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Kinetics of Water Sorption on a $CaCl_2$-in-Silica-Gel-Pores Sorbent: The Effects of the Pellet Size and Temperature

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Abstract—Kinetics of water vapor sorption on the $CaCl_2$-in-KSK-pores composite (SWS-1L) have been studied at $T = 33$–$69°C$ and vapor pressures of 8–70 mbar for pellet sizes of $2R_{pel} = 0.355$–0.425, 0.71–0.85, and 1.2–1.4 mm. Sorption has been measured under isothermal conditions on a thermobalance by abruptly raising the vapor pressure in the measurement cell by a small value and then maintaining the new pressure. In the initial portion of the kinetic curves, the amount of sorbed water (Δm) increases in proportion to the sorption time (t) to the power 1/2. From the slope of the Δm versus $t^{1/2}$ curve, it is possible to derive the sorption rate constant $k_D = D_{eff}/R_{pel}^2$ and the effective diffusivity D_{eff}. The latter is independent of R_{pel} for $2R_{pel} \geq 0.71$ mm. The rate of water sorption on smaller (0.355- to 0.425-mm) pellets grows less rapidly, apparently because of the effect of the heat of sorption. The effective diffusivity is determined by the local slope of the water vapor sorption isotherm for SWS-1L. Applying an appropriate correction enables one to calculate the effective diffusivity for water vapor in the sorbent pores, which appears to be $D_e = (0.35 \pm 0.17) \times 10^{-6}$ m^2/s. This value is approximately 10 times smaller than the Knudsen water diffusion coefficient calculated for a single cylindrical pore with a size equal to the average pore size of the composite. Two possible causes of this discrepancy are discussed, specifically, an increase in the pore tortuosity because of the presence of the salt and the interaction between water and the salt.

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Kinetics of water sorption in porous media have been the subject of numerous studies [1], because such information is necessary in the design of air conditioners and gas driers and in the optimization of their operation. Most of these studies have dealt with the most widely used commercial drying agents, such as zeolites and silica gels. As a rule, the kinetics of water adsorption on these driers is governed by mass transfer in the pores of the material rather than by adsorption itself [1–4]. Three basic mechanisms of water transport in pores are distinguished, namely, molecular, Knudsen, and surface diffusion. In the general case it is these mechanisms that determine the pore diffusion coefficient D_e of water [3]. Many experimental methods have been developed for determining the effective diffusivity D_{eff} [1]. The simplest and most pictorial of them is the differential isothermal method. In this method, after an equilibrium between the sample and water vapor is established at some pressure P_0 (the corresponding water concentration in the gas phase is c_0), the pressure is abruptly changed by a small value ΔP (the water concentration becomes $c_0 \pm \Delta c$) and is then maintained to measure the time variation of the sample weight due to water sorption [5]. This method makes it possible to avoid, to a significant extent, the distortion of the sorption curve due to the sorption-induced heating of the sample and to determine the diffusion coefficient in the case of a nonlinear adsorption isotherm.

The theoretical foundations of this method are described in monographs [1, 5]. The mass balance equation describing the kinetics of matter sorption by identical spherical pellets can be written as

$$(1-\varepsilon)\frac{\partial q}{\partial t} + \varepsilon\frac{\partial c}{\partial t} = \varepsilon D_e\left(\frac{\partial^2 c}{\partial R^2} + \frac{2}{R}\frac{\partial c}{\partial R}\right), \tag{1}$$

where D_e is the effective pore diffusion coefficient (which is considered to be independent of the concentration of sorbed water), ε is the porosity of the pellet, q is the concentration of adsorbed water, c is the water concentration in the gas phase, t is the adsorption time, and R is the radial coordinate. If the concentration step is small ($\Delta c \ll c_0$), then

$$\frac{\partial q}{\partial t} = K\frac{\partial c}{\partial t}, \tag{2}$$

where $K = K(c_0) = \text{const}$. Equation (1) will then appear as

$$\frac{\partial c}{\partial t} = \frac{\varepsilon D_e}{\varepsilon + (1-\varepsilon)K}\left(\frac{\partial^2 c}{\partial R^2} + \frac{2}{R}\frac{\partial c}{\partial R}\right). \tag{3}$$

