

COALESCENCE OF OIL DROPS ON THE SKELETON OF A POROUS MEDIUM IN FILTERING A WATER-OIL MIXTURE

V. I. Pen'kovskii

UDC 532.546

Two mathematical models of filtration coalescence of oil drops when a water-oil mixture moves through a porous material are proposed. In the first model, coalescence is interpreted as the process of sorption, i.e., the accumulation of the oil phase on the pore surface up to a definite critical value above which the larger drops involved by a filtration flow stall. The second model assumes that the motion of the sorbed oil and the entire mixture obeys the generalized Darcy laws.

Introduction. Accidents on oil pipelines frequently lead to oil contamination of the catchment basins of rivers. In high-water periods, water-oil mixtures (emulsions) containing oil drops of various coarseness and solid particles which are water-repelling due to the presence of an oil film inflows from polluted territories into the rivers and their affluents. In contrast to large drops, small-sized oil drops and the solid particles embedded in the oil film can be in an immersed (suspended) state for a long period, which decreases the effectiveness of the existing methods of oil gathering from the surface of the channels. The problem of drop enlargement via their coalescence and, hence, the probability of their rise to the surface can be partially solved by filtering the mixture through the thickness of a water-repelling porous medium in the form of permeable gravel-dikes (dams).

Below, we shall consider two mathematical models of filtration coalescence. It seems to us that these models and the results obtained can be useful for solving the problems of other technological processes.

Basic Equations. We denote the densities of oil, water, and the emulsion (the water-oil mixture) by ρ , ρ_1 , and ρ_e , respectively. Let C be the mass concentration of oil in the mixture. Since oil occupies C/ρ of the unit volume and water occupies $1 - C/\rho$ of this volume, for the density ρ_e of the mixture we obtain

$$\rho_e = \rho_1(1 - \varepsilon C/\rho) \quad [\varepsilon = (\rho_1 - \rho)/\rho_1].$$

In a free flow of a low-concentration mixture, the oil particles float separately, and it is unlikely that they will collide and coalesce with each other [probability of the order of $(C/\rho)^2$]. The probability of coalescence considerably increases if the mixture is filtered through a water-repelling porous medium. In this case, the oil particles touch both the free water-repelling sites of the internal surface of the pores, adsorbing on them, and the precipitated particles, enlarging the latter up to the formation of the coupled films. The adsorption rate j_1 of the oil particles is proportional to the probability of their collision with free sites, which is in turn proportional to the product of the particle concentration in the mixture and the concentration of free sites on the pore surface. If we assume that the free site, earlier occupied by a certain particle, remains free for other particles and, hence, the concentration of the sites remains constant, we obtain $j_1 = k_1 C$, where k_1 is an experimentally determinable factor.

The saturation s of a porous material with oil increases with time. If a certain value of $s = s_*$, which is characteristic of the given material, is exceeded, the oil particles, which have been attached to this material, begin to move. Here, two variants of displacement are possible, depending on the grain sizes, the geometry

of the porous space, and other physicochemical properties of a medium: (1) formations of hydrodynamically coupled oil films on the skeleton of the medium and their filtration under the action of a certain pressure gradient; (2) the stall (desorption) of the enlarged particles from the grain surfaces and their return to the mixture. The first variant of displacement occurs in the filtration through fine porous media like sand, and the second is inherent in the motion through the gravel-crushed stone embankments. Generally, both variants of displacement are not mutually excluding; however, they are described by equations different in form.

Combined Filtration of a Mixture and an Oil Film. Let h and h_1 be the pressures (in meters of the water column) in the films and the water–oil mixture, respectively. They differ by the magnitude of a capillary jump $h_c(s)$ according to the relation

$$h = h_1 + h_c(s). \quad (1)$$

The pressure h_r in a floating oil drop with radius r is determined by the Laplace formula $h_r = h_1 + 2\sigma/r$, where σ is the surface tension on the water–oil boundary. For water-repelling porous media with $h_c \leq 0$, we have $h_r > h$, which promotes the coalescence of the drop when it touches the oil film on the surface of the medium's grains.

