

INFLUENCE OF THE GRAIN SIZE ON THE KINETICS OF WATER SORPTION ON THE SELECTIVE WATER SORBENT "SWS-1L" UNDER TYPICAL OPERATING CONDITIONS OF ADSORPTION HEAT PUMPS

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Abstract

Water sorption kinetics can strongly influence the dynamic behavior of an adsorption heat pump, hence it should be studied and optimized. This communication presents experimental results on water sorption kinetics on the composite sorbent "33.7 wt.% calcium chloride inside mesoporous silica" measured by a "constant-volume /variable-pressure" method. The main aspect of this work is to find out the influence of the grain size of the sorbent on its sorption dynamics. Four samples having different grain sizes have been prepared; namely, 0.34-0.5; 0.71-1.0; 1.3-1.6 and 3.0-3.2 mm. The measurements have been carried out on 3g samples of loose grains on an isothermal plate under three different conditions for starting pressure and sorption temperature. These initial and boundary conditions (60 mbar, 50°C), (40 mbar, 50°C) and (40 mbar, 35°C) are typical for the operation of adsorption heat pumps. The adsorption kinetic curves are non-exponential and can be described by the characteristic times $\tau_{0.5}$ and $\tau_{0.9}$ that correspond to the water dimensionless loadings of 0.5 and 0.9, respectively. The results obtained evidence a remarkable enhancement of the rate of water sorption with the decrease in the sorbent grain size. Indeed, for 3.0-3.2 mm particles the typical half-time of water sorption is measured to be 140-200 s, while for 0.34-0.5 mm particles only 11-15 s. The dependence of $\tau_{0.5}$ and $\tau_{0.9}$ on the average grain radius declares that neither the external heat and mass transfer resistances nor the intercrystalline diffusion resistance play solely the dominant role in characterizing the considered heat and mass transfer problem. Due to the large equilibrium uptake of SWS-1L and fast adsorption kinetics the specific heat power generated inside small adsorbent grains can exceed 20-30 W per 1 g of the SWS, that, in principle, could lead to very compact adsorption units for energy transformation. The effective diffusivity of water was estimated to be $3 \cdot 10^{-10} \text{ m}^2/\text{s}$.

KEYWORDS

Calcium chloride; selective water sorbent; silica gel; adsorption heat pumps; adsorption kinetics; SWS-1L; vapor diffusion.

INTRODUCTION

A family of new working materials, so called Selective Water Sorbents (SWSs), has been recently presented by Aristov *et al.* [1] for sorption air conditioning and heat pumps. These materials are composites "hygroscopic salt inside porous matrix" that demonstrate an inter-mediate behavior between solid adsorbents, salt hydrates and liquid absorbents. The SWS sorption properties can be controllably modified, as depicted by the group of authors [1-4], by varying a) porous structure of the host matrix, b) chemical nature of the impregnated salt, and c) the amount of the salt inside the pores. The study of thermodynamic properties of these materials has shown that composites based on CaCl_2 and LiBr as impregnated salts and silica gels and alumina as host matrices can operate with cycles whose maximum temperature is about 100°C lower than that of the zeolite/water pair with COP values considerably higher than those obtainable by zeolite/water at the same temperature of the heat source [1, 5].

Recently a lab-scale prototype of adsorption chiller with granulated bed of SWS-1L has been built to perform first experimental tests [6, 7]. Advanced sorption properties of this material yield to the high $COP = 0.6$ that gives a promising alternative to the common zeolite or silica gel for application in solid sorption units driven by low temperature heat ($T \leq 90-100^{\circ}\text{C}$). Low specific power of the device is a result of not optimized geometry of the adsorber and of the pelletised adsorbent shape. Thus, the detailed measurement of the water sorption kinetics on SWS-1L pellets under real operating conditions of sorption heat pumps (SHPs) could give a starting point for optimizing the sorbent grain size, salt concentration, etc. In a previous study, Dawoud and Aristov [8] have measured the kinetics of water vapor sorption on two host materials; namely, mesoporous silica gel and alumina in comparison with the two composites SWS-1L and SWS-1A formed by impregnating these host matrices with CaCl_2 . The pellet size of SWS-1L lied between 1-3 mm, while the SWS-1A was in the form of extrudates having a diameter of 2.8 mm and a length between 3-5 mm. The measurements prevailed a remarkable increase in the differential water loading on both SWS-sorbents over that on their host materials. However, and due to the increased diffusion resistance to water sorption resulting from the presence of salt, the kinetics of water sorption into the host matrices is faster than that into the two SWS-composites. Both the salt concentration and the pellet size have to be optimized from the point of view of the adsorption kinetics.