For a stepwise change in the sorbate concentration on the pellet surface, the initial and boundary conditions can be written as follows:

$$c(R_{\text{pel}}, 0) = c_0, \quad q(R_{\text{pel}}, 0) = q_0,$$

$$c(R_{\text{pel}}, \infty) = c_\infty, \quad q(R_{\text{pel}}, \infty) = q_\infty,$$

$$\left.\frac{\partial c}{\partial R}\right|_{R=0} = \left.\frac{\partial q}{\partial R}\right|_{R=0} = 0,$$

where R_{pel} is the pellet radius. Equation (3) has the following solution [5]:

$$\frac{m_t}{m_\infty} = \frac{\bar{q} - q_0}{q_\infty - q_0}$$

$$= 1 - \frac{6}{\pi^2}\sum_{n=1}^{\infty}\frac{1}{n^2}\exp\left(-\frac{n^2\pi^2\dfrac{\varepsilon D_e}{\varepsilon + (1-\varepsilon)K}t}{R_{\text{pel}}^2}\right) \quad (4)$$

$$= 1 - \frac{6}{\pi^2}\sum_{n=1}^{\infty}\frac{1}{n^2}\exp\left(\frac{n^2\pi^2 D_{\text{eff}}t}{R_{\text{pel}}^2}\right),$$

where $\bar{q}$ is the time-dependent average moisture content of the pellet, D_{eff} is the effective diffusivity of water defined as $D_{\text{eff}} = \frac{\varepsilon D_e}{\varepsilon + (1-\varepsilon)K}$, and n is the summation index. Thus, D_{eff} depends on the effective pore diffusion coefficient (D_e), the pellet porosity ε, and the shape of the sorption isotherm (the local slope $K = (dq/dc)$). In the initial portion of the sorption curve, this equation tends to the following form [1]:

$$\frac{m_t}{m_\infty} \approx \frac{2S}{V}\sqrt{\frac{D_{\text{eff}}t}{\pi}} = A\sqrt{t}, \quad (5)$$

where S/V is the ratio of the outer surface area of the pellet to the pellet volume (for a spherical particle, $S/V = 3/R_{\text{pel}}$). Expression (5) can be used in the experimental determination of the sorption rate constant $k_D = \frac{D_{\text{eff}}}{R_{\text{pel}}^2}$ ($1/k_D$ is the characteristic sorption time) and in the subsequent calculation of D_{eff}.

It is this approach that we used in our study of pore diffusion in the composite sorbent $CaCl_2$/KSK (hereafter, SWS-1L). This modified sorbent, which has a higher sorption capacity than pure silica gel, can be used in adsorption heat pumps [6, 7]. Earlier, we carried out only a preliminary study of the kinetics of water sorption on SWS-1L from flowing humid air [8]. Recently, first sorption measurements at a constant-volume and, accordingly, varying pressure have been reported by Dawoud et al. [9, 10]. It was found that the sorption kinetic curves are nonexponential and can be described in terms of the characteristic times $\tau_{0.5}$ and $\tau_{0.9}$, which are the time points at which water sorption is, respectively, 0.5 and 0.9 of its equilibrium value. The sorption rate increases rapidly with increasing pellet size: $\tau_{0.5}$ is 140–200 s for 3.0- to 3.2-mm pellets and is as short as 11–15 s for 0.34- to 0.5-mm pellets. However, Dawoud and his colleagues have been unable to derive, from kinetic curves, any microscopic parameters of the process, such as the water diffusion coefficient. Here, we report detailed kinetics of water sorption on the composite sorbent SWS-1L and the water diffusion coefficient as a function of the sorbent particle size and temperature.

