QUASISTATIONARY SEDIMENTATION WITH ADSORPTION

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Models for the sedimentation of particles suspended in solution are proposed that take into account mass transfer between the liquid fraction of the solution and the particles. The structure and velocity of the concentration wave describing the upward extension of the zone with a high concentration of the solid phase are studied using a kinematic model with the Froude number as a small parameter. It is established that the concentration-wave velocity becomes lower if the sorption parameter is set equal to zero, i.e., if the sorption properties of the suspended particles are ignored.

Key words: sedimentation, adsorption, two-phase continuous medium, concentration wave.

1. Mathematical Models of Sedimentation. Sedimentation — the process of separation of various mixtures into components under gravity — is frequently observed in both nature and technical facilities. In geology, the process of rock formation is studied from the standpoints of sedimentation. Sedimentation has been widely employed in ore mining and chemical industry.

The foundations for the mathematical modeling of sedimentation were laid by Stokes (1851) in his classical paper on the law of fall of a single sphere in a fluid [1]. Since then, this law have been widely used to solve many scientific and practical problems.

An important contribution to research of concentrated suspension solutions was a paper by Kynch (1952), in which he suggested that process of sedimentation of a solid phase be described in terms of concentration waves [2]. A zone with a high concentration of the solid phase is first formed at the bottom of a sedimentation chamber, and then this zone is extended upward — this is a concentration wave. Although the paper was based on the assumption that the inertia forces are negligibly small, the conclusions of this work have been confirmed by a number of experiments. The subsequent development of this theory is summed up in [3].

The present paper considers sedimentation models that take into account the sorption properties of the solid particles suspended in solutions. The need for such models is dictated by a number of applied problems of ecology and chemistry. In addition, there is convincing evidence that adsorption indeed influences sedimentation. Thus, experiments have shown that the sedimentation rate is increased by the addition of surface-active agents, such as cyanides and other electrolytes, to solutions.

Solution and the solid particles suspended in it are treated as two independent phases [4]. The mass and momentum balance equations are formulated with allowance for mass transfer between the phases using a number of assumptions.

The main assumption refers to the role of inertia forces in the total balance of forces. In the case of slow flows there is a small parameter — the Froude number. It is used to perform an ordinary conversion to quasistationary equations ignoring inertia force, as in the Kynch approach.

Another important assumption concerns the adsorption kinetics, which characterizes the mass balance of the active-impurity concentration on the surface of the suspended particles and in the solution. The Langmuir kinetic equation is used as the basis [1].

In addition, it is assumed that the liquid- and solid-phase pressures are identical and the volume compression of horizontal layers of suspended particles depends only on their volume concentration.

As a result, the one-dimensional two-phase sedimentation model with adsorption reduces to the following equations:

$$\frac{\partial \rho_f \varphi_f}{\partial t} + \frac{\partial \rho_f \varphi_f v_f}{\partial x} = -r, \qquad \frac{\partial \rho_s \varphi_s}{\partial t} + \frac{\partial \rho_s \varphi_s v_s}{\partial x} = r,$$

$$\frac{\partial \rho_f \varphi_f c_f}{\partial t} + \frac{\partial \rho_f \varphi_f c_f v_f}{\partial x} = -r, \qquad r \equiv \frac{\partial \rho_s \varphi_s c_s}{\partial t} + \frac{\partial \rho_s \varphi_s c_s v_s}{\partial x},$$

$$\frac{\partial \rho_s \varphi_s c_s}{\partial t} = k_1 c_f \rho_s \varphi_s (c_s^\infty - c_s) - k_2 \rho_s \varphi_s c_s, \qquad \varphi_f + \varphi_s = 1, \tag{1}$$

$$\frac{\partial}{\partial x} p = -g \rho_f + \frac{\alpha(\varphi_s) u}{\varphi_f}, \qquad \frac{\partial}{\partial x} \sigma_e(\varphi_s) = -g(\rho_s - \rho_f)\varphi_s - \frac{\alpha(\varphi_s) u}{\varphi_f}, \qquad u \equiv v_s - v_f.$$

Here ρ is the phase density, v is the phase velocity, $u = v_s - v_f$ is the relative velocity of the phases, α is the interfacial friction factor, φ is the phase volume concentration, g is the acceleration of gravity, c is the impurity mass concentration in the phase, p is the pressure, and σ_e is the volume compression of the horizontal layers of suspended particles. The subscripts f and s denote the liquid and solid phases, respectively. The x axis is directed vertically upward opposite to the gravity. Naturally, the mass transfer between the phases should be accompanied by a variation in the phase densities. However, for many applied problems, the assumption of incompressibility of the phases is justified, and in the present work, the densities ρ_f and ρ_s are considered constant.

Model (1) contains three kinetic constants k_1, k_2, and c_s^∞ and two empirical functions $\alpha(\varphi_s)$ and $\sigma_e(\varphi_s)$, which prevents its application. Therefore, it is reasonable to simplify the model.

If a sorption (or chemisorption) process rapidly reaches a stationary regime, the Langmuir equation can be replaced by a stationary isotherm, from which by linearization it is possible to obtain the relation $\varphi_a = Q\varphi_s$ between the volume concentration of the solid phase φ_s and the volume concentration of the adsorbed surfactant impurity φ_a, where the adsorption parameter Q is determined by the constants k_1, k_2, and c_s^∞ and by a certain average value c_f^* of the concentration c_f. Conversion to the isotherm $\varphi_a = Q\varphi_s$ is justified if the ratio φ_a/φ_s is not negligibly small.

