KINETICS OF THE ENRICHMENT OF BORON—SALT ORES IN A BOILING LAYER

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We give the results of a theoretical and experimental investigation of the kinetics of the dissolution of boron—salt ores of the Inder deposit in a boiling layer.

Boron-producing plants are beginning nowadays to use raw materials with a low concentration of boron oxide — for example, ores from Kazakhstan deposits, which are characterized by a complex mineralogical composition and polydispersity. The enrichment of such ores may be carried out by washing away with water the readily soluble salts, mainly NaCl (over 50%) and KCl (over 30%). If a substantial intensification of the process is desired, it is advisable to use a boiling layer [1, 2].

The theory of dissolution of multicomponent mixtures, as pointed out by the authors of [3], has not been sufficiently developed at the present time. In particular, there are no reliable theoretical methods for determining the mass-exchange coefficients, and little study has been done on the kinetics of dissolution in a fluidized bed. The principal reason for this is that in the general case the rates of dissolution of the individual components are interrelated. If the mass-exchange coefficients for the dissolution of the individual components are known, then the mathematical model for the process can be constructed on the basis of a system of kinetic equations of component-by-component dissolution, taking account of the contribution made to the moving force of the process by all the concentrations that affect it [3].

In the light of the complexity of the process of enrichment of boron—salt ores and the difficulty of experimentally investigating the component-by-component dissolution of a polydisperse material in a boiling layer, we shall confine ourselves in the present study to considering the effective kinetics. We write the linear phenomenological law for the rate of change of the radius of a particle

$$\frac{dr}{dt} = -L[C_s - C(t)] \tag{1}$$

and the material balance equation (per unit volume of the solution), disregarding in the first approximation the variation in the volume of the liquid phase:

$$\beta(1-y) = C(t) - C_0. \tag{2}$$

To close the system of equations (1), (2), we must have an additional relation which will enable us to establish the connection between y and r. We use as such a relation the kinetic equation for the distribution function of the particles in the phase space of their dimensions [4]

$$\frac{\partial f}{\partial t} + \frac{\partial (Wf)}{\partial r} = 0. \tag{3}$$

The distribution function f(r, t) satisfies the conditions

$$dN(r) = N_0 f(r,\ t)\,dr,\ f(r,\ 0) = f_0(r),\ \int\limits_0^\infty f_0(r)\,dr = 1. \tag{4}$$

It should be noted that the kinetic equation (3) has been used repeatedly in the mathematical modeling of mass-exchange processes in various polydisperse systems [5, 6].

The material-balance equation, taking account of (4), is the following:

$$\frac{C(t) - C_0}{\beta} = 1 - \int\limits_0^\infty \frac{r^3}{r_0^3} f(r,\ t)\,dr.$$

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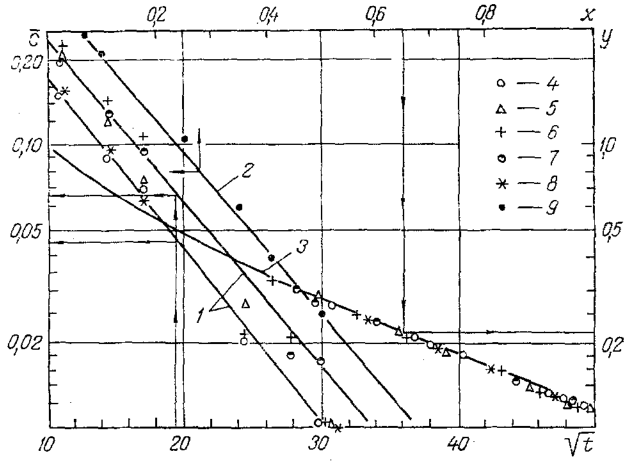

Fig. 1. Kinetics of dissolution in a boiling layer ($\sqrt{t}$, $c^{1/2}$): 1) function $\bar{C} = \bar{C}(\sqrt{t})$, the dots represent our own experiment, and the curves represent calculation according to (15); 2) $\bar{C} = \bar{C}(\sqrt{t})$, the curve represents calculation according to (15), the points according to the data of [3, p. 86, Fig. II.31]; 3) invariant function, the curves represent calculation according to (18), and the dots represent our own experiment; 4) $K_C = 0.16c^{1/2}$, v_S = 0.7 m/sec; 5) 0.15 and 0.9; 6) 0.13 and 1.0; 7) 0.14 and 1.3; 8) 0.18 and 1.73; 9) 0.11.

Thus, the connection between y and r is defined by the integral

$$y = \int_0^\infty \frac{r^3}{\bar{r}_0^3} f(r,\ t)\, dr, \tag{5}$$

$\bar{r}_0^3$ denotes averaging over the initial distribution $f_0(r)$.

