EFFECT OF WETTING ON THE THERMAL CONDUCTIVITY OF GRANULAR MATERIALS

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It is shown that the measured values of the thermal conductivity of a granular system are substantially affected by the wetting of the grains, the nature of the distribution of the liquid, the conditions of wetting of the grains, and the drying of a layer of grains at a heated wall.

The effect of moisture content on the measured values of the effective thermal conductivity of granular systems is most commonly studied with wetted sand. This choice is not based on any theoretical or model study, but rather on the availability of the working material, its widespread use, and traditions.

A comparison of the measured values of the thermal conductivities [1-3] of sands having identical amounts of moisture per unit volume shows a spread of up to 300%. This large spread greatly exceeds the expected error of the measurements and requires a critical analysis.

One of the reasons for the divergence of the experimental values of the thermal conductivity is the use of different methods of measurement without an analysis of systematic errors. Without dwelling on the analysis of the errors of the methods of determining thermal conductivities generally, we consider only the special features of the methods which relate to the study of heat transfer in a moist material. Among these are: a possible increase in the effective thermal conductivity of a material as a result of mass transfer with phase transitions, and a decrease of the thermal conductivity of the material because of the formation of a dried layer at a boundary with a higher temperature. Thus the total heat flux in a wetted material is produced by the collective action of heat conduction through the grains and the liquid and gas in the pores, and diffusive heat transfer by molecules of vapor in pores not filled with liquid. The effective thermal conductivity of a wetted material can be written in the form

$$\lambda = f(\lambda_{\mathrm{fr}}, \lambda_{\mathrm{a}}), \tag{1}$$

where λ_{fr} is the contribution to the effective thermal conductivity from conduction in the wetted material in the absence of diffusive heat transfer in the pores, the so-called "frozen" thermal conductivity, and λ_{a} is the additional contribution to the effective thermal conductivity from diffusive heat transfer, the "mass transfer" thermal conductivity.

Since the "frozen" and "mass transfer" thermal conductivities for a given material depend on the moisture content of the material, the value of the effective thermal conductivity determined by any method will characterize the given material for a given absolute value of the moisture content and distribution of liquid over the volume of the sample.

It is known that it is complicated to establish the nature of the distribution of moisture in a material during an experiment. Moisture, ordinarily uniformly distributed over the volume of the sample at the beginning of the experiment, may, during the experiment, either be redistributed over its thickness if the system is closed so that moisture cannot escape, or partially leave if the system is open so that moisture can escape from the surface of the sample. In neither case is it known to what local or average value of the moisture content the measured values of the effective thermal conductivity should be referred. Most experimenters make the simplest assumption that a uniform distribution of moisture is retained in the sample during the whole experiment, and accordingly the values obtained for the effective thermal conductivities refer to the values of the initial moisture contents m_{m}. From a series of experiments with different initial moisture contents we obtain the relation

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TABLE 1. Characteristics of Instruments for Determining the Thermal Conductivity of Moist Materials

Instrument	h, mm	dT/dx, °K/m	τ_{exp}, min	τ, mm
[6]	10	$3\cdot 10^2$	6—7	8
[6]	34	10^2	30—40	80

$$\lambda = f(m_m). \tag{2}$$

However, if it is assumed that the distribution of moisture in the sample varies during the experiment, in the limit changing from a uniform distribution over the thickness of the sample to a linear distribution, the value obtained for λ is the average value of the thermal conductivity λ_{av} for the sample as a whole, while each cross section of it is characterized by its own value of λ_i depending on the moisture content at the given place.

Since a dry material has the smallest value of the thermal conductivity, the value of λ_{av} for any distribution of moisture in a layer will be larger than that for a dry layer. Consequently, by estimating the error in the measured value of the thermal conductivity arising from the formation of a dried layer we obtain its maximum value. Let us find the maximum duration of an experiment in which the error resulting from the formation of a dried layer of material will be less than a given value.