After introducing the volume concentration of the unfixed liquid phase $\tilde{\varphi}_f$ and reassessing the role of the mass generation rate r, from Eqs. (1) we derive the sedimentation model with equilibrium adsorption:

$$\frac{\partial \rho_f \tilde{\varphi}_f}{\partial t} + \frac{\partial \rho_f \tilde{\varphi}_f v_f}{\partial x} = -\frac{\partial \rho_f \varphi_a}{\partial t}, \qquad \frac{\partial \rho_s \varphi_s}{\partial t} + \frac{\partial \rho_s \varphi_s v_s}{\partial x} = \frac{\partial \rho_f \varphi_a}{\partial t},$$

$$\frac{\partial}{\partial x} \sigma_e(\theta) = -g(\rho_s - \rho_f)\theta - \frac{\alpha(\theta) u}{\tilde{\varphi}_f}, \qquad u \equiv v_s - v_f, \tag{2}$$

$$\tilde{\varphi}_f + \varphi_s + \varphi_a = 1, \qquad \varphi_a = Q\varphi_s, \qquad \theta \equiv \varphi_s + \varphi_a.$$

When adsorption is ignored ($Q = 0$), Eqs. (2) coincide with the well-known equations [3]. In some cases, system (2) can be reduced to one degenerate parabolic equation for the function θ:

$$\frac{\partial \theta}{\partial t} + \frac{\partial F_b(\theta, Q)}{\partial x} = \frac{\partial}{\partial x}\left(a(\theta, Q)\frac{\partial \theta}{\partial x}\right). \tag{3}$$

In particular, if at the sedimentation-chamber bottom there is no removal of the settled particles, the sedimentation is described by this equation.

Equation (3) becomes the scalar conservation law

$$\frac{\partial \theta}{\partial t} + \frac{\partial F_b(\theta, Q)}{\partial x} = 0, \tag{4}$$

if the action of the horizontal layers of the solid phase on each other is insignificant, i.e., if it is possible to set $\sigma_e'(\theta) \equiv 0$.

Most of the present paper deals with an analysis of Eq. (4). Using this equation, it is possible to describe the structure of the wave concentration and to calculate its velocity. It is proved analytically and confirmed by numerical calculations that accounting for adsorption leads to an increase in the wave-concentration velocity.

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2. Sedimentation with Nonequilibrium Adsorption. In two-phase theory, the suspended particles and solution are considered as two material continua overlaid on each other. The mass transfer between the solid and liquid phases is described by the equations [5]

$$\frac{\partial}{\partial t}(\rho_f \varphi_f) + \operatorname{div}(\boldsymbol{v}_f \rho_f \varphi_f) = -r; \tag{5}$$

$$\frac{\partial}{\partial t}(\rho_s \varphi_s) + \operatorname{div}(\boldsymbol{v}_s \rho_s \varphi_s) = r. \tag{6}$$

Here $\boldsymbol{v}$ is the phase velocity and r is the mass generation rate:

$$r \equiv \frac{\partial a}{\partial t} + \operatorname{div}(\boldsymbol{v}_s a)$$

(a is the mass of the adsorbed impurity per unit volume). Let c_s be the mass concentration of the adsorbed impurity in the solid phase. Then,

$$a = \rho_s \varphi_s c_s.$$

The variation in the impurity mass in the liquid phase is described by the equation [6]

$$\frac{\partial}{\partial t}(\rho_f \varphi_f c_f) + \operatorname{div}(\boldsymbol{v}_f \rho_f \varphi_f c_f) = -r. \tag{7}$$

To determine the relation between the concentrations c_s and c_f, we use the Langmuir kinetic adsorption equation [1]

$$\frac{\partial a}{\partial t} = k_1 c_f (\rho_s \varphi_s c_s^\infty - a) - k_2 a, \qquad c_s^\infty = \frac{N\mu S}{\rho_s}. \tag{8}$$

In formula (8), the constants have the following meaning: k_1 and k_2 are the sorption and desorption rate parameters, S is the surface area of the solid phase per unit volume of the solid phase, μ is the mass of one impurity molecule, N is the number of adsorption centers per unit area, and c_s^∞ is the limiting possible impurity concentration in the solid phase. The constant $\tau = 1/k_2$ is the residence time (in seconds) of a molecule at the adsorption center. It is calculated by the formula $\tau = \tau_0 \exp(E/(kT))$, where k is Boltzmann's constant, E is the energy of adhesion to the solid wall, T is the temperature, and $\tau_0 \approx 10^{-13}$ is a factor.

If the third phase is absent, the volume concentrations φ_s and φ_f should satisfy the equality

$$\varphi_s + \varphi_f = 1. \tag{9}$$

In the theory of a two-phase medium, the momentum equations are written as

$$\frac{\partial}{\partial t}(\rho_f \varphi_f \boldsymbol{v}_f) + \operatorname{div}(\rho_f \varphi_f \boldsymbol{v}_f \otimes \boldsymbol{v}_f) = \operatorname{div}\sigma_f + \rho_f \varphi_f \boldsymbol{g} - \boldsymbol{m},$$

$$\frac{\partial}{\partial t}(\rho_s \varphi_s \boldsymbol{v}_s) + \operatorname{div}(\rho_s \varphi_s \boldsymbol{v}_s \otimes \boldsymbol{v}_s) = \operatorname{div}\sigma_s + \rho_s \varphi_s \boldsymbol{g} + \boldsymbol{m}. \tag{10}$$

Here $\boldsymbol{g}$ is the free-fall acceleration, $\boldsymbol{m}$ is the interfacial resistance vector ($\boldsymbol{m} = -\alpha\boldsymbol{u} - \beta\nabla\varphi_f$), and $\boldsymbol{u} = \boldsymbol{v}_s - \boldsymbol{v}_f$. The symbol $\boldsymbol{a} \otimes \boldsymbol{b}$ denotes the tensor product of the vectors $\boldsymbol{a}$ and $\boldsymbol{b}$, so that $(\boldsymbol{a} \otimes \boldsymbol{b})_{ij} = a_i b_j$. We recall that if σ is a matrix, $\operatorname{div}\sigma$ is a vector with the components $(\operatorname{div}\sigma)_i = \partial\sigma_{ij}/\partial x_j$.

