NONSTATIONARY GAS INFILTRATION IN THE PRESENCE OF SORPTION

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A nonlinear equation system is derived for nonstationary gas infiltration in the presence of sorption, which is based on Leibenson's infiltration equation and Langmuir adsorption kinetics.

Sorption has a marked effect on gas infiltration into a porous medium having a high specific surface and results in relaxation effects, e.g., when natural gas or gas-condensate is extracted from a clay collector or in the purification of petroleum products or in drying and separating gases [1-5].

Attempts have been made to describe infiltration with sorption. In [2], a sorption flux was introduced into the infiltration equation, which was taken as a linear function of the gas pressure in the pores.

In [6], observed relaxation effects were described in terms of a double structure for a porous medium, which gave two nonlinear transport equations analogous to those for the infiltration of a liquid into a jointed porous medium [7, 8]. Such systems have been examined in some detail and may be solved for example by the equivalent-equation method [9, 10]. The double structure assumed in [6] greatly restricts the application of that approach because the molecular kinetic theory indicates that the characteristic sorption times are very short by comparison with the observed relaxation ones. Therefore, it was concluded [6] that the relaxation effects were due to mass transfer (diffusion) between macroscopic and microscopic pores, which contained most of the adsorbed gas. However, we consider that the diffusion of natural gas, which has fairly large molecules, in clay grains with complicated surface-layer structures should be very slow.

There is no doubt that the [6] approach is justified, but here we consider an alternative model. We assume that the relaxation is due not to diffusion in a double medium but to the sorption. The gas has a complicated composition, as does the surface layer in the porous body (clay collector), so one gets not adsorption but in fact chemisorption, with its potential barriers and strong binding to the surface. Therefore, the characteristic exchange times may be very considerable.

Leibenson's equation applies for the infiltration of an ideal gas into a homogeneous porous volume on Darcy's law:

$$m\frac{\rho^0}{p^0}\frac{\partial p}{\partial t} = \frac{k}{2\mu}\frac{\rho^0}{p^0}\Delta p^2 - q_s, \tag{1}$$

in which the source q_s on the right incorporates the mass transfer between the pore volume and the surface. For simplicity, we use Langmuir's equation for the sorption [11]:

$$n_*\frac{d\theta}{dt} = k_a p(1-\theta) - k_d\theta. \tag{2}$$

Then for q_s we have

$$q_s = \gamma M[k_a p(1-\theta) - k_d\theta]. \tag{3}$$

(1)-(3) form a closed system of nonlinear differential equations for nonstationary infiltration in the presence of sorption.

If we use the equation of state for an ideal gas, instead of the proportion of filled adsorption centers* θ, one can introduce the sorption pressure $p_s = n_*\theta RT\gamma/(N_A m)$ which is the pressure that would occur in the adsorbed gas if it were distributed in the pore volume. One can also calculate the molecular concentration in unit volume of the body: n in the pore volume and n_S at the surface of the pores:

$$n = \frac{pN_A m}{RT}, \quad n_S = n_*\gamma\theta.$$

We introduce the dimensionless pressure $\eta = p/p_0$, coordinates $\xi = r/L$, and time $\tau = \kappa p_0 t/L^2$, when (1)-(3) may be written as

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*We retain the (2) terminology, and here and subsequently we mean activated sorption.

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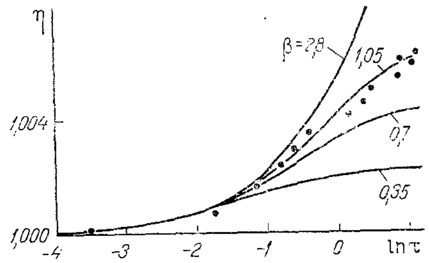

Fig. 1. Dimensionless pressure η as a function of dimensionless time τ, curves constructed from (8) for various β, points from experiment [6].

$$\frac{\partial \eta}{\partial \tau} = \Delta \eta^2 - A\,[\alpha\eta\,(1-\theta) - (1-\alpha)\,\theta], \qquad (4)$$

$$\beta \frac{d\theta}{d\tau} = \alpha\eta\,(1-\theta) - (1-\alpha)\,\theta,$$

in which

$$A = \frac{(k_a p_0 + k_d)\, L^2 \gamma M p^0}{p_0^2 \varkappa m \rho^0};$$

$$\alpha = \frac{k_a p_0}{k_a p_0 + k_d}; \quad \beta = \frac{n_* \varkappa p_0}{(k_a p_0 + k_d\, L^2}.$$

