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Effect of residual gas on the dynamics of water adsorption under isobaric stages of adsorption heat pumps: Mathematical modelling

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ABSTRACT

A mathematical model of the coupled heat and mass transfer in an adsorbent layer was developed to study the effect of a non-adsorbable gas (air, hydrogen) on kinetics of water adsorption on loose grains of the composite adsorbent SWS-1L (silica modified by calcium chloride). The adsorbent monolayer was placed on the surface of an isothermal metal plate at $T = 60$ °C and equilibrated with the mixture of water vapor at constant $P = 10.3$ mbar in the presence of the non-adsorbable gas at a variable partial pressure $P_A = 0.06–14.3$ mbar. After that the metal plate is subjected to a temperature drop down to 35 °C that initiates water adsorption. It is shown that the adsorption of water causes effective gas sweeping to the surface where it was accumulated as a gas-rich layer. This results in dramatic slowing down of the adsorption and heat transfer processes.

1. Introduction

Adsorptive heat transformation (AHT) based on solid adsorption systems has received much attention in recent years as an alternative to conventional compression systems using CFC [1–4]. In order to be competitive with compression refrigerators the specific power of the AHT units has to be improved. A non-adsorbable gas can greatly affect the rate of adsorption and, hence, the AHT specific power. Indeed, an important feature of AHT with water as a working fluid is low pressure during isobaric ad- and desorption phases. Because of this, the presence of even little amount of air (or any other non-adsorbable gas) can significantly affect the AHT performance. This phenomenon is well-known from practical utilization of heat and mass transfer apparatuses. Chlorine production is accompanied by the generation of a modicum of hydrogen which little by little is accumulated in a heat exchanger-condenser. This reduced both the average chlorine concentration and increases the hydrogen concentration in the vicinity of condenser surface [5]. This gradual accumulation is caused by a Stephan flux [6,7], which effectively sweeps hydrogen to the condenser surface. In [7], the authors revealed the reduction of heat transfer in a granulated adsorbent layer in the presence of residual air. It was supposed that this effect can significantly reduce the performance of AHT. In practice a residual gas can present inside evacuated AHT equipment: air due to leakage or desorption, while hydrogen due to corrosion. Detailed study of the mentioned reduction was performed in [8,9]. In [8], the effect of a non-adsorbable gas (air) on kinetics of water adsorption on loose grains of the composite adsorbent SWS-1L (silica modified by calcium chloride) (grain size 0.8–0.9 and 1.4–1.6 mm) was studied. The adsorbent grains were placed on the surface of isothermal metal plate at $T = 60$ °C and equilibrated with the mixture of water vapor at $P_{H2O} = 10.3$ mbar and air at a certain partial pressure P_A. After that the metal plate was subjected to a temperature drop down to 35 °C at almost constant pressure over the grains. Reduction of the adsorption rate was revealed even at the partial pressure of residual air P_A as low as 0.05 mbar. At $P_A > 0.4$ mbar, the kinetic curves were near-exponential and the characteristic adsorption time τ increased as $\tau = \tau_0 + BP_A$, where $B = 700 \pm 50$ s/mbar. Desorption stage was less affected by the residual air. The specific power released during adsorption process was estimated as a function of the amount of residual gas. In [9], the study of this effect was extended over two adsorbents promising for adsorption chilling: silica Fuji type RD and FAM-Z02. The rate of adsorption by the loose grains of Fuji silica RD was found to be less sensitive to the presence of residual air than for SWS-1L. The characteristic time $\tau_{0.8}$ linearly increased with the rise in P_A with the slope $B = 250 \pm 6$ s/mbar. FAM-Z02 demonstrated intermediate behavior with $B = 590 \pm 45$ s/mbar.

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Nomenclature

C	concentration (mole/m^3)
c_p	effective heat capacity (J/(kg K))
D_W	efficient water diffusivity (m^2/s)
ΔH	heat of adsorption (J/mole)
J	molar flux (mole/(m^2 s))
L	characteristic diffusional length (m)
m	mass (kg)
N	uptake (mole H_2O/mole $CaCl_2$)
P	pressure (mbar)
R_p	grain radius (m)
R	universal gas constant (J/(mole K))
t	time (s)
T	temperature (K)
u	convective speed of the gas mixture (m/s)
V	volume (m^3)
x	weight fraction of the salt (kg/kg)
z	spatial coordinate

Greek symbols

α_p	heat transfer coefficient (W/(m^2 K))
ε	grain porosity
ν	dimensionless adsorption
λ	coefficient of heat conductivity (W/(m K))
μ	mass (kg/kmole)
ρ	density (kg/m^3)

Subscripts

0	initial value
a	air
A	residual gas
W	water vapor

The formation of the gas-rich layer in the vicinity of grain surface is a complex process that is influenced by coupled heat and mass transfer between the grain and gas phase as well as inside the grain. In this paper we report a mathematical model which describes the origin of the Stephan flux, the formation and temporal evolution of the gas-rich layer near the surface of the composite sorbent SWS-1L. The description of water sorption process inside the grain was performed in much the same way as in [10]. It was our aim in this work to calculate the evolution of temperature, pressure and concentration of the adsorbed water as a function of time t and the distance r from the grain center. When possible, the calculated values were compared with those experimentally measured in [8] (for residual air) or in this work (for residual hydrogen).

