Introduction

Sustainable development is a common pursuit for people worldwide and energy utilization is a key element. Generally, energy will be consumed in large amounts as the economy of society develops rapidly, and a careful eye needs to be kept on environmental pollution. How to coordinate the balance between energy utilization, economy development, and environmental protection is one of the most important strategies for sustainable development.

With regards to environmental protection, the ozonosphere depletion by chlorofluorocarbons (CFCs), which causes the ultraviolet rays of the sun to be insufficiently blocked and thus threatens life on the earth, has been commonly recognized worldwide. CFCs are very important substances in compression refrigeration. As a type of substitute substance, HCFCs can only be temporally utilized because they also have a negative influence on the ozonosphere. Meanwhile, with regards to central heating systems, the combustion of gases and coal releases \( \text{CO}_2 \) into the environment. Similarly, CFCs produce the greenhouse effect that is becoming more and more serious as the desire for comfortable living conditions all over the world becomes greater and greater. Finding a type of green technology that can be used in air conditioning and heat pumps is very important with regards to solving the problems caused by traditional compression refrigeration technology.

Another critical problem for refrigeration and heat pumps is energy utilization. Traditional compression refrigerators and heat pumps are commonly driven by electricity. Demands for electricity increase as societies develop. According to data provided by the energy department of the US between 2003 and 2004, the electricity consumed by air conditioners in the summer is 15.4% of the total electricity consumption. In China too, for example, in Shanghai City, in summer electricity consumption by air conditioning reached 45–56% according to data collected from 2010. If we analyze the energy utilized through the electricity generation process we find that energy efficiency for electrical generation is only about 40–50%, and there is a large amount of energy being released into the environment as waste heat at temperatures of around 70–200 °C. Meanwhile solar energy and geothermal heat also exist in large amounts in the environment as a low grade energy. Developing refrigeration and heat pump technologies driven by such low grade heat is a solution for energy conservation.

Sorption refrigeration and heat pump technology which is driven by low grade heat and utilizes the green refrigerants, is coordinated with the sustainable requirements of current energy and environmental developments. Firstly, the sorption technology requires little electricity,
secondly, the refrigerants for the sorption refrigeration generally are the substances of water, ammonia, and methanol, and so on, which are green refrigerants with zero ODP (Ozonosphere depletion potential) and zero GWP (Greenhouse warming potential).

As a type of sorption technology, adsorption refrigeration and heat pumps have been paid more and more attention since the 1970s. If compared with other types of sorption technology driven by low grade heat, firstly, adsorption refrigeration has a wide variety of adsorbents, including different physical and chemical adsorbents; which can be used with low grade heat across a large range of temperatures, and generally we find these adsorbents are driven by low grade heat in the range of 50–400 °C. Secondly, adsorption refrigeration doesn’t need the solution pump and rectification equipment, and it also doesn’t have the problems of refrigerant pollution and solution crystallization that often happens in absorption refrigeration technology. But, generally, adsorption refrigeration is not as efficient as absorption, and it also has the disadvantages of being a large volume system. Because of these advantages and disadvantages, adsorption refrigeration is recognized by academics as an essential complementary technology for absorption refrigeration.

1.1 Adsorption Phenomena

According to the different types of adsorption processes, adsorption is divided into physical adsorption and chemical adsorption [1]. Physical adsorption is driven by the van der Waals force among the molecules, and generally happens on the surface of adsorbents. Physical adsorption is not selective, which means multi-layer adsorption can be formed. The phenomena of physical adsorption can be treated as the condensation process of the refrigerant inside the adsorbents, and for most adsorbents the adsorption heat is similar to the condensation heat of the refrigerant. The molecules for the physical adsorption won’t be decomposed in the desorption process.

Chemical adsorption is different to physical adsorption. A chemical reaction will happen between the adsorbent and the adsorbate, and new types of molecules will be formed in the adsorption process. Commonly, the monolayer of the adsorbate will react with the chemical adsorbent, and after this reaction the chemical adsorbents cannot adsorb more layers of molecules. The newly formed molecules will be decomposed in the desorption process. The adsorption/desorption heat produced will be much larger than the physical adsorption heat. The chemical adsorption is selective. For example, H₂ can be adsorbed by W, Pt, and Ni, but cannot be adsorbed by Cu, Ag, and Zn. It is recognized by academics that physical adsorption will happen before chemical adsorption because the effective distance of the van der Waals force is inversely proportional to the power of 7 of distance, and it is much longer than the effective distance for the chemical reaction. Thus, when the adsorbate molecules approach the solid adsorbent the physical adsorption will proceed first, and will transfer into the chemical adsorption when the distance decreases.

The physical adsorption/desorption mainly depends on the heat and mass transfer performances of the adsorbents. For the desorption process, because the pressure is high, correspondingly the mass transfer process will be accelerated by the high pressure, and the heat transfer performance will be the main criterion for the performance. If the heat transfer performance is intensified the main problem for the adsorption systems will be the permeability of the gas inside the adsorbents. Generally, the permeability is higher when the adsorbent granules are smaller. The kinetic reaction rate will also influence the adsorption/desorption rate.
Because the chemical reaction happens in the chemical adsorption process, the chemical adsorption will be influenced by the heat and mass transfer process of the adsorbents, as well as the chemical reaction process and the reaction kinetics of the molecules. Meanwhile, the adsorption hysteresis also exists for the chemical adsorption because the adsorption activated energy is different from the desorption activated energy. The desorption activated energy is always much larger than the adsorption activated energy because it is the sum of the adsorption activated energy and the adsorption heat, and such a phenomenon will lead to a serious hysteresis phenomenon between adsorption and desorption [2].

