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An overview of adsorptive processes in refrigeration systems

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Abstract. Economic reasons and quest for new solutions based on recovering the energy have provoked an increase of interest in the adsorption technology in the refrigeration industry. The confirmation can be the fact that number of published research is on rise. Adsorption appliances may turn out to be an alternative to compression-type coolers. They use ecological chemical agents instead of substances which are aggressive and harmful to the environment. For regeneration of adsorptive refrigeration systems one can use cheap energy in a form of: industrial waste heat, energy of solar radiation and cheap electric power. The paper presents principles of operation as well as advantages and disadvantages of adsorptive refrigeration systems. Basing on literature the most frequently used adsorbent – adsorbate systems – which are employed in refrigeration industry – have been characterized. A review of construction solutions of systems on both laboratory and industrial scale has been made.

1 Introduction

Economic development entails a rise in the demand for electric power [1]. Considerable amounts of energy are used for work of refrigeration appliances which are present in nearly every household [2]. It is assumed that they consume around 45 percent of electric power drawn by households and public facilities - which comprises at the same time 15 percent of world energy consumption. The statistics are risen by countries located in warmer climates. In times of energy crisis the quest for and recovery of thermal energy are particularly justified in case of high levels of sunlight exposure and limited access to electrical energy [3].

Refrigeration appliances can be classified into refrigerators, freezers and air conditioners. These are usually compression-type appliances which are used on a wide scale because of their high performance. Big disadvantage of such appliances is the presence of substances harmful to the environment – mainly chlorofluorocarbons used as the refrigerant [4].

Adsorptive systems may turn out to be an alternative to compression-type refrigerators. Instead of substances harmful to the environment, they operate on non-toxic chemical agents [5]. In the process of recovery of adsorptive cooling systems one can use cheap energy in a form of: waste heat, energy of solar radiation and electric power. The waste heat occurs where one has to do with combustion, especially in combined heat and power stations, steelworks and heat engines with internal combustion. In an internal combustion engine, the emerging heat (50 to 60 percent of energy coming from fuel burning) is removed outside as the waste, while it could be used to power adsorption cooling devices on boats, rail or wheel vehicles [4, 5]. The shift towards a cooling adsorptive appliance from a conventional one may lead to savings in electricity.

The advantages of adsorptive refrigerating equipment are: simple design, easy handling and control of work. Lack of moving parts is connected with quiet work, lower failure rate and absence of vibrations during the work of appliance. Moreover, refrigerators of that type do not occur problems with corrosion and crystallization of refrigerant due to the applied substances [3, 6].

In spite of many advantages, those appliances have some drawbacks such as intermittent work, large size and low coefficient of performance. Yet - because of their specificity - adsorptive systems can be successfully implemented in all places where the levels of sunlight exposure are high or there is waste heat.

2 Principles of operation of adsorptive refrigerating appliances

The basis for the action of refrigerators is a cyclical phase transition gas – liquid of the coolant. When it is in the liquid state, it collects the thermal energy e.g. from a cold chamber (which gives the cooling effect) which is then used for the change of state. Next it returns the absorbed heat in the process of condensation when it changes its state to liquid again [7, 8].

One can adjust the adsorption process through such parameters as pressure and temperature. If we combine the process of endothermic desorption with the exothermic adsorption into closed thermodynamic cycle, then there is a possibility of usage of adsorptive systems for cooling. The heat emitted in the adsorption process is usually higher than the heat of vaporization (condensation) of adsorbate. After the contact of adsorbent with liquid adorbate, transport of mass will occur in the gas phase because the adsorption shows a bigger driving force than the condensation in liquid-vapour setup. During such process the temperature of liquid phase decreases, while the adsorbent's temperature increases. This effect is utilized in air-conditioning and cooling systems.

The operation of adsorptive refrigerators consists in continuous cycles of adsorption and desorption of the refrigerant from the adsorbent. The refrigerant (adsorbate) condenses and evaporate exchanging the energy in a form of heat with the environment [9].

2.1 Construction of adsorptive refrigerator

Adsorptive refrigerating appliances consist of three main elements. The first one of them is a container/adsorber containing a bed of adsorbent. It acts as a generator allowing the refrigerant to circulate through processes of adsorption and desorption occurring cyclically in a consecutive way. Thanks to heating and cooling of the adsorber the execution of both processes is possible. In compressor systems it is the compressor which plays the role of adsorber [10, 11].

Another element is a condenser. On desorption vapours of the refrigerant diffuse to the condenser where occurs the emission of heat which accompanies the condensation process. Vapours of the coolant change the state of matter to liquid .

