Adsorption (also called “solid sorption”) refrigeration systems use solid sorption material such as silica gel and zeolite to produce cooling effect. These systems are attracting increasing attention because they can be activated by low-grade thermal energy and use refrigerants having zero ozone depletion potential and low global warming potential. The adsorption refrigeration system has several advantages compared to the absorption refrigeration system.

Wide range of operating temperatures. A desorption systems can be activated by a heat source with a temperature as low as 50°C (122°F), while the heat source temperature for an absorption system should be at least 90°C (194°F). Also, adsorption systems have less corrosion issues for the adsorbent–refrigerant working pairs when they incorporate high temperature heat sources compared to an absorption system, while severe corrosion might occur in absorption systems when the regeneration temperature is greater than 200°C (392°F).

No crystallization issue. In the lithium bromide (LiBr)/water absorption system, there is a specific minimum solution temperature for any given LiBr solution concentration below which the salt begins to crystallize out of the solution. Crystallization results in interruption of machine operation and possible damage to the unit. By contrast, in adsorption systems the adsorbent remains in a solid state, which means no crystallization issues.

Suitability for application where serious vibration occurs. Absorption systems cannot operate normally under conditions where serious vibration occurs, such as in fishing boats and locomotives, because the absorbent in these systems, which is in a liquid state, may flow from the generator to the condenser or from the absorber to the evaporator. A desorption systems are suitable for such applications, because their adsorbents stay in a solid state.

Depending on the nature of attractive forces existing between the adsorbate and adsorbent, adsorption can be classified as physical adsorption or chemi-
cal adsorption. In physical adsorption, the forces of attraction between the molecules of the adsorbate and the adsorbent are of the Van der Waals’ type. Since the forces of attraction are weak, the process of physical adsorption can be easily reversed by heating. In chemical adsorption, the forces of attraction and chemical bonds between the adsorbate and adsorbent molecules are strong. The adsorbate and adsorbent molecules change their original state after the adsorption process, e.g., complexation occurs between chlorides and ammonia. Moreover, chemical adsorption also exhibits the phenomena of salt swelling and agglomeration, which are critical to heat and mass transfer performance. The major drawbacks of adsorption systems are their low energy efficiency, the COP (coefficient of performance: the ratio of cooling capacity to thermal energy supplied to the system) is usually less than 0.4, due to the thermal coupling irreversibility.5

Adsorbents and Refrigerants

The adsorbents used in adsorption systems are categorized as physical, chemical, or composite adsorbents, according to the nature of the forces involved in the adsorption process. The types, characteristics, advantages, and disadvantages of different adsorbents are summarized in this section. Two parameters are widely used to evaluate the performance of an adsorption system and adsorbents, namely, COP and SCP (specific cooling power: the ratio of cooling capacity to mass of adsorbent in the adsorbers).

Physical Adsorbents

The commonly used physical adsorbents for adsorption refrigeration systems are activated carbon, silica gel and zeolite. Activated carbon is a form of carbon that has been processed to make it extremely porous, and it has a large surface area available for adsorption. Methanol and ammonia are the most common refrigerants paired with activated carbon. Activated carbon–methanol is one of the most promising working pairs in practical systems because of its large adsorption quantity and low adsorption heat (about 1800 to 2000 kJ·kg–1 (773.9 to 859.8 Btu/lb)).1 Low adsorption heat is beneficial to the system’s COP because the majority of heat consumption in the desorption phase is the adsorption heat. Another advantage of activated carbon–methanol is low desorption temperature (about 100°C (212°F)), which is within a suitable temperature range for using solar energy as a heat source. However, activated carbon will catalyze methanol to decompose into dimethyl ether when the temperature is higher than 120°C (248°F).6 Therefore, typical pressures in an activated carbon–methanol system are subatmospheric, a hermetically sealed outer vessel is required.

Activated carbon–ammonia has almost the same adsorption heat as the activated carbon–methanol working pair. The main difference is the much higher operating pressure (about 1600 kPa [232 psia] when the condensing temperature is 40°C [104°F]) of activated carbon–ammonia. The high operating pressure leads to rather small pipe diameters and relatively compact heat exchangers, as compared to activated carbon–methanol. Another advantage of activated carbon–ammonia is the possibility of using heat sources at 200°C (392°F) or above.7 The drawbacks of this working pair are the toxicity and pungent smell of ammonia.

