

REVIEW

Open Access



Current progress in adsorption technologies for low-energy buildings

Yu I. Aristov^{1,2}

Abstract

More than half of the world's population currently lives in cities. An essential constituent of future sustainable cities is energy efficient and ecologically sound buildings which ensure high levels of comfort and convenience without reducing the standards of living. At present, a significant part of primary fossil fuels is spent for heating/cooling of buildings, thus, greatly contributing to total GHG emissions. In this paper, typical heat losses in dwellings are considered taking the United Kingdom and the Russian Federation as examples. The role of adsorption-based technologies for more rational use of heat in buildings is discussed. Fundamentals of inter-seasonal adsorptive heat storage (AHS) are briefly considered. A tentative upper limit of the AHS storage density is estimated. Current practice of inter-seasonal AHS and novel smart adsorbents promising for this emerging technology are overviewed. Since a portion of the heat losses in ventilation system significantly increases in modern buildings, a new approach to regenerating heat and moisture in this system is discussed. Finally, optimization trends of the AHS in buildings are briefly considered.

Keywords: Sustainable city, Low-energy building, Adsorptive transformation of heat, Waste heat, Energy efficiency, Heat storage, Heat regeneration, Nanotailoring new adsorbents, Moisture recovery

Review

Introduction

Past centuries are characterized by persistent growth of urban population. At present, more than half of the world's population currently lives in cities [1]. It is predicted that by 2050 the urban population will reach 70 % [2]. As the major part of population live in cities, future cities must meet severe demands imposed by a sustainability concept, which includes several interrelated areas, such as, energy, ecology, economics, politics and culture [3–5]. In this review, the first domain is mainly addressed and energy efficient buildings, which are an essential constituent of future sustainable cities, are considered. In order such buildings to ensure high levels of comfort and convenience without necessarily sacrificing the standards of living, an input of emerging low-carbon technologies aimed at rational use of thermal energy in dwellings must be decidedly increased [5, 6].

Indeed, at present, a significant part of primary fossil fuels is spent for heating/cooling of buildings, thus, greatly contributing to GHG emissions. In Europe, the

heat consumption in buildings (heating and hot water production, HHWP) is responsible for 24 % of the total energy consumption of the EU-27 (2008) [7]. Forty five percent of total UK final energy consumption for 2012 was for heating purposes; it being known that more than half (24 %) was used for domestic heating [8]. A one fourth of this amount is additionally used for domestic hot water [8, 9]. According to the Parliament Committee [10], residential GHG emissions account for 66 % of buildings emissions. The building sector in Canada accounts for about 30 % of total GHG emissions [11]. In Germany, the share of households in total final energy consumption in 2011 reaches 25 % or 52 Mtoe (million tonnes of oil equivalent), space heating being dominated (72 % of the final households energy consumption [12]). More data for Germany together with similar information for China and the USA can be found elsewhere [13, 14]. In the Russian Federation (RF), 43 % of the produced centralized heat or 138 Mtoe is used for buildings [15]. This agrees well with the data of ref. [16] that Russian residential, public, and commercial buildings in 2005 were responsible for 144.5 Mtoe of final energy use (Table 1), at that 75 % of

Correspondence: aristov@catalysis.ru

¹Boreskov Institute of Catalysis, Ac. Lavrentiev av. 5, Novosibirsk, Russia

²Novosibirsk State University, Pirogova str. 2, Novosibirsk, Russia

Table 1 Evaluation of the energy efficiency potential in buildings (Mtoe) (the data are taken from [16])

Type	Consumption in 2005	Technical potential	Economic potential	Market potential, 2010 prices
Total buildings	144.54	68.61	58.59	49.70
Residential	108.24	53.42	44.78	37.98
Public and commercial	36.31	15.20	13.81	11.72

this heat is consumed in dwellings. Space heating is the leading heat end-user (73.7 % in 2011), while the rest (26.3 %) is used for HHWP [17].

Despite all systematic and active actions that have gone on, heat losses in buildings still remain enormous, hence, there is considerable potential for improving energy efficiency in residential buildings and the related infrastructure. According to the International Energy Agency (IEA), the building sector can reduce energy consumption with an estimated global energy savings of 1509 Mtoe which can possibly mitigate 12.6 Gt (gigatonnes) of CO₂ emissions by 2050 [18]. The UK Government has set an ambitious target to reduce national greenhouse gas emissions by at least 80 % by 2050, and about a half of this reduction is to be due to improved operation of buildings. Similarly, the declared national German policy goal is to reduce nation-wide CO₂ emissions by 80 % till 2050 (against 1990). According to a recent study, about 60 % of that reduction has to come from the building sector [19].

Technical potential of energy saving in the Russian buildings sector exceeds 68 Mtoe or 47 % of the total consumption, the largest potential being evaluated for residential buildings (Table 1) [16]. The major part (67 %) of saving can be implemented through the reduction of district heating use for space heating and hot water. About 85 % of the technical potential is economically viable, while 72 % is market attractive with the 2010 energy prices [16]. Essential saving can be also reached by improving the infrastructure of centralized heat supply [15]. Similar estimations were reported in

[20]: a technical GHG reduction potential for the Russian building stock by 2030 ranges between 26 and 47 % of the national baseline.

The structure of heat losses in dwellings

The UK has around 26.7 million domestic houses and flats [21], and this building stock is one of the oldest in Europe. Old houses have significantly higher heat consumption: e.g. a typical Victorian house demands more than twice as much energy for space heating than a modern house [22]. Much of the heat supplied to UK buildings is wasted, that is mainly due to poor buildings insulation, heating of unoccupied spaces or inappropriate occupant behaviour [21]. As seen from Fig. 1b, for average dwelling, the main losses due to building fabric are related to heat fluxes through the walls (37 %) and windows (19 %) together with those associated with air infiltration in ventilation system (18 %). Heating water for showers, baths and sinks demands around 87 TWh a year, and this heat is completely lost [21].

By the end of 2012, the total floor area of dwellings in Russia reached 3.3 billion m², 72.2 % being related to urban development [17]. In Russia, the space heating is responsible of 58 % of overall energy consumption in residential buildings with district heating systems which cover c.a. 75 % of all dwellings. A small part of dwellings built after 2000 meet acceptable heat efficiency requirements, whereas the majority of older buildings have significantly lower space heating efficiency. The value of Specific Energy Consumption (SEC) for space heating strongly depends on the year of dwelling construction: for buildings

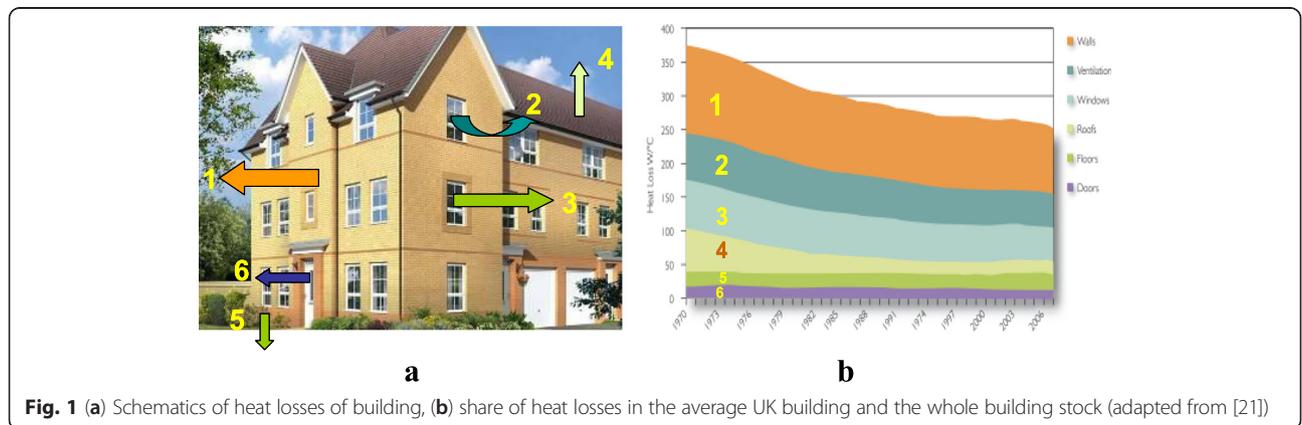


Fig. 1 (a) Schematics of heat losses of building, (b) share of heat losses in the average UK building and the whole building stock (adapted from [21])