According to the theory of two-phase filtration [1], the velocities of the mixture v_1 and of the motion of the coupled oil phase v are determined according to the generalized Darcy laws:

$$v_1 = -K_1 f_1(s, s^*) \frac{\partial h_1}{\partial x}, \quad v = -K f(s, s_*) \frac{\partial h}{\partial x}, \quad (2)$$

where K_1 and K are the filtration coefficients of the medium for the fully oil- or mixture-laden pores, respectively, f_1 and f are relative phase permeabilities satisfying the conditions $f(s, s_*) \equiv 0$ for $s \leq s_*$ and $f_1(0, s^*) = 1$ and $f_1(s, s^*) \equiv 0$ for $s \geq s^*$ and $f(1, s_*) = 1$.

The transfer of the oil particles in a porous medium by the common flow is accompanied by the phenomenon of filtration dispersion. Therefore, according to the Fick law, we write the mass flux j of the particles in a mixture in the form

$$j = -D \frac{\partial C}{\partial x} + v_1 C, \quad (3)$$

where $D = v_1 d/2$ is the dispersion coefficient for granular media [2] and d is the characteristic size of the grains.

The governing equation (1) and the laws of motion (2) and (3) should be supplemented by three laws of conservation — of the oil and water phases in a mixture, respectively:

$$m \frac{\partial}{\partial t} [(1-s)C] + \frac{\partial j}{\partial x} = -k_1 C; \quad (4)$$

$$m \frac{\partial}{\partial t} [(1-s)\rho_1(1-C/\rho)] + \frac{\partial}{\partial x} [\rho_1(1-C/\rho)v_1] = 0, \quad (5)$$

and of the oil phase in the coupled films on the grain surface:

$$m\rho \frac{\partial s}{\partial t} + \frac{\partial}{\partial x} (\rho v) = k_1 C. \quad (6)$$

Equations (1)–(6) represent the closed nonlinear system for the desired functions C , s , h_1 , h , v_1 , v , and j . It is rather complicated, and we failed to obtain explicit solutions for it. Generally, it should be solved numerically with allowance for the corresponding initial and boundary conditions. However, under additional simplifying conditions having an evident physical meaning one can construct explicit solutions. We consider two examples.

Example 1. Let a water–oil mixture be filtered through a specimen of a highly permeable medium with given rate $v_1 = v_0$ at the entry $x = 0$ and the concentration $C = C_0$. As is known [3], highly permeable media are characterized by small jumps of the capillary pressure at the boundary of the water–oil phases and, therefore, one can set $h_c(s) = 0$ in Eq. (1), i.e., $h = h_1$. We assume that the process is steady-state and the length l of the specimen is such that the Peclet number $Pe = v_1 l/D = 2l/d$ is fairly large. In this case, it is

possible to ignore the dispersive scattering of the particles in a mixture, and the problem is reduced to the integration of a simple system of ordinary differential equations

$$\frac{d}{dx}(v_1 C) = -k_1 C, \quad \frac{dv}{dx} = k_1 \frac{C}{\rho}, \quad \frac{d}{dx} \left[\left(1 - \frac{C}{\rho}\right) v_1 \right] = 0 \quad (7)$$

with the boundary conditions

$$v_1(0) = v_0, \quad C(0) = C_0, \quad v(0) = 0 \quad (8)$$

and the final relation of the form

$$v = \alpha v_1 f(s, s_*) / f_1(s, s^*) \quad (\alpha = K/K_1). \quad (9)$$

The last condition in (8) expresses the absence (the continuity) of a flow of coupled films in the input cross section of the specimen.

