

UDC 662.995  
© 2017

**O.V. KOLOMIYETS,**  
*assistant*

**E.A. BELYANOVSKAYA,  
I.V. SUKHA,  
M.P. SUKHYY,**

*Candidates of Engineering Sciences*

**K.M. SUKHYY,**  
*Dr. habil.*

*State Higher Education Institution  
“Ukrainian State University  
of Chemical Engineering”*

**O.M. PROKOPENKO,**  
*Candidate of Engineering Sciences*

*National Metallurgical Academy of Ukraine  
E-mail: ksukhyy@gmail.com*

*Gagarine av. 8, Dnipro  
Gagarine av. 4, Dnipro*

OPERATING PROPERTIES  
OF COMPOSITE MATERIALS  
“SILICA GEL – SODIUM  
SULPHATE” AND “SILICA GEL –  
SODIUM ACETATE” FOR SOLAR  
ADSORPTIVE HEAT PUMPS

*Досліджено експлуатаційні властивості композитних сорбентів “силікагель – натрій сульфат” та “силікагель – натрій ацетат”, які синтезовані золь-гельметодом для адсорбційних сонячних теплових насосів. Показано якісні відмінності кінетичних кривих сорбції води композитними сорбентами та масивними солями. Розроблено конструкцію сонячного адсорбційного теплового насоса. Встановлено коефіцієнти перетворення теплоти запропонованого теплового насоса в разі використання композита “силікагель – натрій сульфат” та “силікагель – натрій ацетат”. Виявлено сезонну залежність експлуатаційного коефіцієнта перетворення теплоти адсорбційного теплового насоса на основі композитів “силікагель – натрій сульфат” та “силікагель – натрій ацетат”.*

*Ключеві слова: композитні сорбенти, сорбційна ємність, температура регенерації, сонячний адсорбційний тепловий насос, енергоефективність.*

Tendencies of monotonic increase in power consumption, cost of primary fuels and energy products stipulate the development of cheaper methods, techniques and devices not only for precluding of primary fuel consumption, but also for reduction of carbon dioxide emissions. Promising devices corresponding to these requirements are heat pumps, ie heat transformers in which work-

ing bodies transfer heat from a lower temperature level to a higher when reverse thermodynamic cycle realized [1]. Compression (air- and steam-driven) heat pumps based on the gradual implementation of the compression and expansion of the working fluid are considered as most abundant of them. In recent years, active research and expanding area of implementation of sorption heat

pumps based on periodically repeating processes of working body sorption and desorption with sorbent, these being accompanied by the release and absorption of heat, respectively. In absorption heat pumps pairs  $H_2O / LiBr$  and  $NH_3 / H_2O$  used in air conditioning and refrigeration technics became the most wide-spread [2]. Recently, heat pump based on metal hydride and pair  $H_2O / LiBr$  is suggested [3]. However, absorption heat pumps are sensitive to gravity. Adsorption heat pumps based on vapor adsorption with solids (adsorbents) are clear from these limitations. Zeolites, silica gel, activated carbon [4] active carbon fiber [5], alumina, mesoporous silica gel [6] and composite sorbents ‘salt in a porous matrix’ [2, 7] are considered as adsorbents. At the same time intensive application such adsorbents is strongly limited by quite complex and expensive technology of manufacturing by impregnation of crystalline porous media with crystalline hydrate solutions [7]. More promising in their sorption capacity and, as a consequence, adsorption heat materials are nanodisperse composites synthesized by sol-gel method [7]. However, the presence of salt in a porous matrix causes a qualitative change not only in sorption capacity, but also in the regularities of adsorption processes kinetic.

The present work is devoted to operating features of composite sorbents “silica gel – sodium sulphate” and “silica gel – sodium acetate” synthesized by sol-gel method for adsorption heat pumps.

**Experimental.** The main structural elements of the adsorption heat pump (fig. 1) is a cylindrical reactor of adsorption-desorption-type (1), a hydraulic circuit (2) with ribs (3) filled with sorbent (4), condenser (5) and an evaporator (7) [8]. As an external source of heat, solar collector (14) ПСК-BC1-2 is used.

