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EFFECT OF CHEMICAL REACTIONS ON FLOW AND MASS TRANSFER IN A LIQUID FILM IN THE PRESENCE OF SURFACE-ACTIVE MATERIALS

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UDC 532.65

To the thin-film approximation an investigation is made of the effect of surface-active materials on the hydrodynamics and mass transfer in liquid films falling under gravity in the presence of surface chemical reactions.

In many chemical engineering processes which occur in film reactors and packed and tray absorbers mass transfer takes place under conditions in which the surface tension at the interface between the liquid film and the adjacent gas stream is not constant, which is caused in particular by the presence of surface-active materials [1]. The surface tension gradients which arise in this case and the shear stresses connected with them as a result of the Marangoni effect can have an important effect on the hydrodynamics and rate of mass transfer of materials dissolving in the film [2]. In a number of industrial processes (such as, for instance, the purification of gases by chemisorption) mass transfer into the film is accompanied by chemical reactions with the participation of surface-active reagents and products [3].

An effect of surface-active materials on mass transfer can arise as follows. In the first place both the material itself and also the chemical reactions can lead to a loss of stability of the flow and to the appearance of convective cells which intensify transfer close to the free surface [4]. Such effects have been investigated, for instance, in [5, 6]. In the second place, the surface-active material can significantly change the velocity at the film surface, which can also influence the mass transfer characteristics. An investigation of the effect of insoluble surface-active materials on mass transfer in a laminar film with a slowly varying thickness not allowing for chemical reactions was carried out in [7].

The aim of the present work was to investigate the effect of surface chemical reactions involving the participation of a surface-active material on the hydrodynamics and mass transfer in a liquid film within the framework of the second of the mechanisms indicated above. Here a film in laminar flow along an inclined plane under the influence of gravity forces is considered, where the film is almost planar and its free surface is in contact with an adjacent gas. The flow rate of the liquid in the film is regarded as being constant and equal to Q.

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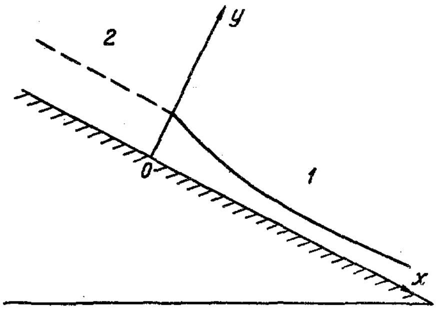

Fig. 1. Liquid film flowing in a gravity field: 1) reaction zone (x > 0); 2) zone without chemical reaction (x < 0).

An insoluble surface-active material is present at the surface of the film which participates in the chemical reactions. The dependence of the reaction rate on the concentration is given by the function $F(\Gamma)$. Since steady-state flow of the film is of interest, it is suitable to consider that the kinetic function $F(\Gamma)$ has one zero Γ_*, $F(\Gamma_*) = 0$. Such a function describes a wide class of surface reactions occurring in adsorption + chemical reaction flowsheets and also in various autocatalytic reactions.

A system of coordinates is selected as shown in Fig. 1. The film will be considered to be semiinfinite in extent (x > 0). The equations and boundary conditions describing the motion of the film to the thin-layer approximation ("quasi-one-dimensional approximation") have the form:

$$\nu\frac{\partial^2 u}{\partial y^2}+g=0, \tag{1}$$

$$\begin{gathered} y=0,\quad u=0;\quad y=h(x),\quad \mu\frac{\partial u}{\partial y}=\delta\frac{\partial\Gamma}{\partial x}; \\ \delta\equiv\frac{d\sigma}{d\Gamma}=\text{const}. \end{gathered} \tag{2}$$

The solution of (1) and (2) is

$$u=-\frac{g}{2\nu}y^2+\left(\frac{g}{\nu}h(x)+\frac{\delta}{\mu}\frac{d\Gamma}{dx}\right)y, \tag{3}$$

from which the velocity at the surface of the film is found as

$$U_s=\frac{gh^2(x)}{2\nu}+\delta h(x)\frac{1}{\mu}\frac{d\Gamma}{dx}.$$

The following condition must be satisfied to ensure the validity of the quasi-one-dimensional approximation [7]:

$$\left|\frac{dh}{dx}\right|\ll 1,\qquad \left|\frac{d^2\Gamma}{dx^2}\right|\ll\frac{1}{h}\left|\frac{d\Gamma}{dx}\right|. \tag{4}$$