We assume that during a time τ a dried layer of thickness h_{dry} with a thermal conductivity of the dried material λ_{dry} is formed in a sample of thickness h. We assume that the effective thermal conductivity of the material corresponding to its moisture content m_m is equal to λ. Then the error Δ resulting from the presence of a dried layer can be estimated as

$$\Delta \geqslant 1 - \frac{q^*}{q},$$

where q* and q are the heat fluxes through the system with and without a dried layer.

Expressing the heat fluxes in terms of the thermal resistances of the layers and the temperature drops we obtain, after some simple transformations,

$$h_{dry} \leqslant \frac{\Delta\lambda_{dry} h}{\lambda - \lambda_{dry}}, \tag{3}$$

i.e., in order for the error to be less than our chosen value of Δ, the thickness of the dried layer must be less than h_{dry}.

We assume that the dried layer is formed by the escape of liquid in the form of vapor. Assuming that we know the vapor flux i_v, we obtain the relation

$$\frac{i_v}{\rho_l}\tau = m_m h_{dry}. \tag{4}$$

The vapor flux can be estimated from a formula obtained from a consideration of relations for the vapor flux and the diffusion of vapor in air given in [4]

$$i_{va} \simeq 0.5\cdot 10^{-17}\frac{P_b P}{P_b - P} H \left(\frac{300}{T}\right)^{0.7} \frac{dT}{dx}. \tag{5}$$

Since the material has an internal resistance to the flow of vapor, it is recommended that an appropriate correction factor α be introduced in (5); Globus [5] recommends using the relation

$$i_v = i_{va}\alpha(m_p - m_m), \tag{6}$$

where α = 0.66 is the tortuosity factor of the vapor path; $(m_p - m_m)$ is the water-free porosity. Then using (3)-(6) we obtain

$$\tau = 2\cdot 10^{17}\frac{h\Delta\lambda_{dry}}{\lambda - \lambda_{dry}}\,\frac{P_b - P}{P_b P}\rho_l\,\frac{\left(\frac{T}{300}\right)^{0.7}}{H\frac{dT}{dx}}\,\frac{m_m}{\alpha(m_p - m_m)}. \tag{7}$$

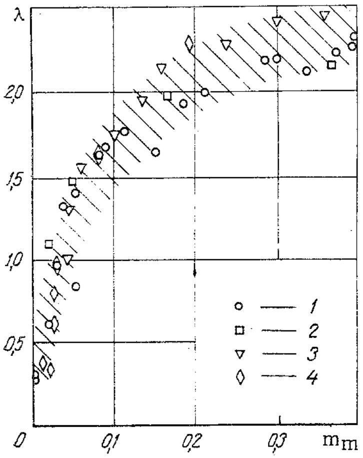

Fig. 1. Experimental results for the dependence of the thermal conductivity of sand on moisture content: 1) obtained in the LITMO (Leningrad Institute of Precision Mechanics and Optics) Laboratory; 2) from [3]; 3) from [2]; 4) from [1]. λ in W/m·°K.

At room temperatures and normal pressure we have

$$\tau = 3.3\cdot 10^{10} h\Delta \frac{\lambda_{\mathrm{dry}}}{\lambda - \lambda_{\mathrm{dry}}} \frac{m_{\mathrm{m}}}{\alpha (m_{\mathrm{p}} - m_{\mathrm{m}})} \frac{1}{\frac{dT}{dx}}. \tag{8}$$

Thus, if the time for the experiment τ_{exp} is shorter than the time τ for the formation of the dried layer, the error in determining the thermal conductivity resulting from the formation of the dried layer is less than Δ.

Measurements of the dependence of the thermal conductivity on the moisture content of various friable materials at room temperatures were performed by the quasistatic method with two instrumental modifications [3, 6].

