

High-efficient thermochemical sorption refrigeration driven by low-grade thermal energy

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Thermochemical sorption refrigeration powered by low-grade thermal energy is one of the energy-saving and environment friendly green refrigeration technologies. The operation principle of sorption refrigeration system is based on the thermal effects of reversible physicochemical reaction processes between sorbents and refrigerants. This paper presents the developing study on the different thermochemical sorption refrigeration cycles, and some representative high-efficient thermochemical sorption refrigeration cycles were evaluated and analyzed based on the conventional single-effect sorption cycle. These advanced sorption refrigeration cycles mainly include the heat and mass recovery sorption cycle, double-effect sorption cycle, multi-effect sorption cycle, combined double-way sorption cycle, and double-effect and double-way sorption cycle with internal heat recovery. Moreover, the developing tendency of the thermochemical sorption refrigeration is also predicted in this paper.

sorption refrigeration, thermodynamic cycle, thermochemical, adsorption, resorption, mass recovery, heat recovery

The problems of environmental pollution and energy resource have received more and more attention as the industrial economy develops all over the world. In the last few years, the amount of energy consumption has been increasing rapidly, and energy shortage has become a major constraining factor to the economic and social development of China. The low average energy source percent population and the low energy utilization efficiency is the current energy status in China. Thus, it is crucial and urgent to improve energy utilization efficiency and develop some advanced energy-saving technology projects for China's energy development. Recently, a new energy development approach with Chinese characteristics was proposed by Jiang^[1] to achieve economic and social rapid development at the expense of low energy consumption in China. The key elements of the new energy development mainly include energy-saving, high-efficient technique, diversified development, environment protection, technology guidance and international cooperation. The new energy development mode with Chinese characteristics will become

one of the dominating strategies in China's sustainable energy development in the future.

The scientific utilization of energy is an essential solution to solve the inconsistency between the insufficient energy supply and the energy consumption. Every year, there exists an enormous amount of low-grade energy resources due to the low energy utilization efficiency in China such as the industrial waste heat, renewable energy, and exhaust gases from engines. These low-grade waste heats would become useful energy resources if they can be reutilized as efficiently as possible. However, a large amount of waste heat is usually directly released to the atmosphere or surface water without rational reutilization. This can be attributed to the lack of high-efficient energy reutilization technology for the low-grade thermal energy in China. To reduce the primary energy consumption and promote the economic and

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social sustainable development, it is desirable to recycle these low-grade waste heats and improve the energy utilization efficiency by developing some advanced energy systems, such as the distributed energy system and the advanced integrated energy technologies.

The exploitation and utilization of primary energy resource promoted the economic development and it also caused the serious ecological problems of the ozone depletion potential (ODP) and the global warming potential (GWP). The chlorofluorocarbons (CFCs) and the hydrochlorofluorocarbons (HCFCs), widely used in refrigeration, air conditioning and heat pump equipment, are the major contributors to the greenhouse effect and the depletion of ozone layer. In consideration of the environment pollution and energy shortage, more and more attentions is focused on the study of new environment friendly refrigerants and the development of high-efficient refrigeration systems in recent years. Thus, increasing recognition of environmental problems associated with CFCs and HCFCs has opened favorable opportunities for the development of green refrigeration technologies. As one of the environment friendly refrigeration technologies, solid-gas sorption refrigeration has been regarded as an effective energy saver to utilize low-grade thermal energy or renewable energy for useful cooling.

Solid-gas sorption refrigeration is a heat-powered green refrigeration technology, and it has a number of advantages in comparison with the conventional heat pumps or refrigeration machines. For example, in comparison with the vapor compression refrigeration systems, solid-gas sorption systems have zero ozone depletion potential (ODP) as well as zero global warming potential (GWP) due to employing environment friendly substance as refrigerant (such as water, methanol, ammonia, etc.). Moreover, these systems can utilize effectively the low-grade waste heat or renewable energy as the main driving energy and thus have a large energy-saving potential^[2]. When compared with the existing heat-powered liquid-gas absorption refrigeration systems, solid-gas sorption systems have a wider range of working temperature and have few problems of corrosion and crystallization. Moreover, energy storage capacity is much higher than the liquid absorption heat pumps due to larger reaction heat, and the heat /cold can be stored for longer time periods with low energy losses. In addition, solid sorption refrigeration systems can be applied to more extensive locations owing to their high

reliability as compared with the liquid absorption refrigeration systems, and these machines can work as ice-making for fish boats and air-conditioning for automobiles by utilizing exhaust gases from engines for useful cooling. Due to the above-mentioned advantages, solid sorption refrigeration has been considered as an important project by the International Energy Agency in its Heat Pump Program in 2007.