This work is the first share in this direction and aims at prevailing the influence of the grain size of SWS-1L on the kinetics of water vapor sorption under the same operating conditions of sorption heat pumps, which have been considered in [8]. The concentration of CaCl_2 in the mesoporous silica gel being measured amounts to 33.7 %.

EXPERIMENTAL SETUP

The sorption kinetics' setup consists, as depicted in Fig. 1, mainly of an isothermal measuring cell and a vapor vessel. The cell and the vessel are connected by a pipe, which can be locked by a valve. Inside the measuring cell the sorbent sample is placed onto the isothermal heat exchanger plate. The sample is regenerated by heating it to 150°C for two hours under vacuum of 1.10^{-2} mbar. The measuring cell is then cooled down to the required sorption temperature. Before starting an experiment, water vapor from the steam generator is to be charged into the vessel to the required starting pressure, which is higher than the vapor pressure of the adsorbed water in the SWS-sample in the measuring cell (thermodynamic unequilibrium).

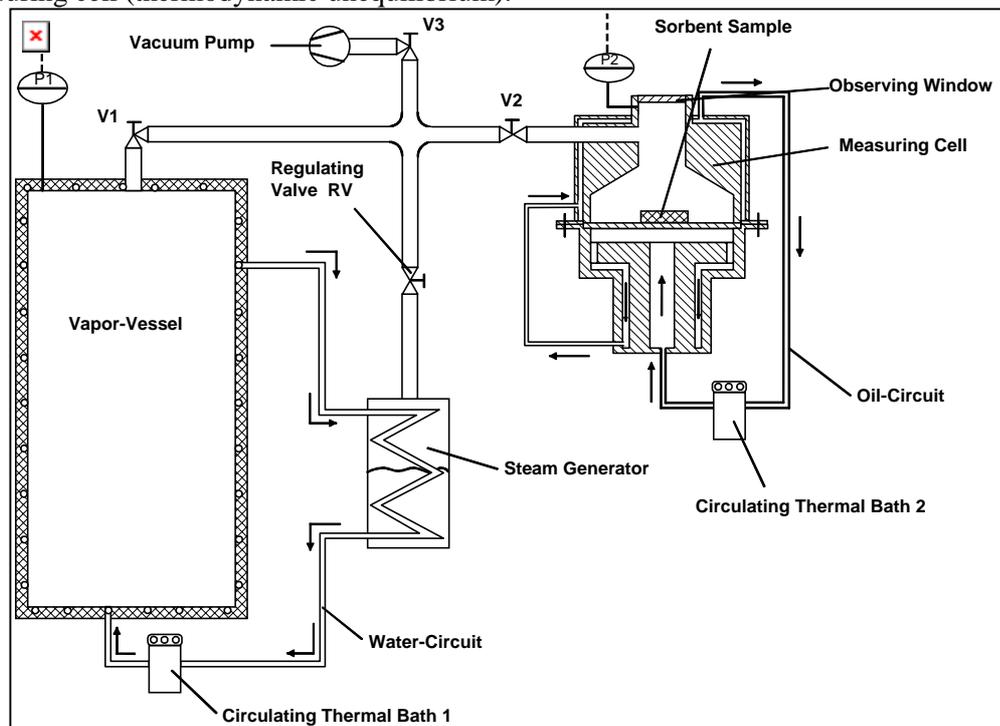


Fig. 1. Setup for measuring the kinetics of water vapor sorption

The course of pressure decrease with time due to sorption, after opening the valve (V2), determines the kinetics of the sorption process. The experimental procedure as well as the dynamic evaluation of the setup are explained in detail by Dawoud and Aristov [8].