The function y(t) at the beginning and the end of the dissolution process takes on the values

$$y(0) = 1;\ y_{\text{end}} = 1 - b;\ b = \frac{C_s - C_0}{\beta}. \tag{6}$$

A number of authors, on the basis of an analysis of experimental data, have established the self-similarity of the process of dissolution in a boiling layer with respect to the characteristic dimension of the particles [3]. This means that the phase velocity W in Eq. (3) depends only on time and is independent of r, the radius of the particles. Using this fact and the equations of motion (1) and balance (2), taking account of (6), we can represent (3) in the form

$$\frac{df}{dt} = \frac{\partial f}{\partial t} + W\frac{\partial f}{\partial r} = \frac{\partial f}{\partial t} + \beta L(1 - b - y)\frac{\partial f}{\partial r} = 0. \tag{7}$$

From this relation it follows that the distribution function f(r, t) is the integral of the motion. Since the latter is multiplicative, it is convenient to pass to the function ln f(r, t), which also satisfies (7). Using the method of characteristics [7], we write the solution of Eq. (7):

$$\ln f(r,\ t) = a\beta\int_0^t L\,[y - (1 - b)]\, dt - \varphi(ar) + \ln A, \tag{8}$$

where $\ln A - \varphi(ar) = \ln f_0(r)$.

The constants of integration a and ln A are found from the normalization condition (4). By directly substituting (8) into (7), we can verify that ln f exactly satisfies (7), where the initial distribution $f_0(r)$ of the particles according to dimensions is approximated by the function

$$f_0(r) = \frac{1}{\bar{r}_0}\exp(-r/\bar{r}_0). \tag{9}$$

If $f_0(r)$ has a more complicated structure, then we can use the methods worked out in [5] in constructing the solution of the kinetic equation (7). Analysis on the basis of these methods shows that starting from some instant of time, the distribution of particles according to dimensions can be represented with sufficient accuracy in the form (9), which means that we can regard (8) as an approximate solution of the problem with arbitrary $f_0(r)$.

Substituting $f(r, t)$ from (8) into (5) and noting that

$$\int_0^\infty \frac{r^3}{\overline{r}_0^3} f_0(r)\,dr = 1,$$

we obtain an integral equation for determining $y(t)$:

$$y(t)=\exp\{-a\beta \int_0^t L\,[y-(1-b)]\,dt\}. \tag{10}$$

The linearized equation (10) in a quasistationary regime of dissolution, when the kinetic coefficient L is independent of t [3, 8], yields an exponential variation for the concentration as a function of time.

The analysis of the experimental kinetics of the enrichment process in a boiling layer, represented in Fig. 1, indicates that the kinetic curves are satisfactorily approximated by representing the concentrations as exponential functions not of t but of $\sqrt{t}$.

Such a kinetic law of dissolution is the solution of Eq. (10) if we assume that L is a function of $1/\sqrt{t}$. This nonstationarity may be caused by the high intensity of the mass-exchange process during dissolution in a boiling layer.

In actuality, the data shown in Fig. 1 indicate that during 0.1 of the total dissolution time there is an increase in the concentration of the solution to 0.9 of its maximum value. As the density increases further, we observe a deviation from the law $\ln\bar{c} \sim \sqrt{t}$; this is obviously due to the establishment of a quasistationary regime. However, these deviations do not exceed 10%, which is entirely acceptable for an engineering calculation method.

Physically, the nonstationarity of the effective kinetics of the mass exchange may be related to the properties of the behavior of the diffusion boundary layer. Because the dissolution rates are different, initially the solution of readily soluble components shields the particles, but in turbulent flow the boundary layer is cyclically disrupted and renewed [9]. As a result, it becomes gradually saturated with slow-dissolving substances. Thus, the effective diffusion resistance changes with the passage of time. This happens because of the changes in the chemical composition of the solution and in the average diameter of the total number of particles.

The kinetic coefficient can be expressed in terms of the mass-exchange coefficient in the usual manner [3, 5, 8]:

$$L(t) = \frac{\varkappa}{\rho_{\text{solid}}} K(t),\ K \sim \frac{D}{d}. \tag{11}$$

Taking into account the function L(t) proposed above, (11), and the relation $a = \overline{r}_0^{-1} = 2d^{-1}$, we represent $a\beta L(t)$ in (10) in the form

$$a\beta L(t) = \frac{K_c}{2\sqrt{t}} \sim \frac{\beta\varkappa\sqrt{D}}{\rho_{\text{solid}} d\sqrt{t}}. \tag{12}$$

