THE MERCURY ELECTROPOROMETRY METHOD

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The capillary distribution function over radius f(r) is one of the basic characteristics of a porous medium defining its filtration properties. Among the known methods of finding f(r) the most widely used is the mercury porometry method [1]. Some imperfections of that method were noted in [2] and an alternative was proposed – electroporometry. However the latter is also not free of shortcomings. First, there is the intrinsic error of the method, related to use of an effective medium model which is the limiting case of the precise percolation model and describes medium properties well only far from the percolation threshold, introducing an error of ~20% into parameter calculations near that threshold [3]. This leads to a narrowing of the radius range over which f(r) can be reliably determined. Second, quite large specimens with a large vertical dimension (~1 m) are required to obtain experimental data, many times the size of rock specimens normally studied.

These shortcomings can be overcome by use of a combined method permitting use of the positive features of both techniques – the mercury electroporometry method. The essence of the method is acquisition of experimental data on the change in electrical conductivity of the specimen when it is filled with a nonwetting electrically conductive liquid with simultaneous measurement of pump pressure and subsequent processing of the data to find f(r). The present study will construct and validate an algorithm for finding the function f(r) for such an approach and demonstrate its effectiveness by calculating model problems.

Study of the change in specimen electrical conductivity as it becomes saturated, in contrast to determining the change in volume of mercury pumped into the specimen under pressure as in the traditional mercury porometry method, will directly provide information on the system of conductive pore channels rather than the integral void system in the material [2]. At the same time use of a nonwetting conductive liquid pumped into the medium under pressure eliminates the problem of specimen size. The most natural liquid to use for this purpose is mercury. As for the mathematical processing of the experimental data which is required, as compared to [2] it can be accomplished using a percolation model of transport processes [4] instead of the approximate effective medium model.

The method used for determining electrical conductivity of the medium σ consists of the following. A specimen with cross sectional area S and height ℓ is placed into a volume with mercury, which is forced into the specimen under a pressure P. We pass a current I through the specimen and measure the voltage drop U across it, then find its resistance $R = U/I$ and electrical conductivity $\sigma = \ell S^{-1} R^{-1}$. By performing a series of such measurements at various pressures $\{P_i\}$ and arranging them in correspondence with the minimum capillary radius $r_i = 2\gamma \cos\theta / P_i$, given by the Laplace formula, into which the mercury can penetrate, we obtain the function $\sigma(r_i)$. Here γ is the surface tension coefficient on the mercury–air boundary, θ is the mercury wetting angle on the pore channel surfaces, whereupon the function $\sigma(r_i)$ can either be represented by an interpolation curve or tabulated for subsequent performance of numerical calculations by computer.

In accordance with [4] the values of $\sigma(r_i)$ can be calculated theoretically for a known f(r):

$$\sigma(r_i) = \frac{A \int\limits_{r_i}^{r_c} \left[\int\limits_{x}^{r_c} f(r)\, dr \right]^{\nu} \int\limits_{x}^{\infty} f(r)\, dr f(x)\, dx}{\int\limits_{x}^{\infty} f(r)\, r^{-2}\, dr}, \tag{1}$$

where A is a numerical coefficient [4], r_c is the critical flow radius, determined by the

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condition

$$\int_{r_c}^{\infty} f(r)\,dr = p_c \tag{2}$$

(p_c is the percolation threshold for the chosen lattice modeling the pore space, ν is the correlation radius index [4, 5]).