The tested SWS-1L has an internal surface area of 230 m²/g, an average pore diameter of 14.5 nm and a salt content of 33.7 wt. %. The samples have been prepared by the Boreskov Institute of Catalysis, Russia. Four samples having different grain sizes have been prepared; namely, 0.34-0.5 / 0.71-1.0 / 1.3-1.6 and 3.0-3.2 mm. The measurements have been carried out on 3g samples of loose grains on an isothermal plate under the three different boundary conditions for starting pressure and sorption temperature. These boundary conditions are given in Table 1. The sorption temperature of 50 °C is the mean temperature of low temperature radiative heating systems in middle Europe (55/45 °C), while the 35 °C is the mean temperature of floor heating systems (40/30 °C). Therefore, the selected boundary conditions are typical for the operation of adsorption heat pumps. The initial water uptake (x_0) has been determined by thermogravimetric tests on the SWS-1L grains under the same activation conditions of 150 °C, 0.01 mbar for 2h and has been found to be equal 0.17 g/100 g.

Boundary condition	Sorption temperature [°C]	Starting pressure, $p_0(\text{H}_2\text{O})$ [mbar]	Starting relative humidity [%]
1	50	60	48.6
2	50	40	32.4
3	35	40	71.1

Table 1. The boundary conditions of the investigated sorption processes

RESULTS AND DISCUSSION

A water vapor mass balance on the measuring cell of the sorption kinetics test-rig was considered in ref. [8]. In order to compare the results of measuring the sorption kinetics under different operating conditions, it is reasonable to represent the time variation of the water loading in a dimensionless form. This may occur by defining the dimensionless differential water loading χ as the ratio between the instantaneous differential water loading to the maximum differential water loading achievable at each operating condition of the sorption process on the sorbent sample:

$$\chi(t) = \frac{x(t) - x_0}{x_\infty - x_0} \quad (1)$$

Figures 2-4 give the kinetic curves of water sorption on the different pellet fractions investigated in a “dimensionless differential water loading vs. time” presentation.

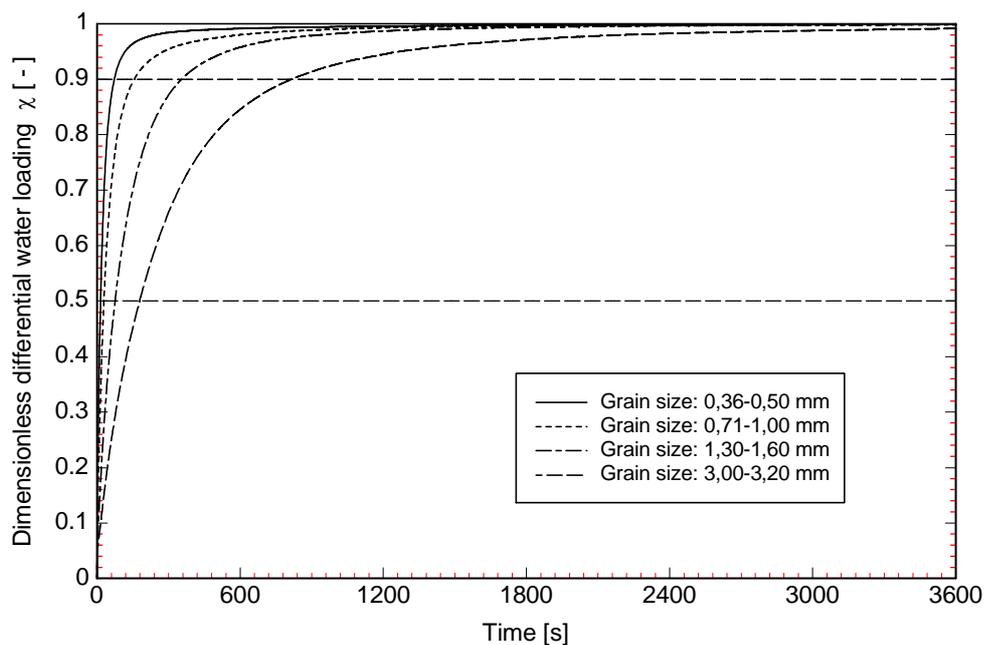


Fig. 2. Comparison between the sorption kinetics of water vapor on different grain sizes of SWS-1L at a starting pressure of 60 mbar and a sorption temperature of 50 °C

