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RETARDATION OF A HEAT FRONT IN A POROUS MEDIUM CONTAINING AN EVAPORATING LIQUID

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We have investigated heat transfer in a layer of silica gel impregnated with a liquid (water, aqueous solutions of calcium and magnesium chlorides, formic acid, and carbon tetrachloride). The layer was arranged on a substrate impenetrable for vapor and it was heated from above by a concentrated light flux. It has been found that the evaporation of the liquid contained in the pores of silica gel substantially slows down the propagation of the heat front into the layer so that the effective thermal conductivity of the layer can be reduced to 0.01 W/(m·K); this value is approximately 4–20 times smaller than the values typical of the majority of standard heat-insulating materials. The time of the front lag depends on the layer thickness, density of the incident heat flux, amount of liquid in the pores, and evaporation heat of the liquid. The observed trends in the motion of the front have been described by a simple one-dimensional model that takes into account phase transition (liquid evaporation) in the interior of the porous matrix.

Description of heat transfer in porous materials that contain an evaporating liquid is a very complicated problem, since it requires simultaneous account for the processes of evaporation and heat transfer and also for the effect of capillary and gravitational forces [1, 2]. There are models that describe evaporation of a liquid from vertical and horizontal porous layers adjacent to a heated impenetrable surface [3–6] and also from a penetrable layer into which the liquid enters from one side, whereas the layer itself is heated from the other side [1]. Heat transfer in a liquid-impregnated horizontal layer adjacent to the impenetrable surface from below and heated from above by a radiative heat flux (Fig. 1) has practically not been investigated despite the fact that objects with heat transfer arranged in this way may hold great interest.

In this work, we present the results of an experimental investigation of the system indicated and suggest a simple one-dimensional model of heat transfer in it.

We prepared samples by impregnating (to moisture capacity) a silica gel powder of SK brand (size of particles less than 100 μm, volume of pores 0.9–1.0 cm^3/g, mean diameter of mesopores 10–15 nm) with water (SG-W sample); with saturated solutions of $CaCl_2$ (SG-$CaCl_2$ sample) and $MgCl_2$ (SG-$MgCl_2$ sample); with a formic acid (SG-FA sample), and with carbon tetrachloride (SG-CT sample). The soaked samples were pressed under a pressure of 200–300 atm as tablets of diameter 24.5 mm and thickness from 4 to 20 mm. The density of the dried tablets was 0.50 ± 0.03 (SG-W, SG-FA, and SG-CT), 0.80 ± 0.05 (SG-$CaCl_2$), and 0.73 ± 0.05 g/cm^3 (SG-$MgCl_2$).

We note that the SG-$CaCl_2$ and SG-$MgCl_2$ samples are efficient sorbents of water that are capable of retaining it in equilibrium in the amount of 30–40 wt.% at a temperature of 20–50°C and a relative air humidity of 50–70% [7, 8]. To investigate the effect of the amount of sorbed water on the heat-protecting properties, the SG-$CaCl_2$ and SG-$MgCl_2$ were dried at a temperature of 200°C and then were held in a desiccator

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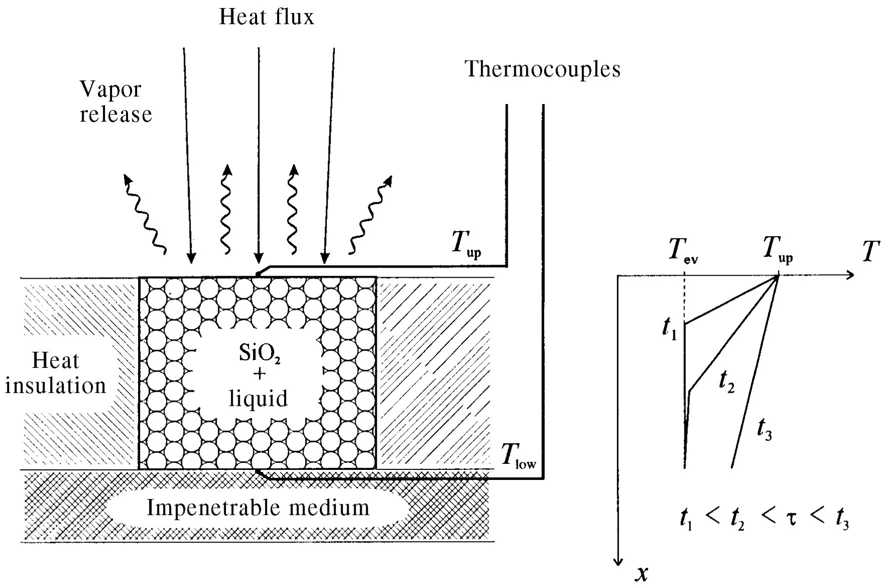
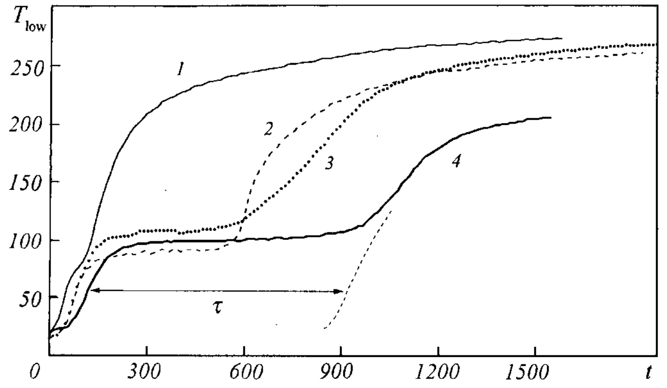


