer in the vapor phase can be neglected. Such conditions occur, for example, in the low-temperature heat treatment of ceramic articles [11], when the binding is paraffin.

As the model pore structure we use a system consisting of capillaries of two different radii; R_1 and R_2, joined over the entire length (Fig. 1). Such a model fully corresponds to a number of ceramic materials for which a pore size distribution of a bimodal character has been established experimentally [12-14].

Before the final firing, articles made of commercial ceramic are subjected to low-temperature heat treatment to remove from them the organic binder, in the given case paraffin. The process of removal of the binder proceeds most efficiently in a medium of disperse fluidized adsorbent [15], when a capillary-porous body is submerged in a fluidized bed at a temperature which excludes the evaporation of the liquid, external mass transfer takes place through the drawing up of liquid by porous particles colliding with the surface of the solid body [16].

Let us write the equations for the liquid fluxes in the model capillary-porous system. In narrow capillaries one observes a viscous flow of liquid due to the difference between the pressures at the menisci of the wide capillaries and the surface of the porous body,

$$j_1 = \frac{\rho R_2^2}{8\eta (L - x_0)} \Delta P, \tag{1}$$

where $\Delta P = P_0 - 2\sigma(x_0)/R_1$. In wide capillaries the liquid flows in the form of a film under the action of the gradient of the disjoining pressure. In contrast to isothermal mass transfer [16], however, flow also occurs in the films under the action of the temperature gradient, which is significant inside the solid body. Adopting the hypothesis of additivity of these fluxes, we can write [17]

$$j_2 = \frac{2\rho h^3}{3\eta R_1} \frac{\partial \Pi}{\partial x} + \frac{\rho h^3}{\eta R_1} \frac{\partial \sigma}{\partial T} \frac{\partial T}{\partial x} = j_{I} + j_{II}. \tag{2}$$

In (2), $\Pi = P - \sigma/R_1$ is the disjoining pressure.

Let us examine the liquid fluxes in Eq. (2) separately. Taking the isothermy of the disjoining pressure for nonpolar liquids in the form [18]

$$\Pi = A/h^3, \tag{3}$$

after differentiation of (3) and its substitution into the first term of Eq. (2), we obtain

$$j_{I} = -\frac{2\rho A}{\eta R_1 h} \cdot \frac{\partial h}{\partial x}. \tag{4}$$

We rewrite (4) in the form

$$\frac{\partial \ln h}{\partial x} = -j_{I} \frac{\eta R_1}{2\rho A} = -\bar{\alpha}, \tag{5}$$

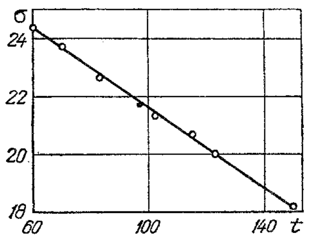

Fig. 2. Dependence of surface tension of paraffin σ (dyn/cm) on temperature.

where $\bar{\alpha}$ is a constant which does not depend on x. Integration of (5) over h in the limits of $h_0 - h(x_0)$ and over x in the limits of $x_0 - L$, with allowance for the relations

$$h_L=\frac{A^{1/3}}{\left(P_0-\frac{\sigma(L)}{R_1}\right)^{1/3}};\quad h_{x_0}=\frac{A^{1/3}}{\left(P_{x_0}-\frac{\sigma(x_0)}{R_1}\right)^{1/3}};\quad P_{x_0}=\frac{2\sigma(x_0)}{R_1},\tag{6}$$

which follow from (3) gives, after the necessary transformations,

$$\frac{1}{3}\ln\frac{P_0-\sigma(L)/R_1}{\sigma(x_0)/R_1}=\bar{\alpha}(L-x_0).\tag{7}$$

Using (5), we obtain the equation for the flow in the film under the action of the pressure gradient in the form

$$j_l=\ln\left\{\frac{P_0-\sigma(L)/R_1}{\sigma(x_0)/R_1}\right\}\frac{2A}{3\eta R_1(L-x_0)}.\tag{8}$$

In connection with the fact that the temperature in a porous body varies over the thickness, the surface tension of the liquid also will be different in different cross sections. The temperature dependence of σ for commercial paraffin of brand A, presented in Fig. 2, was established experimentally by the method of liquid rising in capillaries.