Table 1 lists the characteristics of the measuring cell of these instruments and the values of the time τ calculated by Eq. (8) with a designated error Δ of less than 1%. In this case the minimum moisture content for which the time of formation of the dried layer is somewhat longer than the time to establish a quasistationary regime is 2%. Table 1 also lists data on the duration of the experiments τ_{exp} corresponding to the time to establish a quasistationary regime in the samples.

Since Table 1 shows that $\tau_{\mathrm{exp}} < \tau$, the formation of a dried layer does not distort the experimental results. Figure 1 shows the experimental values of $\lambda = f(m_{\mathrm{m}})$ obtained with these instruments for quartz sand with rounded particles from 0.2 to 0.5 mm in diameter.

Analysis of Eq. (7) shows that the time τ decreases with a rise in temperature, and for a certain value can become still shorter. For a modified version of the instrument in [3] such a relation is obtained even for a temperature of the order of 40°C and higher.

Thus the present arrangement is not suitable for tests of moist materials at high temperatures. It is necessary either to change its size or to decrease the temperature gradient in the material. We note that the above analysis gives a guaranteed value of the time τ for the formation of a dried layer, calculated under the most favorable conditions; in actual systems a reverse flow of liquid can occur from the heated to the cold part, and this leads to a decrease in the size of the dried layer.

A critical analysis of the methods for measuring thermal conductivities at room temperatures from the points of view described above shows that the divergence of experimental results of up to 300% [3] can hardly be accounted for by imperfections of the methods and the production of a dried layer. A more probable cause of this divergence is the difference between the samples of wetted sands studied.

Wetted sands can differ in mineralogical composition, porosity, degree of roundness of the grains, and in the nature of the distribution of moisture among the grains of sand. These parameters are not ordinarily fixed by the experimenters, although they can have an important effect on the thermal conductivity.

In addition, even for a chemically homogeneous granular material, the particles can have different thermal conductivities. Thus solid particles of quartz sands can have thermal conductivities from 10 W/m·°K for crystalline quartz to 1.4 W/m·°K for amorphous. While such a spread in the values of the thermal conductivity of the grain material changes the value of the effective thermal conductivity of a dry material by less than 15%, it has a substantial effect for a moist material as a result of heat transfer through water bridges between grains.

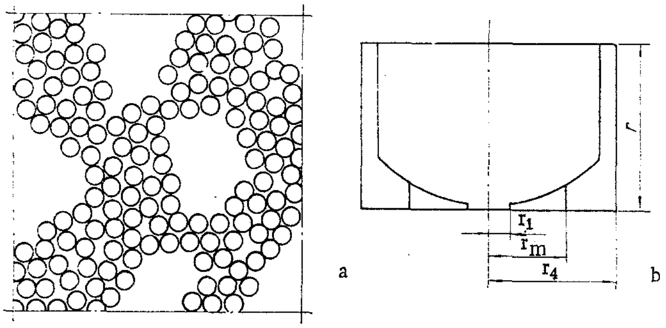

Fig. 2. Structure of a granular material: a) general form of the structure of a dry material; b) elementary cell.

A different porosity of the initial material or the presence of powdered admixtures in the system also make a significant change in the effective thermal conductivity of a moist material [3].

An examination of data reported in the literature on the effective thermal conductivities at room temperature of a single group of sands, for example crystalline quartz with a porosity $m_p = 0.35$-0.40 with rounded particles of diameter $d = 0.5$-2 mm, reveals that the spread of measured values is less than 30%.

We consider now the effect of the nature of the distribution of liquid in the structure of a granular filling on the value of the effective thermal conductivity of a wetted material.

The structure of a granular material can be represented [7] as a skeleton formed by a random but relatively dense stacking of constantly contacting grains — a first-order structure, and a spatial network of voids penetrating the skeleton and forming together with it a second-order structure (Fig. 2a). In considering heat transfer in granular materials an elementary cell is separated out as shown in Fig. 2b. The thermal resistances of such an elementary cell are made up of several terms, including the contact resistances between grains. If the thermal conductivities of a grain (solid component) and the component in the pores (gas) are greatly different, as is the case for granular materials in air ($\nu = \lambda_2/\lambda_1 \simeq 0$), heat transfer occurs mainly near the contacts between grains.

