NEW WATER SORBENT LICL/VERMICULITE FOR THERMAL ENERGY STORAGE

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НОВЫЙ СОРБЕНТ ВОДЫ LiCl/ВЕРМИКУЛИТ ДЛЯ ЗАПАСАНИЯ ТЕПЛОВОЙ ЭНЕРГИИ

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Аннотация. В свете растущего потребления природных ресурсов использование альтернативных источников энергии приобретает особую актуальность. Сорбционное запасание тепла (СЗТ) – энергосберегающая технология, позволяющая использовать низкопотенциальное тепло (солнечная энергия, тепловые отходы промышленности и т.д.). В основе СЗТ лежат обратимые процессы адсорбции/десорбции паров воды. Сорбенты на основе пористых матриц, импрегнированных неорганическими солями, характеризуются высокой энергоаккумулирующей способностью, так как обратимо связывают большое количество воды. Данная работа посвящена синтезу нового материала на основе вспученного вермикулита импрегнированного LiCl для сорбционных циклов сезонного и суточного запасания тепла. Работа состоит из трех частей: 1) синтез композита специализированного для циклов СЗТ ; 2) изучение равновесия и динамики сорбции паров воды синтезированным материалом, 3) оценка энергоаккумулирующей способности нового композита и удельной мощности рассматриваемых циклов. Показано, что LiCl, помещенный в поры вермикулита, реагирует с парами воды с образованием гидратов $LiCl \cdot nH_2O$ (n=1, 2) в рабочих условиях циклов. Энергоаккумулирующая емкость рабочей пары «LiCl/Вер – вода» составляет 2,3 и 2,6 кДж/г в цикле суточного и сезонного СЗТ, соответственно, что превосходит значения для современных материалов, предложенных для СЗТ. Результаты демонстрируют высокий потенциал новых материалов для СЗТ.

Introduction. The depletion of fossil energy resources is a serious reason for development of energy saving technologies. A large barrier to utilization of renewable energy sources (solar, geothermal, and waste heat) for heating/cooling is a mismatch between the production of and demand for the heat generated by them. Thus, the development of thermal energy storage systems is one of hottest topics of scientific researches [1]. Among different ways of thermal energy storage, the sorption one has gained large interest due to its high heat storage density and negligible heat losses during the storage phase [2]. Sorption heat storage (SHS) is based on reversible exothermic sorption (heat releasing) and endothermic desorption (heat accumulation) processes. The development of new advanced sorbents is prerequisite for further SHS elaboration. The composites "salt in porous matrix" (CSPM) – suggested in [3] – are promising sorbents for SHS due to their high Heat Storage Capacity (HSC) and tunable sorption behavior [4]. The main sorbing component of CSPMs is the active salt. Thereby, the matrixes with large pore volume allow us to reach larger salt content in the composite that is

advantageous for SHS. This paper addresses the intent synthesis of novel water sorbent based on expanded vermiculite (specific pore volume V_p = 2,7 cm^3/g) and LiCl for two SHS cycles: seasonal (SS), and daily (DS) heat storage (Table 1).

Table 1

Operating conditions of the SS and DS cycles.

	Cycle	Temperature of discharging,°C	Temperature of evaporation,°C	Temperature of charging,°C	Temperature of condensation,°C
1	SS	35	10	75–85	30
2	DS	35	5	75	15

Materials and methods. To introduce LiCl into pores of vermiculite, the authors employed dry impregnation method. The salt content in the composite LiCl(59)/Ver reached 59 wt.%.

Results and discussion. Isobars of water sorption on LiCl(59)/Ver are S-shaped curves (Fig. 1with the steps of uptake that can be attributed by the complexes LiCl·nH$_2$O (n = 1, 2) formation. Sorption capacity of the composite exceeds 0,75 g/g, whichproves to be profitable for SHS. The narrow sorption-desorption does not exceed 5 °C (Fig 1a), which proves to be acceptable for SHS. At n ≤ 1 mol/mol, the adsorption heat Q_{is} = (61 ± 3) kJ/mol, which can be attributed to monohydrate formation with the strong binding between the salt and water molecules. At higher uptake, the heat decreases down to Q_{is} = (56 ± 3) kJ/mol.