Thus,

$$\sigma=\sigma(T_0)+\frac{\partial\sigma}{\partial T}\Delta T=\sigma_0-\beta(T-T_0),\tag{9}$$

where $\beta = -\partial\sigma/\partial T$ is the tangent of the slope angle of the experimental straight line. In accordance with (9) we obtain the following expressions for σ at the surface of the body and for the meniscus levels of wide capillaries, respectively:

$$\sigma(L)=\sigma_0-\beta(T_a-T_0),\tag{10}$$

$$\sigma(x_0)=\sigma_0-\beta[T(x_0)-T_0].\tag{11}$$

We will be confined to consideration of the solution for an unbounded plate. For this case the temperature $T(X_0, \tau)$ can be written in the form [19]

$$\frac{T_a-T(x_0,\,\mathrm{Fo})}{T_a-T_0}=\sum_{n=1}^{\infty}\frac{2}{\mu_n}(-1)^{n+1}\cos\mu_n\frac{x_0}{L}\exp(-\mu_n^2\mathrm{Fo}).\tag{12}$$

After a small time interval (Fo ≥ 0.45), the terms of the series higher than the first can be neglected, as shown in [19], and one can use the simplified expression

$$\frac{T_a-T(x_0,\,\mathrm{Fo})}{T_a-T_0}=\frac{2}{\mu_1}\cos\mu_1\frac{x_0}{L}\exp(-\mu_1^2\mathrm{Fo}),\tag{13}$$

in which the first root of the characteristic equation is $\mu_1 = \pi/2$. Substituting Eqs. (10), (11), and (13) into (8) gives the final equation for calculating the flow of film moisture in wide capillaries under the action of the pressure gradient. The thermogradient flow in films is written as follows:

$$j_{II} = \frac{\rho h^2}{\eta R_1} \frac{\partial\sigma}{\partial T} \frac{\partial T}{\partial x} = -\frac{\rho h^2}{\eta R_1} \beta \frac{\partial T(x,\ \tau)}{\partial x}. \tag{14}$$

Since j_{II} does not depend on the coordinate, the right side of (14) also does not depend on x. Consequently, the flow can be referred to the surface of the porous body ($x = L$). The film thickness h_L at the surface of the body is described on the basis of (6). Using this dependence, for the flux j_{II}, we will have

$$j_{II} = -\frac{\rho\beta A^{2/3}}{\eta R_1 (P_0 - \sigma(L)/R_1)} \frac{\partial T(L,\ \tau)}{\partial x}. \tag{15}$$

The value of the derivative $\partial T(L, \tau)/\partial x$ at the surface follows from Eq. (13):

$$\frac{\partial T(L,\ \mathrm{Fo})}{\partial x} = \frac{2(T_a - T_0)}{L} \exp\left(-\frac{\pi^2}{4}\mathrm{Fo}\right). \tag{16}$$

The total fluxes in the wide and narrow capillaries of the system are written as

$$J_2 = \frac{F_1(j_I + j_{II})}{F} = \frac{2\rho A n_1}{3\eta R_1 (L - X_0)} \ln\left[\frac{P_0 - \sigma(L)/R_1}{\sigma(x_0)/R_1}\right] - \frac{\rho\beta A^{2/3} n_1}{R_1 \eta (P_0 - \sigma(L)/R_1)^{2/3}} \frac{\partial T(L,\ \tau)}{\partial x}, \tag{17}$$

$$J_1 = \frac{\rho R_2^2 n_2}{8\eta(L - x_0)} \left\{P_0 - \frac{2\sigma(x_0)}{R_1}\right\}. \tag{18}$$

