INTEGRATION OF THE EQUATIONS OF MOTION OF A SORBABLE MIXTURE THROUGH A NONDEFORMABLE POROUS MEDIUM

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Numerical solutions are found for the quasilinear dynamic equations of sorption taking the effective longitudinal mixing into account.

The dynamics of sorption in a nondeformable porous medium is described by a system of quasilinear partial differential equations. Such a system of quasilinear equations can be solved only numerically for an arbitrary nonlinear sorption isotherm.

Numerical solutions were found for the sorption dynamic equations in [1-3] for a Langmuir isotherm without an account of the longitudinal mixing, but the accuracy of the network system for the numerical calculation was not specified, and the conditions for absolute stability of the solution scheme were not examined.

For a convex sorption isotherm there exists an invariant solution [4] corresponding to a traveling-wave mode (a stationary front, the parallel-transport mode). In the stationary-front mode the partial differential equations reduce to ordinary differential equations. In the absence of longitudinal mixing the system of dynamic equations for sorption can be reduced to quadratures [5]. When longitudinal mixing is taken into account, however, the system of dynamic equations for sorption in the stationary-front mode can be solved only numerically, as is shown below.

Below we analyze the conditions for absolute stability of the difference scheme for the dynamic equations of sorption, taking longitudinal mixing into account. We give illustrative numerical solutions. We find analytic solutions for the dynamic equations taking into account longitudinal mixing for a stepped (rectangular) isotherm.

The system of dynamic equations for sorption consists of the mass-balance equation, the kinetic equations for sorption in the porous grains, and the initial and boundary conditions:

$$\frac{\partial c}{\partial z}+\frac{\partial q}{\partial t}+\frac{1}{q_*}\frac{\partial c}{\partial t}=\alpha\frac{\partial^2 c}{\partial z^2}, \tag{1}$$

$$\gamma\frac{\partial q}{\partial t}=c-\varphi(q),\quad f=\varphi^{-1},\quad q=f(c), \tag{2}$$

$$c|_{t=0}=c_0+(c^0-2c_0)\exp\left(\frac{z}{2\alpha}\right)\frac{\operatorname{sh}\lambda(b-z)}{\operatorname{sh}\lambda b},\quad \lambda=\frac{1}{2\alpha}\sqrt{1+\frac{4\alpha}{\gamma}}, \tag{3}$$

$$q|_{t=0}=f(c_0),\quad 0\leqslant z\leqslant b, \tag{4}$$

$$c|_{z=0}=F(t),\quad c|_{z=b}=c_0,\quad F(0)=c^0-c_0,\quad q|_{z=0}=H(t).$$

We would usually have $q_*\gg 1$, so we can neglect the third term in Eq. (1). Conditions (3) and (4) incorporate the continuity condition. The boundary condition, i.e., the function H(t), is found from the solution of the ordinary nonlinear equation by the Runge–Kutta Method:

$$\gamma H_t=F(t)-\varphi(H),\quad H(0)=H_0. \tag{5}$$

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We solve the boundary-value problem for system (1), (2) with conditions (3), (4) numerically, by the pivotal condensation method. Using a six-point pattern with a weight of 0.5 we write the implicit iterative scheme of the second order of accuracy, $O(h^2+\tau^2)$:

$$\overset{(s+1)}{q_i^j} = \overset{(s)}{q_i^j} + \theta\left\{\frac{\tau}{\gamma}\left[\frac{1}{2}(\overset{(s)}{c_i^j} + c_i^{j-1}) - \varphi\left(\frac{\overset{(s)}{q_i^j} + q_i^{j-1}}{2}\right)\right] + q_i^{j-1} - \overset{(s)}{q_i^j}\right\}, \tag{6}$$

$$\overset{(s+1)}{c_i^j} = A_{i+1}\overset{(s+1)}{c_{i+1}^j} + B_{i+1}, \quad 0 \leqslant i \leqslant N-1, \tag{7}$$

