Chinese Science Bulletin 2005 Vol. 50 No. 3 193—204

Adsorption refrigeration-green cooling driven by low grade thermal energy

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Abstract **As a type of environmental benign refrigeration technology powered by low grade thermal energy, adsorption refrigeration have aroused more and more attention in recent years. In this paper, the research frontiers of adsorption refrigeration, including adsorbent, adsorption theory, heat recovery process, technology of adsorber, the research achievements, and the development achievements, are summarized. Typical systems for adsorption refrigeration research facing to applications in the recent years are presented. Future applications of adsorption refrigeration are analysed.**

Keywords: adsorption refrigeration, adsorbent, adsorption cycle, heat transfer, mass transfer.

DOI: 10.1360/982004-62

With the worldwide development of the economy, the energy consumption is quickly increasing, and the problems of environmental pollution and energy shortage are becoming more and more serious. Green cooling (environmental benign refrigeration), such as adsorption refrigeration driven by low-grade thermal energy, has been regarded as an intermediate link between the use of energy and the protection of environment[1] .

There are two reasons to accelerate the researches on adsorption refrigeration. The first is to search for possible ways to solve energy shortage. Energy shortage has been a global problem since the oil crisis caused by the Middle-East War in 1973. One effective way to solve energy shortage is to utilize the low grade thermal energy, which includes renewable energy and the recovery of waste heat[1]. The second reason is that, nowadays, the destruction of ozone layer and global climatic changes are being considered as the main environmental problems worldwide. A large contribution to these problems comes from the use of CFCs and HCFCs refrigerants in mechanical vapour compression refrigeration systems; thus the use of natural refrigerants and the substitution of ways of refrigeration become more and more imperative.

Adsorption refrigeration generates cooling effect through evaporation of refrigerant during adsorption. The adsorption refrigeration process includes mainly two phases: (1) Adsorbent cooling and adsorption reaction, which result in the refrigerant evaporation in the evaporator and hence the refrigeration effect. At this phase, the sensible heat and adsorption heat are consumed by a cooling medium, which is usually water or air. (2) Adsorbent heating and desorption which result in refrigerant condensation in condenser and heat release to the environment. After the adsorption reaction is completed and refrigeration effect is obtained, the low-grade heat (such as solar energy, waste heat, etc), which must have a temperature of at least 50℃, is used to regenerate adsorbent bed. The refrigerants used in adsorption refrigeration are all natural refrigerants, such as water, methanol, ammonia, hydrogen, etc, which are zero ODP and GWP.

In comparison with mechanical vapour compression refrigeration, adsorption refrigeration has the benefits of energy saving, environment protecting, simple control and low operation cost. The range of the heat resources for solid adsorption refrigeration is larger than liquid absorption system. Solid adsorption systems also do not need liquid pump and rectifier, and have no problems of refrigerant pollution, crystallization and corrosion; thus the application of adsorption refrigeration is more extensive. Adsorption refrigeration could be used in places where waste heat is available, such as air conditioner and ice maker powered by the waste heat of power units, and air conditioner powered by solar heated hot water. Distributed energy utilization system of CCHP (combined cooling, heating and power) will be the main direction of energy utilization in China with the extensive use of natural gas, and small type adsorption chillers (10—200 kW) are especially suitable for such systems.

In this paper the development of adsorption refrigeration, which is energy saving and environment protecting is introduced, the achievements of Shanghai Jiao Tong University are presented, and the perspectives of adsorption refrigeration are analyzed.

1 History

The earliest record of the phenomenon of adsorption refrigeration is the ammonia adsorption on AgCl, which was found by Faraday in 1848. In the 1920s, Hulse suggested a refrigerator to store food on train, which utilized silica gel-SO_2 as working pair and reached the evaporation temperature of about −12℃[2]. In this system, propane was burnt to generate the heat necessary to regenerate the adsorbent, and air was used to cool the adsorbent at the adsorption phase. Plank and Kuprianoff developed an activated carbon-methanol adsorption refrigeration system in 1929[3]. An adsorption refrigerator was used on the train from London to Liverpool in 1940—1945, with $CaCl_2$-NH_3 as adsorption working pair and water vapor at 100℃ as the heat source. Since 1930, the development of refrigeration technology was accelerated by the technology innovation brought by the utilization of CFCs as refrigerant

and the utilization of fully closed compressor. Thus, the technology of vapor mechanical compression refrigeration had a fast development, and the adsorption refrigeration could no longer compete with those systems. As the adsorption systems had lower efficiency than the mechanical compression systems, the subsequent research were mainly focused on improvements of the latter.

Worldwide energy crisis in the 1970s intensified the exploitation of new energy resources and the research of energy saving technologies, which attracted attentions again to the sorption systems. In the 1990s, the destruction of ozone layer caused by CFCs and HCFCs and the greenhouse effect were recognized as one of the major environmental problems that could influence living conditions of human beings. Since then, more attention has being devoted to a sustainable development, which in turn gave a good chance for the development of adsorption refrigeration technology.

The researches on adsorption refrigeration technology were accelerated after the first solid sorption refrigeration conference in Paris in 1992. The subsequent conferences, now called International Sorption Heat Pump Conference (ISHPC) have helped a lot to the development of adsorption refrigeration technology.

An adsorption refrigeration system is mainly comprised of adsorber, evaporator and condenser. The first adsorption systems adopted a basic cycle, which only had one adsorber. The basic cycle has the advantage of simple structure, but its efficiency is very low. *COP* of basic cycle is always less than 0.6, and generally less than 0.4, and the second law efficiency is generally less than 0.3[4]. In order to improve thermodynamic efficiency of adsorption system, the concept of heat recovery was introduced. The use of recoverable heat in adsorption refrigeration cycle began in the 1980s[5,6]. And since then great efforts have been made in this realm[7−12]. Recently, some researchers utilized multi-salt[13] and multi-hydride[14] to intensify the heat recovery efficiency in chemical adsorption. Heat recovery is an effective way to enhance *COP* of adsorption system. Jones predicted that *COP* of a heat recovery adsorption system could reach as high as 1.47[15] if six adsorbers are used simultaneously in a zeolite-water system.

The specific cooling power (*SCP*) is another important parameter for adsorption refrigeration cycle besides *COP*. One effective way to improve the *SCP* is to intensify the heat exchange efficiency and decrease the cycle time. Thus another important factor for the design of an adsorption refrigeration system is the heat transfer performance.

Initially, powder and granular adsorbent were mainly used in adsorber. Such an adsorbent has high mass transfer coefficient and low heat transfer coefficient. Two important technologies are adopted to improve heat transfer: one is to increase the heat transfer area of the adsorber, and the other is to use consolidated adsorbent bed or coated adsorber. The cycle time of an adsorption heat pump, which was studied by Miles and Shelton, was about only 5 min[16] after the intensification of heat transfer. The cycle time of the silica gel-water adsorption air conditioner studied in the Shanghai Jiao Tong University was also shortened to about 5 min because of the heat transfer intensification. The *SCP* and hence the cooling power could be improved if the cycle time is shortened and this improvement is the basis for the commercialization of adsorption refrigeration systems.

With the fast development of adsorption refrigeration technology, adsorption refrigerators gradually appeared on the market. Nishiyodo Kuchouki Co. developed a silica gel-water adsorption chiller in 1986. The HIJC Company in USA is now selling such adsorption chillers, (Fig. 1). This chiller is driven by hot water at 50—90℃, and the temperature of chilled water is 3℃. Qianchuan Company in Canada also began to manufacture silica gel-water adsorption chillers in 2003, which are powered by hot water at 75℃ and yield chilled water at 14℃. The reported *COP* for such equipment is 0.6.

