THE ENERGY BOND OF FILM-MENISCUS MOISTURE IN THE MACROPORES OF A DISPERSE MATERIAL

V. M. Kazanskii, P. P. Lutsik,
and M. F. Kazanskii

UDC 541.182.41.6

Direct calorimetric and thermographic tests were used to determine the energy bond for film-meniscus moisture in the macropores of a hydrophilic disperse material. We demonstrate the inapplicability of the theory of capillary condensation to explain the observed bonding energy and we examine the possibility of explaining this effect through the various thermodynamic properties of the body and film water.

It was experimentally observed in [1, 2] that the specific heat of evaporation for a portion of the moisture from the macropores of a disperse material – with a radius of about 10^{-4} m – exceeds the heat of evaporation for free water. Analogous results were confirmed later in [3]. At the same time, we presently assume [4] that the water in the macropores of a material – with a radius in excess of 10^{-7} m in its various states (capillary, film-meniscus, and meniscus) – is free water that is not bound to the solid phase of the material and, consequently, requires no more additional heat for evaporation than is required for the evaporation of free water. Such disagreement between experimental data and existing concepts compelled the authors to undertake a number of additional investigations with regard to this problem. We undertook an experimental determination of the specific heat of evaporation for moisture from the macropores of quartz sand and silica gel, with simultaneous determination of the quantity of moisture for various states in the macropores, by using drying thermograms. A river-bed quartz sand fraction of 0.10-0.15 mm was taken for the test; the sand was first washed and cleansed of all possible impurities. Such sand is hydrophilic with respect to water. The tests were also carried out with sand which was first treated to make it hydrophobic.

The experimental determination of the intrinsic energy bonding moisture to the quartz sand was based on the method of specific heat of evaporation [1] on the laboratory installation described in [5]. The measurements were performed at a temperature of 44.2°C at atmospheric pressure. The sand was moistened to its maximum moisture capacity prior to the test, with a slight excess of free water over the sand surface. The results for the 0.10-0.15 mm sand fraction are shown in Fig. 1 by curve 1a. Curve 2a in this figure shows the evaporation rate as a function of the moisture content of the sand during the course of the test.

We see from Fig. 1 that at the beginning of the test the free water excess is evaporated at a constant rate, followed by the water from water-saturated sand surface. Starting at a moisture content of about 5.5%, the moisture evaporation rate diminishes, indicating a penetration of the evaporation zone, i.e., the evaporation of the moisture from the macropores of the intergrain space in the sand. It is at this time that the moisture in the macropores begins to change from the capillary state to the film-meniscus state, with the menisci at the point of sand grain contact connected to each other by the water films covering the surfaces of the sand grains. Simultaneously, the specific heat of evaporation (curve 1a) is raised slightly in comparison with the specific heat of free-water evaporation – approximately by $3 \cdot 10^4$ J/kg, which corresponds to 1-2% of the heat of free-water evaporation under identical conditions. This slight increase in the heat of evaporation is found in each of the experiments and for each of the sands of various materials [2] and various fractions that we tested, and it was also confirmed in the above-cited work by other authors [3].

Institute of Light Industry Technology. Institute of Civil Engineering, Kiev. Translated from Inzhenerno-Fizicheskii Zhurnal, Vol. 16, No. 5, pp. 798-803, May, 1969. Original article submitted July 12, 1968.

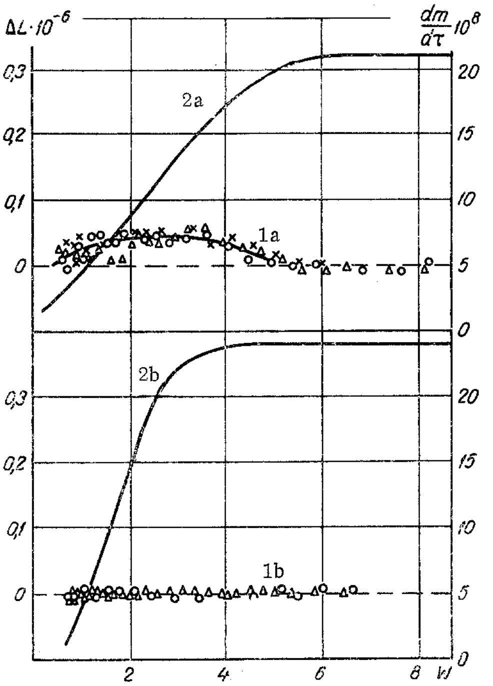

Fig. 1. Increment ΔL (J/kg) (1) in the specific heat of evaporation and in the evaporation rate dm/dτ (kg/sec) (2) for moisture as a function of the moisture content W (%) of ordinary (a) and hydrophobic (b) quartz sand, from the data of various authors.

To determine the physical nature of this increase in the heat of evaporation for the moisture in the macropores, we used the same quartz sand fraction 0.10-0.15 mm for the tests, and the surface of this fraction was first made hydrophobic by treatment in methyltrichlorosilane vapors. The method used to make the sand hydrophobic was taken from [6]. The hydrophobic sand does not become wetted on contact with water; however, when moistened in a cuvette in the installation, under vacuum, in a state of rest, it can retain a certain amount of water in the intergranular state, without forming films about the sand grains.

