MASS TRANSFER IN FILTRATION PROCESSES OF WATERS CONTAINING CORROSIVE COMPONENTS

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A mathematical model of mass transfer for dissolution processes involving the filtration of waters containing corrosive components is suggested. The model is extended to karst formation.

The chemical composition of underground waters reflecting the equilibrium in a water-rock system may change due to different factors disturbing this equilibrium. We consider the case where this change is caused by corrosive components of underground waters (CO_2, O_2, H_2, SO_4, etc.), leading to dissolution of the substance of the rock. Such problems emerge in investigations of the formation of the chemical composition of underground waters, migration of contaminants in underground waters, processes of karst formation, mining of minerals by the underground leaching technique.

If a heterogeneous chemical reaction between a corrosive component and a rock substance proceeds at a sufficiently high rate, the main limiting factor of the reaction is the supply of the reagent to the reaction surface and the removal of the reaction product. For a steady-state reaction, the known stoichiometry ratio of the diffusional flows of a reaction product and a reagent [1] may be used:

$$j_1/\nu_1 = j_2/\nu_2 . \tag{1}$$

Here j_1 and j_2 are the flows of a corrosive component to the reaction surface and a product from the reaction surface expressed in terms of the molar contents; ν_1 and ν_2 are the corresponding stoichiometric coefficients. Ratio (1) is equivalent to the well-known expression for the rate of change of the degree of completeness of the reaction at the interface.

The transfer equation for a corrosive component is

$$\frac{\partial}{\partial t}(m\theta) + v\nabla\theta = \nabla(D_\theta m\nabla\theta) - j_1 . \tag{2}$$

The transfer equation for a reaction product is

$$\frac{\partial}{\partial t}(mc) + v\nabla c = \nabla(D_c m\nabla c) + j_2 . \tag{3}$$

It is noteworthy that the product and corrosive component concentrations are the molar contents of the corresponding substances.

Since the convective diffusion coefficient D_c depends mainly on the porous medium structure and the filtration rate [2], we assume that $D_\theta = D_c = D$.

Dividing Eq. (2) by ν_1 and Eq. (3) by ν_2 and adding the results we arrive at

$$\frac{\partial}{\partial t}(ms) + v\nabla s = \nabla(Dm\nabla s) . \tag{4}$$

Here we have introduced $s = \theta + \nu_1 c/\nu_2$.

The concentration s specifies the content of a corrosive component in both the free state and the state bound, through the reaction product. Equation (4) does not contain any sources (sinks), and thus s is an important characteristic of the process.

The discharge of a reaction product into a solution may be described by choosing the following expression for j_2:

$$j_2 = \beta \, (c_0 \, (\theta) - c) , \qquad (5)$$

where c_0 is the equilibrium (limiting) concentration of the reaction product. The limiting concentration is related to the content of a corrosive component and is determined by an equilibrium constant [3]. For a reaction of the type $\nu_A A + \nu_B B = \nu_C C$ we have

$$K = \frac{[C]^{\nu_C}}{[A]^{\nu_A} \, [B]^{\nu_B}} , \qquad (6)$$

where square brackets designate by tradition the concentrations of the reaction product C and the reagents A and B. If the concentration of the leached substance in the solid phase does not change, then the relationship between θ and c_0 has the form of a power function:

$$\theta = (K_1 c_0)^n ; \quad K_1 , \quad n = \text{const} . \qquad (7)$$

An expression for the flux j_1 follows from (1), (5), and (7):

$$- j_1 = \beta \, (s - \theta - \nu_1 \theta^{1/n} \, (1/K_1)/\nu_2) . \qquad (8)$$

Characteristic features of the mass transfer may be revealed from an analysis of the simplest case, namely, the one-dimensional problem in the nondiffusional approximation. The system of equations

$$v \partial \theta / \partial x = - j_1 , \qquad (9)$$

$$(9) \; v \partial c / \partial x = j_2 \qquad (10)$$

obtained from (2) and (3) generates a solution that is the stationary stage of the general solution of system of equations (2), (3) in the nondiffusional approximation. Since in this case $s = \text{const} = s(0)$, we easily integrate Eq. (9):

$$\int_{\theta(0)}^{\theta} \frac{du}{\nu_1 c_0/\nu_2 + u - s} = - x\beta/v , \qquad (11)$$

and determine c from the relation $\theta + \nu_1 c/\nu_2 = s$.