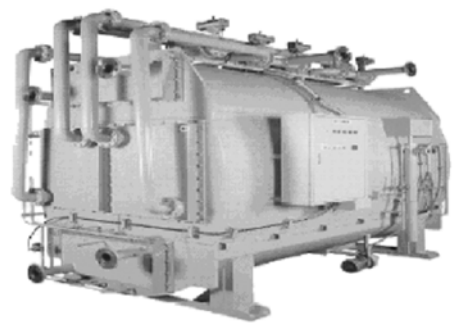


Fig. 1. Silica gel-water adsorption chiller of Nishiyodo Kuchouki Co.

Malteser hospital in Germany first installed a CCHP system in which an adsorption chiller was used to generate cooling power. This CCHP system (Fig. 2) began to operate in May, 2000. The system in Fig. 2 collects solar energy and wasted heat of fuel cell power, and an adsorption chiller with cooling power of 105 kW is used to supply cooling. A mechanical vapour compression refrigerator is also installed in the system to regulate the cooling power. Tokai Optical Company in Nagoya Japan developed another wasted heat powered CCHP system with an adsorption chiller in April, 2003. The wasted heat of diesel engine, 185 kW, is used to power CCHP system. The adsorption chiller in this system is used for dehumidification and refrigeration. This system could decrease the energy consumption by 10% and decrease the emission of CO_2 by 12%.

2 Status of researches on adsorption refrigeration

(ⅰ) Adsorption refrigeration working pairs

Adsorption refrigeration working pairs mainly in-

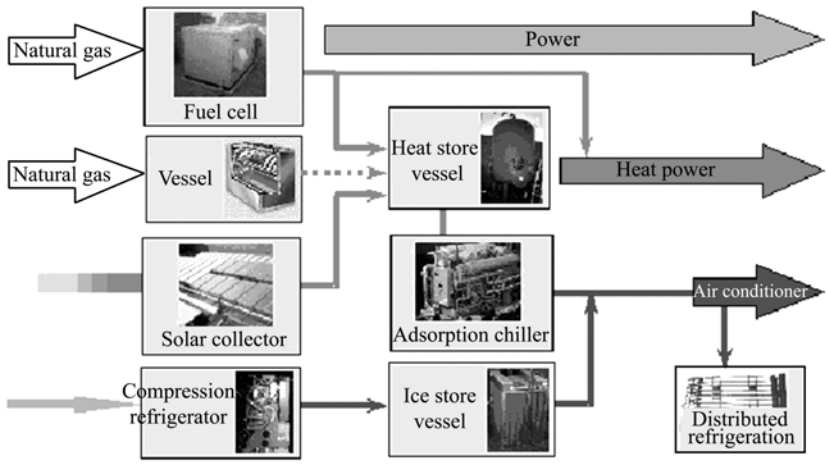


Fig. 2. CCHP system in Malteser hospital.

clude physical adsorption, chemical adsorption and compound/composite adsorption working pairs.

(1) Physical adsorption working pairs.

Zeolite-water, activated carbon-methanol, activated carbon-ammonia and silica gel-water are the main physical adsorption working pairs. The first solar energy adsorption system used the zeolite-water pair[17], and its main feature was high generation temperature of about 250—300℃. Activated carbon has good adsorption performance with methanol or ammonia, but the generation temperature of activated carbon-methanol must be lower than 120℃. The main advantage of silica gel-water system is the low generation temperature, which could be about 70—80℃[18].

(2) Chemical and compound/composite working pairs

The main chemical adsorption working pairs are metal hydride-hydrogen and metal chloride-ammonia. Metal hydride-hydrogen system utilizes the adsorption between hydrogen and metal or alloy to generate cooling effect; it has the advantage of large adsorption and desorption quantities, especially for the developed porous metal hydrides (PMH) or Misch metal (Mm) matrix alloys. The metal hydride-hydrogen system designed by Yanoma[19] has a cycle time of only 10 min, a heating power of 174 kW, and a cooling power of 93 kW. The main advantage of this working pair is the large volume cooling power because of large density of adsorbent; thus it is mainly used for automobile air conditioners[20]. The European Union is supporting now a project of using metal hydride-hydrogen adsorption air conditioners for cars, and the Fiat Automobile Company, the Stuttgart University in Germany, the Warwick University in England, and the Research Center of Energy Resource in Italy undertake this project.

As a kind of chemical adsorption working pairs, the main advantages of metal chloride-ammonia are large adsorption and desorption quantity, while the main disadvantages are the low performances of heat and mass transfer, and the phenomena of swelling and agglomeration in the process of adsorption. Typical metal chlorides are $CaCl_2$, $SrCl_2$, $LiCl_2$, etc. Usually $CaCl_2$ is more widely accepted than other adsorbents because of its low price, but it has the drawback of performance attenuation after successive adsorption and desorption phases.

Because compound and composite adsorbents have both advantages of porous medium and metal chlorides, they have attracted more and more attentions in recent years[21]. Typical achievements are the composite adsorbents made of graphite and chemical adsorbent (IMPEX)[22−25], and the composite adsorbent made of porous graphite and $CaCl_2$[26]. The composite adsorbent used for heat pump, reached a heat transfer coefficient of 90 $Wm^{-2}K^{-1}$[26]. The authors have researched the compound adsorbent made of activated carbon and $CaCl_2$. The results showed that compound adsorbent could improve the mass transfer performance of chemical adsorbent in the case of low pressure, and could control the phenomena of swelling, agglomeration and performance attenuation of chemical adsorbent successfully[27,28].

(ⅱ) Adsorption theory

For chemical and physical adsorption, the adsorption theory is developing from the equilibrium adsorption theory of uniform temperature and uniform pressure to the non-equilibrium adsorption theory. The dynamic characteristics of adsorption and desorption are more and more obvious with the development of adsorption refrigeration and the reduction of adsorption refrigeration cycle time.

Equilibrium adsorption equation for physical adsorption is the D-A equation given by Critoph[29,30]. It has the advantage of simple application, but it cannot reflect the real condition of adsorption dynamics inside adsorbent because it only considers the influence of temperature on adsorption. Considering the dynamics of the adsorption

reaction, Sokoda et al.[31] established the equation for adsorption rate (Eq. (1)) based on reaction dynamics and with the influence of surface diffusion of adsorbates on adsorption rate taken into account

$$\frac{dx}{d\tau} = K_s a_p (x^* - x), \tag{1}$$

$$K_s a_p = \frac{15 D_{so}}{R_p^2} \exp(-E_a / RT), \tag{2}$$

where x^* is the local equilibrium adsorption quantity, $K_s a_p$ is the coefficient of surface diffusion rate, D_{so} is the coefficient of surface diffusion, E_a is activated energy of surface diffusion, and R_p is the average diameter of granular adsorbent. Eq.(1) is mainly used for silica gel-water system. Passos[32] adjusted the coefficient of Eq.(2) and on this basis established the equation for activated carbon-methanol.

The theory of chemical adsorption is more complex than that of physical adsorption. Chemical adsorption mainly includes two types of models for chemical adsorption dynamics. One is the model based on the phenomenon itself, and the other model, which is more generally used, is the dynamic model based on chemical kinetics and global reaction. Spinner and Rheault[33] advanced unreacted shrinking core model based on the researches of dynamic rate. Based on the achievements of Spinner and Rheault, Mazet et al.[34] and Lebrun[35] added a factor to the equation suggested by Tykodi[36] and Flanagan[37]. The new equation could reflect the change in the interface reaction. The equation proposed by Mazet et al.[34] and Lebrun[35] is

$$\frac{dx}{dt} = K_i (1 - x) \exp(-A_0 / T) \ln\left(\frac{P_c}{P_{eq}(T)}\right), \tag{3}$$

where x is adsorption quantity; dx/dt is adsorption rate; subscript i = s represents adsorption process; i = d represents desorption process; K_s, K_d, A_0 are dynamic coefficients, P_c is the constrained pressure of condenser or evaporator; P_{eq} is equilibrium pressure; and T is adsorption temperature. After that Mazet developed Eq. (3) for the reason of small influence of A_0 in the experiments[34], and now the equation that is generally used is the following equation developed by Goetz[38]:

$$\frac{dN_g}{dt} = 4\pi r_c^2 K_i \left(\frac{P_c - P_{eq}(T)}{P_{eq}(T)}\right)^{Ma}, \tag{4}$$

where N_g is molar adsorption quantity, r_c is the diameter of reaction surface, and M_a is the reaction dynamic coefficient. The characteristic of this equation is the involvement of the mass transfer inside granular.

