The value of δ^h was taken in several cases as the theoretical value of the mean pore size. Figure 2a (curve II) shows the results of calculation of δ^h of an RPM from the formula

$$\delta^h = \frac{4}{K_p \gamma} \frac{P}{1-P} d_e; \tag{12}$$

this formula having been obtained on the basis of the relation $\delta^h = f(P; S_{sp})$ and Eq. (4).

Equation (12) is a special case of Eq. (5) with $K_l = 1$ and coincides with the familiar relations proposed by Kozeni [1] and Karnaukhov [2] to calculate the mean size of pores in porous materials from a model with nonintersecting capillary tubes. For this model, δ^h is identical to δ^m_{av}.

NOTATION

d_p, characteristic dimension of particles making up the porous material; d_{wa}, diameter of warp wire; d_{we}, diameter of weft wire; K_1 and K_2, coefficients; K_p, particle form factor; n_{wa}, number of wires of the warp over the length l; n_{we}, number of wires of the weft over the length l; S_Σ, total area of lateral surface of wires in an arbitrary piece of gauze; t, spacing of wires in gauze; V_Σ, total volume of wires in an arbitrary pieze of gauze; γ, accessibility coefficient, accounting for the reduction in the total surface area of the particles in the material due to their mutual obstruction; φ, angle of contact of warp with weft.

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DIFFUSION OF A PASSIVE IMPURITY IN A POROUS MEDIUM. FRACTAL MODEL IN THE CASE OF AN UNSATURATED MEDIUM

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UDC 532.546

The theory of fractal sets is used to describe convective diffusion in a partly-saturated porous medium.

The study of the diffusion of a passive impurity being transported by a liquid or gas in a porous medium is one of the main approaches used to investigate flows in porous materials. By introducing a neutral indicator (such as radioactive isotopes) into the flow and following its distribution, it is possible to obtain a large quantity of information on the motion and mixing of the fluid. Besides isotopes, the neutral indicator may be a pigment or even temperature if the investigator is interested in processes involving convective heat transfer. Helium is often used as the indicator in the study of transport processes in gases.

It is particularly interesting to study convective diffusion in a partly saturated medium, since in this case it is possible to obtain information not only on the flow itself, but also on the geometric characteristics of the regions occupied by a single phase. It is understood that diffusion becomes "anomalous" in an unsaturated medium and differs appreciably from both normal molecular diffusion and convective diffusion in a completely saturated porous medium, since the diffusion coefficient depends not only on the dynamic characteristics of the

All-Union Scientific-Research Institute of Natural Gases, Moscow. Translated from Inzhenerno-Fizicheskii Zhurnal, Vol. 53, No. 4, pp. 612-617, October, 1987. Original article submitted June 20, 1986.

 0022-0841/87/5304-1172$12.50

flow (as in the case of complete saturation) but also on the geometric characteristics of the one-phase regions.

For the sake of determinateness, we will assume that we are studying the diffusion of a neutral impurity in a liquid while its gas (or another liquid) is being forced from a porous medium. Diffusion in the gas will be ignored.

As is known [1, 2], a displacement problem such as that being studied here can be formulated in terms of percolation (flow) theory [3, 4], and in this case the beginning of filtration of the liquid through the gas-saturated sample will be equivalent to the formation of an infinite liquid cluster permeating the sample. An infinite cluster exists at $p > p_c$, while the volume fraction of liquid (saturation coefficient) c_∞ near the percolation threshold, i.e., at small $\Delta p = p - p_c > 0$, exhibits the following scaling behavior: $c_\infty \sim (\Delta p/p_c)^\beta$, where β is a universal exponent dependent on the dimension of the space d, $\beta \simeq 0.39$ at $d = 3$. Similar scaling behavior is exhibited by certain other characteristics of the infinite cluster, such as the correlation length $l_c \sim l_0(\Delta p/p_c)^{-\nu}$ and the permeability coefficient $k \sim m l_0^2(\Delta p/p_c)^{\bar{t}}$. The universal exponents $\bar{t}$ and ν in the three-dimensional space take the values $\bar{t} \simeq 1.7$, $\nu \simeq 0.9$ [2-5].

It follows from the above formulas that $c_\infty \sim (l_c/l_0)^{-\beta/\nu}$. The geometric structure of the liquid cluster near the percolation threshold is extremely complex and cannot be adequately described by the methods of conventional euclidean geometry. However, it turns out that at distances $l_0 \ll l \ll l_c$, the structure of the cluster can be satisfactorily described within the framework of the theory of fractals — sets of fractional dimensionality.

