MEASUREMENT OF THE DIFFERENTIAL CHARACTERISTIC OF THE MACROPOROUS SPACE IN A POROUS BODY

D. P. Litevchuk, M. F. Kazanskii,
and P. P. Lutsik

UDC 541.182.3:537.51

A method has been developed for determining the differential macroporous structure of a dispersed body. The method has been tested on typical standard porous bodies: quartz sand, ceramic, and cellulose.

The structure of the porous base in a body with capillaries is one of the important factors governing the heat and mass transfer, as well as the diffusion and filtration and many other physical processes.

The structural characteristics of porous bodies are of scientific and practical interest in relation to filtration effects in oilfields, soils, water engineering, etc. A basic characteristic of a pore structure is the pore-size distribution; to derive this distribution for a coarse powder of hydrophilic materials one can use the method of [1], which is based on capillary uptake of liquid and involves measurement of the distribution of the water content over the height of a column by cutting up a specimen into parts and drying them.

We [2] have measured the water content as a function of height in the specimen by γ-ray absorption, which avoided disturbing the porous structure and the resulting water distribution.

This method can be extended to the porous structure of bodies with a rigid skeleton in the solid.

The scope for the method is restricted to large pore size; we have extended the method to use it with the larger pores in porous bodies over a wide range of values down to a micropore size (10^{-7} m).

The improvement of the method of [2] consists in balancing the negative capillary pressure from the absorbed dispersed body of liquid by an excess air pressure; balancing of the capillary pressure eliminates the need to measure the distribution of the water content over the height, which greatly simplifies the measurements. It is sufficient to measure the water content only in one section of the body. Also, one needs much less specimen, the height of which in a column constitutes a few centimeters. A further advantage is that the method provides fairly high accuracy in the results with equipment simpler than that used in other methods [3-6].

We tested the method on specimens of quartz sand representing the grain-size fractions 0.16-0.315 mm and 0.063-0.1 mm, as well as a porous ceramic and cellulose.

Washed river sand was taken as a model for a capillary-porous body that will flow; as a model for a brittle gel with a rigid skeleton we took a ceramic plate made in batch 21 at the Slavyensk Works, with an air permeability of 3.6 $m^3 \cdot cm/m^2 \cdot mm\,H_2O \cdot h$, and pore size of 50-70 μ. Cellulose was used in the form of ashless filter papers as a model for a body of colloidal type.

Figure 1 shows the design of the laboratory equipment.

The specimen 1 is first dried at 110°C and is placed in the cylinder 2, whose ends are sealed by the covers 3 and 4. If a loose material is employed, this is poured into a length of 20-25 mm of the cylinder freely with subsequent consolidation by vibration to a given density. A body with a rigid skeleton or one that swells on moistening is used by making it to fit the cylinder and taking additional measures to prevent leakage round the sides.

Light-Industry Technology Institute, Kiev. Translated from Inzhenerno-Fizicheskii Zhurnal, Vol. 19, No. 6, pp. 1031-1037, December, 1970. Original article submitted November 11, 1969.

