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МАТЕМАТИЧЕСКОЕ МОДЕЛИРОВАНИЕ ПРОЦЕССА НЕРАВНОВЕСНОЙ СОРБЦИИ

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Рассматривается система уравнений, моделирующая процесс неравновесной сорбции. Сформулирована разностная аппроксимация дифференциальной задачи по неявной схеме. Решение разностной задачи строится с помощью метода прогонки.

Ключевые слова: система уравнений неравновесной сорбции; разностная аппроксимация; неявная схема; метод прогонки; численные эксперименты.

MATHEMATICAL MODELING THE PROCESS OF NON-EQUILIBRIUM SORPTION

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The article considers the system of equations modeling the process of non-equilibrium sorption. A difference approximation of differential problem by the implicit scheme is formulated. The solution of the difference problem is constructed using the sweep method.

Keywords: the system of equations of non-equilibrium sorption; difference approximation; the implicit scheme; sweep method; numerical experiments.

Introduction. Almost all fluids in nature are solutions, i.e. mixtures of two or more substances (components). Filtering in porous media of liquids and gases containing associated with them (dissolved, suspended) solid substances, is accompanied by the diffusion of the substances and mass transfer between the liquid (gas) and solid phases. The most common types of mass transfer are sorption and desorption, ion exchange, dissolution and crystallization, mudding, sulfation and suffusion. Depending on the physical and chemical interactions of solutions with rock formation are considered the problems of equilibrium and non-equilibrium sorption.

Formulation of the problem. Let $m(x,t)$ is the porosity of the medium, $0 < m(x,t) \leq 1$; pore space is filled with the solution and solid phase precipitated from the solution; $c(x,t)$ is a mass concentration of a certain substance in liquid phase (per unit volume of solution); $s(x,t)$ is a mass concentration of the solid phase of the substance the precipitated (per unit pore volume).

Under equilibrium conditions, when the contact between the solution and the solid phase is maintained for a long enough time, the ratio between the concentrations $c(x,t)$ in solution and $s(x,t)$ on the sorbent is determined by sorption isotherm. At low concentrations of the solution, the amount of absorption is determined by the linear relationship Henry isotherm $s = \Gamma c$, where $\Gamma > 0$ is Henry's constant.

The equation of equilibrium sorption may not always fully characterize the features of the absorption of the two-phase system solution – solid phase. In [1] – [3] have been suggested mathematical models to describe the non-equilibrium sorption. The concentration of the solid phase $s(x,t)$ is associated with the concentration $c(x,t)$ in the liquid phase with the equation

$$\frac{\partial s}{\partial t} = \frac{1}{\tau}(\Gamma c - s), \tag{1}$$

where the positive constant τ is the characteristic relaxation time, Γ is the Henry's constant. The concentrations in the solution satisfy the equation

$$m\frac{\partial c}{\partial t} = D\Delta c - v\nabla c - \frac{\partial s}{\partial t}, \tag{2}$$

where $D(x,t) > 0$ is the diffusion coefficient, $v(x,t)$ is the vector of the filtration rate, which are considered known functions of these arguments.

Let Ω is a bounded domain of n-dimensional space R^n with a sufficiently smooth boundary $S = \partial\Omega$, $Q_T = \Omega \times (0,T)$, $T > 0$; $S_T = S \times (0,T)$.

It is required to find the functions $c(x,t)$, $s(x,t)$, defined in domain Q_T satisfying the equations (1), (2), the initial conditions

$$c(x,0) = c_0(x), x \in \Omega, \tag{3}$$

$$s(x,0) = s_0(x), x \in \Omega, \tag{4}$$

and the boundary condition

$$c(x,t) = c_b(x,t), (x,t) \in S_T. \tag{5}$$

In [4] the global unique solvability of a multi-dimensional boundary value problem (1) – (5) is proved.

Theorem. Let the coefficients m, D, v of the equation (2) belong to the Holder $C^{\alpha, \alpha/2}(\overline{Q}_T)$, $0 < \alpha < 1$; S is $C^{2+\alpha}$ – smooth; functions $c_0(x)$, $c_b(x,t)$, $s_0(x)$ belong to the spaces $C^{2+\alpha}(\overline{\Omega})$, $C^{2+\alpha, 1+\alpha/2}(\overline{S}_T)$, $C^{\alpha}(\overline{\Omega})$ and the compatibility conditions of zero and first order are fulfilled:

$$c_0(x) = c_b(x,0), \quad x \in S,$$

$$m(x,0) \cdot \frac{\partial c_b}{\partial t}(x,0) = D(x,0) \cdot \Delta c_0(x) - v(x,0) \cdot \nabla c_0(x) - \frac{1}{\tau} \cdot (\Gamma c_0(x) - s_0(x)).$$