For adsorption refrigeration most refrigerant molecules are polar molecular gases that can be absorbed under the van der Waals force, such as ammonia, methanol, and hydrocarbons that can be adsorbed by activated carbon, zeolite, and silica gel. For physical adsorption the cycle adsorption quantity is generally from 10 to 20%. The chemical adsorption has greater cycle concentrations than that of physical adsorbents, for example, for CaCl$_2$ the cycle adsorption quantity is always larger than 0.4.

The advantage of chemical adsorption refrigeration is the larger adsorption/desorption quantity, which is essential for the improvement of the specific cooling capacity per kilogram adsorbent (SCP, specific cooling power). But the expansion and agglomeration will happen in the chemical adsorption process, and the expansion space always needs to be kept at two times of the adsorbent volume to ensure high mass transfer performance. In order to improve the heat transfer performance as well as to ensure the mass transfer performance, the solidified compound/composite adsorbents are developed, which uses the porous matrix to keep reasonable permeability of the adsorbent, and then improve the volume filling capacity and volume cooling capacity significantly.

### 1.2 Fundamental Principle of Adsorption Refrigeration

The fundamental principle of adsorption refrigeration is demonstrated by the solar powered adsorption ice maker in Figure 1.1, and the relative thermodynamic cycle is shown in Figure 1.2.

As shown in Figure 1.1, the solar powered adsorption refrigerator is composed of the adsorber, condenser, evaporator, valve, and refrigerant tank. When the adsorber is cooled at night, the pressure inside the adsorber decreases, and the refrigerant inside the evaporator, which evaporates under the pressure difference between adsorber and evaporator, is adsorbed by
Adsorption refrigeration technology is characterized by its ability to operate intermittently, making it an excellent choice for systems that rely on solar energy. The process involves two main stages: heating-desorbing and cooling-adsorbing. This intermittent characteristic is particularly beneficial in scenarios where energy sources are sporadic, such as solar energy.

In the heating-desorbing process, the system starts with the valve closed in the morning, assuming a certain environmental temperature. As the adsorber is heated by solar energy, the refrigerant inside begins to desorb. This continues until the adsorbent reaches its saturated temperature, at which point the refrigeration process stops. In the daytime, the adsorber is heated by solar energy, increasing the pressure inside. The refrigerant, now at a high pressure, is desorbed from the adsorber by the pressure difference between the adsorber and condenser. It then condenses inside the condenser, cooled by the environmental air around.

The whole process can be detailed as follows (Figure 1.2):

1. The valve is closed in the morning, assuming an environmental temperature \( T_{a2} \) of 30°C. As time passes, the adsorber will be heated by solar energy, and the pressure of the adsorber will increase. Finally, the pressure of the refrigerant will be the saturated pressure for the condensing temperature of the refrigerant, which is 30°C. The temperature of the adsorber will be \( T_{g1} \) in Figure 1.2.
2. Open the valve, and the refrigerant desorbed from the adsorber will be condensed inside the condenser, cooled by natural convection. Afterward, the refrigerant will flow from the evaporator and refrigerant tank and accumulate there. In this phase, the final temperature of the adsorber can be as high as \( T_{g2} \) (desorbing temperature).
3. The valve is closed in the evening. The temperature of the adsorber begins to decrease because of the lack of solar energy outside. The pressure of the adsorber also decreases, and it will decrease to the saturated pressure for the evaporating temperature. The corresponding temperature of the adsorber is \( T_{a1} \) (initial adsorption temperature).
4. Open the valve, and the refrigerant inside the evaporator will evaporate and be adsorbed by the adsorbent inside the adsorber because of the pressure difference between adsorber and evaporator. The evaporation process of the refrigerant provides the refrigeration power, and the adsorption heat of the adsorber will release to the environment. This phase will proceed until the next morning, and after that a new cycle will begin.

Adsorption refrigeration has two processes, which are the heating-desorbing process and the cooling-adsorbing process. Because of that, the simple traditional cycle is a type of intermittent refrigeration cycle, which is a very good feature for the utilization of solar energy because solar energy is also a type of intermittent energy. If the heat source can be provided continually and the continuous refrigeration effect is required, two adsorbers or multi adsorbers need to be designed for an adsorption refrigeration system, for which the heating and cooling processes of multi adsorbers will be complementarily arranged.
1.3 The History of Adsorption Refrigeration Technology

In 1848, Faraday found that the cooling capacity could be generated when AgCl adsorbed NH$_3$. This is the earliest record of the adsorption refrigeration phenomenon. In the 1920s, G. E. Hulse proposed a refrigeration system in which silica gel-SO$_2$ was used as the working pair for food storage in a train. It was powered by the combustion of propane and was cooled down by the convection heat transfer of air. The lowest refrigerating temperature could reach 12 °C [3]. R. Plank and J. Kuprianoff also introduced the adsorption refrigeration system with a working pair of activated carbon-methanol [4]. In 1940–1945, the adsorption refrigeration system with working pair CaCl$_2$-NH$_3$ was used for food storage in the train from London to Liverpool, for which the heat source is the steam at 100 °C. From the 1930s, new technologies, such as the discovery of Freon and the successful development of the totally closed compressor improved the efficiency of the compression refrigeration system significantly. Because of that the adsorption refrigeration technology couldn’t compete with the highly efficient CFCs system, it had not been considered by researchers for a long time.

In the 1970s, the energy crisis took hold and it offered a great chance for the development of the adsorption refrigeration technology, mainly because of the fact that the adsorption refrigeration system is driven by a low-grade heat source such as waste heat and solar energy. In the 1990s, environmental pollution became more and more serious, and the shortcomings of the CFCs system had been recognized worldwide as a cause of the ozonosphere depletion and greenhouse warming problems. As a result green refrigeration technology, which is a thermal powered refrigeration technology such as adsorption refrigeration, regained the recognition by the academics. Up until now such a type of technology had been widely researched for heat pump systems, marine refrigeration systems, automobile air conditioning systems [5–7], as well as for the application on aerospace cryogenics because it featured no moving parts, no noise, and had good anti-vibration performance [8, 9].