System (5)–(10) is a sedimentation model with adsorption. Within the framework of this model, the entire diversity of solutions is determined by the parameters k_1, k_2, α, β, and c_s^∞ and the stress tensors σ_f and σ_s. For the tensors σ_f and σ_s, the determining relations will be written below.

Subsequently, we restrict ourselves to the case of one-dimensional motion along the vertical axis x. We introduce the following nondimensional quantities:

$$x' = \frac{x}{L}, \quad t' = \frac{t}{\tau}, \quad v_s' = \frac{v_s}{v_\infty}, \quad v_f' = \frac{v_f}{v_\infty}, \quad u' = \frac{u}{v_\infty}, \quad \sigma_f' = \frac{\sigma_f}{\rho_f g L},$$

$$\sigma_s' = \frac{\sigma_s}{\rho_s g L}, \qquad \frac{\partial}{\partial t'} = \tau\frac{\partial}{\partial t}, \qquad \frac{\partial}{\partial x'} = L\frac{\partial}{\partial x}.$$

Here L is the characteristic height of the solution column and v_∞ is the characteristic sedimentation rate of an individual suspension volume. The characteristic time τ is calculated by the formula $\tau = L/v_\infty$.

We write Eqs. (5)–(10) in dimensionless variables using the Froude number $\mathrm{Fr} = v_\infty/\sqrt{gL}$:

$$\frac{\partial \rho_f \varphi_f}{\partial t'} + \frac{\partial \rho_f \varphi_f v'_f}{\partial x'} = -\frac{\partial \rho_s \varphi_s c_s}{\partial t'} - \frac{\partial \rho_s \varphi_s c_s v'_s}{\partial x'},$$

$$\frac{\partial \rho_s \varphi_s}{\partial t'} + \frac{\partial \rho_s \varphi_s v'_s}{\partial x'} = \frac{\partial \rho_s \varphi_s c_s}{\partial t'} + \frac{\partial \rho_s \varphi_s c_s v'_s}{\partial x'},$$

$$\frac{\partial \rho_f \varphi_f c_f}{\partial t'} + \frac{\partial \rho_f \varphi_f c_f v'_f}{\partial x'} = -\frac{\partial \rho_s \varphi_s c_s}{\partial t'} - \frac{\partial \rho_s \varphi_s c_s v'_s}{\partial x'},$$

$$\frac{\partial \rho_s \varphi_s c_s}{\partial t'} = k_1 c_f \rho_s \varphi_s (c_s^\infty - c_s) - k_2 \rho_s \varphi_s c_s,$$

$$\mathrm{Fr}^2 \left(\frac{\partial \varphi_f v'_f}{\partial t'} + \frac{\partial \varphi_f (v'_f)^2}{\partial x'} \right) = \frac{\partial}{\partial x'} \sigma'_f - g\rho_f \varphi_f + \frac{\alpha v_\infty u'}{g\rho_f} + \frac{\beta}{Lg\rho_f} \frac{\partial}{\partial x'} \varphi_f,$$

$$\mathrm{Fr}^2 \left(\frac{\partial \varphi_s v'_s}{\partial t'} + \frac{\partial \varphi_s (v'_s)^2}{\partial x'} \right) = \frac{\partial}{\partial x'} \sigma'_s - g\rho_s \varphi_s - \frac{\alpha v_\infty u'}{g\rho_s} - \frac{\beta}{Lg\rho_s} \frac{\partial}{\partial x'} \varphi_f.$$

Taking into account that the Froude number is small, we arrive at the quasistationary equations of motion, which in dimensional variables are written as

$$\frac{\partial \rho_f \varphi_f}{\partial t} + \frac{\partial \rho_f \varphi_f v_f}{\partial x} = -r, \qquad \frac{\partial \rho_s \varphi_s}{\partial t} + \frac{\partial \rho_s \varphi_s v_s}{\partial x} = r; \tag{11}$$

$$\frac{\partial \rho_f \varphi_f c_f}{\partial t} + \frac{\partial \rho_f \varphi_f c_f v_f}{\partial x} = -r, \qquad r \equiv \frac{\partial \rho_s \varphi_s c_s}{\partial t} + \frac{\partial \rho_s \varphi_s c_s v_s}{\partial x}; \tag{12}$$

$$\frac{\partial \rho_s \varphi_s c_s}{\partial t} = k_1 c_f \rho_s \varphi_s (c_s^\infty - c_s) - k_2 \rho_s \varphi_s c_s; $$

$$0 = \frac{\partial}{\partial x} \sigma_f - \rho_f g \varphi_f + \alpha u + \beta \frac{\partial}{\partial x} \varphi_f, \qquad 0 = \frac{\partial}{\partial x} \sigma_s - \rho_s g \varphi_s - \alpha u - \beta \frac{\partial}{\partial x} \varphi_f. \tag{13}$$

The determining relations for the stresses σ_f and σ_s are as follows:

$$\sigma_f = -\varphi_f p, \qquad \sigma_s = -\varphi_s p - \sigma_e, \qquad \sigma_e = \sigma_e(\varphi_s). \tag{14}$$

