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Review on sorption materials and technologies for heat pumps and thermal energy storage

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ABSTRACT

Sorption is used for absorption/adsorption heat pumps (sorption refrigeration) and sorption for thermal energy storage (TES). This paper is the first review where the research on both applications is shown together. Sorption has advanced very much due to the immense amount of research carried out around heat pumping and solar refrigeration. Moreover, sorption and thermochemical heat storage attracted considerable attention recently since this technology offers various opportunities in the design of renewable and sustainable energy systems. The paper presents the operation principle of the technology and the materials used or in research are listed and compared. Absorption heat pumping and refrigeration research is today more focussed in the decrease of unit costs and increase of energy efficiency, adsorption is focussed in finding more efficient working pairs, and storage is testing the first prototypes and designing new ones with different or enhanced storage materials and new reactor concepts to optimize energy output.

1. Introduction

Sorption is a technology used for absorption/adsorption heat pumps (sorption refrigeration) and sorption for thermal energy storage (TES). *Although both technologies for heat pumps and sorption for TES use the same or very similar materials and technologies, they have been rarely considered together to learn from one to the other. This review aims on contributing on this collaborative learning by presenting for the first time the materials and technologies used in sorption systems for cooling, heat pumping and storage.*

The existing systems for producing cold, especially when using solar thermal energy, are based mainly on the phenomena of sorption: the process by absorption liquid-gas and the process by adsorption solid-gas [1–3]. The adsorption process concerns separation of a substance from one phase, accompanied by its accumulation or concentration on the surface of another. On the other hand, absorption is the process in which material transferred from one phase to another, (e.g. liquid) interpenetrates the second phase to form a solution. In general, the main differences between absorption and adsorption are located in the nature of the sorbent and the duration of the sorption cycle, which is significantly longer for adsorption [4]; therefore the main difference is that in absorption the sorbent is a pumplable fluid, therefore the heat is recovered easier but movable parts can be a disadvantage. This kind of cold storage system, which can be driven by electricity, industry waste heat, or solar energy, contributes significantly to the concept of sustainable system development.

The key figure describing the efficiency of a sorption refrigeration system is the thermal coefficient of performance ($COP_{thermal}$), which is defined as follows [4,5]:

$$COP_{thermal} = \frac{\text{cooling power}}{\text{energy received by system}} \quad (1)$$

For sorption thermal storage systems, the energy for charging includes sensible heat, a prerequisite energy to heat up the reactor to a required desorption temperature, and the heat of desorption, which includes the heat of condensation and the heat of binding [6]:

$$Q_{char} = Q_{sens} + Q_{des} \quad (2)$$

$$Q_{des} = Q_{cond} + Q_{bind} \quad (3)$$

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Nomenclature

COP	Coefficient of Performance
SCP	specific cooling power
TES	Thermal energy storage
Qchar	heat of charging
Qsens	sensible heat
Qcond	heat of condensation
Qbind	heat of binding
HX	heat exchanger
SHX	solution heat exchanger
PTX	Pressure-Temperature concentration PCPs: porous coordination polymers
MOFS	metal organic frameworks
TCM	Thermochemical material
DHW	domestic hot water
HTDU	high-temperature discharging unit
LTDU	low-temperature discharging unit
T	temperature [°C]
AlPOs	aluminophosphates
SAPOs	silico-aluminophosphates

Subscripts

h	heat

For cold storage, the value of Qcond/Qchar almost equals the cooling coefficient of performance (COPc) [6].

2. Sorption heat pump and cooling

2.1. Technologies

Adsorption cycles for heat pumping or cooling/refrigeration might seem like a relatively new, but the history of solid sorption systems is long dating from Faraday (1823) [7–9]. Patents on refrigeration machines started in early 1900s, being the first one that from Dunsford (1915) for ammonium nitrate as adsorbent for marine applications (Fig. 1) [10]. The technology restarted to rise interest again in the early 1970s, with pioneer work by Alefeld (1975) [11] and Tchernev (1977) [12]. In the late 1980s and 1990s there was an explosion of activity worldwide, with conferences, published papers and the first products appearing in the market. Very recently the environmental and energy cost concerns have led to new research and development of small scale products for air conditioning, solar air conditioning, and heat pumping. Interest in storage is the most recent studied application.