Another formula[39] for the reaction rate, which takes the Darcy equation between reaction surface and grain surface into account, is

$$\frac{dx}{dt} = f(x, r_g)\left(\frac{P_c - P_i}{T_c}\right) K_n(m, c), \tag{5}$$

where K_n is Knudsen diffusion rate related to the diameter of pore and porosity, $f(x,r_g)$ is a function related to adsorption quantity x and the radius of grain r_g, and P_i is the pressure inside the adsorbent pore.

Nowadays there is a wrong point in the chemical adsorption theory, i.e. desorption process is considered as the inverse of adsorption process. Regarding this problem, Furrer[38] had pointed out that a pseudo- equilibrium area exists for chemical solid-gas adsorption, and Goetz[38] had taken it into account in his researches, but unfortunately few people followed with interest in this problem[40]. Recently the authors made some research work on the chemical and compound adsorbent. The results showed serious hysteresis for adsorption and desorption of chemical adsorbents[27], indicating that desorption is really not an inverse process of adsorption for chemical adsorbents. For this reason, the Claperon equation of desorption cannot be replaced by that of adsorption.

Another problem in adsorption theory is compound adsorption theory. Nowadays compound/composite adsorption is mainly analyzed by chemical adsorption theory. This is not reasonable. The mass transfer performance and activated energy of compound and composite adsorption are much different from that of chemical adsorption because of the additives of porous medium, thus the compound and composite adsorption theory needs to be further explored.

(iii) Adsorption refrigeration cycle

The main problem for adsorption refrigeration is the low *COP*, which is generally less than 0.4 for the basic cycle and is mainly caused by the large temperature difference between adsorption and desorption[41]. Heat recovery concept is introduced into the adsorption refrigeration system in order to increase *COP*. The typical heat recovery cycle suggested by Tchernev is shown in Fig. 3[6]. In the process of cooling, the heat transfer fluid is pre-

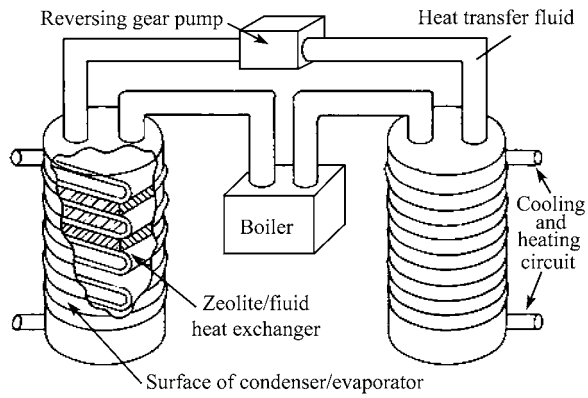


Fig. 3. Heat recovery cycle put forward by Tchernev[6]

heated by the adsorption heat, and then flow to a heating boiler, and finally, flow to the adsorber under desorption condition.

Heat recovery cycles mainly include two-adsorber heat recovery cycle, cascading cycle, multi stage adsorption cycle, thermal wave cycle and fractional regenerative cycle.

(1) Two-adsorber heat recovery cycle, cascading cycle and multi stage adsorption cycle

The common characteristics of these three cycles are that the previously cold adsorber (Adsorber) cannot transfer its heat to the previously hot adsorber (Generator).

Typical values for the coefficient of heat recovery are only about 0.22 for experiments with two-adsorber system[42]. The optimal *COP* of a cascading cycle in experiments is 1.06, and the corresponding heat recovery coefficient is 0.5[41,43], although it could reach about 0.63 in numerical studies[44]. Rockenfeller et al.[45] and Spinner[46] applied cascading cycle in chemical adsorption, and they predicted a *COP* of 1.

The typical heat recovery cycle in these three cycles is the multi stage adsorption cycle, proposed by Saha and K Kashiwagi[47], Fig. 4 is such a cycle with 6-bed. This system uses silica gel-water as working pair, and also uses a triple stage cycle to reduce the temperature lift necessary to drive the cycle. The experiments on this system show that it could provide chilled water at 12℃ when powered by hot water at 50℃, and the second law efficiency could reach about 0.3—0.4. Compared with LiBr water units, this system is very attractive for air conditioning units, as it could be powered by heat source with a temperature as low as 50—60℃.

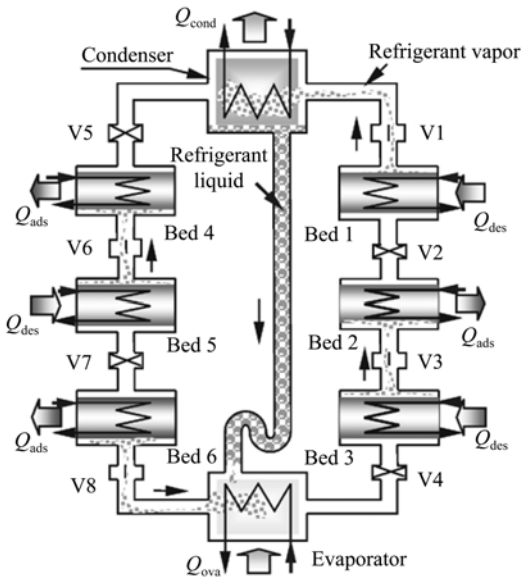


Fig. 4. Working process of multi stage adsorption cycle[47].

(2) Thermal wave cycle and convective thermal wave cycle

Many different cycles have been studied to improve the *COP*, with focus on the improvement of the heat regenerative ratio. One attractive cycle is the thermal wave cycle patented by Shelton[48]. The simulation of this cycle by Shelton showed that the heat regenerative ratio and *COP* for heat pump are as high as 70% and 1.87 respectively. Thermal wave cycle utilizes a simple heat transfer fluid circulating loop to heat and cool the two adsorbent beds, in which part of the adsorbent heat can be recovered from the bed being cooled to the bed being heated[41]. Each cycle consists of two steps, and at the end of each step, the end status of one adsorber becomes the initial status of the other adsorber. The optimal results of thermal wave cycle is reported by Miles and Shelton, which has an experimental cooling *COP* as high as 1.19 with two-bed thermal wave cycle using activated carbon-ammonia pair[16]. This concept has been also introduced into the design of chemical adsorption heat pumps. Typical cycle is the multi-hydride-thermal-wave concept put forward by Willers et al.[14] (Fig. 5). The cycle in Fig. 5 combines low temperature powered metal hydrides with high temperature powered metal hydrides. Beds HT1 and HT2 each contains six metal hydrides, and beds LT1 and LT2 have only two kinds of metal hydrides. A steep thermal wave, which is beneficial for the improvement of heat recovery efficiency, could be obtained because the temperature differences in the adjacent hydrides are the same under the uniform pressure inside bed.