These relations coincide with the well-known formulas for the case of no impurity [3] and imply that all phases are acted upon by identical pressure p and that in the solid phase there are additional stresses σ_e due to the action of horizontal layers of the solid phase on each other. These stresses are especially pronounced at the sedimentation-chamber bottom, where the liquid phase is actually filtered through the "swollen" solid phase. According to this concept, the quantity p is sometimes called pore pressure. The quantity σ_e characterizes the volume compression of the solid sorbent in the solution, and σ_e as a function of φ_s should be determined experimentally. For some types of solution, the function $\sigma_e(\varphi_s)$ is nonnegative and there is a critical value φ_s^* for which the following conditions [3] are satisfied:

$$\sigma'_e(\varphi_s) = 0 \quad \text{at} \quad \varphi_s \leq \varphi_s^*, \qquad \sigma'_e(\varphi_s) > 0 \quad \text{at} \quad \varphi_s \geq \varphi_s^*. \tag{15}$$

When all velocities are equal to zero, the first equation of system (13), in view of equalities (14), reduces to the equation

$$0 = \varphi_f(\beta - p) - \varphi_f(p_x + \rho_f g).$$

However, in the state of rest, $p_x = -\rho_f g$; therefore, in this state $\beta = p$. As a hypothesis, we assume that the equality $\beta = p$ is satisfied always and α is a specified function of φ_s.

In view of this hypothesis, system (13) can be written as

$$\frac{\partial}{\partial x} p = -g\rho_f + \frac{\alpha(\varphi_s)u}{\varphi_f}, \quad \frac{\partial}{\partial x} \sigma_e(\varphi_s) = -g(\rho_s - \rho_f)\varphi_s - \frac{\alpha(\varphi_s)u}{\varphi_f}, \quad u \equiv v_s - v_f. \tag{16}$$

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Thus, we obtain the quasistationary model (1), which describes sedimentation in terms of seven unknown functions: φ_f, φ_s, c_f, c_s v_f, v_s, and p.

3. Equilibrium Adsorption. The adsorbed mass a is attached to the solid phase, carrying with itself a certain volume of the liquid phase. The volume concentration of the fixed liquid phase φ_a is determined from the equality

$$\rho_s \varphi_s c_s \equiv a = \rho_f \varphi_a. \tag{17}$$

The volume concentration of the free liquid phase $\tilde{\varphi}_f$ is equal to $\varphi_f - \varphi_a$. Bearing in mind that mass transfer occurs between the free and fixed liquid phases, we reformulate the mass balance laws (11) and (12):

$$\frac{\partial \rho_f \tilde{\varphi}_f}{\partial t} + \frac{\partial \rho_f \tilde{\varphi}_f v_f}{\partial x} = -r, \qquad \frac{\partial \rho_s \varphi_s}{\partial t} + \frac{\partial \rho_s \varphi_s v_s}{\partial x} = r; \tag{18}$$

$$\frac{\partial \rho_f \tilde{\varphi}_f c_f}{\partial t} + \frac{\partial \rho_f \tilde{\varphi}_f c_f v_f}{\partial x} = -r, \qquad r \equiv \frac{\partial \rho_f \varphi_a}{\partial t} + \frac{\partial \rho_f \varphi_a v_s}{\partial x}. \tag{19}$$

Introducing the volume concentration of the "swollen" solid phases $\theta = \varphi_s + \varphi_a$, we write the momentum equations (16) for the free liquid phase and the "swollen" solid phases as follows:

$$\frac{\partial}{\partial x} p = -g\rho_f + \frac{\alpha(\theta)u}{\tilde{\varphi}_f}, \qquad \frac{\partial}{\partial x} \sigma_e(\theta) = -g(\rho_s - \rho_f)\theta - \frac{\alpha(\theta)u}{\tilde{\varphi}_f}, \qquad u \equiv v_s - v_f. \tag{20}$$

We eliminate from consideration the variable c_s and introduce the variable φ_a by means of equality (17). Then, the Langmuir equation becomes

$$\frac{\partial \rho_f \varphi_a}{\partial t} = k_1 c_f (\rho_s \varphi_s c_s^\infty - \rho_f \varphi_a) - k_2 \rho_f \varphi_a.$$

The sedimentation rate is much lower than the rate of establishment of thermodynamic equilibrium between impurity molecules in the phases. Therefore, the Langmuir equation can be replaced by the Langmuir isotherm

$$\varphi_a = \frac{k_1 \rho_s c_s^\infty c_f}{\rho_f (k_2 + k_1 c_f)} \varphi_s,$$

which is obtained from the last equality if in it the derivative with respect to time is set equal to zero. Linearizing the isotherm for a certain value $c_f = c_f^*$, we arrive at the equality

$$\varphi_a = Q\varphi_s \qquad \left(Q \equiv \frac{k_1 \rho_s c_s^\infty c_f^*}{\rho_f (k_2 + k_1 c_f^*)} \right).$$

Next, we assume that the second term is small compared to the first term in the expression for the mass generation rate r. Assuming that $r = \partial(\rho_f \varphi_a)/\partial t$, we obtain the sedimentation model with equilibrium adsorption (2).

We note that Eqs. (2) do not contain the functions c_s, c_f, and p, which are found from equality (17) and the solutions of Eqs. (19) and (20), respectively. An advantage of model (2) is that instead of the three kinetic constants k_1, k_2, and c_s^∞, it is now necessary to determine just one adsorption parameter Q. To calculate it, one needs to perform a simple experiment to find the degree of reduction in the liquid-solution volume for the case where the solid phase in the form of a dry powder is first placed in the solution and the unadsorbed part of the solution is then poured through a filter.

4. Degenerate Parabolic Sedimentation Equation. For the average velocity

$$q = v_s \varphi_s + (1 - \gamma Q) v_f \tilde{\varphi}_f \qquad (\gamma = \rho_f / \rho_s)$$

equalities (18) imply that $\partial q / \partial x = 0$, i.e., q depends only on time.

