THERMAL CONDUCTIVITY OF POROUS MATERIALS IN RELATION TO THE AGGREGATE STATE OF THE FILLER

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The effective thermal conductivity of porous materials is analyzed as a function of the temperature and in relation to the aggregate state of the filler.

For the design of evaporator–sublimator apparatus with porous metal–ceramic baffles as the main components, one must know the effective thermal conductivity of these porous materials. The performance of the heat exchanger here may vary substantially, depending on that effective thermal conductivity.

The effective thermal conductivity of a porous material depends on many factors, including the kind of filler material and its aggregate state. When the porous element of an evaporator–sublimator type heat exchanger operates under vacuum, also during freezing or thawing of moist media, the water which fills the pore space may exist in three aggregate states (water, ice, vapor). Depending on the thermal flux density, which is variable, the ratio of water volume to ice volume will also change.

We will here analyze the thermal conductivity of porous bodies containing a filler in two aggregate states.

The main purpose of this study was to establish the relation between the effective thermal conductivity of a porous material fully saturated with moisture and the temperature. The authors used for this study porous titanium with $\Pi \approx 42\%$ and $d \approx 10^{-5}$ m, fireclay ceramic with $\Pi \approx 31\%$, charges of densely-packed glass balls with $\Pi \approx 45\%$ and $d \approx 10^{-3}$ m, and metal powder with $\Pi \approx 46\%$ and $d \approx 10^{-5}$ m. The selection of metal ceramic and metal powder was dictated by their different modes of contact between particles, with the same thermal conductivity of the matrix material. In a metal ceramic the particles are welded together, while in a metal powder they are tightly compressed. The same applies to the selection of fireclay ceramic and glass ball packets.

The test specimens were prepared in the shape of thin disks (4-12 mm thick) with thermocouples installed inside and at the surface. The thermal conductivity was measured by the steady-state method. The test procedure and the method of feeding the liquid into specimens has been described in [1] and [2].

For the experiment, a porous specimen was filled with water on one side and with ice on the other. In each test, therefore, the temperature had to be maintained constant at both surfaces of the specimen and the interphase boundary could be regarded stationary.

The results of this study are shown in Fig. 1. Curve *a* represents the relation $\lambda_e = f(T)$ for porous titanium ceramic filled with water; curves b and c represent the same relation for fireclay ceramic and glass ball packets, respectively. For comparison, we also show here the thermal conductivity data for dry porous titanium (curves e and f) and for glass ball packets soaked in naphthalene (curve d). It is to be noted that the measurements of thermal conductivity have, in the case of metal ceramics, revealed a difference between the λ_e values for different layers (curves e and f), owing to the nonuniformity of physical properties across the specimen thickness.

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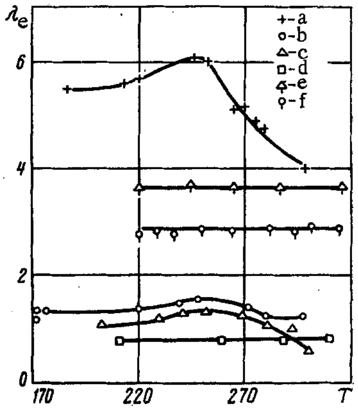

Fig. 1. Effective thermal conductivity of porous materials filled with water, as a function of the temperature: a) porous titanium ceramic; b) fireclay ceramic; c) glass packets; d) glass ball packets filled with naphthalene; e and f) temperature-dependence of λ_e for individual layers in plane metal ceramic body.

As the reference temperature in each test we regarded the mean temperature, namely the average between those of two layers: one containing liquid water and one containing solid ice. The tests were performed within the range of mean temperatures from about 170 to 310°K. In each successive test the temperature was changed at the surfaces, resulting in a different mean specimen temperature and a different location of the interphase boundary.

The diagram indicates that the $\lambda_e = f(T)$ relations for all the porous materials studied here pass through a maximum at some temperature below 273°K.