Adsorptive heat pump is suggested to operate on four-stages cycle included adsorption, heating, desorption and cooling. The heat of adsorption released on the first stage is transferred from the adsorbent granules to the grid and then to the heat-removing media in the hydraulic circuit, it being used for the needs of the consumer. The second and third stages consist in heating to temperatures of sorbent regeneration (composite “silica gel – sodium sulphate” to 90 °C and “silica gel – sodium acetate” to 60 °C) and

desorption of water vapor, respectively. Then, sorbent chilling occur up to the adsorption start temperature (30 °C).

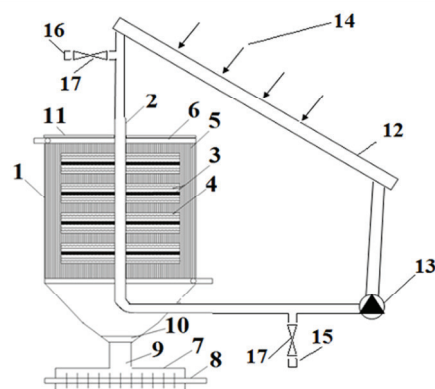
Sol-gel synthesis techniques of the composites is described in detail [9]. Sorption capacities of used composites are 0.85 g/g for “silica gel – sodium sulphate” and 0.42 g/g for “silica gel – sodium acetate”.

**Results and discussion.** Crucial factors for adsorption heat conversion are the ability of composite sorbents to reversible processes hydration and dehydration and temperature ranges for sorption and desorption.

In order to determine these parameters sorption kinetics of water with composites “silica gel –  $Na_2SO_4$ ” and “silica gel –  $CH_3COONa$ ” at temperatures of 20, 40 and 60 °C and pressure of 1010.8 mbar was investigated.

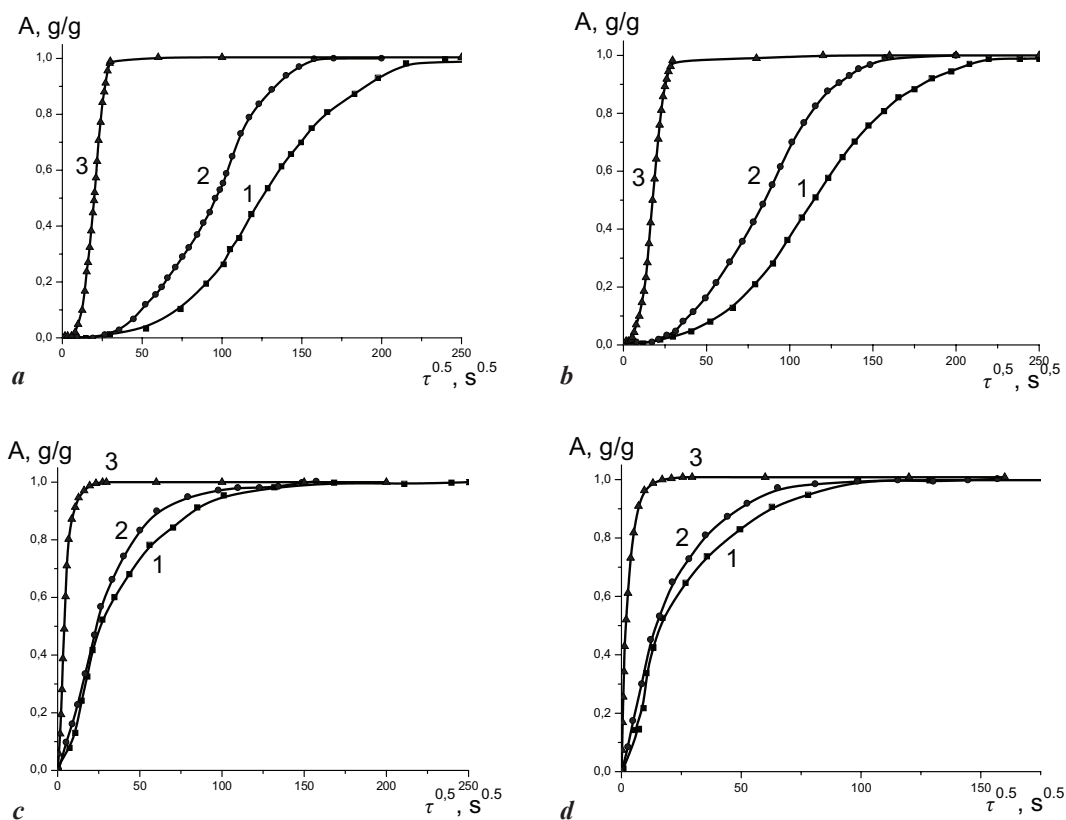
Water sorption kinetic curves of the studied substances in comparison with solid salts are presented in fig. 2.

