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THERMAL CONDUCTIVITY OF A SILICA GEL + CALCIUM CHLORIDE SYSTEM: THE EFFECT OF ADSORBED WATER

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The effective thermal conductivity of a KSK porous silica gel + calcium chloride composite is measured at T = 293 K using the hot-wire method, and the effect of the quantity w of sorbed water on it is studied. It is shown that the w-dependence of the thermal conductivity λ is determined by the degree of filling of the matrix pores with a salt + water system and by the phase transitions in this system. The value of λ increases with a filling increase, this occurring most sharply when a continuous phase of the aqueous solution of salt is formed inside the sorbent layer. The results obtained are adequately described by the Luikov–Bjurström model.

Composites consisting of a porous host matrix and a hygroscopic salt, which is located in the pores, are efficient water sorbents in such important applications as deep drying of gases, sorption heat pumps, Freonless refrigerators, etc. [1-5]. Of basic interest for the analysis of these applications is information on the effective thermal conductivity λ of such composites, which, at constant temperature and pressure, is specified mainly by the thermal conductivity of individual components (the matrix and the impregnated substance), their volume fraction, the porosity of the composite, and its pore size l [6-9]. Since the relative fraction of components can range widely at both the stage of synthesis and directly during the use of composites, for example, due to the water sorption, of great interest is measurement of the thermal conductivity of the composite as a function of the salt and water content, and also an analytical description of the experimental data with the aid of models developed in the literature.

For one-component porous media that do not contain salt (silica gels, zeolites, building materials, rocks, etc.), the effect of the adsorbed water was considered by many authors [8-11]. It was demonstrated that the presence of water in the pores in an amount larger than 5–10 wt.% leads to an increase in the effective thermal conductivity of the system, with λ monotonically increasing with sorption, and when the free volume of the specimen is filled with water by more than 90–95%, the thermal conductivity increases stepwise [11]. For adequate description of the conductivity of moist porous media, various mathematical models, which are reviewed in [11, 12], have been worked out.

Unlike one-component porous sorbents, the sorption in the considered composites is accompanied by phase transitions in a dispersed salt + water system [1-5]. At small magnitudes of the sorption, solid $CaCl_2 \cdot NH_2O$ ($N = 0.33, 1, 2$) crystalline hydrates are formed in the matrix pores, which afterward dissolve in subsequent portions of the sorbed water, producing an aqueous solution of salt that can completely occupy the host-matrix pores [1-5]. In this connection, the analysis of experimental data must allow for the possibility of such phase transitions. The first study of the effect of water sorption on the thermal conductivity of a silica gel + calcium chloride system was carried out in [2, 5] using the "hot-wire" method [13]. It turned out that the thermal conductivity slightly changes at small magnitudes of the sorption ($w < 0.4$) and appreciably increases when $w > 0.5$ (here, w is the water mass referred to the mass of the dry sorbent). At the same time, the small number of experimental points presented in these works makes it possible to speak only of the trend toward variation in the thermal conductivity, whereas a quantitative analysis requires more detailed measurements.

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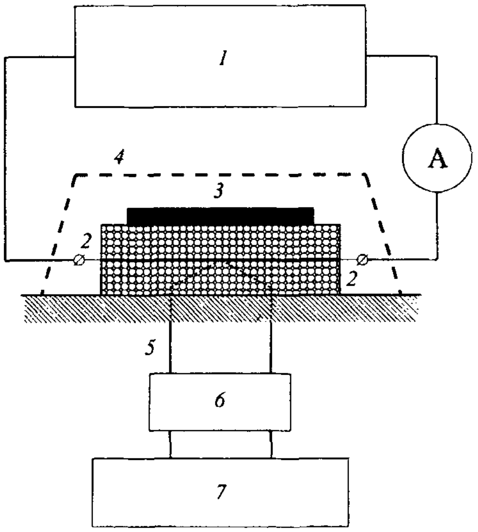

Fig. 1. Diagram of the setup for measuring the thermal conductivity: 1) direct-current source; 2) blocks of the measured specimen; 3) pressing load (100–200 g); 4) hermetic container; 5) thermocouple, 6) amplifier; 7) recorder.

The current work aims at measuring the thermal conductivity of a porous silica gel + calcium chloride composite over a wide sorption range, studying the effect of the content of salt and the sorbed water, and analytically describing the experimental data obtained.

