ELECTROPOROMETRIC METHOD OF DERIVING A CAPILLARY-RADIUS DISTRIBUTION

I. G. Abdul'manov, S. P. Glushko,
V. V. Kadet, and V. I. Selyakov

UDC 532.546

One needs to know the pore and pore-channel size distributions in considering microstructures for porous materials. Mercury porometry is the most widely used, whose main advantage is that it is simple to convert the measurements to the distributions. However, there are major disadvantages, both purely technological [1] and theoretical: the results for the distribution are dependent on the size of the specimen [2], while the unbounded cylindrical-pore model used in mercury porometry is an inadequate representation for many actual structures such as for granular media and ones with cavities [3]. In mercury porometry, one determines the volume of mercury entering the specimen as a function of pressure, which is interpreted as the mercury penetrating steadily smaller capillaries. No allowance is made for the fact that the pore space consists of pore subsystems and links differing considerably in scale, and consequently, the permeability in a given case at a given pressure is governed by the critical size of the linkage pores, but most of the volume of the injected mercury is in the localized pores, which can mean that the interpretation is incorrect.

When one researches any process where the main part is delayed by the connecting capillaries, one needs a method in which the information is provided by a quantity only slightly dependent on the sizes or even presence of the large-scale nodal pore subsystem. The pore-space structure in a cavity or granular medium requires one to abandon the infinite cylindrical-pore model as a physical representation. An alternative is the lattice model, which provides a better fit to the pore-space topology. The data can be provided not by measuring the volume of nonwetting mercury entering the specimen but the conductivity in different parts when the material is saturated with a wetting electrolyte under gravity. This enables one to eliminate the effects from the nodal pore subsystem.

Sensitivity in Electroporometry for Pore Subsystems Differing in Scale: Infinite Cylindrical Pore Model Applicable. If an initially untreated specimen is immersed at one end in a vessel containing a wetting electrolyte (Fig. 1), the uptake decreases along the vertical, because the liquid rises in a vertical capillary having radius $r(\ell)$ under gravity to a height

$$l = (2\gamma \cos\theta)/(\rho g r(l)), \tag{1}$$

in which γ is the surface tension, θ the wetting angle, ρ density, and g the acceleration due to gravity. In general, the vertical capillary chains in the lattice model are isolated, but one can assume that apart from a coefficient of proportionality, the proportion of filled pores at height ℓ is determined by the critical radius $r(\ell)$, which is related to ℓ by (1). Then the conductivity in the vertical direction will be a function of the saturation and thus of the height, which can provide information on the size distribution.

One measures the conductivity at heights $\{\ell_i\}$ in sufficiently narrow layers $\Delta\ell_i \ll \ell_i$ (Fig. 1a), which are such that the specimen can be taken as uniformly saturated within each part. We evaluate the conductivity in any part from the contributions from the two subsystems. Let the electrolyte have conductivity σ_e, while the skeleton of the specimen has $\sigma_s = 0$. The conductivity in the vertical direction will be governed by the vertically oriented chains of electrolyte-filled pores. One can correct for the cross links by means of a correction factor of the order of one, which is unimportant for estimates. We consider a unit cube in an element. If d is the lattice half-width and $\varkappa$ the proportion of vertical chains in unit volume filled by the electrolyte, the concentration of such chains on a cross section having unit area is $N_s = \varkappa/(4d^2)$, with the links in series in each chain, so the conductivity in a vertical chain is $\sigma_i = \left(\sum_{j=1}^{N_l} R_j^i\right)^{-1}$ [R_j^i is the resistance of link j in chain i, with $N_\ell = 1/(2d)$ the number of links in a chain].

Moscow. Translated from Zhurnal Prikladnoi Mekhaniki i Tekhnicheskoi Fiziki, No. 4, pp. 3-10, July-August, 1988. Original article submitted April 13, 1987.