The suggested scheme for solving problems on mass transfer involving filtration of waters containing corrosive elements differs from the conventional one [4], above all, in the fact that it employs explicitly relation (1) and the property that it imparts to the function $s(x, t)$, which, as a rule, is known (in the nondiffusional approximation $s = \text{const}$).

As an example, we consider carbon dioxide leaching of carbonate rocks (carbonate karst). In this case, θ and c_0 are related by the Auerbach formula [5]:

$$\theta = (c_0/17)^3 , \qquad (12)$$

and the stationary distribution of concentrations over the depth is

$$\beta x/v = -3 \ln \left| \frac{\theta^{1/3} - A - B}{\theta^{1/3}(0) - A - B} \right| +$$

$$+ \frac{3^{1/3} (A + B) (2A^2 + 3AB + 2B^2)}{2 |A - B| (A^2 + AB + B^2)} \arctan \frac{2w + A + B}{3^{1/3} |A - B|} \Bigg|_{\theta^{1/3}(0)}^{\theta^{1/3}} +$$

$$+ \frac{2A^2 + AB + B^2}{2 (A^2 + AB + B^2)} \ln \frac{(w + 1)^2}{w^2 + (A + B) w + A^2 - AB + B^2} \Bigg|_{\theta^{1/3}(0)}^{\theta^{1/3}} , \qquad (13)$$

$$\theta(x) + c(x) = s, \quad s = \text{const},$$

where $A = (Q^{1/2} + s/2)^{1/3}$, $B = -(Q^{1/2} - s/2)^{1/3}$, $Q = (17/3)^3 + (s/2)^2$.

Solution (13) is obtained under the assumption that the source of corrosive carbon dioxide in underground waters is biochemical processes occurring both in the water and in the soils with which the water is in contact. The content of the carbon dioxide entering from the atmosphere does not exceed 0.6 mg/liter because of a low partial pressure, while in order to provide mean HCO_3^- concentrations in natural waters (200–250 ml/g), CO_2 must attain approximately 10–12 mg/liter, and therefore the amount of atmospheric CO_2 penetrating into underground waters may be neglected.

Karst formation has long been an object of mathematical modeling. The pioneering karst model is that of N. N. Verigin [7]. Unlike the model suggested in the present work, it does not take into account the CO_2 consumed in the interphase reaction, i.e., in the Verigin model $c_0 = \text{const}$. For zero concentration of the dissolution product at the inlet ($x = 0$) the stationary concentration distribution is

$$c = c_0 (1 - \exp(-\beta x/v)). \qquad (14)$$

Just in our model, for the rate of crack opening $\dot{h}$ the following relation is fulfilled:

$$\rho \dot{h} = \beta (c_0 - c). \qquad (15)$$

We may compare both models because they are parametrically identical. Results of their comparison are shown in Fig. 1. Estimates were made for $\theta(0) = 0.01$ mole/liter (10 mmole/liter), a rate of limestone dissolution of the order of 10^{-7} m/sec, a filtration rate of about 10^{-5} m/sec (1 m/day), and a specific surface of cracks of the order of 10^2 m^{-1} [6]. The curves t_e and c correspond to the contents of free carbon dioxide and calcium hydrocarbonate, respectively, calculated by our model. The curve f_2 corresponds to the concentration distribution according to the Verigin model with $c_0 = 17(s)^{1/3}$. A comparison of the rates of karst development $\rho \dot{h}/\beta$ (the curves f_1 and f_3) showed that the Verigin model (the curve f_3) yields a more rapid karst attenuation (smaller mixing zones) than ours.