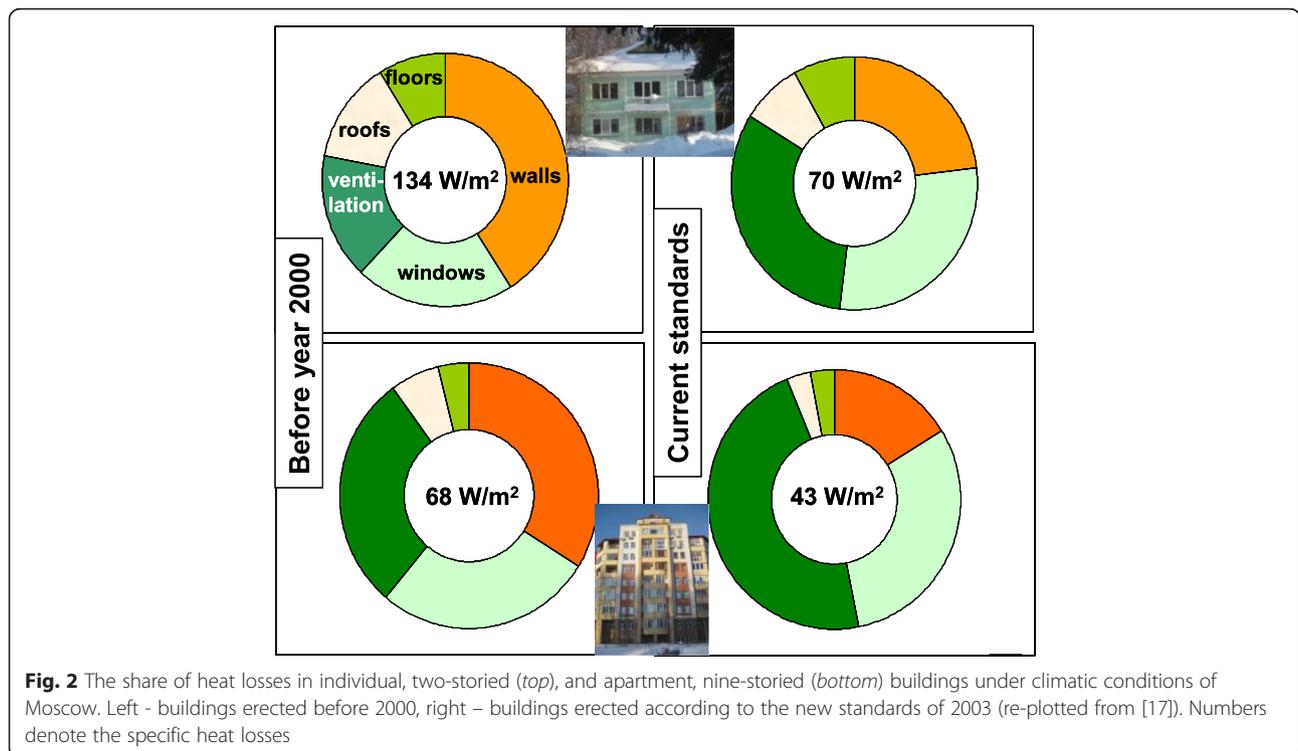
erected before 1990, in 1991–2000 and after 2000, the average SEC is estimated as 0.97, 0.55 and 0.38 GJ/m²/year, respectively [16]. New, and much more severe, standards for thermal protection of buildings were set in 2003 by a new Russian building code (SNiP 23–02–2003 “Thermal Performance of Buildings” [23]). These standards are based on the total number of heating degree-days (HDD) for particular climatic zone/city. The heating period *H* is fixed as a cold season with the mean daily outdoor temperature $T_{ind} \leq 8 \text{ }^\circ\text{C}$. For Moscow, $H = 214$ days and $HDD(T_{ind} \leq 8 \text{ }^\circ\text{C}) = 4,943 \text{ (}^\circ\text{C}\cdot\text{day)/year}$, for Novosibirsk – 230 days and 6,601 (°C·day)/year, and the average HDDs in Russia is 5,140 (°C·day)/year. For comparison, in London the $HDD(T_{ind} \leq 10 \text{ }^\circ\text{C})$ is only 1,860 (°C·day)/year (in 2006) [http://ukclimateprojections.metoffice.gov.uk/media.jsp?mediaid=87928&filetype=pdf]. Thus, in the RF the demand for thermal energy needed for space heating is significantly larger than in the UK.

Another important factor affecting the heating standards is the dwelling size or the number of storeys. Thermal performance of individual low-rise buildings (1–3 storeys) and multi-storied apartment buildings (4–25 storeys) differs essentially: in smaller dwellings, 1 m² of heated rooms area is accompanied by 1.7–3.3 m² of building fabric area, whereas for larger buildings this ratio is considerably less and varies from 0.6 to 1.3 m² [17], which leads to radically

lower heat losses through the building constructions (Fig. 2). It is interesting to mention that the structure of heat losses in the Russian dwellings erected before 2000 (the left half of Fig. 2) is close to that reported for the average building in the UK (Fig. 1b).

Accordingly, the current strategic tendency is a decrease in heat consumption in dwellings by reducing heat losses. The heat consumption can also be reduced by applying inter-seasonal heat storage. During the summer period there is an excess of solar heat available that meets little or no heat demand which is shifted to the winter months. The inter-seasonal *adsorptive heat storage* (AHS) has been considered as a tool to harmonize the heat availability and demand, and, hence, to cover/reduce heating peaks in winter period (see 3.1).

An important tendency clearly seen from Fig. 2 is that, for modern dwellings with better fabric insulation, a portion of the heat losses due to air infiltration significantly increases and becomes dominant (almost 50 %) in high-rise buildings. Therefore, a further improvement of the dwellings thermal efficiency is associated, first of all, with a *decrease in heat losses due to air infiltration*. This can be achieved by implementation of new technologies of indoor climate control, including emerging adsorption methods (see e.g. [24–27] and 3.2 below).



Possible directions of future R&D directed at further improving AHS technologies for dwellings are briefly considered in 3.3.

Adsorption technologies for rational use of heat in buildings

Although there are many applications of adsorption technologies for rational use of energy [29, 30, 31, 32, 33], we consider here those which focus mainly on the building sector.

Adsorptive inter-seasonal heat storage

Inter-seasonal heat storage can be an effective tool to reduce heating peaks in dwellings in winter period [28–34]. Indeed, solar heating potential is high in summer and low in winter, what is just opposite to heat demand (see e.g. Fig. 1 in ref. [35]), therefore a long-term (several months) storage of the excess heat in summer is needed. The inter-seasonal AHS can operate as closed (evacuated) [36] and open (coupled to the ambient) [37] cycles. Useful comparison of these two AHS variations was performed in [38] by using energy and exergy balance analysis. The authors clearly demonstrated that the adsorptive systems may be as efficient as, and more compact than other types of the thermal energy storage systems, however, there is a much room for efficiency improvement for both closed and open AHS systems.

The heat storage density The density A of adsorption heat storage is considered to lie between 100 and 500 kWh/m³ or (0.36–1.8) GJ/m³ being larger than that of sensible (c.a. 50 kWh/m³) and latent (c.a. 100 kWh/m³) heat storage [29, 30, 39–41]. If the annual heating demand is 25 kWh/m²/year that is typical for standards of low energy buildings in Europe a 100 m² house consumes for heating about 9 GJ per year. These heat needs can be, in principle, covered by solar energy, because even in the UK the amount of solar radiation incident on a correctly orientated roof of a typical house exceeds its energy consumption during a year [42]. Accordingly, efficient inter-seasonal heat storage is necessary in this case. The volume of a heat storage material is reasonable (2–10 m³) only if the storage density is above 1 GJ/m³ (270 kWh/m³). In actual practice, the volume of the heat storage unit is larger than the material volume itself by a factor of 2–4 due to volumes of heat exchangers, evaporator/condenser, pumps/fans, pipes, etc.

For countries with colder climate, means, a larger HDD-value, like Russia, the adsorption storage alone can hardly cover the overall heat demand during winter. In this case, the heat storage systems need to work alongside a complementary space heating unit.

It is worthy to make an estimation of tentative upper limit of the AHS storage density. Water has a large heat of evaporation ΔH_{ev} , and is considered as the most promising and ecologically clean working fluid for AHS applications. For making this estimation, let's assume that the heat storage process is simply water evaporation. During this endothermic transition of water molecules from liquid to vapour state, the amount of heat consumed (stored) is $A(H_2O) = \Delta H_{ev} = 2.25 \text{ MJ/kg} = 2.25 \text{ GJ/m}^3 = 630 \text{ kWh/m}^3$ (at 100 °C). For AHS, the amount of heat needed for complete water desorption (or maximal heat storage density A_{max}) is

$$A_{max}^{mas} = \Delta H_{des} \times w_{max} \text{ (per 1 kg dry adsorbent)} \quad (1)$$

or

$$A_{max}^{vol} = \Delta H_{des} \times w_{max} \times \rho \text{ (per 1 m}^3 \text{ adsorbent)}, \quad (2)$$

where ΔH_{des} is the average heat of water desorption [in kJ/kg], w_{max} is the maximal mass of water adsorbed per 1 kg adsorbent, and ρ is the adsorbent apparent density. For adsorbents with high affinity to water vapour, like common zeolites, the ΔH_{des} -value can be 1.5–2 times larger than the heat of water evaporation ΔH_{ev} , $w_{max} = (0.2\text{--}0.4) \text{ kg/kg}$ and $\rho = 600\text{--}800 \text{ kg/m}^3$, hence, $A_{max}(\text{-zeolites}) = (0.67\text{--}1.80) \text{ MJ/kg} = (0.35\text{--}1.45) \text{ GJ/m}^3$ that is $(0.2\text{--}0.7) A(H_2O)$. Several new adsorbents (SWSs, FAMs, MOFs – see below) have an advanced water sorption capacity $w_{max} = 0.7\text{--}1.8 \text{ g/g}$ and the maximal heat storage density A_{max}^{mas} can reach or even somewhat exceed the estimated storage density $A(H_2O)$ (Table 2). The heat A_{max}^{vol} stored per unit adsorbent volume is always lower than $A(H_2O)$. Therefore, the above $A(H_2O)$ -estimation can be used as a reference value that delineates an upper limit of the heat storage density via adsorption process.