When temperature increased in investigated range, noticeable raise of sorption processes rate is observed both for massive salts and composite sorbents. Nevertheless, equilibrium for massive salts is regis-



**Fig. 1. Solar adsorptive heat pump:**

- 1 – cylindrical adsorber; 2 – hydraulic circuit;
- 3 – ribs of hydraulic circuit; 4 – sorptive material; 5 – condenser; 6 – cylindrical rings;
- 7 – evaporator; 8 – нагрівач, 9 – tapered hole;
- 10 – distributor; 11 – lid;
- 12 – polymeric solar collector; 13 – pump;
- 14 – solar rays; 15 – outlet of hot water;
- 16 – inlet of cold water; 17 – valves



**Fig. 2. Kinetic curves of water sorption for massive salts sodium sulphate (a) and sodium acetate (b) and composite sorbents “silica gel – sodium sulphate” (c) and “silica gel – sodium acetate” (d) at a pressure of water vapor 1010.8 mbar and temperatures, °C: 1 – 20; 2 – 40; 3 – 60**

tered later as compared to composite. Coincidentally, qualitative difference kinetic curves for massive salts (Fig. 2a and b) and composite sorbents (Fig. 2c and d) is observed. S-shaped kinetic curves of massive  $\text{Na}_2\text{SO}_4$  and  $\text{CH}_3\text{COONa}$  are typical for kinetic regime of hydration processes. Practically rectilinear

initial section in  $A-\tau_{0,5}$  coordinates confirms diffusion limitations, ie water transport in sorbent pore system is rate-determinant stage.

Temperature dependence of diffusion coefficient of water vapor in pores system is linear in semilogarithmic coordinates for both composite sorbents. This activa-

**Adsorptive heat pump coefficient of energy performance**

Month	The total average daily value of solar radiation (kW-h/m <sup>2</sup> )	“Silica gel – Na <sub>2</sub> SO <sub>4</sub> ”		“Silica gel – CH <sub>3</sub> COONa”	
		COP <sub>c</sub>	COP <sub>s(b)</sub>	COP <sub>It</sub>	COP <sub>s(b)</sub>
May	5.99	2.084	1.130	2.021	1.189
June	5.86	2.084	1.133	2.021	1.193
July	6.06	2.084	1.128	2.021	1.187
August	5.66	2.084	1.137	2.021	1.200
September	4.41	2.084	1.176	2.021	1.257

tion energy for these processes is estimated about 52 kJ/mol for compo-site "silica gel – sodium sulphate" and 64 kJ/mol for "silica gel – sodium acetate".

Further tests of synthesized composite sorbents were carried out in the solar adsorption heat pump. The efficiency criterion for such devices is coefficient of energy performance COP, which is equal to ratio of heat supplied to bodies with a higher temperature to heat expended at that.

COP is calculated by two methods:

1) as ratio of adsorption heat to sum of desorption heat and external heat supplied to sorbent during its heating upto regeneration temperature ( $COP_c$ );

2) as ratio of adsorption heat to heat supplied by solar collector ( $COP_s(b)$ ) (net).