A set F (enclosed in a euclidean space of the dimension d) will be called a fractal if its Hausdorff (fractal) dimension d_f is not a whole number (in particular, does not coincide with d or with the natural topological dimension F) and if F satisfies the property of self-similarity. By self-similarity, we mean local invariance of F relative to a discrete half-group of dilatations. The fractal dimension can be determined as follows:

$$d_f = \lim_{\varepsilon \to 0} \frac{\ln N(\varepsilon)}{\ln(1/\varepsilon)},$$

where $N(\varepsilon)$ is the minimum number of d-dimensional cubes of the dimension ε covering the set F (it is understood that F is compact). It is obvious that $d_f \leq d$.

Along with geometric (regular) fractals, frequent use is also made of stochastic fractals (nearly all "natural" fractals are stochastic fractals). The properties of stochastic fractals are fully analogous to the properties of geometric fractals if we interpret them only in terms of their mean value. For example, in the formula for d_f, instead $N(\varepsilon)$ we write $\langle N(\varepsilon)\rangle$ for a stochastic fractal, where $\langle \cdot \rangle$ denotes averaging over all possible realizations.

Numerous examples of fractal sets and the corresponding definitions can be found in the book [6] (also see [7]).

A percolating cluster (near the percolation threshold) is a typical example of a stochastic fractal. It can be shown that the fractal dimension of the cluster $d_f = d - \beta/\nu$. Thus, at $d = 3$, we have $d_f \simeq 2.56$.

In connection with the use of fractal models in the present study to describe actual physical processes, we make the following observation. A fractal satisfying the property of self-similarity for all length scales is a mathematical object, and the use of fractal models to describe natural processes can be valid only with certain limitations on the scale of the phenomena being investigated.

In the problem being examined here, there are actually two length scales: the microscale from the characteristic dimension of a pore-space capillary l_0 to the correlation length l_c; the macroscale, characterizing the nonuniformity of the physical fields in the problem — such as the pressure field. The macroscale is determined by the dimensions of the sample and in this regard depends on external (in relation to the problem being considered) parameters, while the microscale depends on l_c and thus, on Δp. Here, the fractal approach is used only in the microscale, i.e., for $l_0 \ll l \ll l_c$. All of the power laws governing self-similarity (with anomalous exponents) are also valid only in this region. The problem is "averaged" with the transition to the macroscale, and the fractal internal structure of the liquid cluster disappears. In the macroscale, all of the geometric parameters of the cluster and the percolation processes are characterized by the normal dimension $d = 3$. Thus, in regard to actual physical objects such as the liquid cluster being examined here, the asymptote in the definition of the fractal dimension d_f should be interpreted not as an actual mathematical limit but only as a transition to the lengths $\varepsilon \sim l_0$, i.e., to the lower boundary of the microscale.

Let us examine the case of steady-state filtration in a partly saturated porous medium at $p_c < p$, $p \approx p_c$. We will assume that the mean rate of filtration is constant within the above-mentioned scales and is low enough so that the flow has no effect on the geometry of the liquid cluster. Considering this and the fact that the scales in question are appreciably greater than the size of the capillary, it can be assumed as a first approximation that Darcy's law is valid for the mean filtration velocity:

$$U = -\frac{k}{\mu} q.$$

Darcy's law is usually used to describe flow on the macroscopic scale, and it may not be satisfied for each specific cluster at the microscopic level. However, in our case, we are dealing with the averaged flow velocity for the clusters present. Thus, Darcy's law can be used in this case.

The structure of the cluster is fairly complex and, along with the channels comprising its "skeleton" (and through which, of course, flow takes place), it contains a substantial number of blind channels (so-called "dead ends") through which liquid does not flow and which participate only in normal molecular (not convective) diffusion. Calculations and numerous experiments show [2-5, 8] that the skeleton of the cluster near the percolation threshold can also be regarded as a fractal. Here, the probability of the cluster c_1 being associated with the skeleton obeys the scaling law $c_1 \sim (\Delta p/p_c)^{\beta_1}$, where $\beta_1 > \beta$. In three-dimensional space, $\beta_1 \approx 0.9$. It follows from this that the fractal dimension of the cluster is greater than the fractal dimension of the skeleton $d_{1f} = d - \frac{\beta_1}{\nu} < d_f$, while the mean flow velocity $U_1 \sim U/c_1$ is significantly greater than that which could be expected if an evaluation was made only on the basis of the saturation coefficient.