Eqs. (1) and (2) take into account only the latent heat of material. A useful method of experimental evaluation of both latent and sensible heat was suggested in [41] and then used in [35] and [43]. The sensible heat was found to be 4–7 % of the latent one (in the temperature range 50–200 °C) and can be used either for immediate consumption (e.g. for HHWP) or short-term storage.

Under real conditions the storage density is expected to be lower than the maximal one calculated by eqs. (1) and (2), because only a part of the adsorbed water is involved in the storage process. To realize how much water can be involved, let's consider a simple three temperature (3T) closed cycle of AHS unit. Although the thermodynamics is similar, an open AHS cycle is considered on a psychrometric chart of humid air (not presented) as described in [32]. Practical implementations of the AHS open and closed systems are quite different as well (see 3.1.4).

Table 2 Maximal mass of water adsorbed w_{max} , average desorption heat ΔH_{des} , maximal heat storage densities A_{max}^{mas} and A_{max}^{vol} (calculated by eqs. (1) and (2))

Adsorbent	w_{max} , g/g	ΔH_{des} , MJ/kg	A_{max}^{mas} , MJ/kg	A_{max}^{vol} , GJ/m ³	Reference
Silica gel Fuji RD	0.4	2.40	0.96	0.77	[95]
Zeolite 13X	0.34	3.8	1.29	0.83	[96]
Zeolite 4A	0.22	3.05	0.67	0.49	[97]
Zeolite MgX	0.45	2.68	1.21	-	[53]
SWS-1 L = CaCl ₂ /silica gel	0.65	2.65	1.72	1.55	[98]
SWS-9 V = LiNO ₃ /Vermiculite	1.80	2.30	4.15	1.16	[75]
SWS-1 V = CaCl ₂ /Vermiculite	1.80	2.35	4.2	1.25	[99]
SIM-3b = MgSO ₄ /Vermiculite	1.94	-	0.41 ^a	0.14	[35]
(MgSO ₄ + MgCl ₂)/Attapulgit	-	-	1.59 ^b	-	[54]
AQSOA-Z02	0.33	3.25	1.07	0.55	[100]
AlPO-Tric	0.31	3.17	0.98	-	[56]
MIL-101	1.40	1.83	2.57	-	[62]
MIL-125NH ₂	0.47	2.85	1.33	0.39	[66]
MOF-841	0.48	3.05	1.47	-	[67]

^a the value was obtained by integrating DSC-thermogram of the sample within a temperature range of 30 to 100 °C; it is likely to be underestimated

^b the isothermal heat directly measured during water sorption at 30 °C and a relative humidity of 85 % on the sample preliminarily dried at 130 °C

A 3T cycle of adsorptive heat storage This cycle consists of two isosters and two isobars and is commonly presented on the Clapeyron diagram $\ln(P)$ vs. $(-1/T)$ (Fig. 3). During isobaric desorption (2–3) the amount of water adsorbed reduces from w_{max} to w_{min} , and the heat Q_d consumed for the water desorption is stored. The stored heat can be release during isobaric adsorption (4–1) when the dewatered adsorbent sucks water vapour from an evaporator (for closed AHS cycles) or from the ambient air (for open cycles). The heat of evaporation Q_e is deemed to be taken from the ambient for free. Between the

charging (2–3) and discharging (4–1) stages the heat can be stored as long as needed without any heat insulation.

Three temperatures (those of evaporator T_e , condenser $T_c = T_1$, and external heat source T_g) uniquely define the cycle [44]. The heat Q_a is released for consumers at temperature ranging between T_4 and $T_1 = T_c$, therefore T_c should be at least 30–35 °C (the lowest input temperature for floor heating). The heat of condensation Q_c can also be used for heating at temperature T_c . For simple and relatively cheap flat receivers of solar energy, the temperature of heat carrier T_g available for water desorption commonly is 70–110 °C. Hydration of adsorbent up to the maximal uptake w_{max} occurs at point 1 by absorbing water vapour saturated at temperature $T_e = 5 - 15$ °C. For a model AHS cycle, we have fixed the following set of temperatures: $T_e = 10$ °C, $T_c = 35$ °C, and $T_g = 90$ °C, and calculated the mass of water exchanged along such cycle $\Delta w = w_{max} - w_{min}$ and appropriate cycle heat storage density A_{max}^{vol} that appears to be lower than the maximal one displayed in Table 2 by a factor of 2–12 (Table 3). Significant reduction of the storage density is especially typical for zeolites which need the regeneration temperature much higher than the set temperature $T_g = 90$ °C. This confirms that a high affinity of adsorbent and adsorbate to each other or/ and a large total sorption capacity are not important of themselves. The heat storage density is defined by the amount of adsorbate exchanged within the particular AHS cycle, means, under certain conditions of heat storage process [45].

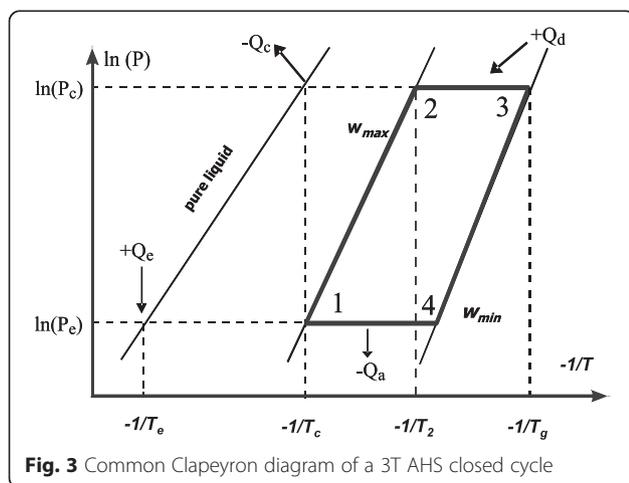


Fig. 3 Common Clapeyron diagram of a 3T AHS closed cycle

Table 3 Mass of water exchanged Δw and appropriate heat storage densities A_{\max} for a model AHS cycle ($T_e = 10$ °C, $T_c = 35$ °C, and $T_g = 90$ °C)

Adsorbent	Δw , g/g	A_{\max}^{mas} , MJ/kg	A_{\max}^{vol} , GJ/m ³	Reference
Silica gel Fuji RD	0.12	0.29	0.23	[101]
Zeolite 13X	0.03	0.11	0.07	[96]
SWS-1 L	0.17	0.45	0.32	[98]
SWS-9V ^a	0.43	1.15	0.45	[75]
SWS-1V	0.33	0.76	0.21	[99]
AQSOA-Z02	0.19	0.62	0.31	[102]
AQSOA-Z02 ^b	0.26	0.84	0.42	[43]
MIL-125NH ₂	0.21	0.64	0.19	[67]

^a $T_e = 10$ °C, $T_c = 30$ °C and $T_{des} = 70$ °C

^b $T_e = 15$ °C, $T_c = 28$ °C and $T_{des} = 90$ °C

Thus, the inter-seasonal heat storage can cover whole winter heating needs for low-energy buildings in a relatively mild climate (reasonable HDD-value). For less perfect buildings and colder climates, the heat stored during summer can yet be used in winter to reduce fossil fuel consumption, smooth heating peaks and, hence, decrease bills for heating. In this case, the AHS can be used as an auxiliary tool for common space heating system.

The 3T cycle on Fig. 3 allows introducing other two parameters important for AHS:

a) a minimal desorption temperature $T_{\min} = T_2$. If the two boundary temperatures T_e and T_c are fixed, this temperature can be estimated from simple Trutoun's rule [44, 46, 47].

$$T_{\min} = (T_c)^2/T_e \quad (3)$$

within an accuracy of ± 1 °C [44]. Evidently, if the temperature of external heat source T_g is lower than T_{\min} , it is not sufficient for adsorbent regeneration and the AHS cycle cannot be realized at all. A low T_2 -value helps in easier adsorbent regeneration that allows storage of heat with appropriately low temperature potential;

b) a temperature lift $L = (T_c - T_e)$. A large temperature lift permits higher temperature level of heat released during heat rejection (discharging) stage. For working pairs that follow Trutoun's rule, the temperature lift can be estimated as [48].

$$L = (T_c - T_e) = [T_c - (T_c)^2/T_g] = T_c(1 - T_c/T_g). \quad (4)$$

Thus, the temperature lift increases if adsorbent has high regeneration temperature, means, strong affinity to water vapour. This affinity can be quantitatively characterized by the Dubinin adsorption potential as suggested

in [49] and applied for analyzing adsorptive transformation of heat in [45].

