

AN OPTIMAL SORBENT FOR ADSORPTION HEAT PUMPS: THERMODYNAMIC REQUIREMENTS AND MOLECULAR DESIGN

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Abstract

In this communication we report the new approach to a choice of solid sorbent for an adsorption heat pump (AHP). First, we discuss requirements to desirable solid sorbent, the thermodynamic characteristics of which could allow perfect realisation of a single-effect non-regenerative adsorption cycle driven by low temperature heat. The conclusion has been made that solid sorbents which match the theoretical requirements for the mentioned cycle in the best way are those with a monovariant equilibrium, namely, salts and their crystalline hydrates both pure and confined to a porous host matrix (so called Selective Water Sorbents).

In the second part of the paper we suggest and discuss practical tools available to design and synthesise such optimal sorbent. These are the chemical nature and content of the confined salt, the average size of pores of the host matrix and synthesis conditions. All these tools can be used to adjust the properties of real composite adsorbent to the optimal one.

KEYWORDS: adsorption equilibrium, water vapour, adsorption chilling, adsorption heat pumps, low temperature heat, molecular design

INTRODUCTION

In many adsorption heat pumps water is used as an ecologically sound refrigerant with large heat of evaporation. The choice of solid sorbent for reversible water exchange is of high importance because it can strongly affect output parameters of AHP.

Commonly the selection of the sorbent is performed in two steps:

a) specification of the main parameters of the adsorption cycle. The simple adsorption cycle can be schemed in the Clapeyron diagram (Fig.1). The cycle operation is determined by three temperatures: the temperatures of the coolant in the condenser T_c and in the evaporator T_e , and the maximum desorption temperature $T_3 = T_{des}$. In the case of a standard cycle of adsorptive chiller the condenser temperature T_c is commonly dictated by the temperature of the environment where the condensation heat is dissipated to. Usually, this temperature depends on a climatic zone and can be fixed by convention as 25°C for moderate climate and 45°C for a hot one [1]. The temperature maintained in the evaporator is that needed for cooling and is usually in the range of 0 to 10°C. Finally, the maximum desorption temperature T_{des} is the temperature of heat source available for dehydration of adsorbent (stage 2-3). For solar cooling it is 70-110°C.

If these three temperatures are chosen the next step is

b) scanning of already available solid sorbents to select one the thermodynamic properties of which better (even if not perfectly) fits the determined cycle. This choice is usually made among solid sorbents which are already known and commercially produced, such as zeolites, silica gels, inorganic salts, their crystalline hydrates, etc., for which data on the sorption equilibrium with water are available (see for example, [2]). Such a screening can be a very time-consuming process, and this approach, in general, is a palliative one as it gives an intermediate solution rather than an ultimate one.

Here we suggest and discuss **the alternative approach** to making a choice of solid sorbent for AHP:

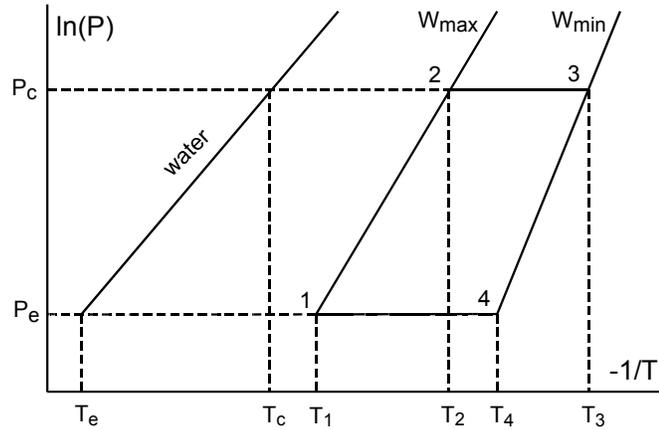


Fig. 1. Standard cycle of an adsorption heat pump

After parameters of the particular AHP cycle have been determined, the next step is the formulation of requirements to a desirable (ideal) solid sorbent the thermodynamic characteristics of which could allow perfect performance of this cycle. Then, the final step of this approach is a **design** of a new solid sorbent with sorption properties close or even equal to those determined before as properties perfectly fitting the cycle. In this communication we analyse this approach in detail.

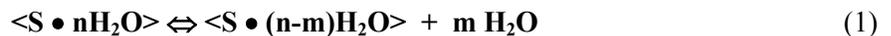
DESCRIPTION OF THE NEW APPROACH

To specify the requirements to an ideal solid sorbent which ensures the perfect performance of a particular cycle, we consider here as an example a single-effect non-regenerative adsorption cycle driven by low temperature heat.