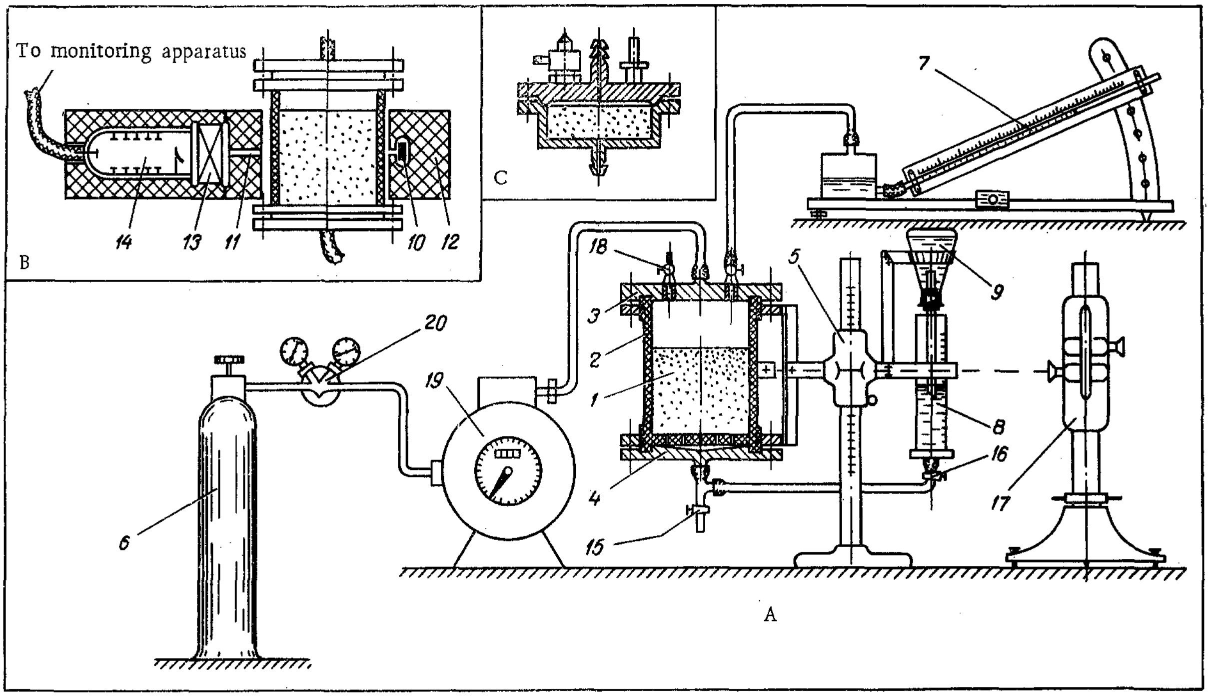

Fig. 1. Scheme of experimental installation.

The cylinder and specimen are fixed firmly in the micrometer device 5, which provides for vertical movement and for locating of the specimen in a definite position. The top cover 3 of cylinder 2 bears three tubes with stopcocks which are joined via hoses to the unfilled part of the cylinder and the source 6 of compressed air, as well as the micromanometer 7 and the atmosphere. The perforated base of the cylinder 2 is joined via the pipe to the lower closure 4 and by a rubber pipe to the measuring vessel 8 in which water from the balancing bulb 9 maintains a given height.

This chamber was used with excess air pressures not exceeding $5 \cdot 10^5$ N/m^2. Tests at higher excess pressures were done with a special strong chamber (Fig. 1B).

The local water content of the specimen was measured by γ-absorption [7] without disrupting the porous structure; the content was measured only in one layer of thickness 1 mm placed 10 cm from the upper end. The horizontal section of the specimen was placed in a plane in which lay the γ-source 10 and the collimation slit 11 (Fig. 1B). The γ-source was of ^{60}Co placed in the lead shield 12, which also acted as a preliminary collimator; the final narrow beam was isolated by the horizontal collimation slot 11 which was 1 mm wide, and which was formed between two lead plates. Direction beyond the slot was the γ-ray detector for the radiation passed by the specimen; this detector was a scintillation counter consisting of the NaI(Tl) single crystal 13 and the photomultiplier 14 type FÉU-14b, whose pulses were recorded by standard equipment.

The γ-ray unit and specimen diameter were chosen on the basis of all the factors [7] needed to provide optimum conditions for water content measurement in this way.

The method was operated as follows. The cylinder 2 containing the dry specimen was fixed rigidly in the micrometer device and set so that the upper end of the specimen was 10 mm above the collimation slit 11. Then a measurement was made of the γ-ray passed by the layer of dry specimen. Stopcock 15 was closed and stopcock 16 was opened to communicate with the balancing bulb 9 in such a way that the water in the measuring vessel 8 coincided in height with the upper edge of the specimen. The horizontal water level was monitored with the microcathetometer 17. With stopcock 18 open, the water from vessel 8 passed via the perforated base into the cylinder 2 and filled the entire pore space in the specimen; then the γ-ray intensity was measured with this maximum water content. These two measurements served to calibrate the γ-system.