New adsorbents promising for AHS For advanced AHS performance, it is necessary to have an adsorbent with high heat storage density A_{\max}^{vol} , large temperature lift L , and low regeneration temperature T_g . It is evident, that two last requirements are in a certain conflict. Indeed, the regeneration process is easier for adsorbents with low affinity to water vapour, whereas a large temperature lift, on the contrary, needs high affinity. Therefore, intelligent compromise between these tendencies is necessary. We do not consider here dynamic parameters of the promising adsorbents, because the overall dynamics in real AHS units is more dependent on the organization of heat and mass transfer in the overall unit "adsorber – heat exchanger", Ad-HEx (see 3.1.4 and 3.5).

The largest overall storage density A_{\max}^{vol} (up to 1.55 GJ/m³) was documented for composites "salt in porous matrix" that are known as Selective Water Sorbents (SWSs) [50]. They present a family of solid sorbents specifically developed in the Boreskov Institute of Catalysis (Novosibirsk, Russia) for adsorptive transformation and storage of low temperature heat [50, 51]. The SWSs were shown to exhibit an intermediate behaviour between solid adsorbents, salts hydrates and liquid absorbents. Combination of high storage density of the salts and good mass transfer of the porous matrix allows the design of advanced materials and AHS units with high efficiency and specific power. Very important advantage of SWSs is an opportunity for nano-tailoring their sorption properties by varying the salt chemical nature and content, porous structure of the host matrix and synthesis conditions [51, 52]. It is especially valuable for inter-seasonal AHS, because allows adaptation of a heat storing adsorbent to particular climatic conditions at the location of AHS unit. At present, these materials are comprehensively tested in many laboratories all over the world [28, 29, 35, 53].

Loose grains of clay mineral attapulgite impregnated with mixture of MgSO₄ and MgCl₂ hydrates was investigated for suitability as a heat storage material [54]. It was shown that the partial substitution of MgSO₄ by MgCl₂ resulted in higher sorption heat. This larger heat release was accompanied with higher temperature lift. The energy density of the composite containing a mixture of 20 wt.% MgSO₄ and 80 wt.% MgCl₂ and saturated at $T_a = 30$ °C and $RH = 85$ % was 1590 kJ/kg. The desorption temperature of 130 °C was sufficient for the composite regeneration, that makes the new material promising for solar thermal energy storage.

Systematic study of the SWS-type composites for AHS was performed in refs. [35, 55]. The authors tested various hygroscopic salts (CaCl_2 , MgSO_4 , $\text{Ca}(\text{NO}_3)_2$, LiNO_3 , and LiBr) and host matrices (silica gel, zeolite, activated carbon and mineral vermiculite) to obtain their combinations promising for open AHS systems and studied them by a variety of physico-chemical methods (BET, BJH, TG, DSC, SEM, EDX, etc). It was found that the sorption capacity of all composite materials is significantly higher (up to 1.9 g/g) compared to their raw host matrices alone suggesting the addition of the salt is beneficial for moisture and, hence, heat storage. It was demonstrated that the pore structure damage may occur for the non-vermiculite matrices, however no damage was observed in the vermiculite as a host. Vermiculite with either lithium bromide or calcium chloride appears to have significantly larger AHS potential when compared to both the raw matrices and the other composites [35].

A recent survey of the current-state-of-the art of the SWS materials can be found elsewhere [52]. In particular, the authors considered potential troubles that could impede an actual reduction of these new composites to practice. This is, first of all, a leakage of the salt solution formed during sorption out of the matrix pores, which can cause a corrosion of metal parts of AHT unit and emission of non-condensable gas. Several ways to avoid,

or at least lessen, this shortcoming were considered in [52].

Quite interesting storage parameters were obtained for new zeolite-like materials that do not contain silicon, namely, pure and substituted aluminophosphates [56–59]. E.g. an APO-Tric material was suggested for use in low temperature solar energy storage [56], because it exchanges 0.25 g $\text{H}_2\text{O}/\text{g}$ in an extremely narrow range of the relative pressure $P/P_0 = 0.12\text{--}0.15$ and can be regenerated at 80–90 °C. Quite promising storage properties were revealed for SAPO-34, AlPO-18, AlPO-17, AlPO-5, etc [58]. The disadvantages of this class of materials are a relatively small pore volume (e.g. 0.33 cm^3/g for AQSOA-Z02, Table 2) and high cost. The main practical strength is an availability of several commercial adsorbents (AQSOA-Z01, AQSOA-Z02 and AQSOA-Z05) in the form of coated heat exchangers produced by the Mitsubishi Plastics Ltd. (see refs. [59–61] and Fig. 4d).

Among new AHS adsorbents, metal organic frameworks (MOFs) are attracting an increasing attention (e.g. MIL-101, MIL-125 NH_2 and MOF-841 in Table 2) due to their unique combination of properties such as high surface area, crystalline open structure, tunable pore size and functionality [62–64]. These materials can exhibit very large water adsorption capacity (e.g. 1.4 g/g for MIL-101, Table 2) and low regeneration temperature, however, their affinity to water is, in general, too low to

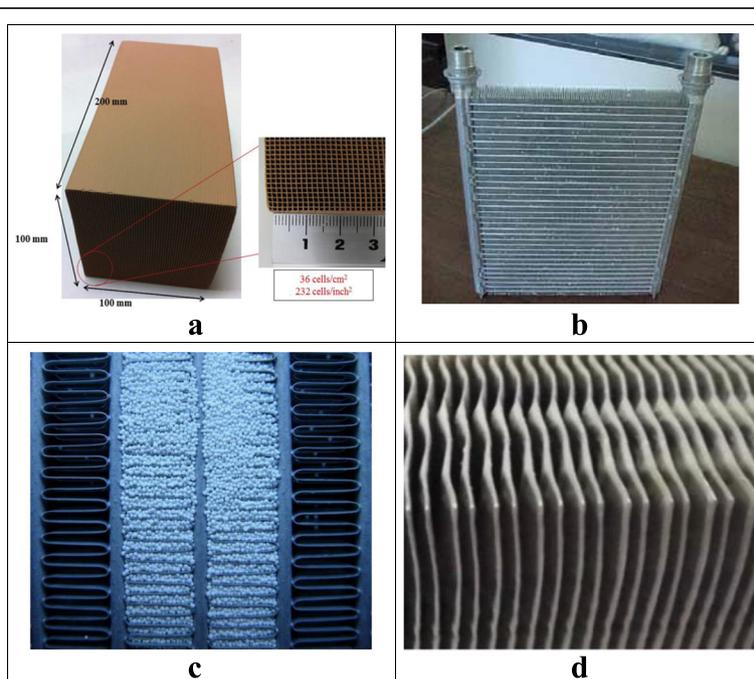


Fig. 4 Various configurations of “adsorber – heat exchanger” unit: open systems - a honeycomb ceramic element made of WSS [71] (a); closed systems - overall (b) and fragment (c) views of the Ad-HEX with loose grains [76], (d) - fragment of the fin-and-tube heat exchanger coated with AQSOA-Z01 [60]

ensure sufficient temperature lift. In our opinion, the potential of MOFs for AHS has not been unveiled yet, and it is quite possible that a target-oriented modification or screening of MOFs will reveal novel working pairs highly efficient for AHS. In particular, very promising results have been reported for UiO-66NH₂ [65], MIL-125NH₂ [66], MOF-801 and MOF-841 [67].

The above analysis is mainly based on considering the storage density, temperature lift and regeneration temperature, and do not take into account other important practical requirements to adsorbent optimal for AHS. These are minimal or no adsorption/desorption hysteresis, low costs and easy availability, high cyclic stability, free from poison, non-combustibility, no environmental effects, low maintenance requirements, etc. Some of these issues have become clear during practical testing of the advanced adsorbents as reported below.

Current practice of inter-seasonal adsorptive heat storage Since a large variety of adsorbents have already been tested for AHS, we consider here only several selected, mostly recent, examples of both open and closed AHS systems, and refer a Reader to appropriate review papers (e.g. [28–40, 68–70]) and references therein.

Among open AHS systems the most famous and well tested is an open heat storage system installed in a school building in Munich (Germany) and connected to the local district heating network [32]. It contained 7,000 kg of zeolite 13X as beads. The unit was tested during the heating period 1997/98 under the following conditions: the air flow rate—6,000 m³/h, the desorption temperature—130 °C, the pressure of water vapour at the heat release stage—32 mbar that corresponds to a dew-point of 25 °C. For a large temperature lift of 40 °C, a maximal energy density is estimated to be 0.49 GJ/m³ (or 0.55 GJ/m³ if the sensible heat can be utilized), whereas in the experiments a lower value of 0.446 GJ/m³ was recorded, which is 81 % of the theoretical one. Such a large storage density is due to a relatively high regeneration temperature of 130 °C. It is worthy to remind that for the above model AHS cycle with lower regeneration temperature of 90 °C, $A_{\max}^{vol} = 0.07 \text{ GJ/m}^3$ (Table 3).

