SELECTION CRITERIA OF WORKING PAIRS ADSORBENT - ADSORBATE FOR THERMAL ENERGY TRANSFORMERS

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In the manuscript the main factors that affect the thermal mass of open and closed types of heat storage devices are shown. Also, the main requirements for adsorption modules are given. The calculation procedure has been refined, which includes the determination of heat load, heat of adsorption, adsorbent mass, as well as integral, structural, and specific thermal mass. The specific thermal masses of adsorption heat-accumulating modules of open and closed types were evaluated. The main factors affecting their value are analysed. It is shown that the specific thermal mass of the adsorption heat storage module increases significantly due to the adsorption of water during the discharge of the device. It is shown that it reaches its maximum values at the end of the discharge stage, when the maximum values of adsorption in the cycle are reached. The influence of the design of the heat storage module on the value of the specific thermal mass has been confirmed. It is shown that the maximum values of these changes correspond to the composites containing 80% salt and 20% silica gel, due to the maximum values of the limiting adsorption and the heat of adsorption, which contributes to the lower values of the adsorbent mass, which is required to cover the thermal load. Specific thermal masses of adsorption modules based on "silica gel - sodium sulphate" and "silica gel - sodium acetate" composites are compared. The composition of the composite is 80% sodium sulphate and 20% silica gel, which corresponds to the minimum dimensions of the adsorption module, and therefore the maximum value of the specific thermal mass.

KEYWORDS

thermal mass, adsorption conversion of thermal energy, composite adsorbent, adsorption, marginal adsorption

1 INTRODUCTION

Decarbonization of the energy sector, improvement of energy efficiency and energy security are the main directions for achieving a number of climate requirements during the next decade. One of the promising technical solutions, which allows to compensate the mismatch between the periods of active production and energy consumption during the exploitation of renewable energy resources, is the adsorption conversion of thermal energy [Belyanovskaya 2019a and 2020]. At the same time, the key factor that determines the mode and affects the efficiency of the adsorption modules is the working pair "adsorbent - adsorbate" [Belyanovskaya 2019b, Serhiienko 2019].

The mode of operation of most adsorption heat energy converters involves heating and cooling, which periodically replace each other [Farulla 2020, Holubcik 2022]. In these conditions, the main influence on the operation of similar devices of the thermal mass, has, the heat capacity of the device (kJ/K), which includes the product of its mass and specific heat capacity [Sangwon 2021]. In the literature and the research community, there is a fairly clear division between the thermal masses of adsorbent and other materials. They are contrasted as active and inactive (inert) masses, host / guest [Gluesenkamp 2020]. The division into live and dead thermal masses is considered illogical, since the adsorbent itself has a thermal mass. In this work, only the term thermal mass is used. There is an integral relationship between thermal mass and the efficiency of heating or cooling processes. Such a characteristic can be decisive during the design of adsorption devices. This requires an analysis of the main factors that influence this characteristic.

There is an inherent trade-off between the thermal mass of an adsorption device and its efficiency. The maximum efficiency of the adsorber corresponds to zero thermal mass, but this results in a lower heat exchange surface, higher cycle time and lower power compared to a less efficient design at a higher thermal mass. Demir and others considered thermal mass as a key parameter that affects the efficiency of cycles [Demir 2008]. Paul and others studied the possibility of increasing the efficiency by reducing the thermal mass during the introduction of microchannel heat exchangers [Paul 2018]. Li and others studied the influence of the mass ratio of the metal parts of the reactor and salt in the thermochemical refrigeration system using a thermodynamic model and established the optimal mass ratio of the solid-gas sorption system at about 5:1 [Li 2009]. A higher ratio leads to an increase in heat consumption during desorption and heat release during adsorption, without changing the cooling capacity, which reduces the cooling coefficient. Gluesenkamp and others consider it necessary to consider the total thermal mass, which is the sum of the thermal masses of the adsorbent (i.e. non-negative) and the sum of the thermal masses of the coolant (HTF) and structural materials (structural) [Gluesenkamp 2020]. The integral thermal mass is simply defined as the product of the mass and heat capacity of the adsorbent [Gluesenkamp 2020]. At the same time, the thermal mass of the adsorbent during the cycle obviously changes as a result of the adsorption of the working substance, which is determined by the properties of the adsorbent, but this change is mostly neglected, which can be assumed only in the case of insignificant adsorption or low heat capacity of the adsorbate. It is appropriate to compare the change in the thermal mass of the adsorption heat-accumulating module during the cycle.

