ENHANCEMENT OF THE INTERNAL MASS TRANSFER UNDER ISOTHERMAL CONDITIONS

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A study has been made concerning the effect of an electric and a magnetic field as well as the effect of exchange ions on the internal mass transfer in the case of moisture sorption in grade KSM-5 silica gel in a constant-temperature and constant-pressure atmosphere of water vapor.

The intensity of external electromagnetic fields relaxes in moist capillary-porous materials so that, as a consequence, a constant nonuniform electric or magnetic field applied to such a system induces additional thermodynamic forces involved in mass transfer [1] which, depending of the direction of the field gradient, can either accelerate or decelerate the flow of moisture. This phenomenon should be reflected most clearly in the curves of sorption kinetics $W(\tau)$ and in the trend which the coefficients a_m, λ_m of internal mass transfer follow as functions of the moisture content at a fixed temperature in a capillary-porous body.

These relations have been established by methods shown in [2, 3] on the basis of measurements made with vacuum-type sorption balances thermostatized within $\pm 0.05°C$ and modified for weighing a test specimen in the form of a pellet 4 mm in diameter, such a specimen placed inside a cylindrical capacitor along the electric field axis or between two knife-edge poles of a permanent magnet along the axis of maximum nonuniformity [4].

A specimen, moist after sorption of water vapor at an air humidity $\varphi \cong 1$, was here located in a highly nonuniform electric field ($dE/dx = 4 \cdot 10^7$ (V/m)/m in vacuum) or magnetic fields ($dH/dx = 1.4 \cdot 10^8$ (A/m)/m in vacuum), with the respective field gradient directed toward the center of the specimen.

Static and kinetic characteristics of sorption were determined at a temperature of 303°K.

The object of this study was homogeneously porous grade KSM-5 silica gel with the effective radius of the dominant pore size equal to $13 \cdot 10^{-10}$ m [5].

The specimens of grade KSM-5 silica gel were saturated appropriately with Ca^{2+} and K^+ ions according to the method in [6]. The equilibrium concentration of sorbed ions did not exceed 2.5 mg-equ/g.

The position and the shape of the sorption isotherms shown in Fig. 1 indicate both quantitative and qualitative changes in the sorptive properties of silica gels during their saturation with ions of various valences. The test data which have been obtained with a specimen of industrial grade KSM-5 silica gel intentionally not saturated with ions indicate, meanwhile, that the sorption equilibrium remains, within measurement accuracy, stable in uniform as well as in nonuniform fields, because such fields with intensities as high as in these tests have almost no effect on the maximum content of hygroscopic moisture and altogether do not affect the trends of the curves in both the adsorption and the desorption range.

According to Fig. 1, the sorption capacity of specimens is appreciably affected by ion complexes of either kind in the pores.

The data pertaining to the amount of vapor sorption in specimens of grade KSM-5 silica gel saturated with various ions lead to the conclusion that the Ca^{2+} ions have less effect than the K^+ ions. The difference

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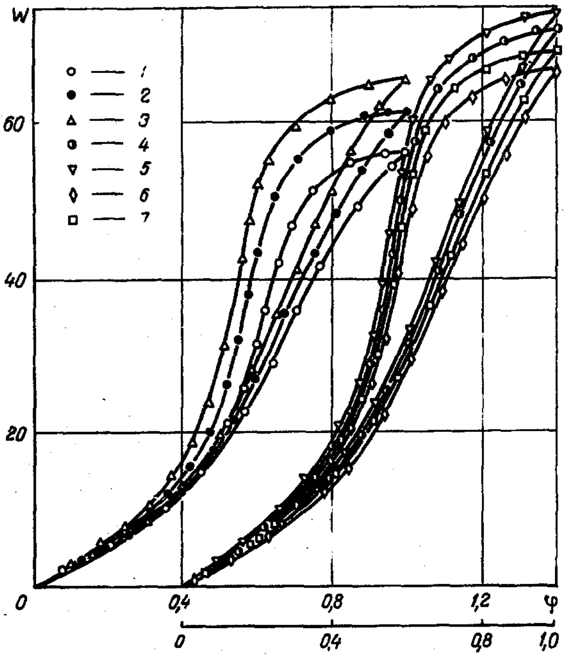