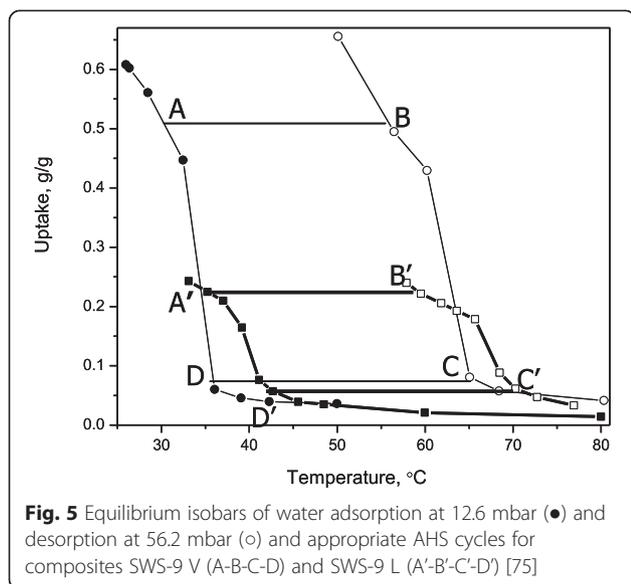
The authors of [55] analysed the performance of several candidate materials (1.5 dm³ of adsorbent) under experimental hygrothermal cycling tests together with energy and exergy analysis of the results obtained. They tested eight composites “salt in porous matrix” identified before in [35] as well as raw zeolite 13X and mesoporous silica gel (Geejay Chemicals, UK) under typical conditions of open AHS cycle. The studied adsorbents were located in a test tray as a bed of loose grains. It was found that the zeolite provided the highest temperature

lift, however, after the initial period (1–2 h), the moisture adsorption rate and thus heat generation decreased sharply. A sharp drop in performance over the four cycles was found for zeolite 13X which requires a higher regeneration temperature (>180 °C) than that used (100 °C) for the research. The composite SIM-3a (vermiculite doped with CaCl₂) was found to be the most promising candidate for open TES systems due to its larger heat generated (120–160 kWh/m³) and rapid mass uptake at higher RH levels. Moreover, SIM-3a is non-toxic material, has a low regeneration temperature, good cyclic ability, and low cost (~0.48 \$/kg) [55]. It is worthy to note that for inter-seasonal heat storage the material cost is far more important than for short-term heat storage.

The authors of ref. [71] used as a host porous matrix another cheap mineral material, that was a Wakkanai siliceous shale (WSS). The WSS is a type of siliceous mudstone that is widely distributed in Wakkanai, the northern part of Hokkaido (Japan). It is a natural mesoporous material composed of silicon dioxide (SiO₂) with pores of 5–40 nm size. A new AHS composite was formed by inserting LiCl into the WSS pores. To overcome the problems of low heat and mass transfer and high hydrodynamic resistance in an open AHS system, the WSS was formed by adding a binder into a honeycomb ceramic element of 10 cm x 10 cm x 20 cm with 36 cells/cm² and a cell wall thickness of 0.28 mm (Fig. 4a). The composite containing 9.6 wt.% LiCl showed a good potential for storing heat with a volumetric heat storage density of 0.180 GJ/m³ and could supply air heated up to 53 °C. No material degradation was observed during at least 250 cycles at a quite low desorption temperature of 60 °C.

An open-type AHS setup equipped with 40 kg of composite sorbent CaCl₂/(mesoporous silica gel) was tested as a batch adsorber in [72, 73]. The concentration of the CaCl₂ impregnating solution was found to be an important factor affecting the storage properties of the composites. The composite prepared by impregnating silica gel with a 30 wt.% CaCl₂ solution showed a high storage capacity of 1.02 MJ/kg (0.81 GJ/m³) that remained stable after 500 consequent sorption/desorption cycles. The heat discharging temperature varied from 47 °C to 30 °C and the sorbent can be charged at temperature 90 °C or below. Mathematical modelling of the AHS process predicted that the specific heat storage capacity can be increased up to 1.35 MJ/kg at a regeneration temperature of 100 °C [74].

SWS-type materials were successfully used also in closed AHS systems [75]. For instance, lithium nitrate was introduced into silica gel [76] and vermiculite [75] matrices and tested in typical AHS cycle (Fig. 5). LiNO₃ is a salt which bounds water less strongly than calcium

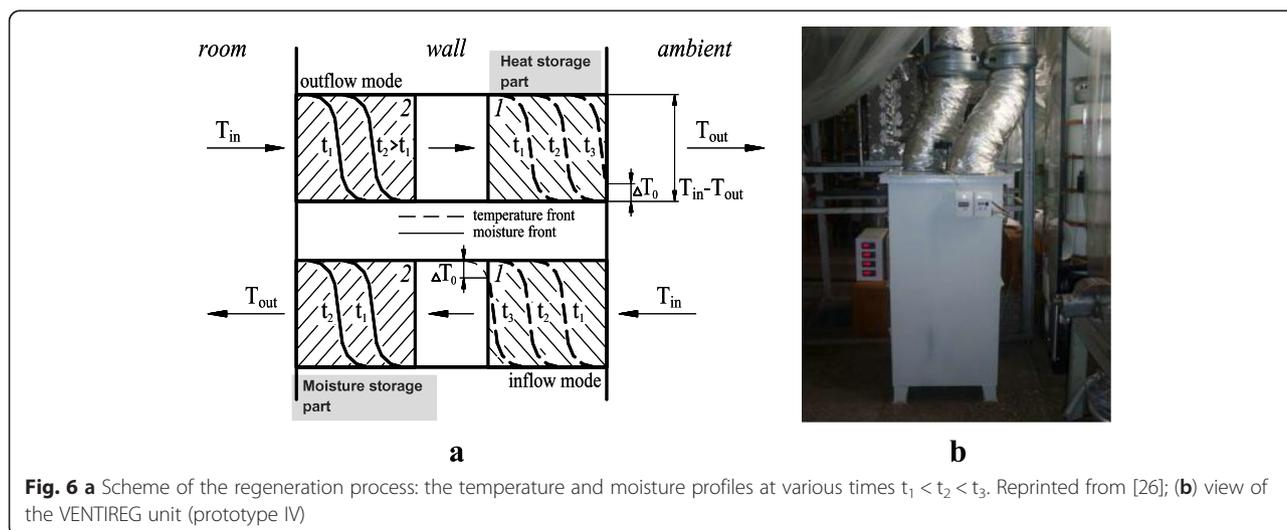


chloride, lithium bromide or calcium nitrate already reported for AHS applications. Therefore, this composite sorbent was specifically developed to operate at low regeneration temperature (<65–70 °C). The sorbent particles were embedded inside a compact heat exchanger of a finned flat-tube type (Fig. 4b, c). This Ad-HEX configuration has the following advantages: a) compactness and low weight, as the heat exchanger is made of aluminium; b) good heat transfer properties due to the high heat transfer area and a high thermal conductivity of aluminium; c) high vapour permeability as provided by granular packing. Fig. 4b, c shows the overall and the detailed view of the Ad-HEX with loose silica gel grains.

The distance between the fins was about 2 mm, so that 2–4 grains could be housed in this gap.

The composite LiNO₃/vermiculite (SWS-9 V) exchanges 0.43 (g H₂O)/(g sorbent) in an exceptionally narrow temperature range, 33–36 °C (heat rejection) and 62–65 °C (adsorbent regeneration), corresponding to a remarkable heat storage capacity of 1.15 MJ/kg. It is much larger than for similar composite based on mesoporous silica gel, SWS-9 L (Fig. 5). If relate the storage capacity to the *total volume* of the Ad-HEX unit (Fig. 4b), it is equal to 0.45 GJ/m³. This is superior to common adsorbents and Ad-HEX units suggested for storage of heat with temperature potential of 60–70 °C.

Another solution for enhancing heat and mass transfer was investigated for the residential application in [60]. A commercial heat exchanger was adopted for an adsorption bed to quicken the charging process by improving heat and mass transfer. It is a copper tube and aluminium plain fin type heat exchanger with 12 parallel four-pass circuits, 1.8 mm fin spacing and a 0.25 mm thickness adsorbent coating on all fin and tube surfaces (Fig. 4d). The commercial material AQSOA-Z01 (Mitsubishi Plastics) [77] was used as the adsorbent bed material. When the regeneration and heat rejection temperatures were 70 °C and 30 °C, respectively, the heat storage density was found to be 0.805 MJ/kg or 0.15 GJ/(m³ of the Ad-HEX). The loading difference was 0.164 kg water/kg adsorbent. The authors suggested several possible solutions for the system performance improvement, e.g. adding more adsorbents into the fin spacing of the Ad-HEX or onto heat transfer tubes to form consolidated layer.



