MASS TRANSFER IN THE LEACHING OF A SOLID FROM A POROUS SPHERE

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UDC 66.015.23

We derive a sequence of approximate solutions of the problem of the kinetics of the extraction of a solid material uniformly filling the volume of a porous particle when it interacts with a liquid which selectively dissolves this material.

We consider solid porous particles (Fig. 1) which contain the desired component in the solid state. This component is extracted in the contact of these porous particles with a liquid which selectively dissolves it. As this component is dissolved and carried outside the particle by diffusion, the volume a of the particle containing the desired component in the solid state is systematically decreased, while the region b containing this component in solution increases. In region b the material is transferred by diffusion from the interface $r = r_0$ to the outer boundary of the porous body $r = R$.

Processes of this kind, widely used in the chemical industry and in hydrometallurgy, are called leaching. A mathematical model of this process involves the difficulties of solving problems with a moving boundary $r_0 = r_0(t)$ when the convective component of material transfer cannot be neglected. The assumptions made include the following: 1) the particles are spherical; 2) the desired component is uniformly distributed over the volume of the particle; 3) the diffusion is isotropic (mass transfer by diffusion is the same in all directions); 4) there is no external diffusion resistance; 5) the concentration of the component at the outer boundary $r = R$ is constant; 6) the liquid filling the porous structure of the body has a constant density.

The first results, published in 1951 by Piret et al. [1], established an approximate relation for the position of the interphase boundary r_0 at any time t in the form

$$\frac{1}{6}-\frac{\varphi_0^2}{2}+\frac{\varphi_0^3}{3}=\gamma\tau,\ \tau=\frac{Dt}{R^2},\ \varphi_0=\frac{r_0}{R},\quad \gamma=\frac{c_{AS}-c_{A1}}{\rho_{Aa}-\varepsilon c_{AS}}.$$

In 1959 Aksel'rud [2] used an integral relation to derive the result

$$\tau=\sigma^*\left(\frac{1}{6}-\frac{\varphi_0^2}{2}+\frac{\varphi_0^3}{3}\right)-\frac{1}{6}\left(\ln\varphi_0+\varphi_0-\varphi_0^2\right),$$

$$\sigma^*=\frac{\rho_{Aa}-c_{AS}+(1-\varepsilon)c_{A1}}{c_{AS}-c_{A1}}.$$

This result has the advantage of encompassing a wide range of variation of the parameter σ^*, including $\sigma^* = 0$ which corresponds to the extraction of a soluble material with an initial concentration c_{AS} [3]. In 1981 Protod'yakonov et al. [4] treated the problem by making the following assumptions, which are by no means self-evident: 1) the radius r_0 decreases linearly with time $r_0 = R - \alpha t$; 2) the amount of dissolved material M leaving the interphase surface is determined by $dM/dt \approx \beta 4\pi r_0^2 c_S$ instead of the generally accepted $dM/dt = -D4\pi r_0^2\left(\frac{\partial c}{\partial r}\right)_{r=r_0}$. It is debatable whether the mass-transfer coefficient β can be introduced when material transfer is of the nature of molecular diffusion.

In the present article we present two types of results: The first is based on the direct integration of the differential equation of convective diffusion, and the second on the use of an integral relation similar to that employed in hydrodynamics (the Karman–Pohlhausen

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Lenin Komsomol Polytechnic Institute, Lvov. Translated from Inzhenerno-Fizicheskii Zhurnal, Vol. 44, No. 5, pp. 787-793. Original article submitted November 10, 1981.