Fig. 1

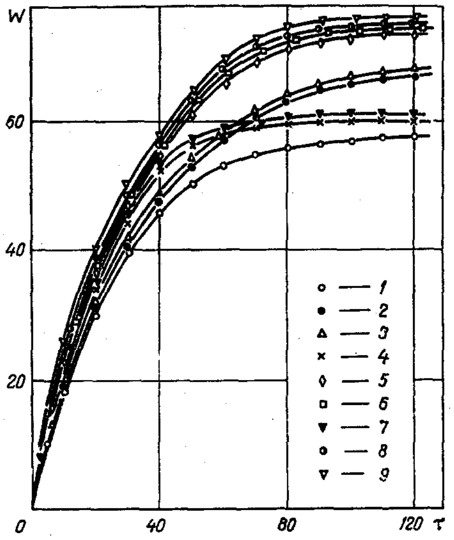

Fig. 2

Fig. 1. Sorption isotherms for plain and ion-saturated specimens of grade KSM-5 silica gel: without a field: 1) plain KSM-5; 2) with K^+; 3) with Ca^{2+}: in a magnetic field; 4) with K^+; 5) with Ca^{2+}; in an electric field: 6) with K^+; 7) with Ca^{2+}.

Fig. 2. Moisture content W (%) in plain and in ion-saturated specimens of grade KSM-5 silica gel, as a function of the sorption time τmin, at a temperature of 303°K: without a field: 1) plain KSM-5; 2) with K^+; 3) with Ca^{2+}; in an electric field: 4) plain KSM-5; 5) with K^+; 6) with Ca^{2+}; in a magnetic field: 7) plain KSM-5; 8) with K^+; 9) with Ca^{2+}.

between sorption capacities under the given conditions indicates the presence of additional sorption centers at the inner surface of micropores in specimens, which in a definite way coordinate with sorbed water molecules. Evidently, the strong effect of bivalent ions on the amount of sorption is associated with the appreciable change in the molecular structure of the silica gel surface. Bivalent ions produce a closer packing of sorbed water molecules, inasmuch as two monovalent K^+ ions occupy more space than one bivalent Ca^{2+} ion [6]. An appreciable widening of the hysteresis loop in the low-pressure range is characteristic of ion-saturated specimens. This can probably be explained by the hydration of ions during capillary condensation. The isotherms which have been thus obtained indicate, furthermore, that the presence of ions affects not only the total amount of sorption water but also the very mechanism of sorption and desorption processes in nonuniform electric and magnetic fields. The latter applies mainly to specimens saturated with bivalent ions. Within the range of our sorption measurements, this effect is apparently due to a redistribution of moisture toward higher densities ρ_L accompanied by a drop in concentration of hydrated ions in regions of a capillary-porous body where the electric or the magnetic field gradient and intensity are highest. At that time, the number of ions within the surface layer of capillary condensate changes, causing the surface tension σ to change and thus also the free energy of the bond in capillary moisture $\Delta F = 2V_L\sigma/r$. Probable is also a deformation of the charged surface of menisci and a change in the density of the vapor ρ_V above them, due to ponderomotive forces associated with the field nonuniformity [7], causing a change in the radius of curvature

$$r = \frac{2\sigma\cos\theta\rho_V}{\rho_L P_N \ln\left(\frac{1}{\varphi}\right)}.$$

It is to be noted that the mechanism of ion adsorption in the micropores of silica gel differs from the mechanism of exchange-ion adsorption in clay. Namely, it has been suggested in [8] that the cation adsorption in silica gels is molecular and that, consequently, the bond of cations to the surface of silica gel is weaker than their bond to the surface of clay particles. At the same time, having studied the location of exchange ions in laminate minerals, the author of [9] suggests that these ions move freely in the