0021-8944/88/2904-0461$12.50

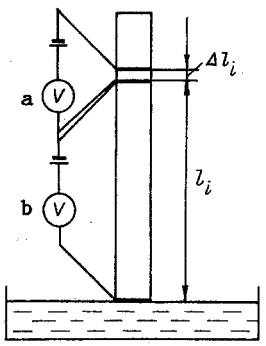

Fig. 1

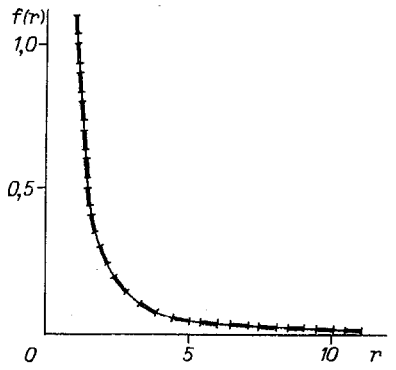

Fig. 2

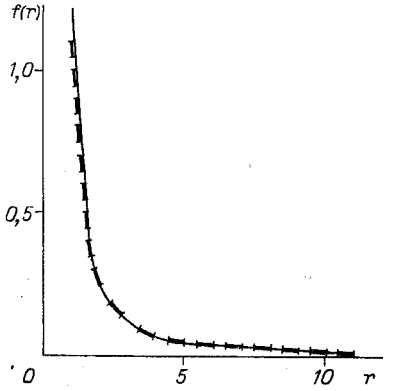

Fig. 3

We estimate the contribution from each subsystem to σ_i on the basis that the characteristic radius of the nodes is $r_b = d/2$, while the connections are cylinders having characteristic radii $r_s \ll d$ and lengths $l \sim d$. Then the resistances in the chain links are $R_s \sim (1/\sigma_e)(d/r_s^2)$, $R_b \sim (1/\sigma_e)(d/d^2)$,, and the ratio of these is $\varepsilon = R_b/R_s \sim (r_s/d)^2 \ll 1$, so $\sigma_i \approx \left(\sum_{j=1}^{N_l/2} (R_s)_j^i\right)^{-1} \sim \sigma_e r_s^2$, from which we get an estimate for the conductivity of the material:

$$\sigma_0 \sim \sum_{i=1}^{N_s} \sigma_i \sim \sigma_e (r_s/d)^2. \tag{2}$$

We see from (2) that the conductivity for a specimen consisting of these subsystems with different scales is dependent only on the linkage resistances, so in electroporometry, one can transfer from a lattice model having bulky nodes to one with point ones, in which the volume, resistance, and filtration impedance of the nodes are zero. The parameters in such a lattice as regards electroporometry are determined by the size distribution for the linkage pores, while the radii for the different links in the capillary chains with any orientation are of the same order (this is a difference from chains containing nodes, where capillaries with differing scales link up in each lattice period, $r_s \ll r_b \sim d$), which enables one to relate the variable-radius capillaries to cylindrical ones having certain effective radii.

We also make some simplifying assumptions: we take the lattice as a simple cubic one, with the field vector **E** collinear with the vertical lattice edges. With this orientation and lattice type, there are marked effects only from the vertical capillary chains (the transverse links have little effect on the current flow pattern because they are perpendicular to **E**). Here again one can use the infinite cylindrical pore approximation, which has much more basis for electroporometry than it does in the mercury case. That model enables one to solve the forward and inverse electroporometry problems in an explicit fashion.

Let the pore space consist of vertical cylindrical pores having the radius distribution f(r). We derive a relation between the electrical conductivity σ for a part of a specimen as a function of the height l on the one hand and the capillary radius distribution on the other (Fig. 1b shows the measurement scheme). All the pores are connected in parallel, so

$$\sigma(l) = \sum_{i=1}^{n_l} \frac{1}{R_i}\Bigg|_{r_i < r(l)} = SN_s\pi \int_0^{r(l)} f(r)\,\sigma_e (r^2/d)\,dr,$$

where S is the cross-sectional area and n_l the total number of filled pores at height l.

The mean-square radius at height l is $\langle r^2\rangle_l = \frac{\sigma(l)\,l}{\sigma_e \pi S N_s} = \int_0^{r(l)} f(r)\,r^2 dr$. We pass to the limit $l \to 0$ to get $\langle r^2\rangle_{l=0} = \lim_{l\to 0} \frac{\sigma(l)\,l}{\sigma_e \pi S N_s} = \int_0^{\infty} f(r)\,r^2 dr$.

We consider $X = \langle r^2\rangle_l / \langle r^2\rangle_{l=0}$, which can be expressed in terms of σ(l) and f(r):

$$X = \frac{\sigma(l)\,l}{\lim\limits_{l\to\infty}[\sigma(l)\,l]} = \int_0^{r(l)} f(r)\,r^2 dr / \langle r^2\rangle_{l=0}. \tag{3}$$

Clearly, $\lim_{l\to 0}[\sigma(l)\,l] = \sigma_0 S$ (σ_0 is the conductivity of the completely saturated specimen). Then $X = \sigma(\ell)/(\sigma_0 S)$ has a one-to-one relationship to $\sigma(\ell)$ and is measurable. On the other hand, we differentiate (3) with respect to $r(\ell)$ and use the normalization $\int_0^\infty f(r)\,dr = 1$ to get

$$f(r(l)) = \frac{1}{r(l)^2}\frac{dX}{dr(l)}\Big/\int_0^\infty \frac{1}{r(l)^2}\frac{dX}{dr(l)}\,dr(l). \tag{4}$$