Within this temperature range, in the absence of moisture or without change of the aggregate state of the filler substance, λ_e almost does not vary with temperature (curves e and f). Filling the specimen pores with moisture, on the other hand, causes a sharp increase in the effective thermal conductivity, by different amounts in different materials. For example, filling a specimen with water causes the thermal conductivity to increase by 0.5 W/m • deg in the case of glass ball packets and by somewhat more (0.6 W /m • deg) in the case of fireclay ceramic, but by 2.0 and 2.8 W/m • deg in the case of metal powder and metal ceramic, respectively. These different increments of λ_e indicate that the thermal conductivity of porous materials depends not only on the thermal conductivity of the filler λ_f and of the matrix λ_m, but apparently also on the purity of the surface and on the structure of particles comprising the porous material. The surface of glass balls is smooth and almost flawless, and filling the interstices with liquid results in a higher thermal conductivity mainly on account of the thus closed contact gaps between particles, but also on account of a liquid filling the pores now. Particles of metal powder and metal ceramic are full of microcracks, protuberances, and asperities which offer a high resistance to the flow of heat. Therefore, filling such materials with liquid causes their thermal conductivity to increase not only on account of better and new heat paths as well as on account of a liquid filling the pores now, but also because the intrinsic thermal conductivity of the particles becomes higher when their microcracks are filled with liquid.

When one side of a porous body is at a temperature below 273°K while its other side is at a temperature above 273°K, then water filling the pores begins to freeze first within a thin layer near the cold surface then, as its temperature drops, the solid zone begins to extend deeper into the porous body. It would seem that λ_e should continue to increase with decreasing temperature, because more water filling the pores transforms into ice and the already higher thermal conductivity of the latter increases further with decreasing temperature [3]. Our experiment has shown, however, that at some temperature T, λ_e begins to decrease as the temperature drops further. This trend is apparently due to the fact that, as the temperature drops, the volume of ice in the pores decreases faster than the volume of the pores ($\alpha = 50 \cdot 10^{-6}$ deg^{-1} for ice, $4 \cdot 10^{-6}$ deg^{-1} for glass, and $1 \cdot 10^{-6}$ deg^{-1} for titanium, at T = 258°K). As a consequence, the heat paths may be broken up inside the pores between ice crystals or between ice crystals and matrix particles. Furthermore, as the material is cooled, water freezes first inside the large pores while remaining liquid inside the micropores – even at temperatures down to 250°K [4]. The ice crystals which form inside large pores and the volume of which decreases at a faster rate than the volume of pores when the temperature drops, act like a suction pump and withdraw water from smaller pores (from the contacts between particles). This partial dehydration of micropores and breakup of thermal contacts between matrix and ice crystals filling the pores does, apparently, cause the effective thermal conductivity λ_e of a porous specimen to decrease, when the latter is cooled through a certain temperature interval. This hypothesis has been confirmed indirectly by tests, indicating that the $\lambda_e = f(T)$ relation is linear when porous materials are filled with a solid such as naphthalene, for example, which do not change state within

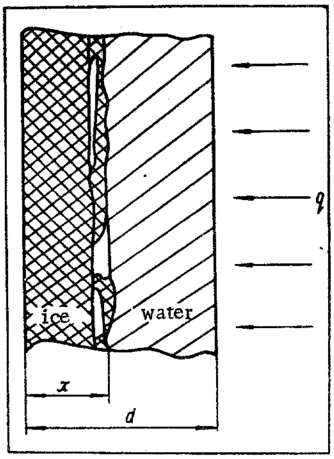

Fig. 2

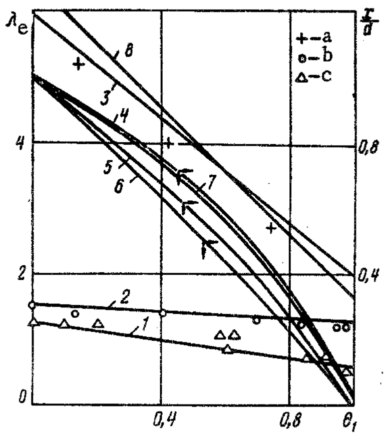

Fig. 3

Fig. 2. Schematic diagram of the model for calculations.

Fig. 3. Curves of λ_e and x/d as functions of θ_1, plotted on the basis of Eqs. (2) and (3): 1, 4) glass balls; 2, 6) fireclay ceramic; 3, 5) porous titanium ceramic; 7, 8) iron powder. Test points: a) porous titanium; b) fireclay ceramic; c) glass balls.

the same temperature interval. Those tests have shown that, as the temperature decreases, the effective thermal conductivity λ_e of nonmetallic porous materials filled with naphthalene increases but decreases in the case of metallic porous materials filled with naphthalene.