The research on the adsorption refrigeration originated from Europe. The famous researchers such as F.E. Meunier, M. Pons et al. from France [10–12], G. Cacciola et al. from Italy [13, 14], R.E. Critoph et al. from England [15–17], Shelton et al. from America [18–21], and Leonard L. VASILIEV et al. from Belarus [22] contributed quite a lot to the development of the technology. In China the research on adsorption refrigeration started during 1980s [23–27]. Shanghai Jiao Tong University (SJTU) started the research in 1991 [28–35] and pursued this work for more than 20 years. The research scopes of SJTU include the adsorption working pairs, adsorption refrigeration cycles, and heat and mass transfer intensification technologies.

From the point of view of its development history, the research on adsorption refrigeration can be summarized according to the research goals, the research contents, and the research methods. In the early years the research started with the performance of the adsorbent-refrigerant working pairs, and most of this research work was performed by chemistry and physics academics instead of refrigeration specialists. The main object was to apply this technology to a real application. The research methods were mostly based on the objects of basic adsorption refrigeration systems, and combined the experimental results with the chemical and physical theories for the analysis of the performance. Such research work improved the basic theory of the adsorption refrigeration, and typical adsorbents and refrigerants were focused mainly on activated carbon, zeolite, silica gel, CaCl$_2$, hydride, and so on, and refrigerants were mainly methanol, ammonia, water, Hydrogen, and so on [36, 37].

The early research work pointed out that the basic adsorption refrigeration cycles needed to be improved in many ways, especially the intermittent refrigeration process. Adsorption/
Adsorption Refrigeration Technology

Desorption rate and capacity were related to the properties of the adsorption working pairs and the heat and mass transfer performance in the adsorption bed. Such problems resulted in low COP (coefficient of performance) and low SCP (specific cooling power per kilogram adsorbent). In order to solve these problems, the research concerned many interrelated aspects such as heat transfer, mass transfer, and adsorption properties. Some advanced adsorption cycles, such as continuous heat recovery cycle, thermal wave cycle [28, 38], mass recovery cycle, convective thermal wave cycle [16, 28], and cascading cycle [11], and so on, were proposed and their thermal performances were analyzed at that time. Meanwhile some adsorbents-refrigerants working pairs with better adsorption characteristics, for instance, the composite adsorption working pairs, were proposed in many references [32, 39, 40], for which the adsorption cycles were evaluated as a combination of the adsorption cycle and thermodynamic analysis more than just from the point of view of adsorption capacity.

The references produced up until about 1992, was mostly about the analysis and simulations of different cycles theoretically, especially about how the cycle parameters influenced the performances [41–43]. Those contents were even studied in the last few years. The superiority, feasibility, and enormous potential of some advanced systems were proved [20, 44]. Though the feasibility needed to be proved for some of more advanced cycles such as thermal wave cycle, convective thermal wave cycle, and cascading cycle, the research offered the possibility of continuous refrigeration and provided a bright future for the performance improvement of adsorption refrigeration systems. For the system design, the heat and mass transfer intensification attracted a great deal of attention. As a result, researchers paid more attention to the design of an adsorption bed that could improve heat and mass transfer and achieve better performance of continuous regeneration [13, 45, 46] based on the combination of the theoretical analysis and experimental study. In 1992, the first sorption conference held in Paris brought this technology even more to world’s attention. Since then the key research aspects of this technology were uniformly recognized by worldwide researchers [47] because numerous new ideas had been put forward on how to improve the adsorption refrigeration performance.

In the 1990s, the research project of the adsorption refrigeration (JOULE0046F) was listed into the JOULE research plan of the European Union (EU). In that plan the research groups such as Meunier from France (zeolite-water), Critoph from England (activated carbon-ammonia), Cacciola from Italy (zeolite-water), Groll from German (metal hydrides-Hydrogen), Zigler from German, Spinner from France (nickel chloride-ammonia/lithium bromide-water adsorption/absorption) had all studied the adsorption refrigeration technology. The research results had been published in the special issue of International Journal of Refrigeration in 1999. The adsorption technology and absorption technology were paralleled in the heat pump plan published by the International Energy Association (IEA). In 1994 the adsorption heat pump was taken as an important issue in the International Absorption Heat Pump Conference (ISHPC) which was held in Louisiana in the United States in 1996, the paper for adsorption refrigeration contributed one-third of all the papers in the ISHPC held in Montreal, Canada. Since 1996 the conference for adsorption heat pumps and absorption heat pumps were combined into sorption heat pump and the conference was renamed ISHPC, which is held every three years. In 1999, adsorption refrigeration was the main topic of the sorption heat pump conference held in Munich, Germany. In the conferences of 1996 and 1999, most of the topics were about the composite adsorbent, polymetallic hydrides for heat recovery cycle, thermal wave cycle, and so on. After that the topics expanded over the following sessions of the conference. For example, ISHPC 2002 was held in SJTU. In this conference, the topics
included heat transfer intensification, the multi-stage cycle, thermal wave cycle, heat and mass recovery cycle, triple effect cycle of adsorption/absorption refrigeration, solar adsorption system and locomotive adsorption air conditioner, and so on.

1.4 Current Research on Solid Adsorption Refrigeration

In the last 20 years study on solid adsorption refrigeration and heat pump has been reported from USA, France, Japan, UK, Italy, India, and other countries, and the contents are mainly connected to promoting the development of adsorption refrigeration in the field of adsorption working pairs, heat and mass transfer performance, and adsorption refrigeration cycles, and so on. With the progress of adsorption refrigeration technology, some silica gel-water adsorption chillers have been commercialized successfully in the market. The development of the adsorption refrigeration technology can be summarized more in detail as follows: adsorption working pairs and their mechanism; system structure of adsorption refrigeration; improvement of heat and mass transfer of the adsorption bed, as well as thermal properties of many advanced regenerative cycles.

