

DETERMINING THE MACROPORE STRUCTURE OF
CAPILLARY-POROUS MATERIALS BY
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The macropore structure of quartz sand has been studied experimentally by various methods on the basis of various physical phenomena.

In a study of the pore structure, it is scientifically and practically very important to obtain the structural characteristics of disperse materials by a composite determination. Such a study program concerning the pore structure will establish to what extent various methods complement one another and how closely the true values of the structural pore parameters are approached.

Among the basic characteristics of a pore structure of disperse systems are the pore size and the size distribution.

While various methods of determining the distribution function of micropore sizes have been thoroughly dealt with in the technical literature [1-6], not sufficient attention has been paid to the determination of the macropore distribution function.

The authors have made a composite study of the macropore structure on model capillary-porous materials by various independent methods. As the test object we used quartz sand from river beds, with various dispersion spectra.

The distribution function of pore sizes in the quartz sand specimens was determined experimentally by five methods on the basis of different physical phenomena. We used indirect methods based on capillary and on filtration effects as well as the direct statistical method.

The method by Dumanskii [7] is based on the capillary absorption of liquid by the disperse body and it includes a measurement of the moisture distribution over the column height by cutting the specimen into segments with a subsequent drying of the pieces. In order to prevent a distortion of the pore structure and thus a redistribution of moisture in the specimen, an inevitable result of such an operation, we measured the moisture content over the specimen height by means of gammascopy [8].

The second method is based on compensating the negative capillary pressure in the liquid by means of an external air pressure and, at the same time, measuring the moisture content in the given specimen as well as the excess air pressure [9].

Among the filtration methods we selected the filtering of a "tracer" liquid [8, 10], which is based on the volume displacement of liquid presence in the disperse body by another "tracer" liquid.

We also used the "first bubble" method [11], which is simultaneously based on filtration and capillary effects, with the distribution function of pore sizes determined by applying the Poiseuille law to the volume of a given pore size fraction and with the pore size determined by the Laplace formula.

For an evaluation of our results, we compared them with the pore size distributions in quartz sand which had been obtained in [12] by the statistical method.

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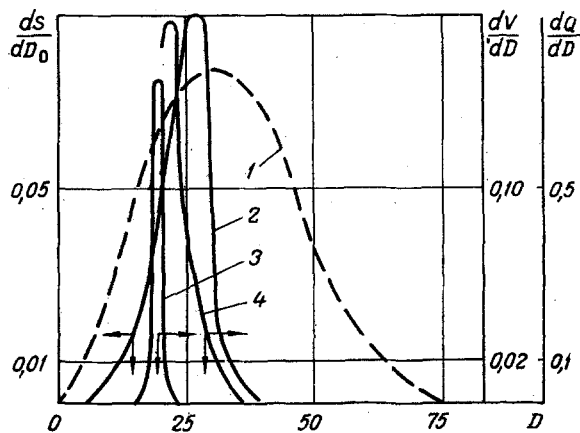


Fig. 1. Differential curves dS/dD_0 (2), dQ/dD (3), dV/dD (4) (μm^{-1}) of pore distribution, with respect of dimension D (μm), in the <0.16 mm sand fraction: statistical method (1), compensation method (2), "tracer" water filtration method (3), "first bubble" method (4).

For plotting the distribution curves, we processed the test data each time in the same manner. First we calculated the integral distribution and then, by discrete differentiation [13], we found from it the differential distribution curve.

The differential curves in Fig. 1, representing the pore size distributions in the fine sand fraction <0.16 mm, have been obtained by four different methods.

According to the diagram, these distribution curves differ from one another appreciably in terms of both the general trend and of the peak "sharpness." They cover different ranges of pore sizes. The maxima correspond to different pore sizes: $29 \mu\text{m}$ (curve 1), $27 \mu\text{m}$ (curve 2), $19 \mu\text{m}$ (curve 3), $21 \mu\text{m}$ (curve 4). The entire range of pore sizes covered by the differential curves based on indirect methods (2, 3, 4) does not extend, however, beyond the limits of the distribution curve obtained by the statistical method but remain within the middle range of the latter. Differential curve 3 obtained by the filtration method covers the narrowest range of pore sizes.