Properties of the silica gel KSK and the SWS-1L composite

Property	KSK	SWS-1L
Pore volume, cm^3/g	1.0	0.51
Salt content, wt %	–	33.7
Density, g/cm^3	0.72	1.08
Pellet porosity	0.72	0.57
Pellet size, mm	–	0.355–0.425, 0.71–0.85, 1.2–1.4

EXPERIMENTAL

The adsorbent was synthesized by impregnating dry pellets of KSK silica gel with a saturated aqueous $CaCl_2$ solution at 25°C followed by drying at 200°C. This procedure allows the water sorption capacity to be increased to 0.6–0.7 g per gram of dry sorbent [11]. Some properties of KSK and SWS-1L are presented in the table. The sorbent pellets had a size of 0.355–0.425, 0.71–0.85, or 1.2–1.4 mm.

Kinetic curves of water sorption were obtained by thermogravimetric analysis on a CAHN C2000 thermobalance by a standard procedure [5]. Before measurements, the sample was dried at 150°C for 5–6 h under continuous pumping down to $\sim 10^{-3}$ mbar. The dry weight of the sample was typically 22–25 mg. The sample temperature was controlled with an accuracy of ±0.3 K using a temperature regulator. Next, the sample in the measurement cell was cooled to a temperature T, pumping was ceased, and the cell was connected to a thermostated water evaporator, whose temperature was maintained at T_1. The vapor pressure in the measurement cell grew rapidly to become equal to the vapor pressure in the evaporator ($P(T_1)$) and then remained invariable (Fig. 1). From the time-dependent, sorption-induced weight gain of the sample, we derived a kinetic curve for water sorption at the temperature T and pressure $P(T_1)$. Thereafter, the evaporator was disconnected from the measurement cell and was thermostated at a temperature T_2 (usually, $T_2 > T_1$). The temperature T_2 was chosen so that the pressure change $\Delta P = P(T_2) - P(T_1)$ was small. Next, the evaporator was again connected to the cell, in which some pressure $P(T_2)$ (Fig. 1) was then rapidly established. The time variation of the

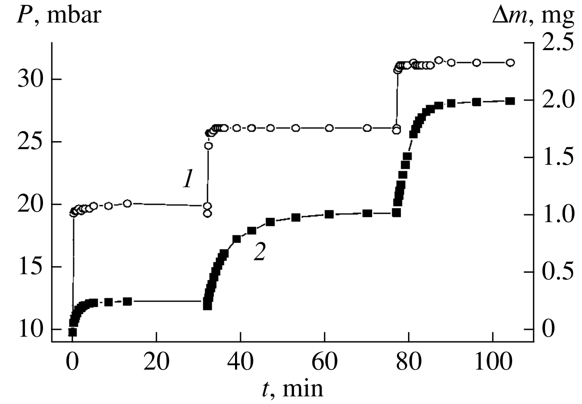

Fig. 1. Typical plots of (*1*) the water vapor pressure over the sample and (*2*) the weight gain of the sample versus sorption time ($T = 59$°C; pellet size, 0.355–0.425 mm).

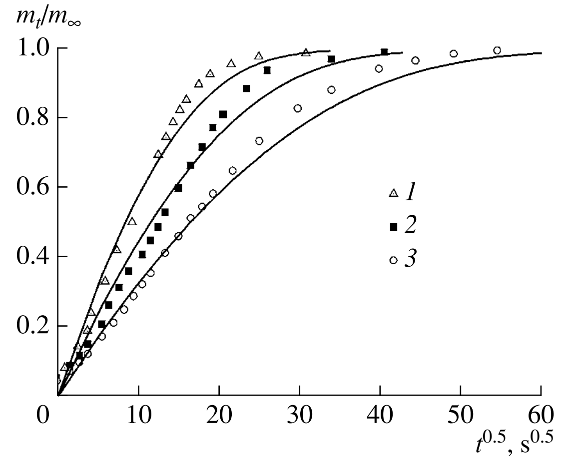

Fig. 2. Kinetics of water sorption on pellets in size ranges of (*1*) 0.355–0.425, (*2*) 0.71–0.85, and (*3*) 1.2–1.4 mm. The initial and final water vapor pressures are 26.0 and 31.0 mbar, respectively. The solid lines represent the data calculated using Eq. (4) and the D_{eff} values derived from the slopes of the initial portions of experimental kinetic curves.