If we consider the function $\sigma(r_i)$ known, and $f(r)$ unknown, then Eq. (1) is a nonlinear integral equation in $f(r)$. Differentiating that expression once with respect to r_i and performing obvious transformations, we have

$$f(r_i) = -\frac{\frac{d\sigma}{dr_i}\int_{r_i}^{\infty} f(r)\,r^{-2}\,dr}{\left[\int_{r_i}^{r_c} f(r)\,dr\right]^{\nu}\left[\int_{r_i}^{\infty} f(r)\,dr\right]} \tag{3}$$

Or, introducing the notation

$$\lambda(r_i) = -\frac{d\sigma/dr_i}{A}\left[\int_{r_i}^{r_c} f(r)\,dr\right]^{-\nu}\left[\int_{r_i}^{\infty} f(r)\,dr\right]^{-1}, \tag{4}$$

$$z(x) = \int_{x}^{\infty} f(r)\,r^{-2}dr, \quad z_c = z(r_c), \quad \varphi(r_i) = z_c\lambda(r_i).$$

We obtain a nonlinear inhomogeneous Volterra equation of the second sort in standard form

$$f(r_i) = \lambda(r_i)\int_{r_i}^{r_c} f(r)\,r^{-2}dr + \varphi(r_i). \tag{5}$$

Commencing from both the physical meaning of the percolation model of transport processes in an inhomogeneous medium, as well as directly from analysis of Eq. (3), it can easily be seen that it, and consequently, Eq. (5), are valid over the range $0 < r_i < r_c$.

In measuring $\sigma(r_i)$ there may be segments $r_i < r < r_i + \Delta_i$ in which the conductivity of the medium does not change, i.e., $d\sigma(r_i)/dr_i = 0$. If Δ_i does not include r_c, then in such intervals $\lambda(r_i) = \varphi(r_i) = 0$, which according to Eq. (5), leads to $f(r_i) = 0$ at $r_i < r < r_i + \Delta_i$. This implies that the medium does not have capillaries with $r_i \in \Delta_i$. If some Δ_i includes a segment with r_c, then, substituting $\lambda(r_i) = \varphi(r_i) = 0$ in Eq. (5), we also obtain $f(r_i) = 0$. Since in Eq. (4) the integral of $f(r)$ is in the denominator, we formally have a zero by zero indeterminacy. However the equality $d\sigma/dr_i = f(r_i) = 0$ near the initially introduced r_c merely implies absence of capillaries with r_i close to r_c. Therefore it is sufficient to decrease r_c down to the closest r_i for which $d\sigma/dr_i \neq 0$ and take this value for a new r_c, which does not change the meaning or content of all the expressions and avoids the formal indeterminacy. Such cases are found only in media having a function $f(r)$ with two global maxima, i.e., having two different forms of porosity (for example, media with block and interblock pores or in cavernous-fissured rock).

Considering the new definition of r_c, we evaluate $\lambda(r_i)$ and $\varphi(r_i)$.

With consideration of the limitation $0 \leq f(r) \leq M < \infty$ from Eqs. (1) and (4) we have

$$\begin{gathered} |d\sigma(r_i)/dr_i| \leqslant A(1-p_c)^{\nu}M/z_c, \\ |\lambda(r_i)| \leqslant \frac{M}{z_c p_c}\left(\frac{1-p_c}{N_c\delta}\right)^{\nu}, \quad |\varphi(r_i)| \leqslant \frac{M}{p_c}\left(\frac{1-p_c}{N_c\delta}\right)^{\nu}. \end{gathered} \tag{6}$$

Here N_c is the mean value of $f(r)$ in the first interval $r_c - r_1$ ($r_c - r_1 \equiv \delta$).

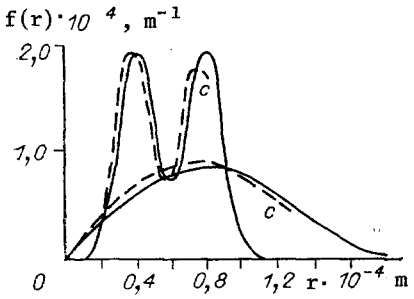

Fig. 1

Since for an integral Volterra equation of the second sort the principle of constringent transformations is valid for any finite λ and φ [6], Eq. (6) makes possible positive solution of the question of existence and uniqueness of the solution of Eq. (5), as well as the validity of using for its determination the method of successive approximations with arbitrary initial function $F^{(0)}(r)$.