For solid sorption refrigeration systems, the working performance is mainly dependent on the sorption material, the heat and mass transfer performance inside the sorption bed and the sorption thermodynamic refrigeration cycle^[3]. The solid sorption refrigeration can be divided into physical sorption refrigeration and thermochemical sorption refrigeration in terms of the constraining force during the adsorption process. The working principle of the former sorption is based on the Van der Waals force between the sorbent and the refrigerant, and the adsorption heat of the sorbent is almost equal to the condensation heat of the refrigerant. For the thermochemical sorption refrigeration, the operation principle is based on the thermal effect of reversible chemical reaction between the reactive sorbent and the refrigerant, and the adsorption heat of the sorbent is higher than the condensation heat of the refrigerant. Usually, chemical working pairs have the advantages of large sorption capacity and high volume cooling density over physical adsorbents. The most investigation of the thermochemical refrigeration systems is focused on the metal chlorides-ammonia sorption working pairs, and these thermochemical sorption systems have received considerable attention in recent years^[4-12].

However, low system performance is the biggest drawback for solid sorption refrigeration machine in terms of specific cooling power (SCP) and coefficient of performance (COP), which has been still limiting the extensive application of sorption refrigeration technology. Besides the basic intermittent sorption thermodynamic refrigeration cycle, many advanced sorption thermodynamic cycles have been proposed and investigated to improve the performance of sorption refrigeration system. The representative cycles mainly include the thermal wave sorption cycle^[13], the forced convection sorption cycle^[14], the cascading sorption cycle^[15], the mass recovery cycle^[16], the heat and mass recovery sorption cycle^[17], and the multi-stage sorption cycle^[18], etc. The above-mentioned sorption refrigeration cycles were conducted on the physical sorption working pairs,

and the detailed reviews of these different physical thermodynamic refrigeration cycles were presented in the reference [19]. However, little work has been performed on different thermochemical sorption refrigeration thermodynamic cycles. Due to the different sorption principle between the chemisorption and the physisorption, solid sorption refrigeration machines have different working performances when these advanced physisorption thermodynamic refrigeration cycles are applied to the thermochemical sorption refrigeration systems. For example, the mass recovery thermodynamic cycle can be used to enlarge the cycle mass of the refrigerant for physisorption machine, while it would become useless for the chemisorption machine based on the single chemical plateau reaction between the sorbent and the refrigerant; the multi-stage thermodynamic cycle can reduce the regeneration temperature of physisorption machine, but it can not decrease the regeneration temperature of the chemisorption machine based on the single chemical plateau reaction; and the resorption thermodynamic cycle is feasible in the thermochemical sorption system while it would not take place in the sorption system using physical sorption working pair.

In the paper, several different advanced thermochemical sorption refrigeration cycles are presented. Some representative high-efficient thermochemical sorption refrigeration cycles, such as the heat and mass recovery sorption cycle, double-effect sorption cycle, multi-effect sorption cycle, combined double-way sorption cycle, and double-effect and double-way sorption cycle with internal heat recovery, are also evaluated and analyzed based on the conventional thermochemical sorption cycle.

1 Thermochemical sorption refrigeration cycle

Chemisorption is different from physisorption because the former is monovariant and the latter is bivariant, and the schematic diagram of the physisorption refrigeration cycle and the thermochemical sorption refrigeration cycle are shown in Figure 1 and Figure 2, respectively.