Since all the liquid supplied to the surface of the body is drawn off by porous particles colliding with it, the fluxes from Eqs. (17) and (18) can be equated to the external moisture flux, for which an expression was obtained earlier [16],

$$i_{ex} = \alpha W_s (1 - W_p) \sqrt{P_p - P_0}, \tag{19}$$

in which α is the coefficient of external mass exchange; W_s, W_p, surface moisture of the body and of the particles; P_p, capillary potential of the particles. Thus, we can write

$$J_1 + J_2 = \alpha W_s (1 - W_p) \sqrt{P_p - P_0}. \tag{20}$$

The equation which we lack, for determining the pressure P_0 at the surface, is obtained from the condition of lowering of the menisci of liquid in wide capillaries:

$$n_1 \rho \frac{dx_0}{d\tau} = -\alpha W_s (1 - W_p) \sqrt{P_p - P_0}. \tag{21}$$

We will consider the case of a sufficiently large number of porous particles, which makes it possible to set $W_p = 0$ in future calculations. The surface moisture of the capillary-porous system in the first stage of the process is written under the assumption that the film thickness is small in the mouths of wide capillaries:

$$W_s = n_1 \frac{2h_0}{R_1} + n_2 \approx n_2. \tag{22}$$

Substituting the expressions for the fluxes into (20), after the necessary transformations we obtain, with allowance for (22), the equation

$$\begin{aligned} -\frac{dx_0}{d\tau} = {} & \frac{\gamma_1}{L - x_0} \ln\left\{\frac{2\sigma/r - \gamma_2 (dx_0/d\tau)^2 - \sigma(L)/R_1}{\sigma(x_0)/R_1}\right\} - \\ & -\frac{\gamma_3 (T_a - T_0) \exp\left(-\frac{\pi^2}{4}\frac{a}{L^2}\tau\right)}{\{2\sigma/r - \gamma_2 (dx_0/d\tau)^2 - 2\sigma(x_0)/R_1\}^{2/3}} + \frac{\gamma_4}{L - x_0} \{2\sigma/r - \gamma_2 (dx_0/d\tau)^2 - 2\sigma(x_0)/R_1\}, \end{aligned} \tag{23}$$

which establishes the dependence between the amount of liquid in the capillary-porous system and the rate of fall of the menisci in the wide capillaries.

The condition under which falling of the menisci in the narrow capillaries will not yet occur has the form $P_0 \leq P_{0e} = 2\sigma/R_2$ or $x_0 \leq x_{0e}$. At the initial time the porous body is completely filled with liquid and $P_0 = 0$. After a brief time interval, however, a pressure $P(0) = 2\sigma/R_1$ is established in the narrow capillaries [16]. The position of the menisci in the large capillaries at which the menisci in the small capillaries start to fall (the start

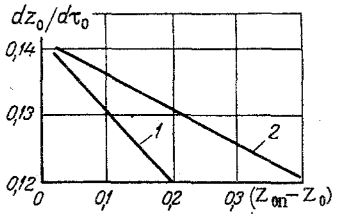

Fig. 3

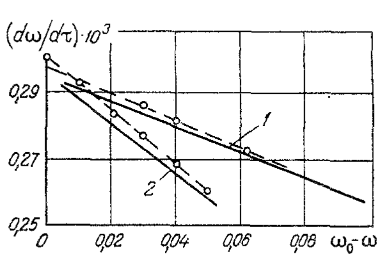

Fig. 4

Fig. 3. Dependence of dimensionless intensity of mass transfer on dimensionless coordinate of meniscus in narrow capillaries; 1) nonisothermal; 2) isothermal conditions.

Fig. 4. Comparison of calculated and experimental values of intensity of liquid removal; 1) isothermal; 2) nonisothermal conditions; ($d\omega/d\tau$), 1/sec.

of the second stage of the process) can be obtained from (23) by the substitution $P_{0e} = 2\sigma/R_2$. Equation (23) can be solved on a computer using the Runge–Kutta method [20]. For this purpose it is more convenient to represent it in dimensionless form:

$$-\frac{dz_0}{d\tau_0}=\frac{\gamma_1'}{1-Z_0}\ln\left\{\frac{2\sigma/r-\gamma_2'(dz_0/d\tau_0)^2-\sigma(L)/R_1}{\sigma(Z_0)/R_1}\right\}-$$
$$-\frac{\gamma_3'(T_a-T_0)\exp\left(-\frac{\pi^2}{4}\frac{a\tau_0\tau_{00}}{L^2}\right)}{\{2\sigma/r-\gamma_2'(dz_0/d\tau_0)^2-\sigma(Z_0)/R_1\}^{2/3}}+\frac{\gamma_4'}{1-Z_0}\left\{2\sigma/r-\gamma_2'\left(\frac{dz_0}{d\tau_0}\right)^2-\frac{2\sigma(Z_0)}{R_1}\right\}. \tag{24}$$