With allowance for conditions (8), the integration of system (7) gives

$$v = \frac{v_0(u_0 - u)}{1 - u}, \quad v_1 = \frac{v_0(1 - u_0)}{1 - u}, \quad \frac{k_1}{a} x = \ln \frac{u_0(1 - u)}{u(1 - u_0)} + \frac{u_0 - u}{(1 - u_0)(1 - u)}$$

$$[a = (1 - u_0)v_0, \quad u = C/\rho, \quad u_0 = C_0/\rho, \quad 0 < u \leq u_0],$$

The distribution of the saturation s of the specimen's porous space with the oil precipitated on the particle surface can be obtained by formula (9), into which it is necessary to introduce the expressions for v and v_1 .

Example 2. The estimates show that for mixtures with the concentration C_0 of the order of 10^{-4} g/cm³ (100 mg/liter), in the initial system (1)–(6) the value of C/ρ may be ignored in comparison with unity. With this in mind, we consider the same problem as in Example 1, leaving the dispersion term in Eq. (3). In addition to (9), we obtain $v_1 = v_0 = \text{const}$ and the problem is reduced to the integration of the system

$$D \frac{d^2 C}{dx^2} - v_0 \frac{dC}{dx} - k_1 C = 0; \quad \frac{dv}{dx} = k_1 C/\rho \quad (10)$$

with the boundary conditions

$$x = 0: \quad v = 0, \quad -D \frac{dC}{dx} + v_0 C = v_0 C_0; \quad x = l: \quad \frac{dC}{dx} = 0. \quad (11)$$

The conditions for the function $C(x)$ express the continuity of a dropwise oil flow at the specimen edges.

With allowance for the boundary conditions (11), the combination of the equations in system (10) produces the first integral of the form

$$\rho v = D \frac{dC}{dx} + v_0(C_0 - C).$$

Substituting here the value of $D = v_0 d/2$ and introducing the notation

$$\xi(x) = \frac{d}{2\rho\alpha} \frac{dC}{dx} + \frac{C_0 - C}{\rho\alpha}, \quad (12)$$

we find the distribution of the saturation s of the porous space with the film oil as an implicit function from relation (9): $f(s, s_*)/f_1(s, s^*) = \xi(x)$. In particular, if the experimentally determinable relative phase permeabilities are approximated by functions of the form

$$f(s, s_*) = ((s - s_*)/(1 - s_*))^n, \quad f_1(s, s^*) = ((s^* - s)/s^*)^n \quad (n \approx 3.5, \quad s^* \approx 1 - s_*),$$

we have $s(x) = (s_* + \xi^{1/n}(x)s^*)/(1 + \xi^{1/n}(x))$.

The function $C(x) = A_1 \exp(\alpha_1 x) + A_2 \exp(\alpha_2 x)$, where $\alpha_{1,2} = (1 \pm \sqrt{1 + 2k_1 d/v_0})/d$ are the roots of the corresponding characteristic equation (the subscript 1 corresponds to the plus sign), is the solution of the first equation in system (10), which satisfies the boundary conditions (11). Since $d/l \ll 1$, one can set $\alpha_1 \approx 2/d$

and $\alpha_2 \approx -k_1/v_0$ with a good approximation. In this case, $A_2 = C_0/(1 + \delta_1)$, $A_1 = C_0\delta_1 \exp(-Pe + \delta)/(1 + \delta_1)$ ($\delta = v_k/v_0$ and $\delta_1 = \delta/Pe$, where $v_k = lk_1$ is the total adsorption rate), and the function $C(x)$ takes the form

$$C/C_0 = (\exp(-\delta x_1) + \delta_1 \exp[-(\delta + Pe(1 - x_1))]) / (1 + \delta_1),$$

where $x_1 = x/l$. Substituting it into expression (12), we obtain

$$\xi(x) = C_0[1 - \exp(-\delta x/l)] / (\rho\alpha).$$

Clearly, the process of filtration dispersion greatly affects neither the velocity of the motion of the film oil nor the distribution of the latter over the specimen length.