Sorption systems are either open or closed cycles [2–5,13–16]. Open cycles are mainly desiccant systems, while closed cycles are adsorption or absorption systems. The main differences between adsorption and absorption are located in the nature of the sorbent and the duration of the sorption cycle. The general operating principal of solar closed cycle sorption refrigerator is presented in Fig. 2. The process of adsorption concerns separation of a substance from one phase and its concentration on the surface of another. Adsorption systems are based on a physical or chemical reaction process in which the molecules of one substance are adsorbed on the internal surface of another substance [4,17].

Absorption systems are the oldest and most common heat driven refrigeration systems [4,16,19,20]. On the low-pressure side, an evaporative refrigerant is absorbed by the absorbent formulating a weak absorbent solution. The weak solution is directed to

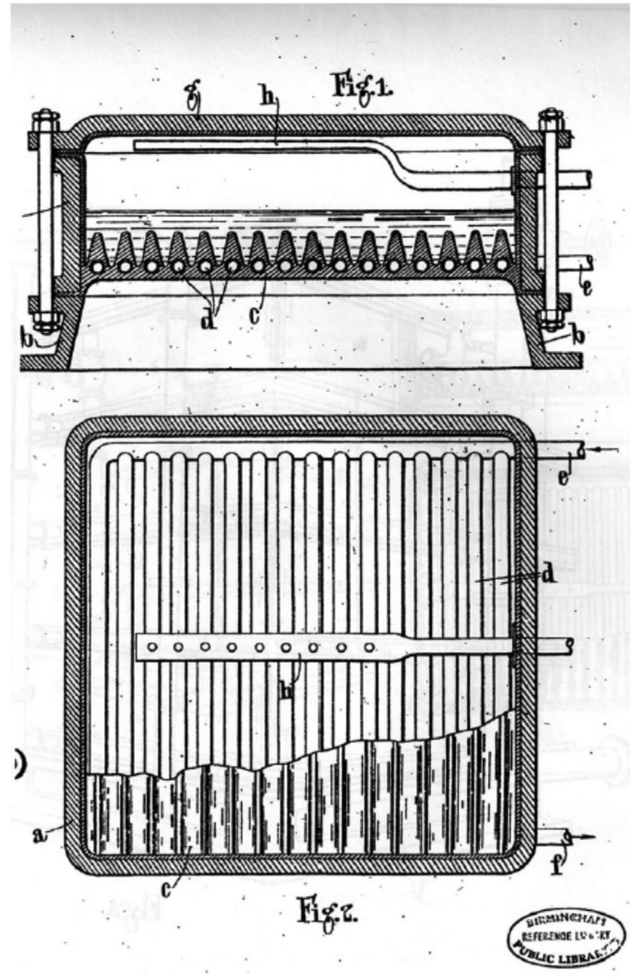

Fig. 1. Dunsford's generator of 1915 [7,10].

the generator where the pressurisation takes place by desorption of the refrigerant. The refrigerant then undergoes a common cooling cycle, while the weak solution is directed to the absorber and the cycle is repeated.

Ziegler [13] carried out a comparison between liquid (absorption) and solid (adsorption) sorption (Fig. 3), claiming that sorption chillers can be operated with low driving temperature, but the specific costs will be high and the COP will be low. Such comparison is done based on the characteristic temperature difference, ΔΔT, defined as:

$$\Delta\Delta T = (t_G - t_A) - (t_C - t_E)\cdot B \tag{4}$$

where t_G is the temperature of the generator (desorber), t_A is the temperature of the absorber, t_C is the temperature of the condenser, t_E is the temperature of the evaporator, and B is the Düring coefficient.

Demir at al. [21] and Sarbu and Sebarcievici [5] compared the different characteristics of both systems (Table 1).

The sorption refrigerator includes one or several reactors, i.e. regenerator(s), absorber(s), adsorber(s), generator(s) etc., depending on the specific cycle and the sorption pair, and of course the condenser and the evaporator, which exchange refrigerant vapour with the thermal compressor. The working principle of solid physisorption is based on the Van der Waals force between a sorbent and a refrigerant gas. The basic adsorption cycle for cooling