2 MATERIALS AND METHODS

The purpose of the study is to establish the main factors that affect the thermal mass of the adsorption heat storage device. To achieve this goal, the following tasks have been set:

- set the limit values of thermal masses of heat-accumulating devices during the cycle;
- identify the main factors that affect the amount of thermal mass of heat-accumulating devices;
- establish the conditions under which the thermal mass of the adsorbent reaches maximum values.

Also the thermal mass of heat storage devices of two types was compared according to the nature of mass exchange with the environment - closed and open. Operation of the closed-type device is carried out in two-phase mode: discharge - adsorption and charge - adsorbent regeneration, i.e., desorption [Li 2009]. The operation of the open-type device is also carried out in a two-phase mode, which involves the stages of discharge (adsorption) and charge (desorption, i.e., regeneration of the adsorbent). The closed-type device is operated in a two-phase mode: discharge – adsorption and charge – adsorbent regeneration, i.e., desorption.

The operation of the open-type device is also carried out in a two-phase mode, which involves the stages of discharge (adsorption) and charge (desorption, i.e., regeneration of the adsorbent). As a result, the temperature of the adsorbent layer increases to 90–115 °C. The second stage (regeneration) is carried out by supplying hot air, which warms the adsorbent layer to temperatures of at least 90ºC, which promotes desorption. The calculation of non-separable thermal masses of the adsorption module was carried out according to the formulas given in [Sukhyy 2020].

$$TM_{inherent} = m_{ads}c_{ads} \tag{1}$$

$$TM_{inherent} = m_{ads}(c_{ads} + Ac_{ad-te}) \tag{2}$$

where

$TM_{inherent}$ is the integral thermal mass of the adsorption module,

m_{ads} is the mass of the adsorbent, kg;

c_{ads} – heat capacity of adsorbent;

A – adsorption (kg of adsorbate/kg of adsorbent), which changes during the cycle;

$m_{ads}Ac_{ad-te}$ is the thermal mass of the substance absorbed by the adsorbent.

The thermal mass of the adsorption device was determined as the sum of the integral thermal mass and the structural mass, which includes the thermal mass of non-absorbing materials, i.e. structural parts and the coolant. Another important characteristic is the specific thermal mass (STM) according to the method given in [Belyanovskaya 2019b].

$$STM = \frac{TM}{m_{ads}} \qquad kJ/K\ kg_{sorb} \tag{3}$$

where

TM is the specific thermal mass of the device, kJ/K,

A comparison of the specific thermal masses of adsorption heat accumulators of closed and open types is shown in Figs. 3 and 4. Composites "silica gel - sodium sulphate" and "silica gel - sodium acetate" were used as heat-accumulating media, which are promising environments for adsorption heat energy converters [Rupam 2018, Sukhyy 2018, Belyanovskaya 2020b].

According to equation (2), the thermal mass will reach its maximum values at the end of the discharge stage, when adsorption is close to the limiting values of Alim.

Various options for the purpose condition and determine the selection of the working fluid, adsorbent and basic parameters of the cycle. During this selection, the peculiarities of the operation of this device should be taken into account, in particular, sanitary and hygienic norms should be observed.

First of all, the working substance should be determined. Typical requirements for it:

a) low specific volume in the liquid state;
b) low molecular weight;
c) low viscosity;
d) high thermal conductivity;
e) chemical stability in the operational temperature range;
f) non-toxic, non-aggressive, non-flammable;
g) absence of environmental problems during operation;
h) accessibility;
i) low cost;
j) lower heat of vaporization is possible;
k) low saturation pressures are possible at operating temperatures.

Direct contact of the working fluid with a person, obviously, requires not only an available fluid, but also a safe one. Water, which should be used primarily for heating supply air in open-type devices, as well as coolants in heat supply systems, obviously meets these requirements. The positive qualities of water include high heat capacity and small specific volume in the liquid state. Otherwise, i.e., for cooling, it is advisable to use other substances, including methanol, ethanol, ammonia, etc.

As is known, the key criterion that allows to evaluate the change in enthalpy and entropy during adsorption is precisely the isotheric heat of adsorption, which is determined precisely by the amount of absorbance of the adsorbate, that is, the working fluid [Chua 2003]. In addition, the regeneration temperature of the adsorbent is important, and in case of human contact, it must meet current sanitary standards. At the same time, the amount of adsorption, that is, absorption of the adsorbate, and the heat of adsorption determine the mass of the adsorbent in the adsorption module, that is, in the final sense, the design parameters of the heat transformer. Thus, it was shown that the limit adsorption should be at least 0.5 kg/kg, which allows the use of a compact size of the adsorption module [Belyanovskaya 2019c].