Fig. 1. Schematic representation of the experiment. On the right, the distribution of the temperature of the porous-coating layer at different time moments which is used in the calculation.



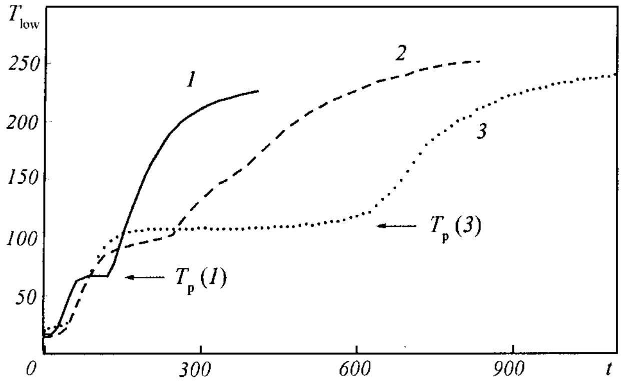
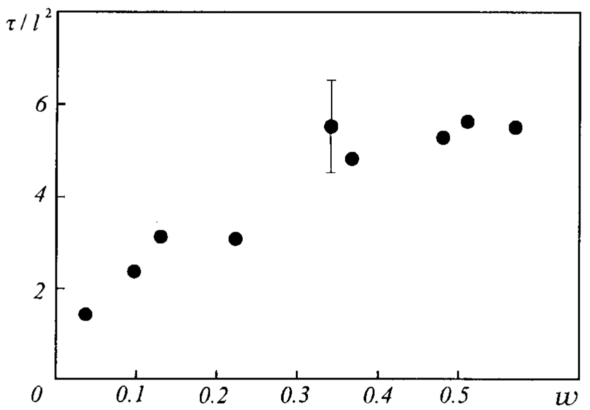


Fig. 2. Experimental dependence of the temperature of the lower face of the porous coating preliminarily held at a relative air humidity of 60% (except for 2) on the time of heat effect at $q = 150 \pm 30$ kW/M^2: 1) the SG-W sample, $w = 0.05$, $l = 10$ mm; 2) the same, $w = 0.9$ (impregnation before irradiation); 3) the SG-$MgCl_2$ sample, $w = 0.6$, $l = 10$ mm; 4) the SG-$CaCl_2$ sample, $w = 0.55$, $l = 13$ mm (also given is the curve for heating the lower face of this sample at $w = 0$ that was transposed from the coordinate origin by the value of τ). T_{low}, ^{o}C; t, sec.

Fig. 3. The function $T_{low}(t)$ for the SG-CT (1), SG-FA (2), and SG-$CaCl_2$ (3) samples impregnated to moisture capacity. $q = 150 \pm 30$ kW/m^2, $l = 10$ mm.

with a fixed moisture content up to the establishment of the needed weight content w of water in the pores, which is defined as the mass of H_2O related to the mass of a dry sample.