This brief overview of the current practice in inter-seasonal AHS shows that

- a) for several AHS systems tested the storage density are approaching a desired level of $1 \text{ GJ}/\text{m}^3$;
- b) the composite sorbents “salt in porous matrix” demonstrated great potential to obtain a high AHS density and to reduce an AHS system size as compared to the other heat storage materials. The main advantages of these composites are as follows:
 - i) low charging temperature (solar energy absorbed by flat receivers can be stored),
 - ii) large storage capacity, and
 - iii) possibility to controllably modify their sorption properties to match conditions of particular heat storage cycles (e.g. variation of the salt and matrix nature, etc). The main shortcoming is a relatively low temperature lift. It can be enhanced by applying salts with higher affinity to water vapour at the expense of appropriate increase in the charging temperature.

To summarize, despite the significant progress in adsorbent synthesis and applications in various AHS cycles, still there is a big room for their further optimization and development of new adsorbents with advanced and pre-requested properties.

Regeneration of heat and moisture in ventilation system of dwellings in cold climates

As manifested above, an efficient way of further improvement of the dwellings thermal efficiency is associated with heat recovery from the ventilation systems. This is especially important for countries with a cold climate (typical of Russia, Canada, the North Europe and USA), where the difference between indoor and outdoor temperatures can reach in winter up to $60 \text{ }^\circ\text{C}$ or even more. This leads to enormous heat losses, therefore efficient exchange of heat between the exhaust and supply air fluxes is absolutely necessary for reducing the heat losses. Numerous experimental and modelling studies have clearly demonstrated that up to a 90 % heat recovery can be reached by using modern plate [78, 79] and regenerative [80, 81] air-to-air heat exchangers. Another problem that appears during cold winter is continuous losing of moisture through ventilation system [82, 83]. Indeed, the absolute humidity of supplied (outdoor) air is extremely low (e.g. $\leq 0.29 \text{ g}/\text{m}^3$ at $-30 \text{ }^\circ\text{C}$), that results in dramatic reducing the indoor relative humidity (down to 10–20 % or even below) in winter season that greatly disbalances the indoor thermal comfort. Therefore, in cold countries it is extremely important to organize not only heat exchange, but moisture exchange between the fluxes as well to maintain the indoor humidity within the reasonable range. One of the solution is the

application of porous and polymer membranes partially permeable for moisture as suggested in [83–85]. A new approach (the so called VENTIREG) was suggested in [26] for simultaneous regeneration of both heat and moisture in ventilation systems for cold climate countries. This approach was deemed to ensure an efficient moisturizing of the supplied air to approach indoor conditions of human thermal comfort which is extremely important because people spend more than 90 % of their time in buildings [86].

The main principal of the VENTIREG method is as follows (Fig. 6a). To exchange the sensible heat between the inlet (fresh) and outlet (exhausted) air fluxes, a granulated layer (1) of heat storing material is placed closer to the unit exit. Before this layer, layer 2 of water adsorbing material is located closer to the room side. It serves as a water buffer. The unit operates in two modes:

outflow mode: a warm and humid indoor air is blown by an extract fan through the relatively dry adsorbent, which captures and retains the indoor moisture. Dried and warm air enters layer 1 and heats it up. After that, the air flux switches;

inflow mode: a dry and cold outdoor air is blown by a supply fan through the warm layer 1 and is heated up to the temperature close to that in the room T_{in} , thus, recovers the stored heat. Passing through the layer of the humid adsorbent, warm and dry air causes the retained water to be desorbed and come back to the room, thus, maintaining the indoor moisture balance. Because of the finite heat capacities of layers 1 and 2, the temperature of incoming air is slowly decreasing, and the air flux switches when the temperature difference ($T_{in} - T$) reaches a predetermined value ΔT_0 , and so on.

To study and optimize the heat and moisture recovery, four experimental units with the air flux up to 25 (I), 40 (II) and 135 (III and IV) m^3/h were built and tested. Both common (silica, alumina) and novel (SWS-1A = alumina impregnated with CaCl_2) adsorbents were used as buffers of water. The composite sorbent SWS-1A was found to demonstrate better performance than the common commercial adsorbents. Owing to higher adsorption capacity of this composite, the adsorbent loading is less by a factor of 2–3 that leads to smaller unit size and much lower hydrodynamic resistance of the unit. This could allow the using of cheap blade-type fans instead of centrifugal ones and give a reduction of the electricity consumption. Units III and IV consume for air blowing 20–40 W of electric power and give the heating load of about 600–1400 W that corresponds to a Coefficient of Performance of 25–35. So little electricity

consumption is a very important advantage of the VENTIREG approach. Prototype IV (Fig. 6b) was constructed in a way to ensure a continuous operation, not intermittent as for units I-III [26].

Thus, the tested VENTIREG units exchange stale, contaminated room air with fresh outdoor air, recovering up to 95 % of heat and 70–90 % of moisture from the exhaust air. Moreover, it prevents the formation of ice at the unit exit that is one more severe problem to be solved under real winter conditions [87]. According to the data of Table 3 of the recent review paper [82], the VENTIREG unit demonstrates the best properties among different heat and mass recovery systems tested under various cold climate conditions.

Future R&D for AHS optimization

Despite a significant progress in AHS achieved, still there is a much room for further developing this emerging technology [48, 88, 89]. To reach this ambitious goal, systematic R&D must be made at least, but not last, in the following directions:

- development of new efficient adsorbents with the cycle heat storage density larger than 1.0 GJ/m^3 . Their adsorption properties have to be harmonized with boundary temperatures of appropriate heat storage cycles [45];
- improvement of heat and mass transfer in the unit “adsorbent – heat exchanger”. This can be obtained by using new advanced heat exchangers [78, 81, 90], heat pipes [91], coating a heat exchanger fins with an adsorbent [60, 61], etc.;
- optimization of AHS cycles due to a proper choice of durations of isobaric stages [76], heat and mass recovery [92], cascade cycles [93], etc.;
- improvement of AHS hardware [94], first of all, an evaporator that operates at low temperature and pressure [88].

Conclusion

In this paper we consider the role of adsorption-based technologies for more rational use of heat and better thermal comfort in buildings. Based on the structure of typical heat losses in modern dwellings, two adsorption technologies can be selected for reaching the mentioned goals, namely, the inter-seasonal heat storage and the regeneration of heat/moisture in dwelling ventilation systems. Both technologies have not reached yet a degree of perfection that is needed for successful commercialization. The appropriate units have to be more robust, compact and provide better heat and mass transfer, whereas the adsorbents must exhibit larger heat storage capacity and lower cost. To reach two above mentioned targets and make the adsorption technologies better competitive with more

mature technologies, like PCM or sensible heat storage, further R&D is required in the field of adsorbents, heat and mass transfer, and advanced components.

We hope that this review will give new impulses to further consolidating international R&D activities in materials science and applied thermal engineering to obtain novel revolutionary adsorbents and technologies for improving energy efficiency and thermal comfort in buildings.

Abbreviations

Ad-HEX: Adsorbent – heat exchanger; AHS: Adsorptive heat storage; EU: European union; GHG: Green house gases; HDD: Heating degree-days; HHWP: Heating and hot water production; IEA: International energy agency; MOF: Metal organic frameworks; Mtoe: Million tonnes of oil equivalent; PCM: Phase change materials; RF: Russian Federation; RH: Relative humidity; SEC: Specific energy consumption; SWS: Selective water sorbents; UK: United Kingdom; USA: United States of America; WSS: Wakkanai siliceous shale.

Competing interests

The authors declare that they have no competing interests.

Acknowledgments

The author thanks the Russian Foundation for Basic Researches (project 14-08-01186a) for partial financial support.