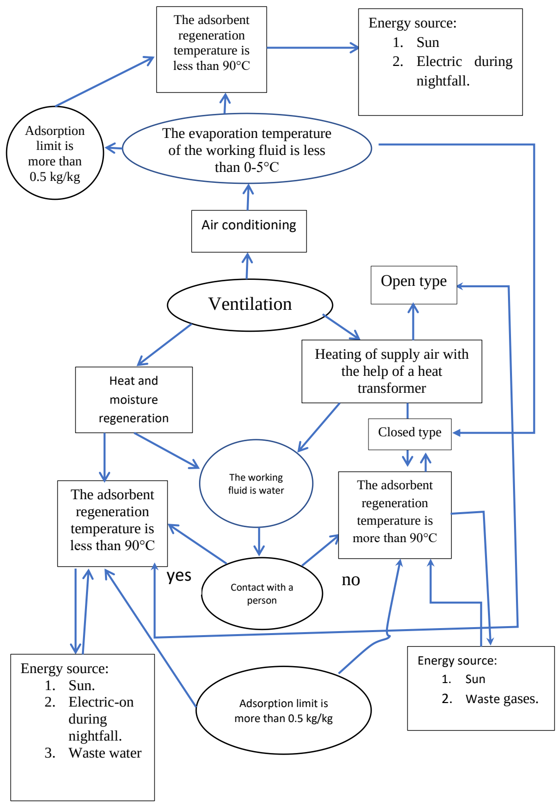

Figure 1. Algorithm for selection of adsorbent for adsorption heat transformers in the ventilation system

The algorithm for selecting adsorbents and working fluids for ventilation systems is shown in Fig. 1. The main areas of use of heat transformers in ventilation systems are air conditioning (i.e., air cooling), supply air heating (air heating) and heat and moisture regeneration.

For air conditioning, working fluids with evaporation temperatures of no more than 0-5°C should be used. The properties of the adsorbent must meet the following requirements: the maximum adsorption is not less than 0.5kg/kg, and the regeneration temperature is not more than 90°C. Taking into account the required potential, such sources of energy as solar or electric energy should be used during the period of the night-time minimum of consumed power, or the so-called "night-time failure" of electric energy consumption. The advantage of using such resources is the technical possibility of their use in household appliances for air conditioning, in particular, for residential and warehouse premises in the absence of a centralized power supply or to compensate for peak loads.

For open-type heat transformers and regenerators of heat and moisture, it is advisable to use water as a working fluid. It is advisable to select adsorbents with a regeneration temperature of no more than 90°C in view of operational safety. At regeneration temperatures above 90°C or if alternative heat carriers are used, heat transformers of the closed type should be chosen. These restrictions also determine the type of thermal energy source: when using adsorbents with a regeneration temperature of less than 90°C - solar or electric during the period of night failure, more than 90°C - solar, waste gases and sewage. Similar requirements and restrictions exist for the selection of working pairs for heat supply systems, in particular, heating (Fig. 2).

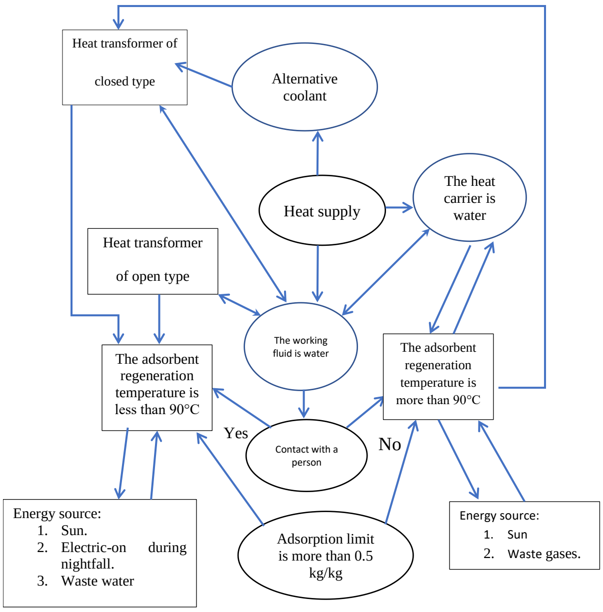

Figure 2. Algorithm for selection of adsorbent and working fluid for heat supply systems

The most promising is the use of water as a working fluid and coolant. In this case, you can use heat transformers of both open and closed types. But the type of device used should be chosen, taking into account the presence of contact with a person during operation and/or the temperature of regeneration of the adsorbent. Thus, the presence of contact with a person limits the selection of the adsorbent according to the regeneration temperature below 90°C, which allows the use of open-type heat transformers. Adsorption modules of the closed type must be used under the condition of using an alternative heat carrier and/or adsorbent regeneration temperature above 90°C. These conditions obviously require the impossibility of contact between the working substance and the person during the operation of the module.