$$A_{ik}\overset{(s+1)}{c_k^j} = P\overset{(s+1)}{c_{i-1}^j} - Q\overset{(s+1)}{c_i^j} + R\overset{(s+1)}{c_{i+1}^j} = -F_i, \quad 1 \leqslant i \leqslant N-1, \tag{8}$$

$$A_1 = 0, \quad B_1 = F(t), \quad A_{i+1} = R(Q-PA_i)^{-1}, \quad P = \frac{\alpha}{h^2} + \frac{1}{2h},$$

$$B_{i+1} = (PB_i + F_i)(Q-PA_i)^{-1}, \quad Q = \frac{2\alpha}{h^2} + \frac{1}{\gamma},$$

$$R = \frac{\alpha}{h^2} - \frac{1}{2h}, \quad F_i = \frac{2}{\gamma}\varphi\left(\frac{\overset{(s)}{q_i^j} + q_i^{j-1}}{2}\right) + \frac{\alpha}{h^2}(c_{i-1}^{j-1} - 2c_i^{j-1} + c_{i+1}^{j-1}) - \frac{1}{2h}(c_{i+1}^{j-1} - c_{i-1}^{j-1}) - \frac{1}{\gamma}c_i^{j-1}, \quad \alpha > \frac{h}{2}.$$

Implicit iterative scheme (6)-(8) is not absolutely stable, so we must find the conditions under which it is stable. We denote the error of the difference scheme by

$$\overset{(s)}{\varepsilon_i^j} = \overset{(s)}{c_i^j} - c_i^j, \quad \overset{(s)}{\xi_i^j} = \overset{(s)}{q_i^j} - q_i^j. \tag{9}$$

The linearized difference scheme is

$$A_{ik}\overset{(s+1)}{\varepsilon_k^j} = -\frac{1}{\gamma}\varphi'\left(\frac{q_i^j + q_i^{j-1}}{2}\right)\overset{(s+1)}{\xi_i^j}, \tag{10}$$

$$\overset{(s+1)}{\xi_i^j} = \theta\frac{\tau}{2\gamma}\overset{(s)}{\varepsilon_i^j} + \overset{(s)}{\xi_i^j}\left[1 - \theta - \theta\frac{\tau}{2\gamma}\varphi'\left(\frac{q_i^j + q_i^{j-1}}{2}\right)\right]. \tag{11}$$

After some calculation, we find from (10), (11)

$$A_{ik}\overset{(s+1)}{\varepsilon_k^j} = B_{ik}\overset{(s)}{\varepsilon_k^j}, \quad A_{ik}\overset{(s+1)}{\xi_k^j} = B_{ik}\overset{(s)}{\xi_k^j}, \tag{12}$$

$$B_{ik} = \left(1 - \frac{\tau\theta}{2\gamma}\varphi' - \theta\right)A_{ik} - \frac{\tau\theta}{2\gamma^2}\varphi'\delta_{ik}. \tag{13}$$

A sufficient condition for the absolute stability of difference equations (10), (11) is

$$|\lambda_i(B)| < |\lambda_i(A)|, \tag{14}$$

where $\lambda_i(B)$ and $\lambda_i(A)$ are the eigenvalues of the matrices B_{ik}, A_{ik}. We find the eigenvalues from the characteristic equation. After some calculation we find

$$\lambda_i(A) = -Q + 2\sqrt{PR}\cos\frac{\pi i}{n+1}, \quad i = 1, 2, \ldots, n. \tag{15}$$

The pivotal condensation method is stable for $Q > 0$, $P > 0$, $R > 0$, $Q > P + R$. Under these conditions we have $Q > 2\sqrt{PR}$, so that the eigenvalues of matrix A_{ik} are always negative. From condition (14), and using (13) and (15), we find restrictions on the time step:

$$\tau \leqslant \frac{(2-\theta)2\gamma}{\theta\max|\varphi'|}\left(1 - \frac{1}{\gamma\max|\lambda(A)|}\right)^{-1}. \tag{16}$$

We see from (16) that by varying θ $(0 < \theta \leq 1)$ in the appropriate manner we can increase the time step τ.