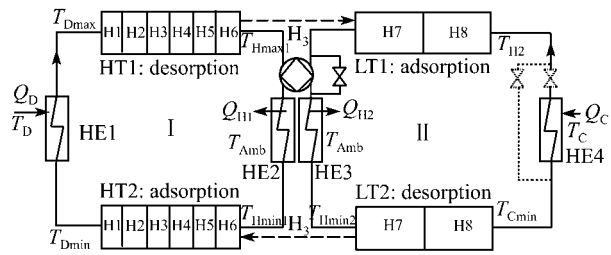


Fig. 5. Multi-hydride-thermal-wave cycle[14].

Critoph suggested a convective thermal wave cycle with refrigerant serving as the heat transfer fluid. Refrigerant vapour generates a convective thermal wave directly within the solidified adsorbent thus raising the heat recovery efficiency[49].

(3) Fractional regenerative cycle

All the refrigeration cycles above utilize fixed adsorbers, while the fractional regenerative adsorption cycle, as those used for dehumidification and studied by Douglas[50], utilizes rotated adsorbers. The latter cycle has two steps for regeneration. The first step is adsorbing water from the air to dry it and to preheat the adsorber by the adsorption heat. The second step is heating the adsorber

until it reaches the generation temperature. Spraying water into the dried air generates the desirable cooling effect. Dakin Company of Japan has utilized dehumidification/humidification wheel in its room air conditioner products since 2003. The desiccant wheel is used to adsorb the water moisture from air outside room, and then to humidify the indoor air for heat pump application, thus making the indoor air more comfortable in winter.

(4) Mass recovery cycle

Besides the thermal recovery, there is another type of vapour mass recovery cycle that could be used to enhance the *COP* and the *SCP*. The mass recovery between two beds is driven by the vapour pressure difference between them, which transfers refrigerant vapour from the high temperature bed to low temperature bed, and enhances the cooling power and *COP* of adsorption system effectively. A group in Shanghai Jiao Tong University (SJTU) improved the *COP* of adsorption refrigeration system by 10%~100% with mass recovery technology[1]. It is also coupled with heat recovery cycle[54] by performing mass recovery first and then heating recovery to improve system performances of adsorption cooling. The *COP* of activated carbon-methanol adsorption air conditioning with such a cycle could reach 0.8[51]. This technology is used in the commercialized adsorption chillers now in SJTU. The process of mass recovery can be simply performed by the connection of two beds with piping and valve.

(ⅳ) Technology of adsorbers

The main method to enhance *SCP* of system is to shorten the cycle time. There are two ways to shorten cycle time: one is to improve the mass transfer performance of low-pressure system, and the other is to intensify the heat transfer performance.

The improvement of mass transfer is mainly for the chlorides of chemical adsorbents. Agglomeration exists for metal chlorides in the process of adsorption, and this phenomenon will influence the mass transfer performance in the case of low pressure. Using compound adsorbent, the authors successfully improved the mass transfer performance of calcium chloride [27,28].

There are three main ways to improve the overall heat exchange coefficient: to increase the heat exchange area, to use consolidated adsorbent bed or coated adsorber, and to use heat pipe technology.

(1) Extended surfaces for heat exchangers

Several types of extended surfaces are used: finned tubes[41], plate heat exchangers, plate-fin heat exchangers. The drawback of the extended surfaces is that they increase the thermal capacity of the adsorber, and therefore the extended surfaces heat exchangers require advanced cycle (heat recovery) to use heat source effectively. SJTU has designed a silica gel-water adsorption air conditioner with plate-fin heat exchanger, with a cycle time of only 5 min because the heat transfer was intensified. To make use of this technology, Meunier[41] considered that at high operation pressure, under which Knudsen effect limitations could be avoided, heat transfer coefficient depends on the adsorbent grain size, and small grain size will facilitate high wall heat transfer performance[41]. Miles and Shelton shortened the cycle time to about 5min with small pellet sizes[16].

(2) Consolidated adsorbers

Another way to get high heat transfer coefficients is to develop consolidated adsorbent with higher thermal conductivity. This is particularly interesting when the simple powder beds are not suitable. This approach has been developed a long period for metal hydrides[41]. Later, researchers found that consolidation of the adsorbent with expanded natural graphite will be helpful for the heat transfer intensification[52]. The optimal result is the 3000 W/m^2 wall heat transfer coefficient[53]. The utilization of aluminum powder foam as a heat conduction matrix in consolidate compound is another method to intensify the heat transfer within the adsorber. An effective thermal conductivity as high as 12 $Wm^{-1}K^{-1}$ has already been measured by Groll[54]. Optimal results were also obtained from solidified adsorbent by agglomerant. The authors studied the consolidated activated carbon with agglomerant, and obtained a heat transfer coefficient improvement of about 58—100% when compared to the powder activated carbon[55]. One drawback of the consolidated adsorber is the deterioration of the mass transfer performance, especially for refrigerants evaporating under atmospheric pressure, such as water, methanol, etc.

(3) Coated adsorbers

This technology is especially suitable for the case where *COP* is not a big issue. This technology is to increase the wall heat transfer coefficient by the effectively decreasing the contact thermal resistance between heat exchange surface and adsorbent. Dunne[56] developed coated tubes with zeolite crystals monolayers coated on its surface. The heating rate of such an adsorber is more than 1500 W per kg of adsorbent. The drawback of this technology is the very high ratio of metal mass to adsorbent mass; therefore it requires a very effective heat recovery regenerative process. Another way to get coated heat exchangers is to insert the adsorbent bead in an expanded natural graphite plate[57]. With this technology, the contact between the heat transfer fluid and the adsorbent is not as close as in the previous coated tube, but the ratio of mass of adsorbent to the mass of inert conducting material is much higher， since the adsorbent bead size can reaches few millimeters.

(4) Heat pipe technology

Meunier[41] deemed that the use of heat pipe would enable us to enhance the heat exchange efficiency in adsorber due to the high heat transfer coefficient that could be obtained by the evaporation and the condensation of the heat transfer fluid inside the heat pipe. The condensation of the heat transfer fluid releases the heat necessary to

regenerate the adsorber and the vaporization of the former absorbs the heat necessary to cool down the adsorber. The study performed at LIMSI[41] showed that extremely high heat transfer coefficients of 10 kWm^{-2} were obtainable. Vasiliev proposed pulsating heat pipe for adsorption system (Fig. 6), in which propane was used as heat transfer fluid. The adsorber was made by flat aluminum (multi-channel) heat pipe panel, only 7mm in width[58]. SJTU has introduced the heat pipe concept into adsorption ice makers on fishing boats and the adsorption chillers powered by low temperature heat source, and applied for several patents on compound heat pipe type adsorbers and split heat pipe adsorbers[59,61].

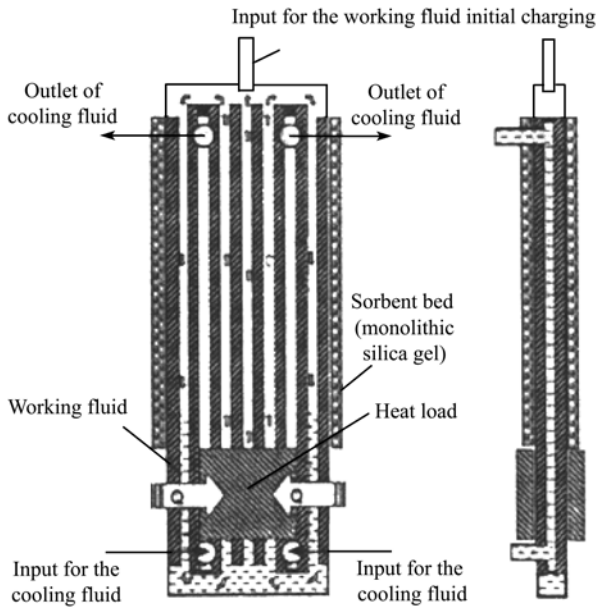


Fig. 6. Multi-channel pulsating heat pipe type adsorber[58]

3 Researches Facing Applications

The work facing the applications of adsortion refrigeration have been well demonstrated in Shanghai Jiao Tong University (SJTU), which can be shown as follows:

(ⅰ) Heat transfer intensification and advanced cycle of heat and mass recovery

Researches on heat transfer intensification include extended heat transfer area and consolidated adsorbent.

a) Heat and mass recovery adsorption ice maker with consolidated adsorbent

Typical application of consolidated adsorbent technology for activated carbon is shown in Fig. 7(a)[55]. Consolidated adsorbent could improve the heat conductivity coefficient by 58—100% in comparison with granular adsorbent. A two-bed activated carbon-methanol adsorption icemaker, which uses such technology, is shown in Fig. 7(b)[55].

