



ADSORPTION-DESORPTION PROCESSES IN ADSORPTION CHILLERS¹

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ABSTRACT

The aim of this paper is to present the adsorption chillers technology. The operating principle of these systems, the adsorbent-adsorbate pairs that are frequently applied and the enhancement techniques that allow improvement of their efficiency are presented. Analysis of the mass transfer and principles of mathematical modeling of such systems are also discussed. In the further part of the text, the results of experimental studies and comparison of these results with calculations based on the mathematical model of adsorption were presented.

Symbols:

- a – specific surface area of an adsorbent layer, ($\text{m}^2 \cdot \text{m}^{-3}$)
- C – component concentration in a bulk of a gas phase, ($\text{kg} \cdot \text{m}^{-3}$)
- C_i – component concentration in a gas phase at the interphase, ($\text{kg} \cdot \text{m}^{-3}$)
- C_0 – component concentration in the inlet gas, ($\text{kg} \cdot \text{m}^{-3}$)
- D_s – solid diffusion coefficient, ($\text{m}^2 \cdot \text{s}^{-1}$)
- k_g – mass transfer coefficient, ($\text{m} \cdot \text{s}^{-1}$)
- k_s – LDF equation coefficient,
- K_F – Freundlich equation coefficient,
- L – length of the adsorbent layer, (m)
- q – component concentration in a solid phase, ($\text{kg} \cdot \text{kg}^{-1}$)
- q_i – concentration in a solid phase at the interphase, ($\text{kg} \cdot \text{kg}^{-1}$)
- q^* – concentration of the adsorbed component in a solid phase in equilibrium with, gas phase concentration, ($\text{kg} \cdot \text{kg}^{-1}$)
- \bar{q} – average concentration of the adsorbed component in a solid phase, ($\text{kg} \cdot \text{kg}^{-1}$)
- r_p – radius of an adsorbent grain, (m)
- t – time, (s)
- u – apparent gas velocity, ($\text{m} \cdot \text{s}^{-1}$)
- z – position coordinate in an adsorber: $z = 0$ for gas inlet, $z = L$ for gas outlet, (m)

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Greek letters:

- ε – external porosity,
- v – Freundlich equation exponent,
- ρ_s – solid phase density, ($\text{kg}\cdot\text{m}^{-3}$)
- φ_i – gas phase (air) relative humidity.

Introduction

Cooling systems are necessary in many aspects of human life, for instance, for food storage or air conditioning in buildings or vehicles. Environmental pollution and considerable energy consumption causes that conventional electricity-driven compression chillers are against the concept of sustainable development. Therefore, the importance of adsorption chillers has increased in recent years. Their operating principle is based on the utilization of the thermal effects of consecutive adsorption-desorption cycles. Environmentally friendly refrigerants, for example water, can be used. Moreover, they can be driven by low temperature heat sources, such as solar energy or waste heat produced, for example, by vehicles such as fishing boats or trucks (Daßler and Mittelbach, 2012; Sharafian and Bahrami, 2014). Consumption of electricity in an adsorption chiller is low (Ng et.al, 2001). Despite their advantages, adsorption chillers are not used commercially because of their low efficiency (Daßler and Mittelbach, 2012). The problems in the adsorber bed design come from poor thermal conductivity of adsorbents and also from internal and external mass transfer resistances (Gwadera and Kupiec, 2015; Solmus et.al, 2012). Therefore, design of an efficient system requires studying the mass and heat transfer properties of an adsorbent bed carefully.

The aim of this work is to present the adsorption chillers technology. The operating principle of these systems, the adsorbent-adsorbate pairs that are frequently applied and the enhancement techniques that allow one to improve adsorption chillers efficiency are presented. The analysis of the mass transfer in an adsorber and principles of developing mathematical models for such systems are discussed. Moreover, the results of experimental studies and comparison of these results with calculations based on the mathematical model of the process are shown.

Operating principle and working pairs for adsorption chillers

The principle of adsorption chiller operation is based on alternate adsorption and desorption of an adsorbate (refrigerant) in a bed of adsorbent. The adsorbent bed, condenser and evaporator are the main elements of an adsorption chiller. The adsorber plays a similar role to a compressor in a traditional electricity-driven refrigeration system. A complete cycle of work consists of four steps: heating of the bed, desorption (adsorbent regeneration), cooling and adsorption. During the adsorption stage, vapors produced as a result of refrigerant boiling are adsorbed in the adsorbent bed. The cooling effect results from taking the heat necessary for adsorbate boiling from the space to be cooled.