Another example is Lekhov's model of karst formation [8–10]. As a basis, this model employs the model of a crack as a slit with parallel smooth walls. The equation of mass balance for the internal space of a crack is [8]

$$D_m \partial^2 c/\partial y^2 = 1.5 u_w (1 - (y/b)^2) \partial c/\partial x, \qquad (16)$$

where D_m is the diffusion coefficient; c is the concentration of the components of the dissolved rock; u_w is the mean velocity of underground water; x is the coordinate running along the middle of the slit in the flow direction; y is the coordinate perpendicular to the slit walls.
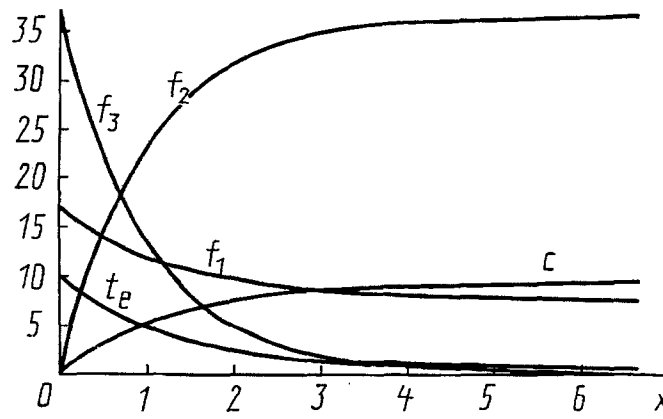
Fig. 1. Curves illustrating the content of carbon dioxide (curve t_e) and calcium hydrocarbonate (curves c and f_2) in the solution and the reduced rate of opening of cracks (curves f_1 and f_3). c, mmole/liter; x, m.

The boundary conditions are the concentration distribution at the crack inlet, the symmetry condition of the problem, and the equation of equality of the rate of appearance of the dissolved rock due to the reaction to the rate of its removal by diffusion:

$$c(0, y) = c_1,$$ (17)

$$\partial c(x, 0)/\partial y = 0,$$ (18)

$$D_m \partial c(x, b)/\partial y = -k_e(c_m - c)^r.$$ (19)

Here (in the author's notation) c_m is the equilibrium concentration of the dissolved rock; k_e is the dissolution rate ratio; r is the formal order of the reaction; b is the crack opening, equal to half the distance between its walls [9].

The main drawback of model (16)−(19), in our opinion, is use of the boundary condition in form (19). Indeed, it is easy to show that for any x, generally speaking, $c(x, b) > c(x, y)$, i.e., the concentration distribution over the crack width has the form of a concave curve. At some time (or at some distance x_0 from the crack inlet) the concentration at the boundary may attain its equilibrium value, i.e., $c(x_0, b) = c_m$. In this case, as is known [1], the diffusion stage of the dissolution process will operate. But the Lekhov model leads to a contradiction in this case since the r.h.s. of (19) is strictly equal to zero, while the l.h.s. is not equal to zero. The sole possibility of considering $c(x, y) = c_m$ at $x > x_0$ and $0 < y < b$ is too strong an assumption. Thus, the choice of boundary condition (19) excludes the diffusion stage of the dissolution process in the Lekhov model. Since precisely the diffusion stage of dissolution is described by our model (i.e., it is assumed that thermodynamic equilibrium is instantaneously established over the interphase surface of a physical volume element) but the Lekhov model excludes this stage, we have not compared these models.

NOTATION

j_1 and j_2, flows of the aggressive component of underground waters and the reaction product expressed in terms of molar contents; ν_1 and ν_2, stoichiometric coefficients of the aggressive component and the reaction product; t, time; x, y, coordinates; m, porosity; v, filtration rate; θ, molar concentration of the aggressive component; c, molar concentration of the reaction product; D_θ, D_c, D, coefficients of convective diffusion; s, concentration of the aggressive component in the free state and the state bound through the reaction product; β, mass transfer constant;

c_0, rock solubility; K, chemical equilibrium constant; ρ, density of the soluble rock; ∇, gradient operator; D_m, molecular diffusion coefficient; U_w, mean velocity of the flow of the underground water in the crack; $h(= b)$, opening of the crack (half the distance between its walls); k_e, dissolution rate ratio; c_m, equilibrium concentration of the dissolved rock (in the Lekhov model of karst).

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