Then stopcocks 16 and 18 were closed, and with 15 open compressed air was supplied to the cylinder from the source 6 up to a set value. After the necessary equilibration time had been allowed, we measured the intensity of the γ-rays corresponding to the set pressure. The pressure was maintained constant

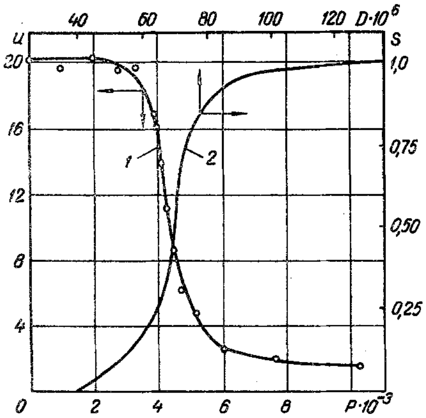

Fig. 2

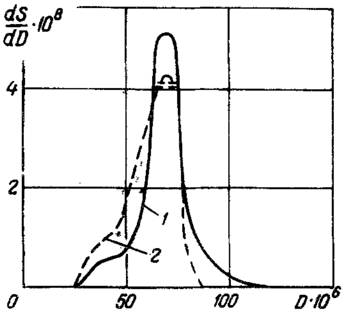

Fig. 3

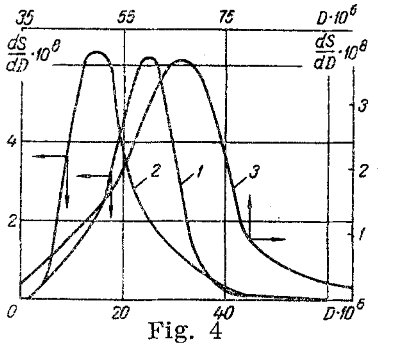

Fig. 4

Fig. 2. Moisture content u, % versus excess pressure P, N/m^2 (1) and integral curve S(D) of pore distribution by size D, m in quartz sand of fraction 0.315-0.16 mm (2).

Fig. 3. Differential curves dS/dD (m^{-1}) of pore distribution by size D, m in quartz sand: 1) fractions 0.315-0.16 mm; 2) 0.3-0.2 mm [9].

Fig. 4. Differential curves dS/dD (m^{-1}) of pore distribution by size D, m in: 1) quartz sand of fraction 0.1-0.063 mm; 2) cellulose; 3) porous ceramic.

via the air reduction valve 20. During the tests, the air pressure was raised in steps to a point where one obtained a constant γ-ray intensity transmitted by the body. The last step was to measure the integral water content corresponding to a maximal wetting of the body; for this purpose, water was passed again into the cylinder from the measuring vessel, and the initial γ-ray intensity was recorded, after which the integral content was determined by weighing and by drying at 110°C to constant weight.

The excess pressure required was dependent on the pore size; to displace the liquid from the largest pores one employed a pressure that was measured by the micromanometer 7, while the smaller pores were examined with water and mercury manometers. For the very smallest pores, the excess pressure was measured with a membrane gauge.

The differential distribution by pore size was deduced by processing the pressure results and corresponding water contents; the integral distribution curve was also deduced in the same way.

Figure 2 shows the recorded water content in a layer of quartz sand of the 0.16-0.315 mm fraction as a function of excess air pressure (curve 1) and the integral pore size distribution S(D) (curve 2).