Preparation of Specimens. As a porous matrix, silica gel of the KSK grade with open mesopores was used (the particle size of the powder was 50–100 μm, the mean diameter of the pores was $l = 15$ nm, and the volume of the mesopores was $V_\mu = 0.9–1.0$ cm^3/g). The matrix was impregnated, according to moisture capacity, with aqueous solutions of calcium chloride with a salt concentration of 20 ± 1 wt.% (specimen 1) and 40 ± 2 wt.% (specimen 2). Furthermore, a part of specimen 2 after drying at $T = 473$ K was impregnated once more with a saturated $CaCl_2$ solution (specimen 3). The ratio M_C/M_S = $CaCl_2$ mass/SiO_2 mass was 0.23–0.24 (1), 0.51–0.55 (2), and 1.00–1.04 (3). The impregnated specimens were compacted under a pressure of 150–200 atm into rectangular blocks that measured 70 × 30 × 10 mm and were calcined at $T = 473$ K until the weight loss discontinued, following which they were saturated with water vapor in the desiccator with a fixed humidity up to the establishment of sorption equilibrium. The content of the sorbed water was determined by weighing as $w = M_H/(M_S + M_C)$, where M_H is the water content of the specimen.

Measurement of the Thermal Conductivity. The effective thermal conductivity λ was measured using the "hot-wire" method (Fig. 1) [13, 14]. A thin constantan wire 0.127 mm in diameter was placed between two blocks of the considered specimen and was heated via a dc source, and its temperature was recorded with the aid of an iron-constantan thermocouple welded to the center of the wire. In conformity with the theory of heat-flux propagation from a uniformly heated thin rod in an infinite homogeneous medium, the thermal conductivity of the considered system can be calculated with good accuracy from the dependence of the wire temperature T_w on the heating time t as [14]

$$\lambda = \frac{q}{4\pi} \frac{dT_w}{d(\ln t)}, \tag{1}$$

where $q = \rho I^2/s$ is the power released per unit length of the wire, I is the current strength, ρ is the specific resistance of the wire, and s is its cross section.

The measurements were performed at the room temperature $T_{room} = 290–300$ K and atmospheric pressure. The specimens were placed in a hermetic container, inside which an air humidity close to that in the

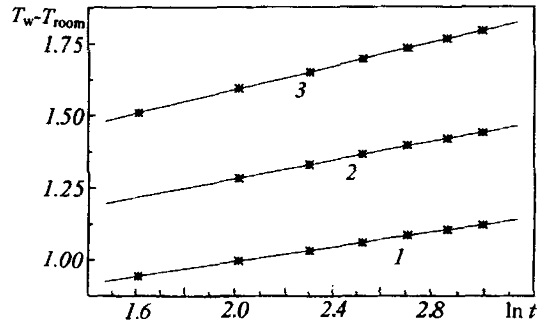

Fig. 2. Temperature of the constantan wire vs. its heating time (specimen 2, w = 0.04): 1) I = 0.07 A; 2) 0.08; 3) 0.09. $T_w - T_{room}$, K; t, sec.

TABLE 1. Experimental Values of the Thermal Conductivity for the Considered Specimens with a Different Weight Content of the Sorbed Water

Specimen	M_C/M_S	w	N	y	Density, g/cm^3	λ, W/(m·K).
KSK	–	0	–	0	0.51	0.089±0.006
KSK	–	0.05	–	0.03	0.51	0.095±0.006
1	0.23	0.01	0.2	0.06	0.65	0.112±0.007
1	0.24	0.34	10.8	0.30	0.82	0.153±0.008
1	0.23	0.58	18.8	0.51	1.01	0.216±0.012
2	0.51	0.04	0.7	0.13	0.80	0.127±0.008
2	0.51	0.48	8.9	0.57	1.15	0.233±0.011
2	0.55	0.75	13.1	0.88	1.42	0.44±0.03
3	1.00	0.02	0.3	0.21	0.88	0.138±0.008
3	1.03	0.42	5.1	0.65	1.28	0.305±0.025
3	1.03	0.60	7.3	0.79	1.44	0.43±0.03

desiccator was maintained. The absence of substantial water migration from the specimen to air or inversely was checked by the thermocouple reading, specifically, λ was measured, if the deviation of the thermocouple readings from zero (with no current) was not greater than 10 μV (0.2 K). The current strength was selected so that the increase in the wire temperature over the measurement time ($t \leq 25$ sec) did not exceed 2 K. Under these conditions, the effect of the water desorption on a measured λ could be disregarded [2, 5]. The tests using reference materials (Plexiglas and Teflon) indicated that the convective heating of air in a gap formed between the blocks (about 0.1 mm) can lead to an overestimate of 10–15% for λ. To avoid this, the constantan wire was immersed in a groove made in the lower block. The accuracy of the determination of the effective thermal conductivity by the described procedure was 5–7%.