Neglecting surface diffusion, an equation can be written for describing the steady-state distribution of the surface-active material at the surface:

$$\frac{d(U_s\Gamma)}{dx}=F(\Gamma). \tag{5}$$

Taking into account the constancy of the liquid flow rate, a system of equations is obtained for describing the dependence of the film thickness and of the concentration of the surface-active material on the longitudinal coordinate:

$$\frac{1}{3}\frac{gh^3}{\nu}+\frac{1}{2}\frac{\delta h^2}{\mu}\frac{d\Gamma}{dx}=Q, \tag{6}$$

$$\frac{d}{dx}\left(\Gamma\left(\frac{1}{2}\frac{gh^2}{\nu}+\frac{\delta h}{\mu}\frac{d\Gamma}{dx}\right)\right)=F(\Gamma). \tag{7}$$

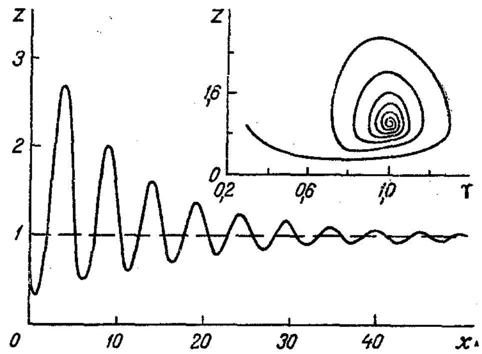

Fig. 2. Relationship z(x) and the phase diagram of the system (9), (10) for $\varepsilon = 10$, $f(\gamma) = 10(1 - \gamma)$.

Using the dimensionless variables

$$x' = x/L, \quad z = h/h_0, \quad \gamma = \Gamma/\Gamma_*, \quad \varepsilon = (9/\nu Q g^2)^{1/3}\delta\Gamma_*/2L\rho,$$
$$L = Q/h_0 k, \quad f(\gamma) = 2F(\Gamma_*\gamma)/3k\Gamma_*, \quad h_0 = (3\nu Q/g)^{1/3}, \tag{8}$$

the system of equations (6), (7) can be reduced to the following form:

$$\frac{dz}{dx} = \frac{(1 - z^3)(4 - z^3)}{\varepsilon z(2z^3 + 4)\gamma} - \frac{3z^2 f(\gamma)}{\gamma(2z^3 + 4)}, \tag{9}$$

$$\frac{d\gamma}{dx} = \frac{1 - z^3}{\varepsilon z^2}. \tag{10}$$

Here and subsequently the prime on the dimensionless variable x' is omitted.

The state of equilibrium of the system (9), (10): $z = 1$, $\gamma = 1$ ($f(1) = 0$), corresponds to steady-state flow of the film with respect to the longitudinal coordinate.

Let us first consider the case where z and γ differ slightly from the uniform values which have been indicated. In the neighborhood of the singular point the linearized system becomes the following:

$$\frac{dz_1}{dx} = -\frac{3}{2\varepsilon} z_1 - \frac{f'(1)}{2}\gamma_1, \qquad \frac{d\gamma_1}{dx} = -\frac{3}{\varepsilon} z_1. \tag{11}$$

Here $z_1 = z - 1$, $\gamma_1 = \gamma - 1$, $|z_1| \ll 1$, $|\gamma_1| \ll 1$, $f' \equiv df/d\gamma$.

From the system (11) a characteristic equation is obtained, the roots of which are

$$\lambda_{1,2} = -\frac{3}{4\varepsilon} \pm \left(\frac{9}{16\varepsilon^2} + \frac{3}{\varepsilon}\frac{f'(1)}{2}\right)^{1/2}. \tag{12}$$

It can be seen from Eq. (12) that the type of the singular point on the phase plane (z, γ) and the corresponding nature of the distributions of the concentration of the surface-active material and of the film thickness with respect to the flow depends strongly on the ratio of the quantities $f'(1)$ and ε. In the case of inactive materials ($\varepsilon > 0$) the following situations are possible: $f'(1) > 0$, $\lambda_1 > 0$, $\lambda_2 < 0$ represents a saddle; $-3/(8\varepsilon) < f'(1) < 0$, $\lambda_1 < 0$, $\lambda_2 < 0$ is stable node; $f'(1) < -3/(8\varepsilon)$, $\lambda_{1,2} = \omega_r \pm i\omega_i$, $\omega_r < 0$ is a stable focal point. In the case of a surface-active material, strictly speaking (where $\varepsilon < 0$), it is found correspondingly that: $f'(1) < 0$, $\lambda_1 < 0$, $\lambda_2 > 0$ represents a saddle; $0 < f'(1) < -3/(8\varepsilon)$, $\lambda_1 > 0$, $\lambda_2 > 0$ is an unstable node; $f'(1) > -3/(8\varepsilon)$, $\lambda_{1,2} = \omega_r \pm i\omega_i$, $\omega_r > 0$ is an unstable focal point.