Sorption-Desorption Model. The dropwise displacement of oil, which is attributed to the desorption of coarse particles, is accompanied by the generation of a new water-oil mixture, in which the radii of the coarser drops are $r \geq r_*$. The characteristic minimum radius r_* depends on the shapes and sizes of the grains in a porous medium and, possibly, on other physicochemical factors.

Let C_1 and C_2 be the concentrations of the fine ($r < r_*$) and coarse ($r \geq r_*$) oil particles in a mixture. The total oil concentration is $C = C_1 + C_2$. The basic source of the coarser particles in the common flow is their desorption from the grain surface when the oil saturation s of the porous space of the medium exceeds a certain limiting value s_* . We assume that the desorption rate j_2 is proportional to this exceeding, i.e.,

$$j_2 = k_2(s - s_*)\eta(s - s_*),$$

where k_2 is the coefficient of desorption rate and $\eta(x)$ is the Heaviside unit function. The precipitation-separation process is then described by the kinetic equation

$$m\rho \frac{\partial s}{\partial t} = k_1 C - k_2(s - s_*)\eta(s - s_*), \quad (13)$$

which is the analog of Eq (6). Accordingly, the conservation law of the total mass of the dropwise oil in the mixture takes the form

$$m \frac{\partial}{\partial t} [(1 - s)C] = \frac{\partial}{\partial x} \left(D \frac{\partial C}{\partial x} - v_1 C \right) - k_1 C + k_2(s - s_*)\eta(s - s_*). \quad (14)$$

Equations (13) and (14) should be supplemented by the analog of Eq. (4) written for the function C_1 and by Eq. (5). For problems with a given rate of the mixture (v_0 at the entrance), the four equations are the closed system for determining the four desired functions C_1 , C , s , and v_1 .

As applied to low-concentration mixtures ($C/\rho \ll 1$), the system becomes simpler. In this case, one can conclude from Eqs. (5) and (13) that $v_1 \approx v_0$, and, ignoring an insignificant decrease in the porous space of the medium owing to the presence of the sorbed oil (s is small compared to unity), we obtain the system of three quasi-linear equations

$$\begin{aligned} m \frac{\partial C_1}{\partial t} &= D \frac{\partial^2 C_1}{\partial x^2} - v_0 \frac{\partial C_1}{\partial x} - k_1 C_1, \\ m \frac{\partial C}{\partial t} &= D \frac{\partial^2 C}{\partial x^2} - v_0 \frac{\partial C}{\partial x} - k_1 C + k_3(N - N_*)\eta(N - N_*), \\ \frac{\partial N}{\partial t} &= k_1 C - k_3(N - N_*)\eta(N - N_*). \end{aligned} \quad (15)$$

Here $N = m\rho s$, $N_* = m\rho s_*$, and $k_3 = k_2/(m\rho)$. The boundary and initial conditions for system (15) can be written in the form

$$\begin{aligned} x = 0: \quad C_1 &= C_1^0, \quad C = C_0, \quad x = l: \quad \frac{\partial C_1}{\partial x} = 0, \quad \frac{\partial C}{\partial x} = 0, \\ t = 0: \quad C_1 &= \varphi_1(x), \quad C = \varphi(x), \quad N = N_0(x). \end{aligned} \quad (16)$$

We note that problem (15)–(16) is partially split, because the first equation can be solved irrespective of the other two equations. In addition, for the zero initial data $N = \varphi = \varphi_1 = 0$ and all $t < t_* = N_*/(k_1 C_0)$ the function $\eta(N - N_*)$ vanishes, and the second equation of system (16) coincides in form with the first equation,

and their solutions — the functions $C_1(x, t)$ and $C(x, t) = C_1 + C_2$ — are expected to differ from each other only by a factor in this time interval, since the boundary conditions for them are the same. We find this solution by the Laplace transform method. For brevity, we replace t/m by t and consider the problem