1.4.1 Adsorption Working Pairs

The adsorption working pair is a key element for the adsorption refrigeration and heat pump system. Thermal properties of working pairs have a great influence on the performance coefficient of the system, the temperature increment velocity of the adsorber, and the initial investment. For efficient refrigeration output, the suitable adsorption working pairs need to be selected according to the heat source temperatures, and the suitable adsorption refrigeration cycles need to be selected according to the actual requirements. The application scope and properties are different for different adsorption refrigeration working pairs. The common adsorption refrigeration working pairs mainly include: activated carbon-methanol, activated carbon fiber-methanol, activated carbon-ammonia, zeolite-water, silica gel-water, metal hydrides-hydrogen, calcium chloride-ammonia, and strontium chloride-ammonia, and so on (physical and chemical adsorption) [48]. Recent studies also show that composite adsorption, which is a type of effective heat and mass transfer intensification technology for a chemical adsorbent, is a prospective technology for refrigeration [32, 39, 40].

For working pairs of physical adsorption, the carbon-methanol working pair has a large adsorption and desorption concentration. Its desorption temperature is around 100 °C, which is not high, and it also has the advantage of low adsorption heat, which is around 1800–2000 kJ/kg. Methanol refrigerant can be applied to make ice because its freezing point is below 0 °C. For activated carbon-methanol working pairs, the highest desorption temperature cannot exceed 120 °C, otherwise methanol will decompose. The advantages of the activated carbon-ammonia system is the low evaporation temperature of the refrigerant which is commonly used for making ice. Characterized by being less sensitive to temperature changes for adsorption capacity, it is generally used for higher heat source temperature. For the working pair of silica gel–water, desorption temperature cannot be too high. If it is higher than 120 °C, silica gel will be destroyed. Thus it is a common adsorbent for the low temperature heat source. The zeolite-water working pair has a wide range of desorption temperature (70–250 °C). Its adsorption heat is about 3200–4200 kJ/kg, and the evaporation
latent heat of water is 2400–2600 kJ/kg. Zeolite–water is quite stable and won’t be destroyed at a high temperature as happens to silica gel. However, it has the disadvantages of a higher adsorption heat, which will lead to the low COP, as well as an evaporation temperature that needs to be higher than 0°C, which cannot be utilized for making ice. In addition, the system is a vacuum system, which leads to a high requirement of vacuum sealing; meanwhile the low evaporation pressure also makes the adsorption process slower.

Chemical adsorption working pairs mainly include Hydrides-hydrogen, metal chlorides (salt)-ammonia, metal oxides-water and metal oxides-carbon dioxide, and so on. The metal hydrides-hydrogen system utilizes the adsorption process as well as desorption process between metals or alloys and hydrogen for refrigeration, which is characterized by large adsorption and desorption heat, especially for advanced porous metal hydrides (PMH) or Misch metal (Mm) alloy matrixes including Ni, Fe, La, and Al. Such types of working pairs are generally utilized for the adsorption heat pump because they have high adsorption heat as well as high adsorption concentration. Metal chloride-ammonia working pairs are featured as having a large adsorption capacity. For example, for calcium chloride-ammonia working pair 1 mol of calcium chloride can adsorb 8 mol of ammonia. Simultaneously, the boiling point of ammonia is lower than −34°C so that can be used for making ice, meanwhile the refrigerator works under the condition of positive pressure, which is a feature of simpler manufacture techniques required for the system. Metal oxides-water and metal oxides-carbon dioxide have the advantages of being able to store high levels of energy in hydration and carbonation processes [49, 50]. Take calcium oxide for example, storage energy in the hydration and carbonation process is 800–900 kJ/kg, which makes it possible to develop efficient heat pump systems by the application of such types of working pairs.

But chemical adsorption has the disadvantages of agglomeration and swelling phenomena, which will lead to problems of low permeability and poor mass transfer performance of adsorbents. In order to overcome this problem, recently the porous heat transfer matrixes were put forward for the improvement of mass transfer as well as the heat transfer (by solidified adsorbents) of chemical adsorbents. Studies on such types of adsorbents mainly focus on the composite adsorbents with the matrixes of expanded natural graphite (ENG), activated carbon fiber, and activated carbon. Research shows that such types of composite adsorbents could improve the volume filling quantity and volumetric cooling capacity [32, 39, 40] of adsorbent.

1.4.2 Heat Transfer Intensification Technology of Adsorption Bed

An important indicator when evaluating the adsorption system is the specific cooling power per kilogram adsorbent (SCP, W/kg), which is defined as [51]:

\[
SCP \approx \frac{L \Delta x}{t_c}
\]  

(1.1)

where \( L \) is the latent heat of vaporization of the refrigerant, \( t_c \) is cycle time, and \( \Delta x \) is cycle adsorption quantity. Equation 1.1 shows that for a given operating condition and a given cycle, the main method used to improve the cooling capacity is to shorten the cycle time. Generally there are two ways to shorten the cycle time; one is to improve the mass transfer performance of an adsorbent in the low pressure system, and another way is to enhance the heat transfer performance of the adsorption bed.
Two main technologies for the heat transfer intensification of the adsorption bed are the performance improvement of adsorbent and adsorber. The former one concentrates on the development of the novel types of adsorbents, and the latter one concentrates on the development of the new type of heat exchangers for the adsorber. If the technologies were summarized more in detail, there are three major ways to improve the overall heat transfer coefficients. The first one is to increase the heat transfer area of heat exchanger, the second one is to utilize a compact adsorption bed or coated adsorber, and the last one is to use heat pipe technology.