Thus, all the possible equilibrium positions of the system (6), (7) appear to be unstable in the case where the surface-active material is present, i.e., the concentration at the film surface and the film thickness do not lead towards uniform states, but conversely, the system "speeds up" and enters a regime which is not described by the quasi-one-dimensional approximation. On the other hand, in the case of inactive materials the equilibrium state at $f'(1) < 0$ is stable, and the film thickness and concentration tend towards the constant values $z = 1$ and $\gamma = 1$. The existence of a stable equilibrium position of the "focal point" type is particularly interesting. This means that when $f'(1) < -3/(8\varepsilon)$ the film thickness and the surface concentration experience undergo damped oscillations along the coordinate (Fig. 2). Thus, in the direction of the flow a wavy, three-dimensional structure of the rippled type is formed on the surface of the film. For the quasi-one-dimensional approximation to remain valid it is necessary to satisfy conditions equivalent to the inequality (4):

$$\left|\frac{dz}{dx}\right| \ll \frac{gh_0}{3\nu k}, \quad \left|\frac{d^2\gamma}{dx^2}\right| \ll \frac{gh_0\,|d\gamma/dx|}{3\nu kz}, \tag{13}$$

which are valid for sufficiently small initial deviations of t_1 and γ_1.

It does not appear to be possible to find an analytical solution of the system (6), (7) even in the case of kinetics described by the linear function $F(\Gamma)$. However, in the case of heavy films with large liquid flow rates, or in the case of films containing dilute surface-active materials, the parameter ε appears to be small, and for solving the system (6), (7) it is possible to use perturbation theory with given boundary conditions. It will be assumed that the film flows into the "reactor" zone ($x > 0$) from a prereaction zone ($x < 0$), where the distribution of the surface-active material along the surface is not influenced by the chemical changes. Far from the reaction zone ($x \to -\infty$) the film will be regarded as unperturbed: $h(x) = h_0$, $\Gamma = \Gamma_0$ (dashed line in Fig. 1). Then for the steady-state distribution of the surface-active material it is found that $d(U_S\Gamma)/dx = 0$, whence $U_S\Gamma = q = \text{const}$, where the given flow of the surface-active material is equal to $q = \Gamma_0 gh_0^2/2\nu$. The system of equations describing the distribution of the concentration of the surface material and the film thickness than have the forms

$$\frac{gh^3}{3\nu} + \frac{\delta h^2}{2\mu}\frac{d\Gamma}{dx} = 0, \qquad \left(\frac{gh^2}{2\nu} + \frac{\delta h}{\mu}\frac{d\Gamma}{dx}\right)\Gamma = q. \tag{14}$$

or, in terms of the dimensionless variables

$$z^3 + \varepsilon z^2\gamma_x' = 1, \qquad \gamma\left(z^2 + \frac{4}{3}\varepsilon z\gamma_x'\right) = \alpha, \quad \alpha \equiv \Gamma_0/\Gamma_*. \tag{15}$$

It has been shown in [7] that equations (14) or (15) have the solution $z \equiv 1$, $\gamma \equiv \alpha$, and also a neutral solution giving an implicit dependence of z and γ on x; in particular, the following integral system of (15) exists:

$$2\varepsilon\left(\frac{1}{3}\ln\left|\frac{4-z^3}{1-z^3}\right| - \frac{2}{4-z^3}\right) = x + C, \tag{16}$$

where C is a constant determined from the boundary conditions.

The relationship (16) coincides with the analogous relationship from [7] to within the accuracy of selecting the non-dimensional parameters. Furthermore, according to [7] the solution $z \equiv 1$, $\gamma \equiv \alpha$ is stable for inactive materials ($\varepsilon > 0$) and unstable for surface-active materials ($\varepsilon < 0$) with respect to steady-state perturbations distributed in the direction of flow of the film. This provides a basis for starting that in the case $\varepsilon > 0$, the steady-state of the film in the prereaction zone will be $z \equiv 1$, $\gamma \equiv \alpha$, while in the case $\varepsilon < 0$ it will be described by the relationship (16), where the constant C is determined from the condition for merging with the solution at $x > 0$ (the implicit dependence of γ on x is not used here because of its very unwieldy nature). From what has been said above, it follows that for establishing the shape of the film, and the distribution of the concentration of the reacting inactive material it is necessary to set up the following boundary condition: $z = 1$, $\gamma = \alpha$ at $x = 0$. Then, as in the case of the surface-active material, the boundary condition at $x = 0$ will be the condition for the conservation of its flux: $\gamma(z^2 + 4/3\varepsilon z\gamma'_x) = \alpha$.