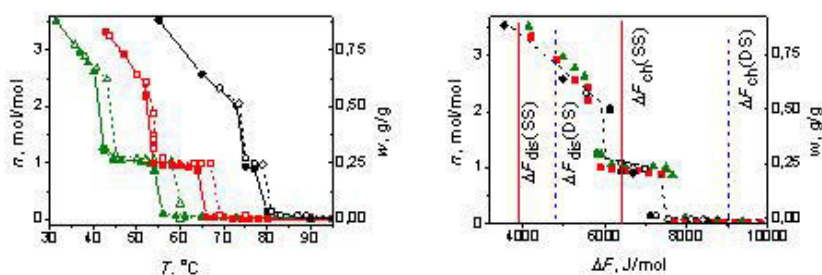*Fig. 1. Isobars (a) and temperature-independent curve (b) of water sorption on the composite LiCl(59)/Ver (a) at P = 0,88 (▲,△), 1,72 (■,□), and 4,28 (●,○) kPa. Open symbols stand for desorption, solid symbols stand for sorption. The lines (b) represent the adsorption potential at charging (ΔFch) and discharging (ΔFdis) stages of the DS (dash) and SS (solid) cycles*

The sorption isobars measured at various pressures coincide with each other if presented as function of adsorption potential ΔF = - RTln(P/P$_0$), where P is the vapor pressure, P$_0$ is the saturation vapor pressure at temperature T (Fig. 1b). That corresponds to the Polanyi principle of temperature invariance and allows evaluation of the amount of water exchanged under conditions of the SS and DS cycles as Δw = w(ΔF$_{dis}$) - w(ΔF$_{ch}$) (Table 2, Fig. 1b). The HSC of the composites is estimated as HSC = ΔwΔH$_{ads}$. During the DS and SS cycles, the LiCl(59)/Ver exchanges 0,75 and 0,6-0,85 g/g, respectively (Fig. 1b, Table 2). The values of HSC obtained for the new composites equal to 1,8–2,6 MJ/kg are superior to appropriate values (0,1–0,9 MJ/kg) reported for the adsorbents proposed for SHS, like silica gel, zeolites, AlPO-18 and SWS-1L [2].

Table 2

The uptake variation Δw_c and HSC of the new composite under conditions of the DS and SS cycles.

Cycle	Δw_c, g/g	HSC, MJ/kg
DS cycle	0,75	2,3
SS cycle (T_{ch} = 75°C)	0,60	1,8
SS cycle (T_{ch} = 85°C)	0,85	2,6

The data on water sorption dynamics on the loose grains of LiCl/Verm (Fig. 2) allow the estimation of the Specific Power of SHS unit as SP=$0{,}8\Delta w_c Q_{is}/(t_c)$, where t_c is the cycle duration. The conversion in the cycle was restricted by q = 0,8 in order to avoid strong falling down the power at approaching to the equilibrium. For the SS cycle , the SP = 3,4–15,6 kW/kg are obtained for the studied configurations. For the DS cycle, the SP for discharging and charging stages is essentially lower: 1,6–2,4 kW/kg. However, even under conditions of the ST cycle one needs only 0,5–1,3 kg or 1,5–3,5 dm^3 of the new sorbent to realize a 2 kW heating power that is very promising.
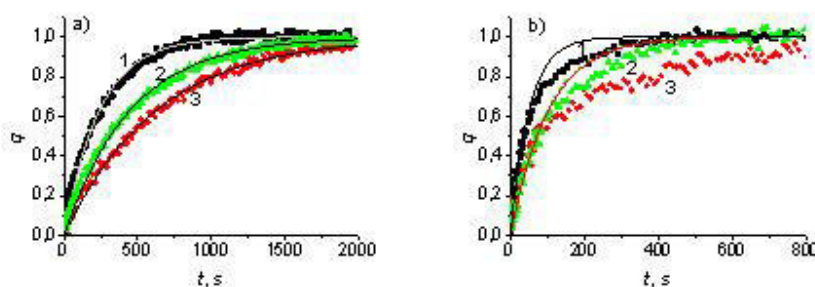

Fig. 2. The kinetic curves (symbols) of water sorption on LiCl(59)/Ver composite and their exponential fitting (lines) under conditions of the DS cycle, P = 0,88 kPa, ΔT = 65–35 °C (a), and the SS cycle, P = 1,23 kPa, ΔT = 54–35 °C (b). Dgr = 0,8–0,9 (1, 2) and 1,6–1,8 mm (3), N = 1 (1, 3) and 2 (2)

Conclusion. Owing to high HSC and SP values, the new composite LiCl/Verm provides a great potential capacity for further realization of the SS and DS heat storage cycles.

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