The differential curves in Fig. 2, representing the pore size distributions in the medium sand fraction (0.16-0.30 mm), have been obtained by five methods.

Curves 2, 3, and 4 in Fig. 2 have been obtained by indirect methods and, as in the previous case, they cover the middle range of the statistical curve in the same order as in Fig. 1. These distribution curves, too, cover differential ranges of pore sizes: curve 2 the widest range (25-100 μm) and curve 3 the narrowest range (40-50 μm). The peaks of the curves correspond to different pore sizes: $42 \mu\text{m}$ (1), $67 \mu\text{m}$ (2), $43 \mu\text{m}$ (3), $52 \mu\text{m}$ (4), and $167 \mu\text{m}$ (5).

Curve 5 in Fig. 2 (according to the Dumanskii method) is shifted toward large macropores. The most likely pore sizes are approximately three times larger than the most likely pore sizes in the same specimen based on the other methods of determination. The curve extends beyond the limits of the statistical curve.

The differential curves in Fig. 3, representing the pore size distributions in the coarse sand fraction (0.40-0.63 mm), have been obtained by three methods.

Curves 2 and 4 in Fig. 3, obtained by the method in [9] and the method in [11], respectively, are shifted from one another in the same sense as the corresponding curves for the two smaller sand fractions. An appreciable difference is noted here between the most likely pore sizes. The peak of curve 2 corresponds to $150 \mu\text{m}$, the peak of curve 4 corresponds to $107 \mu\text{m}$, and the peak of curve 3 corresponds to $570 \mu\text{m}$.

Curve 3, which is based on the Dumanskii method, differs here too from curves 1 and 2.

We could not obtain the differential distribution in the 0.40-0.63 sand fraction by the "tracer" water filtration method, because water from this sand was displaced so very fast that the process had been completed in too short a time.

The results of this composite study concerning the macropore structure of quartz sand can, evidently, be interpreted as follows.

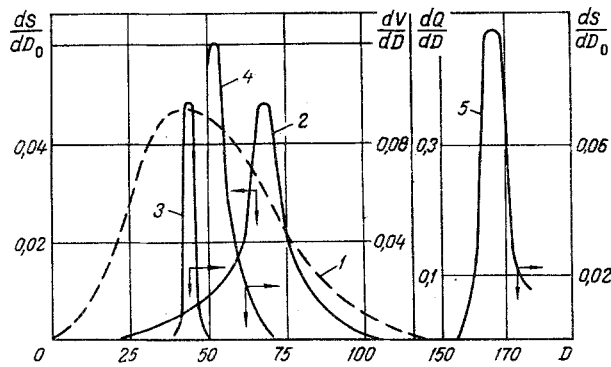


Fig. 2

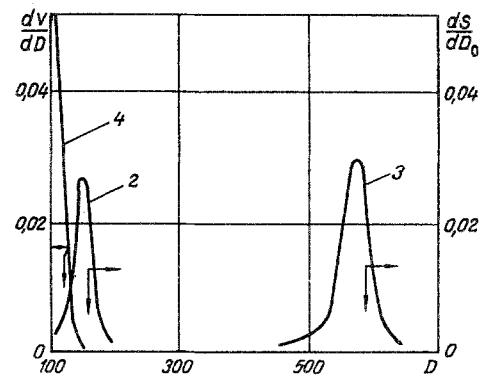


Fig. 3

Fig. 2. Differential curves dS/dD_0 (2), dQ/dD (3), dV/dD (4) (μm^{-1}) of pore distribution, with respect to dimension D (μm), in the 0.16-0.30 mm sand fraction: statistical method (1), compensation method (2), "tracer" water fraction method (3), "first bubble" method (4), A. V. Dumanskii method (5).