“What should be an optimal solid sorbent for this cycle?”

This question is considered here only from thermodynamic point of view, no kinetic features are taken into account. For cycle involved, the temperature level of a heat source which drives the cycle is of key practical significance. Indeed, huge amount of waste heat is rejected at temperature 50-80°C (liquid from cooling circuit of engines, geothermal water, etc.). Similar temperature level is typical for solar heat obtained using cheap flat solar receivers [3]. So, it is very attractive to utilize this low temperature heat for sorbent dehydration (stage 2-3, Fig. 1).

Thus, the first step of our analysis is aimed to estimate the minimum temperature T_{\min} of an external heat source sufficient for isobaric water desorption at $P = P_c$. Looking at the cycle on Fig. 1 it is evident that $T_{\min} \geq T_2$. The limiting case $T_{\min} = T_2$ corresponds to the complete removal of water immediately at T_2 as it takes place in chemical heat pumps which utilise chemical reactions of a gas-solid type. Indeed, an equilibrium of dehydration reaction of a hydrated solid $\langle S \bullet nH_2O \rangle$ ($S \bullet nH_2O$ = a crystalline hydrate)



is monovariant, and at fixed P the decomposition occurs at unique $T_r = f(P)$ [4]. For conventional solid adsorbents the equilibrium is divariant, and the removal of water proceeds in a temperature interval ΔT , resulting in $T_{\min} = T_2 + \Delta T > T_2$ as shown in Fig. 1. For divariant systems the difference of water uptakes corresponding to the rich (1-2) and weak (3-4) isosters has to be as large as possible [5]. It means that the isosters should be concentrated within the ΔT mentioned above [5, 6].

For estimation of T_2 we fix the temperatures of evaporator T_e and condenser T_c and assume that both the equilibrium P-T line for water and isosteres of the sorbent are straight lines in the $\ln P(\text{H}_2\text{O}) \div 1/T$ presentation and approximately follow the Trouton's rule (the intersection of vapour pressure lines for T approaching infinity [7]). Under these assumptions it can be shown [1, 8] that $T_1 T_c = T_2 T_e$ or $T_2 = T_1 T_c / T_e$. If consider the simplest case when $T_1 = T_c$, then

$$T_2 = T_c^2 / T_e . \quad (2)$$

Fig. 2 presents as calculated T_2 vs T_c for the three cooling applications, namely, the freezing ($T_e = -30^\circ\text{C}$), ice making ($T_e = -5^\circ\text{C}$) and air conditioning ($T_e = 10^\circ\text{C}$). The value of T_2 considerably differs for various climatic zones and covers the ranges of $80\div 156$, $47\div 116$ and $30\div 96^\circ\text{C}$ for the above applications (Fig. 2, see also [1]). One might thus expect that optimal adsorbents for these particular applications and climatic conditions should be quite different and, hence, to be a subject of careful choice.

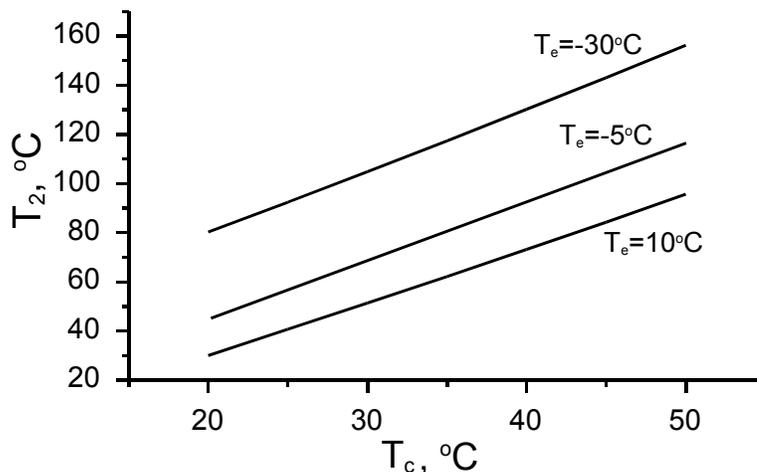


Fig. 2. T_2 vs. T_c calculated according to eq. (2) for various cooling applications: freezing ($T_e = -30^\circ\text{C}$), ice making ($T_e = -5^\circ\text{C}$) and air conditioning ($T_e = 10^\circ\text{C}$)

Thus, for an optimal adsorbent to be used in a single-effect non-regenerative adsorption cycle driven by low temperature heat

a) the temperature $T_{\min} = T_2 + \Delta T$ of water removal at $P = P_c$ has to be as close to T_2 as possible. This would minimise the temperature of the external heat source;

b) the amount of water removed within the temperature range ΔT between T_2 and T_{\min} (for chemical reaction, immediately at $T_{\min} = T_r = T_2$) has to be as large as possible. It could maximise the coefficient of performance [5].