We introduce the function

$$f(\theta) = -g(\rho_s - \rho_f)\theta^2 (1 - \theta)^2 / \alpha(\theta).$$

The phase velocities can be expressed in terms of q and u as follows:

$$v_f = \frac{q - \varphi_s u}{(1 - \gamma Q)\tilde{\varphi}_f + \varphi_s}, \qquad v_s = \frac{q + (1 - \gamma Q)\varphi_f u}{(1 - \gamma Q)\tilde{\varphi}_f + \varphi_s}, \qquad \varphi_s = \frac{\theta}{1 + Q}, \qquad \tilde{\varphi}_f = 1 - \theta.$$
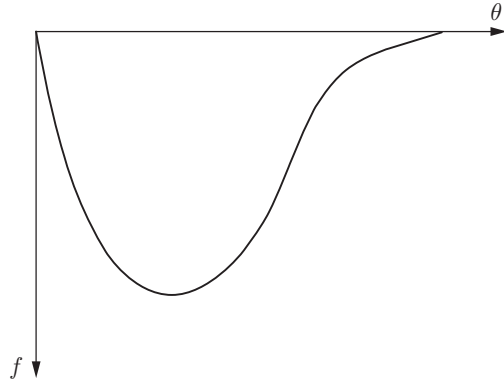
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Fig. 1

Eliminating the function u by means of the second formula in (20), from the second equation of system (18), we obtain the equation for θ

$$\frac{\partial \theta}{\partial t} + \frac{\partial F(\theta, q, Q)}{\partial x} = \frac{\partial}{\partial x}\left(a(\theta, Q)\frac{\partial \theta}{\partial x}\right), \tag{21}$$

where

$$F(\theta, q, Q) = \frac{(1+Q)f(\theta)}{r(\theta, Q)} + \frac{1+Q}{(1-\gamma Q)}\frac{q\theta}{r(\theta, Q)}, \qquad a(\theta, Q) = -\frac{(1+Q)f(\theta)\sigma_e'(\theta)}{g(\rho_s - \rho_f)\theta r(\theta, Q)},$$

$$r(\theta, Q) := \theta + \nu(Q)(1-\theta), \qquad \nu(Q) := (1+Q)(1-\gamma Q).$$

Equation (21) belongs to the type of degenerate parabolic equations if the function $\sigma_e(\theta)$ obeys conditions (15) in which φ_s is replaced by θ and φ_s^* by a certain number θ^*. As is obvious, Eq. (21) is determined by the kinetic constant Q and two empirical functions $\alpha(\theta)$ and $\sigma_e(\theta)$, where α is the interfacial friction factor and σ_e characterizes the compression of horizontal layers of the solid phase. For $Q = 0$, Eq. (21) becomes the well-known equation of sedimentation without adsorption [3].

An analysis of Eq. (21) is based on the empirical representation of the function $f(\theta)$ used to describe sedimentation of a number of suspensions [3]:

$$f(\theta) = -a_0\theta(\theta_\infty - \theta)^n, \qquad a_0 = \text{const} > 0, \quad 0 < \theta_\infty \le 1, \quad n > 0. \tag{22}$$

Here θ_∞ is the limiting possible concentration of the settled solid particles. In particular, for some suspensions, the constants in formula (22) have the following values [3]: $a_0 = 6.05 \cdot 10^{-4}$ m/sec, $n = 12.59$, and $\theta_\infty = 0.65$. For such values, the function $f(\theta)$ exhibits the following properties:

$$f(\theta) \text{ has one point of inflection, } f(0) = f(\theta_\infty) = 0, \text{ and } f(\theta) < 0 \text{ for } 0 < \theta < \theta_\infty. \tag{23}$$

A plot of such a function is given in Fig. 1.

Below, Eq. (21) is studied under the assumption that $\sigma_e'(\theta) \equiv 0$, which is equivalent to ignoring the compression interaction between horizontal layers of the solid phase. In this case, Eq. (21) becomes the kinematic-wave equation [7]:

$$\theta_t + F(\theta, q)_x = 0.$$

The properties of the function $F(\theta, q)$ are determined by conditions (22) and (23). We note that $\nu > 1$ for $Q < (1 - \gamma)/\gamma$.

5. Sedimentation with a Closed Bottom. Under conditions where there is no removal of solid particles at the sedimentation-chamber bottom, the average mass flux q vanishes and the model of noncompression sedimentation reduces to the conditions

$$\theta_t + F_b(\theta)_x = 0, \quad \theta|_{t=0} = \theta_0, \quad \theta|_{x=0} = \theta_\infty, \quad F_b = \frac{(1+Q)f}{\theta + \nu(Q)(1-\theta)}. \tag{24}$$

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It is assumed that the initial solid-phase concentration has the same value θ_0 over the entire column height and that at the bottom a certain limiting concentration θ_∞ occurs instantaneously and remains unchanged during the entire process. Recall that the function $F_b(\theta)$ depends on the constant θ_∞ [see (22)].

Let us show that for a small value of the number Q, the function $F_b(\theta)$ obeys conditions (23). It suffices to check that the second derivative $F_b''(\theta)$ vanishes only at a single point in the interval $(0, \theta_\infty)$. We have

$$F_b''(\theta) = (\nu - 1)^2 a r^{-3}(\theta_\infty - \theta)^{n-2} p(\theta, Q), \quad r(\theta, Q) := \theta + \nu(1 - \theta), \quad a = a_0(1 + Q),$$

where $p(\theta, Q)$ is a third-degree polynomial in the variable θ:

$$p = 2(n + 1)(\theta - \theta_\infty')(\theta - \theta_\infty)(\theta - 1/\delta) - 2\theta(\theta - \theta_\infty)^2 - n(n + 1)(\theta - 2\theta_\infty')(\theta - 1/\delta)^2. \tag{25}$$

Here we used the notation $\theta_\infty' = \theta_\infty/(n + 1)$ and $\delta = (\nu - 1)/\nu$.