Results and Discussion. The characteristic dependences of the temperature T_w of the constantan wire on the logarithm of its heating time (Fig. 2) are of the form of straight lines. Their slope permits a determination of the thermal conductivity λ of the considered composites at different contents w of the sorbed water (see Eq. (1)). For water-free composites ($w \approx 0$), the values of λ_0 are 0.11 (specimen 1), 0.13 (specimen 2), and 0.14 W/(m·K) (specimen 3), which is larger than λ = 0.09 W/(m·K) measured for the initial silica gel that was molded in a similar fashion. Thus, an increase in the thermal conductivity due to the addition of salt correlates with an increase in the ratio M_C/M_S.

Table 1 and Fig. 3 present measurement results for various weight contents of the sorbed water. On the experimental curve, four different types of λ variation with increase in w can be isolated conventionally: a) a weak rise, b) an approximate constancy, c) a sharp rise, and d) a monotonic increase. For the subsequent analysis it is convenient to introduce the parameter v, which characterizes the degree of filling of the free space

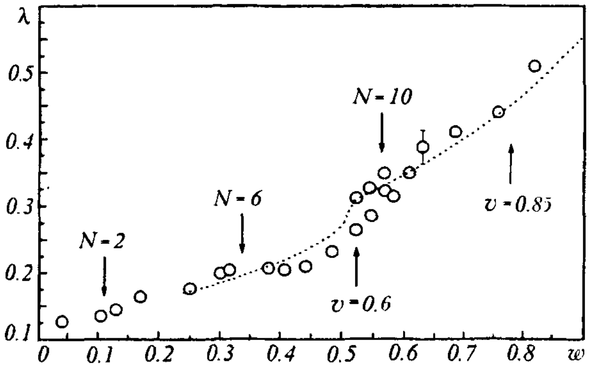

Fig. 3. Thermal conductivity of composite 2 vs. water content. The dotted line denotes the calculation by the Luikov–Bjurström model. λ, W/(m·K).

inside the host matrix: $v = V_{liq}/(V_{\mu} + V_m)$, where V_{liq} is the volume of the salt + water system and V_m is the macropore volume. It should be noted that the free space inside the specimens is of a bimodal structure: the initial silica-gel particles with a size of 50–100 μm contain mesopores, and when this powder is compacted into blocks, voids with a size of several tens of microns (macropores) are formed between the initial particles. The volume fraction of the macropores in the blocks is about 0.3, and of the mesopores, 0.5. The water content of the specimens was varied over a wide range, including the region of complete filling of the mesopores ($w \approx 0.52$ and $v = 0.6$ for specimen 2) and of subsequent egress of the solution to the macropores ($0.6 < v < 0.9$). The analytical relation between the parameters v and w is of an intricate character; in the case with no crystalline hydrates of salt in the pores ($w > 0.3$ for specimen 2 [1, 3]), $v = M_C/(cW_{liq}(V_{\mu} + V_m))$, where $c = (1 + w(1 + M_S/M_C))^{-1}$ and $W_{liq} = f(c)$ is the density of the aqueous solution of salt.

The effect of the sorbed water on the variation in the thermal conductivity in the aforementioned regions (a)-(d) was analyzed using the notions of the character of water sorption in porous host matrix + hygroscopic salt composites, which were previously developed in [1-5]. Further on, the data for specimen 2 are discussed.

a) Weak rise in λ at small magnitudes of the sorption. At sorption magnitudes smaller than $w \approx 0.20$, the dispersed salt forms low crystalline hydrates that contain from $N = 0.33$ to $N = 2$ water molecules per salt molecule [1-5, 15]. Since, on the one hand, the thermal conductivity of the hydrates is somewhat lower than that of the anhydrous salt [16] but, on the other hand, the specimen density and the degree of filling of the free volume increase, the resultant outcome of these trends is a relatively weak rise in λ at the initial stages of sorption.