Then, having the n-th approximation the normalized function $f^{(n)}r$, to obtain the next approximation we initially consider in Eq. (5) the unnormalized value

$$f_0^{(n+1)}(r_i) = \lambda^{(n)}(r_i)\int_{r_i}^{r_c} f^{(n)}(r)\, r^{-2}\, dr + \varphi^{(n)}(r), \tag{7}$$

and then normalize

$$f^{(n+1)}(r) = \frac{f_0^{(n+1)}(r)}{C^{(n+1)}}, \quad C^{(n+1)} = \left(\int_0^{\infty} f_0^{(n+1)}(r)\, dr\right)^{-1}. \tag{8}$$

Use of Eqs. (2), (4), (7), (8), where the function $\sigma(r_i)$ is considered known from experiment, allows determination of $f(r)$ over the interval $0 \leq r \leq r_c - \delta$. For $r > r_c - \delta$ the function $f(r)$ cannot be determined directly within the framework of the given approach, since "pressure scanning" becomes impossible due to disintegration of the infinite cluster. Certain a priori assumptions are required as to the behavior of $f(r)$ in this region, where in the great majority of cases, it decreases monotonically. We may assume that at $r > r_c - \delta$ $f(r) \sim r^{-k}$, where $k > 1$. Then, for example, for the case $k = 2$ with consideration of Eq. (2) we write

$$f(r) = p_c (r_c - \delta) r^{-2}, \; r_c - \delta < r < \infty. \tag{9}$$

Correspondingly the quantity z, also defined in the range $r - \delta < r < \infty$, must be calculated on the basis of an expression of the type of Eq. (9). In the example presented $z_c = (p_c/3)(r_c - \delta)^{-2}$.

Thus, Eqs. (2), (4), (7)-(9) form a complete algorithm for determining $f(r)$ from the experimentally known function $\sigma(r_i)$. To verify its operation model calculations were performed on a computer. The initial data used were functions $\sigma(r_i)$, obtained by direct calculations with Eq. (1) for specified $f_i(r)$. These functions were then reconstructed by the iteration procedure described, and the $f(r)$ distributions thus found compared to the original $f_i(r)$.

In all cases the function $f^{(0)}(r) = \text{const}$ was used as the zeroth approximation. The calculations showed that the iteration process converged quite rapidly, with 5-10 iterations being required. With proper choice of the function $f(r)$ in Eq. (9) the reconstructed and initial $f(r)$ coincided quite well (~0.1%). Introduction of significant error into Eq. (9), and thus, into the quantity z_c leads to distortion of $f(r)$ near r_c(≲50%). However on the whole the function $f(r)$ is also reconstructed satisfactorily in this case, most accurately in the range of small r, which is of special importance in a number of applications.

To illustrate the efficiency of the method Fig. 1 shows results of reconstruction for two cases: "one-peak"

$$f_i(r) = \left(2r/r_0^2\right) \exp\left[-(r/r_0)^2\right] \quad \left(r_0 = 10^{-4}\ \text{m}\right)$$

and the "two-peak" mentioned above

$$f_i(r) = B^{-1}\{\exp[-(x - x_1)^2/\Sigma^2] + \exp[-(x - x_2)^2/\Sigma^2]\}$$

($x = r/r_0$, $x_i = r_i/r_0 = 0.4$, $x_2 = r_2/r_0 = 0.8$, $r_0 = 10^{-4}$ m, $\Sigma = 0.15$, $B = 2\sqrt{\pi}\Sigma r_0$) original distributions. In both cases the original $f_i(r)$ is shown by a solid line, and the reconstruction by dashes. The $f(r)$ curves are compared over the interval $0 \le r \le r_c$. To the right of r_c the function $f(r)$ can be joined to the point c with a power function $f(r) \sim r^{-k}$, as noted above.

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