It is not convenient to carry out a study of the behavior of the film in the presence of a real surface-active material within the framework of our present approach, since it is clear from the analysis which has been carried out that the steady state which is uniform in three dimensions is unstable and the flow always passes into a regime which is not described by the quasi-one-dimensional approximation.

Below we will restrict ourselves to a study of the film properties in the presence of inactive (i.e., not surface-active) materials which react at the free surface. The parameter ε will be assumed to be small: $0 < \varepsilon \ll 1$. The system of equations (6) and (7) can then be written in the following dimensionless form supplemented by boundary conditions:

$$z^3 + \varepsilon z^2\gamma_x' = 1, \qquad \left(\gamma\left(z^2 + \frac{4}{3}\varepsilon z\gamma_x'\right)\right)_x' = f(\gamma); \tag{17}$$

$$x = 0, \qquad z = 1, \qquad \gamma = \alpha. \tag{18}$$

Since the small parameter occurs in the higher derivatives, the problem proves to be singularly perturbed. It is easy to show that if the solution is sought according to regular perturbation theory in the form of a power series in ε, then two of the boundary conditions in (18) are not satisfied. The method of merging asymptotic expansions will therefore be used in seeking the solution. By introducing a "stretched-out" variable $\xi = x/\varepsilon$ which is close to zero, the system of relationships

$$\tilde{z}^3 + \tilde{z}^2 \tilde{\gamma}'_\xi = 1, \qquad \left(\tilde{\gamma}\left(\tilde{z}^2 + \frac{4}{3}\tilde{z}\tilde{\gamma}'_\xi\right)\right)'_\xi = \varepsilon f(\tilde{\gamma}), \tag{19}$$

$$\tilde{z} = 1, \qquad \tilde{\gamma} = \alpha, \qquad \xi = 0, \tag{20}$$

is obtained, where $\tilde{z}$ and $\tilde{\gamma}$ are functions of ξ.

The zeroth and first terms of the expansions are then determined in turn:

$$\tilde{z} = 1 + \frac{\varepsilon}{3} f(\alpha)\left(\exp\left(-\frac{3}{2\alpha}\xi\right) - 1\right) + o(\varepsilon), \tag{21}$$

$$\tilde{\gamma} = \alpha + \varepsilon\left(f(\alpha)\xi + \frac{2}{3}\alpha f(\alpha)\left(\exp\left(-\frac{3}{2\alpha}\xi\right) - 1\right)\right) + o(\varepsilon). \tag{22}$$

Let us now pass on to determining the external approximation. The solution is sought in the form $\gamma = \gamma_0 + \varepsilon\gamma_1 + \ldots$, $z = z_0 + \varepsilon z_1 + \ldots$ From (17), the zeroth approximation is found to be $z_0 = 1$, $\gamma_0' = f(\gamma_0)$, or

$$\int_\alpha^{\gamma_0} \frac{d\gamma}{f(\gamma)} = x + C. \tag{23}$$

The constant C is determined from the condition for merging with the internal solution. On converting in equation (23) to the internal variables, we can write

$$\int_\alpha^{\gamma_0} \frac{d\gamma}{f(\gamma)} = \varepsilon\xi + C, \quad \text{or} \quad \gamma_0 = \psi(\varepsilon\xi + C) = \psi(C) + \psi'(C)\varepsilon\xi.$$

From the relationship (21), (22) it is found that $\psi(C) = \alpha$, whence $C = \psi^{-1}(\alpha) = 0$. The zeroth external approximation is given by the implicit function of $\gamma_0(x)$:

$$\int_\alpha^{\gamma_0} \frac{d\gamma}{f(\gamma)} = x. \tag{24}$$

Then, using (24) and solving the equation for the first approximation, expressions are found for γ_1 and z_1:

$$z_1 = -\frac{1}{3} f(\gamma_0), \quad \gamma_1 = A\frac{f(\gamma_0)}{f(\alpha)} - \frac{2}{3} f(\gamma_0)\left(\gamma_0 - \alpha + \int_\alpha^{\gamma_0} \frac{yf'}{f}\, dy\right). \tag{25}$$