b) Approximate constancy of λ. As is well known, the thermal conductivity of $CaCl_2 \cdot NH_2O$ crystals is at least twice that of an aqueous solution [8, 16]; therefore, the emergence of the liquid phase in the mesopores and the dissolution of the crystalline hydrates slow down an increase in the thermal conductivity ($0.2 < w < 0.3$). With w ranging from 0.3 to 0.45, when only the liquid phase (a supersaturated salt solution [1, 3]) is present in the mesopores, λ remains practically constant. Such behavior seems anomalous, since, with increase in w, (1) the sorbent density increases due to the displacement of the gas phase, which conducts heat poorly, by the solution and (2) the concentration c of the dispersed salt solution decreases (as is well known, the thermal conductivity of a massive $CaCl_2$ solution increases in proportion to its dilution [8, 17]). The observed effect can be explained, for example, assuming a significant difference of the physicochemical properties of the dispersed and massive supersaturated solutions (see below).

c) Sharp rise in the thermal conductivity. In the narrow range of $v = 0.53$–0.60, there is a jump of the thermal conductivity to values that are larger than λ_0 by a factor of 2–2.5. It should be noted that the degree of the volume filling of the pores in the indicated interval (which corresponds to $w = 0.45$–0.52 and $c > 40$ wt.%) was evaluated by extrapolating the polynomial dependence of the solution density on the salt concentration c, which was constructed on the basis of reference data (also see below).

Such threshold effects for moist porous media are known in the literature [11] and, specifically, are the subject of analysis within the framework of the percolation theory [12]: it is assumed that a "threshold of flowing" exists, i.e., a certain volume concentration $v = v_{cl}$ of the heat-conducting element, above which its continuous phase (infinite cluster) originates in the system. The effective thermal conductivity near this threshold increases rapidly [12]. For the considered systems, this continuous phase can be formed by the solution that fills the pores. Indeed, in the discussed range of sorption, the solution completely occupies the mesopores and emerges on the surface of the primary particles the host matrix, where it begins to form a film (droplets). Here, the heat transfer between neighboring particles can additionally occur through this film. The number of such "joined" granules increases, and at a certain threshold value of $v \approx 0.60$, a continuous phase of the solution is formed, which sharply increases the thermal conductivity of the entire system.

d) Monotonic increase in the thermal conductivity. The subsequent adsorption of water vapor, which leads to the filling of the macropores, entails a monotonic increase in the thermal conductivity. Such a character of the dependence $\lambda(w)$ at $T = 293$ K is typical of moist macroporous structures presented in the literature [8-10]. The reasons for the increase in λ are, in this case, evident: (1) a decrease in the relative volume of the poorly conducting gas phase in the macropores and (2) an increase in the intrinsic thermal conductivity of the solution in proportion to a decrease in the salt concentration [8, 17]. It should be noted that with a degree of filling of the macropores up to 80–90%, the solution is completely contained in the specimen due to the predominance of capillary forces over gravitational ones. When the specimens were further saturated with moisture, measurements were not performed, since the solution partially outflowed from the specimens.

In the limiting case where the entire free space inside the silica gel is filled with a calcium chloride solution (here, $w = 0.95$ and $c = 26.8$ wt.%), the effective thermal conductivity of the system is specified by the intrinsic thermal conductivity of the skeleton (amorphous silicon dioxide) $\lambda_S = 1.35$ W/(m·K) [9] and the solution $\lambda_{liq} = 0.567$ W/(m·K) [17], and by their volume concentrations $v_S = 0.21$ and $v_{liq} = 0.79$. Using a simple relation for the thermal conductivity of a three-dimensional, two-component system from [18], it is not difficult to estimate the limiting value to which the thermal conductivity must tend:

$$\lambda = \lambda_S v_S^2 + \lambda_{liq} v_{liq}^2 + 4 \frac{\lambda_S \lambda_{liq}}{\lambda_S + \lambda_{liq}} v_S v_{liq} = 0.68 \text{ W/(m·K)} .$$