Received: 24 August 2015 Accepted: 7 November 2015

Published online: 01 December 2015

References

1. United Nations Population Fund. (2012). State of the World population 2011
2. UN-HABITAT (2008). State of the world's cities report 2008–9: Harmonious cities: <http://www.fastcodesign.com/1669244/by-2050-70-of-the-worlds-population-will-be-urban-is-that-a-goodthing> (accessed November 13, 2015)
3. Dresner S (2002) *The Principles of Sustainability*. Earth Scan Publications, London
4. Gurusprasad M, Oakley B, Green D, Koon D, Low P (2013) *Practicing Sustainability*. Springer, New York
5. James P, Magee L, Liam S, Scerri A, Steger M (2015) *Urban Sustainability in Theory and Practice: Circles of Sustainability*. Routledge, London
6. Rassa S, Pardalos P (2015) *Cities for Smart Environmental and Energy Futures, Impacts on Architecture and Technology*. Springer, New York
7. Eurostat, *Energy Yearly Statistics 2008*, Publication Office of the European Union, 2010
8. DECC (Department of Energy & Climate Change), *Energy Consumption in the UK. Overall Energy Consumption Factsheet*, Department of Energy & Climate Change, 2013, Available from <https://www.gov.uk/government/publications/energy-consumption-in-the-uk> (last accessed 13/11/15)
9. Abdellatif M, Al-Shamma'a A (2015) Review of sustainability in buildings. *Sustainable Cities and Society* 14:171–177
10. Parliament Committee. (2013). Meeting Carbon Budgets: Progress Report on Climate Change, Chapter 3: Progress reducing emissions from buildings
11. NRC (2006). *Operating energy in buildings*. Retrieved from <http://cn-sbs.cssbi.ca/operating-energy-buildings> (last access - 13/11/15)
12. Ziesing H-J, Schlomann B, Rohde C, Eichhammer W, Kleeburger H, Tzscheutschler P. (2011). *Anwendungsbilanzen für die Endergiegiesektoren in Deutschland im Jahr 2008*. In AG Energiebilanzen beauftragt vom BMWiProjekt Nummer 40/08
13. *Buildings Energy Efficiency in China, Germany, and the United States*, Climate Policy Initiative, April 2013, <http://climatepolicyinitiative.org/wp-content/uploads/2013/04/Buildings-Energy-Efficiency-in-China-Germany-and-the-United-States.pdf> (last access 13/11/15)
14. *Energy Efficiency Policies and Measures in Germany, ODYSSEE- MURE 2010*, Monitoring of EU and national energy efficiency targets, Karlsruhe, November 2012, http://www.isi.fraunhofer.de/isi-wAssets/docs/x/de/publikationen/National-Report_Germany_November-2012.pdf (last access 13/11/15)
15. Report «On enhancement of energy efficiency of the Russian economy». Arkhangelsk, April 2009; <http://www.cenef.ru/file/Report%2025.05.09.pdf> (last access 13/11/15)

16. Bashmakov I, Borisov K, Dzedzichik M, Gritsevich I, Lunin A: *Resource of energy efficiency in Russia: Scale, costs and benefits*. 2008. Moscow: CENEF – Center for Energy Efficiency. Developed for the World Bank 102p. <http://www.cenef.ru/file/Energybalances-final.pdf> Accessed 13/11/15
17. Filippov SP, Dilman MD, Ionov MS (2013) The Optimum Levels of the Thermal Protection of Residential Buildings under Climatic Conditions of Russia. *Therm Eng* 60:841–851
18. International Energy Agency (2010) *Energy Technology Perspectives 2010: Strategies and Scenarios to 2050*. OECD/IEA, Paris
19. Arbeitsgemeinschaft Prognos AG/Öko-Institut/Dr. Hans-Joachim Ziesing, *Modell Deutschland: Klimaschutz bis 2050-Vom Ziel her denken*, WWF Deutschland, Germany, 2009
20. Ürgü-Vorsatz D, Novikova A (2008) Potentials and costs of carbon dioxide mitigation in the world's buildings. *Energy Policy* 36:642–661
21. *The Future of Heating: A strategic framework for low carbon heat in the UK*, Department of Energy and Climate Change, March 2012
22. Space heating demand modelled using the Cambridge Housing Model v2.6
23. SNiP 23-02-2003, *Thermal Performance of Buildings* (Moscow, the State Construction Committee of the Russian Federation, The Central Institute for Type Designing, 2004)
24. Riffat SB, Zhao X, Doherty PS (2006) Application of sorption heat recovery systems in heating appliances - Feasibility study. *Appl Therm Engn* 26:46–55
25. Zheng X, Ge TS, Wang RZ (2014) Recent progress on desiccant materials for solid desiccant cooling systems. *Energy* 74:280–294
26. Mezentshev YI IV, Mukhin VA (2008) A new approach to regenerating heat and moisture in ventilation systems. *Energy and Buildings* 40:204–208
27. Mardiana-Idayu A, Riffat SB (2012) Review on heat recovery technologies for building applications. *Renew Sustain Energy Rev* 16:1241–1255
28. Yu N, Wang RZ, Wang LW (2013) Sorption thermal storage for solar energy. *Prog Energy Combust* 39:489–514
29. Ding Y, Riffat SB (2012) Thermochemical energy storage technologies for building applications: a state-of-the-art review. *Int J Low-Carbon Tech*. doi: 10.1093/ijlct/cts004
30. N'Tsoukpoe KE, Liu H, Le Pierrès N, Luo L (2009) A review on long-term sorption solar energy storage. *Renew Sustain Energy Rev* 13:2385–2396
31. Kuznik F, Johannes K (2014) A review of chemisorption heat storage in low energy buildings. *Energy Procedia* 57:2333–2341
32. Hauer A (2007) Evaluation of adsorbent materials for heat pump and thermal energy storage applications in open systems. *Adsorption* 13: 399–405
33. Xu J, Wang RZ, Li Y (2014) A review of available technologies for seasonal thermal energy storage. *Sol Energy* 103:610–638
34. Aydin D, Casey SP, Riffat S (2015) The latest advancements on thermochemical heat storage systems. *Renew Sustain Energy Rev* 41:356–367
35. Casey SP, Elvins J, Riffat SB, Robinson A (2014) Salt impregnated desiccant matrices for 'open' thermochemical energy storage—Selection, synthesis and characterisation of candidate materials. *Energy and Buildings* 84:412–425
36. Raldow WM, Wentworth WE (1979) Chemical heat pumps - a basic thermodynamic analysis. *Sol Energy* 23:75–79
37. Close D, Dunkle R (1977) Adsorbent beds for energy-storage in drying of heating systems. *Sol Energy* 19:233–238
38. Abedin AH, Rosen MA (2012) Closed and open thermochemical energy storage: Energy- and exergy-based comparisons. *Energy* 41:83–92
39. Michel B, Mazet N, Mauran S, Stitou D, Xu J (2012) Thermochemical process for seasonal storage of solar energy: characterization and modeling of a high density reactive bed. *Energy* 47:553–563
40. Hadorn JC. *Thermal Energy Storage for Solar and Low Energy Buildings—State of the Art*. Servei de Publicacions de la Universitat de Lleida, 2005
41. Aristov YI, Restuccia G, Tokarev MM, Cacciola G (2000) Selective water sorbents for multiple applications: 10. Energy storage ability. *React Kinet Catalysis Letters* 69:345–353
42. CIBSE (2006) *Guide A - Environmental Design*, 7th edn. Chartered Institute of Building Services Engineers, London
43. Frazzica A, Sapienza A, Freni A (2014) Novel experimental methodology for the characterization of thermodynamic performance of advanced working pairs for adsorptive heat transformers. *Appl Therm Engn* 72:229–236
44. Aristov YI, Tokarev MM, Sharonov VE (2008) Universal relation between the boundary temperatures of a basic cycle of sorption heat machines. *Chem Eng Sci* 63:2907–2912
45. Aristov YI (2014) Concept of adsorbent optimal for adsorptive cooling/heating. *Appl Therm Engn* 72:166–175
46. Critoph RE (1988) Performance limitation of adsorption cycles for solar cooling. *Sol Energy* 41:21–31
47. Saha BB, Chakraborty A, Koyama S, Srinivasan K, Ng K, Kashiwagi T, Dutta P (2007) Thermodynamic formalism of minimum heat source temperature for driving advanced adsorption cooling device. *Appl Phys Lett* 91:11902
48. Aristov YI (2013) Challenging offers of material science for adsorption heat transformation: a review. *Appl Therm Engn* 50:1610–1618
49. Dubinin MM (1960) Theory of physical adsorption of gases and vapour and adsorption properties of adsorbents of various natures and porous structures. *Bull Div Chem Soc* 9:1072–1078
50. Aristov YI, Restuccia G, Cacciola G, Parmon VN (2002) A family of new working materials for solid sorption air conditioning systems. *Appl Therm Engn* 22:91–204
51. Aristov YI (2007) Novel materials for adsorptive heat pumping and storage: screening and nanotailoring of sorption properties (review). *J Chem Engn Japan* 40:1242–1251
52. Gordeeva LG, Aristov YI (2012) Composites "salt inside porous matrix" for adsorption heat transformation: a current state of the art and new trends. *Int J Low Carbon Techn* 7:288–302
53. Stach H, Mugele J, Jaenchen J, Weiler H (2005) Influence of cycle temperatures on the thermochemical heat storage densities in the systems water/microporous and water/ mesoporous adsorbents. *Adsorption* 11:393–404
54. Posern K, Kaps C (2010) Calorimetric studies of thermochemical heat storage materials based on mixtures of MgSO₄ and MgCl₂. *Thermochim Acta* 502:73–76
55. Casey SP, Aydin D, Riffat SB, Elvins J (2015) Salt impregnated desiccant matrices for 'open' thermochemical energy storage - Hygrothermal cyclic behaviour and energetic analysis by physical experimentation. *Energy and Buildings* 92:128–139
56. Ristic A, Zabukovec Logar N, Henninger SK, Kaucic V (2012) The performance of small-pore micro-porous aluminophosphates in low-temperature solar energy storage: the structure–property relationship. *Adv Funct Mater* 22:1952–1957
57. Kakiuchi H, Iwade M, Shimooka S, Ooshima K, Yamazaki M, Takewaki T (2005) Water vapour adsorbent FAM-Z02 and its applicability to adsorption heat pump. *Kagaku Kogaku Ronbunshu* 31:273–277
58. Jänchen J, Ackermann D, Weiler E (2005) Calorimetric investigation on zeolites, AlPO₄s and CaCl₂ impregnated attapulgite for thermochemical storage of heat. *Thermochim Acta* 434:37–41
59. Shimooka S, Ooshima K, Hidaka H, Takewaki T, Kakiuchi H, Kodama A, Kubota M, Matsuda H (2007) The evaluation of direct cooling and heating desiccant device coated with FAM. *J Chem Engn Jpn* 40:1330–1334
60. Li G, Qian S, Lee H, Hwang Y, Radermacher R (2014) Experimental investigation of energy and exergy performance of short term adsorption heat storage for residential application. *Energy* 65:675–691
61. Myat A, Ng K, Kyaw T, Kim Y-D (2013) Experimental investigation on the optimal performance of Zeolite–water adsorption chiller. *Appl Energy* 102: 582–590
62. Akiyama G, Matsuda R, Sato H, Hori A, Takata M, Kitagawa S (2012) Effect of functional groups in MIL-101 on water sorption behaviour. *Microporous Mesoporous Materials* 157:89–93
63. Yaghi OM, O'Keeffe M, Ockwig NV, Chae HK, Eddaoudi M, Kim J (2003) Reticular synthesis and the design of New materials. *Nature* 423:705–714
64. Henninger S, Habib H, Janiak C (2009) MOFs as adsorbents for Low temperature heating and cooling applications. *J Am Chem Soc* 131: 2776–2777
65. Jeremias F, Lozan V, Henninger SK, Janiak C (2013) Programming MOFs for water sorption: aminofunctionalized MIL-125 and UiO-66 for heat transformation and heat storage applications. *Dalton Trans* 42:15967–15973
66. Gordeeva LG, Solovyeva MV, Aristov YI. NH₂-MIL-125 as a promising material for adsorptive heat transformation and storage, 2015, *Energy* (accepted)
67. Furukawa H, Gándara F, Zhang Y-B, Jiang J, Queen WL, Hudson MR, Yaghi OM (2014) Water adsorption in porous metal – organic frameworks and related materials. *J Am Chem Soc* 136:4369–4381
68. Deng J, Wang RZ, Han GY (2011) A review of thermally activated cooling technologies for combined cooling, heating and power systems. *Prog Energy Combust* 37:172–203