Silica gel is a granular, highly porous form of silica made synthetically from sodium silicate. For the silica gel–water working pair, the adsorption heat is about 2500 kJ/kg (1074.8 Btu/lb) and the desorption temperature could be as low as 50°C (122°F).1 Such a low desorption temperature makes it suitable for solar energy use. There is about 4% to 6% (by weight) of water connected with a single hydroxyl group on the surface of a silica atom, which cannot be removed; otherwise the silica gel would lose its adsorption capability. Thus, the desorption temperature cannot be higher than 120°C (248°F), and it is generally lower than 90°C (194°F).1 One of the drawbacks of the silica gel–water working pair is its low adsorption quantity (about 0.2 kg water/kg [0.2 lb water/lb] silica gel). Another drawback is the limitation of evaporating temperature due to the freezing point of water.

Zeolite is a type of alumina silicate crystal composed of alkali or alkali soil. The adsorption heat of zeolite–water is higher than that of silica gel–water, at about 3300 to 4200 kJ·kg–1 (1418.7 to 1805.7 Btu/lb).1 The desorption temperature of zeolite–water is higher than 200°C (392°F) due to its stable performance at high temperatures. The drawbacks of zeolite–water are the same as for silica gel–water, low adsorption quantity and inability to produce evaporating temperatures below 0°C (32°F).

Chemical Adsorbents

Chemical adsorption is characterized by the strong chemical bond between the adsorbent and the refrigerant. The chemical bond mainly includes the functions of complexation, coordination, hydrogenation and oxidation.1 The chemical adsorption reaction is represented in Equation 1:8

$$
\text{S} + \nu(G) \rightarrow \langle \text{S} \rangle + \nu \Delta H
$$

(1)

The equilibrium of this reaction is monovariant. Since the liquid–vapor equilibrium is also monovariant, the solid–gas and liquid–vapor equilibrium lines can be calculated using the Clausius-Clapeyron equation,8

$$
\ln(P_{eq}) = -\frac{\Delta H}{RT} + \frac{\Delta S}{R}
$$

(2)

$\Delta H$ is the reaction enthalpy, $\Delta S$ is the reaction entropy, $R$ is the gas constant. The most commonly used chemical adsorbent–refrigerant pair is metal chlorides and ammonia, which exhibits the complexation force. The metal chlorides include calcium chloride (CaCl2), strontium chloride (SrCl2), magnesium chloride (MgCl2), barium chloride (BaCl2), manganese chloride (MnCl2), and cobalt chloride (CoCl2), among others.
As an example, the complexation reaction of CaCl₂ and ammonia (NH₃) can be written as

$$\text{CaCl}_2 \times (n_1 - n_2) \text{NH}_3 + n_2 \text{NH}_3 \leftrightarrow \text{CaCl}_2 \times n_1 \text{NH}_3 + n_2 \Delta H \quad (3)$$

where the numbers of $n_1$ and $n_2$ could be 2, 4 and 8. The advantage of metal chloride–ammonia working pairs is the higher adsorption quantity than that of physical adsorbent–refrigerant pairs. The drawbacks of metal chloride–ammonia pairs are: 1) they require more energy to remove the adsorbed molecules than in physical adsorption, and 2) adsorption performance is degraded because of salt swelling and agglomeration in repeated adsorption/desorption processes.

**Composite Adsorbents**

The composite adsorbents (or complex compounds) are made from porous media, and chemical sorbents are commonly a combination of metal chlorides and expanded graphite, activated carbon, active carbon fiber, zeolite or silica gel. The objectives of using composite adsorbents are: 1) improve heat and mass transfer of chemical adsorbents, 2) increase the adsorption quantity of physical adsorbents. The addition of chemical sorbents to the physical adsorbents could result in higher adsorption quantity than that of physical adsorbents alone.

The main composite adsorbents–refrigerants in the recent literature can be categorized as silica gel and chloride–water, and chlorides and porous media–ammonia.