Operation of an adsorption chiller depends largely on the working pair used. A well-designed system should be characterized by large adsorption capacity and large capacity changes with temperature. Costs and availability in the market also affect the choice of an

adsorbent-adsorbate pair. Table 1 presents the most common adsorbents and adsorbates used in adsorption cooling technology. A properly chosen adsorbent (Anyanwu, 2004) must adsorb large quantities of a refrigerant at low temperatures and effectively desorb it when temperature increases. Its properties should not change with age and use. A good refrigerant (Fan et.al, 2007; Wang et.al, 2009; Wang et.al, 2010) should be characterized by high latent heat of vaporization, small size of molecules and evaporation temperature below 0°C. It should also be chemically and thermally stable, non-flammable, non-toxic and non-corrosive.

Table 1.
Working pairs for adsorption chillers

Adsorbent	Adsorbate (refrigerant)
Activated carbon/Activated carbon fibers	Methanol, ethanol, ammonia, 134a
Silica gel	Water
Zeolite	Water

Rezk, (2012)

Heat and mass transfer enhancement for adsorption chillers

Nowadays, the commercial application of adsorption chillers is difficult because of their low efficiency. It is expressed by the Coefficient of Performance (COP) and Specific Cooling Power (SCP). COP is a ratio of the cold production (kJ) to the heat supplied to a chiller (kJ). SCP is the ratio of the cooling power (kW) to the adsorbent mass (kg). Low values of SCP lead to big sizes of the chillers and high investment costs. COP can be improved by the application of advanced adsorption refrigeration cycles (e.g. heat or mass recovery cycle). SCP may be enhanced by advanced adsorber technology and by utilization of adsorbents with good heat and mass transfer properties.

The methods for heat transfer enhancement in adsorption chillers reported in literature (Bonaccorsi et.al, 2006; Chang et.al, 2005; Demir et.al, 2008; Freni et.al, 2009; Rezk, 2012; Wang et.al, 1999) are as follows:

- *Covering adsorbent grains with electrically conductive substances* – covering the grains with, for example, polyaniline, enhances thermal conductivity of an adsorbent bed and increases its thermal performance. The disadvantage of this technique is blocking the adsorbent pores and reducing the bed uptake.
- *Adding metal particles to adsorbent bed* – thermal conductivity and thus the heat transfer performance of an adsorbent bed can be improved by adding metal particles to the bed of grains. Aluminum, copper or graphite is applied for this purpose.
- *Covering heat exchanger pipes with adsorbent grains* – in most commercial adsorption chillers, granular packed adsorbent beds are used. To improve the mass transfer between thermal fluid flowing in heat exchanger pipes and adsorbent grains, the pipes can be covered with grains. It allows the reduction of the thermal resistance between grains and heat exchanger surface which constitutes 25% of the total thermal resistance.
- *Shaping adsorbent bed* – compression of an adsorbent bed leads to increasing its density and reducing the thermal resistance between the grains and the thermal resistance between the bed and the heat exchanger. Consolidating or sintering processes can be applied for this purpose. Consolidated adsorbents may be obtained from zeolite and

expanded graphite, zeolite and metallic foam, activated carbon and CaCl_2 , silica gel and expanded graphite.

- *Adsorbent deposition on metallic foam* – it was proposed to deposit the zeolite powder on metal foam in order to improve the adsorbent thermal conductivity.

Mass transfer resistances during adsorption

Adsorption, which is the key mass transfer process occurring in adsorption chillers, is a complex phenomenon that consists of the following steps:

1. Transport of an adsorbed component to the external surface of an adsorbent (external diffusion),
2. Transport of an adsorbed component inside an adsorbent grain (internal diffusion),
3. Condensation of an adsorbed component in adsorbent pores (the act of adsorption).

The act of adsorption is usually very fast so the rate of the whole process is limited by the internal and external diffusion. Therefore, two types of mass transfer resistances during adsorption (Ruthven, 1984) can be mentioned: internal (in grains) and external (in fluid) one. If adsorption of a pure substance occurs, the resistance is related only to diffusion in an adsorbent grain (internal resistance). When adsorption from a binary or multi-component

mixture takes place, a film around an adsorbent grain can form and mass transfer resistances result from diffusion of an adsorbed component through this laminar film (external resistance) and transport of an adsorbed component inside adsorbent grains (internal resistance). The external resistance may be reduced by mixing of the fluid.

The distribution of an adsorbed component concentration during the mass transfer between fluid (gas) and solid phases for the case of adsorption of a component from a binary mixture with an inert component is presented in figure 1. The thick solid lines in figure 1 mark real concentrations in solid and gas phases, while the dotted line refers to concentration in the solid phase in equilibrium to the concentration in the gas phase.