Calculation of the Thermal Conductivity Using the Luikov–Bjurström Model. A great many models have been proposed in the literature for describing the thermal conductivity of porous composites [6-12, 18], with some of them allowing for the presence of the liquid phase in the pores. In [11], the applicability of these models to describing the thermal conductivity of the system of a porous silica gel particle and water has been analyzed, and calculation results have been compared with experimental data. Here, the water content of the silica-gel pores was varied over a wide range, up to a maximum filling. The considered system is the most similar to that analyzed in the present work; therefore, as the basic model, we subsequently used the model recommended by Bjurström et al. [11], namely, the elementary-cell model proposed by Luikov [6]. Within its framework, the porous system is viewed as a periodic three-dimensional structure with voids, in which an elementary cell of simple geometry can be isolated. The thermal conductivity of the entire system is equal to the thermal conductivity of the cell that is amenable to accurate calculation. Bjurström and his coauthors supplemented this model, having introduced, into the cell, a liquid film that envelopes the quartz skeleton [11]. Figure 4 presents a diagram of the Luikov–Bjurström elementary cell and indicates the basic geometric parameters of the model. The relation between h, l, and L can be calculated proceeding from the specific weight W_S of the skeleton-forming material and from the volume V_μ of the pores of the modeled system by solving the equation

$$\left(\frac{L}{l}\right)^3 - 3B\left(\frac{L}{l}\right) + 2B = 0 ,$$

where $B = 1 + 1/(W_S V_\mu)$. Thus, for KSK silica gel ($W_S = 2.4 \pm 0.2$ g/cm^3), we obtained $L/l = 1.579$ and $L/h = 2.727$. The parameter m was found from the equation

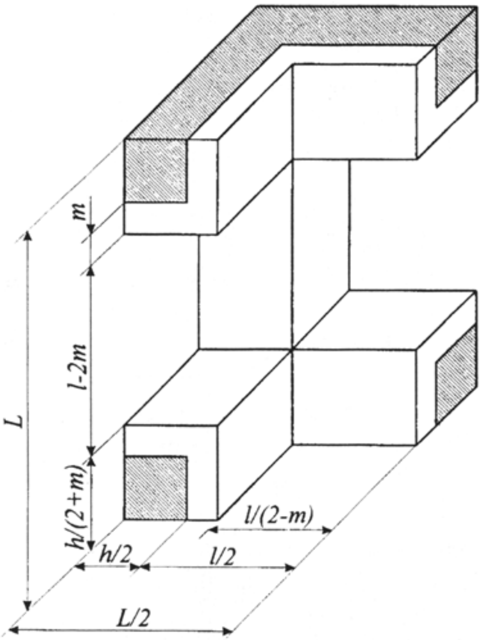

Fig. 4. Quarter of an elementary cell by the Luikov–Bjurström model of moistened porous material.

$$4\left(\frac{m}{L}\right)^3-3\left(\frac{l-h}{L}\right)\left(\frac{m}{L}\right)^2-3\frac{h}{L}\frac{l}{L}\frac{m}{L}+\frac{1}{4}\frac{W_S}{W_{\text{liq}}}\left(3\frac{l}{L}+\frac{h}{L}\right)\left(\frac{h}{L}\right)^2\left(w+\frac{M_C}{M_S}(1+w)\right)=0,$$

where $W_{\text{liq}} = f(c)$ is the liquid density. Most importantly, W_{liq} for $w < 0.52$ refers to a supersaturated ($c > 42\%$) $CaCl_2$ solution. The tabular dependence $W_{\text{liq}}(c)$ for ($c < 42\%$) [19] is well approximated by the function $W_{\text{liq}}(c) = 1 + c/126 + c^2/20{,}243$. The density of the supersaturated solution in the mesopores was evaluated by extrapolating the above dependence to the region of $c > 42\%$.

The thermal conductivity of the elementary cell was calculated from the equation [11]

$$\lambda_p=\left(\frac{h}{L}\right)^2\lambda_S+4\left(\frac{m}{L}\right)^2\lambda_{\text{liq}}+\left(\frac{l-2m}{L}\right)^2\lambda_g+\frac{4m/l}{\frac{L}{l}\frac{1}{\lambda_S}+\frac{L}{h}\frac{1}{\lambda_{\text{liq}}}}+$$

$$+\frac{4(l-2m)\,m/L}{\frac{h+2m}{\lambda_{\text{liq}}}+\frac{l-2m}{\lambda_g}}+\frac{2}{\frac{L}{l}\frac{1}{1-2m/l}\left(\frac{1}{\lambda_S}+\frac{2m}{h}\frac{1}{\lambda_{\text{liq}}}\right)+\frac{L}{h}\frac{1}{\lambda_g}}, \qquad (2)$$