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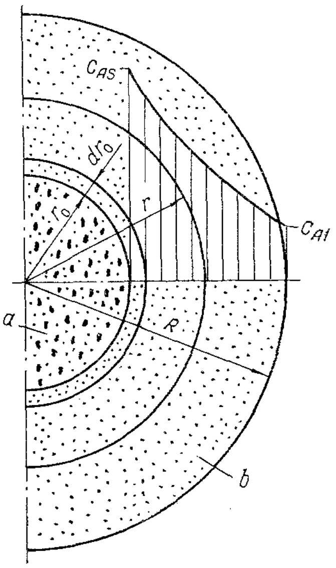

Fig. 1. Schematic diagram of a porous body in the process of extraction of a soluble solid. Region (*a*) contains the desired component in the solid state, and region (*b*) in the dissolved state.

method) [5]. The concentration field of the desired component c_A in the continuously expanding region b is determined by the system [6]

$$\begin{cases} \dfrac{\partial c_A}{\partial t} + (v \cdot \nabla c_A) = D \Delta c_A, \\ (\nabla \cdot v) = 0 \end{cases}$$

or in expanded form in spherical coordinates

$$\begin{cases} \dfrac{\partial c_A}{\partial t} + v_r \dfrac{\partial c_A}{\partial r} = D \dfrac{1}{r^2} \dfrac{\partial}{\partial r} \left(r^2 \dfrac{\partial c_A}{\partial r} \right), \\ \dfrac{1}{r^2} \dfrac{\partial}{\partial r} (r^2 v_r) = 0. \end{cases} \tag{1}$$

The boundary conditions on the outer and moving boundaries are written in the form

$$\begin{aligned} r = R, \quad c_A &= c_{A1}; \\ r = r_0, \quad c_A &= c_{AS}. \end{aligned} \tag{2}$$

The velocity of the moving boundary $-dr_0/dt$ is determined by analyzing the mass fluxes of the desired component and the solvent

$$n_A = c_A v - D_{AB} \frac{\partial c_A}{\partial r}, \quad n_B = c_B v - D_{BA} \frac{\partial c_B}{\partial r}. \tag{3}$$

It follows from Fig. 1 that

$$(n_A dt)_{r=r_0} = -(\rho_{Aa} - c_{AS})\, dr_0, \quad (n_B dt)_{r=r_0} = (c_{BS} - \rho_{Ba})\, dr_0. \tag{4}$$

Combining and using the familiar relation $(n_A + n_B)_{r=r_0} = \rho_S v_{r=r_0}$ [6], we obtain

$$v_{r=r_0} = -\left(\frac{\rho_t}{\rho_S} - 1 \right) \frac{dr_0}{dt}, \tag{5}$$

where $\rho_t = \rho_{Aa} + \rho_{Ba}$; $\rho_S = c_{AS} + c_{BS}$. The simultaneous transformation of Eqs. (3)-(5) gives

$$\frac{dr_0}{dt} = \frac{D_{AB}\gamma}{c_{AS} - c_{A1}} \left(\frac{\partial c_A}{\partial r} \right)_{r=r_0}, \tag{6}$$

where

$$\gamma = \frac{c_{AS} - c_{A1}}{\rho_{Aa} - c_{AS}\dfrac{\rho_t}{\rho_S}} = \frac{c_{AS} - c_{A1}}{\rho_T (1-\varepsilon)\left(1 - \dfrac{c_{AS}}{\rho_S}\right)}. \tag{7}$$

It follows directly from the second of Eqs. (1) that

$$v_r = v_{r=r_0} \left(\frac{r_0}{r} \right)^2. \tag{8}$$

We now have sufficient material to reduce Eqs. (1) to a form suitable for integration. We introduce dimensionless parameters, a dimensionless function and arguments by the relations [7, 8]:

$$\tau = \frac{D_{AB}t}{R^2}, \quad \varphi = \frac{r}{R}, \quad \varphi_0 = \frac{r_0}{R}, \quad \Phi = \varphi \frac{c_{AS} - c_A}{c_{AS} - c_{A1}},$$

$$\sigma = \frac{1-\varphi}{1-\varphi_0}, \quad y = 1 - \varphi_0, \quad \nu = \frac{\rho_t}{\rho_S}, \quad \left(\frac{\rho_T}{\rho_S} - 1 \right)(1-\varepsilon) = \nu - 1,$$

after which we find that

$$\frac{\partial^2 \Phi}{\partial \sigma^2} = \gamma \left(\frac{\partial \Phi}{\partial \sigma} \right)_{\sigma=1} \left[\frac{1}{1-y} \left(\sigma \frac{\partial \Phi}{\partial \sigma} - y \frac{\partial \Phi}{\partial y} \right) + (\nu - 1) \frac{1-y}{(1-\sigma y)^2} \left(\frac{y\Phi}{1-\sigma y} + \frac{\partial \Phi}{\partial \sigma} \right) \right], \tag{9}$$