sample weight was measured at the new pressure, and so on. Measurements were carried out at sample temperatures of 33, 49, 59, and 69°C. The evaporator temperature was varied between 1.0 and 41.0°C.

RESULTS AND DISCUSSION

Typical time dependences of the water vapor pressure in the measurement cell and of the sample weight are plotted in Fig. 1. In the initial portion of the sorption curve, $m_t/m_\infty = A\sqrt{t}$ (Fig. 2). This observation is in agreement with Eq. (5), and it is, therefore, possible to calculate the slope $A = \frac{6}{\sqrt{\pi}}\sqrt{\frac{D_{\text{eff}}}{R_{\text{pel}}^2}}$ and the effective sorption rate constant $k_{\text{D}} = \frac{D_{\text{eff}}}{R_{\text{pel}}^2} = \pi A^2/36$. The constant k_{D} thus determined was substituted into Eq. (4) in order to calculate the complete sorption kinetic curve. The calculated curve appeared to coincide closely with the observed curve (Fig. 2).

Figure 3 plots the effective water sorption rate constant versus water vapor pressure for various pellet sizes. Clearly, k_{D} decreases as the pellet size is increased. For pellet sizes of 0.71–0.85 and 1.2–1.4 mm,

$$k_{\text{D}} \sim R_{\text{pel}}^{-2}, \tag{6}$$

that is, the effective diffusivity is independent of the pellet size. For smaller pellets with a size of 0.355–0.425 mm, the increase in k_{D} is smaller than is expected from relationship (6). This finding points to a significant contribution from the heat of water sorption.

The constant k_{D} depends on the water vapor pressure in a rather complicated way (Fig. 3) because of the nonlinearity of the sorption isotherm for SWS-1L. This dependence is primarily determined by the local slope of the $K = \mathrm{d}q/\mathrm{d}c$ isotherm. The $K(P)$ relationship can be established by numerically differentiating the water vapor sorption isotherm $q(P)$ obtained by thermogravimetric analysis (Fig. 4a). Note that, although numerical differentiation is inaccurate, it is clear that the $K(P)$ maximum at $P \approx 27$ mbar in Fig. 4b corresponds to a $k_{\text{D}}(P)$ minimum in Fig. 3a.

Now, it is possible to calculate the $\frac{D_{\text{e}}}{R_{\text{pel}}^2} = \frac{D_{\text{eff}}}{R_{\text{pel}}^2}\frac{\varepsilon + (1-\varepsilon)K}{\varepsilon}$ value, which depends only on the pellet size at a fixed temperature (Fig. 3b). From this value, the effective pore diffusion coefficient for the pellet sizes of 1.2–1.4 and 0.71–0.85 mm is determined to be $D_{\text{e}}(59°\text{C}) = (0.46 \pm 0.12) \times 10^{-6}$ m^2/s. The diffusion coefficient calculated in the same way for the pellet size of 0.355–0.425 mm has a smaller value of $D_{\text{e}} = 0.26 \times 10^{-6}$ m^2/s. We believe that this difference is due to a significant contribution from the heat of water sorption in the case of smaller pellets. Indeed, the rate of sorption on these pellets is much higher, and the evolved heat has no time to dissipate into the environment. As a consequence, the pellet temperature rises, resulting in a decrease in the equilibrium water sorption. This effect is allowed for in the nonisothermal model [12], which is briefly described in the appendix. By substituting $D_{\text{e}} = 0.46 \times 10^{-6}$ m^2/s into Eq. (A.1) (see Appendix) and optimizing the parameters α and β, one achieves a good fit to the experimental data (Fig. 5) at $\alpha = 342$ and $\beta = 24.8$ (these values are close to the theoretical estimates of α and β; see Appendix).