A merging of the internal and external expansions is carried out in order to determine the constant A. To do this, a change is made in the external expansion to the internal variable ξ:

$$\begin{aligned}\gamma = \gamma_0 + \varepsilon\gamma_1 = \gamma_0(\varepsilon\xi) + \varepsilon\Bigg(A\frac{f(\gamma_0(\varepsilon\xi))}{f(\alpha)} - \frac{2}{3} f(\gamma_0(\varepsilon\xi)) \times \\ \times\left(\gamma_0(\varepsilon\xi) - \alpha + \int_\alpha^{\gamma_0(\varepsilon\xi)} \frac{yf'}{f}\, dy\right)\Bigg) + o(\varepsilon) = \alpha + f(\alpha)\varepsilon\xi + \varepsilon A + o(\varepsilon).\end{aligned} \tag{26}$$

The expression (22) exists for the internal expansion. By comparing (26) and (22) and taking into account that the last term in (22) is exponentially small, it is found that $A = -2/3\ \alpha f(\alpha)$.

Thus, finally we have the following composite expansions for z and γ respectively:

$$z = 1 - \varepsilon\frac{1}{3}\left(f(\gamma_0) - f(\alpha)\exp\left(-\frac{3x}{2\varepsilon\alpha}\right)\right) + o(\varepsilon), \tag{27}$$

$$\gamma = \gamma_0 - \varepsilon\frac{2}{3} f(\gamma_0)\left(\gamma_0 + \int_\alpha^{\gamma_0} \frac{yf'}{f}\, dy\right) + \varepsilon\frac{2}{3}\alpha f(\alpha)\exp\left(-\frac{3x}{2\varepsilon\alpha}\right) + o(\varepsilon). \tag{28}$$

It is not difficult to show that when $f'(1) < 0$, the expansions (27) and (28) are uniformly applicable over the entire region of the reaction zone $x > 0$. It can be shown that γ_1 tends towards a finite limit when $x \to \infty$. To do this, let us consider the external expansion $\gamma = \gamma_0 + \varepsilon\gamma_1$. The dependence of γ_0 on x is given by the implicit function (24). Assuming that $f(\gamma)$ has only a single zero $\gamma = 1$ and that $f'(1) < 0$, it is seen that when $\gamma_0 \to 1$, $f(\gamma) \sim f'(1)(\gamma - 1) + o(\gamma - 1)$. The integral (24) can then be split up so that

$$\int_{\alpha}^{\gamma_0} \frac{d\gamma}{f(\gamma)} \sim \frac{1}{f'(1)} \ln|\gamma_0 - 1| + C_0,$$

whence $\gamma \sim 1 + C_1 \exp(f'(1)x) \to 1$ when $x \to \infty$.

The quantity γ_1 satisfies the differential equation

$$\gamma_1' - f'(\gamma_0)\gamma_1 = -\frac{2}{3}(\gamma_0 f(\gamma_0))'.$$

Bearing in mind that $f(\gamma)$ is the necessary number of times that differentiation can be carried out continuously, the following equation is found for γ_1 when $x \to \infty$:

$$\gamma_1' - f'(1)\gamma_1 = -\frac{2}{3}((1 + C\exp(f'x))Cf'\exp(f'x)), \quad f' \equiv f'(1),$$

the general solution of which is

$$\gamma_1 = A\exp(f'x) - \frac{2}{3}Cf'\exp(f'x)\left(x + \frac{C}{f'}\left(\exp(f'x) - 1\right)\right).$$

From this it is easy to see that $\gamma_1 \to 0$ when $x \to \infty$, since $f' \equiv f'(1) < 0$. From what has been said it can be concluded that the expansions (27) and (28) are applicable over the entire region of the reaction zone $x > 0$.

It should also be noted that the case of small values $\varepsilon > 0$ corresponds to a stable node on the phase plane (z, γ).

The results which have been obtained are strongly dependent on the value of α. From equation (9) it is seen that $z'(0) = -f(\alpha)/2\alpha$. Hence, for the quasi-one-dimensional approximation to be valid when $\alpha \to 0$ it is necessary that $\lim\limits_{\alpha \to 0} (f(\alpha)/2\alpha) < \infty$.