$$\Phi = \Phi(\sigma, y), \ \Phi(0, y) = 1, \ \Phi(1, y) = 0, \tag{10}$$

$$\frac{d\varphi_0}{d\tau} = + \frac{\gamma}{(1-y)} \frac{1}{y} \left(\frac{\partial \Phi}{\partial \sigma} \right)_{\sigma=1}. \tag{11}$$

Equations (9)-(11) can be solved numerically, but an approximate analytic result can be obtained by using the fact that in the important practical cases $\gamma = 0.01\text{-}0.5$:

$$\Phi(\sigma, y) = \Phi_0 + \gamma\Phi_1 + \gamma^2\Phi_2 + \ldots \tag{12}$$

The function Φ_0 is determined from the equation $\dfrac{\partial^2 \Phi_0}{\partial \sigma^2} = 0$ with boundary conditions (10), which gives $\Phi_0 = 1 - \sigma$ or

$$\frac{c_{AS} - c_A}{c_{AS} - c_{A1}} = \frac{1 - \dfrac{\varphi_0}{\varphi}}{1 - \varphi_0}, \tag{13}$$

and substitution into (11) leads to the final expression

$$\frac{1}{6} - \frac{\varphi_0^2}{2} + \frac{\varphi_0^3}{3} = \gamma\tau, \tag{14}$$

which is valid for $\gamma \ll 1$, and differs from the result in [1] in the value of γ. Further refinement involves the determination of the function Φ_1 by the substitution of $\Phi_0 = 1 - \sigma$ into the right-hand side of Eq. (9) and the subsequent integration in the boundary conditions $\Phi_1(0, y) = 0$ and $\Phi_1(1, y) = 0$ [7]. After performing all the operations we finally obtain the second approximation

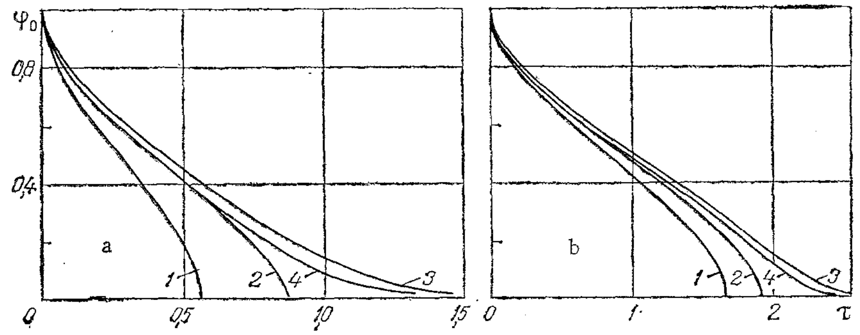

Fig. 2. Dependence of relative radius φ_0 on dimensionless time for a) $\gamma = 0.3$ and b) $\gamma = 0.1$: 1) Eq. (14); 2) (15); 3) (20); 4) (22).

$$\left(\frac{1}{6}-\frac{\varphi_0^2}{2}+\frac{\varphi_0^3}{3}\right)+\frac{\gamma}{\varkappa}\left(\frac{1}{6}-\frac{\varphi_0}{3}+\frac{\varphi_0^2}{6}\right)=\varkappa\gamma\tau, \tag{15}$$

$$\varkappa = 1-0.5\gamma(\nu-1).$$

We turn to a consideration of a method of solution based on the use of the integral relation

$$-\frac{d}{dt}\left[\frac{4}{3}\pi r_0^3\rho_{Aa}+\int\limits_{r_0}^{R} c_A 4\pi r^2 dr\right] = -D_{AB}4\pi R^2\left(\frac{\partial c_A}{\partial r}\right)_{r=R}+v_{r=R}\,c_{A1}4\pi R^2. \tag{16}$$