Mathematical modeling of adsorption

The process in a gas phase is considered. It is assumed that adsorption occurs on spherical grains when gas flows through an adsorbent bed of height L and porosity ε . Assumptions that the process is isothermic and adsorption equilibrium is non-linear are also taken. The mass balance for

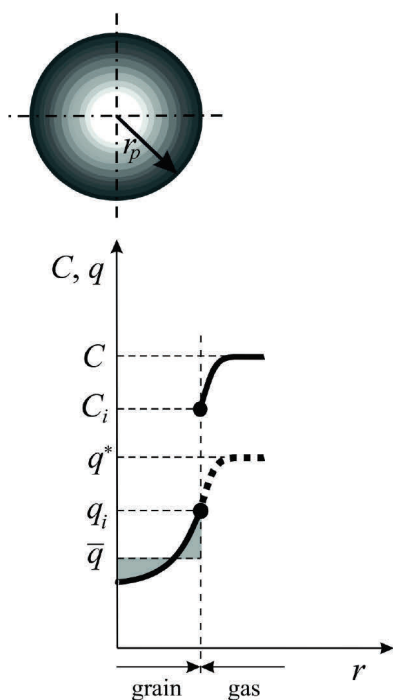


Figure 1. The distribution of the adsorbed component concentration in solid and fluid phases.

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the adsorbed component in the gas phase is (Ruthven, 1984):

$$\varepsilon \frac{\partial C}{\partial t} = -u \frac{\partial C}{\partial z} - k_g (C - C_i) a \quad (1)$$

The specific surface area of an adsorbent layer is defined by the formula:

$$a = \frac{3(1 - \varepsilon)}{r_p}$$

The left side of eq. (1) presents accumulation of a component in a fluid phase, the first term on the right side – convective inflow of the component, while the second one – the amount of the component transferred between phases as a result of adsorption. The form of this second term results from the mass transfer equation.

The following equation presents the mass balance of the adsorbed component in the solid phase:

$$\frac{\partial \bar{q}}{\partial t} = k_s (q_i - \bar{q}) \quad (2)$$

The left side of this equation describes the component accumulation, while the right side – the amount (flux) of the component transferred between phases. This amount (per unit of time) is expressed by the LDF (*Linear Driving Force*) equation as proportional to the driving force of the process $q_i - \bar{q}$ (Glueckauf, 1955; Yang, 1987). Since the solid phase is stationary, the convective term is equal to zero. For a spherical grain, the LDF equation coefficient k_s is given by the formula (Seader and Henley, 2006):

$$k_s = \frac{15D_s}{r_p^2}$$

The balance equations are coupled by the equation of continuity for the adsorbed component at the interface:

$$k_s (q_i - \bar{q})(1 - \varepsilon) \rho_s = k_g (C - C_i) a \quad (3)$$

The left side of formula (3) presents the stream of the component adsorbed by the solid phase, while the right side – the stream of the component lost by the fluid phase.

The equilibrium at the interface between the solid and gas phases may be described by the Freundlich equation:

$$q_i = K_F \phi_i^v \quad (4)$$

The initial conditions have the form:

$$t = 0; \quad C = 0, \quad \bar{q} = 0$$

The boundary condition results from maintaining the inlet component concentration constant:

$$z = 0; \quad C = C_0$$

The model for desorption is similar as for adsorption but the initial and boundary conditions are different; namely $\bar{q} \neq 0$ in the initial condition and $C = 0$ in the boundary condition.

Experiments and results



Figure 2. A glass adsorber with a silica gel-coated copper pipe

Experiments were conducted with the use of the experimental setup illustrated in figures 2 and 3. The main element of the setup was a glass adsorber, which had a coaxially-located metal (copper) pipe coated with adsorbent grains. Orange silica gel grains purchased from the Centro-chem company (Poland) was used. The size of grains was between 3.0 (mm) and 3.5 (mm). Polyvinyl alcohol (PVA) was used as a binder to coat the metal pipe with grains. The length of the adsorbent layer was 130 (mm). Air saturated with water vapor flew into the adsorber from its bottom and water was adsorbed from this stream in silica gel grains. The gas apparent velocity was $0.276 \text{ (m}\cdot\text{s}^{-1})$. Concentration of water in the inlet gas was $C_0 = 0.0178 \text{ (kg}\cdot\text{m}^{-3})$. All the measurements were performed at a temperature of 296 (K).