Then the problem (1) – (5) has a unique classical solution:

$$c(x,t) \in C^{2+\alpha, 1+\alpha/2}(\overline{Q}_T), \quad s(x,t) \in C^{\alpha, 1+\alpha/2}(\overline{Q}_T).$$

Difference approximation of the differential problem by the implicit scheme. Let us consider the one-dimensional case of the variable x. In this case equation (2) can be written in the form

$$m \frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2} - v \frac{\partial c}{\partial x} - \frac{\partial s}{\partial t}. \tag{6}$$

Let the concentration $c(x,t)$ of the substance in liquid phase satisfies the initial condition

$$c(x,0) = c_0(x), x \in (0,1), \tag{7}$$

and the boundary conditions

$$c(0,t) = c_{b0}(t), c(1,t) = c_{b1}(t), t \in [0,T], \tag{8}$$

and the concentration $s(x,t)$ of the solid phase satisfies the initial condition

$$s(x,0) = s_0(x), x \in (0,1). \tag{9}$$

It is required to find a solution $c(x,t)$, $s(x,t)$ of equations (1) and (6) in the rectangle $(x,t) \in (0,1) \times (0,T)$ that satisfies the initial conditions (7), (9) and the boundary conditions (8).

The main unit of the numerical solution of partial differential equations is finite difference method. To find an approximate solution of this problem, consider a rectangular grid nodes, formed by the intersection of two families of parallel lines $x = ih$, $i = \overline{0,k}$, $h = 1/k$; $t = jq$, $j = \overline{0,p}$, $q = T/p$.

For each node (i,j), we denote $c_{i,j} = c(ih, jq)$, $s_{i,j} = s(ih, jq)$ and write difference approximation of differential equations (1) and (6)

$$\frac{s_{i,j+1} - s_{i,j}}{q} = \frac{1}{\tau}(\Gamma c_{i,j} - s_{i,j}), i = \overline{0,k}, j = \overline{0,p-1}, \tag{10}$$

$$m_{i,j} \frac{c_{i,j+1} - c_{i,j}}{q} = D_{i,j} \frac{c_{i+1,j+1} - 2c_{i,j+1} + c_{i-1,j+1}}{h^2} - v_{i,j} \frac{c_{i+1,j+1} - c_{i-1,j+1}}{2h} - \frac{s_{i,j+1} - s_{i,j}}{q} \tag{11}$$

From equation (10) we find

$$s_{i,j+1} = s_{i,j}\left(1 - \frac{q}{\tau}\right) + \frac{q\Gamma}{\tau} c_{i,j}. \tag{12}$$

From equation (11) we obtain

$$\frac{q}{h}\left(\frac{v_{i,j}}{2} - \frac{D_{i,j}}{h}\right)c_{i+1,j+1} + \left(m_{i,j} + \frac{2D_{i,j}q}{h^2}\right)c_{i,j+1} - \frac{q}{h}\left(\frac{D_{i,j}}{h} + \frac{v_{i,j}}{2}\right)c_{i-1,j+1} = m_{i,j}c_{i,j} + s_{i,j} - s_{i,j+1}. \quad (13)$$

To find the values $c_{i,j+1}$ from (13), first find the value of the function $s_{i,j+1}$ from (12).

The initial and boundary conditions (7), (9), (8) for functions $c(x,t)$, $s(x,t)$ can be rewritten as

$$c_{i,0} = c_0(ih), s_{i,0} = s_0(ih), c_{0,j} = c_{b0}(jq), c_{k,j} = c_{b1}(jq), i = \overline{0,k}, j = \overline{0,p}.$$

A sweep method for difference equations. We introduce the following notation:

$$c_{i,j+1} = y_i, \ c_{i+1,j+1} = y_{i+1}, \ c_{i-1,j+1} = y_{i-1}, \ m_{i,j}c_{i,j} + s_{i,j} - s_{i,j+1} = \varphi_i,$$

$$-\frac{q}{h}\left(\frac{D_{i,j}}{h} + \frac{v_{i,j}}{2}\right) = a_i, \ m_{i,j} + \frac{2D_{i,j}q}{h^2} = b_i, \ -\frac{q}{h}\left(\frac{D_{i,j}}{h} - \frac{v_{i,j}}{2}\right) = d_i.$$