For the physisorption refrigeration cycle (Figure 1), the working region between the sorbent and the refrigerant ranges from the 0 % equilibrium line to the 100 % equilibrium line during both the heating desorption and the cooling adsorption phases. Moreover, the working pressure and the working temperature is not the func-

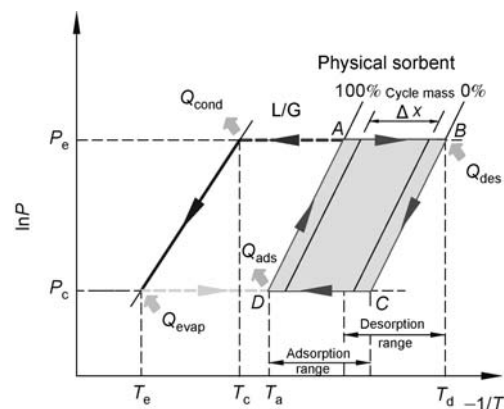


Figure 1 Schematic diagram of physical sorption refrigeration cycle.

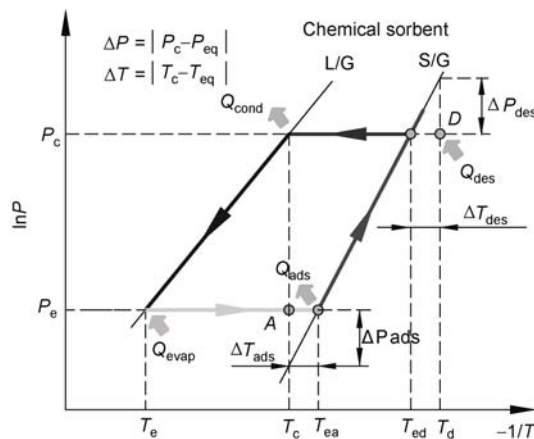
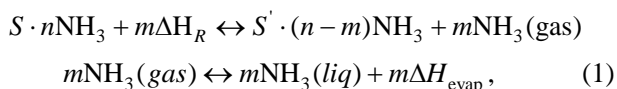


Figure 2 Schematic diagram of thermochemical sorption refrigeration cycle.

tional equation of one variable, and the adsorption or desorption process occurs when the temperature or pressure locates in the working region. However, in the thermochemical sorption cycle, the relation between the sorbent and the refrigerant is the functional equation of one variable, which means that for a given working temperature, the relevant working pressure is automatically specified. The working region between the sorbent and the refrigerant is the solid-gas equilibrium line. During the cooling adsorption phase, the synthesis reaction between the sorbent and the refrigerant takes place when the constraining temperature/pressure is lower than the solid-gas equilibrium temperature/pressure at the evaporation pressure of the refrigerant. Whereas, when the constraining temperature/pressure is higher than the solid-gas equilibrium temperature/pressure at the condensation pressure of the refrigerant, the decomposition reaction between the sorbent and the refrigerant occurs during the heating desorption phase. Thus, it indicates that the driving equilibrium temperature/pressure

drop is the only contributor to the chemical reaction between the sorbent and the refrigerant in the thermochemical sorption refrigeration system. Moreover, the higher the driving equilibrium drop, the faster is the chemical reaction rate.

The operation principle of the thermochemical sorption refrigeration is based on the thermal effect of the reversible chemical reaction between the sorbents and the refrigerants. For the metal chlorides–ammonia chemisorption working pairs, the chemical reaction equation is as follows:



in which S is the metal chloride, ΔH_R is the enthalpy of transformation (J/mol), ΔH_{evap} is the evaporation enthalpy of the refrigerant (J/mol), n , m is the mole number of the refrigerant (mol).

The thermochemical sorption thermodynamic cycle can be divided into adsorption cycle (Figure 3) and resorption cycle (Figure 4) in terms of the different mode of cold production. The operation principle of the adsorption refrigeration cycle is based on the evaporation process, and the useful cold is produced by the vaporization heat of the refrigerant during the adsorption phase, and the synthesis heat released by the sorbent is removed by a heat sink. During the regeneration phase, the decomposition heat required by the sorbent is supplied by an external low-grade heat source (such as solar energy, industrial waste heat, and exhaust gas). The refrigerant gas desorbed by the sorbent is transferred to the condenser and then flows into the evaporator.