The prepared samples were placed in the focus of a DKSShRB-10,000 xenon lamp in the URAN apparatus of radiant heating (Fig. 1). During irradiation, the temperature of the upper surface of the layer T_{up} substantially exceeded the boiling temperature T_{ev} of the liquid introduced into the layer. The mean den-



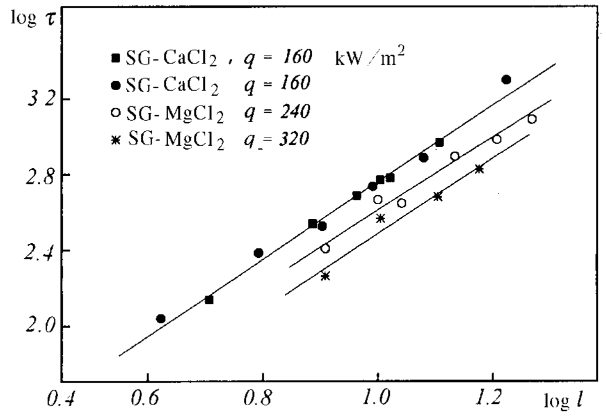


Fig. 4. The dependence of the parameter τ/l^2 on water content in the SG-CaCl$_2$ sample at $q = 200 \pm 30$ kW/m^2. τ, sec; l, mm.

Fig. 5. The experimental dependence of the time τ on the sample thickness at different values of the decreasing power; the samples were preliminarily held at room temperature in a desiccator at a relative air humidity of 60%.

sity q of the heat flux incident on the upper surface of the tablet was determined calorimetrically (with the use of a light-absorbing water-cooled cavity) and was varied approximately from 50 to 500 kW/m^2. The temperature T_{up} of the upper and T_{low} lower (adjacent to the impermeable substrate) surfaces of the layer were measured by Chromel–Alumel thermocouples (Fig. 1). To decrease heat losses, the side surface of the tablet was insulated.

In the course of irradiation the temperature T_{up} rises rapidly (for several minutes) up to a stationary value of the order of 700–1100°C for q = 150–300 kW/m^2, while the temperature T_{low} of the "protected" surface is retained for a long time at a much lower level (Figs. 2 and 3). The dependence $T_{\text{low}}(t)$ for the samples filled with a liquid is characterized by an extended plateau at T_{p} = 70–120°C demonstrating substantial retardation of the heat front. The effect observed can be characterized quantitatively by the retardation time τ, i.e., by the "length" of the plateau (Fig. 2). The retardation time increases with increase in the amount of liquid in the pores (Fig. 4), and the temperature T_{p} corresponding to the plateau closely coincides with T_{ev}: for example, for the SG-CT sample, T_{p} = 70–75°C (Fig. 3) and for CCl$_4$ T_{ev} = 76.5°C.

It has been established that the retardation time is the strongest function of the sample thickness l, with the function $\tau(l)$ being nearly quadratic:

$$\tau \sim l^n, \tag{1}$$

where $n = 2.0 \pm 0.2$ (Fig. 5). This behavior is typical of the kinetics of the heat-front propagation in a medium with a pendant phase transition of the first kind, for example, melting [9–11]. The consequence of expression (1) is that the ratio τ/l^2 is independent of l and can be selected as a convenient parameter for comparing different samples and studying the effect of other factors.

The observed effect is associated much more weakly with the incident heat flux within the range q = 200–500 kW/m^2; however, with a heat loading below a certain limit ($q \sim 150$ kW/m^2) the value of τ increases sharply (Fig. 6a). Probably, this points to the existence of the threshold value of $q = q_{\text{cr}} > 0$, i.e., of a minimum heat flux needed for complete removal of the liquid from the pores. This conclusion agrees with the theory of liquid evaporation from a porous medium [1] claiming that for the "vapor layer" to appear in the pores the heat-flux density must exceed a certain value q_{cr} that depends on the properties of the liquid and of the porous medium. It seems that when $q \le q_{\text{cr}}$ the sample as a whole is heated right through to a

