SORPTION DYNAMICS IN POROUS MEDIA

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The accuracy of different model equations of sorption dynamics in porous media is analyzed. Analytical solutions of the equations are obtained for a rectangular isotherm.

The motion of a mixture of gases (liquids) through porous media is described by a quasilinear system of equations. Such a system has invariant parallel transport solutions (travelling wave) only under certain conditions (convexity of sorption isotherm for sorption dynamics and concavity of the isotherm for desorption dynamics) [1].

It is shown in [2] that for the equations of sorption dynamics in the outer diffusion kinetic region under parallel transport conditions the resistance to mass transfer due to the finite rate of sorption dynamics and longitudinal mixing can be added up in the first approximation and the equations of sorption dynamics can be appropriately simplified. In [3] it is shown phenomenologically that the resistance to mass transfer can be approximately added up for all regimes of sorption dynamics; it is also shown how approximate model equations can be derived. However, the question of accuracy of different approximate model equations of sorption dynamics remained open. A rigorous estimate of the accuracy of different model equations can be obtained by comparing numerical computations of the exact and approximate equations.

The computations for different types of isotherms (linear, convex, concave, s-shaped) were carried out on a BÉSM-6 computer.

The computations for the convex isotherm are presented below by way of example, although all the conclusions about the accuracy of approximate model equations will be valid for any type of isotherm.

The sorption dynamics is described by the equation of mass balance and the equation of outer diffusion sorption kinetics

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

We shall solve this quasilinear equation with appropriate initial and boundary conditions numerically by the screw die method. The implicit iteration scheme of second order accuracy is absolutely stable for

$$\tau\leqslant\frac{2\gamma}{\max|\varphi_q'|}. \tag{2}$$

Langmuir sorption isotherm has the form

$$q=\frac{(1+p)c}{1+pc},\ 0\leqslant c\leqslant 1. \tag{3}$$

The output dynamic curves corresponding to the motion of a rectangular perturbation through a porous medium were computed for (3) with p = 10 for different values of the parameters α, γ. The dynamic curves of distribution of the concentrations in the porous medium are shown in Fig. 1 by continuous lines for $\alpha = \gamma = 0.5$, by dashes for $\alpha = 0.05$, $\gamma = 0.95$, and by dash–dots for $\alpha = 0.925$, $\gamma = 0.075$.

The exact system of equations ($\alpha \neq \gamma \neq 0$) has form (1). The approximate systems are

$$(\alpha=0,\ \gamma=1)\ \frac{\partial c}{\partial z}+\frac{\partial q}{\partial t}=0,\ \frac{\partial q}{\partial t}=c-\varphi(q), \tag{4}$$

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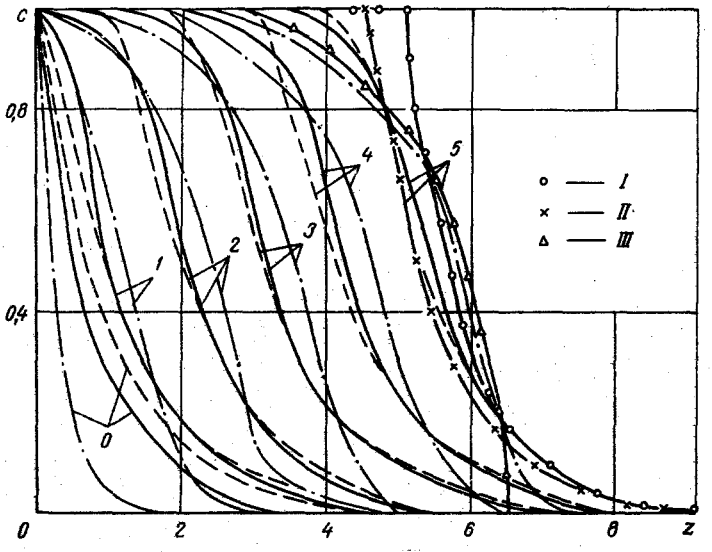

Fig. 1. Distribution of concentration in flow through a porous medium at different instants of time. The numbers on the curves are values of t.

$$(\alpha = 1,\ \gamma = 0)\ \frac{\partial c}{\partial z} + \frac{\partial f(c)}{\partial t} = \frac{\partial^2 c}{\partial z^2}\ . \tag{5}$$

The accuracy of the different approximate equations can be estimated by varying the parameters α, γ. Actually, let us assume that it is required to compute the dynamic output curves of motion of concentrations along a porous medium when the rates of mass transfer due to outer diffusion sorption kinetics and longitudinal mixing are equal, i.e., $\alpha = \gamma = 0.5$. In this case an exact numerical solution can be obtained from the solution of system (1). However, it is possible to use the approximate model equation (4), in which the equivalent resistance to outer diffusion mass transfer is equal to the sum of the true resistance to outer diffusion mass transfer and the resistance due to longitudinal mixing ($\alpha = 0$, $\gamma = 1$, $\alpha + \gamma = 1$). The approximate equation (5) can also be used in which the equivalent resistance due to longitudinal mixing is equal to the sum of the true resistance due to longitudinal mixing and the resistance of outer diffusion mass transfer ($\alpha = 1$, $\gamma = 0$). It is evident from a comparison of the exact and the approximate model equations that in outer diffusion kinetics the sorption dynamics can be advantageously described by the approximate model equation (4), since this equation is more exact than (5).