This way of presentation clearly shows that the sorption rate considerably increases if the grain size decreases (Fig. 2-4). Experimentally determined characteristic times $\tau_{0,5}$ and $\tau_{0,9}$ are displayed in Tables 2-4. We tried to fit the dependence of $\tau_{0,5}$ (and $\tau_{0,9}$) on the average radius of the tested grains R_{av} with a power law according to equation 2.

$$\tau \propto R_{av}^n \quad (2)$$

The obtained values of n are presented in Table 5, lie between 1.2 and 1.45 and do not depend on χ . If the sorption rate is limited by the surface resistance to the heat or mass transfer the value of efficient rate constant k_{eff} (that in first approximation is proportional to $\tau_{0,5}^{-1}$) should be proportional to the specific external surface area of grains (that means the surface related to the grain volume), that means increases as R_{av}^{-1} (or $\tau_{0,5} \sim R_{av}^1$) [9]. If the water diffusion inside a grain (intercrystalline diffusion) is the slowest (or dominant) stage, the relation should be $k_{eff} \sim R_{av}^{-2}$ (or $\tau_{0,5} \sim R_{av}^2$). We found that $1 < n < 2$ (Table 5), hence, we can conclude that both resistances are sharing in dominating the characteristics of the considered heat and mass transfer problem.

Rapid increase of $\tau_{0,5}$ for pellets that are larger than 1.0-1.5 mm (Tables 2-4) select this size as the upper limit for applying in adsorption heat pumps with loose adsorbent layer [10]. For such units the specific heat power generated by adsorption can be very large. Indeed, for the smallest pellets ($R_{av} = 0.212$ mm) a half of equilibrium adsorption (0.12 g water per 1 g SWS) is reached after 15 s of the sorption process that corresponds to a sorption heating power of 31.4 W per 1 g SWS. For these calculations we consider the average heat of water adsorption to be 70 kJ/mol [11]. Thus, a 1 kW unit needs theoretically just $M_{0,5} = 32$ g of SWS-1L.

Diameter [mm]	Time [min] $\tau_{0,5}$	Time [min] $\tau_{0,9}$	x_{∞} [g/100 g]	$x_{\infty} - x_0$ [g/100 g]	$W_{0,5}$ W/g	$W_{0,9}$ W/g	$M_{0,9}$ g/kW
0.335-0.5	0.25	1.20	24.342	24.172	31.4	11.8	85.0
0.71-1.0	0.48	2.58	24.424	24.254	16.3	5.5	182.7
1.3-1.6	1.26	5.09	24.485	24.315	5.9	2.8	359.1
3.0-3.2	2.97	13.55	24.405	24.235	2.6	1.04	959.8

Table 2: Comparison between the sorption kinetics characteristics of the different grain sizes of SWS-1L at a starting pressure of 60 mbar and a sorption temperature of 50 °C