The following notation is adopted in Eqs. (23) and (24):

$$\gamma_1=\frac{2\rho A}{3\eta R_1}\ ;\ \ \gamma_2=\left(\frac{n_1\rho}{\alpha n_2}\right)^2;\ \ \gamma_3=\frac{2\beta A^{2/3}}{LR_1\eta}\ ;\ \ Z_0=\frac{x_0}{L}\ ;\ \ \tau_0=\frac{\tau}{\tau_{00}}\ ;$$
$$\gamma_4=\frac{R_2^2n_2}{n_18\eta};\ \ \gamma_1'=\gamma_1\tau_{00};\ \ \gamma_2'=\gamma_2\frac{L^2}{\tau_{00}^2};\ \ \gamma_3'=\gamma_3\frac{\tau_{00}}{L};\ \ \gamma_4'=\gamma_4\tau_{00}.$$

In Fig. 3 we present the results of calculations of the dimensionless rate of fall of the menisci, $dz_0/d\tau_0$, as a function of $(Z_{0n}-Z_0)$ for steatite ceramic. The calculations were made for the following conditions: $R_1 = 10^{-5}$ m; $R_2 = 0.5\cdot10^{-7}$ m; $r = 10^{-8}$ m; $\rho = 820$ kg/m^3; $A = 10^{-13}$ erg; $T_a = 373$°K; $\alpha = 0.97\cdot10^{-6}$ kg/m · sec · N$^{0.5}$; $L = 5\cdot10^{-3}$ m; $\beta = 0.072\cdot10^{-3}$ N/m °K; $\sigma_0 = 25\cdot10^{-3}$ N/m; $\tau_{00} = 120$ sec; $\alpha_1 = 300$ W/m^2 · °K; $\lambda = 4.5$ W/m · °K; $\eta = 10^{-2}$ N · sec/m^2 with (straight line 1) and without (2) allowance for the nonisothermal flux. As seen from Fig. 3, the presence of a temperature gradient considerably reduces the intensity of the process of removal of the bound substance.

Introducing the average moisture, corresponding to the degree of filling of the pore space with liquid,

$$\omega=n_2+n_1\cdot Z_0, \tag{25}$$

we can change from a dependence of the type of $i(Z_0)$ to equations of the form $i(\omega)$. The results of calculation of the mass-transfer intensity $d\omega/d\tau$ as a function of the volumetric moisture are shown in Fig. 4. The experimental data for steatite ceramic (points) were obtained during the removal of paraffin binder in a fluidized bed under nonisothermal and isothermal conditions. In the latter case the specimen, in the form of a plate, was heated in the fluidized bed without mass transfer. The comparison of the experimental and calculated values of $d\omega/d\tau$ indicates their satisfactory agreement with allowance for the tentative nature of the adopted values of the parameters appearing in the expression for α.

If the porous body has a large enough extent, then when $x_0 = x_{0e}$ the second stage of the process starts—the absence of menisci in the narrow capillaries. This stage should correspond to a sharp decrease in the intensity of liquid removal [21].

NOTATION

t, T, temperature; a_m, coefficient of moisture conductivity; ρ, η, σ, density, viscosity, and surface tension of liquid; h, thickness of liquid film; Π, disjoining pressure; A, Hamaker constant; α, coefficient of external mass exchange; α_1, coefficient of heat transfer; λ, coefficient of thermal conductivity; Fo, Fourier number; ω, volumetric moisture content of porous body; W_s, surface moisture content of body; $n = n_1 + n_2$, porosity; r, pore radius in the particles; $F = F_1 + F_2$, surface area of porous body; R_1, R_2, radii of wide and narrow capillaries; $\bar{u}$, moisture content; x_0, x_{0e}, coordinates of menisci in wide capillaries and at end of first stage, respectively; P_0, P_{0e}, pressures at surface of body and at end of first stage, respectively.

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