The left-hand side of Eq. (16) denotes the change of mass content in both zones of the porous particle. The right-hand side shows that the reasons for this change are the diffusion of material and its removal by the solution moving with the velocity $v_{r=R}$. By introducing the dimensionless concentration $c^* = (c_A - c_{A_1})/(c_{AS} - c_{A_1})$ and the other dimensionless variables mentioned previously, we obtain the relations

$$\frac{d}{d\tau}\left[\frac{\varphi_0^3}{3}(1+\gamma\nu)+\gamma\int\limits_{\varphi_0}^{1} c^*\varphi^2 d\varphi\right]=\gamma\left(\frac{\partial c^*}{\partial\varphi}\right)_{\varphi=1}, \tag{17}$$

$$\begin{gathered} c^* = 0 \quad \text{for} \quad \varphi = 1, \\ c^* = 1 \quad \text{for} \quad \varphi = \varphi_0, \end{gathered} \tag{18}$$

$$\frac{d\varphi_0}{d\tau}=\gamma\left(\frac{\partial c^*}{\partial\varphi}\right)_{\varphi=\varphi_0}. \tag{19}$$

The use of the integral relation (17) is based on a rough approximation of the distribution $c^*(\varphi)$ in the range $\varphi_0<\varphi<1$, which satisfies boundary conditions (18), substitution into (17), and the subsequent performance of all the operations. If we take

$$c^* = \frac{\dfrac{1}{\varphi}-1}{\dfrac{1}{\varphi_0}-1}$$

as the approximating function, the final result takes the form

$$[1+\gamma(\nu-1)]\left(\frac{1}{6}-\frac{\varphi_0^2}{2}+\frac{\varphi_0^3}{3}\right)-\frac{\gamma}{6}(\ln\varphi_0+\varphi_0-\varphi_0^2)=\gamma\tau. \tag{20}$$

Another version is based on the substitution of the distribution

$$c^* = \eta\left(\frac{\dfrac{1}{\varphi}-1}{\dfrac{1}{\varphi_0}-1}\right)+(1-\eta)\left(\frac{\dfrac{1}{\varphi}-1}{\dfrac{1}{\varphi_0}-1}\right)^2, \tag{21}$$

into the integral relation and the boundary condition (19). As before, this distribution satisfies conditions (18), but contains the parameter η. We obtain

$$\left\{\begin{aligned}&[1+(\nu-1)\gamma]\left(\frac{1}{6}-\frac{\varphi_0^2}{2}+\frac{\varphi_0^3}{3}\right)-\gamma\left[\frac{\eta}{6}(\ln\varphi_0-\right.\\&\left.-3\varphi_0+\varphi_0^3+2)-\frac{1}{3}(1-\varphi_0)^2\right]=\gamma\eta\tau, && (22)\\&\frac{1}{6}-\frac{\varphi_0^2}{2}+\frac{\varphi_0^3}{3}=\gamma(2-\eta)\tau. && (23)\end{aligned}\right.$$

The calculation of the mass content of the desired component A leads to the expression

$$\frac{M}{M_0}=\varphi_0^3+\frac{c_{A1}}{\rho_{Au}}(1-\varphi_0^3)+\frac{c_{AS}-c_{A1}}{\rho_{Au}}\left[\eta\left(\frac{\varphi_0}{2}+\frac{\varphi_0^2}{2}-\varphi_0^3\right)+(1-\eta)\varphi_0^2(1-\varphi_0)\right]. \tag{24}$$

The parameter η can be chosen so that Eqs. (22) and (23) give nearly the same result. For small values of γ this can be done by equating the coefficients of $\left(\frac{1}{6}-\frac{\varphi_0^2}{2}+\frac{\varphi_0^3}{3}\right)$. We obtain

$$\eta=\frac{1+\gamma(\nu-1)}{1+0.5\gamma(\nu-1)}. \tag{25}$$

A more accurate result is based on approximation "in the mean" by using the relation

$$\int\limits_0^1[\tau_1(\eta,\ \varphi_0)-\tau_2(\eta,\ \varphi_0)]\,d\varphi_0=0, \tag{26}$$

where τ_1 is determined from Eq. (22), and τ_2 from (23):