69. Saha B, Chakraborty A, Ng KC (2010) *Innovative Materials for Processes in Energy Systems*. Research Publishing, Singapore. ISBN 981-08-7614-9
70. *Advances in Adsorption Technologies*, Eds. B. Saha and K.S. Ng; 2010, Nova Science Publishers, ISBN: 978-1-60876-833-2
71. Liu H, Nagano K, Togawa J (2015) A composite material made of mesoporous siliceous shale impregnated with lithium chloride for an open sorption thermal energy storage system. *Sol Energy* 111:186–200
72. Zhu D, Wu H, Wang S (2006) Experimental study on composite silica gel supported CaCl₂ sorbent for low grade heat storage. *Int J Therm Sci* 45: 804–813
73. Wu H, Wang S, Zhu D (2007) Effects of impregnating variables on dynamic sorption characteristics and storage properties of composite sorbent for solar heat storage. *Sol Energy* 81:864–871
74. Wu H, Wang S, Zhu D (2009) Numerical analysis and evaluation of an open-type thermal storage system using composite sorbents. *Int J Heat Mass Transfer* 52:5262–5265
75. Sapienza A, Glaznev IS, Santamaria S, Freni A, Aristov YI (2012) Adsorption chilling driven by low temperature heat: New adsorbent and cycle optimization. *Appl Therm Eng* 32:141–146
76. Aristov YI, Sapienza A, Freni A, Ovoschnikov DS, Restuccia G (2012) Reallocation of adsorption and desorption times for optimizing the cooling cycle parameters. *Int J Refrig* 35:525–531
77. Mitsubishi Plastics. Inc. AQSOA - Product Brochure: <http://www.aasaveenergy.com/products/001/temperature/> (last access 13/11/15)
78. Li Q, Flamant Q, Yuan X, Neveu P, Luo L (2011) Compact heat exchangers: a review and future applications for a new generation of high temperature solar receivers. *Renew Sust Energy Rev* 15:4855–4875
79. Amin MR, Lindstrom JD (2012) Transient thermal simulation of counter flow compact recuperator partition plates. *Appl Therm Eng* 48:11–17
80. Dallaire J, Gosselin L, da Silva A (2010) Conceptual optimization of a rotary heat exchanger with a porous core. *Int J Therm Sci* 49:54–62
81. Mert Cuce P, Riffat SB (2015) A comprehensive review of heat recovery systems for building applications. *Renew Sust Energy Rev* 47:665–682
82. Alonso MJ, Liu P, Mathisen HM, Ge G, Simonson C (2015) Review of heat/energy recovery exchangers for use in ZEBs in cold climate countries. *Build Environ* 84:228–237
83. Zhang L-Z (2012) Progress on heat and moisture recovery with membranes: from fundamentals to engineering applications. *Energy Convers Manag* 63: 173–195
84. Zhang L-Z, Zhang XR, Miao Q, Pei L (2012) Selective permeation of moisture and VOCs through polymer membranes used in total heat exchangers for indoor air ventilation. *Indoor Air* 22:321–330
85. Kistler KR, Cussler EL (2002) Membrane modules for building ventilation. *Chem Eng Res Des* 80:53–64
86. Spengler JD, Sexton K (1983) Indoor air pollution: a public health perspective. *Science* 221:9–17
87. Nasr MR, Fauchoux M, Besant RW, Simonson CJ (2014) A review of frosting in air-to-air energy exchangers. *Renew Sust Energy Rev* 30:538–554
88. Meunier F (2013) Adsorption heat powered heat pumps. *Appl Therm Eng* 61:830–836
89. Ziegler F (2009) Sorption heat pumping technologies: comparisons and challenges. *Int J Refrig* 32:566–576
90. Bahrami M, Sharafian A (2014) Assessment of adsorber bed designs in waste-heat driven adsorption cooling systems for vehicle air conditioning and refrigeration. *Ren Sust Energy Rev* 30:440–451
91. Vasiliev LL (2006) Heat pipes in modern heat exchangers (review). *Appl Therm Eng* 25:1–19
92. Wang RZ (2001) Performance improvement of adsorption cooling by heat and mass recovery operation. *Int J Refrig* 24:602–611
93. Pons M, Poyelle F (1999) Adsorptive machines with advanced cycles for heat pumping or cooling applications. *Int J Refrig* 22:27–38
94. Aristov YI, Girkis IS, Glaznev IS (2012) Optimization of adsorption dynamics in adsorptive chillers: loose grains configuration. *Energy* 46:484–492
95. Ng KS, Chua HT, Chung CY, Loke CH, Kashiwaga T, Akisawa A, Saha BB (2001) Experimental investigation of the silica gel - water adsorption isotherm characteristics. *Appl Therm Eng* 21:1631–1642
96. Dubinin MM (1966) Adsorption equilibrium of water on NaX zeolite. *Coll Czech Chem Commun* 31:406–414
97. Gorbach A, Stegmaier M, Eigenberger G (2004) Measurement and modeling of water vapor adsorption on zeolite 4A - equilibria and kinetics. *Adsorption* 10:29–46
98. Aristov YI, Tokarev MM, Cacciola G, Restuccia G (1996) Selective water sorbents for multiple applications: 1. CaCl₂ confined in mesopores of the silica gel: sorption properties. *React Kinet Cat Lett* 59:325–334
99. Aristov YI, Restuccia G, Tokarev MM, Buerger H-D, Freni A (2000) Selective water sorbents for multiple applications. 11. CaCl₂ confined to expanded vermiculite. *React Kinet Cat Lett* 71:377–384
100. Goldsworthy MJ (2014) Measurements of water vapour sorption isotherms for RD silica gel, AQSOA-Z01, AQSOA-Z02, AQSOA-Z05 and CECA zeolite 3A. *Microporous Mesoporous Materials* 196:59–67
101. Glaznev IS, Aristov YI (2010) The effect of cycle boundary conditions and adsorbent grain size on the water sorption dynamics in adsorption chillers. *Int J Heat Mass Transfer* 53:1893–1898
102. Sapienza A, Santamaria S, Frazzica A, Freni A, Aristov YI (2014) Dynamic study of adsorbers by a new gravimetric version of the large temperature jump method. *Appl Energy* 113:1244–1251

Submit your manuscript to a SpringerOpen[®] journal and benefit from:

- Convenient online submission
- Rigorous peer review
- Immediate publication on acceptance
- Open access: articles freely available online
- High visibility within the field
- Retaining the copyright to your article

Submit your next manuscript at ► springeropen.com