Inasmuch as the structure of porous materials is nonhomogeneous and the freezing point of water is not the same in capillaries of different cross sections, the water–ice interface here becomes a rather moot concept. The interface should be regarded as some layer where both phases penetrate each other. On the liquid side this layer is bounded by an isothermal surface at $T = T_0$; on the solid side it is bounded by an isothermal surface at the freezing point of water in the thinnest capillaries. Obviously, the thickness of such a transition layer depends on the structure and the mean pore dimensions of the body as well as on the temperature difference between hot and cold surfaces of a specimen. The presence of such a transition layer should tend to somewhat decrease the effective thermal conductivity but, if any small difference between the thermal conductivity of the transition layer and that of the ice-filled material layer λ_2 is disregarded, then the boundary between the filler phases will be characterized by the location of the $T = T_0$ isothermal surface.

In this case a porous specimen may be tentatively treated as a system of two layers containing liquid water in one and solid ice in the other (Fig. 2). For the layer filled with water we have $q = \lambda_1(T_1-T_0)/(d-x)$; for the layer filled with ice we have $q = \lambda_2(T_0-T_2)/x$; for a specimen of thickness d we have $q = \lambda_3(T_1-T_2)/d$. Eliminating x and q from these equations, we obtain for λ_e

$$\lambda_e = \lambda_1 \frac{T_1 - T_0}{T_1 - T_2} + \lambda_2 \frac{T_0 - T_2}{T_1 - T_2}. \tag{1}$$

We introduce the dimensionless temperatures $\theta_1 = (T_1-T_0)/T_1-T_2)$ and $\theta_2 = (T_2-T_0)/(T_1-T_2)$ for locating the interphase boundary inside a specimen of thickness d ($0 \le x \le d$), finding that they can vary over the intervals $0 \le \theta_1 \le 1$ and $-1 \le \theta_1 \le 0$; in the extreme cases $\theta_1 = 1$ and $\theta_2 = 0$ when $x = 0$ or $\theta_1 = 0$ and $\theta_2 = -1$ when $x = d$. Obviously, θ_1 and θ_2 are related as follows: $\theta_1 - \theta_2 = 1$. Inserting the dimensionless temperature into (1) and expressing θ_2 in terms of θ_1, we can write for λ_e:

$$\lambda_e = \lambda_2 - (\lambda_2 - \lambda_1)\theta_1. \tag{2}$$

Assuming the thermal resistance of a porous body of thickness d to be equal to the sum of the thermal resistances of both layers, we may write $d/\lambda_e = (d-x)/\lambda_1 + x/\lambda_2$. Solving this equation for x/d and substituting expression (2) for λ_e then yields

$$\frac{x}{d} = \frac{\lambda_2(1-\theta_1)}{\lambda_2 - (\lambda_2 - \lambda_1)\theta_1}. \tag{3}$$

The semiempirical relations (2) and (3), which are based on the most simple considerations, make it feasible to plot $\lambda_e(\theta_1)$ and $x/d(\theta_1)$ curves for a porous body containing liquid in one layer and ice in the other layer, and then to compare these curves with test data.

Such curves representing Eqs. (2) and (3) are shown in Fig. 3. The convexity of curves 4, 5, 6, and 7 depends on the relative thermal conductivity $\Delta\lambda/\lambda_2$. A strongly convex curve corresponds to a large value of $\Delta\lambda/\lambda_2$, typical of loose materials. Test points have been plotted on the same diagram, where they come close to the curves based on Eqs. (2) and (3) for porous materials with a poorly heat conducting matrix. The departure of other test points from these curves is evidently explainable by the presence of a transition layer, which can be quite thick in a material with an excellently heat conducting matrix.

NOTATION

λ_e is the effective thermal conductivity of a porous material;
λ_1 and λ_2 are the effective conductivities of a porous material filled with water or ice, respectively;
$\Delta\lambda = \lambda_2 - \lambda_1$;
x is the depth of the solid-phase zone;
d is the thickness of a plane porous body;
T is the temperature, °K;
α is the thermal expansivity;
$T_0 = 273.16$:K;
T_1 and T_2 are the temperatures of the hot surface and cold surface, respectively.

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