### 1.4.2.1 Heat Transfer Intensification by Extending the Heat Transfer Area

The heat transfer area of the adsorber can be extended by the following heat exchangers: finned tube [51], plate heat exchanger, plate-fin heat exchanger. Such technology could shorten the cycle time effectively, such as that a SJTU utilizing plate-fin heat exchanger reduced the cycle time of the system by about 5 minutes. The disadvantage of increasing the heat transfer area is the increment of the heat capacity of the metal materials for adsorbers, thus an advanced cycle is usually required for the recovery of heat among adsorbers. For granular adsorbents, with the application of this technology, the wall heat transfer coefficient generally depends on the granularity of the adsorbent, and a small size adsorbent is believed to be necessary for the improvement of the heat transfer coefficients [51]. For example, Miles and Shelton, using small particle size of adsorbent, shortened the cycle time to 5 minutes [52].

### 1.4.2.2 Compact Adsorption Bed

This technology is particularly suitable for the occasion when the bulk sorbent is not applicable. Such technology had been used for metal hydrides for a long time [51]. The following study found that combining ENG with the adsorbent can enhance heat transfer performance, which was firstly proposed by Spinner and Le Carbone Lorraine and the thermal conductivity can reach 3000 W/m² [40]. The other method is to use aluminum as a heat transfer matrix, and thermal conductivity can reach 12 W/(mK) [40]. Curing the composite adsorbents with the binders is also proposed. By using this technology, SJTU improves the thermal conductivity of activated carbon by 58–100% [53]. The disadvantage of compact adsorbent technology is that the mass transfer performance will be influenced in the adsorption bed, especially for the refrigerant working under the vacuum conditions such as water and methanol, and so on.

### 1.4.2.3 Coated Heat Exchanger

This technique is particularly suitable for the occasion when COP is not important. The coated adsorbent bed can effectively enhance the thermal conductivity of the adsorb by reducing the contact resistance between heat transfer surface and the absorbent. Dunne utilized zeolite [54] coated on the surface of the metal tube thereby improving the SCP to the level of 1500 W/kg. The disadvantage of this technique is that the metal heat capacity is too high, so usually an efficient heat recovery process is required. Another method of developing coated adsorbers is to insert adsorbents into the ENG plates [55], for which the contact between the heat transfer fluid and the adsorbent is not as close as a coated pipe, but since the diameter of the granular adsorbents is only a few microns, the ratio of the adsorbent heat capacity is greatly improved.
1.4.2.4 Heat Pipe Technology

Meunier put forward a novel idea for the improvement of the heat transfer performance, which used the phase change processes, such as condensation and evaporation processes, for heating and cooling adsorbers to obtain a high heat transfer coefficient [51]. LIMSI has studied this idea, and the heat transfer coefficient is about 10 kW/m² [51]. Vasiliev also introduced the concept of pulse heat pipe into the adsorbent bed by using propane as the working medium in the design of the pulse heat pipe, for which the adsorption bed is a tablet-shaped heat pipe made of aluminum, and the width of the heat pipe is only 7 mm [56]. As well as that SJTU applied the heat pipe principle to the marine adsorption ice-making system and chillers driven by low-temperature heat and successfully improved the heat transfer performance [57–59].

1.4.3 Low Grade Heat Utilization

The low grade heat exists abundantly in the environment, and it has great potential for the recovery of such a type of heat for energy conservation. The adsorption refrigeration technology is suitable for the recovery of most low grade heat resources by different adsorption working pairs. For example, the silica gel–water working pair can be utilized as a heat source with a low temperature, whereas the zeolite–water system is applicable for a high temperature heat source. Compared with the liquid absorption refrigeration system, the solid adsorption refrigeration system has the advantage of simple structure and low cost. Moreover, it is believed that adsorption technology is more suitable for the vibratory occasions than absorption technology because the adsorbent is solid. Therefore, the application research of solid adsorption refrigeration has been carried out extensively for low grade heat utilization in recent years.

Suzuki [5] applied the zeolite–water working pair on an adsorption automobile air conditioner and analyzed the performance of the system, and the results showed that the key element for reducing the cycle time and the weight of the system is to improve the heat and mass transfer performance of the adsorption bed effectively. Zhu et al. [60] studied the adsorption refrigeration system used for the fish storage on boats. Lavan [61] investigated the probability of the absorption refrigeration system driven by the exhaust gas of trucks. Saha [62] presented a double-stage adsorption refrigeration cycle with four beds driven by a low temperature heat source. Such a double-stage cycle has a higher efficiency than that of single-stage cycle when the heat source temperature is very low (<54°C). However, its efficiency decreased dramatically once the heat source temperature is relatively high. Yonezawa Y et al. carried out a great deal of research on continuous double-bed adsorption chillers with silica gel–water as the working pair and driven by the waste heat, and obtained a series of patents [63, 64]. Ron M studied the application of metal hydride–hydrogen system in automobile air conditioners. Goetz put forward the concept of resorption on the basis of the utilization of PbCl₂ and MnCl₂, for which the desorption state of PbCl₂ is closely bonded with the MnCl₂ adsorption state. The principle for this cycle is to use the desorption process of PbCl₂ for refrigeration, and the desorbed ammonia is adsorbed by MnCl₂. The pressure and temperature of the adsorption bed need to be controlled in the cooling process, otherwise the desorption state of PbCl₂ won’t match the adsorption state of MnCl₂. This study provides a new idea for adsorption refrigeration [65, 66].

On the utilization of the low grade heat, SJTU [29] designed and manufactured a 5 kW adsorption air conditioner using activated carbon–ammonia as the work pair. SJTU also developed a zeolite–water adsorption air conditioning system with the function of energy
storage, which was applied in a locomotive cab. The average cooling power of this system is 5 kW. Meanwhile, SJTU developed a physical adsorption ice maker for fishing boats with activated carbon–methanol as the working pair [67]. In addition, combining the heat pipe principle with the adsorption system, SJTU developed the siphon heat pipe type adsorber and a split heat pipe type compound adsorption ice-making system for fishing boats [68].