These criteria use the value of T_2 calculated from eq. (2) as the main parameter for determination of optimal adsorbent. Practical means directed to match these requirements will be discussed below. Here we briefly consider what is the minimum set of experimental data, which is sufficient to learn to what extent an adsorbent follows the above criteria. In order to minimize the time consumption one could measure just one isobar of water desorption at $P = P_c$ and $T \geq T_2$. The ideal case corresponds to a complete dehydration immediately at $T_r = T_2$ (monovariant chemical reaction, curve **a** in Fig. 3a), while for divariant systems the isobar is a smooth line and the desorption occurs in more or less wide temperature range (respectively, curves **c** and **b** in Fig. 3a). Typical isotherms and isosteres corresponding to isobars of **a**, **b** and **c** type are displayed on Fig. 3b and 4.

Although we have considered water as a refrigerant, this approach is a general one. It can be applied for formulating requirements to a desirable solid sorbent of ammonia, methanol and other refrigerants used in any non-regenerative adsorption cycle.

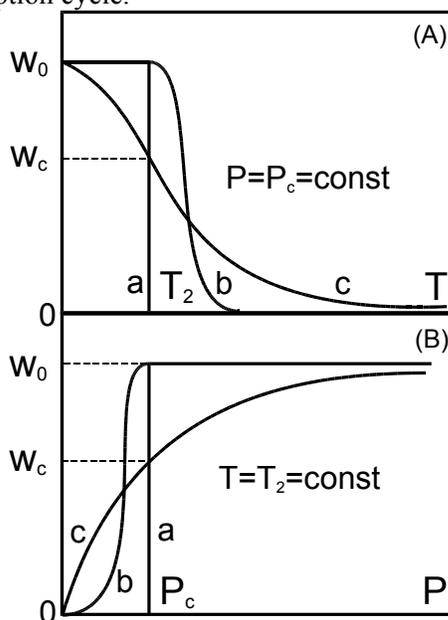


Fig. 3. Typical isobars (A) and isotherms (B) corresponding to mono- (a) and divariant equilibrium (b and c)

Thus, we can conclude that solid sorbents which best match the theoretical requirements for mentioned cycle driven by low temperature heat are those with a monovariant equilibrium, namely, salts and their crystalline hydrates which exchange water due to reaction (1).

It is well known that in actual practice these materials can have several shortages [9-11]:

- a) salt swelling/expansion during chemical reaction;
- b) hysteresis between decomposition and synthesis reactions;
- c) kinetic limitations due to the formation of core on the salt external surface ,
- d) corrosive properties, etc.

How to overcome or reduce these problems? One of the most efficient way appeared to be a dispersion of a salt by its confinement to pores of a host matrix as it was suggested in [11, 12]. Several years ago these new hybride sorbents "salt in porous host matrix" (so called Selective Water Sorbents, SWSs) were suggested for solid sorption cooling/heating driven by low temperature heat [13, 14]. We believed that the SWSs, taking an intermediate position between salt hydrates and solid adsorbents, can combine advantages of both these materials. Here we review the results on SWSs obtained so far and try to answer the second question declared above:

“Which tools has material science to design optimal adsorbent?”

The second part of this presentation is directed to summarise the activity of the Boreskov Institute of Catalysis in the synthesis of SWSs and study of their water sorption properties (sorbent characterisation was partially done in co-operation with the ITAE/CNR, Italy). So far, more than 30 new sorbents based on halides (CaCl_2 , LiBr , LiCl , MgCl_2), sulphates (Na_2SO_4 , MgSO_4 , CuSO_4) and nitrates ($\text{Ca}(\text{NO}_3)_2$, LiNO_3 , $\text{Mg}(\text{NO}_3)_2$) of metals incorporated into hydrophilic (silica gels, alumina, clays) or hydrophobic (porous carbons) matrices have been synthesised and studied. The results of the study were presented in more than 50 publications and have been summarised in [15-17].