Let $n > 2$. The polynomial $(\nu(Q) - 1)^2 p(\theta, Q)$ for $Q = 0$ has one root $\theta = 2\theta_\infty'$. By virtue of continuity, in the interval $(\nu(Q) - 1)^2 p(\theta, Q)$ the polynomial $(0, \theta_\infty)$ also has one root. Thus, for small values of Q, the function $F_b''(\theta)$ vanishes in the interval $(0, \theta_\infty)$ only at one point. Let us find the range of the parameter Q that *a priori* ensures that property (23) is satisfied for the function $F_b(\theta)$.

Statement 1. *If*

$$\frac{\nu(Q) - 1}{\nu(Q)} \equiv \delta(Q) < 2n \Big/ \left(\theta_\infty + \sqrt{\theta_\infty^2 + \frac{2n^2(n - 1)}{\theta_\infty(n + 1)}} \right) \equiv \delta_*,$$

the function $F_b(\theta)$ satisfies conditions (23).

Proof. The polynomial p can be written as

$$p = -n(n - 1)(\theta^3 - \alpha_2 \theta^2 + \alpha_1 \theta - \alpha_0),$$

where

$$\alpha_2 = \frac{2(n + 1)}{\delta n}, \quad \alpha_1 = \frac{n + 1}{\delta^2(n - 1)} + \frac{2(n - 2)\theta_\infty}{\delta n(n - 1)}, \quad \alpha_0 = \frac{2\theta_\infty(n + 1)}{\delta n(n - 1)} \left(\frac{n}{\delta} - \theta_\infty \right).$$

Let the condition $\alpha_0 > 1$ be satisfied. We denote the roots of the equation $p(\theta) = 0$ by $\bar{\theta}_i$ and assume that $\bar{\theta}_1 \leq \bar{\theta}_2 \leq \bar{\theta}_3$.

Representation (25) implies the inequalities $p(2\theta_\infty') > 0$ and $p(\theta_\infty) < 0$. Therefore, one of the roots is positive and lies in the interval $(2\theta_\infty', \theta_\infty)$.

The condition $\bar{\theta}_1 \bar{\theta}_2 \bar{\theta}_3 = \alpha_0 > 1$ implies that all roots are positive or that exactly two negative roots exist. In the latter case, it is clear that $(2\theta_\infty', \theta_\infty) \ni \bar{\theta}_3$ is a single point in the interval $(0, \theta_\infty)$ at which the function p vanishes.

Let now all roots be positive. Since $\alpha_0 > 1$, we have $\bar{\theta}_3 > 1$. Representation (25) implies that $p(\theta) < 0$ for $\theta_\infty < \theta < 1/\delta$. Therefore, $\bar{\theta}_3 \geq 1/\delta > 1$. There is an alternative: $\max\{\bar{\theta}_1, \bar{\theta}_2\} < \theta_\infty$ or $\max\{\bar{\theta}_1, \bar{\theta}_2\} > 1/\delta$. In the first case, $p(\theta) > 0$ for $\min\{\bar{\theta}_1, \bar{\theta}_2\} < \theta < \max\{\bar{\theta}_1, \bar{\theta}_2\}$. In the second case, $p(\theta) \to \infty$ as $\theta \to -\infty$ and $p(\theta) \to -\infty$ as $\theta \to \infty$. Therefore, the function $p(\theta)$ should have four different points at which $p'(\theta) = 0$, which is impossible because $p(\theta)$ is a third-degree polynomial.

Thus, $\max\{\bar{\theta}_1, \bar{\theta}_2\} > 1$. Hence, $(2\theta_\infty', \theta_\infty) \ni \min\{\bar{\theta}_1, \bar{\theta}_2\} = \bar{\theta}_1$ is the unique solution of the equation $p(\theta) = 0$ in the interval $(0, \theta_\infty)$. Thus, for $\alpha_0 > 1$, the polynomial p has a unique root in the interval $(0, \theta_\infty)$.

It is easy to verify that the condition $\alpha_0 > 1$ is equivalent to the inequality $\delta < \delta_*$. Statement 1 is proved.

Next, it is assumed that the function $F_b(\theta)$ satisfies conditions (23). This assumption makes it possible to describe the sedimentation dynamics and show that the discontinuity wave of the function $\theta(x, t)$, called a concentration wave, propagates up the column.

Before characterizing the velocity σ of this wave, we shall describe the structure of the solution of problem (24) on the plane of variables (x, t) (Fig. 2) invoking the theory of entropy solutions for the scalar conservation laws [8] in the case where the function $F_b(\theta)$ has one point of inflection and $\theta_0 < \theta_\infty$.

In the sector between the half-lines $t = 0$ and $x/t = \sigma$, the function θ takes a constant value θ_0. Since the wave propagates in the increasing direction of the variable x, the number θ_0 is reasonably called the value of the quantity θ ahead of the front. On the line $x/t = \sigma$, the function undergoes a discontinuity. The value of θ_1^a behind the front and the velocity σ are found from the Hugoniot condition