Composite adsorbents of silica gel and chloride are usually produced using the impregnation method. The silica gel is immersed in a chloride salt solution and is then dried to remove the water. The adsorption characteristics of silica gel and chloride composite adsorbents could be modified by 1) changing the silica gel pore structure, 2) changing the type of salt, and 3) changing the proportions of chloride and silica gel. Daou, et al., impregnated silica gel with calcium chloride, which improved the COP by 25% and increased the SCP by 283% compared to pure microporous silica gel.

Four types of porous media reported in the recent literature were used to produce composite adsorbents with chlorides: expanded graphite, activated carbon, and activated carbon fiber as well as vermiculite. Han, et al., measured the effective thermal conductivity and gas permeability of a composite adsorbent made from expanded graphite impregnated with MnCl₂ using the consolidation method. The measured effective thermal conductivities ranged from 14.0 to 25.6 W·m⁻¹·K⁻¹ (8.1 to 14.8 Btu/h·ft·°F) and permeability ranged from $8.1 \times 10^{-15}$ to $2.5 \times 10^{-13}$ m² (8.7 × 10⁻¹⁴ to 2.7 × 10⁻¹² ft²). Wang, et al., used the same method to produce the composite adsorbents.
adsorbent of expanded graphite and CaCl₂. Effective thermal conductivities of the expanded graphite–CaCl₂ consolidated composite adsorbent are in the range of 7.05 to 9.2 W·m⁻¹·K⁻¹ (4.07 to 5.3 Btu/h·ft·°F). The obtained results indicated that the thermal conductivity of the composite adsorbent has a strong dependence on the bulk density, the mass fraction of expanded graphite and the ammoniated state of CaCl₂. Wang, et al.,²⁰ investigated the effective thermal conductivity of a composite consolidated adsorbent of expanded graphite and activated carbon, and test results showed that its thermal conductivity could reach as high as 30 W·m⁻¹·K⁻¹ (17.3 Btu/h·ft·°F).

Adsorption Cycle Description

Basic Adsorption Cycle

A basic adsorption cycle consists of four steps (Figure 1): heating and pressurization, desorption and condensation, cooling and depressurization, and adsorption and evaporation. In the first step, the adsorber is heated by a heat source at a temperature of $T_H$. The pressure of the adsorber increases from the evaporating pressure up to the condensing pressure while the adsorber temperature increases. This step is equivalent to the "compression" in the vapor-compression cycle. In the second step, the adsorber continues receiving heat and its temperature keeps increasing, which results in the desorption (or generation) of refrigerant vapor from adsorbent in the adsorber. This desorbed vapor is liquefied in the condenser and the condensing heat is released to the first heat sink at a temperature of $T_C$. This step is equivalent to "condensation" in the vapor-compression cycle.

At the beginning of the third step, the adsorber is disconnected from the condenser. Then, it is cooled by heat transfer fluid at the second heat sink temperature of $T_M$. The pressure of the adsorber decreases from the condensing pressure down to the evaporating pressure due to the decrease in the adsorber temperature. This step is equivalent to the "expansion" in the vapor-compression cycle. In the last step, the adsorber keeps releasing heat while being connected to the evaporator. The adsorber temperature continues decreasing, which results in the adsorption of refrigerant vapor from the evaporator by adsorbent, pro-

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Advanced Adsorption Cycle
Since the efficiency of the basic adsorption refrigeration cycle is low, and the cooling output is not continuous, many advanced adsorption refrigeration cycles (such as the heat recovery cycle, mass recovery cycle, thermal wave cycle, forced convective thermal wave cycle, etc.) have been developed to improve efficiency and practicability.

The heat recovery cycle is an advanced adsorption cycle used in a system with two or more adsorbers. Figure 2 shows the heat recovery system on the P-T diagram. After the adsorption phase and desorption phase are finished in the adsorbers, the heat from the hot adsorber is transferred to the cold adsorber by circulating heat transfer fluid between them in a closed loop. The experimental results show that the COP of the system will increase by up to 25% with the heat recovery cycle.21,22

The mass recovery cycle uses refrigerant mass recovery between two adsorbers to effectively increase cooling output and COP of the system. Figure 3 presents a diagram of the mass recovery cycle of an adsorption system. In the end of the desorption–adsorption phase, the high-pressure adsorber...
is connected to the low-pressure adsorber in a closed loop. The refrigerant in the high-pressure adsorber will be re-adsorbed by the adsorbent in the low-pressure adsorber due to the pressure difference between the two adsorbers. In a mass recovery process, the adsorption quantity of adsorbent is increased, which causes the cooling capacity and COP to increase. The experimental results showed the mass recovery cycle may help obtain a COP increase of more than 10%.