Linearizing (10) and taking account of (12), we obtain a differential equation for determining the function $y(t)$:

$$\frac{dy}{dt} = -\frac{K_c}{2\sqrt{t}}[y-(1-b)]. \tag{13}$$

The solution of this equation, taking account of (6), is the following:

$$y = 1-b\,[1-\exp(-K_c\sqrt{t})] \tag{14}$$

or, using (2) to pass to concentrations, we find

$$\overline{C} = \frac{C_s-C(t)}{C_s-C_0} = \exp(-K_c\sqrt{t}). \tag{15}$$

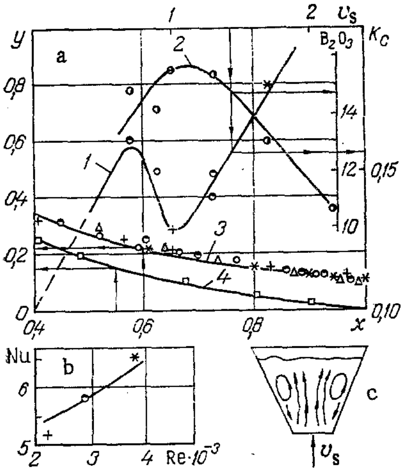

Fig. 2. Effect of boiling-layer hydrodynamics on the dissolution kinetics (the notation for the points is the same as in Fig. 1; K_c, $\sec^{1/2}$; v_s, m/sec); a) 1: K_c as a function of the superficial velocity (experiment); 2: percentage of enriched substance in the final product as a function of the superficial velocity (experiment); 3: invariant function y = y(x), our own experiment; 4: invariant function y = y(x) according to the data of [3]; b) the curve shows calculations according to the formula of [11]; c) scheme of circulation of the material at minimal mass-exchange intensity. B_2O_3, %

In treating experimental data on the kinetics of dissolution, it is very convenient to use invariant functions [3, 8, 10]. In the present case a function invariant with respect to the hydrodynamic regime can be found theoretically; this is usually a fairly complicated matter. We introduce a new variable by using the relation [3, 10]

$$x(t) = \frac{\int\limits_0^t [C_s - C(t)]\,dt}{\int\limits_0^\infty [C_s - C(t)]\,dt}. \tag{16}$$

Using (15) and (16), after integrating, we obtain

$$x(t) = 1 - e^{-K_c\sqrt{t}}(K_c\sqrt{t} + 1). \tag{17}$$

Eliminating t from (14) and (17), we finally find

$$x = 1 - \frac{y-(1-b)}{b}\left[1 - \ln\frac{y-(1-b)}{b}\right]. \tag{18}$$

The experimental investigation of the kinetics of enrichment of boron–salt ores was carried out in a conical apparatus with periodic action [1]. The choice of the shape of the apparatus enabled us to ensure practically ideal mixing conditions. The brine was circulated by means of a pump through an overflow tank. The dissolution was carried out at room temperature at superficial velocities of v_s = 0.70, 0.90, 1.0, 1.30, and 1.73 m/sec (according to the inlet cross section of the apparatus). In the experiments we determined the instantaneous density (concentration) of the brine, its chemical composition, and the yield of the desired product (the B_2O_3 content in the undissolved residue). The data obtained in the experiments are shown in Figs. 1 and 2.

The variation of the concentration of the dissolved substance as a function of time was approximated by Eq. (15), curve 1 in Fig. 1. The coefficients K_c were determined by the method of least squares. Figure 2 shows K_c as a function of the superficial velocity. It has a minimum at v_f = 1 m/sec. The existence of this minimum can be explained by the scheme of circulation of the material (Fig. 2c), observed visually (the walls of the apparatus were made of transparent plastic). In this regime a minimal amount of B_2O_3 is washed out from the solid residue (curve 2 in Fig. 2a). All the fluidization regimes are described by the invariant function (18) (curves 3 in Figs. 1 and 2). From the values found for the coefficients K_c for the ascending branch of curve 1 in Fig. 2a, we calculated the dimensionless mass-exchange coefficients Nu as functions of the Reynolds numbers, $Re = v_s d/\nu$ (Fig. 2b). As the determining parameters we used the superficial velocity v_s and the average particle diameter d calculated from the initial distribution (according to sieve-analysis data). The average mass-exchange coefficients K were found by means of the empirical formula obtained by taking account of (12):

$$\mathrm{Nu} = \frac{Kd}{D} = 0.07\frac{K_c\rho_{solid}d}{\beta\varkappa\sqrt{D}}.$$