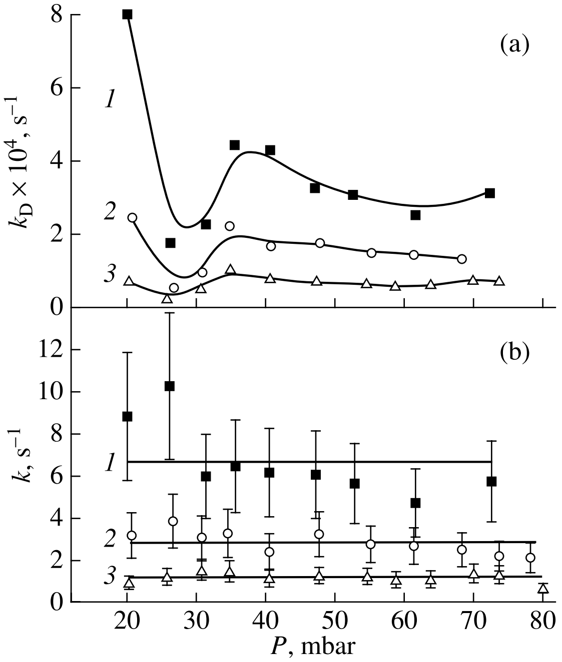

Fig. 3. Effective sorption rate constants (a) $k_D = D_{eff}/R^2_{pel}$ and (b) $k = D_e/R^2_{pel}$ at 59°C versus water vapor pressure for SWS-1L pellets in size ranges of (*1*) 0.355–0.425, (*2*) 0.71–0.85, and (*3*) 1.2–1.4 mm.

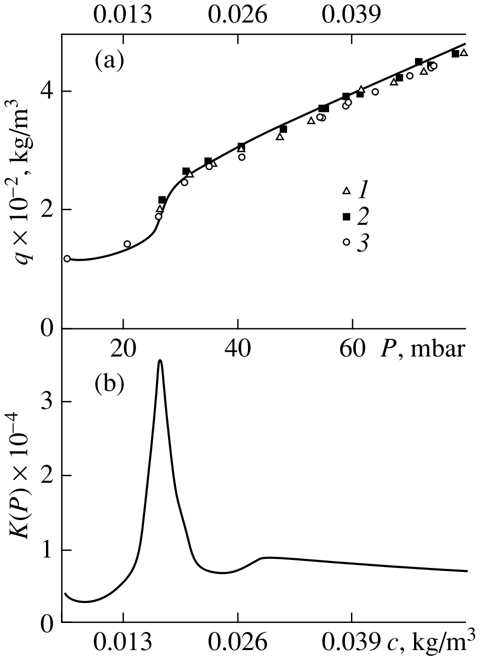

Fig. 4. (a) Water sorption isotherm for SWS-1L pellets in size ranges of (*1*) 0.355–0.425, (*2*) 0.71–0.85, and (*3*) 1.2–1.4 mm (T = 59°C). (b) Coefficient $K(P)$ numerically calculated from this isotherm.