Then (13) can be written as a system of (k+1) equations:

$$y_0 + 0 \cdot y_1 = c_{0,j+1},$$

$$a_i y_{i-1} + b_i y_i + d_i y_{i+1} = \varphi_i, \ i = \overline{1,k-1},$$

$$0 \cdot y_{k-1} + y_k = c_{k,j+1},$$

for every $j = \overline{0, p-1}$ it is a linear system with three-diagonal matrix. The solution exists, is unique and can be found using the sweep method.
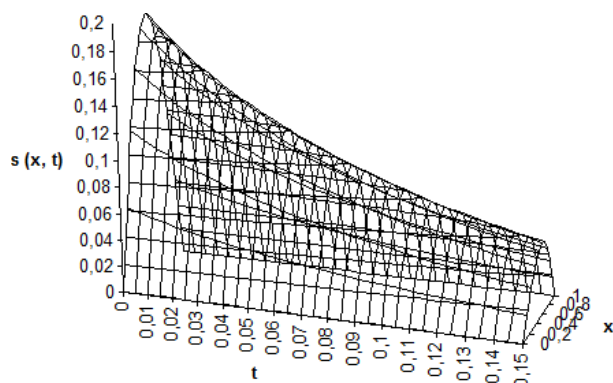

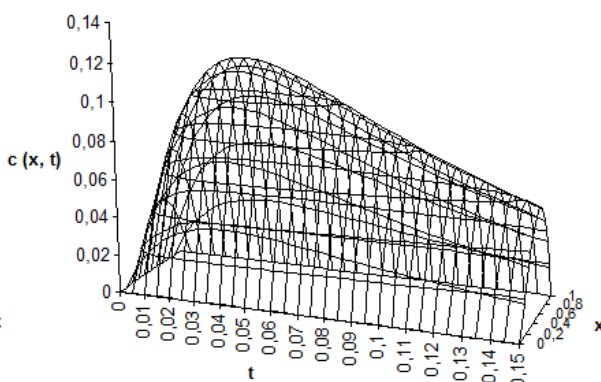Figure 1. The concentration in the solid phase
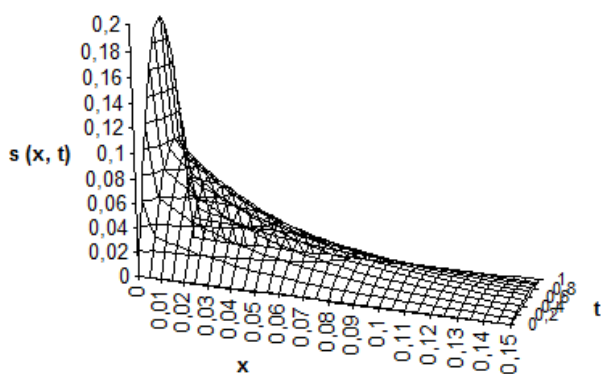

Figure 2. The concentration in the liquid phase
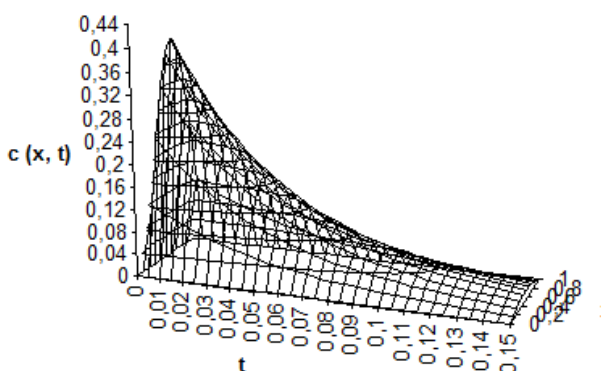

Figure 3. The concentration in the solid phase

Figure 4. The concentration in the liquid

Numerical experiments. After constructing a difference scheme, numerical calculations have been carried out. As an illustration, we present the results corresponding to the following data: $m = 0.1$, $D = 1$, $v = v(x) = 0, x \in (0,1)$, $\Gamma = 0.2$, $c_0(x) = 0, x \in (0,1)$; $s_0(x) = 0.2\sin \pi x, x \in (0,1)$; $c_{b0}(t) = 0, c_{b1}(t) = 0, t \in (0,T)$, $T = 0.15; h = 0.1; q = 0.005$, $\tau_1 = 0.1, \tau_2 = 0.01$ are two characteristic relaxation time values.

Graphical visualization of calculations when $\tau = 0.1$ for $s(x,t)$ is shown in Figure 1, and for $c(x,t)$ is shown in Figure 2.

Graphical visualization of calculations when $\tau = 0.01$ for $s(x,t)$ is shown in Figure 3, and for $c(x,t)$ is shown in Figure 4.

Conclusion. Based on the numerical results and their visualization in the form of graphs we can conclude the following: when the relaxation time τ decreases to 0, then the solution of non-equilibrium problem tends with increasing time to solution of the equilibrium problem, i.e. $s \rightarrow \Gamma c$.

The obtained results allow to confirm the predictions of theoretical studies and the results obtained analytically.

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