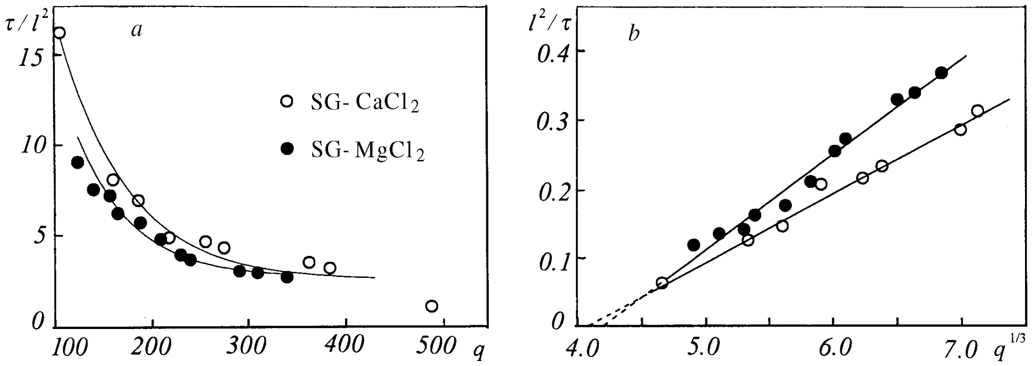


Fig. 6. Effect of the heat-flux density on the parameter τ/l^2 (a) and the determination of the value of q_{cr} (b).

temperature smaller than T_{ev}, with the evaporation being additionally retained by capillary forces, precisely which leads to the considerable increase in τ.

The samples containing the solutions of $CaCl_2$ (SG-$CaCl_2$) and $MgCl_2$ (SG-$MgCl_2$) in their pores, demonstrate approximately the same retardation time under all other conditions being equal (Figs. 5 and 6). On termination of irradiation, the heat-protecting properties of these materials are restored entirely (SG-$CaCl_2$) or partially (SG-$MgCl_2$) (when the samples are kept in air) due to spontaneous sorption of steam from the surrounding air at a relative moisture content of the latter of 60–70%. We note that under these conditions the initial, not salt-impregnated, silica gel adsorbs only 5–7 wt.% H_2O; therefore, to restore the heat-protecting properties of the SG-W sample (see Fig. 2) it should be impregnated with water immediately prior to the exposure to heat.

As was already noted, a successive description of heat transfer inside of the porous layer saturated with liquid requires simultaneous account for heat transfer, evaporation, and capillary and gravitational forces [1, 2]. In the present work, we suggest a simplified model of the process using the approach developed earlier in the theory of heat transfer accompanied by phase transition of the type of melting [9–11]. For the system considered we make the following assumptions: (a) the temperature T inside of the cover depends on the distance x up to the upper (heated) surface and on the time t; (b) the temperature T_{up} of the upper surface is constant; (c) the thermal conductivity of the porous medium is independent of the temperature in the range $T_r - T_{ev}$; (d) the intrinsic heat capacity of the layer can be neglected, i.e., the heat losses in heating the layer are small in comparison with the heat spent to evaporate the liquid. Then the heat balance in the layer of a coating of thickness dx, in which phase change (evaporation) occurs during the time interval from t to $t + dt$, can be written as

$$\lambda\,(dT/dx)_x\,dt = \rho \Delta H_{ev} dx\,, \tag{2}$$

where λ is the thermal conductivity of the layer, $(dT/dx)_x$ is the temperature gradient at the distance x, ρ is the density of the layer saturated with the liquid, and ΔH_{ev} is the evaporation heat given in J/kg of the saturated layer. Assuming $(dT/dx)_x = (T_{up} - T_{ev})/x$ (see Fig. 1), it is not difficult to integrate Eq. (2) with the boundary condition $T|_{x=0} = T_{up}$ and to obtain an expression for the time τ during which the phase change occurs, i.e., the liquid is completely removed from the coating of thickness l:

$$\tau = \rho \Delta H_{ev} l^2 / [2\lambda\,(T_{up} - T_{ev})]\,. \tag{3}$$

We can easily see that the obtained relation describes the experimental dependence $\tau(l)$. The function $\tau(w)$ here (see Fig. 4) is determined by three increasing functions: $\rho(w) = \rho(0)(1 + w)$, $\Delta H_{ev}(w)$ [7], and $\lambda(w)$ [12].

Moreover, relation (3) predicts a sharp increase in the quantity τ on approach of the surface temperature to the value T_{ev}, which confirms, in an explicit form, the threshold effect discussed above.