The liquefied refrigerant flows then to an evaporator. Its role is opposite to the condenser. At adequately selected pressure the liquid evaporates (boils) absorbing the heat from the environment and emerging vapours are adsorbed in the adsorbent bed. The evaporator is usually placed in the cold chamber as it is the element which generates the cooling effect [12].

2.2 Efficiency of adsorptive refrigeration system

For comparison and assessment of performance of refrigerating appliances two coefficients are used: coefficient of performance (COP) and specific cooling power (SCP).

The COP is the quantity of achieved cooling effect by a refrigeration machine per unit of heat delivered. It is described by the following general formula [13]:

$$COP = \frac{Q_p}{Q_o + Q_d} \tag{1}$$

where: Q_p – the evaporation heat ; Q_o – heat used for bed heating; Q_d – heat of desorption.

The coefficient of SCP [W/kg] indicates what cooling capacity is obtained from a unit of mass of adsorbent. It is connected with the adsorption capacity of the adsorbent deposit. The higher its value is, the more efficient is the use of applied sorbent. The SCP is expressed by the formula [10]:

$$SCP \cong \frac{L \cdot \Delta x}{t_c} \tag{2}$$

where: L – latent heat of evaporation, Δx – adsorptive capacity of cycle; t_c – time of adsorptive cycle.

3 Adsorbent - adsorbate working pairs for adsorptive cooling systems

The selection of proper working pair of adsorbent-adsorbate type is the crucial issue during designing of refrigerating appliance as the performance and work of the refrigerator depend on that. The choice of appropriate substances depends first of all on the intended use and work condition of the device [10].

3.1 Adsorbates applied in adsorptive refrigerating systems

The adsorbate, attending as the refrigerant, should fulfil certain criteria so that its properties turns into the maximum possible performance of cooling system.

Good adsorbate must be characterized with the following features: have low temperature of evaporation, high latent heat of evaporation, small size of particles easily adsorbed and desorbed from adsorbent, show thermal stability in the range of operating temperature, possess low pressure of saturation and be environmentally-friendly, non-toxic, non-flammable, non-corrosive [14].

In reality, however, substances that would meet all the above mentioned criteria do not exist. In adsorptive refrigerating systems it is most frequently the ammonia, water and methanol or ethanol which is applied as the adsorbate. Their most important properties are presented in the table 1 [10].

Table 1. The physical properties of the most commonly used adsorbents in the adsorption refrigeration systems [10].

Refrigerants	Normal boiling point [°C]	Density [kg/m^3]	Latent heat of vaporizati [kJ/kg]	Latent heat of vaporizati [MJ/m^3]
Ammonia	-34	681	1368	932
Water	100	958	2258	2163
Methanol	65	791	1102	872
Ethanol	79	789	842	665

3.2 Adsorbents in adsorptive refrigerating systems

The performance of adsorbents is largely dependent on their surface properties such as: specific surface area, type and number of pores, size of granules, size of powder, size of grains or packets. Adsorbents used in systems of adsorptive cooling should demonstrate the ability to adsorb large quantities of the refrigerant at low temperatures and the desorption of maximum possible amount of the coolant at increased temperature. They should be marked by: high latent adsorption heat (in comparison to emitted adsorption heat), high coefficient of thermal conductivity, the consistency of characteristics over time and reusability, being non-toxic and non-corrosive, being cheap and easily accessible.

Good porous materials, which are most frequently used in systems of adsorptive refrigeration, are: carbonic adsorbents (activated carbon, activated carbon non-woven fabrics, carbon molecular sieves, monoliths [15]), silica gels and zeolite.

3.3 Characteristics of adsorptive system: adsorbent – adsorbate

In literature one can find numerous research in which various systems of adsorbent – adsorbate type are proposed that fulfil requirements of work in adsorptive cooling systems. The most frequently described and applied working pair are: activated carbon-methanol, activated carbon- ammonia, silica gel - water and zoelite - water.

The activated carbon-methanol is often utilized for the production of ice and air-conditioning systems because of high adsorption capacity (up to 0,45 g/g_{carbon}), high latent adsorption heat (ca. 1229 kJ/kg·°C at -30°C) and the ability to work in a temperature below zero. Low values of adsorption heat (1800–2000 kJ/kg) and relatively low temperature of desorption translate into a high COP value for those systems. In spite of many advantages, the pair has several drawbacks and namely: activated carbon catalyses a decomposition reaction of methanol into formaldehyde (HCHO) and dimethyl ether (CH_3OCH_3) at temperatures higher than 150 °C and thus the temperature of desorption should not exceed 120°C. Methanol is a toxicant and this is why it should be handled with precautions taken. The system operating on the pair methanol-activated carbon requires the use of vacuum which makes the construction of appliance somehow more difficult [5,9,10].