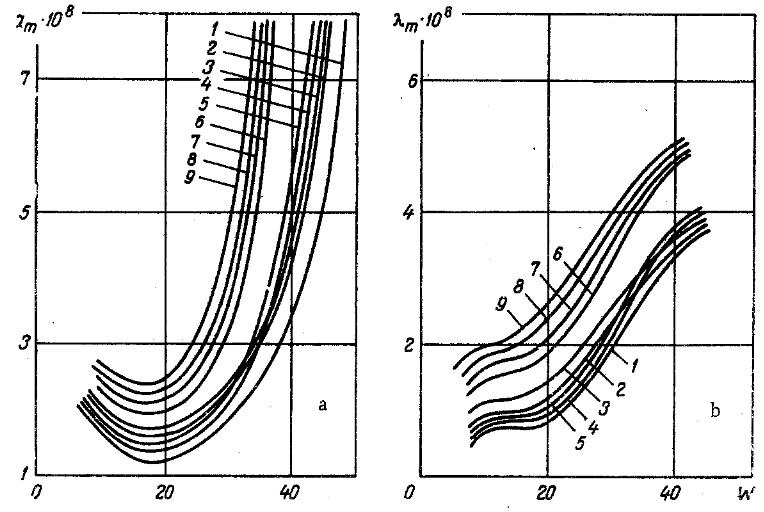

Fig. 3. (a) Hygrodiffusivity a_m (m^2/sec) and (b) hygroconductivity λ_m ($kg^2/m \cdot sec \cdot J$) as functions of the moisture content W (%): 1) plain KSM-5 silica gel without a field; 2, 6) KSM-5 saturated with K^+ ions in an electric field; 3, 7) in a magnetic field; 4) without a field; 5) KSM-5 saturated with Ca^{2+} ions without a field; 8) in an electric field; 9) in a magnetic field.

interlaminar space (along equipotential surfaces) together with the water molecules, the latter being exchangeable by transilience. Inasmuch as the bond between ions and the surface of a silica gel is still weaker than their bond with clay, the mobility of ions should result here in a higher rate of moisture sorption in ion-saturated specimens. Indeed, according to Fig. 2, the curves of sorption kinetics for ion-saturated specimens lie above the respective $W(\tau)$ curve for a plain KSM-5 specimen.

It would appear that the existence of additional sorption centers should result in a more effective deceleration of molecules during their diffusion through the micropores of silica gel, because of their longer life in the adsorbed state. This lifetime, as is well known, depends on the heat of adsorption of molecules [10]. According to the tests in [6], however, exchange ions have no significant effect on the heat of wetting of silica gel and, therefore, no appreciable difference should have been noted between the sorption rates in both cases. The experiment has shown, on the other hand, that the sorption rate increases appreciably in the cases of ion-saturated silica gel. Consequently, it may be concluded that the process is accelerated because of the lower potential barrier which a molecule must overcome in order to move from one location to another.

The test data shown in Fig. 2 lead to the conclusion that nonuniform electric or magnetic fields shift the sorption kinetics toward higher process rates. Tests performed in uniform electric and magnetic fields of intensity $2 \cdot 10^5$ V/m and $2.4 \cdot 10^5$ A/m respectively have not revealed any significant effect on the kinetics of water adsorption in those specimens.

Generally, when adsorptive and capillary condensation occur simultaneously in nonuniform fields, this can be explained thermodynamically by the finite rate at which all phases in a moist material become polarized: the solid phase, the water vapor, the adsorbed moisture, and the capillary moisture.

Known concepts about the dynamic character of the sorption process [10] lead to the conclusion that, within the range of adsorptively bonded moisture, the process of moisture transfer is enhanced most by the molecules of water vapor with electric and magnetic moments orienting them along the force lines and pulling them into the region where the given field is most nonuniform. Thus, the gradient of either kind of field within the specimen accelerates the diffusion of vapor molecules along the system of microcapillaries into the body. Moreover, according to [11], it seems that polarized molecules which have been adsorbed at the surface of a body are also pulled by a nonuniform electric field into the region where the intensity of this field within the body is maximum.

