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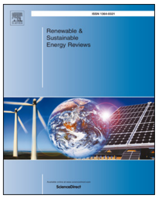

A review on recent developments in physisorption thermal energy storage for building applications

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ABSTRACT

On one hand, physical adsorption, also named physisorption, is a process that can be used to storage thermal energy with an energy density higher than sensible or latent storages. On the other hand, in Europe, 26% of the final energy consumption is related to the energy systems of households [1] and 80% of this energy is needed for heating purposes [2]. The consequence is the development of thermal energy storage systems, based on physisoprtion, for building application. The objective of this paper is first to present the basics concerning physisorption heat storage. Then, experimental developments from the literature are reviewed, based on three scales: the material scale, the reactor scale and the system scale. From the review, development of commercial systems faces with scientific and technological issues that must be addressed to reach a higher technology readiness level with an acceptable system cost.

1. Introduction

Adsorption heat storage is, nowadays, a concept widely studied in the literature…but this concept is coming from the '70s! Solid/gas sorption/thermochemical materials have a relatively high potential of heat storage density and is subject of interest to both scientists and engineers. It is worth mentioning that sorption/thermochemical heat storage is also identified as a key challenge for a more rational use of energy [3,4].

Basically, there is a lot of reviews dealing with sorption and thermochemical as these processes can be used for heat storage in a wide range of applications and,also, for cooling applications [5–16]. The point of view of this review is to focus on physisorption heat storage in buildings. Our point of view is a multi-scale analysis: **material ⇔ reactor ⇔ system**. This choice is justified by the different steps required to design and develop a heat storage system. The objective of the paper is to analyze recent developments in order to propose guidelines for future works.

Let's first define sorption: according to [17], sorption is *the process by which a substance (sorbate) is sorbed (adsorbed or absorbed) on or in another substance (sorbent)*. The process can be caused by physical bonding, i.e. physical sorption, or chemical bonding, i.e. chemical sorption. The main difference between physical and chemical sorption lies in the nature of created bonds. Physical sorption is weak, long range bonding mostly Van der Walls interactions and hydrogen bonding. Chemical sorption is strong, short range bonding involving orbital overlap and charge transfer. Another main difference between physical and chemical sorption is that the latest requires activation energy whereas it is not the case for the first process.

Sorption can be absorption or adsorption. Definitions of both processes can be found in [17]:

- Absorption is *the process of one material (absorbate) being retained by another (absorbent); this may be the physical solution of a gas, liquid, or solid in a liquid, attachment of molecules of a gas, vapor, liquid, or dissolved substance to a solid surface by physical forces, etc.*
- Adsorption is *an increase in the concentration of a dissolved substance at the interface of a condensed and a liquid phase due to the operation of surface forces. Adsorption can also occur at the interface of a condensed and a gaseous phase.*

While molecule undergoing absorption are taken up through the bulk of the absorbent (for example by diffusion), adsorption is a surface process.

Physical sorption can be split into absorption and adsorption:

- In physical absorption, the mass transfer takes place at the interface between the absorbate and the absorbent. This type of absorption depends on the solubility of absorbate, the pressure and the temperature. The rate and amount of absorption also depend on the

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surface area of the interface and its duration in time.

- *Physical adsorption is called physisorption. Physisorption is adsorption in which the forces involved are intermolecular forces (Van der Waals forces) of the same kind as those responsible for the imperfection of real gases and the condensation vapors, and which do not involve a significant change in the electronic orbital patterns of the species involved. The term van der Waals adsorption is synonymous with physical adsorption, but its use is not recommended* [17].

On the whole, physisoprtion is a surface process, mainly depending on the material and the specific surface of the solid. Consequently, physisoprtion materials should have a high porosity to increase the sorption surface between the solid and the gas.

We propose, in this paper, to develop a multi-scale analysis of the experiments related to physisorption heat storage in buildings. The Section 2 is dedicated to basics of physical adsorption heat storage, including material, reactor and system considerations. Then, the materials, reactor and systems are developed, respectively, in Sections 3, 4 and 5. Finally, in Section 6, guidelines are given to tackle the remaining scientific and technological issues on the road to commercial systems.

2. Basics of physisorption heat storage

2.1. Material basics

Physisorption, or physical adsorption is a process in which atoms or molecules move from a bulk phase (that may be solid, liquid, or gas) onto a solid or liquid surface [18,17]. Attractive interactions occur between the surface (*adsorbent*) and molecules being adsorbed (*adsorbate*). An equilibrium point is reached when attractive and repulsive (Pauli) forces compensate each other. Lennard-Jones potential describes this equilibrium (Eq. (1) and Fig. 1).

$$V_{LJ}(r) = 4\epsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right] \tag{1}$$

σ is the distance for which the potential is zero and ϵ is the depth of the potential well. The higher ϵ is, the more the energy is released during adsorption (and required for desorption). This exothermic/endothermic process is used to release/store heat.