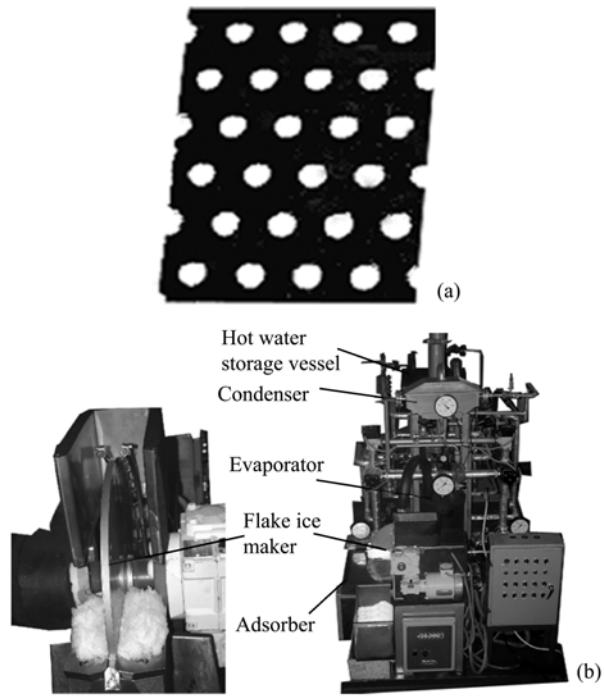


Fig. 7. Heat transfer intensification technology: solidified adsorber[55]; (a) Solidified activated carbon, (b) solidified adsorption icemaker for fishing boats[62]

In the case of 60kg adsorbent per bed, experimental results of the adsorption icemaker are as follows (Fig. 7(b)):

(1) The heat transfer performances of consolidated beds are much better than that of granular beds. Heat transfer coefficients of consolidated beds are about 80—100 $Wm^{-2}℃^{-1}$, while the heat transfer coefficients of granular beds are only 20—25 $Wm^{-2}℃^{-1}$.

(2) *SCP* and *COP* of adsorption icemaker are effectively improved by heat and mass recovery. In experiments on consolidated adsorbent icemaker, *COP* is improved by 20%—30% and *SCP* is improved by 7%—11% with heat and mass recovery.

(3) Compared with granular adsorption system, consolidated adsorption system improves *COP* and *SCP* respectively by 15% and 23%. Ice productivity of adsorption icemaker is about 432 kg ice per day.

b) Adsorption chiller with extended heat transfer area and powered by low temperature heat source[63]

The studies on the adsorption refrigeration system with extended heat transfer area of finned tubes heat exchangers, spiral plate exchangers, and plate-fin exchangers to intensify heat transfer have been carried out. The principle of typical finned tubes adsorption system driven by low temperature heat source is shown in Fig. 8(a)[63]. For the system in Fig. 8(a), the adsorption refrigeration unit

comprises an adsorber, a condenser and an evaporator, all of which are enclosed in the same vacuum chamber, and there are no refrigerant valves. Two adsorption units that perform heat and mass recovery at switch time serve to continuously refrigerate. Because the mass recovery is performed by the heat exchange of the liquid in evaporator, it is called "mass recovery like". Adsorbers, condensers and evaporators are all made by finned-tube heat exchangers to intensify heat transfer. Fig. 8(b) is a photo of this system. Experiments are performed with this system and the results show that the maximum cooling power is 7.43 kW and *COP* is 0.42 when the temperature of heat source is 85℃. Cycle time is only about 5 min because the extended heat transfer area effectively improves the heat transfer performance.

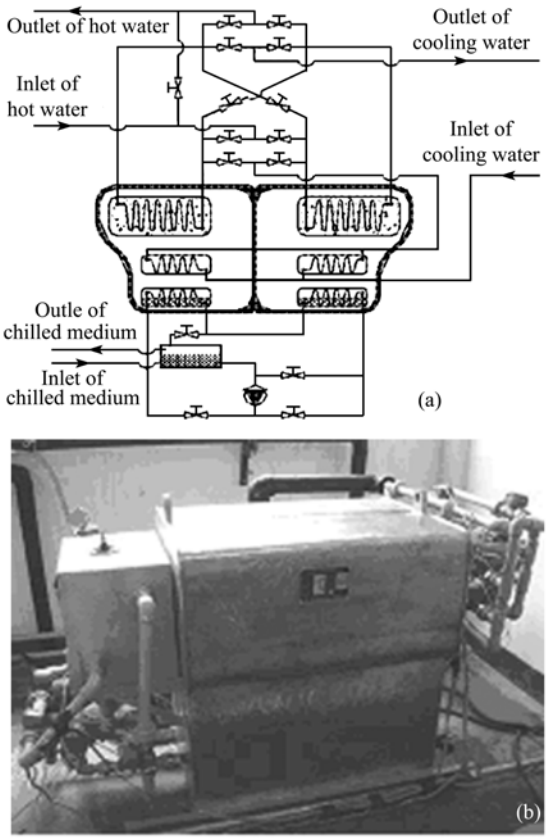


Fig. 8. Heat transfer intensification technology: extended heat transfer area. (a) Principle of Adsorption chiller that is powered by low temperature heat source[63]. (b) Adsorption chiller driven by low temperature heat source.

c) Heat pipe theory applied in adsorption refrigeration system

A type of heat intensification technology, in which a heat pipe device is coupled to an adsorption refrigeration system has been developed. This technology effectively uses a heater and a cooler with phase changes to perform heating, cooling, adsorption and desorption process without extra driven force. Typical adsorption system is shown in Fig. 9[61].

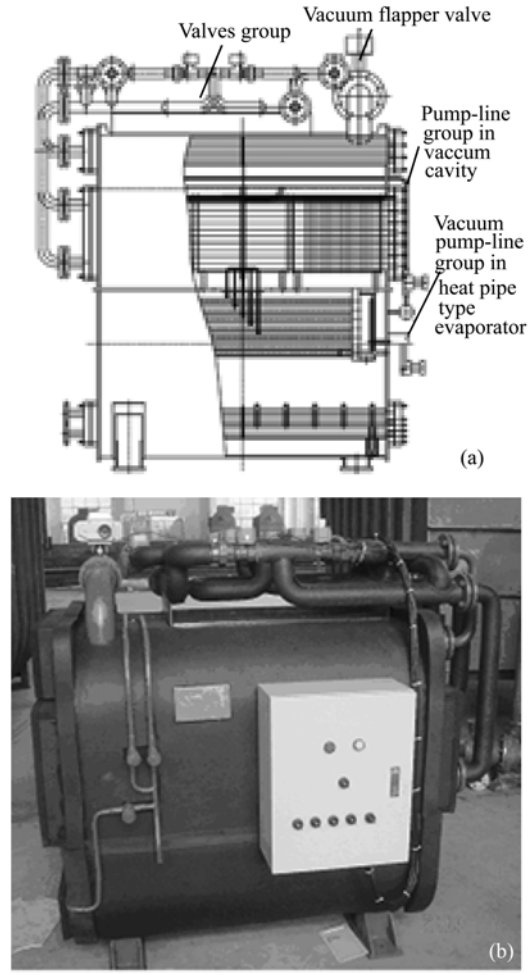


Fig. 9. Adsorption chiller of two types of separate heat pipes with heat and mass recovery: (a) Structure of system; (b) Photo of chiller.