Based on these characteristics, you can choose an energy source for adsorbent regeneration. Under the condition of using an adsorbent with a regeneration temperature below 90°C, it is advisable to use solar collectors or resistive heating elements for heating during the period of night-time failure of electricity consumption, which is promising for domestic use or in the housing and communal sector, as well as wastewater of enterprises.

When using adsorbents with a regeneration temperature higher than 90°C, exhaust gases from the operation of boiler units and solar collectors can be used to supply heat to the adsorbent layer.

Obviously, the mass and volume of the adsorbent will be determined by the required amount of consumed thermal energy per day (Fig. 3). The adsorption module itself should be compact and convenient for installation in accordance with building regulations and standards. But at the same time, it must provide the necessary heat load for 8-10 hours.

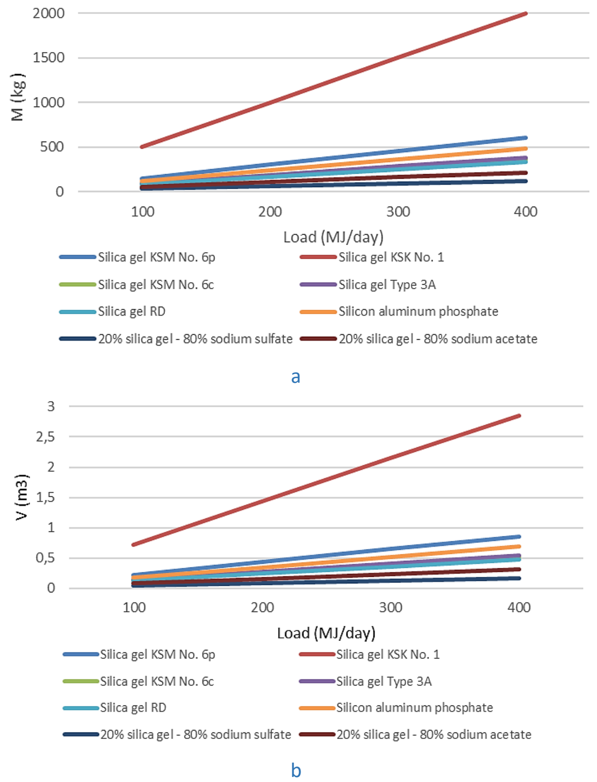

Figure 3. Correlation of heat load and adsorbent mass or volume

Obviously, the low amount of absorption of the adsorbate, that is, water, leads to low values of the heat of adsorption, and, therefore, large masses of adsorbent, which are necessary to compensate for the necessary heat load. For example, silica gel KSK No. 1 with a sorption capacity of 0.06 kg/kg requires more than 0.75 m^3 to compensate heat loads of 100-400 MJ/day. Silica gels KSP No. 6p, KSM No. 6c, silica gel Type 3A, silica gel RD, and silicoaluminophosphate with a sorption capacity of 0.2-0.36 kg/kg, which could be used to compensate for peak loads of 100 MJ/day, which in conditions of a typical three-room apartment corresponds to 2 hours of operation of the device. To compensate for higher values of heat loads (device operation 8-10 hours per day), composites "20% silica gel - 80% sodium acetate" with a limit adsorption of 0.557 kg/kg are more promising.