The order of magnitude concerning adsorption heat, given per mole of solid, is 5 kJ mol^{-1} to 45 kJ mol^{-1} in [19]; 2 kJ mol^{-1} to 29 kJ mol^{-1} in [20]. It is interesting to compare the previous values with latent heat of water vaporization, given per mole of water, i.e. about 44.2 kJ mol^{-1}.

Physisorption is mainly due to Van der Vaals interaction forces. Adsorbed molecules remain intact and the process is fully reversible. The extent of adsorption depends on intrinsic properties of material such as the adsorbent specific surface area and the affinity of the couple adsorbent/adsorbate. It also depends on operating conditions such as temperature, pressure and concentration in the bulk phase. High pressures, high concentrations, high surface areas, high affinities and low temperatures generally foster adsorption process.

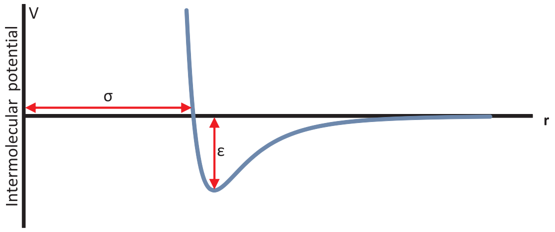

Fig. 1. Lennard Jones potential.

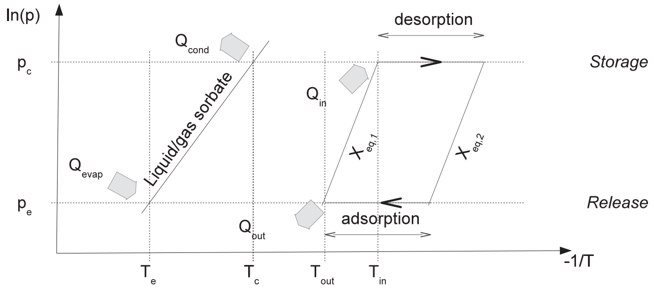

Fig. 2. Theoretical Clausius–Clapeyron sorption cycle.

2.2. Reactor basics

2.2.1. Principle

The sorbent/sorbate equilibrium is bivariant meaning that the quantity of adsorbed gas, x_{eq}, depends on both, temperature T and sorbent partial pressure p. The schematic diagram of a perfect sorption thermal battery for energy storage is presented in the Clausius–Clapeyron diagram of Fig. 2.

The principle of a physisorption heat storage system can be decomposed into storage and release phases. Initially, sorbent is under the $x_{eq,1}$ form, where $x_{eq,1} > x_{eq,2}$. During the storage phase, Q_{in} heat is transferred to the material at the temperature T_{in}. Then, desorption occurs to reach the state $x_{eq,2}$. There is a quantity of energy in the sorbate under the gas state that can be recovered during the phase change to liquid state, Q_{cond}. During the release phase, adsorption occurs at temperature T_e, eventually requiring a heat of vaporization, Q_{evap}. A quantity of heat Q_{out} is then released during the sorption process in the material.

2.2.2. Reactor types

Reactors can be classified into a lot of categories. A first distinction occurs between batch reactors and continuous reactors. **Batch reactors** are often characterized by a mechanical agitation, and a heating or cooling system that enables heat transfers. Mass transfers are limited to vapor discharge through the top of the vessel. No airflow is intended to cross the reactor. This is typically used in chemistry from laboratory scale to industrial scale.

Continuous reactors are more appropriate to heat and mass transfers applications. Continuous reactors are made of a vessel filled with small beads that can be a catalyst (in case of fluid-fluid reaction) or a reactant (in case of solid-fluid reaction). In adsorption heat storage, the bed is filled with adsorbent beads. There are numerous reactor types with different shapes and characteristics. In a general way, reactors are designed to enhance heat and mass transfers. Reactor design is often optimized for a given application.

Nonetheless, a large distinction occurs between fixed bed reactors and fluidized bed reactors.

- **Fixed bed** reactors are commonly used in a wide range of applications. In adsorption heat storage, the solid reactant remains in the vessel while the fluid crosses the bed (Fig. 3a). It ensures mass transfers between fluid and solid phases. The use of baffles can enhance fluid mixing and hence heat and mass transfers (Fig. 3b).
  Heat is either carried by the inlet fluid or transferred to the reactor through a heat exchanger that separates heat and mass carriers. In this case, the use of fins allows to ensure a good conduction within the adsorbent bed to carry heat from or to the heat transfer fluid, as illustrated in Fig. 4 extracted from [21]. [22] proposed an alternative solution to fins for heat transfers enhancement. They show it is possible to increase the bed thermal conductivity by an order of 100 by replacing pure adsorbent beads with a mixture containing a metallic foam in addition of zeolite powder. It can fairly reduce heat exchanger size and hence lead to a more compact system.