The results from the measurement of the specific heat of evaporation for the water from the hydrophobic sand are shown by curve 1b in Fig. 1. Curve 2b in that same figure shows the rate of moisture evaporation. As in the case of the drying of ordinary (hydrophilic) quartz sand, the rate of moisture evaporation from the hydrophobic sand (curve 2b) for higher moisture content is constant, and then, beginning with a moisture content of about 4%, begins gradually to diminish. This indicates the penetration of the evaporation zone, i.e., the evaporation of the water from the intergranular space of the sand. Unlike the previous experiments with hydrophilic sand, the heat of evaporation for the intergranular moisture from the hydrophobic sand, for all of its moisture contents, does not change and remains equal to the heat of free-water evaporation (curve 1b).

The experiments with ordinary and hydrophobized quartz sands thus demonstrate that the cause of the increase in the heat of evaporation for the moisture from the macrocapillaries is the interaction of the intergranular moisture in the macropores of the sand with the solid phase as the moisture makes the transition from the capillary state to the film-meniscus state.

The existence of energy to bind the moisture in the macrocapillaries to the solid phase of a porous material shows up clearly in the tests to record the drying thermograms. The drying thermograms for quartz sands in this case were recorded on the installation described in [7]; however, unlike the earlier described experiments the specimen was not placed into a metallic cuvette, but into a Teflon cuvette. Curves 1a and 1b in Fig. 2 are typical drying thermograms for ordinary and hydrophobic quartz sands of fractions 0.10-0.15 mm at a constant air temperature of 52°C and an air pressure of 120 mm Hg. The same figure, curves 2a and 2b, shows the rate of evaporation for the moisture from the same sands during the recording of the thermograms.

Examining the thermogram and drying-rate curve for ordinary quarz sand (curves 1a and 2a in Fig. 2), we see that at the beginning of the test, with the evaporation of the excess free water over the surface of the sand, the evaporation rate is constant, as is the temperature difference between the specimen and the air, which is given in the form of a thermogram. The quantity of heat spent on the evaporation of the water is supplied to the specimen in this case through the constant exchange of heat with the ambient air. With a drop in the drying rate (curve 2a) corresponding to the onset of the transition of the moisture from the intergranular space of the sand from the capillary state to the film-meniscus state, the temperature of the sand rapidly drops, as a consequence of which the temperature difference between the specimen and the air, written in the form of thermogram 1a, increases by 1-2°C, reaching a clear maximum, and it is only after this point that it diminishes. The transition of the moisture from the capillary to the film-meniscus state in the macropores as it is being evaporated is accompanied by an additional endothermic effect, which stands out clearly on the drying thermogram in the form of a slight peak.

It is impossible to explain the endothermic effect by a change in the drying rate, since the drying rate (curve 2a in Fig. 2) at the instant of time corresponding to the cited thermogram maximum not only does not increase, but actually diminishes somewhat in comparison with the evaporation of the free water. This endothermic effect on the thermogram can be recorded only when the intensity of the external heat transfer of the

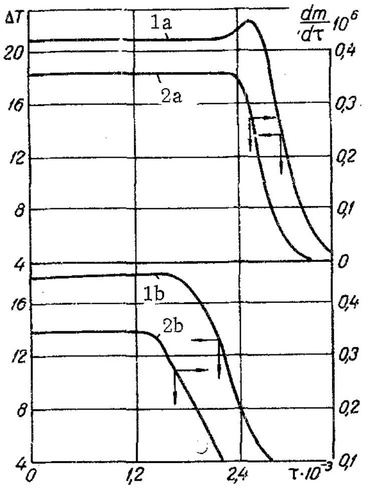

Fig. 2

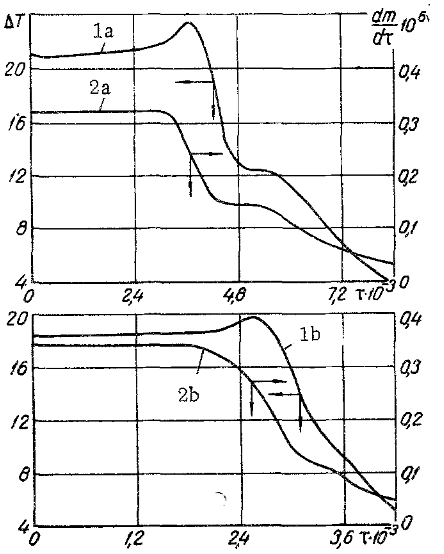

Fig. 3

Fig. 2. Thermograms (1) and drying-rate curves (2) for ordinary (a) and hydrophobic (b) quartz sand (ΔT denotes the temperature difference between the specimen and the air, °C; dm/dτ is the drying rate, kg/sec; τ is the test duration, sec).