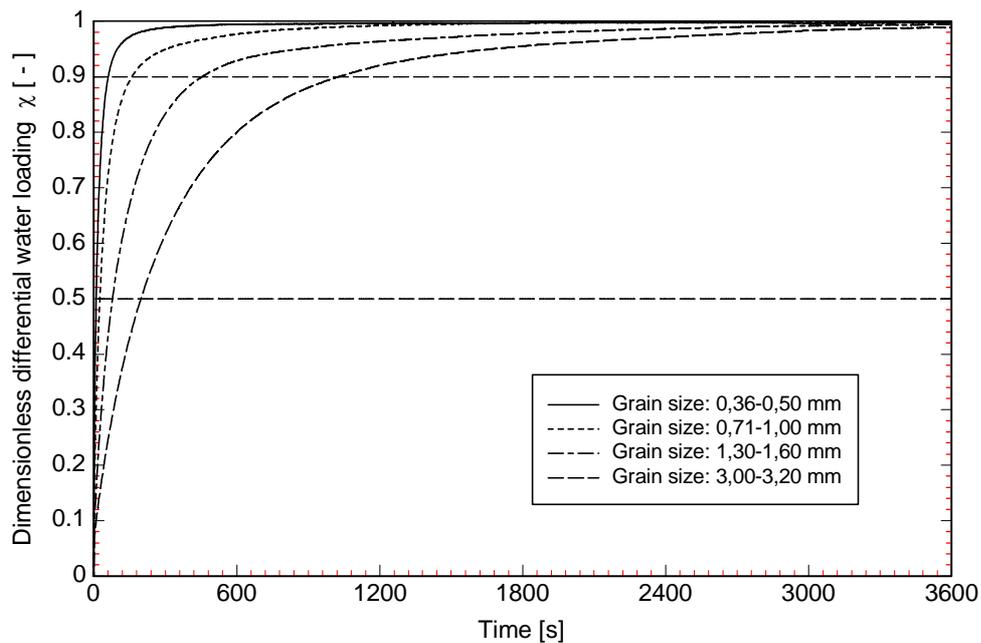


Fig. 3. Comparison between the sorption kinetics of water vapor on different grain sizes of SWS-1L at a starting pressure of 40 mbar and a sorption temperature of 50 °C

For more equilibrated operation (for instance, with $\chi = 0.9$) the time of the adsorption stage is almost 5 times longer; that corresponds to $W_{0.9} = 11.8$ W/g and $M_{0.9} = 85$ g/kW. Even for 3 mm grains the adsorption generates a heat power of 2.6 and 1.04 W/g at $\chi = 0.5$ and 0.9, respectively, that is still very promising for compact adsorption devices for energy transformations. The results on estimating $W_{0.5}$, $W_{0.9}$ and $M_{0.9}$ are also given in Tables 2-4. To transfer this sorption heating power from a pellet to a heat carrier fluid, a very efficient heat conductance has to be provided [12].

Diameter [mm]	Time [min] $\tau_{0.5}$	Time [min] $\tau_{0.9}$	x_{∞} [g/100 g]	$x_{\infty} - x_0$ [g/100 g]	$W_{0.5}$, W/g	$W_{0.9}$, W/g	$M_{0.9}$, g/kW
0.335-0.5	0.18	1.00	14.684	14.514	26.1	8.5	118.2
0.71-1.0	0.43	2.63	14.641	14.471	10.9	3.2	310.9
1.3-1.6	1.32	7.52	14.612	14.442	3.5	1.1	895.2
3.0-3.2	3.30	17.05	14.763	14.593	1.4	0.49	2030

Table 3: Comparison between the sorption kinetics characteristics of the different grain sizes of SWS-1L at a starting pressure of 40 mbar and a sorption temperature of 50 °C

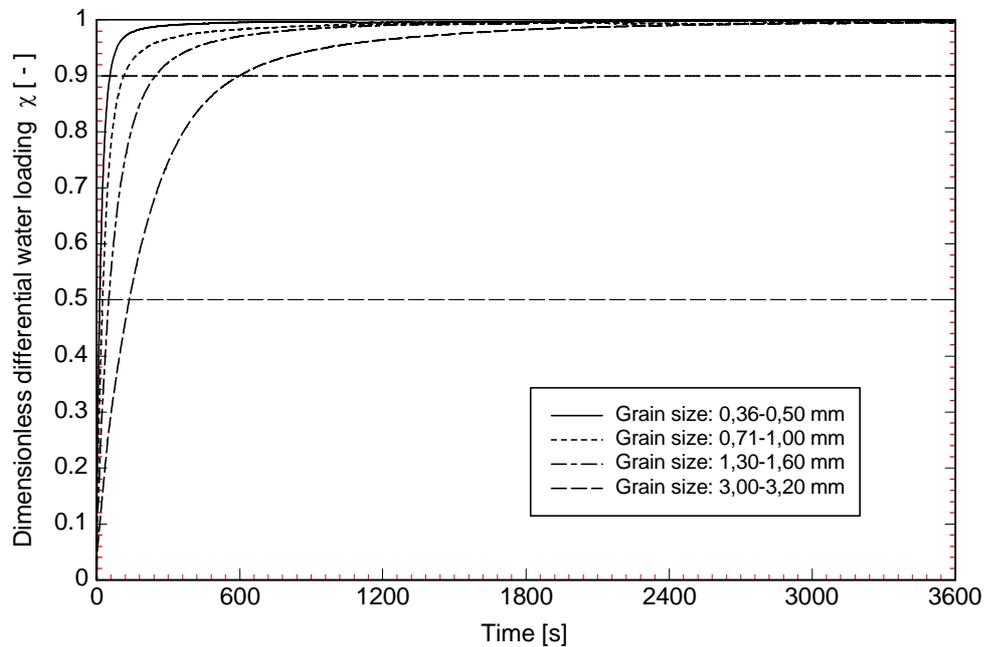


Fig. 4. Comparison between the sorption kinetics of water vapor on different grain sizes of SWS-1L at a starting pressure of 40 mbar and a sorption temperature of 30 °C