The function $\tau(q)$ in its analytical form can be obtained from (3) if the relationship between T_{up} and q is known. We assume that the dependence $q(T_{up})$ can be approximated by the function αT_{up}^{γ}, where the effective parameter γ characterizes the relative contribution of reflection and of convective and radiative heat losses on the upper surface of the sample (it is evident that in the case of purely radiative losses $\gamma = 4$). Special measurements at $T_{up} = 700$–1200^{o}C $\gg T_{ev}$ showed that for the systems investigated $\gamma = 3.0 \pm 0.5$. Thus, a large portion of the incident radiant energy is scattered from the sample surface in the form of radiative losses, thus indicating the possibility of using the approximation mentioned. Consequently, Eq. (3) will be written in the form

$$\tau = \rho \Delta H_{ev} l^2 / (2\lambda\beta\,(q^{1/\gamma} - q_{cr}^{1/\gamma}))\ , \tag{4}$$

where $\beta q_{cr}^{1/\gamma} = T_{ev}$. Thus, if we represent the function $\tau(q)$ in the l^2/τ–$q^{1/\gamma}$ coordinates, then the intersection of the obtained straight line with the abscissa axis easily yields the value of the "critical" heat flux $q_{cr} \approx 60$–70 kW/m^2 (Fig. 6b). This estimate has also been confirmed experimentally: the measurement of the retardation time of the front for the SG-CaCl$_2$ sample for $q \approx 50$ kW/m^2 (with T_{up} attaining in this case 250^{o}C) showed that the value of τ exceeds at least 150 min.

As is known, the characteristic time τ_0 of the motion of the heat front in an isotropic solid medium without phase changes can be described as $\tau_0 \approx \rho c l^2 / 2\lambda$ [11]. In a medium with a phase transition of the first kind the heat front is retarded additionally and, as a consequence, the apparent heat conduction decreases. Using Eq. (3), the retardation effect can easily be evaluated numerically:

$$k = \tau/\tau_0 = \Delta H_{ev} / [c\ (T_{up} - T_{ev})]\ .$$

Here, for the effective thermal conductivity λ_{app} we may write

$$\lambda_{app} = \lambda / k = \lambda c (T_{up} - T_{ev}) / \Delta H_{ev}\ .$$

In particular, the effective thermal conductivity of the SG-CaCl$_2$ and SG-MgCl$_2$ systems ($c \approx 1.5$ J/(g·K); $\Delta H_{ev} \approx 1.5$ kJ/g) will decrease due to water evaporation approximately by a factor of 10 for $T_{up} - T_{ev} = 100^{o}$C, which makes it possible to obtain efficient heat-protecting coatings with $\lambda_{app} \approx 0.01$ W/(m·K). This value turns out to be much smaller than that for typical "passive" heat insulators for which $\lambda > 0.04$ W/(m·K) at $T = 20^{o}$C and $\lambda > 0.1$–0.3 W/(m·K) at $T = 1000^{o}$C [13].

It follows from Eq. (3) that the retardation time can be increased substantially by using liquids with a high evaporation heat and porous matrices with a low stationary thermal conductivity. The effect of the evaporation heat of the impregnating liquid on the effect of heat-front retardation was fixed experimentally by comparing the SG-W and SG-MgCl$_2$ samples (Figs. 2 and 3). Formic acid has an evaporation temperature closely coinciding with that of water ($T_{ev} = 100.6^{o}$C) and a smaller value of ΔH_{ev}, precisely which leads to the decrease in the parameter τ in comparison with the SG-W sample.

The data given indicate that porous coatings containing liquid are capable of substantially retarding the heat front and demonstrate an abnormally low thermal conductivity when $T > T_{ev}$. We have studied the dependences of the retardation time on the incident heat-flux density, coating thickness, amount of liquid, and the heat of its evaporation. It is shown that these dependences can be described satisfactorily within the framework of a simple one-dimensional model that takes into account evaporation of liquid inside a porous medium. The results obtained may serve as a basis for practical development of new efficient and recovered heat- and fire-protecting active coatings.

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NOTATION

c, heat capacity; $k = \tau/\tau_0$, dimensionless coefficient; l, thickness of coating; n, exponent in Eq. (1); q, heat-flux density; q_{cr}, minimum heat-flux density needed for complete removal of a liquid from a porous medium; T, temperature; T_{ev}, boiling temperature of liquid; T_{low}, temperature of the lower surface of the porous layer; T_p, temperature of heat front retardation in a layer; T_r, temperature of the surrounding medium; T_{up}, temperature of the upper surface of the layer; t, time; w, weight content of the liquid in the layer; x, coordinate; $\alpha = q/(T_{up})^{\gamma}$, parameter; β and γ, parameters in Eq. (4); ΔH_{ev}, heat of liquid evaporation in a porous medium; λ, stationary heat-conduction coefficient; λ_{app}, effective heat-conduction coefficient (with a correction for evaporation); ρ, density; τ, time of heat-front retardation; τ_0, characteristic time of heat-front propagation in a medium without a phase change.

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