where λ_g is the thermal conductivity of the gas phase. In the calculation of λ_g, the effect of water vapor was disregarded (its contribution to the effective thermal conductivity of the system at T = 293 K is no greater than 0.01% and, taking into account that in the mesopores $l < l_a$, the relation $\lambda_g \approx 0.026\ (l-2m)/l_a$ W/(m·K) was used, where $\lambda_a \sim 60$ nm is the free path length of air molecules at P = 1 atm and T = 293 K [8]. The thermal conductivity λ_{liq} of the dispersed $CaCl_2 + H_2O$ system with $0.3 < w < 0.52$ ($c > 42\%$) that represents, as has already been mentioned, a homogeneous supersaturated solution, was calculated by extrapolating the dependence $\lambda_{\text{liq}}(c)$ for a massive solution with $c < 42\%$: $\lambda_{\text{liq}} \approx 0.597 - c/1229 - c^2/80{,}989$ (according to the data of [17]).

The above relations permit a calculation of the effective thermal conductivity λ_p for a moist mesoporous particle of composite 2. Since the size of the macroporous system, which is a dense packing of such particles, is much larger than the size of the latter ones, $L' \sim 100$ μm, its effective thermal conductivity can be calculated using the Luikov model [6, 7, 11]:

$$\lambda = \left(\left(\frac{L'}{h'} \right)^2 + A_{\text{res}} \right)^{-1} \lambda_p + \left(\frac{l'}{L'} \right)^2 \lambda_g + \frac{2}{\frac{L'}{l'} \frac{1}{\lambda_p} + \frac{L'}{h'} \frac{1}{\lambda_g}}, \tag{3}$$

where the parameter A_{res} takes account of the resistance to the heat flux in the region of particle contact. The geometric parameters h', l', and L' have a similar meaning (see Fig. 4) and were calculated with allowance for the specific weight of SiO_2 (0.5 g/cm^3 after the compaction) and the volume of the macropores of the modeled system: $L'/l' = 2.665$ and $L'/h' = 1600$. In order to simplify the procedure of calculating λ, the parameter A_{res} was neglected (the latter could lead to a certain overestimate of the calculation results [11]) and it was assumed that $\lambda_g = 0.026$ W/(m·K).

The calculations of λ in the case where a $CaCl_2$ solution is present in the macropores was also carried out in two stages: first, we determined λ_p, which is the thermal conductivity of a particle whose pores are filled with solution with concentration $c < 42\%$. For this, we used Eq. (3), setting $A_{\text{res}} = 0$ and replacing λ_p by λ_S, λ_g by λ_{liq}, L' by L, h' by h, and l' by l. Then we calculated the parameter m', which is the thickness of the solution film in the macropores, and afterward we calculated λ from Eq. (2) with an inverse substitution of the geometric parameters (L' in lieu of L, etc.) and the replacement of λ_S by λ_p.

It turned out that the employed model in the large reflects the main regularities of the behavior of the function $\lambda(w)$ (Fig. 3). Thus, the model predicts a substantial jump in the thermal conductivity at $v \approx 0.50$. The greatest qualitative difference from experimental data – the absence of a "plateau" – takes place in the region of $0.30 < w < 0.45$, i.e., when the mesopores are incompletely filled with a supersaturated solution. This is, evidently, linked with deviations that arise in the extrapolation of the properties of diluted massive solutions – density and thermal conductivity – to the region of a supersaturated dispersed solution. On the whole, however, the deviation of the calculated values of λ from the experimental ones is no greater than 10–15%, which is close to the experimental accuracy.

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NOTATION

c, weight concentration of salt in the aqueous solution; h, characteristic dimension of the solid skeleton of the porous matrix (the model parameter); $L = h + l$, size of the elementary cell in the porous-system model; l, pore size (the model parameter); M, mass; m, thickness of the salt + water film in the pores (the model parameter); N, molar ratio of water and salt in the solution and the crystalline hydrate; T, temperature; t, time; V, pore volume; v, degree of volume filling of the pores with salt and water; W, density; w, weight content of water in the sorbent; λ, thermal conductivity; λ_0, thermal conductivity in the absence of water.

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