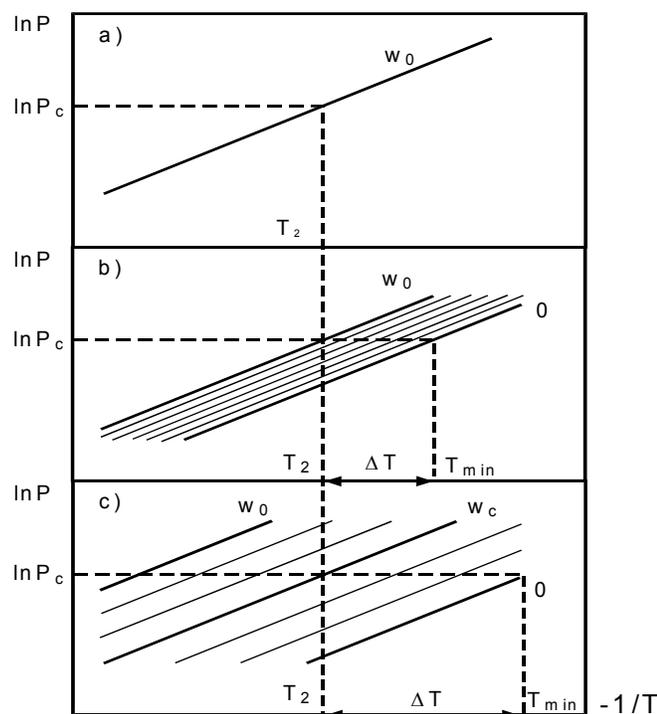


Fig. 4. Typical isosteres corresponding to the isobars and isotherms displayed in Fig. 3

The main findings can be summarised as follows:

- three mechanisms of water sorption have been found: a) adsorption by the host matrix, b) chemical reaction between water and salt resulting in the formation of crystalline hydrates, and c) absorption by the salt aqueous solution in the pores (Fig. 5);
- sorption by composite is not a linear combination of that of the host matrix and salt (Fig. 6);
- the matrix can accommodate the salt swelling caused by a chemical reaction;
- gas-solid reaction is much faster for a confined salt than for a bulk one, so that the rate of sorption process is commonly controlled by inter- or intrapartical diffusion;
- inside pores, the synthesis-decomposition hysteresis can be reduced or even avoided (see below).

Moreover, a host matrix provides a network for efficient transfer of heat and reagent which greatly enhances these processes, as it was conceived and reached for composite sorbents of ammonia “salt + expanded graphite” [18] or “salt + carbonaceous textile” [19].

The data obtained so far are a fundamental to answer the question **“Which practical tools are available to design the optimal adsorbent?”**

First, we shall list these tools and then give examples of how do they affect sorption properties of a composite “salt in porous matrix”. In our previous studies [14-17, 20-24] it has been clearly shown that sorption properties of SWSs can be peculiarly changed in a wide range by varying

- a) **chemical nature of confined salt,**
- b) **average size of pores of the host matrix,**
- c) **salt content,**
- d) **synthesis conditions.**

Effect of the chemical nature of the confined salt

Since the active substance in SWSs is inorganic salt, its chemical nature is of prime importance. Fortunately, a plenty of salts can form crystalline hydrates which undergo dehydration according to

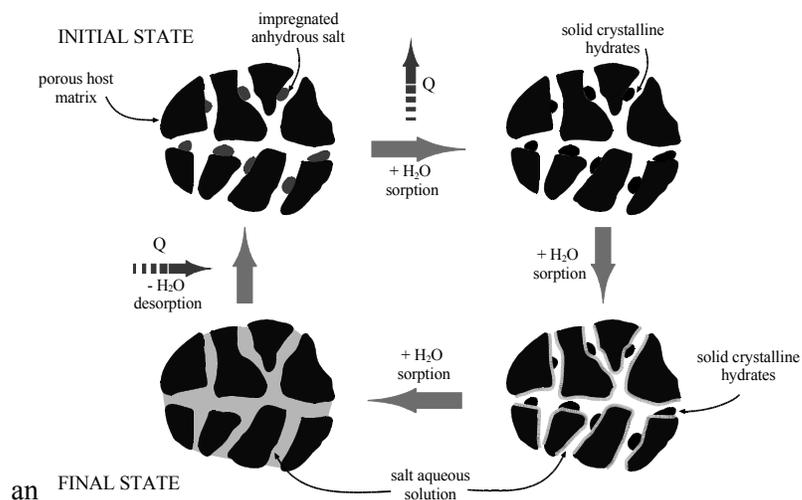


Fig. 5. Scheme of water sorption on SWSs

reaction (1). As these systems are monovariant, the temperature of reaction T_r depends only on vapour pressure P . The link between them is given by Van't Hoff equation [4]