As an example we choose the Langmuir isotherm

$$q = \frac{(1+p)c}{1+pc}, \quad 0 \leqslant q \leqslant 1, \quad 0 \leqslant c \leqslant 1, \tag{17}$$

and integrate system (1)-(4) for the following parameters: $\alpha = \gamma = 0.5$; $c_0 = 0$; $c^0 = 1$, $F(t) = 1$; $H_0 = 0$; $h = 0.06$; $b = 15$; $\tau = +1/51$; $p = 50$. The solid curves in Fig. 1a and b, respectively, show the distributions in the column of the concentration of the material, $c(z, t)$, and the concentration of the absorbed material, $q(z, t)$. The stationary-front regime sets in at

$$|\mu_2^j - \mu_2^{j-1}| < \varepsilon, \tag{18}$$

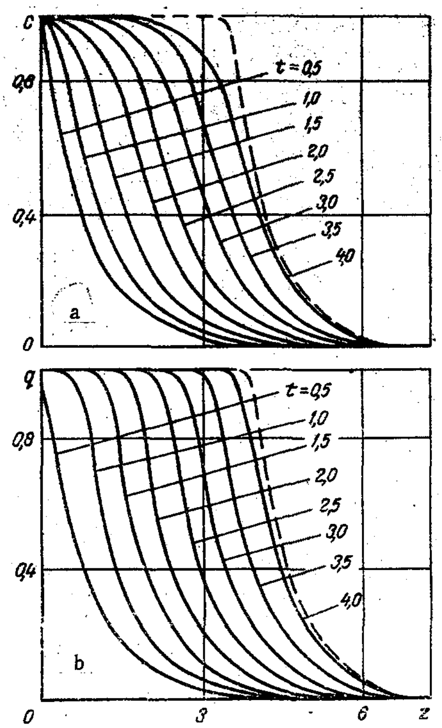

Fig. 1. a) Distribution of the concentration of material, c(z, t); b) that of the concentration of absorbed material, q(z, t). The dashed curves are the asymptotic solutions (24), (25).

where ε is the error of the calculation, μ_2 is the second central moment, α_1 and α_2 are the first and second initial moments, $\mu_2 = \alpha_2 - \alpha_1^2$; $\alpha_n = n \int\limits_0^\infty z^{n-1} c(z, t)dz$.

Using condition (18) we showed that the stationary-front regime sets in at $t \geq t_* = 3.6$ and $z \geq z_* = 6.75$ and that the distribution curves can be calculated within 1% from the asymptotic equations corresponding to the stationary-front regime.

Using the methods of Lie-group theory [4] we can show that system (1)-(4) permits an invariant solution corresponding to a Galilean transport operator (the stationary-front regime). In this case we can write system (1)-(4) as

$$c - wq = \alpha \frac{dc}{dy}, \quad -\gamma w \frac{dq}{dy} = c - \varphi(q), \quad y = z - wt, \tag{19}$$

$$w = \left.\frac{c}{q}\right|_{y\to-\infty} = 1,$$

$$c\big|_{\substack{z=0\\ t=\infty}} = c(-\infty) = 1, \quad q(-\infty) = f(1) = 1,$$

$$c\big|_{\substack{z=\infty\\ t=0}} = c(\infty) = 0, \quad q(\infty) = 0, \quad \left.\frac{dc}{dy}\right|_{y\to\pm\infty} = \left.\frac{dq}{dy}\right|_{y\to\pm\infty} = 0. \tag{20}$$

On the basis of physical considerations we can conclude that, under conditions (20), the functions c(y) and q(y) must be monotonically decreasing functions, so that from (19), (20) we conclude that the following conditions must hold:

$$wq > c > \varphi(q). \tag{21}$$

Condition (21) always holds for sorption dynamics in the case of a convex isotherm, i.e., one which begins at the origin, $f(0) = 0$, and lies above the straight line connecting the origin (0, 0) and the point (1,1) on the interval $0 \leq c \leq 1$.