Sorbents having an almost rectangular isotherm are often used in applications for processes of desication etc. This isotherm may be regarded as a limiting Langmuir isotherm ($p \gg 1$)

$$q = \begin{cases} 1, & 0 < c \leqslant 1, \\ 0, & c = 0, \end{cases} \qquad \varphi(q) = \begin{cases} 0, & 0 \leqslant q < 1, \\ 1, & q = 1. \end{cases} \tag{6}$$

Isotherm (6) is of certain interest, since on one hand for it the equations of sorption dynamics can be solved analytically, and on the other hand using such solutions it is possible to estimate the time and the length of the porous medium after which parallel transport conditions set in. In this formulation the boundary value problem (1) of sorption dynamics reduces to Stefan's problem [4] with unknown movable boundary $l(t)$:

$$\frac{\partial c}{\partial z} + \frac{c}{\gamma} = \alpha \frac{\partial^2 c}{\partial z^2}\ ,\quad \gamma \frac{\partial q}{\partial t} = c,\ 0 \leqslant z \leqslant l(t),\ 0 < q \leqslant 1,\ 0 < c \leqslant 1,$$
$$c = q = 0,\ z > l(t),\ l(0) = 0. \tag{7}$$

Solving (7) with the boundary condition $c(l, t) = 0$, we obtain

$$c(z, t) = \gamma\psi'(t)\ \{\exp(\lambda_2 z) - \exp[\lambda_1 z + (\lambda_2 - \lambda_1) l]\},$$
$$q(z, t) = \psi'(t)\{\exp(\lambda_2 z) - \exp[\lambda_1 z + (\lambda_2 - \lambda_1) l]\}$$
$$+ \Phi(z),\ \lambda_{1,2} = \frac{1}{2\alpha} \pm \frac{1}{2\alpha}\sqrt{1 + 4\frac{\alpha}{\gamma}}\ , \tag{8}$$

where Φ is an arbitrary function.

We divide the second equation of (8) by the first. After some reorganization we have

$$q(z,\ t) = \frac{q(0,\ t) - \Phi(0)}{c(0,\ t)}\, c(z,\ t) + \Phi(z). \tag{9}$$

From the second equation in (7) we get

$$q(0,\ t) = \frac{t}{\gamma}. \tag{10}$$

Comparing (9), (10) we see that parallel transport conditions set in at $t \geq t_*$, when saturation occurs at the boundary ($\max q = 1$). Therefore considering the boundary condition $c(0,\ t) = 1$, from Eq. (8) we obtain the solution

$$c(z,\ t) = \{\exp(\lambda_2 z) - \exp[\lambda_1 z + (\lambda_2 - \lambda_1)\, l]\}\, \{1 - \exp[(\lambda_2 - \lambda_1)\, l]\}^{-1}. \tag{11}$$

We shall find the equation for determining the unknown boundary $l(t)$ from the integral form of the equation of mass balance. After some manipulations we get

$$\int_0^l q(z,\ t)\, dz = t - \alpha \int_0^t \frac{dc(0,\ t)}{dz}\, dt,$$

from which we have

$$\frac{1}{\gamma} \int_0^l c(z,\ t)\, dz = 1 - \alpha \frac{dc(0,\ t)}{dz}. \tag{12}$$

Substituting (11) into (13) we obtain

$$(\lambda_2 - \lambda_1) \exp(\lambda_2 l) \cong 0.$$

With an accuracy up to a few percents the parallel transport conditions set in for

$$l \geqslant l_* = \frac{4{,}6}{|\lambda_2|}, \tag{13}$$

since $\exp(-4.6) \leqslant 0.01$.

Taking (13) into consideration we write solution (9), (11) in the following form:

$$c(z,\ t) = \exp(\lambda_2 z),\ q(z,\ t) = Ac(z,\ t),\ A = \text{const}. \tag{14}$$