The relation between $r(\ell)$ and ℓ is defined by (1), and we use this with the relation between X and $\sigma(\ell)$ to convert to the variable ℓ in (4):

$$f\left(\frac{G}{l}\right) = \frac{1}{G}\,l^4\frac{d(\sigma(l)\,l)}{dl}\Big/\int_0^\infty l^2\frac{d(\sigma(l)\,l)}{dl}\,dl \quad (G = 2\gamma\cos\theta/\rho g). \tag{5}$$

Then one can measure $\sigma(\ell)$ for a sequence of ℓ and use (5) to recover the capillary radius distribution.

If we abandon strict constraints on the lattice type and orientation, which are taken as arbitrary, the infinite cylindrical pore approximation becomes inapplicable, and one must use the lattice model. However, this involves major difficulties, and only early steps have so far been made in that direction. It is quite complicated even to solve the direct case (calculating macroscopic characteristics with a given size distribution), and it has so far been done mainly numerically [4-6]. There is no discussion in the literature of the inverse treatment for the lattice model, i.e., recovering the size distribution from macroscopic characteristics as functions of the variable external conditions.

Direct Electroporometry Treatment for any Capillary Structure. One approach is to consider the lattice model approximately to obtain an analytic solution in the forward treatment and thus get an analytic relation between the size distribution and certain characteristics, which can then be inverted at least by some numerical method.

We first consider the first part of this: deriving an approximate analytic solution. We assume that the measurements are made as in Fig. 1a and also that only capillaries having radii less than the critical $r(\ell)$ are filled at a given ℓ, with the latter defined by (1). Then we take the radius distribution as known and the system as infinite because the specimen's dimensions are much larger than the lattice period, and thus the conductivity can be derived.

This is a classical problem in percolation theory, namely calculating the conductivity in a lattice with links (the conductivity in an individual capillary is related to the radius by $q = \sigma_e \pi r^2/d$). Only numerical methods can be used, apart from the case of a classical Bethe lattice [7], so one cannot apply that technique in the inverse treatment. One needs an analytic relation between $\sigma(\ell)$ and the size distribution, which can however be obtained approximately in the effective-medium model [7, 8], which gives approximate results in satisfactory agreement with exact percolation calculations. There are appreciable discrepancies (about 20%) only near the penetration threshold $p_c = \int_0^{r_c} f(r)\,dr$ (r_c is the radius corresponding to that threshold), which is a structural constant governed by the lattice type. Therefore, if one assumes that the $\sigma(\ell)$ measurements are not carried to an excessive height, such that $\int_0^{r(l)} f(r)\,dr \geqslant 1.2p_c$, one is correct in using that model.

The basis of the effective-medium model is that the random-resistance network is replaced by a network containing identical effective resistors subject to the condition that the conductivity of the entire medium as a whole is unaltered. Then the conductivity q_m in one link in the effective medium is [8] defined by

$$\int_0^\infty f_0(q)\,\frac{q_m - q}{(z/2-1)\,q_m + q}\,dq = 0. \tag{6}$$

Here $f_0(q)$ is the link conductivity distribution, while z is the number of nearest neighbors for the lattice type. In what follows, it is convenient to convert from (6) for q_m to the analogous expression for r_m. We incorporate the relation between the capillary conductivity

and radius and use the equality of the random quantities with the functional relationship [9]: $f_0(q)dq = f(r)dr$, so (6) can be rewritten as $\frac{1}{(z/2-1)}\int_{r(l)}^{\infty} f(r)\,dr + \int_0^{r(l)} f(r)\frac{r_m^2 - r^2}{(z/2-1)\,r_m^2 + r^2}\,dr = 0$, from which the f(r) normalization condition gives us the final equation for r_m:

$$\int_0^{r(l)} \frac{zr^2}{(z/2-1)\,r_m^2 + r^2} f(r)\,dr = 2. \tag{7}$$

For definiteness, we put z = 6 in the subsequent calculations, which corresponds to a simple cubic lattice. Then (7) becomes

$$\int_0^{r(l)} \frac{r^2}{2r_m^2 + r^2} f(r)\,dr = \frac{1}{3}, \tag{8}$$

from which we see for example that p_c, which is defined in this model, is 1/3 for this lattice type. The exact value found from percolation theory is 1/4. To obtain a reliable test for using this model, we take $p_c = 1/3$, and then (8) is applicable to describing this lattice for the range $r' < r < \infty$, where r' is defined by

$$\int_0^{r'} f(r)\,dr = 0{,}4. \tag{9}$$

The capillary radius distribution is then used with (8) and (1) to derive $r_m(l)$ and consequently

$$\sigma(l) = \sigma_e \pi \left[\frac{r_m(l)}{d}\right]^2 \frac{S}{\Delta l} \tag{10}$$

(for simplicity, we take the measurement intervals Δl_i as identical and equal to Δl), which solves the direct electroporometry case for this lattice model.