Activated carbon and ammonia is another widely used pair. It can be characterized with similar adsorption heat as in case of methanol adsorption. Working in pair with ammonia requires increased pressure which is necessary due to the low boiling point for that substance. Employing high pressure (around 16 bar) results in improving the processes of exchange of mass and shortening the time of refrigeration cycle and is also connected with an increase of SCP indicator. Another benefit is the possibility of using higher temperatures – in a range of 200°C – in the desorption process. Disadvantage of the system is the corrosivity of NH_3 especially in case of use of copper materials. In case of any leakiness an immediate leakage of ammonia into the environment happens. As it is known the ammonia is an irritant with unpleasant smell. One should also mention about a lower adsorption capacity of that pair comparing to activated carbon- methanol systems [5, 10]. The latter ones are used for the manufacture of ice and as refrigerating appliances.

Table 2. Properties comparison of chosen working pairs [18].

Working pair	Operating temperature [°C]	Working pressure [bar]	Adsorption heat [kJ/kg]	Specific cooling capacity	Application
Silica gel – water	Below 90	0.01 – 0.3 (Vacuum conditions)	1000 – 1500	High	Air conditioning
Activated carbon – methanol	Below 120	0.01 – 0.35 (Vacuum conditions)	1800 – 2000	Normal	Ice making
Activated carbon – ammonia	Up to 150	3 – 10.4	2000 – 2700	Higher than silica gel- water	Refrigeration/ Ice making
Zeolite – water	Up to 200	3.4 – 8.5	3300 – 4200	Normal	Air conditioning
Zeolite – ammonia	150 – 200	3.5 – 7	4000 – 6000	High	Refrigeration/ Ice making

The silica gel - water system is marked by slightly higher adsorption heat (about 2500 kJ/kg) than it is in case of carbon and methanol. A big advantage of that pair is low desorption temperature beginning already at 55°C. However, it cannot exceed 120°C as the silica gel loses its sorption properties and this is why one uses in practice desorption temperatures in a range of 75 – 90°C. The disadvantage of the system is low sorption capacity of silica gel (0,2 kg_{water}/$kg_{adsorbent}$) and the range of temperature of water evaporation which cannot be lower than 0°C. This system is successfully used in air-conditioning, cold storage appliances [16] and solar energy-powered systems because of its characteristics [5].

Zeolite – water pair shows the highest adsorption heat among the above-mentioned working pairs which amounts to 3300 – 4200 kJ/kg. The system is stable at high temperatures and enables the occurrence of desorption at temperatures exceeding 200°C. The isotherm of adsorption in that working pair is virtually flat and because of that it can work with similar performance in a wide range of temperatures. High adsorption heat causes a lower value of COP coefficient than in previous cases in low and middle temperature ranges. That situation changes in case when the temperature of heat source for desorption exceeds 200°C. Then the system works with constant effectiveness, while all other pairs reach their maximum of temperature or are not capable to work at all. The drawback for the system is, as in the previous case, the low-end range of water evaporation as well as limited rate of mass exchange arising from the need of using lowered pressure. For the above reasons, that pair can be successfully used in air-conditioning systems with the high-temperature source of waste heat and heat pumps [17]. The table 2 presents properties of the selected adsorbent – adsorbate systems.

4 Review of design solutions of adsorptive refrigerating systems

The type of source of delivered heat can be one of criteria for classification of adsorptive cooling appliances. In literature one can find many various construction solutions. Yet, in every case one can distinguish three basic elements of the system: generator – condenser – evaporator.

4.1 Solar energy-powered systems

The solar energy is often utilized as in adsorptive refrigerating systems because of the possibility of their use in areas of limited access to electricity. In the figure 1 a prototype of refrigerator designed for storing food in countries having a Mediterranean climate is presented.