Let us now consider how changes in the flow of the film caused by the presence of an insoluble, chemically reacting, surface-inactive material on its surface influence mass transfer between the film and the adjacent gas. As in [7], it will be assumed that the material diffusing in the film does not enter into chemical reactions and does not influence the surface tension of the film, and that the corresponding Peclet number is large. The following formula can then be used for the local diffusion flux:

$$J = C_0\left(\frac{DU_s}{\pi}\right)^{1/2}\left(\frac{1}{U_s}\int_0^x U_s(x)\,dx\right)^{-1/2}. \qquad (29)$$

The integral flux into the film is

$$I = \int_0^x J\,dx = 2C_0\sqrt{\frac{D}{\pi}}\left(\int_0^x U_s\,dx\right)^{1/2}. \qquad (30)$$

If $U_S = U_0 + \varepsilon U_1$, then $I = I_0(1 + 1/2\varepsilon\langle\delta U\rangle)$, where $I_0 = 2C_0(DU_0x/\pi)^{1/2}$, $\delta U = U_1/U_0$.

$$\langle \delta U \rangle = \frac{1}{x}\int_0^x \delta U\,dx.$$

In our case, $U_S = U_0 + \varepsilon U_1 = U_0(1 + \varepsilon\delta U)$, $\delta U = U_1/U_0$. Then from (30) and the expression for U_S it follows that $\delta U = 2/3(f(\gamma_0) - f(\alpha)\exp(-3x/(2\varepsilon)))$. Then $\langle\delta U\rangle = 2/3(\gamma_0 - \alpha)/x - (4/9)\varepsilon\alpha f(\alpha)\exp(-3x/(2\varepsilon))$. Neglecting terms of the order $o(\varepsilon)$, the following expressions are obtained for the integral flux and the value of the relative change

$$I = I_0\left(1 + \frac{1}{3}\varepsilon\frac{\gamma_0 - \alpha}{x}\right), \qquad \Delta(x) = \frac{I - I_0}{I_0} = \frac{\varepsilon}{3}\,\frac{(\gamma_0(x) - \alpha)}{x}.$$

Thus, the dependence of the relative change on the flux as a result of the reacting surface-active material $\Delta(x)$ decreases with $1/x$ as the film length increases, since when $x \to \infty$, $\gamma_0(x) \to 1$, and the film tends towards the unperturbed state $z = 1$.

NOTATION

u, velocity component along x axis; ν, μ, kinematic and dynamic viscosities; ρ, density of liquid; g, projection of the acceleration of free fall onto the x axis; σ, surface tension at the liquid–gas interface; Γ, surface concentration of insoluble surface-active material; h(x), film thickness; F(Γ), kinematic function expressing the dependence of the rate of the chemical surface reaction on the concentration of the surface-active material; k, reaction rate constant of dimensions 1/T; C_0, concentration of component of the gas which dissolves in the liquid close to the film surface; D, diffusion coefficient of gas dissolved in the film.

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INFLUENCE OF LONGITUDINAL MIXING ON DISSOLUTION KINETICS OF A POLYDISPERSE SYSTEM OF PARTICLES

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The problem of dissolution of a polydisperse system of particles in a semibounded channel is formulated and investigated with longitudinal mixing in the solid phase taken into account.

To describe processes proceeding in polydisperse systems, methods of the mechanics of heterogeneous media [1, 2] have recently received greater and greater currency. According to [1], utilization of the so-called continuity equations for functions of the particle size distribution density type turns out to be most productive when studying the motion of inclusions interacting with a dispersion medium and hence changing size. Thus on the basis of this approach mathematical models of certain processes of such nature are obtained and investigated in [3, 4].

Let us examine the steady process of dissolution of a polydisperse system of solid inclusions entrained by a fluid flow moving in a semibounded channel. Such a representation can be used if it is assumed that the main particle mass is dissolved without succeeding in reaching the opposite boundary of the channel. Let us take the quasihomogeneity hypothesis [5] that the spacings in which the mixture flow parameters change substantially, are much greater than the particle size and their separation. We will consider the inclusions whose sizes are a continuous random variable, to be sufficiently numerous so that their granulometric composition could be described by a continuous function of the size distribution density type (not normalized to one) that satisfies the continuity equation in the space of their linear dimensions. If the fluctuations of the linear rate of particle dissolution is neglected, then for the developed turbulent flow case, the continuity equation can be written in the form

$$w\frac{\partial f}{\partial l}+\frac{\partial}{\partial r}(fv)-D\frac{\partial^2 f}{\partial l^2}=\delta(l-l_0)\,wf_0(r). \qquad (1)$$

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