Since the adsorption of molecules is accompanied by a partial deformation of their electron shells [12], which results in a change of their magnetic moment, hence a nonuniform magnetic field also aids the surface diffusion of adsorbed molecules.

As the polymolecular moisture film at the surface of microcapillaries becomes thicker and the latter become filled with moisture during capillary condensation, the vaporized portion of moisture inside the body decreases and with it diminishes the effect of a field on the moisture transfer.

This does not mean, of course, that no electrically or magnetically induced migration occurs when the space in microcapillaries has been filled. Indeed, according to the results in [13], an electric field causes moisture to flow even when a bulk wetting water film exists at the surface of a quartz capillary. Since industrial specimens of silica gel always contain at least small amounts of various ions which become hydrated while water vapor is sorbed, hence the moisture transfer rate within the range of capillary condensation is obviously affected more appreciably by the ion-relaxative polarization of a specimen than by any other mode of polarization of the solid phase in a capillary-porous body due to a nonuniform field [14, 15]. Of course, in various nonuniform fields the ions affect the transilience of water molecules to somewhat different degrees.

A rise in the concentration of K^+ or Ca^{2+} ions in a specimen causes a change in the rate and in the degree of polarization, in any of these modes, which a moist body undergoes and, under the given conditions, this is followed by a stronger effect of a constant nonuniform field on the moisture transfer rate.

The trend of the $a_m(W)$ curves in Fig. 3 is generally not different from that of such curves for typical capillary-porous materials. Lower values of the coefficient a_m correspond to larger ions in the pores of silica gel.

The application of a nonuniform field, at a fixed moisture content and a fixed temperature of ion-saturated grade KSM-5 silica gel, also results in a higher value of the coefficient a_m. This effect is more pronounced in specimens of capillary-porous material with Ca^{2+} ions.

A higher a_m in the presence of ions has to do with the exchange of ions caused by a field during diffusion. A hydrated ion, after receiving sufficient energy as a result of fluctuating thermal oscillations, can leave a potential well (by breaking away from a given hydroxyl group) and occupy the place of an adjacent ion it has repelled. The latter falls into the gap between hydroxyl groups, i.e., into a potential well which is not so deep, whereupon, if it has not yet been hydrated, it becomes an additional adsorption center and immediately thereafter repels another adjacent ion. Exchange ions may thus be regarded as a supplementary vehicle for the transport of water molecules which the gradient of the chemical potential of mass transfer drives through the pores of a specimen, either by way of Knudsenian diffusion or by way of surface diffusion [16]. Such a mass transfer can occur in any direction and thus enhances the diffusion of vapor in a capillary-porous material.

According to [17], such a mass transfer requires that an ion receive an activation energy $E = E_1 + E_2$ (E_1 denoting the energy of ion-hydroxyl interaction and E_2 denoting the energy of ion-by adjacent-ion repulsion). In the presence of a field an ion needs only an activation energy $E = E_1$ for a transilience to the adjacent state, because the adjacent ion is displaced in the same direction already. Thus, there remains no doubt that external fields enhances the diffusion of vapor through a system of interlinked pores in an ion-saturated specimen of a disperse material.

Under isothermal conditions, as is well known, coefficient λ_m determines the magnitude of the moisture current per unit gradient of the chemical potential of mass transfer.

As the relative positions of the $\lambda_m(W)$ curves in Fig. 3b indicate, external nonuniform fields do appreciably enhance the internal moisture transfer in a capillary-porous material, over the entire range of hygroscopic moisture content levels. As the ion concentration rises, coefficient λ_m increases and the effect of a field becomes stronger. This effect differs in silica gel with different kinds of ions.

On the basis of the preceding analysis, it appears feasible to use nonuniform electric and magnetic fields as well as exchange ions for effectively regulating the rate of internal mass transfer in capillary-porous bodies at constant temperature, and thus for improving the efficiency of various technological processes in terms of better energy utilization.

NOTATION

W is the moisture content in a body;
τ is the sorption time;
a_m is the hygrodiffusivity;
λ_m is the hygroconductivity.

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