Fig. 9 is the split heat pipe type adsorption chiller driven by low temperature heat source. There are two vacuum chambers inside this chiller, and each of the chamber encloses one adsorber, one condenser, and one evaporator. Mass recovery piping is installed between the two chambers. Cooling power of this adsorption chiller is 6~10 kW. The 6 kW cooling power and the 0.35 *COP* are obtained when the system is powered by hot water at 65°C, which is the lowest working temperature of hot water, while 10 kW cooling power and 0.4 *COP* are obtained when the temperature of hot water is 85℃. This adsorption chiller could be used as solar powered air conditioner and also as the chiller for CCHP system. Adsorption system could provide 10—15℃ chilled water for normal air conditioning systems, or 15—20℃ chilled water for dry fan coils according to the requirements, and *COP* could be

more than 0.5 in this case.

Nowadays, this adsorption system is applied in the Shanghai Green Building to serve as solar powered air conditioner, and another set of this system is used at the National Grain Storage to cool grains during hot summer. In addition, several adsorption chillers have been installed as chiller for CCHP systems. They are commercially available now with the help of Jiangsu Shuangliang Air Conditioner Equipments Company, the range of product are rated as 10 kW, 20 kW, 50 kW, 100 kW, 200 kW, etc.

Besides the application of the split heat pipes in the adsorption chiller powered by low temperature heat source, SJTU is also applying this technology, together with the technology of complex alternate heat pipes in the development of adsorption ice maker for fishing boats. The application of these technologies prevents adsorber from corrosion at the heating phase by exhausted gases and at the cooling phase by seawater, and also has the advantage of high heat transfer performance. Furthermore, with the use of this technology adsorption icemaker can be directly heated by the exhausted gases and cooled by seawater[59,60].

(ⅱ) Chemical and compound adsorption

In comparison with physical adsorbents, chemical adsorbents have the disadvantages of swelling, agglomeration, performance attenuation, and low mass transfer performance under the condition of low pressure. Compound adsorbent is researched in SJTU in order to solve these problems.

a) Adsorption performances of calcium chloride and compound adsorbent

Two types of adsorbents, $CaCl_2$ and compound adsorbent ($CaCl_2$ mixed with activated carbon) are tested; the test unit is shown in Fig. 10.

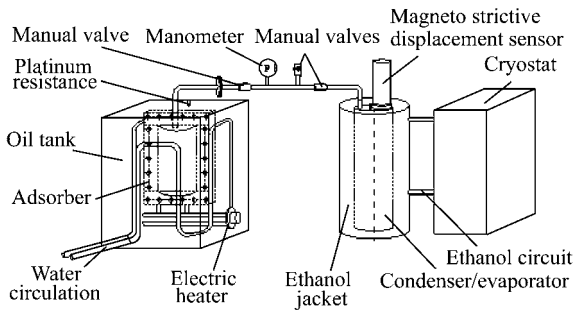


Fig. 10. Test unit for chemical and compound adsorption performance.

The test unit in Fig. 10 mainly includes two parts: adsorber and condenser/evaporator. The adsorption and desorption quantities are measured by magnetostrictive level sensor, and its relative error is about only 0.05%. Three main achievements on theory have been obtained[27,28]:

(1) Serious adsorption hysteresis phenomenon exists for chemical and compound adsorbent, which cannot be explained by the current adsorption hysteresis theory.

(2) Complex formation processes with adsorption performance attenuation exist for chemical and compound adsorbents, and complex formation processes without adsorption performance attenuation also exist for chemical and compound adsorbents, which is related to the precursor chemical adsorption state.

(3) Vapor will condense in the porous medium in the compound adsorbent, which induces the phenomenon of compound adsorbent, such as activated energy.

The achievements that can be used in the design of an adsorption system are shown as follows:

(1) Best results are obtained when the compound adsorbent is made at the radio of 4∶1 between $CaCl_2$ and activated carbon, and it is also solidified with cement. Performance attenuation does not appear when the volume filling quantity of such an adsorbent is 75%.

(2) Compound adsorbent can effectively improve the mass transfer performance of adsorbent in adsorber, and consequently volumetric cooling power and filling quantity of $CaCl_2$ are effectively improved. In comparison with the optimal volumetric cooling power of $CaCl_2$, the volumetric cooling power of consolidated compound adsorbent was improved by 35% when the temperature of saturated refrigerant was −15℃.

b) Compound adsorbent of silica gel-$CaCl_2$

Another compound adsorbent, $SiO_2{\cdot}xH_2O{\cdot}yCaCl_2$, is mainly designed for the adsorption system to uptake water from air[64]. Such a system, as shown in Fig. 11[65], consists mainly of two adsorbers, one reversing valve, one condenser, and one hot water vessel and could continuously uptake water from air during the adsorption process.

Achievements of compound adsorbent of $CaCl_2$ and silica gel are as follows[64]:

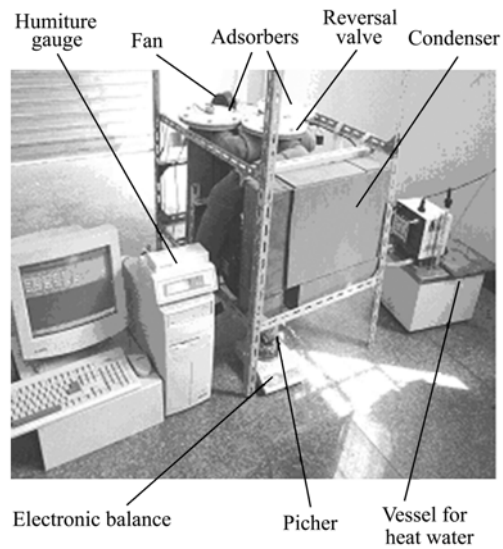


Fig. 11. Continuous adsorption system to intake water from air[65].

(1) Compound adsorbents with 13.0%, 27.3%, 38.4%, and 51.0% of $CaCl_2$ are defined as CA1, CA2, CA3, and CA4, respectively. The isothermal curves of water adsorption for compound adsorbents are compared with conventional solid desiccant (spherical silica gel with coarse pores, spherical silica gel with fine pores, and 13X zeolite molecular sieve). The results show that equilibrium water adsorption quantities of compound adsorbent are obviously higher than that of conventional adsorbents, especially in high humidity condition. The equilibrium adsorption quantity of CA4 is 2.7—8.5 times that of silica gel with coarse pores, 2.6—8.6 times that of silica gel with fine pores, and 2.1—9.2 times that of 13X molecular sieve.

(2) The outer diffusion rate coefficients are far less than inner diffusion rate coefficients for compound adsorbent, which means that the outer diffusion is the main factor for mass transfer. The adsorption rate will be effectively enhanced by using a method to improve the outer diffusion conditions.

(3) Adsorption system to uptake water from air could perform continuous water adsorption from environment. When the filling quantity of CA3 in each adsorber is 1.5 kg and cycle time is 2 h, the cycled water uptake during the daytime (temperature of air is 22.2℃, and relative humidity is 44%) and the night-time (temperature of air is 10.4℃, and relative humidity is 77%) are 0.15kg and 0.27kg respectively.

This compound adsorbent is now already used as the desiccant material for dehumidification wheels.