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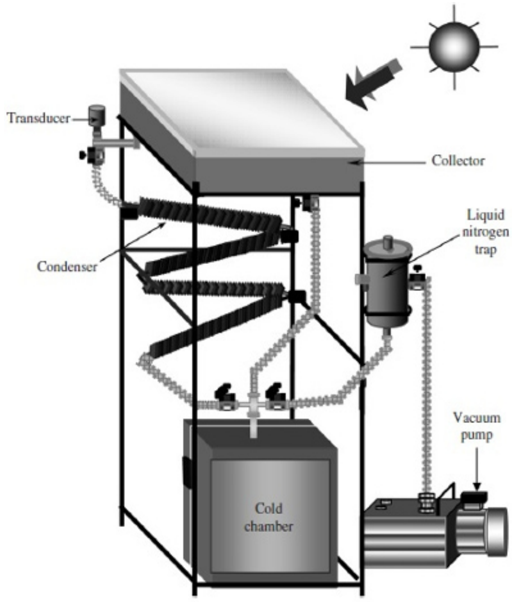

Figure 1. Scheme of solar adsorption refrigerator [19].

The system consists of an adsorber which is the sun collector at the same time. It has a form of chest filled with 14.5kg of activate carbon. The box is separated inside with copper ribs for better transport of heat in the bed. The copper ribbed pipe placed under the collector plays the role of condenser in which the refrigerant (methanol) change its state matter as well as flows into the evaporator, also made of copper, which is simultaneously a collecting container for the methanol. That part is situated in a thermally-insulated cold chamber. There are also a vacuum pump together with a trap with liquid nitrogen linked with the system. The pump enables lowering the pressure in the system without losses of methanol, pressure transmitter and thermocouple for process control.

The refrigerator works periodically – during the day high sunlight exposure causes desorption of the coolant, while at night the re-adsorption of methanol is possible as well as achieving the cooling effect when the temperature falls. The capacity of work depends on weather conditions and because of that the COP varies from 0.02 to 0.07 and the output is low temperature obtained in the cold chamber – from + 6.2 to – 11.1 °C [19].

Another example of use of the solar energy in adsorptive refrigeration is a solar refrigerator designed for the production of ice (figure 2). The working pair in this case is also activated carbon and methanol. The adsorber is made of stainless steel and accommodates 24 kg of activated carbon. It is distinguished by a condenser cooled with water thanks to which the methanol passes directly to the evaporator in the liquid phase. The evaporator is situated in a thermally-insulated water tank [20].

The COP coefficient of performance for this system varies from 0.083 to 0.127 depending on weather conditions, while the quantity of ice produced within one cycle is from 30 to 35 kg.

The drawback of adsorptive refrigerators powered by solar energy is undoubtedly very long time of cycle dependant on daily insolation phases (recovery of bed occurs by day and adsorption at night) and work productivity which also depends on weather conditions.

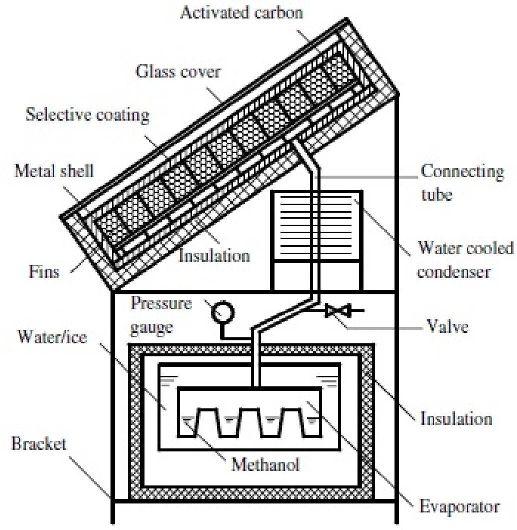

Figure 2. Scheme of adsorption device for ice production [20].

4.2 Systems powered by waste heat of exhaust fumes

The next group of cooling appliances are systems using the waste heat of internal combustion engines. The temperature of exhaust fumes and internal combustion engine can be utilized for air-conditioning of compartments in vehicles which may bring the reduction of fuel consumption.

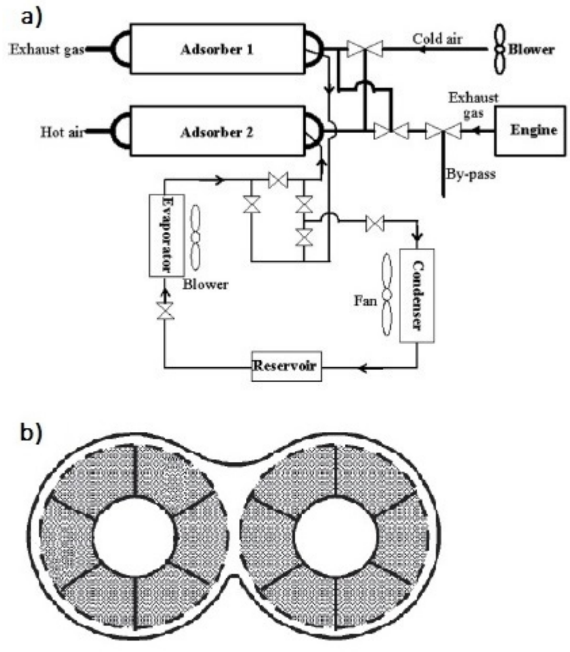

Figure 3. a) Scheme of adsorption cooling system working on car engine exhaust gases waste heat; b) A cross section of applied adsorber [21].