In the stationary front regime with $t \geq t_*$, $z \geq l_*$ with (14) taken into consideration problem (7) reduces to the following:

$$\frac{\partial c}{\partial z} + \frac{A}{\alpha\lambda_1} \frac{\partial c}{\partial t} = 0,\ c|_{t=t_*} = \exp(\lambda_2 z),$$

the solution of which is

$$q(z,\ t) = \begin{cases} \exp[\lambda_2 (y - y_0)], & y_0 \leqslant y < \infty,\ y_0 = -t_* = -\alpha\gamma\lambda_1, \\ 1, & -\infty < y \leqslant y_0,\ y = z - wt, \end{cases}$$

$$w = \frac{A}{\alpha\lambda_1} = 1,\ A = \alpha\lambda_1,$$

$$c(z,\ t) = \begin{cases} \exp[\lambda_2 (y - y_0 - y^0)], & y_0 + y^0 \leqslant y < \infty, \\ 1, & -\infty < y \leqslant y_0 + y^0, \end{cases}$$

$$y^0 = \frac{1}{\lambda_2} \ln(\alpha\lambda_1).$$

Let us consider the approximate model equation (4) when $\alpha = 0$, $\gamma \neq 0$. As follows from (14), in this case the solution has a simple form

$$c(z,\ t) = q(z,\ t) = \begin{cases} \exp\left(-\dfrac{y - y_0}{\gamma}\right), & y_0 \leqslant y < \infty,\ y_0 = -\gamma, \\ 1, & -\infty < y \leqslant y_0, \end{cases} \tag{15}$$

since $\lambda_2 = -1/\gamma$, $y^0 = 0$.

For the approximate model equation (5) ($\alpha \neq 0$, $\gamma = 0$) system (1) goes over into the following:

$$\frac{1}{q_*}\frac{\partial c}{\partial t} + \frac{\partial c}{\partial z} = \alpha \frac{\partial^2 c}{\partial z^2},\ q = 1,\ c > 0,\ q_* \gg 1,\ c(0, t) = 1,$$
$$c(l, t) = 0. \tag{16}$$

Usually $q_* \gg 1$ and the first term can be neglected. The solution of (16) without the first term is

$$c(z, t) = \psi_1(t) + \psi_2(t) \exp\left(\frac{z}{\alpha}\right),$$

When the boundary conditions are taken into consideration we get

$$c(z, t) = \left[1 - \exp\left(\frac{z-l}{\alpha}\right)\right]\left[1 - \exp\left(-\frac{l}{\alpha}\right)\right]^{-1}. \tag{17}$$

We obtain the equation for the movable boundary from the integral form of the equation of mass balance:

$$l(t) = t - \alpha \exp\left(-\frac{l}{\alpha}\right) + \alpha,\ l(0) = 0. \tag{18}$$

The parallel transport conditions set in for a linear time dependence of the boundary (constant velocity of the movable boundary); therefore

$$\alpha \exp\left(-\frac{l}{\alpha}\right) \cong 0.$$

Hence we get

$$l \geqslant l_* = 4{,}6\,\alpha.$$

For $t \geq t_* = 3.6\,\alpha$; $z \geq 4.6\,\alpha$ the solution in the parallel transport regime is of the form

$$c(z, t) = \begin{cases} 1 - \exp\left(\dfrac{y - y_0}{\alpha}\right), & -\infty < y \leqslant y_0,\ y_0 = \alpha, \\ 0, & y_0 \leqslant y < \infty,\ y = z - t, \end{cases}$$
$$q(z, t) = \eta\left(\frac{y_0 - y}{\alpha}\right). \tag{19}$$

As an example solutions (14), (15), (19) for t = 5.0 are shown in Fig. 1 by the points I, II, III respectively. It is evident from a comparison of the numerical and analytical solutions that for the rectangular isotherm the dynamic output curves in the outer diffusion kinetic region in parallel transport regime can be described by Eqs. (14), (15).

NOTATION

c	is the concentration of matter in the gas (liquid) flow;
q	is the concentration of the absorbed matter;
$\alpha = \tau_D \tau_\Sigma^{-1}$;	
$\gamma = \tau_e \tau_\Sigma^{-1}$;	
$\tau_\Sigma = \tau_D + \tau_e$;	
$\tau_D = ((1 + k)\delta D_*)/u^2$;	
$\tau_e = ((1 + k)a)/((1 + \nu)\beta_0)$;	
$k = df(0)/dc$;	
$\delta = (1-\sigma)/\sigma$;	
$\alpha + \gamma = 1$;	
τ_D	is the relaxation time due to longitudinal mixing;
τ_e	is the relaxation time due to finite rate of mass transfer at the outer boundary of the grain;
σ	is the fraction of free space in the porous medium;
D_*	is the coefficient of effective longitudinal mixing;
u	is the linear velocity of gas (liquid) flow;

ν	is the symmetry parameter ($\nu = 2$ for spehrical grains with radius a, $\nu = 1$ for cylindrical grains with radius a, $\nu = 0$ for grains in the form of sheets of thickness $2a$);
β_0	is the mass transfer coefficient at the outer boundary of the grain;
t', $2'$	are the dimensional time and coordinate respectively;
$t = t'\tau_\Sigma^{-1}$, $z = z'\delta k u^{-1}\tau_\Sigma^{-1}$	are the dimensionless time and coordinate, respectively;
$q = f(c)$	is the sorption isotherm.

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