$$\text{Ln}P = -\Delta G^\circ/RT_r \text{ or } \text{Ln}P = -\Delta H^\circ/RT_r + \Delta S^\circ/R, \quad (3)$$

where ΔG° , ΔH° and ΔS° correspond to the variation of the standard Gibb's potential, enthalpy and entropy, respectively. As there is a large difference in values of ΔH° and ΔS° for various massive hydrates, one might expect that transition (1) can occur at quite different temperatures T_r . Thus, it gives a chance to select a hydrate which at $P = P_c$ undergoes transformation (1) at temperature T_r close to the required T_2 determined by equation (2).

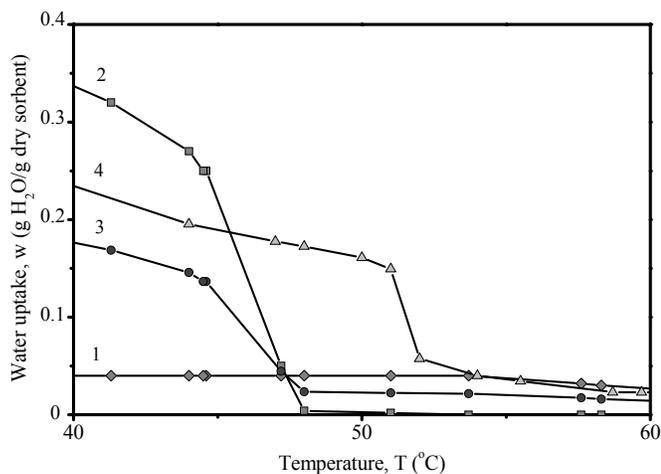


Fig. 6. Isobars of water sorption by silica gel (pore size 12 nm) (1), by bulk Ca(NO₃)₂ (2), their linear superposition (3) and isobar for composite Ca(NO₃)₂/silica (4) [20]. $P(\text{H}_2\text{O}) = 17 \text{ mbar}$

Over a narrow range of temperature variation $-\Delta G^\circ/RT$ can be considered constant, hence dehydration reaction (1) occurs approximately at constant relative pressure $\eta = P/P_o$. It is confirmed by Fig. 7 where both our experimental and literature data measured at different T are plotted as a function of η . Hence, for

fast selection η can be used as a single parameter instead of common two parameters (T and P). Fig. 7 and Table 1 demonstrate that reaction (1) for various hydrated salts (in bulk) does occur at values of P/P_0 distributed over a wide range. Thus, the first step of salt selection should be the calculation of relative pressure η_2 which corresponds to point 2 of the cycle diagram (Fig. 1) and searching the salt hydrate decomposed at η_r equal or close to η_2 . The chosen salt can be placed inside pores of a host matrix to eliminate or reduce shortages listed above.

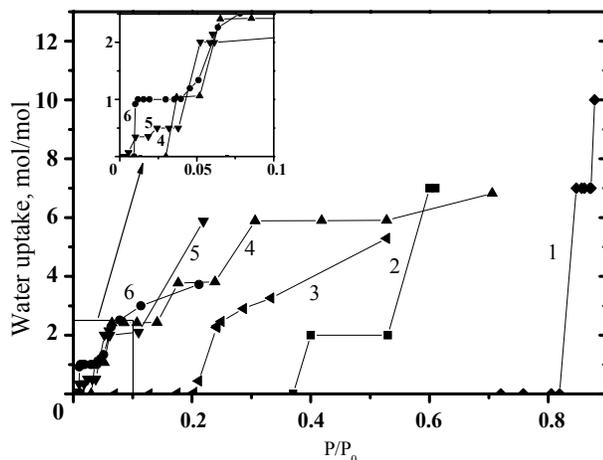


Fig. 7. Equilibrium amount of water in various hydrated salts (in bulk) vs P/P_0 : Na_2SO_4 (1), Na_2HPO_4 (2), $\text{Ca}(\text{NO}_3)_2$ (3), MgSO_4 (4), CaCl_2 (5) and LiBr (6)

Fig. 8 displays experimental isobars of water sorption on commercial silica gel KSK both pure (1) and modified by CaCl_2 (2) and LiBr (3). The modification, first, leads to larger amount of water sorbed in comparison to that for pure silica. Second, the transition temperature T_r (or humidity η_r) for confined hydrate can differ from that in bulk (Table 1). Thus, confining hydrate to small pores can result in shifting the equilibrium of its decomposition, what gives a valuable **tool for adjusting** the transition temperature T_r closer to T_2 . Preliminary analysis on how the host matrix and synthesis procedure can influence T_r is presented below.