The integral distribution was calculated as follows. The range used in the excess pressure was divided into n equal parts, and for each change ΔP_i in excess pressure we deduced the corresponding change in water content Δu_i from the observed curve; by definition, the specific water content is

$$\Delta u_i = \frac{S_i \Delta h_i \rho_1}{P_d}\,100 = \frac{S_i \Delta P_i}{P_d g}\,100, \tag{1}$$

where ΔP_i is the change in the excess pressure of the air. For each pore size calculated from Laplace's equation, we deduced the integral distribution function as the ratio of the total change in area of the pores free from liquid at a given excess pressure to the total area of pores free from liquid at the end of the experiment

$$S(D) = \frac{\sum\limits_{i=n}^{k} S_i}{\sum\limits_{i=1}^{n} S_i} \qquad 1 \leqslant k \leqslant n. \tag{2}$$

The values of the S_i in (2) were calculated from (1) via

$$S_i = \frac{P_d g \Delta u_i}{100 \Delta P_i}.$$

The differential characteristic dS/dD for the pores in the above quartz sand is shown as curve 1 in Fig. 3, which was derived by stepwise differentiation of the integral curve [8].

Figure 3 shows for comparison the differential curve for quartz sand of the 0.2-0.3 mm fraction as recorded by others [9]. It is clear that the two curves cover approximately identical integral values of pore sizes, and also there is good agreement between the most probable sizes for the pores.

Figure 4 shows differential curves obtained in this way for: 1) the 0.063-0.1 mm fraction of quartz sand; 2) cellulose; and 3) porous ceramic.

Curve 2 of Fig. 4 shows that cellulose had most of its pores near 15 μ in size, which agrees well with the maker's values for this cellulose (a graded white strip, mean pore size 3-10 μ [11]).

The position of the peak in curve 3 of Fig. 4 shows that the ceramic had 65 μ as its most probable pore size, which agrees quite well with the maker's figure.

This apparatus thus allows one to examine the macroporous structure of such bodies with rigid skeletons and also colloidal ones over a wide range of pore sizes. The laboratory apparatus allows not only the above method to be used but provides also two independent methods of examining pore structure on the basis of capillary phenomena [2] and liquid flow [10]. To process the data by the method of the first bubble [10], we additionally measured the flow of air with the flowmeter 19 (Fig. 1A). This enabled us to process results obtained simultaneously from one run by two different methods, in which sense the laboratory equipment is universal.

NOTATION

$S(D)$	is the integral function of pore distribution by size D;
ΔP_i	is the change of excess air pressure;
Δu_i	is the change of local moisture content of body;
Δh_i	is the change of the height of liquid in capillaries of diameter D_i;
S_i	is the area of pores free from liquid at certain section of body;
P_d	is the weight of dry sample;
ρ_l	is the density of liquid;
g	is the acceleration due to gravity.

LITERATURE CITED

1. A. V. Dumanskii and M. S. Ostrikov, Koll. Zh., 2, 727 (1936).
2. P. P. Lutsik, D. P. Litevchuk, and M. F. Kazanskii, Izv. VUZ, Tekh. Legkoi Prom., No. 2, 112 (1967).
3. E. W. Washburn, Proc. Nat. Acad. Sci., 7, 115 (1921).
4. H. L. Ritter and L. G. Drake, Ind. Eng. Chem. An., 17, 782 (1945).
5. T. G. Plachenov, V. A. Aleksandrov, and G. M. Belotserkovskii, in: Methods of Structure Examination for Powder and Porous Bodies [in Russian], Izd. AN SSSR (1953).
6. Yu. B. Mekler, Koll. Zh., 30, No. 6, 908 (1968).
7. P. P. Lutsik, Legka Prom., No. 4, 17 (1967).
8. N. Lanczos, Practical Methods of Applied Analysis [Russian translation], Fizmatgiz (1961).
9. M. M. Gorokhov, V. I. Lashnev, and N. V. Churaev, in: Heat and Mass Transfer [in Russian], Vol. 6, Part 1, Naukova Dumka (1968).
10. I. P. Ishkin and M. G. Kaganer, Zh. Fiz. Khim., 24, No. 8, 943 (1950).
11. Short Chemist's Handbook [in Russian], Khimiya, Moscow–Leningrad (1964).