We examine the solution to (4). We consider the situation where there are only small pressure differences in the porous body relative to the absolute pressure. We put $\tilde{\eta} = \eta^2$ and linearize (4) with respect to $\tilde{\eta}$. Then

$$\frac{d\tilde{\eta}}{\partial \tau} = \Delta\tilde{\eta} - A\,(\alpha - \theta), \quad \beta \frac{d\theta}{d\tau} = \alpha - \theta. \qquad (5)$$

The second equation in (5) is readily integrated to $\theta = \alpha + (\theta_0 - \alpha) \exp(-\tau/\beta)$, and for $\tilde{\eta}$ we get the unique equation

$$\frac{\partial \tilde{\eta}}{\partial \tau} = \Delta\tilde{\eta} + A\,(\theta_0 - \alpha) \exp(-\tau/\beta). \qquad (6)$$

For gas release from a specimen under pressure $\eta = \eta' > 1$ to the pressure $\eta = 1$, one can neglect the dependence of $\tilde{\eta}$ on the spatial coordinates in (6), since experiment [6] shows that the pressure equalizes along the specimen very rapidly. Then

$$\frac{\partial \tilde{\eta}}{\partial \tau} = A\,(\theta_0 - \alpha) \exp(-\tau/\beta), \quad \tilde{\eta}|_{\tau=0} = 1, \quad \theta_0 = \frac{\alpha\eta'}{\alpha\eta' + 1 - \alpha}, \qquad (7)$$

so

$$\tilde{\eta} = A\,(\theta_0 - \alpha)\,\beta\,(1 - \exp(-\tau/\beta)) + 1. \qquad (8)$$

As $\theta_0 - \alpha$ is always positive and becomes zero for $\alpha = 0$ and $\alpha = 1$ and attains its maximum for $\alpha = \hat{\alpha} = (\sqrt{\eta'} - 1)/(\eta' - 1)$, we have for $\eta' = 4$, 2, and 1.21 correspondingly that $\hat{\alpha} = 0.33$, 0.4, and 0.48, so we conclude that the relaxation will be most prominent when the adsorption and desorption occur at approximately equal rates, i.e., $x \approx 0.5$, which for unaltered specimen parameters is shown by (4) to be dependent primarily on the gas pressure.

Here β is governed by the length of the relaxation caused by the sorption; $\tau_r = 3\beta$, or in dimensional form

$$t_r = 3n_*/(k_a p_0 + k_d), \qquad (9)$$

is the relaxation time. During it, $\tilde{\eta}$ shows 95% of its possible change. (9) shows that t_r is also dependent on the pressure.

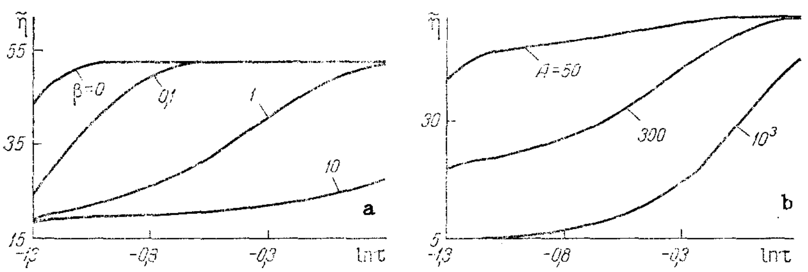

Fig. 2. Relaxation in $\tilde{\eta}$ in time τ at $\xi = 0.5$: a) for various β, $\eta' = 10$, $\alpha = 0.5$, $A = 300$; b) for various A, $\eta' = 10$, $\alpha = 0.5$, $\beta = 1$.

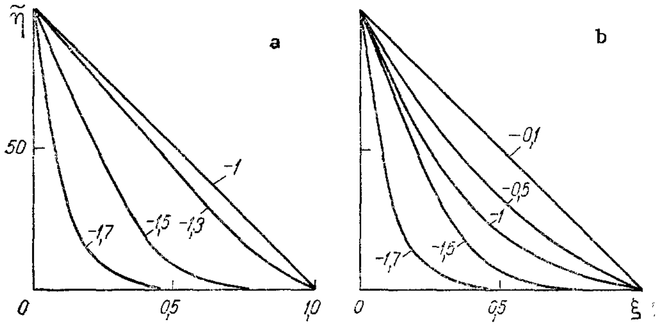

Fig. 3. Distributions of $\tilde{\eta}$ along the specimen for various log τ (numbers on curves) for $A = 0$ (a) and $A = 300$ (b); $\eta' = 10$; $\alpha = 0.5$; $\beta = 1$.