$$\eta=\frac{6+2\gamma+3\gamma(\nu-1)}{2\gamma}\left\{\sqrt{1+\frac{8\gamma[3+3\gamma(\nu-1)+4\gamma]}{[6+2\gamma+3\gamma(\nu-1)]^2}}-1\right\},$$

from which it follows that $\eta_{\gamma\to 0}=1$ and $\eta_{\gamma\to\infty}=2$, since $\gamma(\nu-1)=\text{const}$ for all values of ε. The advantage of Eq. (22) is that it is approximately true even in the special case $\gamma\to\infty$, $\varepsilon\to 1$ (extraction of a dissolved material with an initial concentration c_{AS}). From (22) and (24) we obtain

$$\left\{\begin{aligned}&\ln\varphi_0-\varphi_0+1=-6\tau,\\&\frac{M}{M_0}=\varphi_0,\end{aligned}\right. \tag{27}$$

which is close to the exact solution [9] over a wide range of variation of τ. Figure 2 compared all four results obtained for $\nu = 2$ and $\gamma = 0.3$ and $\gamma = 0.1$. These curves show that (14) is acceptable only for $\gamma < 0.1$.

NOTATION

R, radius of sphere; r, running radius; r_0, radius of sphere containing desired component in the solid state; D, diffusion coefficient: t, time; c_A, concentration of desired component; c_{AS}, saturation concentration; c_{A1}, concentration at surface of sphere; ε, porosity in region a relative to porosity in the region b; ρ_{Aa}, volume density of desired component A in region a; $\rho_{Ac} = \varepsilon c_{AS} + (1 - \varepsilon)\rho_T$; ρ_T, density of desired solid component A; ρ_{Ba}, volume of solvent in region a; $\rho_{Ba} = c_{Bs}\varepsilon$; ρ_t, average density of two-phase system; $\rho_t = \rho_{Aa} + \rho_{Ba} = \rho_T(1 - \varepsilon) + \rho_S\varepsilon$; ρ_S, density of saturated solution; c_B, concentration of solvent; c_{Bs}, concentration of saturated solvent; n_A, flux density of component A; n_B, flux density of component B; v_r, mass average velocity of liquid.

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HEAT TRANSFER IN BOILER FURNACE, TAKING ACCOUNT OF THE SCATTERING OF RADIATION

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UDC 536.33:621.181.7

A method of zonal calculation of the radiational heat transfer in scattering media is outlined. The influence of scattering of the radiation on the heat-transfer coefficient in a furnace is considered.

The presence of a large number of particles (coal, coke, ash in the combustion of coal dust; soot in the flame combustion of natural gas and oil) suspended in high-temperature flows of furnace gases creates the preconditions for radiation scattering. Therefore, it is of practical interest (especially in connection with the appearance of detailed information on the radiative characteristics of dust flows and luminous flames; see [1-3], etc.) to solve the problem of external heat transfer, within the framework of the zonal method, taking account of scattering in complex three-dimensional multizonal systems filled with an emitting–absorbing and scattering medium.

In the present work, the zonal method is used to investigate the combined heat transfer in a furnace chamber of a BKZ-320-140PT boiler. Isotropic scattering in volume zones is taken into account using the method developed earlier in [4]. In calculating the heat transfer in real aggregates, it is necessary to take account of the complexity of the scattering index in volume zones and the reflection coefficient at boundary surfaces. Generalization of the method of [4] to the case of anisotropic scattering of radiation and nondiffuse reflection — in the presence of both diffuse and nondiffuse components in the reflection of radiation from surface zones ($R - R^{\text{dif}} + R^{\text{nondif}}$), there are both isotropic and anisotropic components in the scattering at particles in the volume zones ($\beta = \beta^{\text{is}} + \beta^{\text{anis}}$) — may be accomplished using the following system of linear algebraic equations

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I. M. Kalinin Krasnoyarskii Institute of Nonferrous Metals. Translated from Inzhenerno-Fizicheskii Zhurnal, Vol. 44, No. 5, pp. 793-801, May, 1983. Original article submitted January 19, 1982.