Since the motion of a single impurity particle does not possess universality, we will examine the relative motion of two impurity particles. We will designate $\mathbf{r}_i(t)$ as the position of the i-th particle (i = 1, 2) at the moment of time t, $\xi(t) = \mathbf{r}_1(t) - \mathbf{r}_2(t) = \xi(0) + \int_0^t \mathbf{V}(\tau)\,d\tau$.

Since $\langle \mathbf{V}(t) \rangle = 0$, we have $\langle \xi(t) \rangle = \langle \xi(0) \rangle$. This equality means that $d/dt \langle \xi(t) \rangle = 0$, but at the same time $\xi = \langle |\xi(t)|^2 \rangle^{1/2}$, $\frac{d}{dt}\xi^2$, $\left\langle \left| \frac{d}{dt}\xi(t) \right|^2 \right\rangle$ may be nonvanishing. Let us investigate these quantities. It is evident that

$$\left\langle \left| \frac{d}{dt}\xi(t) \right|^2 \right\rangle = \langle \mathbf{V}(t)\,\mathbf{V}(t) \rangle, \tag{1}$$

$$\frac{d}{dt}\xi^2 = 2\int_0^t \langle \mathbf{V}(t)\,\mathbf{V}(\tau) \rangle\, d\tau. \tag{2}$$

The quantity (1) is easily calculated, since it is a simultaneous correlation function and is equal to the mean of the square of the difference in velocities at the points $\mathbf{r}_1(t)$ and $\mathbf{r}_2(t) = \mathbf{r}_1(t) + \xi(t)$. Thus,

$$\langle \mathbf{V}(t)\,\mathbf{V}(t) \rangle = \langle |\mathbf{v}(\mathbf{r}_1(t)) - \mathbf{v}(\mathbf{r}_1(t) + \xi(t))|^2 \rangle \sim U_c^2 f_0(U_c, \xi, l_c, \eta),$$

where U_c is the mean velocity of the impurity particle; $f_0 = f_0(U_c, \xi, l_c, \eta)$ is a weight factor associated with the fractal structure of the cluster; η is the kinematic viscosity.

Considering the self-similarity of the liquid cluster, it can be assumed that the function f_0 is invariant relative to the scale transformations $x \to ax$, $t \to bt$. This leads us to the following equation

$$f_0\left(\frac{a}{b} U_c,\ a\xi,\ a l_c,\ \frac{a^2}{b}\eta\right) = f_0(U_c, \xi, l_c, \eta),$$

thus, $f_0(U_c, \xi, l_c, \eta) = f(Re_c, \xi/l_c)$, where $Re_c = U_c l_c/\eta$.

In the fractal region, f determines the probability that points separated by the distance $\xi(t)$ will belong to the active flow region, i.e., to the liquid cluster.

For the scales $l_0 \ll \xi \ll l_c$, we have

$$f(\mathrm{Re}_c, \xi/l_c) \sim c_\infty \frac{(\xi/l_0)^{d_f-1}}{(\xi/l_0)^{d-1}} \sim c_\infty^2 (\xi/l_0)^{-\delta},$$

where $\delta = d - d_f$, while the coefficient in the above asymptote f may depend on Re_c.

Accordingly, in the regularity region $\xi \gtrsim l_c$, we have $f(Re_c, \xi/l_c) \sim c_\infty^2$. The specific form of the function f in the transitional region $\xi \sim l_c$ is fairly complex and depends on the geometric properties of the porous medium.

An impurity particle introduced into the flow participates in two types of motion: it is transported by the liquid over the skeleton of the cluster at the velocity U_1; having entered a "dead end," the particle is slowed and moves only as a result of molecular diffusion. It leaves the blind channel after the characteristic drift time $\tau_1 \sim l_c^2/D_1$, where $D_1 \simeq D_0(\Delta p/p_c)^{\bar{t}-\beta}$ [8]. The mean drift velocity U_2 is evaluated by the quantity $l_c/\tau_c \simeq D_1/l_c$. Considering that the relative probability of the cluster being associated with the skeleton is $\sim c_1/c_\infty$, we have $U_c \sim \frac{c_1}{c_\infty} U_1 + \left(1 - \frac{c_1}{c_\infty}\right) U_2 \sim U/c_\infty + U_2$. Since $U_2 \sim (\Delta p/p_c)^{\bar{t}+\nu-\beta}$ and $U/c_\infty \sim (\Delta p/p_c)^{\bar{t}-\beta}$, at small Δp it can be assumed that $U_c \sim U/c_\infty$.