A sample of such solution is a prototype of car air-conditioner on laboratory scale operating on the activated carbon-methanol system which is presented in the figure 3. It is made of two adsorbers working in opposite phases

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of the cycle which ensures an almost continuous cooling effect. Each of them consists of two carbon beds (mass is 08, kg for each). They have a form of concentrically placed pipes among which the sorbent material is located (external pipe is made of steel grid). Hot exhaust fumes coming from the internal combustion engine or cool air from the surroundings flow through internal pipes (150 - 200 °C) (figure 3b). The whole is locked in airtight case made of stainless steel which enables the transport of refrigerant from or to remaining part of the system. In the bed there are steel fins for improving the exchange of heat. The condenser is a finned aluminum pipe which is cooled by air from the fan. The role of evaporator in the system is to chill the air pressed to it by the fan. The air is then used for cooling the interior of compartment in vehicle [21].

Another system making use of waste heat of exhaust fumes is an air-conditioner cooling the interior of cockpit in a locomotive which is made on a scale allowing to use it practically (figure 4). In that case the working pair is zeolite 13X and water. In this system there is one generator with a mass of bed of 140 kg which is heated by hot exhaust fumes and cooled by ambient air depending on the phase cycle. In the evaporator there is a separate external water cycle which is chilled during the adsorption phase. Cooled water is transported by a pipeline and pump to the cockpit where it collects heat from the air present over there. This air-conditioner is able to chill the air on the cockpit of locomotive from 33 to 25 °C. Its cooling capacity is 4.1 kW and the COP value is 0.25 [22].

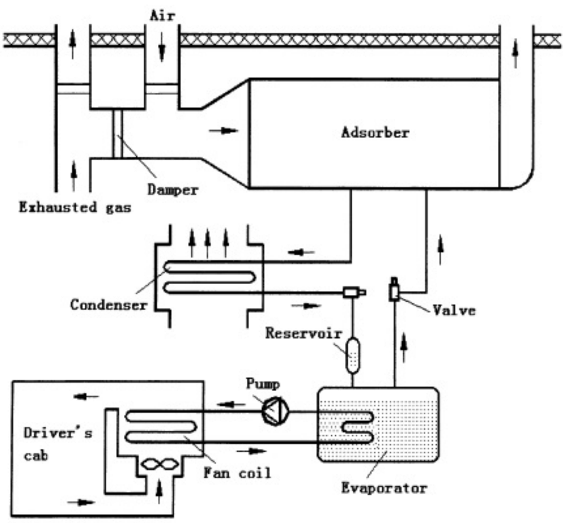

Figure 4. Adsorption air conditioner working on locomotive engine exhaust gases waste heat [22].

Adsorptive refrigerating appliances using the waste heat from internal combustion engines appear to be a promising solution which could replace widely used air-conditioning systems in vehicles. There are also some disadvantages related to them such as the necessity of using a set of generators in order to ensure continuous cooling and requirements connected with appropriately long working time of the engine for the purpose of assuring proper working conditions for adsorptive appliance.

5 Commercially produced adsorptive refrigerators

Significant part of adsorptive refrigerating systems described in the literature is a prototypical appliance usually made on a small laboratory scale and theoretical models constructed on the basis of experimental data with the aid of computer programs. There are also appliances created on a bigger scale serving till today as air-conditioners for facilities, but they are still a single instance. The development of technology of adsorptive refrigeration is primarily limited by high costs of the design of equipment and still low efficiency of such appliances.

In the market there are several companies which deal with the manufacture of adsorptive cooling systems. Their products are air-conditioners operating on the working pair of silica gel- water and zeolite – water. The main producers offering appliances of that type are: German SorTech and InvenSor, Japanese Mayekawa and American HIJC and Eco – Max.