1.4.4 Solar Energy Utilization

The sorption refrigeration driven by solar energy attracted broad attention because the heat supply and cool demand are very well matched with the season and the heat quantity. Compared with the absorption system, the adsorption system can be driven by the heat sources of lower temperatures, which makes the application of solar energy more feasible on the adsorption system.

The solid adsorption refrigeration technology driven by solar energy has been researched extensively since Tchernev [38] successfully developed the refrigeration system with zeolite–water as the working pair. In France, Pons and Guillemirot studied activated carbon–methanol and zeolite–water adsorption systems driven by solar energy, in which the COP of the activated carbon–methanol ice maker [69] is 0.12–0.14 with a collector area of 6 m² (four collectors) and adsorbent mass of 20–24 kg/m², and the COP of a zeolite–water refrigerator [70] is about 0.10 with the collector area of 20 m² (24 collectors) and the adsorbent mass of 360 kg. K. Sumathy et al. investigated an activated carbon–methanol ice maker powered by solar energy, and results showed that the daily ice production is 4–5 kg and the COP is 0.1–0.2 [71] when the area of flat plate collector is 0.92 m². Y.K. Tan [23–25] in South China University of Technology and Z.F. Li et al. in Guangzhou Institute of Energy Conversion [72] also developed the solid adsorption refrigeration system driven by solar energy, which had a similar performance to the system developed by K. Sumathy.

Different from the refrigeration system with the integrated solar collector–adsorption generator, multi types of solar energy powered adsorption refrigeration systems were developed. Iloeje et al. [73, 74] utilized a tubular type of absorber, for which the adsorbent (such as calcium chloride, activated carbon) is filled inside the metal pipes. The concentric tube arranged at the center of the metal pipe served as the mass transfer channel of the refrigerant, and the metal tube is boned on the collector surface. Erhard [75] arranged the condensation part of the horizontal heat pipe inside the adsorbent bed to improve the heat flux density. Headley et al. [76] studied the activated carbon–methanol adsorption refrigerating system utilizing the compound parabolic concentrator (CPC) as the heat source. The system could realize refrigeration even if the solar radiation is very feeble, but the efficiency of the refrigeration system is very low. Bansal et al. [77] studied the SrCl₂-NH₃ adsorption refrigerating system driven by the vacuum tube type collector. Vasiliev [56] developed a continuous adsorption heat pump with heat recovery process driven by solar energy and natural gas, using a parabolic concentrator for collecting the solar energy to heat the circulating water. The system employed solar energy as a main power supply, and the natural gas served as an auxiliary heat source when solar energy is not enough. The system can accomplish continuous refrigeration with the cycle time of 12 minutes Z.Y. Liu [78, 79] put forward the refrigeration system which combined the unit adsorption tube with the collector for the solar energy. For such a design the adsorbent bed can be heated by solar energy directly.

On the topic of solar energy utilization, SJTU [80] developed a compound system of water heater and refrigerator driven by solar energy to improve energy efficiency. Meanwhile, SJTU
also developed the silica gel–water adsorption chiller in 2004, which had been applied to the building and grain storage hall with solar energy as the driving power.

1.4.5 Advanced Adsorption Refrigeration Cycle

A prominent problem for adsorption refrigeration is that the COP is low. For a traditional simple cycle under the condition of air conditioning, generally COP is less than 0.4 [51]; if during ice making with a refrigerating temperature lower than 0 °C, commonly COP is less than 0.2 and under some conditions is even lower than 0.1 [53, 67, 81] due to the fact that the adsorption performance usually decreases with the evaporation temperature. The reason for the low COP is mainly caused by the big temperature fluctuation of the adsorption bed under the condition of alternating heating and cooling processes. In order to improve the COP of the adsorption refrigeration system, the concept of heat recovery was proposed. The principle of heat recovery was put forward by Tchernev initially [38], for which the heat transfer fluid was preheated by the adsorption heat, then was heated by the boiler and passed into the adsorber to provide the desorption heat. Nowadays the heat recovery cycles studied by researchers mainly include double-bed heat recovery cycle, cascading cycle, multi-stage cycle, thermal wave cycle, and so on.

1.4.5.1 Double-Bed Heat Recovery Cycle, Cascading Cycle, and Multi-stage Cycle

For such type of cycles in the heat recovery process the heat from a high-temperature adsorption bed is delivered to the low-temperature adsorption bed by the temperature potential. Because the heat recovered is mainly the sensible heat of the adsorbers, the heat cannot be recovered from the low temperature bed to the high temperature bed. Thus the coefficient of heat recovery is limited.

In the research for the continuous refrigeration cycle with double-bed heat recovery process [82–87], the heat recovery coefficient gleaned from experiments is 0.22 [44]. The best result of heat recovery coefficient for the cascading cycle is 0.5 [11, 51], although in the simulation it is as high as 0.63 [88].

Among three types of cycles, i.e., double-bed heat recovery cycle, cascading cycle and multi-stage cycle, the typical cycle is a multi-stage and six-bed adsorption cycle proposed by Saha and Kashiwagi [89]. The three-stage cycle system using silica gel–water as the working pair can decrease the driven temperature effectively. The experimental results showed that it can obtain a chillier water of 12 °C when the heat source temperature is 50 °C and the second law of thermodynamics efficiency is 0.3–0.4. Its driven temperature is lower than that of the LiBr absorption system. Such a technology provided an effective way for the recycling use of low grade heat of 50–60 °C. SJTU also developed a type of two-stage cycle for the freezing conditions, such a type of cycle can be driven by a heat source with the temperature lower than 100 °C, and can generate the cooling power with temperatures as low as −15 °C when the environmental temperature is around 25–35 °C [90].