Inverse Electroporometry Treatment: Analytical and Numerical Approaches. We now consider the inverse electroporometry treatment for a given lattice model. We assume that $\sigma(l)$ has been measured at k heights satisfying (9), from which we derive the size distribution; $\sigma(l)$ can readily be converted to the effective radii $r_m(r(l))$ from (1) and (10), which involves solving an integral Volterra equation of the first kind, which is (8) in terms of the unknown f(r). A difficulty is that we do not know the analytic dependence of the kernel here as a function of the upper limit, or rather $r_m(r(l))$ appearing in the kernel has to be determined from experiment and therefore always contains errors. In that case, deriving the solution to (8) is an ill-posed problem and classical methods are not applicable. To derive the size distribution from (8), one must use some regularized method stable under small errors in the input data.

One possibility is to reduce (8) to linear algebraic equations to be solved by regularization. Here we convert to those equations by means of approximating functions, which are based on expanding the size distribution in terms of some linearly independent functions. As usual the a priori information on the size distribution is very limited; it is difficult to give preference to any one approximating-function system over another. Then one can use Weierstrass's theorem on the expansion of a function as a polynomial [10]:

$$f(r) = \sum_{i=-\infty}^{\infty} a_i r^i. \tag{11}$$

General considerations show that f(r) is different from zero only in the range $[r_1, r_2]$, in which r_1 is the minimal capillary radius and r_2 the maximal one. One retains a finite number of terms in (11), and substitution into (8) gives

$$\sum_{i=-n}^{n} a_i F_{ik} = \frac{1}{3} \quad (k = 1, \ldots, m), \tag{12}$$

in which

$$F_{ik} = \int_0^{(r(l))_k} \frac{r^{2+i}}{r^2 + 2\left(r_m^2\right)_k}\,dr.$$

Direct use of (11) will give a system containing an infinite number of unknowns, which does not have a unique solution.

For $m > 2n + 1$, (12) is an overdefined system of algebraic equations for the unknown coefficients $\{a_i\}$ having an inaccurately specified matrix F_{ik}. Regularization [11, 12] can be used to derive the normal pseudosolution, where the regularization parameter should be chosen to match the input-data errors. However, one cannot evaluate the error in using the lattice model to describe the pore space structure exactly, so in fact the error in specifying F_{ik} is unknown and one cannot emply the usual discrepancy condition to choose the optimum regularization parameter. Instead, one can use a quasioptimality criterion or ratio [11], as these do not require a knowledge of the input-data errors.

This has been tested on recovering a known distribution:

$$f(r) = \begin{cases} \dfrac{r_1 r_2}{r_2 - r_1} \dfrac{1}{r^2}, & r_1 \leqslant r \leqslant r_2, \\ 0, & r > r_2,\ r < r_1 \end{cases} \quad (r_1 = 1, r_2 = 11). \tag{13}$$

The Newton–Raphson method was used to solve (8) and determine $\{(r_m((r(\ell))_k)\}$ in the forward treatment from (13) for f(r) and the given set of upper limits $\{(r(\ell))_k\}$. From (9) we first determined the threshold r' for using the model and all the $(r(\ell))_k$ were then selected in the $[r', r_2]$ segment.

The resulting $r_m((r(\ell))_k)$ was used as input for the inverse treatment by solving (12) by regularization with a quasioptimality criterion. The approximating function system decreased as the radius increased:

$$f_{\text{app}}(r) = \begin{cases} \sum_{i=0}^{n} \dfrac{a_i}{r^i}, & r_1 \leqslant r \leqslant r_2, \\ 0, & r > r_2,\ r < r_1. \end{cases}$$

We supplemented (12) with an equation corresponding to the normalization condition $\sum_{i=0}^{n} a_i F_{i,m+1} = 1 \left(F_{i,m+1} = \int_{r_1}^{r_2} \frac{1}{r^i}\, dr \right)$.

Figures 2 and 3 show the inverse treatment to recover (13) [the dashed lines show the true f(r) curve]. In the first case (Fig. 2), exact input data were used to solve the initial problem, while in the second (Fig. 3), the $\{(r_m)_k\}$ were corrupted with about 1% errors when the direct problem had been solved. If the approximating-function system is properly chosen and the input errors are small, the distribution is recovered accurately.