Fig. 3. Thermograms (1) and drying-rate curves (2) for MSM silica gel (a) and Belgorod Portland cement (b) (ΔT is the temperature difference between the specimen and the air, °C; dm/dτ is the drying rate, kg/sec; τ is the test time, sec).

disperse material being dried is smaller than the intensity of the given effect, for which the experiments on the recording of the thermograms must be performed in a special Teflon cuvette. However, the metal cuvettes – as a consequence of their greater thermal conductivity – are not suitable for the investigation of this effect. The endothermic effect recorded on the thermogram, accompanying the transition of the moisture from the capillary to the film-meniscus state in the pores, generally amounts to several degrees, which substantially exceeds the error in the recording of the thermogram.

The drying rate for the hydrophobized quartz sand (curve 2b in Fig. 2) in the recording of the drying thermograms under the same conditions is similar in curve shape to the drying rate for ordinary sand. However, we do not observe the above-described endothermic maximum on the thermogram 1b for the hydrophobic sand.

The cited maxima are found on the thermograms under various experimental conditions in the evaporation of the intergranular moisture of hydrophilic sand. Thus, curves 1a and 2a in Fig. 3 are the thermogram and drying rate for sand of fine-porosity MSM silica gel, while curves 1b and 2b show the thermogram and drying rate for sand from the stone of Belgorod Portland cement.

The results of the thermographic investigation of moisture evaporation from the macropores of disperse materials, as well as the above-described results of direct calormetric tests, thus show that the moisture in the film-meniscus state in the macropores of a disperse material is bound to the solid phase of the material. The thermal effect of this bond is approximately $3 \cdot 10^4$ J/kg, i.e., 1-2% of the free-water heat of evaporation.

It is fundamentally important, from our standpoint, that the above-described thermal effect for the bonding of film-meniscus moisture cannot be explained exclusively by the effect of the surface tension of the water, i.e., that which serves to explain the bonding of the moisture in the microcapillaries of the disperse material [4]. Indeed, the most probable radius for the capillaries of the intergranular space of the 0.10-0.15 mm sand fraction is given by quantities on the order of 10^{-4} m. Calculation of the increment in the heat of moisture evaporation on the basis of conventional formulas for capillary condensation [8] yields a magnitude of the order of Joule units per kilogram of moisture, which is smaller by 4 orders of magnitude than the observed effect of moisture bonding. It might be assumed that the moisture in the sand, at the instant of its transition from the capillary to the film-meniscus state, enveloping the sand grains with a thin film, markedly increases its specific surface, which requires the additional expenditure of heat in evaporation. However, the quantitative calculation does not bear out this assumption. Indeed, even if we assume that at a moisture content for the sand of 2-4%, the water covers each sand grain with an even layer, so that the mass of the water per single sand grain will be equal to

$$m = \frac{4}{3}\pi R^3 \rho W,$$

the surface of this water will be given by

$$F = 4\pi R^2,$$

and, consequently, the specific surface of the water is

$$\frac{F}{m} = \frac{3}{R\rho W}.$$

In this connection, the increments in the specific heat of evaporation must amount to

$$\Delta L = \left(\sigma - T\frac{d\sigma}{dT}\right)\frac{\Delta F}{m} = \frac{3\left(\sigma - T\frac{d\sigma}{dT}\right)}{R\rho W}.$$

For the case of sand with a grain diameter of 0.10 mm, with a moisture content of 2%, and at temperatures of 20-70°C, we have

$$\Delta L = 1.5 \cdot 10^2 \text{ J/kg}.$$

Although this estimate is clearly overstated, it is nevertheless still smaller by 2 orders of magnitude than the measured effect.

The results of the calculation thus show that the bonding energy for the moisture in the film-meniscus state in the macropores of a disperse material – a quantity which we have measured experimentally – cannot be explained on the basis of the ordinary concepts of capillary condensation.

It was noted in the work of Deryagin et al. [9] that films of anomalous water may exist in the stable state on a flat quartz surface, with the vapor tension above that surface amounting to 0.93–0.95 of that of ordinary water, which corresponds to a free bonding energy for such moisture of $(1.0\text{–}0.7) \cdot 10^4$ J/kg. If in analogy with the capillary water, we assume for the anomalous water an internal bonding energy (the thermal effect) that is approximately two times greater than the bonding energy of free water [10], we will obtain $(2.0\text{–}1.5) \cdot 10^4$ J/kg, which is close to the magnitude of the bonding energy which we measured for film-meniscus water in the macropores of a disperse material. We can therefore assume that the experimentally determined energy bond for moisture in the film-meniscus state in the macropores of a disperse material is explained by the difference between the thermodynamic properties of free and film water.

Unfortunately, the thermodynamic properties of anomalous water have not been adequately studied and these calculations are therefore exceedingly tentative in nature. However, the inapplicability of the theory of capillary condensation for this case compelled us to seek other possible explanations.

NOTATION

m	is the mass of the water;
R	is the radius of the sand grain;
p	is the density of the sand;
W	is the moisture content;
F	is the surface;
σ	is the surface tension of the water;
T	is the absolute temperature;
ΔL	is the increment in the heat of water evaporation in comparison with free water.

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