Diameter [mm]	Time [min] $\tau_{0.5}$	Time [min] $\tau_{0.9}$	x_{∞} [g/100 g]	x_{∞} [g/100 g]	$W_{0.5}$, W/g	$W_{0.9}$, W/g	$M_{0.9}$, g/kW
0.335-0.5	0.23	0.93	19.602	19.602	27.6	12.3	81.3
0.71-1.0	0.42	1.82	19.584	19.584	15.1	6.3	159.2
1.3-1.6	0.85	4.03	19.669	19.669	7.5	2.8	359.1
3.0-3.2	2.28	9.90	19.691	19.691	2.8	1.15	865.9

Table 4: Comparison between the sorption kinetics characteristics of the different grain sizes of SWS-1L at a starting pressure of 40 mbar and a sorption temperature of 35 °C

Initial conditions	$\chi = 0.5$	$\chi = 0.9$
1	1.24	1.25
2	1.45	1.46
3	1.16	1.20

Table 5: Values of the exponent (n) after fitting the characteristic times of the adsorption process to equation (2)

For quantitative description of the kinetic curves as well as for extracting the information about the water diffusivity, a mathematical analysis should be done. This analysis may be based either on analytical or on numerical solutions of a suitable model for the adsorption process under constant-volume / variable-pressure conditions. Several analytical solutions are known and related to the isothermal case of micropore, macropore and dual diffusion controls [9, 13-16] and non-isothermal case (see Table 9.7 in ref. [9] as well as [17-20]). Unfortunately, only few of them considered adsorption kinetics under constant-volume / variable-pressure conditions. In this communication, we've applied the model suggested by Cočičík et al. [21] for the quantitative description of experimental curves. The model considers that the sorption rate is controlled by both intercrystalline diffusion and external heat transfer that is probably the closest model to our case. The model gives for dimensionless concentration of the sorbate (water) the following analytical equations:

$$\frac{c(0_+) - c(\tau)}{c(0_+) - c(\infty)} = 1 - \sum_{n=1}^{\infty} \frac{9(1 + \alpha^*) [Y_n / (-q_n^2)]^2 \exp(-q_n^2 \tau)}{\frac{1}{\beta_n} + \frac{3}{2} \frac{\beta}{\beta_n} [q_n \cot(q_n) (\frac{Y_n}{q_n^2} + 1)] + \frac{3}{2} \frac{\alpha^* B_n}{q_n^4 \beta_n}} \quad (3)$$

where q_n are the roots of the following equation

$$(-q_n^2 + \alpha) + 3\beta \cdot Y_n - \frac{3\alpha^*}{q_n^2} (-q_n^2 + \alpha) Y_n = 0, \quad (4)$$

where

$$Y_n = q_n \cot(q_n) - 1 \quad (5)$$

$$\beta^* = \beta \cdot (1 - \frac{3\alpha^* Y_n}{q_n^2}), \quad (6)$$

$$B_n = Y_n [(q_n^2 - \alpha) q_n \cot(q_n) - 2\alpha] + q_n^2 (q_n^2 - \alpha), \quad (7)$$

$$\text{and } \alpha^* = \frac{c(0_+) - c(\infty)}{c(\infty) - c(0_-)} = \frac{p(0_+) - p(\infty)}{p(\infty) - p(0_-)}, \quad (8)$$

where $p(0_+)$ is the vapor pressure directly after the step change in pressure (after opening the valve V2 in Fig. 1), $p(0_-)$ is the vapor pressure prior to the step change, and $p(\infty)$ is the final (equilibrium) pressure.

$$\alpha = \frac{ha}{\rho_s c_s} (\frac{R_{av}^2}{D}) \text{ and} \quad (9)$$

$$\beta = \frac{\Delta H}{\rho_s c_s} \frac{\partial q^*}{\partial T}, \quad (10)$$

are parameters have to be found by comparison of calculated kinetic curve with experimental one (here ρ_s - adsorbent density, C_s - adsorbent specific heat).