2. Experimental

To measure the dynamics of water sorption on SWS-1L in the presence of hydrogen, we used the same methodology (the so-called large temperature jump (LTJ) method [11]) and equipment as it was carefully described in [8] for the residual air. The adsorbent grains were placed on the surface of an isothermal metal plate at $T = 60$ °C and equilibrated with the mixture of water vapor at $P = 10.3$ mbar and air (hydrogen) at a certain partial pressure P_A between 0.06 and 14.3 mbar. After that the metal plate was subjected to a temperature drop down to 35 °C at almost constant pressure over the grains. The data of the pressure evolution P(t) required for calculating the water uptake $m(t)$ were recorded each 1 s by a data acquisition system. Dimensionless uptake was calculated as $\nu = m(t)/m(\infty)$.

The tested adsorbent SWS-1L was prepared by a silica KSK impregnation with a saturated aqueous solution of $CaCl_2$ at $T = 25$ °C. The salt content amounted to 33.7 wt% (dry base). The average pore diameter of SWS-1L was 15 nm. Grain sizes of the sample was selected as 1.6–1.8 mm. Typical weight of the dry sample was 0.420–0.425 g that corresponded to a one layer of loose grains covering the metal plate.

3. Sorption dynamics in the presence of hydrogen

After initiating the holder cooling, its temperature reached the final temperature within approximately 1 min, while the pressure reduction was slower and lasted some tens minutes or even hours (Fig. 1). At any P_A, the kinetic curves of water sorption were near-exponential over the whole range of uptake so that $m(t) = m_0 + (m_f - m_0)[1 - \exp(-t/\tau)]$ that is similar to the sorption dynamics in the presence of air [8]. A thorough look at the curves reveals that the experimental uptake is slightly larger than exponential at short and long times, and somewhat smaller – at intermediate times. The difference does not exceed 0.03 and increases at elevated P_A (Fig. 1). Interestingly, that in the presence of air no deviation was observed and the uptake curves were very close to exponential [8].

The characteristic time of sorption increased as $\tau = \tau_0 + BP_A = 261$ s + 177 s/mbar, where τ_0 is the characteristic time in a pure vapor ($P_A = 0$) and B is the slope that characterizes an impact of residual gas (Fig. 2). This figure demonstrates that the effect of residual hydrogen is less dramatic as compared with air, and the ratio of the slopes $B(\text{air})/B(H_2)$ is equal to 3.64. This ratio is close to the ratio of effective diffusivities (cm^2/s) in the binary mixture "air–vapor"

$$D_a = 292/(P_W + P_A),$$

and "hydrogen–vapor"

$$D_h = 1136/(P_W + P_A),$$

where P_W is the vapor partial pressure (in mbar), equal to $D_h/D_a = 3.89 \approx (\mu_a/\mu_h)^{1/2}$, where μ_a and μ_h are the molecular masses of air and hydrogen [12].

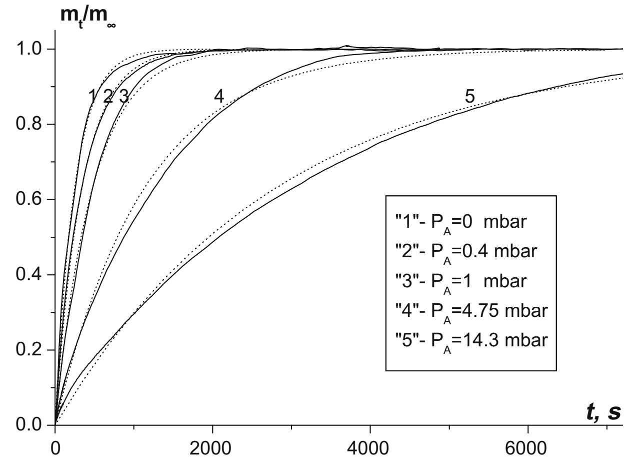

Fig. 1. Dimensionless uptake curves of water sorption on SWS-1L at various partial pressures of hydrogen (dashed lines). Solid lines give an exponential approximation.