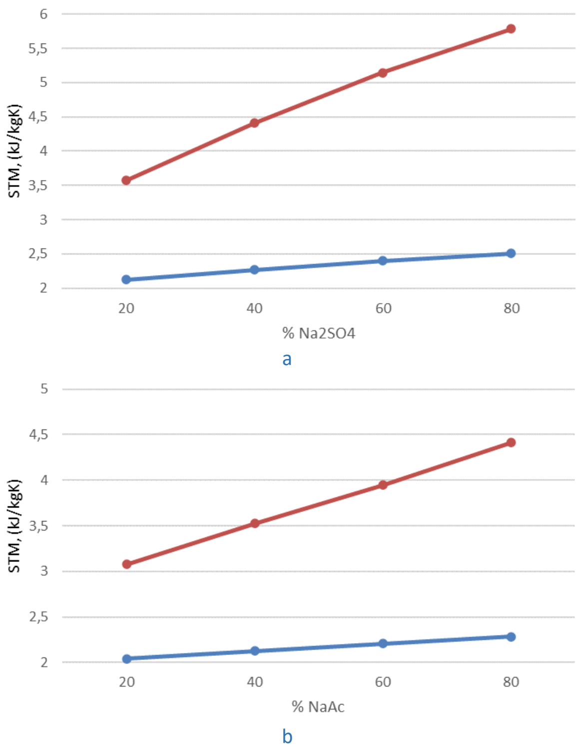

Figure 4. The influence of the composition of the composite on the specific thermal mass of the heat-accumulating device of the closed type. Composites: a - "silica gel - sodium sulfate", b - "silica gel - sodium acetate"

No more than 0.3 m^3 is needed to compensate heat loads of 200-400 MJ/day. But materials with a maximum adsorption of more than 1 kg/kg, i.e., "20% silica gel - 80% sodium sulphate" appear to be more effective, the volume of which does not exceed 0.16 m^3 for the entire considered range of heat loads.

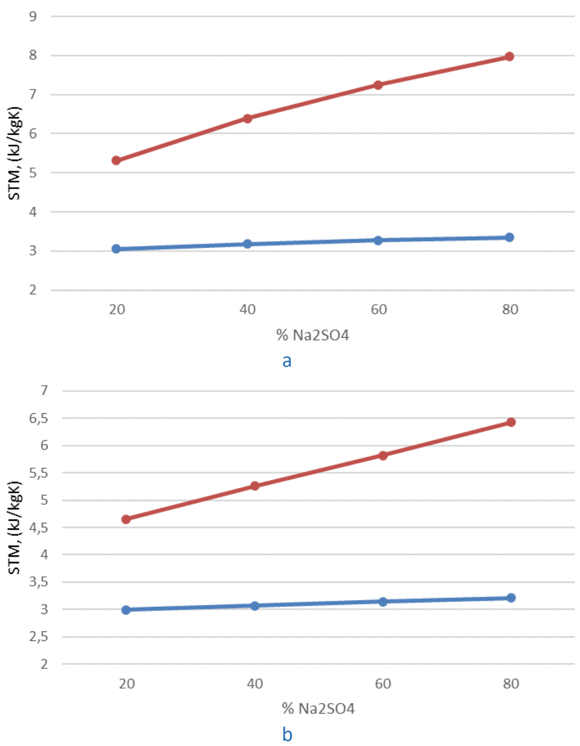

Figure 5. The influence of the composition of the composite on the specific thermal mass of the open-type heat storage device. Composites: a - "silica gel - sodium sulphate", b - "silica gel - sodium acetate"

For devices of both open and closed types, the maximum values of specific thermal mass correspond to adsorbents that contain 20% silica gel and 80% salt (Figs. 4-5). The increase in thermal mass in the case of increasing salt content obviously corresponds to an increase in the limit of adsorption and the heat of adsorption, which contributes to a decrease in the mass of the adsorbent, which is necessary to cover the heat load. In addition, the smaller mass of the adsorbent contributes to the reduction of the structural thermal mass due to the reduction of the volume of the adsorption module. Regarding specific thermal mass at the beginning of the cycle (1) and at the end of the cycle (2), the mass of the adsorbent is calculated to cover the thermal load of 339.5 MJ/day.

3 CONCLUSIONS

The main criteria for the selection of working pairs for heat transformers of open and closed types are considered. The main factors affecting the thermal mass of adsorption devices are analysed. The change in thermal mass during the operation of adsorption devices based on composite adsorbents "silica gel - sodium sulphate" and "silica gel - sodium acetate" is shown. The specific thermal masses of adsorption heat storage devices are compared and the nature of their changes during the cycle is shown.

It was established that the specific thermal masses reach their maximum values when the composite contains 80% salt and 20% silica gel. With the same composition of the adsorbent, the largest changes in the specific thermal mass were established, which correlates with the maximum values of the adsorption limit.

The maximum values of specific thermal masses are reached when using "silica gel - sodium sulphate" composites, which corresponds to the maximum values of the limiting adsorption and heat of adsorption and, therefore, the minimum dimensions of the adsorption module.

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