Compare the experimental pore diffusion coefficient for the large pellets to the Knudsen diffusion coefficient D_{Kn} calculated for a cylindrical pore with a radius of r_{por} = 7.5 nm at T = 332 K [1]: $D_{Kn} = 9700 r_{por}\sqrt{T/M}$ = 3.1×10^{-6} m^2/s (here, M is the molecular weight). Thus, the salt present in the pores makes D_e smaller than D_{Kn}. A possible cause of this effect is that the salt blocks access to part of the pores, thus markedly increasing their tortuosity. The given D_{Kn}/D_e leads to $\chi/\varepsilon \approx$ 7–10 [1], where χ is the tortuosity factor of the sorbent pores. Setting ε = 0.57 (table), we obtain χ = 4–6 for the SWS-1K composite. This value is well above the typical value of $\chi \approx$ 2–3 [1]. The above effect may also be caused by the interaction between water molecules and dispersed salt in sorbent pores. As a result of this interaction, the water molecules stay on the surface for a longer time and are less rapidly transferred into the pellet bulk. In this case, the characteristic on-surface "wait" time varies with temperature as $\exp(-B/T)$ [13], where B is a temperature-independent coefficient, and, therefore, D_e depends strongly on temperature.

We have obtained kinetic curves for water vapor sorption between 33 and 69°C and have calculated the corresponding effective pore diffusion coefficients for water in 0.71- to 0.85-mm SWS-1L pellets. The diffusion coefficient D_e is temperature-independent within the measurement error and is equal to $(0.35 \pm 0.17) \times 10^{-6}$ m^2/s (Fig. 6). Therefore, the assumption that the decrease in the effective diffusivity of water in the pores is due to steric effects is more plausible.

Thus, we have investigated the kinetics of water vapor sorption on a composite consisting of CaCl$_2$ confined in the mesopores of KSK silica gel pellets (0.355–1.4 mm) at temperatures of 33–69°C and H_2O

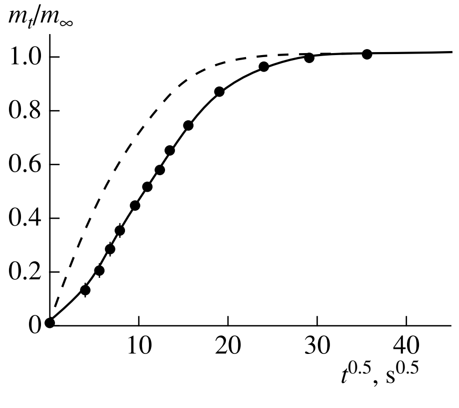

Fig. 5. Water sorption kinetics at 59°C. The points are experimental data for 0.355- to 0.425-mm pellets (the initial and final water vapor pressures are 35.6 and 40.6 mbar, respectively). The solid line is the least squares fit of the nonisothermal model to the experimental data (α = 342, β = 24.8, and $D_e = 0.46 \times 10^{-6}$ m^2/s). The dotted line represents the data calculated using the isothermal equation (4) (D_e = 0.46×10^{-6} m^2/s).

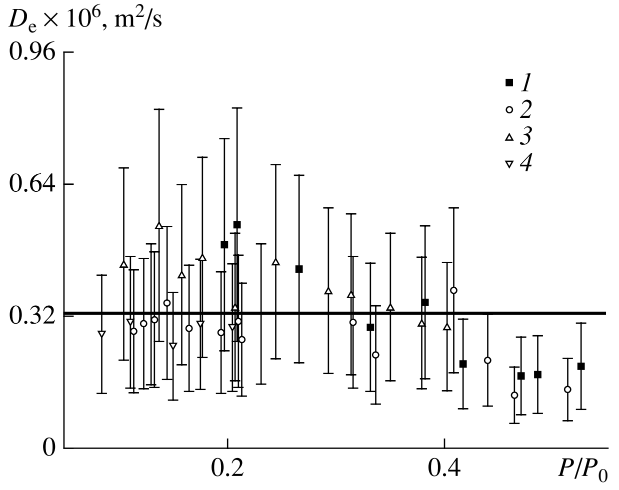

Fig. 6. Calculated pore diffusion coefficients for 0.71- to 0.85-mm SWS-1L pellets at (*1*) 33, (*2*) 49, (*3*) 59, and (*4*) 69°C. The solid line is the weighted average.