System (19) can be reduced to a single nonlinear second-order equation, which can be solved by the pivotal condensation method. For a stepped isotherm, like the limiting ($p \gg 1$) Langmuir isotherm (17),

$$q = \begin{cases} 1, & 0 < c \leq 1, \\ 0, & c = 0, \end{cases} \qquad \varphi(q) = \begin{cases} 0, & 0 \leq q < 1, \\ 1, & q = 1, \end{cases} \tag{22}$$

we can find the solution of system (19), (20) analytically. For isotherm (22) with $\alpha \neq \gamma \neq 0$ we find from (19)

$$\alpha \frac{d^2c}{dy^2} - \frac{dc}{dy} - \frac{c}{\gamma} = 0. \tag{23}$$

Using (19) and (20), we find the solution of (23) to be

$$q(y) = \begin{cases} \exp[\lambda_2(y - y_0)], & y_0 \leq y < \infty, \quad y_0 = \text{const}, \\ 1, & -\infty < y \leq y_0, \quad \lambda_{1,2} = \dfrac{1}{2\alpha} \pm \dfrac{1}{2\alpha}\sqrt{1 + \dfrac{4\alpha}{\gamma}}, \end{cases} \tag{24}$$

$$c(y) = \begin{cases} \exp[\lambda_2(y - y_0 - y^0)], & y_0 + y^0 \leq y < \infty, \\ 1, & -\infty < y \leq y_0 + y^0, \\ & y^0 = \dfrac{1}{\lambda_2}\ln(1 - \alpha\lambda_2). \end{cases} \tag{25}$$

In the case $\alpha = \gamma = 0.5$ we have $y^0 = -0.39$.

We find the constant y_0 from the integral form of the mass-balance equation. Multiplying (1) by dzdt and integrating over $z (0 \leq z \leq z_1)$ and $t (0 \leq t \leq t_1)$, using solutions (24) and (25), and taking the limits $z_1, t_1 \to \infty$, we find a transcendental equation for y_0:

$$y_0 = -\int_{y_0}^{\infty} q dy + \alpha [1 - c(0)], \tag{26}$$

We then find

$$y_0 = \frac{1}{\lambda_2} + \alpha [1 - \exp(-(y^0 + y_0)\lambda)]. \tag{27}$$

In the case $\alpha = \gamma = 0.5$ we find from (27) the result $y_0 = -0.475$. We see from solutions (25), (24) that q(y) is displaced by an amount $|y^0|$ with respect to c(y). In the case $\alpha = 0$ ($|y^0| = 0$) the solutions coincide.

Solutions for the particular case $\alpha \neq 0$, $\gamma = 0$ can be found from (25), (24).

In the case $\alpha \neq 0$, $\gamma = 0$, the second equation in (19) converts into the isotherm $c = \varphi(q)$ or $q = f(c)$. In this case we find from (19), after integrating,

$$c - 1 = \alpha \frac{dc}{dy}, \tag{28}$$

and we then find

$$q = f(c), \quad c(y) = \begin{cases} 1 - \exp\left(\dfrac{y - y_0}{\alpha}\right), & -\infty < y \leqslant y_0, \\ 0, & y_0 \leqslant y < \infty. \end{cases} \tag{29}$$

We find the integration constant y_0 from the integral form of Eq. (1):

$$y_0 = \frac{\alpha}{w} [1 - c(0)] = \alpha \exp\left(-\frac{y_0}{\alpha}\right). \tag{30}$$

From the solution of transcendental Eq. (30), we have $y_0 = 0.567\alpha$. Solutions (24) and (25) for t = 4.0 are shown by the dashed curves in Fig. 2a and b. In practice, porous zeolite grains are frequently used; the corresponding isotherm is rectangular. We see from Fig. 1 that in this case the asymptotic solutions corresponding to the stationary-front regime can be described by analytic solutions (24), (25).

NOTATION

c	is the concentration of the sorbed gas (or liquid) in the filtration flow;
q	is the concentration of the material absorbed by the medium from the porous grains;
α	is the relative longitudinal-mixing coefficient (longitudinal dispersion);
γ	is the relative kinetic coefficient;
f, φ	are the functions describing the forward and reverse sorption isotherms;
h, τ	are the coordinate and time steps, respectively.

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