If we assume that there are 10^{19} adsorbed molecules per m^2 and $t_r \approx 10^3$ sec, then $k_A p_0 + k_d$ should be about 10^{16} m^{-2}/sec. The total change in $\tilde{\eta}$ is $\Delta\tilde{\eta} = A\beta(\theta_0 - \alpha) = (\theta_0 - \alpha)\gamma M p^0/(\rho^0 p_0 m)$, so this change determines A for given α, θ_0, and β.

Figure 1 shows curves constructed from (8) for $A = 0.08$, $\alpha = 0.5$, and various β, along with measurements [6]. The η for the observed points have been transformed with respect to the pressure values ($\eta' = 1.37$), while the log τ have been determined by displacing the points along the abscissa to coincide with the theoretical curves (explicit determination of τ is impossible because the experimental parameters are incompletely given in [6]).

For large pressure differences, one needs to use (4). As an example, we consider the filling of a one-dimensional porous specimen whose ends are kept at constant pressures. We have

$$\begin{gathered}\frac{\partial\eta}{\partial\tau} = \frac{\partial^2\eta^2}{\partial\xi^2} - A\left[\alpha\eta(1-\theta) - (1-\alpha)\theta\right],\\ \beta\frac{d\theta}{d\tau} = \alpha\eta(1-\theta) - (1-\alpha)\theta,\\ \eta(0, \xi) = 1, \ \theta(0, \xi) = \alpha,\\ \eta(\tau, 0) = 10, \ \eta(\tau, 1) = 1.\end{gathered} \tag{10}$$

The solutions to (10) have been derived numerically by an inexplicit difference treatment [12]. Figures 2 and 3 show some results. The curves in Fig. 2a show how the relaxation time for the pressure at a certain point in the specimen varies with β for a given A. Figure 2b shows that with a fixed β and various A, the relaxation times remain constant but the shapes of the curves alter. For large A, the relaxation due to sorption is most prominent. Figure 3 shows the distribution for the square of $\tilde{\eta}$ in the dimensionless coordinate ξ for various times and two A. The sorption (Fig. 3b) results in the equilibrium time being increased by an order of magnitude for the given values relative to the absence of sorption (Fig. 3a).

We note some distinctive features of our approach and [6].

1. As the grain size d decreases, the relaxation should weaken according to [6], since the proportion of micropore volumes decreases and the proportion of macropores rises. The relaxation time should vary as d^2 [6]. With our model,

the relaxation is accentuated by reduced d, since the specific surface of the pores is increased, and so one gets $A \sim \gamma \sim 1/d$. As β is independent of the grain size, t_r should remain unchanged as it varies.

2. A difference from the [6] model is that in ours one should get a marked dependence of the relaxation time and amplitude on pressure.

These differences if used in tests may enable one to elucidate the relaxation mechanism due to sorption and select the best model.

NOTATION

A, α, and β, dimensionless parameters in (4); d, mean grain radius; k, permeability; k_a and k_d, adsorption and desorption constants; L, characteristic dimension; M, gas molecular weight; m, porosity; N_A, Avogadro's number; n and n_s, gas molecule concentrations in unit volume of the body correspondingly in the volume of the pores and at the surfaces of them; n_*, maximum possible number of gas molecules per unit surface; p, pressure; p_s, sorption pressure; p^0 and ρ^0, reference values of pressure and density; q_s, sorption flux; R, gas constant; r and ξ, dimensional and dimensionless spatial coordinates; T, absolute temperature; t, time; τ, dimensionless time; t_r and τ_r, dimensional and dimensionless relaxation times; $\hat{\alpha}$, value of α for which $\theta_0-\alpha$ is maximal; γ, proportion of surface in unit volume; η, dimensionless pressure; $\tilde{\eta}$ and η', dimensionless quantities introduced correspondingly in (5) and (7); θ, proportion of adsorption centers occupied by gas molecules; $\kappa = k/(2\mu m)$; μ, viscosity. A subscript 0 corresponds to initial value.

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