pressures of 8–70 mbar. Our results suggest that, as the pellet diameter is decreased, the sorption rate and the effective diffusivity increase approximately as R_{pel}^{-2} (at $2R_{\text{pel}} \geq 0.71$ mm). The effective diffusivity depends on the water vapor sorption isotherm and is, accordingly, a function of the amount of sorbed water. Applying the correction for the local slope of the sorption isotherm, we calculated the effective pore diffusion coefficient of water to be $D_e = (0.35 \pm 0.17) \times 10^{-6}$ m²/s. This diffusion coefficient does not depend on the sorption value or temperature. It is 7–10 times smaller than the Knudsen diffusion coefficient of water calculated for a single cylindrical pore whose size is equal to the average pore size of the composite examined. Two possible causes of this decrease in the diffusion coefficient have been considered, specifically, an increase in the pore tortuosity due to the presence of the salt and the interaction between water and the salt. The former cause is in better agreement with experimental data.

APPENDIX

The mass and heat balance equations describing the nonisothermal kinetics of matter sorption on identical spherical pellets can be written as [12]

$$\begin{cases} (1-\varepsilon)\dfrac{\partial q}{\partial t} + \varepsilon\dfrac{\partial c}{\partial t} = \varepsilon D_e\left(\dfrac{\partial^2 c}{\partial R^2} + \dfrac{2}{R}\dfrac{\partial c}{\partial R}\right) \\ (-\Delta H)\dfrac{\partial \bar{q}}{\partial t} = C_p\dfrac{\mathrm{d}T}{\mathrm{d}t} + ha(T-T_0), \end{cases}$$

$$\bar{q} = \frac{3}{R_{\text{pel}}^3}\int_0^{R_{\text{pel}}} qr^2\,\mathrm{d}r.$$

In the case of a small concentration change in the gas phase, the solution appears as

$$\frac{m_t}{m_\infty} = 1 - \sum_{n=1}^{\infty}\frac{9[(p_n\cot p_n - 1)/p_n^2]\exp(-p_n^2 D_{\text{eff}}t/R_{\text{pel}}^2)}{\beta^{-1} + 1.5[p_n\cot(p_n(p_n\cot p_n - 1)/p_n^2 + 1)]}, \tag{A.1}$$

where p_n is the root of the equation $3\beta(p_n\cot p_n - 1) = p_n^2 - \alpha$, $\alpha = \dfrac{ha}{C_p}\dfrac{R_{\text{pel}}^2}{D_{\text{eff}}}$, and $\beta = \dfrac{\Delta H}{C_p}\left(\dfrac{\partial q^*}{\partial T}\right)_p$. Here, h is the heat transfer coefficient, a is the heat transfer area per unit weight of the sorbent, ΔH is the heat of sorption, and q^* is the equilibrium moisture content of the pellets.

The limiting case of isothermal kinetics (Eq. (4)) takes place at $\alpha \longrightarrow \infty$ (infinitely rapid heat transfer) or $\beta \longrightarrow 0$ (infinitely high heat capacity). In practice, sorption kinetics is indistinguishable from isothermal at $\alpha/\beta > 60$ [1].

Let us estimate α and β for 1-mm pellets under the assumption that the main mechanism of heat removal is transfer from the sorbent pellets to the substrate. In this case, heat is mainly transferred through the water vapor layer between the pellets and the substrate and the heat transfer coefficient can be estimated using the formula $h = \lambda/R_{\text{pel}}$, where $\lambda = 0.02$ W m^{-1} K is the heat conductivity of water vapor. For the pellets considered, h = 20 W m^{-2} K^{-1}. For the sorbent density $\rho = 1300$ kg/m³, C_p = 1 kJ kg^{-1} K^{-1}, $D_{\text{eff}} = 3 \times 10^{-11}$ m²/s, ΔH = 2600 kJ/kg, and $\partial q/\partial T$ at T = 59°C and P = 32 mbar estimated at 0.0126 K^{-1}, we obtain $\alpha = 1800$ and $\beta = 32$.

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