To examine the effects from errors due to a poorly fitting approximating-function system, we recovered the distribution $f(r) = 6(r_2 - r)(r - r_1)/(r_2 - r_1)^3$, $r_1 = 1$, $r_2 = 4$ with the previous $f_{app}(r)$.

Figure 4 shows the results (the dashed line shows the exact distribution). Although on the whole the distribution is recovered fairly well, it is in principle impossible to obtain a fairly close approximation to the exact distribution over a finite interval, so considerable deviations occur. If $f_{app}(r)$ is to be chosen to fit well, one thus needs additional a priori information on f(r). One can then expect high accuracy in recovering f(r), and the result can be represented analytically. If on the other hand the condition for f(r) as an analytic expression is not obligatory and one can instead represent f(r) as a graph, one can adopt the following procedure.

The integral on the left in (8) is replaced by an integral sum in accordance with some quadratic formula. For example, we can divide up the interval $[r_1, r_2]$ with the net $\{r_i = r_{i-1} + h,\ h = (r_2 - r_1)/(n + 1),\ i = 1, \ldots, n\}$ and use the trapezium formula to get

$$\sum_{i=1}^{i_k} f_i A_{ik} = \frac{1}{3}, \tag{14}$$

in which

$$f_i = f(r_i);\ A_{ik} = \begin{cases} \dfrac{r_i^2}{r_i^2 + 2(r_m)_k^2}, & 1 < i < i_k, \\ \dfrac{1}{2} \dfrac{r_i^2}{r_i^2 + 2(r_m)_k^2}, & i = 1,\ i = i_k \end{cases} \quad (r_{i_k} = (r(l))_k).$$

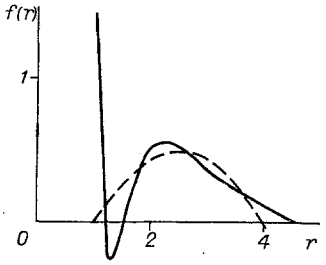

Fig. 4

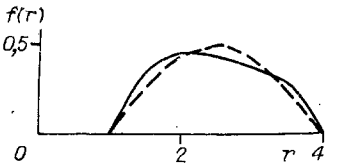

Fig. 5

Then (14) can be solved by regularization as above, which gave values for $\{f(r_i)\}$ as a set of points $\{r_i\}$. Figure 5 shows the inverse solution for the distribution (dashed line) based on (14).

LITERATURE CITED

1. Yu. M. Vol'fkovich, V. S. Bogotskii, et al., "Standard porometry methods and electrochemical applications," Élektrokhimiya, 16, No. 11 (1980).
2. Yu. G. Chirkov and V. I. Rostokin, "Effects of specimen size on mercury porometry curves," Élektrokhimiya, 17, No. 6 (1981).
3. Yu. G. Chirkov and A. A. Chernenko, "Interpreting mercury porometry results," Élektrokhimiya, 15, No. 5 (1979).
4. V. M. Entov, A. Ya. Fel'dman, and E. P. Chen-Sin, "Software simulation for capillary displacement in a porous medium," Programmirovanie, No. 3 (1975).
5. V. M. Entov, A. Ya. Fel'dman, V. A. Yudin, and E. P. Chen-Sin, Simulating Equilibration and Motion for Immiscible Liquids in a Capillary Network [in Russian], Dep. VINITI No. 3608-80, May 10, 1980, Moscow (1980).
6. É. O. Manucharyants, A. Yu. Mishina, and V. A. Yudin, "Simulating nonequilibrium immiscible-liquid displacement in a capillary network," in: Abstracts for the All-Union Seminar on Current Topics in Mathematical Filtration Theory [in Russian], Moscow (1984).
7. J. Ziman, Disorder Models [Russian translation], Mir, Moscow (1982).
8. S. Kirkpatrick, "Percolation and permeation," in: Theory and Properties of Disordered Materials [Russian translation], Mir, Moscow (1977), Issue 7.
9. V. S. Pugachev, Probability Theory and Mathematical Statistics [in Russian], Nauka, Moscow (1979).
10. N. I. Akhiezer, Lectures on Approximation Theory [in Russian], Nauka, Moscow (1965).
11. A. N. Tikhonov and V. Ya. Arsenin, Methods of Solving Ill-Posed Problems [in Russian], Nauka, Moscow (1979).
12. A. N. Tikhonov, A. V. Goncharskii, V. V. Stepanov, and A. G. Yagola, Regularizing Algorithms and A Priori Information [in Russian], Nauka, Moscow (1983).