$$\sigma = \frac{F_b(\theta_1^a) - F_b(\theta_0)}{\theta_1^a - \theta_0}.$$
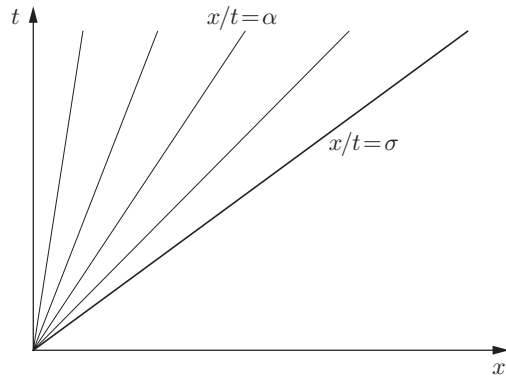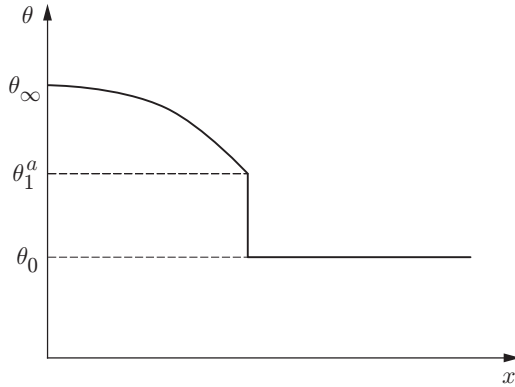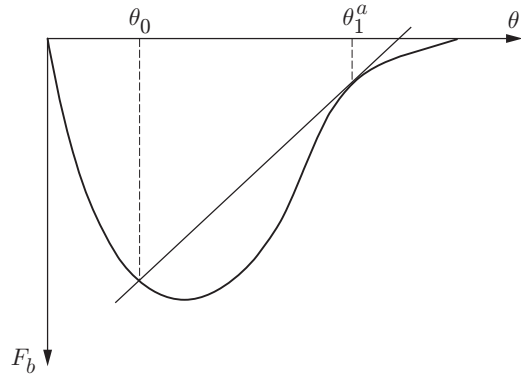
Fig. 2

Fig. 3

Fig. 4

In the sector between the half-lines $x/t = \sigma$ and $x = 0$, the function θ is constant along each half-line $x/t = \alpha = \mathrm{const}$ and increases continuously from θ_1^a to θ_∞ as α decreases from σ to 0. In this case, θ is found from the equality

$$\alpha = \frac{dF_b}{d\theta}(\theta(\alpha)), \qquad \theta(\alpha) = (F_b')^{-1}(\alpha).$$

Thus, the shock wave propagates up the column and is followed by a centered wave. A qualitative curve of the concentration θ versus the height x at any fixed time t is given in Fig. 3.

The values of σ and θ_1^a are found uniquely, as follows from the geometrical method of their determination. On the plane of variables (θ, F_b), straight lines are drawn that lie above the plot of the function $F_b = F_b(\theta)$, $\theta_0 < \theta < \theta_\infty$ pass through the point $(\theta_0, F_b(\theta_0))$, and among these straight lines one needs to choose the one that has the minimum slope to the positive semiaxis $t = 0$. It is clear that this straight line is tangent to the plot of the function $F_b = F_b(\theta)$ and the tangency point determines the parameters σ and θ_1^a (Fig. 4):

$$\sigma = \sup_{\theta_0 \leq \theta \leq \theta_\infty} \frac{F_b(\theta) - F_b(\theta_0)}{\theta - \theta_0} = \frac{F_b(\theta_1^a) - F_b(\theta_0)}{\theta_1^a - \theta_0} = F_b'(\theta_1^a), \qquad \theta_0 < \theta_1^a < \theta_\infty. \tag{26}$$

In the case where the solid phase is not a sorbent, the concentration wave velocity is found in a similar way:

$$\sigma_0 := \sup_{\theta_0 \leq \theta \leq \theta_\infty} \frac{f(\theta) - f(\theta_0)}{\theta - \theta_0} = \frac{f(\theta_1) - f(\theta_0)}{\theta_1 - \theta_0} = f'(\theta_1), \qquad \theta_0 < \theta_1 < \theta_\infty.$$

Since

$$\frac{F_b(\theta) - F_b(\theta_0)}{\theta - \theta_0} = \frac{1 + Q}{r(\theta_0)} \left(\frac{f(\theta) - f(\theta_0)}{\theta - \theta_0} + \frac{(\nu - 1)f(\theta)}{r(\theta)} \right), \qquad \nu = 1 + O(Q),$$

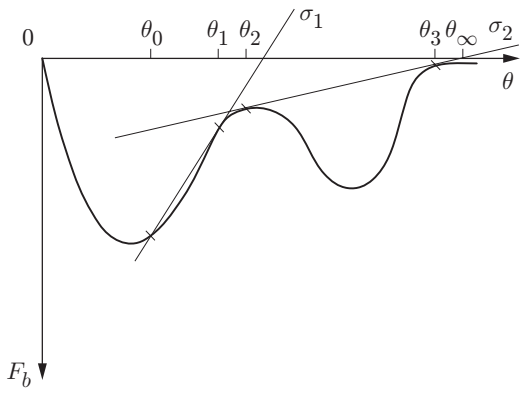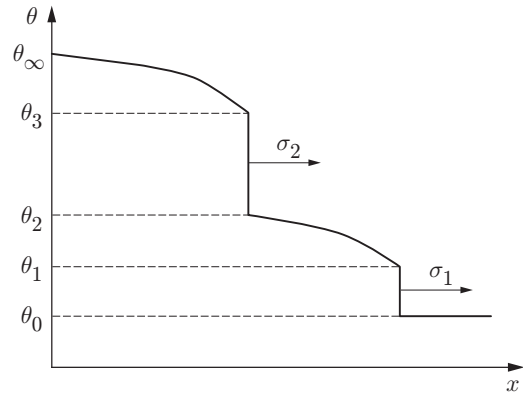we have

$$|\sigma - \sigma_0| \leq cQ.$$

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Fig. 5

Fig. 6

Thus, the effect of small adsorption on the concentration-wave velocity is insignificant. Statement 1 forbids the occurrence of new points of inflection for the function $F_b(\theta)$ if the parameter Q varies from zero to a certain value Q_*. To understand the importance of this property, we consider a hypothetical situation where for any small $Q > 0$, the function $F_b(\theta)$ have three points of inflection and a shape similar to that in Fig. 5. In this case, the solution $\theta(x, t)$ would be represented by two shock waves which travel over the unperturbed medium and are separated by a centered rarefaction wave, and the second wave would also be followed by a centered rarefaction wave. For each $t > 0$, the function $\theta = \theta(x, t)$ would have a shape similar to that in Fig. 6.