1.4.5.2 Thermal Wave and Convective Thermal Wave Cycle

Thermal wave cycle was proposed by Shelton [18]. His theory indicated that the heat recovery coefficient of a thermal wave cycle can reach 0.7 and the COP of the heat pump is 1.87.
The principle of the thermal wave cycle is to use the flow of the thermal fluids, which transferred the heat within the adsorbers to form a steep temperature wave. For such technology the heat can be transferred from the low temperature adsorber to the high temperature adsorber [51]. This concept has been applied to chemical heat pumps. Willers et al. have studied a multi-hydride–thermal-wave concept [91]. For this cycle, through the combination of low-temperature and high-temperature metal hydride, with the same equilibrium temperature difference for both metal hydrides under the condition of same pressure, a very steep thermal wave can be generated by the accumulating temperature effect in the adsorption bed. Critoph [16] suggested a convective thermal wave cycle. In such a cycle, the refrigerant served as the heat transfer fluid, which could improve the heat recovery efficiency effectively because of the direct contact between the heat transfer fluid and the solid adsorbent.

1.4.5.3 Stages Regeneration Cycle for Dehumidification Refrigeration System

All the refrigeration cycles mentioned above are for the closed adsorption refrigeration cycles. Nowadays there is also a type of stage regenerative dehumidification cycle. The regenerative process of the adsorbent is divided into two stages while the adsorber rotates. The first stage is to heat the adsorbent with the air preheated by the heat of adsorption, and then to heat the adsorbent to the maximum desorption temperature with the air heated by the heat source. For the adsorption phase the dehumidification effect will be achieved by absorbing the water in the environment, and the cooling power can be generated by spraying the water into the dry air in a dehumidification process. The early research can be seen in a report from Douglas [92]. By using the rotary beds, the Daikin company in Japan successfully humidified the indoor air by desorbing the water indoor and adsorbing the water outside. Such a mode made the indoor more comfortable during the heat-pump condition of winter.

1.4.5.4 Mass Recovery Cycle

In addition to the heat recovery cycle there is a mass recovery cycle. The mass recovery cycle is that the refrigerant gas in the high pressure generator after desorption is transferred to the low pressure generator of adsorption as a result of the pressure difference between two adsorption beds. It can effectively improve the adsorption/desorption quantity because of the large pressure difference between two beds, thereby enhance the cooling capacity and improving the COP. If compared with the basic cycle, the largest COP increment of the system can reach 100%.

1.4.5.5 Combined Adsorption-Absorption Refrigeration Cycle

Two-stage or three-stage combined adsorption-absorption refrigeration cycle is composed of the adsorption refrigeration system driven by a high temperature heat source and the absorption refrigeration system driven by the exhaust heat from the adsorption system. The total theoretical COP of the combination refrigeration cycle with adsorption chiller of NiCl₂-NH₃ (COP = 0.27) or two-bed zeolite–water adsorption chiller (COP = 0.50) as the first stage cycle, and absorption chiller of lithium bromide–water (COP = 0.75) as the second stage cycle is 1.52. The theoretical COP of the combination refrigeration cycle with metal hydride adsorption
chiller as the first stage cycle, and silica gel–water or lithium bromide–water absorption chiller as the second stage cycle is expected to reach 1.5. The COP of combination refrigeration cycle is high, but the system is very complicated.

1.4.5.6 Adsorption Refrigeration System Driven by Compressor

Compared with the conventional adsorption refrigeration system for which the adsorption quantity is relative to the temperature difference of the adsorption bed, the difference for this system is that the adsorption is relative to the pressure difference between two adsorption beds, which is formed by the compressor. Thus the adsorption quantity decreased with the pressure of the adsorption bed, and the temperature decreased during the desorption process, for which the cooling power was generated. The main problem for such a system is the high requirements on the pressure ratio of the compressor.

1.4.5.7 Internal Heat Recovery Process and Double Way Cycle

An internal heat recovery process is proposed by P. Neveu and J. Castaing [93]. In this cycle they used two types of salts and recovered the reaction heat of the high temperature salt as the heat source for the desorption process of the low temperature heat source. In such a way, SJTU had established the double way and multi-effect refrigeration cycle, which combined the adsorption and resorption process together for the refrigeration output, as well as combining the internal heat recovery with the sensible heat recovery processes to improve the COP, and the study indicated that the COP could be improved by more than 1 through such a novel cycle [94, 95].

1.4.6 Commercialized Adsorption Chillers

With the rapid development of the adsorption refrigeration technology, adsorption chillers appeared in the market. Nishiyodo Kuchouki Co., Ltd invented the silica gel–water adsorption chiller in 1986, and the schematic diagram was shown in Figure 1.3. The adsorption system used water for heating and cooling. HIJC Company in the United States sold such a type of

![Figure 1.3 Schematic diagram of silica gel-water adsorption system from Nishiyodo Kuchouki Co., Ltd.](image)
adsorption chillers. The chiller produced 3 °C chilling water when the heat source temperature was 50–90 °C.

The Malteser Hospital in Kammenz of Germany were the first to install a CCHP (cogeneration system for cooling, heat, and power) system for which an adsorption chiller was utilized. The system started running from May 2000 and the system diagram is shown in Figure 1.4. The heat collector of the system collected the waste heat from the fuel cell and the low grade heat from solar energy, combined with the adsorption chiller the system supplied the heating and cooling power simultaneously. The cooling power of the adsorption chiller was 105 kW. A complimentary compression chiller is also installed in the system for the regulation of the cooling power.

Macom, a Japanese company, began to produce a silica gel–water adsorption refrigeration chiller since 2003. It can obtain 14 °C chilled water when the driven temperature is 75 °C, and the COP is 0.6.

Tokai Optical Co., Ltd., in Nagoya of Japan, introduced an adsorption CCHP system powered by waste heat in April 2003. A 185 kW diesel engine is used in the system. The waste heat can supply heat, and simultaneously the refrigeration can be generated for dehumidification and cooling. By such a system the annual energy consumption could be reduced by 10%, and CO₂ emissions could be reduced by 12%.