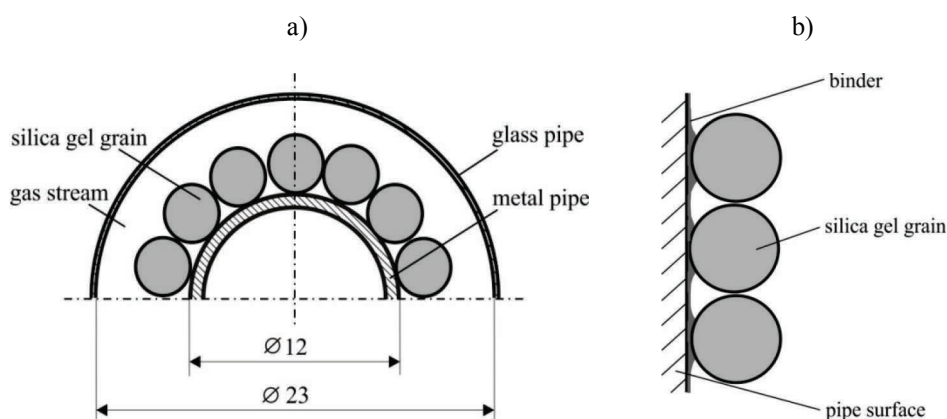


Figure 3. An adsorber with a grains-coated pipe: a) adsorber cross-section b) grains on pipe surface

Figure 4 shows the breakthrough curve, which presents the temporal change of the component concentration (water) in the outlet gas. The symbols refer to experimental values and the solid line presents the values obtained from the model of the process presented in this work. As can be seen, the model predicts the experimental curve quite good, which indicates that it can be used for process simulation. The mean percentage error for the model predictions is 6.3%. The temporal increase of component concentration in the outlet gas stream that can be observed in the figure is a result of saturation of grains during adsorption. The breakthrough curve shape depends primarily on the type of the adsorption equilibrium isotherm but it is also influenced by transport processes in the bed and in adsorbent grains. The shape of the breakthrough curve presented in fig. 4 corresponds to the type B isotherm (Yang, 1987; Demir et. al, 2011) which is the favorable one. It is typical for most of commercially significant adsorption systems.

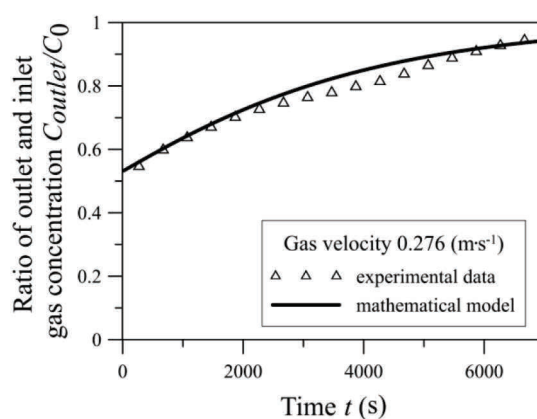


Figure 4. Experimental and numerical breakthrough curves.

Conclusions

Adsorption refrigeration technology is a promising environmentally-friendly technique for food or drugs storage or air conditioning. It allows the reduction of electricity consumption because cold can be produced with the use of thermal energy, for instance, solar energy or waste heat. Moreover, ecological refrigerants such as water are used in these systems.

The process in an adsorption chiller is affected by many factors, which causes that elaboration of experimental results is burdensome. The influence of these factors on chiller performance is difficult to determine without the theoretical knowledge on partial processes. In such a case it is useful to develop a mathematical model that is based on the mass and heat transfer phenomena.

Studies on heat and mass transfer in the system, especially for an adsorber which is the main part of the chiller, can help to improve the efficiency of adsorption chillers which nowadays is low. In this case, mathematical modeling and process simulation may play a significant role.

The model presented in this work gives results consistent with experiments therefore it can be used for simulation of the behavior of an adsorber and for the analysis of the mass transfer in an adsorption chiller.

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PROCES ADSORPCJI I DESORPCJI W AGREGACIE ADSORPCYJNYM

Streszczenie. Niniejsza praca ma na celu zaprezentowanie technologii agregatów adsorpcyjnych. Przedstawiono zasadę działania takich systemów, a mianowicie par adsorbat-adsorbent, które są często stosowane oraz technik ulepszania, które pozwalają na poprawę ich wydajności. Przedyskutowano także analizę przepływu masy oraz zasad modelowania matematycznego takich systemów. W dalszej części przedstawiono wyniki badań eksperymentalnych oraz porównanie takich wyników z obliczeniami na podstawie modelu matematycznego adsorpcji.

Słowa kluczowe: agregaty adsorpcyjne, ulepszenie przepływu ciepła i masy, modelowanie matematyczne