In a moist granular system the third component, water, can be distributed in various ways between the other two components. We consider one of the possible variants of the disposition of the wetting liquid: The water collects in the narrowest places near contacts between grains and forms water bridges with an area πr_w^2 (Fig. 3a). As the moisture content is increased, the area of these bridges increases until they merge and fill up the whole pore space. Since the thermal conductivity of water under normal conditions is almost 20 times as large as that of air ($\lambda_{water} \simeq 0.60$ W/m·°K and $\lambda_{air} \simeq 0.03$ W/m·°K), the thermal conductivity of the whole system increases sharply as a result of the decrease in contact resistance. It is assumed that the bridges are formed uniformly over the whole volume of the material. Thus a moist granular material can be represented by a structure with interpenetrating components in which the thermal conductivity of the skeleton sharply increases with increasing moisture content in comparison with a dry granular material.

Another possible variant of the disposition of water, if it does not wet the grain surfaces, is the formation of individual disseminations of noncontacting drops (Fig. 3b). In this case the dry skeleton can be represented as a uniform component, and the water in it as noncontacting disseminations. As the moisture content is increased, both the absolute value of the disseminations and the number of them per unit volume may increase. The effective thermal conductivity of the whole system for small moisture contents increases much more slowly than in the preceding case, since the dry skeleton exerts an isolating effect. For a large moisture content $m_m \to m_p$ when there is so much liquid that the individual initial disseminations begin to merge, the thermal conductivity of the system increases sharply, and when the water content of the system is equal to its porosity, the effective thermal conductivity does not depend on the method of wetting but is equal to the thermal conductivity of a two-component system consisting of solid particles and a liquid completely filling the pores.

We have considered two limiting cases of the distribution of water in a moist material for which the effective thermal conductivity of the system and its dependence on moisture content differ most strongly. Of course intermediate variants of the distribution of moisture in the structure of a granular material are also possible, but the thermal conductivities of such systems will be intermediate between those of the above cases.

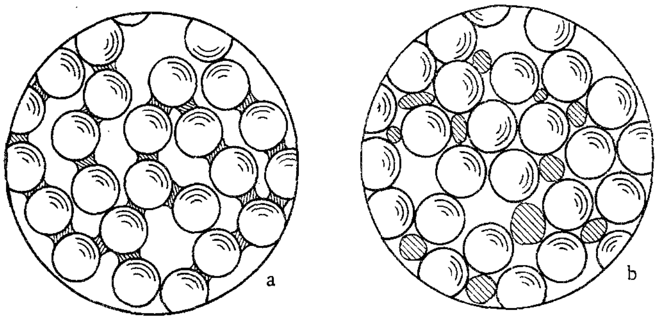

Fig. 3. Distribution of water in a granular material: a) with wettable grain surfaces; b) with nonwettable surfaces.

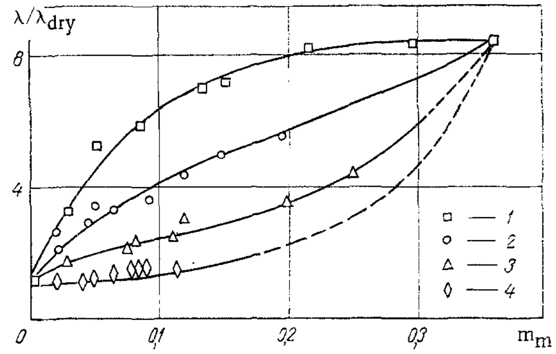

Fig. 4. Dependence of thermal conductivity of sand on moisture content: 1) clean degreased washed sand ($\theta < 3°$); 2) particle surfaces lightly coated with silicone oil ($\theta \leq 30°$); 3) some of the grains coated with a water-repellent film ($\theta \geq 150°$); 4) all grains coated with a water-repellent film ($\theta \geq 150°$); the dashed parts of the curves were obtained by extrapolation.