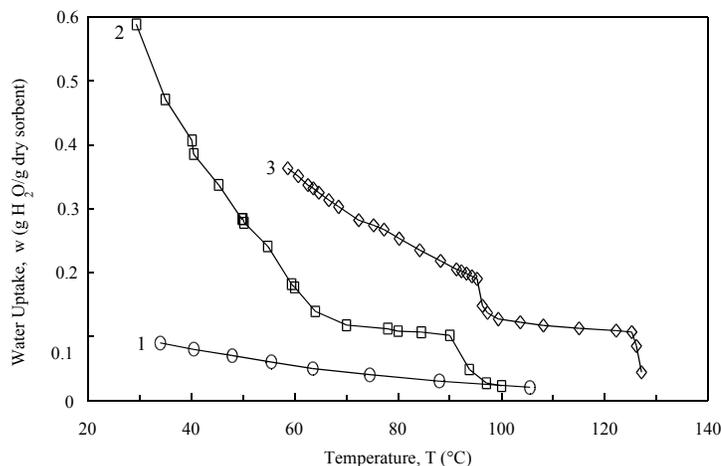


Fig. 8. Comparison of the 25 mbar isobars of pure silica KSK (1) and composites CaCl_2/KSK (2) and LiBr/KSK (taken from [13])

Effect of the pore size of the host matrix

This effect was comprehensively studied by confining $\text{Ca}(\text{NO}_3)_2$ to silica with different pore size [23]. A gradual shift was found for the transition between anhydrous $\text{Ca}(\text{NO}_3)_2$ and its dihydrate (synthesis reaction) from 45-48°C for bulk salt to 53-58°C and 83-105°C for the salt confined to silica pore of 12 and

3.5 nm in size, respectively (Fig. 9). Thus, for selected host matrix, the proper choice of its pore size provides a way to change the temperature of synthesis in a wide range. For the dihydrate studied a hysteresis between synthesis and decomposition reactions was found. Indeed, for decomposition

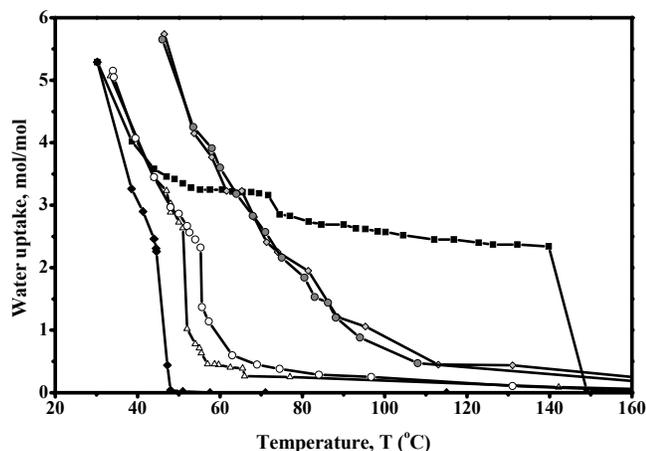


Fig. 9. Isobars of sorption/desorption for $\text{Ca}(\text{NO}_3)_2$: bulk ($\blacklozenge/\blacksquare$), confined to pores of 12 nm (Δ/o) and 3.5 nm ($/ /$)

the bulk strong overheating does not allow to use the bulk salt for heat pumping. Confining the salt inside the pores of silica reduces the hysteresis, which becomes almost negligible for 3.5 nm pores (Fig. 9).

Table 1. Relative pressure η_r corresponding to various transitions between different salt hydrates, both bulk and confined to silica pores of 15 nm in size