The solid curve in Fig. 2b was calculated from the equation

$$\mathrm{Nu} = 11.14\cdot10^{-5}\mathrm{Re}^{0.35}\mathrm{Ar}^{0.28}\mathrm{Pr}^{0.63},$$

obtained by Bogomolov [11] in his investigation of the dissolution of sylvinite in a fluidized bed. We give below the numerical data obtained for the parameters of the process of enrichment of boron—salt ores and used in the experiments we have described: $C_s = 220$ kg/m³; $\rho_{solid} = 2700$ kg/m³; $b = 0.88$; $V_{liq} = 100$ liters; $M_{0\cdot solid} = 25$ kg; $\beta = 250$ kg/m³; $d = 4$ mm; $\varkappa = 2$; $D = 1.69\cdot10^{-9}$ m²/sec; $\nu = 1.78\cdot10^{-6}$ m²/sec (D and ν were calculated by Bogomolov's method). In addition to the results of our own experiments, we also processed by the method given in this study the experimental data on the dissolution of the binary mixture NaCl—KCl which are given in [3, pp. 82 and 87]. The results of the calculations are shown in the straight line 2 of Fig. 1 and curve 4 of Fig. 2a. The kinetic curves $\overline{C}(t)$ are satisfactorily approximated by Eq. (15).

Thus, the theoretical model is in satisfactory agreement with the experimental data on the kinetics of the dissolution of multicomponent mixtures.

NOTATION

L, kinetic coefficient; $C(t)$, C_0, C_s, instantaneous, initial and saturation concentrations of the dissolved substance; $M_{solid}(t)$, $M_{0\cdot solid}$, instantaneous and initial mass of the solid substance; $y(t) = M_{solid}(t)/M_{0\cdot solid}$; $\beta = M_{0\cdot solid}/V_{liq}$; V_{liq}, volume of the liquid phase; r, particle radius; t, time; $W = dr/dt$, velocity of displacement of the image point in the phase space; N_0, initial number of solid particles in the system; $\overline{r}_0 = 1/a$, average initial particle radius; a, A, constants of integration in (8); $\varkappa$, particle-shape coefficient; ρ_{solid}, density of the solid material; D, diffusion coefficient; K, mass-exchange coefficient; K_c, coefficient in (12); Ar, Archimedes number; Pr, Prandtl number.

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NUMERICAL SOLUTION OF A NONSTEADY EXTRACTION PROBLEM IN THE CASE OF NONLINEARITY OF THE MASS-TRANSFER-COEFFICIENT RELATION

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A numerical solution is presented to an extraction problem with a variable mass-transfer coefficient and variable concentration of the external medium and a nonlinear condition of equilibrium on the surface of the body.

Well-known analytical solutions [1, 2] to the problem of nonsteady mass transfer during extraction were obtained for relatively simple cases, when the mass-transfer coefficient was assumed constant over the duration of the process. These solutions often differ significantly from the empirical data. In these cases, there is no regular regime [3], which can be attributed to several factors. Among these factors are a variable mass-transfer coefficient, polydispersity [4], the simultaneous extraction of several substances, and kinetic nonequivalence of the pores [5].

The study [2] examined special cases of mass transfer. The study [1] found the region of a regular regime with $\beta = 0$. The report [6] approximately solved the problem with allowance for the linear dependence of the mass transfer coefficient on concentration. The investigation [7, 8] obtained a solution in the case of a mass-transfer coefficient dependent on concentration without approximations limiting the form of the function but with $\mathrm{Bi} = \infty$. These studies investigated exponential and rational dependences of the mass-transfer coefficient on concentration. Other particular solutions were obtained for a constant mass transfer coefficient and $\beta \neq 0$ [9-14].

This article presents a numerical solution of the above problem for three classic forms (plate, $T = 0$; cylinder, $T = 1$; sphere, $T = 2$) with a variable mass-transfer coefficient, variable concentration of the external medium, and nonlinear condition of equilibrium on the surface of the body.

Formulated in this way, the problem is described by the equation

$$\frac{\partial C_2}{\partial \tau} = \frac{1}{x^T} \frac{\partial}{\partial x}\left[x^T D_{\mathbf{e}}(C_2) \frac{\partial C_2}{\partial x}\right]. \tag{1}$$

Equation (1) is supplemented by the following boundary and initial conditions:

$$\frac{\partial C_2}{\partial x} = 0;\ x = 0;\ \tau \geqslant 0, \tag{2}$$

$$W \frac{\partial C_1}{\partial \tau} = -N \varepsilon_1 D_{\text{э}}(C_2)\, S \frac{\partial C_2}{\partial x};\ x = R, \tag{3}$$

$$C_1 = \varkappa(C_2);\ x = R, \tag{4}$$

$$C_2 = C_{20};\ C_1 = C_{10};\ \tau = 0. \tag{5}$$

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