In China, SJTU, South China University of Technology, Guangzhou Institute of Energy Conversion, Chinese Academy of Sciences, Hunan University, and so on, carried out the practical research work on the adsorption refrigeration. Adsorption chillers of series “DY” had been developed by the Hunan University, such as an ice-maker powered by the exhaust heat of the diesel engine on fishing boats and on automobiles. SJTU successfully developed small types of silica gel–water adsorption refrigerators of 10–200 kW using a heat and mass recovery process, which can be driven by the heat source with the temperature of 65 °C. The second generation of the prototype developed by SJTU in 2009 is shown in Figure 1.5. Such a chiller had been successfully utilized for the building and grain storage.

1.4.7 Current Researches on the Adsorption Theory

For physical as well as for chemical adsorption refrigeration, the research direction on the adsorption refrigeration is from the equilibrium adsorption refrigeration with uniform
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Figure 1.5 Silica gel–water adsorption refrigerator developed in China

temperature and pressure to the non-equilibrium adsorption refrigeration technology. The
dynamic features of the adsorption and desorption is more and more important for the analysis
on the adsorption refrigeration theories with the development of the heat and mass transfer
intensification technology.

For physical adsorption Critoph proposed a simplified format of the D-A equation [15,
17], for which only the temperature is considered. It is an experiential equation utilized
extensively for the equilibrium adsorption performance evaluation, but cannot be utilized for
the non-equilibrium adsorption performance analysis. For this problem Sokoda established a
model for the adsorption velocity for which the dynamic process of adsorption is considered
with the mass transfer process of the gases inside the adsorption systems, and they are:

\[
\frac{dx}{dt} = K_s a_p (x^* - x)
\]

(1.2)

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

(1.3)

where \(x^*\) is the local adsorption quantity, \(K_s a_p\) is the coefficient for the velocity of surface dif-
fusion, \(D_{so}\) is the surface diffusion coefficient, \(E_a\) is activated energy for the surface diffusion,
and \(R_p\) is the average diameter of the adsorbent granules. This equation is mainly for the silica
gel–water adsorption working pair. The equation can be utilized for other working pairs but
needs the amendment of the coefficients in the equations, such as that which E. F. Passos et al.
[12] had performed on this equation for the activated carbon-methanol working pair.

Compared with physical adsorption the chemical adsorption theories are very complex.
There are mainly three categories: local, global, and analytical models. Local models con-
sider mass and heat transfer, and kinetics of small volume that result in partial derivatives
equations, which are numerically solved. Global models consider variables and average values of reactor features such as permeability, thermal conductivity, heat capacity, and so on, for simulation. Numerical solutions for the global models give sets of differential equations. Analytical models consider average values of the variables during reaction time and these differential equations are related to the space variable only. Spinner and Rheault [96] researched non-uniform dynamics based on the study of dynamic adsorption rate. Then, based on the achievements of Spinner and Rheault, Mazet et al. [97] and Lebrun [98] amended the equation that is suggested by Tykodi [99] and Flanagan [100], it is:

$$\frac{dx}{dt} = K_i (1 - x) \exp\left(-\frac{A_0}{T}\right) \ln\left(\frac{p_c}{p_{eq}(T)}\right)$$

(1.4)

where $x$ is adsorption quantity, $\frac{dx}{dt}$ is adsorption rate, $K_i$ is dynamic coefficient, subscript $i = s$ for adsorption process, and $i = d$ for desorption process. $p_c$ is the constrained pressure of condenser and evaporator, $p_{eq}$ is equilibrium pressure, and $T$ is adsorption temperature.

Mazet makes a logarithm transformation in Equation 1.4 because the influence of $A_0$ is not great in the experiments [97]. Based on that Goetz [101] developed a model that considered the mass transfer performance inside the grain, which is

$$\frac{dN_g}{dt} = 4\pi r_c^2 K_i \left(\frac{p_c - p_{eq}(T)}{p_{eq}(T)}\right)^{Ma}$$

(1.5)

where $N_g$ is the molar adsorption quantity, $r_c$ is the diameter of reaction surface, and $Ma$ is the reaction dynamic coefficient.

Another formula [102] for the reaction rate which considered the Darcy equation for reaction surface and grain surface is

$$\frac{dx}{dt} = f(x, r_g) \left(\frac{p_c - p_i}{T_c}\right) K_n(m, c)$$

(1.6)

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

One question that comes out of the chemical adsorption theory is the models for the adsorption and desorption processes. Generally the models for adsorption are also utilized for the desorption process. Furrer once pointed out that there is a quasi-equilibrium region for the solid-gas reaction, and Goetz and Marty [101] had considered this region in his research work [103]. SJTU had studied the chemical and composite adsorption under the condition of non-equilibrium heating and cooling processes, and results showed that a serious hysteresis phenomenon exists for the adsorption and desorption processes [2]. The real refrigeration process is always under the condition of non-equilibrium states, thus such type of hysteresis needs to be considered for the chemical adsorption model.

Another question from the chemical adsorption is the difference between the chemical adsorption models and composite adsorption models. The main adsorbent inside the composite adsorbent is the chemical adsorbent, thus for the simulation of the adsorption process generally the models of chemical adsorbent are utilized for the composite adsorbent. Such a simulation is acceptable for the equilibrium process. For the non-equilibrium process the composite adsorption is complex because it includes the heat and mass transfer processes in
chemical adsorbent and porous media. In the reaction phase the volume of chemical adsorbent, as well as the density of porous additive will all be changed, and such a phenomenon will influence the adsorption performance. Thus the heat and mass transfer performances for both chemical and porous materials need to be considered for the non-equilibrium adsorption models.

To summarize the contents above, as a type of energy saving and environmental benign technology the adsorption refrigeration has received more and more attention. Quite a lot of achievements had been made by the researchers with their continuous efforts, and this has established a good foundation for further development. But there is still a long way for the extensive application of the technology. The achievements and problems in the research work will be summarized and analyzed in detail in the following chapters.

References

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