The concept of thermal wave cycle, proposed by Shelton, et al., is shown in Figure 4. The heat transfer fluid circulates through four components: (1) Adsorber 1 in adsorption phase, (2) the heat source; (3) Adsorber 2 in desorption phase, and (4) heat sink. The adsorption heat released from Adsorber 1 is recovered by the heat transfer fluid and transferred to Adsorber 2, and only limited thermal energy is required from the heat source since about 65% of the total energy received by each adsorber can be internally recovered. Experimental results showed the COP of a two-bed adsorption air conditioner (zeolite–water) with thermal wave cycle was approximately 1.0 in cooling season. Critoph invented and theoretically investigated the convection thermal wave cycle, which uses refrigerant as a heat transfer medium for internal heat recovery. The simulation results predicted a COP of 0.95 for this system when the evaporating temperature and condensing temperature are 0°C and 42°C (32°F and 107.6°F), respectively.

Figure 2: Pressure-temperature diagram of heat recovery cycle.

Figure 3: Diagram of mass recovery cycle.

Figure 4: Thermal wave adsorption cycle.

Performance of Adsorption Systems

Table 1 summarizes the performance of some typical adsorption refrigeration systems that were manufactured and tested in the last 20 years for use of waste heat and solar energy. These results were obtained under various operating conditions; hence they should not be compared to one another.

However, they could be used as a reference to what can be expected from adsorption refrigeration systems.

Summary

Compared to the vapor compression refrigeration systems, adsorption systems have the following advantages: 1) they can be driven by waste heat and low-grade heat such as solar energy; 2) they use environmentally friendly fluids such as water or ammonia as refrigerants. The major drawbacks of adsorption systems are their low energy efficiency (low COP and SCP).

Silica gel–water and activated carbon–methanol are suitable working pairs for low temperature waste heat and solar energy due to their relatively low desorption temperatures. Zeolite–water, activated carbon–ammonia, and metal chlorides–ammonia, as well as composite adsorbents–ammonia can be used in adsorption systems driven by high temperature waste heat. Since the typical pressures in silica gel–water, zeolite–water, and activated carbon–methanol systems are subatmospheric, a hermetically sealed outer vessel is essential to maintain good machine performance.

The basic adsorption refrigeration cycle is an intermittent system and the cooling output is not continuous. A minimum of two adsorbers are required to obtain a continuous cooling effect (when the first adsorber is in the adsorption phase, the second adsorber is in the desorption phase). Several advanced adsorption cycles (such as heat recovery cycle, mass recov-
Advanced cycles (such as the mass recovery cycle and thermal wave adsorption cycle) have been developed to improve efficiency and practicality. Although the advanced cycles can improve the adsorption system performance, the complexity and the initial costs of the system also increase. In these advanced cycles, the mass recovery cycle has the potential to be a cost-effective way to boost the COP and SCP of the adsorption systems.

Although the adsorption refrigeration systems have several advantages over vapor compression refrigeration systems, there are several challenges (such as improvement in systems’ energy efficiency and/or reduction of manufacturing costs, advanced cycles with less thermal coupling irreversibilities, and formulation of new composite adsorbents with enhanced adsorption capacity and improved heat and mass transfer properties) to overcome before they can be considered as possible alternatives to replace the present vapor compression systems, especially in regions with abundant waste heat or solar energy resources available. These challenges also point to new research and development opportunities and leave opportunity for considerable creativity.

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Note
Figure 4 and Table 1 are reprinted from Progress in Energy and Combustion Science, 32(4), R.Z. Wang, R.G. Oliveira, “Adsorption refrigeration—An efficient way to make good use of waste heat and solar energy,” pp. 424–458 with permission from Elsevier.

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