To calculate (2), we assume that $\langle \mathbf{V}(t)\mathbf{V}(\tau)\rangle = \langle \mathbf{V}(t)\mathbf{V}(t)\rangle g\left(\frac{t-\tau}{\tau_c}\right)$, where g is a correlation function. We will assume that $g(0) = 1$ and that as $x \to \infty$, $g(x)$ decreases more rapidly than any power of x; $\tau_c \sim l_c/U_c$.

Equation (2) can now be rewritten in the form

$$\frac{d}{dt}\xi^2 \sim U_c^2 f\left(\mathrm{Re}_c, \frac{\xi}{l_c}\right)\tau_c \int_0^{t/\tau_c} g(x)\,dx. \quad (3)$$

First we will examine the case $\xi \ll l_c$ (and $t \ll \tau_c$). Then the integral in (3) can be replaced by the quantity $\sim g(0)t/\tau_c$. Thus

$$\frac{d}{dt}\xi^2 \sim 2U_c^2 \left(\frac{\xi}{l_c}\right)^{-\delta} t c_\infty^2.$$

From this we find (under the condition $\xi_0 = \xi(0)$)

$$\xi^{2+\delta} - \xi_0^{2+\delta} \sim U_c^2\, l_c^\delta\, t^2 c_\infty^2.$$

Assuming that $\xi \gg \xi_0 \sim 0$, we obtain

$$\frac{d}{dt}\xi^2 \sim c_\infty^{2\alpha} U_c^{2\alpha}\, t^{2\alpha-1}\, l_c^{\alpha\delta}, \quad \alpha = \frac{2}{2+\delta} \leqslant 1.$$

At $t \geq \tau_c$, we find that $f(Re_c, \xi/l_c) \sim c_\infty^2$. Thus, Eq. (3) takes the form

$$\frac{d}{dt}\xi^2 \sim 2U_c^2 \tau_c c_\infty^2 \sim 2U\lambda, \ \lambda = c_\infty l_c.$$

Since the diffusion coefficient $D_c \sim \frac{1}{2}\frac{d}{dt}\xi^2$, we find that in the fractal region ($\xi \ll l_c$)

$$D_c \sim c_\infty^{-\alpha\delta} U^{2\alpha}\, t^{2\alpha-1} \lambda^{\alpha\delta}, \quad (4)$$

while outside this region ($\xi \gtrsim l_c$)

$$D_c \sim U\lambda. \quad (5)$$

Equations (4) and (5) can have a somewhat different form. At $\xi \ll l_c$, we have

$$D_c \sim \left(\frac{\Delta p}{p_c}\right)^{\alpha_1} t^{\gamma_1},$$

where $\alpha_1 = \alpha(2\bar{t} - \beta) \approx 2.47$, $\gamma_1 = 2\alpha - 1 \approx 0.64$, while at $\xi \geq l_c$

$$D_c \sim \left(\frac{\Delta p}{p_c}\right)^{\alpha_2},$$

where $\alpha_2 = \bar{\bar{t}} + \beta - \nu \approx 1.19$.

Thus, we differentiate two diffusion regimes — an anomalous regime in the fractal region and the normal convective regime outside this region.

In the calculations performed above, we used numerical values of the critical percolation indices obtained for network models. Since percolation is important in a number of critical phenomena, these indices have the property of universality, i.e., they are nearly independent of the type of network. However, they may also depend on its dimensionality. In the case of porous materials, with the pore space having the structure of a fractal [9], this may be significant. Thus, the numerical values of the above-cited indices α_1 and γ_1 may change. The index α_2 corresponds to the diffusion coefficient outside the fractal region and in this case should be fairly universal.

There has been considerably less study of percolation theory on fractal sets than on regular networks, so it is not yet possible to obtain sufficiently reliable values of the critical percolation in relation to the dimensions of fractal sets.

The above estimates are definitely valid when the porous materials have a sufficiently regular structure or a high porosity and the pore space is not fractal.

NOTATION

P, displacement pressure; p_c, breakthrough pressure (percolation threshold); $\Delta p = p - p_c$; c_∞, saturation coefficient; β, ν, $\bar{t}$, β_1, characteristic indices of the percolating cluster; l_c, correlation length; l_0, characteristic dimension of a pore-space capillary; m, porosity; k, permeability; μ, viscosity; d_f, fractal dimension of the cluster; q, pressure gradient; $\mathbf{r}(t)$, coordinate of the impurity at the moment of time t; $\mathbf{v}(t)$ relative coordinate of particle at the moment of time t; D_0, coefficient of molecular diffusion; U, filtration velocity; f, influence function; D_1, diffusion coefficient in a partly saturated medium τ_1 and τ_c, time of particle drift from the "dead end" and correlation time; D_c, effective diffusion coefficient.

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