$$C_t = DC_{xx} - v_0 C_x - k_1 C, \quad N_t = k_1 C,$$

$$x = 0: C = C_0, \quad x = l: C_x = 0, \quad t = 0: C = 0, \quad N = 0.$$

The Laplace image $\bar{C}(x, p) = \int_0^\infty e^{-p\tau} C(x, \tau) d\tau$ of the desired function $C(x, t)$ is found by integrating the respective ordinary differential equation with allowance for the boundary conditions and has the form

$$\bar{C}(x, p) = C_0 \exp(v_0 x / (2D)) (\cosh \alpha x - \sinh \alpha x (v_0 / (2D) \cosh \alpha l + \alpha \sinh \alpha l) / (v_0 / (2D) \sinh \alpha l + \alpha \cosh \alpha l)) / p,$$

where $\alpha = \alpha(p) = \sqrt{v_0^2 + 4D(k_1 + p)} / (2D)$.

The image has a countable set of simple poles at the point $p = 0$ and the points $p = p_n = -D\mu_n^2/l^2 - v_0^2/(4D) - k_1$. Here μ_n are the roots of the equation $\tan \mu_n = -2\mu_n/Pe$ ($Pe = v_0 l/D$). Returning to the preimage by calculating the residues in these singular points, we obtain

$$C(x, t) = C_\infty - \frac{2C_0 D}{l^2} \exp\left[-\frac{k_1 t}{m} + \frac{Pe}{2l}(x - x_*(t))\right] \times \sum_{n=1}^{\infty} \frac{\exp(-D\mu_n^2 t / (ml^2))}{k_1 + v_0^2/(4D) + D\mu_n^2/l^2} \frac{\mu_n (Pe + 4\mu_n^2)/Pe}{Pe + 2 + 4\mu_n^2/Pe} \sin \mu_n \frac{x}{l}, \quad (17)$$

$$C_\infty = C_0 \exp\left(\frac{v_0 x}{2D}\right) \left(\cosh \alpha_0 x - \frac{v_0/(2D) \cosh \alpha_0 l + \sinh \alpha_0 l}{v_0/(2D) \sinh \alpha_0 l + \alpha_0 \cosh \alpha_0 l} \sinh \alpha_0 x\right), \quad \alpha_0 = \alpha(0), \quad x_* = vt/m.$$

The function $N(x, t)$ for $t < t_*$ is calculated by the simple quadrature $N(x, t) = k_1 \int_0^t C(x, \tau) d\tau$. Similarly, one can obtain an analytical representation of the solution of system (15) if $N(0, x) \geq N_*$ at the initial moment of time $t = 0$. In this case, we have $\eta(N - N_*) = 1$, and system (15) becomes linear. Omitting the cumbersome calculations, we present the final form of the solution:

$$\frac{C(x, t)}{C_0} = 1 - \frac{l^2}{D} \exp\left(\frac{v_0 x}{D}\right) \sum_{n=1}^{\infty} \left(\frac{(k_3 - p_n^+)^2 \exp(-p_n^+ t)}{p_n^+ (k_1 k_3 + m(k_3 - p_n^+)^2)} + \frac{(k_3 - p_n^-)^2 \exp(-p_n^- t)}{p_n^- (k_1 k_3 + (k_3 - p_n^-)^2)} \right) \frac{Pe^2 + 4\mu_n^2}{Pe(Pe + 2)4\mu_n^2} \mu_n \sin \mu_n \frac{x}{l},$$

$$N(x, t) = N_* + k_1 \int_0^t C(x, \tau) \exp(-k_3(t - \tau)) d\tau.$$

The notation here is as follows: $p_n^\pm = (b_n \pm \sqrt{b_n^2 - 4c_n})/2$, $b_n = k_1 + k_3 + Dm_n^2/l^2$, $c_n = m_n^2 k_3 D/l^2$, and $m_n^2 = \mu_n^2 + l^2 v_0^2/(4D)$. The function $C_1(x, t)$ is calculated by formula (17), in which C_0 should be replaced by C_1^0 . In the general case, problem (15)–(16) is solved numerically.