The figure 5 presents an adsorptive aggregate eCoo 2.0 by SorTech company along with its plan. The system is made of two absorbers working in opposite cycles. The working pair is silica gel and water and the cooling capacity is up to 16 kW. It also chills the water which is utilized later on in air-conditioning in a temperature range from 8 to 21°C. For the proper operation of the system a source of heat is necessary – it is water at a temperature from 50 to 95°C. For that purpose the water can be heated by an optional source of waste heat, with the aid of sun collectors or with use of both variants in a manner of cogeneration [23].

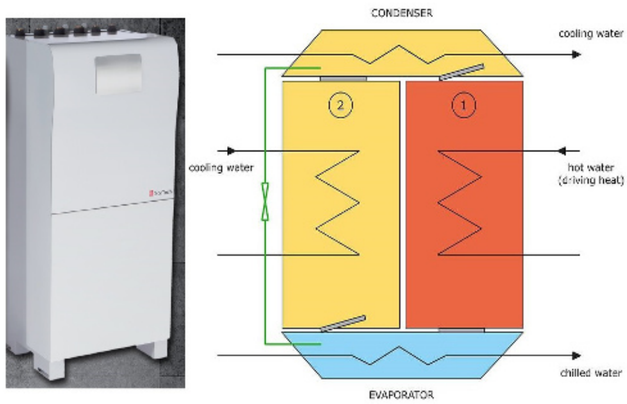

Figure 5. Adsorption cooling unit eCoo 2.0 produced by SorTech company. Photograph and scheme of the system (1 – adsorber in desorption phase, 2 – adsorber in adsorption phase) [23].

They only differ by values of COP, the cooling capacity and sizes. Commercial adsorptive refrigerating apparatus is often installed in associated cooling systems in which several different types of heat source are used. In the year 2000 in a hospital in Kammenz (Germany) for example an associated Cogeneration system for Cooling, Heat and Power (CCHP) was installed for the very first time in which the heat collector is powered by the waste heat from a fuel cell and solar energy. It delivers both heat and cold to hospital spaces

In combination with adsorptive refrigerating system. The aggregate's cooling capacity is 105 kW.

In Japan Macom company has been dealing with the production of adsorptive refrigerator with a working pair of silica gel and water since 2003. In Japan, too, Tokai Optical Co. company from Nagoya introduced an associated adsorptive system (CCHP) with the use of waste heat from the diesel engine in 2003.

6. Directions of improvement and development of adsorptive refrigerators

In spite of many advantages, adsorptive refrigerating appliances have also some disadvantages. The main drawbacks are a relatively low COP effectiveness, cyclicity, big sizes and weight of systems. As far as the intermittent operation can be easily changed by the use of two or more generators in the system, then the increase in COP is combined with the necessity of improving the heat exchange in the generator bed which is still quite problematic. As it is known, adsorbents are marked by low heat conductivity coefficient. Adsorbents undergo various modifications in order to intensify the exchange of heat in the adsorbent's bed. According to the literature, there are many ways as for example: placing metal partitions in the bed [19, 21], mixing the adsorbent with metal filings and formulation of composites like e.g. composite of zeolite and aluminum in a form of foam surrounding particles of adsorbent [24]. Adsorbents undergo modifications with the purpose of improving sorption properties and packing in the bed through processing. That processing consists in the abrasion of external layers of adsorbent grains and the change of nature of surface through oxidation [25].

The COP coefficient can also be increased by the improvement of energy use – delivered and emitted during the process. Due to that reason, advanced adsorption cycles for systems consisting of at least two generators were worked out. Their purpose is more effective energy usage, improvement of mass and heat transport in the adsorbent deposit.

One can distinguish the following advanced adsorption cycles: heat recover cycle, mass recover [18], thermal wave cycle, convective thermal wave cycle, cascade cycles [5, 10]. The cycles are still being investigated and developed in order to obtain the best possible effects and cooling capacities. One also attempts to combine the above described cycles with each other. This, however, results in increase of complexity of systems and makes them sophisticated and that, it turn, has an effect in failure rate of adsorptive refrigerating appliances. Despite that the advanced adsorption cycles are a promising direction for development for this branch of practical use of the desorption phenomenon.

The main direction of development of adsorptive cooling technologies are works over increasing the process efficiency, intensification of the heat exchange in the bed and lowering the costs of system production. In order to achieve that numerous actions are taken on challenges of development of generator/adsorber design, improvement of use and recovery of heat and modification and quest for more and more effective adsorbents.

As one can see from variety and number of research on that topic it is still current and interesting issue both from the scientific and practical point of view.

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