According to calculation results given in Table  $COP_c$  and  $COP_s(b)$  of heat pumps based on both composite sorbents are values of the same magnitude, it being resulted from lower regeneration temperature of composite "silica gel – sodium acetate" (60 °C) as compared to "silica gel – sodium sulphate" (90 °C). Unsignificant decrease of  $COP_c$  when composite "silica gel –  $CH_3COONa$ " used is accounted for by lower sorption capacity as compared to "silica gel –  $Na_2SO_4$ ".

Higher values of  $COP_s(b)$  when composite "silica gel –  $CH_3COONa$ " used are interpreted by its lower regeneration temperature.

### Conclusions

*The properties and kinetic regularities of water vapor adsorption with composite materials "silica gel –  $CH_3COONa$ " and "silica gel –  $Na_2SO_4$ " are studied. Distinction in kind of sorption processes by massive salts and composite sorbents synthesized by sol-gel method is shown.*

*Operating characteristics of solar adsorption*

*heat pumps based on composites "silica gel –  $CH_3COONa$ " and "silica gel –  $Na_2SO_4$ " are studied. Such heat pumps are shown to be very attractive for further development and potential alternative to conventional heating systems in the future because of their environmental benefits and independence from traditional energy sources.*

### References

1. Botticella F. Seasonal Performance Analysis Of a Residential Heat Pump Using Different Fluids With Low Environmental Impact / F. Botticella, L. Viscito // Energy Procedia. – 2015. – Vol. 82. – P. 878–885.
2. Романова Е.В. Возможности использования тепловых насосов в процессе сушки / Е.В. Романова, А.Ю. Орлов // Вестник ТГТУ. – 2008. – Т. 14, № 3. – С. 591–596.
3. Muthukumar P. Thermodynamic analysis of a thermally operated cascade sorption heat pump for continuous cold generation / P. Muthukumar, D.V.N. Lakshmi // Int. J. of Energy and environment. – 2013. – Vol. 3, № 1. – P. 161–174.
4. Demir H. A review on adsorption heat pump: Problems and solutions / H. Demir, M. Mobedi, S. Ülkü // Renewable and Sustainable Energy Reviews. – 2008. – Vol. 18. – P. 2381–2403.
5. Jr. Solar – gas solid sorption heat pump / L.L. Vasiliev, D.A. Mishkinis, A.A. Antukh, L.L. Vasiliev // Applied Thermal Engineering. – 2001. – Vol. 21. – P. 573–583.
6. Dawoud B. Experimental study on the kinetics of water vapor sorption on selective water sorbents, silica gel and alumina under typical operating conditions of sorption heat pumps / B. Dawoud, Yu. Aristov // Heat and mass transfer. – 2003. – Vol. 46. – P. 273–281.
7. Gordeeva L.G. Composites "salt inside porous matrix" for adsorption heat transformation: a current state-of-the-art and new trends / L.G. Gordeeva, Yu.I. Aristov // International Journal of Low-Carbon Technologies Advanced Access. – 2012. – P. 1–15.
8. Пат. 91481 Україна, МПК F 25 В 30/00, F 25 В 17/00 Адсорбційний тепловий насос / Сухий К.М., Сухий М.П., Коломієць О.В. [та ін.]; заявник і патентовласник Державний вищий навчальний заклад "Український державний хіміко-технологічний університет". – № у 2013 15448; заявл. 30.12.2013; опубл. 10.07.2014. Бюл. № 13.
9. Structure and Adsorption Properties of the Composites "Silica Gel – Sodium Sulphate", obtained by Sol-Gel Method / K.M. Sukhyy, E.A. Belyanovskaya, Ya.N. Kozlov, E.V. Kolomiyets, M.P. Sukhyy // Applied Thermal Engineering. – 2014. – Vol. 64, № 1–2. – P. 408–412.