4 Perspectives for the development of adsorption refrigeration technology

There are mainly two directions for the development of adsorption refrigeration: one is low efficiency applications but with simple system structure, such as locomotive air conditioners and solar powered adsorption icemakers. Recently, adsorption chiller powered by low temperature heat source was successfully developed by SJTU. The adsorption water chiller is commercialized. The heat source of this chiller is only 65—90℃, and it could be coupled with solar powered water heating system to work as a solar air conditioner. Nowadays, these types of adsorption chillers have already been used at Shanghai Green Building, National Grain Storage, and at CCHP systems.

The second direction is high efficiency applications. Here, the competition will be very serious with electrical powered mechanical vapour compression systems where air conditioning is considered only for cooling applications. From the point of view of energy and environment, for air conditioning, the cooling *COP* must be higher than 1 and possibly higher than 1.2[66], to compete favourably with a mechanical vapour compression unit (*COP* = 3) powered with electricity provided by a thermal power station ($\eta \sim 1/3$)[41]. However, the situation may be much more favourable if one considers both cooling mode in summertime and heating mode in wintertime. Meunier[41] claimed that the whole energy consumption for heating in winter and for cooling in summer should not exceed the consumption of energy just for heating in winter time with a conventional heating method if the heat recovery efficiency could reach 0.75[41,42].

The researches are not perfectly completed in the direction of adsorption refrigeration theory. The researches on the adsorption theory of metal chlorides should couple the molecular dynamics theory with chemical theory of complex compound. Considering the phenomena of swelling and agglomeration of chemical adsorbents, nonlinear and non-equilibrium concepts should be introduced into researches on the heat and mass transfer. The additives of porous mediums in compound adsorbents makes the compound adsorption phenomena more complex; thus the compound adsorption theory must be further developed.

The main problems of the adsorption refrigeration technology are the poor heat transfer in the adsorbent and its operation performances that leads to low *COP*. For the adsorption system with chlorides as adsorbents and ammonia as refrigerant, the metal heat capacity of the system is very high because the system is under high pressure. As a result it is very difficult to shorten cycle time even with the heat transfer intensification in the bed. The main problem of operation performance of an adsorption system is its low heat recovery coefficient that is much lower than liquid absorption system and limits the *COP* of adsorption system and hence the application of adsorption system when high efficiency is requested. Thus high efficient heat transfer and heat recovery processes are still the main directions for the study of the adsorption refrigeration technology in the future.

Acknowledgements This work was supported by the National Natural Science Foundation for Distinguished Young Scholars of China (Grant No. 50225621), the National Key Fundamental Research Program (Grant No. G2000026309), the Teaching and Research Award Program for Outstanding Young Teachers in High Education Institutions of MOE, China, and the Shuguang Training Program of Shanghai Education Commission (Grant No. 02GG03).

References

1. Wang, R. Z., Wu, J. Y., Dai, Y. J. et al, Adsorption refrigeration (in Chinese), Beijing: Mechanical Industry Press. 2002.
2. Hulse, G. E., Refroidissement d'un wagon frigorifique a marchandises par un system a adsrption utilisant le gel de silice, Revue Gen Froid, 1929, 10: 281—284.
3. Plank, R., Kuprianoff, J., In die Kleinltemaschin, Berlin: Springer-Verlag, 1960.
4. Meunier, F., Kaushik, S. C., Neveu, P. et al., A comparative ther-

modynamic study of sorption systems: second law analysis, International Journal of Refrigeration, 1996, 19(6): 414—421.[DOI]
5. Shelton, S., Miles, D., Solid/vapor thermally driven heat pump development, In: Prodeedings of the International Workshop on Research Activities on Advanced Heat Pumps, Austria: Technical University of Graz, 1986, 403—420.
6. Tchernev, D. I., Emerson, D. T., High-efficiency regenerative zeolite heat pump, ASHRAE Transactions, 1988, 14: 2024—2032.
7. Jones, J. A., Carbon/ammonia regenerative adsorption heat pump, Proceedings of the International Absorption Heat Pump Conference, ASME, AES, 1993, 31: 449—455.
8. Miles, D. J., Sanborn, D. M., Nowakowski, G. A. et al., Gas fired sorption heat pump development, Heat Recovery Systems and CHP, 1993, 13(4): 347—351. [DOI]
9. Zheng, W., Worek, W. M., Nowakowski, G., Effect of operating conditions on the performance of two-bed closed cycle solid-sorption heat pump systems, Journal of Solar Energy and Engineering, ASME Transactions, 1995, 117, 181—186.
10. Sun, L. M., Ben, A. N., Meunier, F., Numerical study on coupled heat and mass transfers in an adsorber with ecternal fluid heating, Heat Recovery Systems and CHP, 1995, 15(1): 19—29.
11. Critoph, R. E., Gas-fired air conditioning using a carbon-ammonia convective thermal wave cycle, In: Proceedings of the International Absorption Heat Pump Conference, Quebec, Montreal, 1996, 353—360.
12. Pons, M., Laurent, D., Meunier, F., Experimental temperature fronts for adsorptive heat pump applications, Applied Thermal Engineering, 1996, 16(5): 395—404. [DOI]
13. Istria, S., Castaing-Lasvignottes, J., Neveu, P., Energetic analysis, application field and performance of a new thernochemical sorption cycle: the multisalt system, Applied Thermal Engineering, 1996, 16(11): 875—889. [DOI]
14. Willers, E., Groll, M., Isselhorst, A. et al., Advanced concept of a metal hydride solid sorption device for combined heating and air-conditioning, In: Proceedings of the International Absorption Heat Pump Conference, Quebec, Montreal, 1996, 169—175.
15. Jones, J., Sorption refrigeration research at JPL/NASA, Heat Recovery Systems and CHP, 1993, 13: 363—372. [DOI]
16. Miles, D., Shelton, S., Design and testing of a solid-sorption heat-pump system, Applied Thermal Engineering, 1996, 16: 389—394. [DOI]
17. Tchernev, D. I., Solar refrigeration utilizing zeolites, In: 14th Inter. Conv. Engng. Conf. Amer. Chem. Soc., 1979: 2070—2074.
18. Srivastava, N. C., Eames, I. W., A review of adsorbents and adsorbates in solid-vapour adsorption heat pump systems. Applied Thermal Engineering 1998,18: 707—714. [DOI]
19. Yanoma, A., Yoneta, M., Nitta, T. et al., The performance of a large scale metal hydride heat pump, JSME International Journal, 1988,31(4): 741—747.
20. Ron, M., A hydrogen heat pump as a bus air conditioner, Journal of Less-Common Metals, 1984, 104(2): 259—278. [DOI]
21. Valkov, V., Cote, R., Perron, G. et al., Experimentation of a new thermochemical material based on carbon fiber. In: Proceedings of the International Sorption Heat Pump Conference, Germany: Munich, 1999: 239—245.
22. Mauran, S., Prades, P., Haridon, F. L., Heat and mass transfer in consolidated reaction beds for thermochemical systems, Heat Recovery Systems & CHP, 1993, 13: 315—319. [DOI]
23. Mauran, S., Coudevylle, O., Lu, H. B., Optimization of porous reactive media for solid sorption heat pumps. In: International Absorption Heat Pump Conference, Quebec, Montreal, 1996: 3—8.
24. Han, J. H., Cho, K. W., Lee, K. H. et al., Characterization of graphite-salt blocks in chemical heat pumps, In: Ab-sorption Heat Pump Conference, Quebec, Montreal, 1996: 67—73.
25. Mauran, S., Lebrun, M., Prades, P. et al, Active composite and its use as reaction medium, US Patent 5283 219, 1994.
26. Groll, M., Reaction beds for dry sorption machines, In: Proceedings of Symposium of Solid Sorption Refrigeration, France: Paris, 1992: 208—214.
27. Wang, L. W., Wang, R. Z., Wu, J. Y., Wang, K., Adsorption performances and refrigeration application of adsorption working pair of $CaCl_2$-NH_3, Science in China, Ser. E, 2004, 47(2): 173—185. [Abstract] [PDF]
28. Wang, L. W., Wang, R. Z., Wu, J. Y. et al., Compound adsorbent for adsorptin ice maker on fishing boats, International Journal of Refrigeration, 2004, 27(4): 401—408. [DOI]
29. Critoph, R. E., Performance limitations of adsorption cycles for solar cooling,. Solar Energy, 1997, 14(1): 21—31.
30. Tamainot, Z. T., Critoph, R. E., Adsorption refrigerator using monolithic carbonammonia pair, International Journal of Refrigeration, 1997, 20(2): 146—155. [DOI]
31. Sokoda, A., Suzuki, M., Fundamental study on solar powered adsorption cooling system, Journal of Chemical Engineering of Japan, 1984, 17(1): 52—57.
32. Passos, E. F., Escobedo, J. F., Meunier, F., Simulation of an intermittent adsorptive solar cooling system, Solar Energy, 1989, 42(2): 103—111. [DOI]
33. Spinner, B., Rheault, F., Kinetics models in solid/gas reactions under imposed pressure and temperature constraints, In: Proc. of International Workshop on Heat Transformation and Storage, ISPRA, 1985, 9—11.
34. Mazet, N., Amouroux, M., Spinner, B., Analysis and experimental study of the transformation of non-isothermal solid/gas reacting medium, Chemical Engineering Communication, 1991, 99: 155—174.
35. Lebrun, M., Models of heat and mass transfers in solid/gas reactor used as chemical heat pumps, Chemical Engineering Science, 1990, 45: 1743—1753. [DOI]