Salt	Transition	η_r (bulk)	η_r (confined)
Na_2SO_4	$1 \Rightarrow 7$	0.80	0.5 – 0.6
	$7 \Rightarrow 10$	0.91	-
Na_2HPO_4	$0 \Rightarrow 2$	0.37-0.39	-
	$2 \Rightarrow 7$	0.52 -0.57	-
$\text{Ca}(\text{NO}_3)_2$	$0 \Rightarrow 2$	0.21-0.23	0.15 – 0.19
MgSO_4	$0 \Rightarrow 1$	0.03	0.001-0.003
	$1 \Rightarrow 2$	0.05-0.06	0.003-0.01
	$2 \Rightarrow 4$	0.15-0.17	-
CaCl_2	$0 \Rightarrow 1/3$	< 0.01	-
	$1/3 \Rightarrow 2$	0.04-0.05	0.03-0.04
	$2 \Rightarrow 4$	0.16-0.18	0.12-0.14
LiBr	$0 \Rightarrow 1$	0.01	0.01
	$1 \Rightarrow 2$	0.04-0.05	0.02-0.03
LiCl	$0 \Rightarrow 1$	0.09-0.12	0.04-0.05
	$1 \Rightarrow 2$	0.12-0.13	0.06-0.09

Effect of the salt content

If the shift of reaction temperature due to discussed effect of pore size is not sufficient, as it is the case for CaCl_2 , next attempt can be done by varying salt content [24]. In practice, it is easily to do by changing the concentration of the salt aqueous solution used for matrix impregnation. Smaller solution concentration results in decreasing salt content in composite and influences the crystallisation process as well.

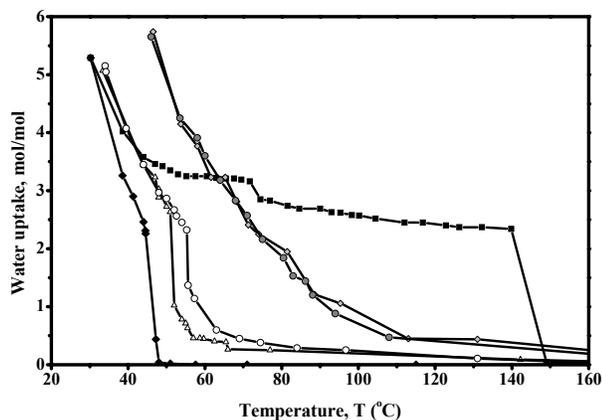


Fig. 9. Isobars of sorption/desorption for $\text{Ca}(\text{NO}_3)_2$: bulk ($\blacklozenge/\blacksquare$), confined to pores of 12 nm (\blacktriangle/\circ) and 3.5 nm (\blacklozenge/\circ)

It was found that reducing the salt content from 33.4 to 22.3 wt.% shifts the transitions ($0.33 \Rightarrow 2$) and ($2 \Rightarrow 4$) to lower relative pressure (Fig. 10). This effect is caused either by smaller size of salt nanocrystallites deposited on the silica surface from less concentrated salt solution or by the salt-silica ion exchange interaction discussed below.

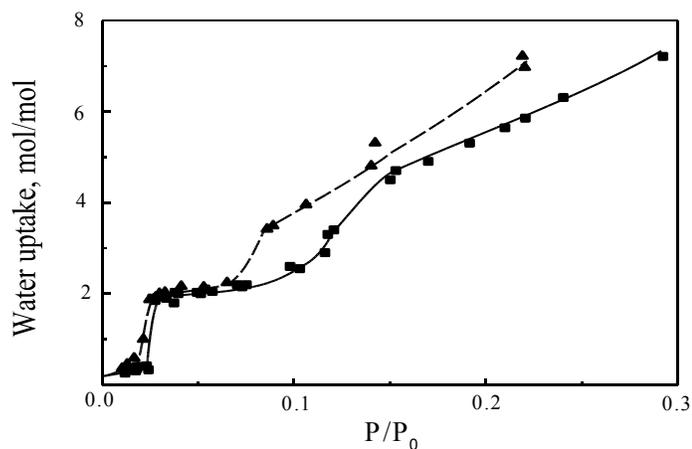


Fig. 10. Temperature independent curves for $\text{CaCl}_2/\text{SiO}_2$ with the salt content 22.3 (\blacktriangle) and 33.4% (\blacksquare)

Effect of the synthesis conditions

We have found that among the conditions, which can be varied during synthesis procedure the most important are pH of the impregnating solution [24, 25] and calcination temperature [26].

Both these effects are illustrated by Fig. 11, which shows that the increase of pH and T_{calc} leads to qualitatively similar impacts: the transition becomes less sharp and proceeds over wider range of the relative pressure.