The case of a steady-state regime is important for practice and the laboratory determination of the parameters of the problem. Assuming that $\partial N/\partial t = \partial C/\partial t = \partial C_1/\partial t \equiv 0$ and $D = v_0 d/2$ in Eqs. (15), with allowance for the boundary conditions (16), for $x = 0$ and $x = l$ we obtain the simple solution

$$C_1(x) = C_1^0 \exp(x/d) \left(\cosh \mu x/l - \frac{l/d \cosh \mu_0 + \sinh \mu_0}{l/d \sinh \mu_0 + \mu_0 \cosh \mu_0} \sinh \mu_0 x/l \right),$$

$$C = C_1 + C_2 \equiv C_0, \quad N = N_* + C_0 k_1/k_3 \quad (\mu_0 = l\alpha_0).$$

Since the Peclet number $Pe = 2l/d$ is usually large in comparison with unity, keeping the first-order quantities in the expansion of the function $C_1(x)$ with respect to the small parameter Pe^{-1} , for the concentration $C_1(l)$

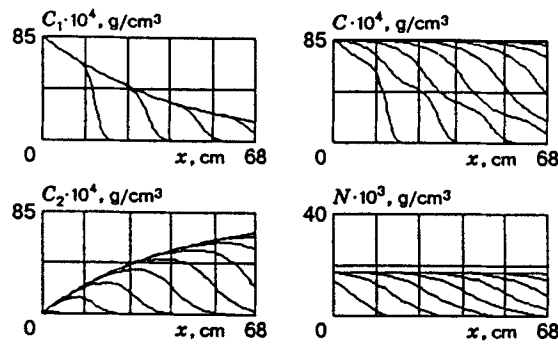


Fig. 1

of small-sized particles at the exit, and for $x = l$ we obtain

$$C_1(l) = C_1^0(1 + \delta Pe^{-1}) \exp(-\delta),$$

where $\delta = k_1 l / v_0$ is the ratio of the integral sorption rate to the filtration rate. It is evident from this formula, which is useful for processing experimental data, that the effective work of the filtering layer mainly depends on the magnitude of the dimensionless parameter δ of the problem.

Figure 1 shows the numerical results obtained for problem (16) and (17) for the initial data of the laboratory experiment: $m = 0.45$, $v = 19$ cm/h, $C_0 = 85 \cdot 10^{-4}$ g/cm³, $C_1^0 = C_0$, $l = 68$ cm, $\varphi(x) = \varphi_1(x) = N_0(x) = 0$, $d = 0.2$ cm, $k_1 = 0.45$ h⁻¹, $N_* = 10^{-3}$ g/cm³, and $k_3 = 5$ h⁻¹. The curves correspond to the subsequent moments of time with an interval of 0.4 h. It is seen that in the adopted conditions, the sorption almost reaches a steady-state regime after 4 h of continuous filtering of a water-oil mixture.

Preliminary results of the experiments performed on a filtering element (the filtration coefficient is $K_1 = 7.8$ m/h) shaped like a tube of cross section $2 \cdot 10^{-4}$ m² and length $l = 0.68$ m, which is filled with glass crumb, agree qualitatively with the theoretical results.

Additional experiments on the specimens of porous media with a different degree of particle coarsity are necessary for solving the problem of the range of applicability for each of the proposed mathematical models for filtration coalescence.

REFERENCES

1. *Development of Filtration Theory in the USSR (1917-1967)* [in Russian], Nauka, Moscow (1969).
2. V. G. Levich, V. S. Markin, and Yu. A. Chizmadzhiev, "A study of the longitudinal hydrodynamic mixing in porous media with stagnation zones using a harmonic analysis," *Dokl. Akad. Nauk SSSR*, 168, No. 6, 1902-1904 (1966).
3. R. E. Collins, *Flow of Fluids through Porous Materials*, Reinhold, New York (1961).