Thus, by virtue of Statement 1, the sorption properties of the solid phase does not imply the occurrence of new concentration waves and the sedimentation process remains one-wave.

Let us consider the effect of the sorption properties of the solid phase on the sedimentation dynamics. For at least rather large values of the initial concentration θ_0, we can show in a mathematically rigorous way that accounting for adsorption leads to an increase in the concentration-wave velocity.

Statement 2. *There exists a certain number θ_0^* dependent on Q such that $\sigma > \sigma_0$, if $\theta_0 \geq \theta_0^*$.*

Proof. We introduce the function

$$g(\theta) = f(\theta) - F_b(\theta) \equiv -r^{-1}f(\theta)(\theta(\nu - 1) + \gamma(1 + Q)Q).$$

It is clear that

$$g(0) = g(\theta_\infty) = 0 \quad \text{and} \quad g(\theta) > 0 \quad \text{for} \quad 0 < \theta < \theta_\infty.$$

From formulas (22) and (24), we obtain the value of the derivative $g'(\theta)$

$$g' = a_0(\nu - 1)^2 r^{-2}(\theta_\infty - \theta)^{n-1}p,$$

where p is a third-degree polynomial:

$$p = (n + 1)(\theta + \gamma_2)(\theta - \theta_\infty')(\theta - 1/\delta) - (1/\delta + \gamma_2)\theta(\theta - \theta_\infty).$$

Here

$$\theta_\infty' = \theta_\infty/(n + 1), \quad \delta = (\nu - 1)/\nu, \quad \gamma_1 = \gamma Q(1 + Q), \quad \gamma_2 = \gamma_1/(\nu - 1).$$

Because

$$p(-\infty) = -\infty, \quad p(0) > 0, \quad p(\theta_\infty) < 0, \quad p(+\infty) = +\infty,$$

it follows that in the interval $(0, \theta_\infty)$, the equation $p = 0$ has a unique root $\theta = \theta_0^*$. Thus, the function $g(\theta)$ decreases monotonically in the interval $(\theta_0^*, \theta_\infty)$.

We assume that $\sigma \leq \sigma_0$. Then, for $\theta_0 < \theta < \theta_\infty$, the plot of the function $F_b(\theta)$ does not lie above the plot of the function $\sigma_0(\theta - \theta_0) + F_b(\theta_0)$. This, however, is impossible since at the point $\theta = \theta_1$,

$$\sigma_0(\theta_1 - \theta_0) + F_b(\theta_0) - F_b(\theta_1) = g(\theta_1) - g(\theta_0) < 0.$$

Hence, $\sigma > \sigma_0$, and the statement is proved.

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From (26) it follows that the equality $F_b'(\theta)(\theta - \theta_0) = F_b(\theta) - F_b(\theta_0)$ is the equation to find θ_1^a. With allowance for formulas (22) and (24), it has the form

$$(\theta - \theta_0)(\theta_\infty - \theta)^n(-n\theta^2 + (n+1)\theta/\delta - \theta_\infty/\delta)$$

$$= (\theta - 1/\delta)\theta(\theta_\infty - \theta)^n - (\theta - 1/\delta)^2\theta_0(\theta_\infty - \theta_0)^n/(\theta_0 - 1/\delta). \tag{27}$$

We note that θ_1^a is a unique solution of this equation in the interval $(\theta_0, \theta_\infty)$. Apparently, there are no accurate formulas for the numbers θ_1^a and σ; therefore, the indicated parameters can be found only numerically. Because the solution of Eq. (27) cannot be found in implicit form, it is difficult to prove the inequality $\sigma > \sigma_0$. Generally, without any constraints on the initial value of θ_0, calculations using the Mathematica 5.0 program confirm the validity of this inequality.

Conclusions. Some sedimentation models taking into account sorption transfer of mass and volume between the liquid and solid dispersion phases were proposed. The sorption transfer is described by the Langmuir kinetic equation.

One of the simplest models is a one-dimensional kinematic sedimentation model with equilibrium adsorption, which is based on a number of assumptions. It is assumed that the Froude number is small; this is characteristic of slow sedimentation processes. Another assumption is that the sorption process rapidly reaches a stationary regime, so that the Langmuir equation can be replaced by a stationary isotherm. One more assumption is related to neglect of the compression of horizontal layers of the solid phase.

The kinematic model was used to study the structure of the concentration wave which describes the upward extension of the high-concentration zone of the solid phase in the problem of a sedimentation chamber with a closed bottom. This is done invoking some representative empirical dependences of the interfacial friction factor on the solid-phase concentration. In terms of the theory of hyperbolic systems, the concentration wave is an upward traveling shock wave which adjoins a centered rarefaction wave from below and a zone with a lower constant (initial) solid-phase concentration from above. The concentration-wave velocity is taken to be the shock wave velocity.

An advantage of the simple kinematic model is that it includes only one adsorption parameter Q, whereas the fuller model contains three kinetic constants. Mathematical investigation of the dependence of the kinematic model on the parameter Q shows that the concentration wave moves more slowly in the case $Q = 0$ than in the case $Q > 0$. Physically, this is apparently due to the fact that in contrast to neutral particles, the settling sorbent particles entrap a certain volume of the liquid-phase impurity and the total entrapped volume increases with time.

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