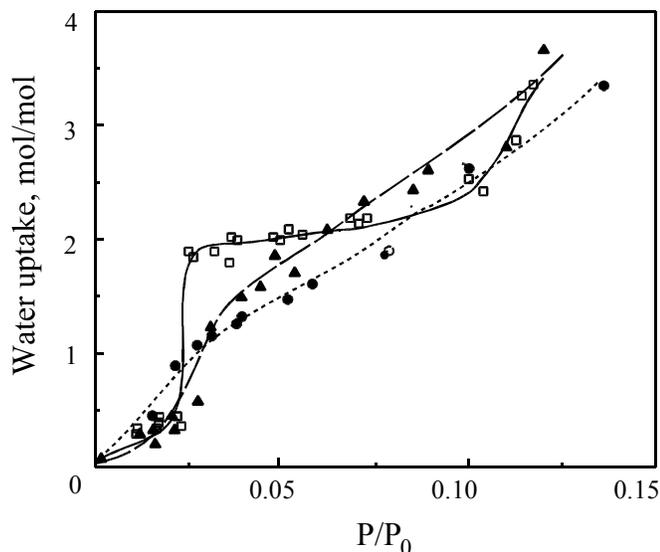


Fig. 11. Temperature independent curves of water sorption by composite $\text{CaCl}_2(33.4 \text{ wt.}\%)/\text{SiO}_2$ prepared at pH of salt solution 5.5 (\square) and 8.0 (\bullet), both calcined at $T_{\text{calc}} = 200^\circ\text{C}$; and prepared at pH = 5.5 and $T_{\text{calc}} = 370^\circ\text{C}$ (\blacktriangle)

More detailed study was performed to analyse the ion exchange interaction between the silica surface and the salt solution, which occurs during the impregnation procedure [24-26]. This interaction was found to cause the formation of the surface complexes $\equiv\text{Si}-\text{O}^-\text{Ca}^{2+}\cdots\text{Cl}^-$, which stabilizes two phases of the confined salt, namely, the volume crystalline phase and the surface X-ray amorphous phase. The fractions of the crystalline and amorphous phases depend on the salt content and pH of salt solution and affect the sorption equilibrium between the composites and water vapor. Water sorption by the composites, which contain predominantly crystalline salt, leads to the formation of crystalline hydrates of the salt with monovariant equilibrium. Water sorption by the composites, containing predominantly X-ray amorphous phase, monotonically changes with the increase of relative pressure, which is typical for salt solutions and hydrates of the lacunary structure [27]. Relative contributions of the mentioned phases can be also controllably changed by varying the temperature T_{calc} of SWS final treatment [26].

Thus, the sorption properties of SWSs can be efficiently monitored by varying the synthesis conditions: the pH and concentration of impregnating solution, and the calcination temperature.

CONCLUSIONS

In this communication we suggest and discuss the new approach how to make a choice of solid sorbent for AHP. It consists of a) **formulation** of the requirements to desirable solid sorbent the thermodynamic characteristics of which could allow perfect realisation of the cycle, and b) the **design** of a new solid sorbent with sorption properties close or even equal to those perfectly fitting the cycle.

In the first part the mentioned requirements are formulated for a particular single-effect non-regenerative cycle driven by low temperature heat. The conclusion has been made that solid sorbents which match in the best way the theoretical requirements for mentioned cycle are those with a monovariant equilibrium, specifically, salts and their crystalline hydrates capable of exchanging water due to reaction (1). Several years ago at the Borskov Institute of Catalysis (Russia) it was suggested to confine such salts to porous host matrices, thus obtaining so called Selective Water Sorbents (SWSs). Later, SWSs were studied and presented for sorption cooling/heating together with the ITAE/CNR (Italy).

The second part of the paper is devoted to practical tools, which are available to design and synthesise an optimal composite sorbent of water for a particular ATH cycle. It was proved that the sorption properties of SWSs can be monitored by a proper choice of the chemical nature and content of the

confined salt, the average size of pores of the host matrix and synthesis conditions. All these tools can be used to adjust the real composite adsorbent to an optimal one. Thus, this part reviews the current state-of-the-art on the new family of the SWS composites.

It is important to mention that although we have considered here water as a refrigerant, this approach is a general one. It can be applied for formulating requirements to a desirable solid sorbent of ammonia, methanol and other refrigerants used in any non-regenerative adsorption cycle.

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Nomenclature:

T - temperature, K, C

ΔT - temperature interval, K, C

P - pressure, mbar

η - relative pressure

w - uptake, g/g

Δw - change of uptake, g/g

ΔG° - variation of the standard Gibb's potential, kJ/mol

ΔH° - variation of the standard enthalpy, kJ/mol

ΔS° - variation of the standard entropy, J/(mol K)

R - universal gas constant, J/(mol K)

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