Using this model, we obtained quite fair description of the experimental data with the following values for the fitted parameters: the effective diffusivity $D = 3 \cdot 10^{-10} \text{ m}^2/\text{s}$, $\beta = 35$, and $h = 4.5 \text{ W}/(\text{m}^2\text{K})$. Although these values look quite reasonable, we consider them as a rough estimation because two assumptions of the model of Cočičík et al. [21] do not match with our experimental conditions. First, the real water sorption isotherm on SWS-1L is not linear and, second, the obtained water loading increments under the boundary and initial conditions of our experiments are quite high. The later fact implies that the temperature dependence of the intercrystalline diffusion has to be considered in the model. Moreover, the external mass transfer resistance due to the formation of a solution film near the external pellet surface, as it was found by Koptuyug et al. [22] has also to be taken into account. Considering all these peculiarities of the coupled heat and mass transfer problem under study shows the necessity for setting up a more sophisticated model which can't then be solved analytically but numerically. A step by step approach towards the numerical solution of the sophisticated model and comparing its results with experimental data will be the aims of our following communications in the field.

CONCLUSION

The kinetics of water vapor sorption on different grain sizes of SWS-1L has been experimentally studied. The measurements have been carried out on 3g samples of loose grains on an isothermal wall under three different operating conditions of sorption heat pumps. The results obtained evidence a remarkable enhancement of the rate of water sorption with the decrease in the sorbent grain size. Indeed, for 3.0-3.2 mm particles the typical half-time of water sorption is measured to be 140-200 s, while for 0.34-0.5 mm particles only 11-15 s. This indicates that the water adsorption rate is limited mainly by water or/and heat transport in adsorbent grains. Due to the large equilibrium uptake of SWS-1L and fast adsorption kinetics the specific heat power generated inside small adsorbent grains can exceed 20-30 W per 1 g of the SWS, that, in principle, could lead to very compact adsorption units for energy transformation. The efficient diffusivity of water was estimated to be $3 \cdot 10^{-10} \text{ m}^2/\text{s}$.

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Nomenclature

a	specific surface area per unit volume of a pellet [m^{-1}]
B_n	variable defined by equation (7)
c	specific heat capacity [$\text{kJ kg}^{-1} \text{K}^{-1}$] / sorbate concentration in the gas phase [kg m^{-3}]
COP	coefficient of performance [-]
D	diffusion coefficient [$\text{m}^2 \text{s}^{-1}$]
h	heat transfer coefficient [$\text{W m}^{-2} \text{K}^{-1}$]
k_{eff}	effective rate constant
n	exponent in equation (2) and Table (5) [-]
p	pressure [mbar]
q^*	equilibrium sorbed phase concentration [kg m^{-3}]
q_n	roots of equation (4)
R	radius of a grain [mm]
t	time [s]
T	temperature [K]
V	volume [m^3]
x	water loading [g / 100 g]
W	Specific absorption heating power of SWS-1L [W g^{-1}]
Y_n	variable defined by equation (5)

Greek symbols

α	dimensionless parameter defined by equation (9)
α^*	quotient defined by equation (8)
β	dimensionless parameter defined by equation (10)
β^*	variable defined by equation (6)
ΔH	heat of adsorption [kJ kg^{-1}]
Φ	pore diameter [nm]
ρ	density [kg m^{-3}]
τ	characteristic time [s] / dimensionless time in equation (3) [-]
$\tau_{0.5}$	time requirement for χ to reach 0.5
$\tau_{0.9}$	time requirement for χ to reach 0.9
χ	dimensionless differential water loading [-]

Subscripts

0_-	prior to the step change in pressure (before opening the valve V2 in Fig. 1)
0_+	directly after the step change in pressure
0.5	at the time, when χ reaches 0.5
0.9	at the time, when χ reaches 0.9
av	average
o	initial value
s	Sorbent
∞	final value (equilibrium)

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