Fig. 3. Diffractional curves dS/dD_0 (2), dV/dD (4) (μm^{-1}) of pore distribution, with respect to dimension D (μm), in the 0.4-0.63 mm sand fraction: compensation method (2), A. V. Dumanskii method (3), "first bubble" method (4).

The statistical method yields a distribution of intergranular distances in quartz sand with the minimum and the maximum dispersion.

The methods based on capillary and filtration effects characterize various aspects of the pore structure in dispersion systems. For this reason, these methods yield different calculated pore sizes.

Churaev has shown [12, 14] that the differential curve obtained by the filtration method (curve 3 in Figs. 1 and 2) described the distribution of filtering pores with respect to their equivalent diameter (D). Curves 2 (Figs. 1, 2, and 3), which are based on capillary effects, characterize the distribution of likely surface-to-surface distances (D_0) between neighboring grains and the peak of each curve corresponds to the average of pore sizes most frequently occurring in a specimen.

Thus, a differential curve based on the compensation of the negative capillary pressure corresponds to the distribution of likely surface-to-surface distances between grains, ranging from D_{\min} to D_{\max} , and the peak of such a curve corresponds to the average most frequently occurring length ($D_{m.l.} = D_{av}$) in a specimen.

According to Figs. 1 and 2 (curves 2 and 3), the water duct dimension (D) fluctuates within narrower limits (18-21 and 42-46 μm) than the distance between surfaces of neighboring grains (10-35 and 25-100 μm). This indicates that the equivalent diameter of water ducts is determined essentially by the average intergranular surface-to-surface distance.

It has been shown in [4] that curves 5 and 3 (Figs. 2 and 3), which are based on the rise of water in dry sand, must characterize the distribution of likely intergranular surface-to-surface distance ranging from D_{\max} to D_{av} . Differential curves 5 and 3 in Figs. 2 and 3 characterize the distribution of entirely different pore dimensions, however, which extend far beyond the pore sizes covered by the distribution curves according to the statistical and the indirect methods.

We suggest that the considerable discrepancy between pore size obtained experimentally by capillary rise of water in dry sand and in moist sand respectively is due to the indeterminacy of the wetting angle θ .

In the Dumanskii method of obtaining the distribution function one calculates the pore dimension by the Jouren formula and the wetting angle is assumed zero. At the same time, it has been shown by Deryagin [15] that, during capillary impregnation of porous bodies, this critical angle can be within 60-70°. With a correction for the critical angle ($\theta = 70^\circ$) and the minimum, the most likely, and the maximum pore dimension calculated by the Jouren formula, one obtains the following results: for the differential curve 5 (Fig. 2) $D_{\min} = 53 \mu\text{m}$, $D_{m.l.} = 57 \mu\text{m}$, $D_{\max} = 62 \mu\text{m}$ and for the differential curve 3 (Fig. 3) $D_{\min} = 171 \mu\text{m}$, $D_{m.l.} = 195 \mu\text{m}$, $D_{\max} = 214 \mu\text{m}$. These numerical values of pore dimensions including a correction for the critical wetting angle agree, according to Figs. 2 and 3, fairly well with the distribution curves obtained for the given specimens by other methods.

Distribution curve 4 (by the "first bubble" method, Figs. 1-3) lies in all cases between the distribution curves obtained by compensation of capillary pressure and by filtration of "tracer" water respectively.

Since the "first bubble" method is based simultaneously on filtration and on capillary effects, hence the corresponding distribution curve does apparently describe the distribution of intermediate pore dimensions between D and D_0 .

Thus, the results of our experimental determinations of size distributions by methods suitable for a composite study have led to the following conclusions.

The discrepancies in the results of the pore size determinations are due to the fact that the various methods have been based on different physical phenomena. Moreover, the methods based on capillary effects yield the distribution of likely intergranular surface-to-surface distances.

The methods based on filtration effects, on the other hand, yield the distribution of equivalent pore diameters.

The statistical method yields the closest to actual size distribution of pores in porous bodies.

The "first bubble" method is suitable for determining only the most likely and the maximum size of intermediate pores, inasmuch as the distribution curve does not continue into the range of small sizes.

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