An experimental test of the above was performed by using the method described in [6] to measure the dependence of thermal conductivities on moisture content for four cases of different distributions of moisture.

Ordinary river sand with a porosity $m_p \simeq 0.36$–0.40 and particle diameters $d \simeq 0.1$–0.2 mm was used as the test material. In order to obtain a uniform distribution of water through the material, and to produce water bridges only at the contacts between grains, the sand was carefully washed, baked, and degreased. In this case the grain surfaces were readily wetted by water, and even for a moisture content of 0.5-1% the water was uniformly distributed over the whole volume and collected at the contacts between particles, as was observed with a 50-power binocular microscope (Fig. 3a).

The contact angle formed at the solid — liquid — gas boundary was used to characterize the wetting of the surface. This was measured separately with a very simple arrangement consisting of a magnifying optical system with a drop of liquid on a substrate of the same material as the particles (quartz glass) placed at the focus. In the first case the surface of the substrate was degreased, and the contact angle θ was smaller than 3°, which agrees with the value in [8]. The contact angle was measured on the screen of the apparatus where the image of the drop was obtained with a 10-fold magnification.

To obtain a structure with a nonwetting liquid in which water is distributed in the form of individual disseminations which are not in contact with one another, the particles of sand were coated with a thin organosilicon film not more than a few microns thick. The water-repellent film was obtained by placing the grains in a 10% solution of dimethyldichlorosilane and benzine and then drying them at 120°C. The quartz-glass plate for measuring the contact angle was coated at the same time. The angle turned out to be about 150-160°. Water did not wet the grains coated with the water-repellent film, but accumulated as individual noncontacting drops in the voids of the large pores (Fig. 3b).

Intermediate structures were obtained in the following way: The particle surfaces were coated with a film of silicone oil ($\theta \simeq 30°$) and a certain number of grains with the water-repellent organosilicon film were added.

The latter two structures had an intermediate distribution of water; i.e., they showed individual water bridges between particles and unconnected drops. As the moisture content was increased the bridges and the individual drops began to merge with one another, and in the limit formed a two-component structure. It was impossible to obtain completely water-saturated sand whose particles were coated with a water-repellent film, since in the mechanical mixing it was difficult to eliminate the air from the sand. The largest amount of water which could be introduced into a system of grains coated with an organosilicon film was 11% of its total volume.

Wetted samples were placed in a cell, weighed to determine the porosity, and then the thermal conductivity was measured. The temperature of the sand did not exceed 25°C, and therefore the change in moisture content of the sample resulting from mass transfer in the moist material could be neglected. The weight of the water added to the sand was determined to ±0.001 g (1%). The error in measuring the thermal conductivity was ~5%.

The experimental results for four different distributions of water in granular material are shown in Fig. 4. The figure shows that the thermal conductivity of a single material with the same moisture content varies by a factor of four depending on the nature of the distribution of the water in the material.

NOTATION

λ, λ_{fr}, λ_a, effective, "frozen," and "mass transfer" thermal conductivities, W/m·°K; m_m, m_p, volumetric moisture content of material and its porosity, m^3/m^3; i_{va}, i_v, vapor fluxes in air and in moist material, $kg/m^2 \cdot sec$; H, heat of vaporization, J/kg; T, temperature, °K; α, tortuosity factor; P, P_b, saturated vapor pressure and barometric pressure, N/m^2; Δ, error in measurement of thermal conductivity resulting from formation of dried layer; h, h_{dry}, thicknesses of test and dried layers, m; ρl, density of liquid, kg/m^3; τ_{exp}, duration of experiment, min; τ, time for formation of dried layer, min; λ_{dry}, thermal conductivity of dried layer, W/m·°K; d, particle diameter, mm; λ_1, λ_2, thermal conductivities of particles and component in pores, W/m·°K.

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