36. Tykodi, R. J., Thermodynamics of steady state resistance change transitions in steady-state systems, Bulletin of the Chemical Society of Japan, 1979, 552(2): 564—568.
37. Flanagan, T. B., Hydrides for Energy Storage, England: Oxford Press, 1978, 135.
38. Goetz, V., Marty, A., A model for reversible solid/gas reactions submitted to temperature and pressure constraints; simulation of the rate of reaction in solid gas reactors used in chemical heat pump, Chemical Engineering Science, 1992, 47(17-18): 4445—4454[DOI].
39. Neveu, P., Castaing-Lasvignottes, J., Development of a numerical sizing tool for a solid-gas thermochemical transformer I—impact of the microscopic process on the dynamic behaviour of a solid-gas reactor, Applied Thermal Engineering, 1997. 17(6): 501—518. [DOI]
40. Huang, H. J., Wu, G. B., Yang, J. et al., Modeling of gas–solid chemisorption in chemical heat pumps, Separation and Purification Technology, 2004, 34: 191—200. [DOI]
41. Meunier, F., Solid sorption heat powered cycles for cooling and heat pumping applications, Applied Thermal Engineering, 1998, 18: 715—729/[DOI]
42. Douss, F., Meunier, F., Sun, L. M., Predictive model and experimental results for a two-adsorber solid adsorption heat pump, Industry & Engineering Chemistry Research, 1988, 27: 310—316.
43. Douss, N., Meunier, F., Experimental study of cascading adsorption cycles, Chemical Engineering Science, 1989, 44: 225—235. [DOI]
44. Meunier, F., Second law analysis of a solid adsorption heat pump operating on cascade cycles, Heat Recovery Systems, 1985b, 5: 133—141.
45. Rockenfeller, U., Kirol, L., Sarkisian, P. et al., In: Proceedings of "Solid Sorption Refrigeration" Symposium, France: Paris, 1992: 171—177.
46. Spinner, B., Les transformateurs thermochimiques a ammoniac, In: Proceedings of "Solid Sorption Refrigeration" Symposium, France: Paris, 1992: 163—170.
47. Saha, B. B., Kashiwagi, T., Performance evaluation of advanced adsorption cycle driven by near-environment temperature waste heat, In: Proceedings of the International Ab-sorption Heat Pump Conference, Quebec, Montreal, 1996: 277—284.
48. Shelton, S., Solid adsorbent heat pump system, US Patent, 4 610 148, 1986.
49. Critoph, R. E., Gas-fired air conditioning using a carbon-ammonia convective thermal wave cycle, In: Proceedings of the International Absorption Heat Pump Conference, Quebec, Montreal, 1996: 353—360.
50. Douglas, K., Linking indoor air quality (IAQ), ventilation, moisture control, and desiccants to future air conditioning practices, In: Proceedings of the International Absorption Heat Pump Conference, Quebec, Montreal, 1996: 128—137.
51. Wang, R. Z., Performance improvement of adsorption heat pump by heat and mass recovery operations, International Journal of Refrigeration, 2001, 24(7): 602—611. [DOI]
52. Coste, C., Mauran, S., Crozat, G., Procede de mise en oeuvre de reaction gaz-solide, US Patent, 4 595 774, 1983.
53. Mauran, S., Prades, P., Haridon, F. L., Heat and mass transfer in consolidated reacting beds for thermochemical systems, Heat Recovery Systems, 1993, 13: 315—319. [DOI]
54. Groll, M., Reaction beds for dry sorption machines, In: Proceedings of "Solid Sorption Refrigeration" Symposium, France: Paris, 1992: 225—232.
55. Wang, L. W., Wu, J. Y., Wang, R. Z. et al., Experimental study of a solidified activated carbon- methanol adsorption ice maker, Applied Thermal Engineering, 2003, 23: 1453—1462. [DOI]
56. Dunne, S., Carousel heat exchanger for sorption cooling process, US Patent, 5 503 222, 1996.
57. Bou, P., Guilleminot, J. J., Pons, M., Composite actif a structure feuilletee comprenant un agent actif sous forme de granules, French pending patent, 96 12762, 1996.
58. Vasiliev, L. L., Sorption refrigerators with heat pipe thermal control. In: Proceedings of ICCR'2003, Zhejiang: Hangzhou, 405—415.
59. Xia, Z. Z., Wang, R. Z., Wu, J. Y. et al., Compound alternate heat pipe reactor powered by waste heat (in Chinese), Chinese Patent 200410018291.3, 2004.
60. Wang, L. W., Wang, R. Z., Wu, J. Y., Separate heat pipe adsorption ice maker for fishing boats (in Chinese), Chinese Patent 200310108924.5, 2003.
61. Xia, Z. Z., Wang, R. Z., Wu., J. Y. et al., New type of effective adsorption chiller adopt separate heat pipe (in Chinese), Chinese Patent 200410025398.0, 2003.
62. Wang, S. G, Wang, R. Z., Wu, J. Y. et al., Experimental results and analysis for adsorption ice-making system with consolidated adsorbent, Adsorption, 2003,9 (4): 349—358. [DOI]
63. Liu, Y. L., Wang, R. Z., Xia, Z. Z., Experimental performance of a silica gel–water adsorption chiller, Applied Thermal Engineering, 2005, 25(2-3): 359—375. [DOI]
64. Liu, Y. F., Wang, R. Z., Pore structure of new composite adsorbent SiO_2 xH_2O $yCaCl_2$ with high uptake of water from air, Science in China SCI, Ser E, 2003, 46 (5): 551—559. [Abstract] [PDF]
65. Liu, Y. F., Wang, R. Z., Xia, Z. Z., Continuous adsorption system to intake water from air, Journal of Chemical Engineering (in Chinese), 2004, 55(6): 1002—1005.
66. Meunier, F., Solid sorption: an alternative to CFC's, Heat Recovery Systems and CHP, 1993,13: 289—295. [DOI]

(Received August 2, 2004)