For solid-gas chemical sorption machine based on the resorption thermochemical process (Figure 4), the evaporator/condenser is replaced by another solid-gas

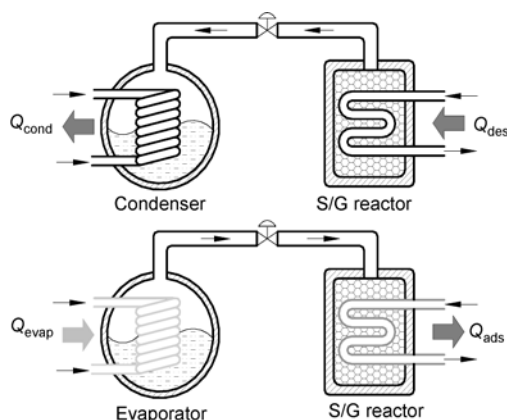


Figure 3 Thermochemical sorption refrigeration cycle.

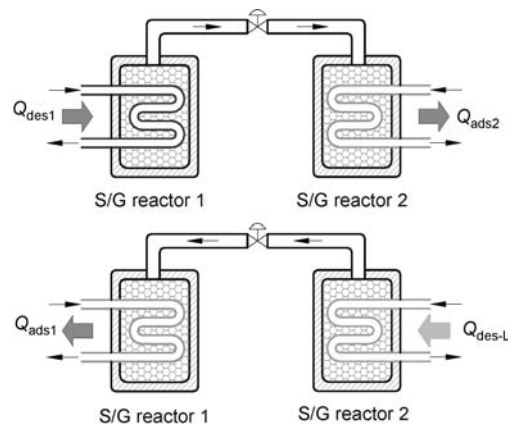


Figure 4 Thermochemical resorption refrigeration cycle.

reactor. Its working principle is based on the different thermochemical equilibrium characteristics for different reactive sorbents. To accomplish the resorption refrigeration, at least two different sorbents are employed in a thermochemical resorption cycle. It consists of a solid-gas reactor 1 operating at a high temperature (R1) and a solid-gas reactor 2 operating at a low temperature (R2). The former S/G reactor is filled with a reactive sorbent that has higher equilibrium temperature than the reactive sorbent filled inside the latter S/G reactor at the same constraint pressure. Thus, the two kinds of reactive sorbents are referred as high-temperature sorbent (HTS) and low-temperature sorbent (LTS), respectively. During the resorption refrigeration phase, the refrigerant is transferred from the LTS reactor to the HTS reactor due to the pressure difference between the two S/G reactors, and the decomposition reaction heat consumed by the LTS at a low temperature is utilized to produce a useful cooling-effect (desorption cooling). During the regeneration phase of the HTS, the HTS reactor is heated by an external heat source at a high temperature to desorb the refrigerant to the LTS reactor.

For the same amount of refrigerant adsorbed and specified heat input, the resorption process could achieve a higher theoretical cooling capacity and COP in comparison with the adsorption process with a liquid-gas evaporator. This is because the reaction enthalpy of the sorbent is almost 2–3 times the vaporization enthalpy of the refrigerant. However, the resorption refrigeration machine usually has a low chemical reaction rate due to the low driving equilibrium pressure drop, and thus the long cycle time could reduce the system performance. In addition, the thermal capacity of the metallic parts of the reactor usually has a strong influence on

the working performance of the resorption refrigeration machine.

The Clapeyron diagram of different metal chlorides-ammonia is shown in Figure 5, in which the solid-gas and liquid-vapour thermodynamic equilibrium lines are calculated by the following equation^[20]:

$$\ln(P_{\text{eq}}) = -\frac{\Delta H}{RT} + \frac{\Delta S}{R}, \quad (2)$$

in which P_{eq} is the thermodynamic equilibrium pressure (Pa), T_{eq} is the thermodynamic equilibrium temperature ($^{\circ}\text{C}$), ΔH_{R} is the enthalpy of transformation (J/mol), ΔS is the entropy of transformation (J/mol $\cdot^{\circ}\text{C}$).

It can be seen that the different sorbents have different sorption characteristics, and the dynamical equilibrium temperatures and pressures are largely different at the same heat sink temperature, condensation pressure and evaporation pressure. As shown in Figure 5, the condensation pressure is about 1.2×10^3 kPa when the condensation temperature of ammonia is 30°C . To regenerate the sorption working pair during the decomposition reaction phase, the sorbent is heated by an external heat source at a high temperature. In order to keep a driving temperature drop, the sorbent should have a constraining temperature higher than its dynamical equilibrium temperature at the condensation pressure of ammonia. For different reactive sorbents, it was observed in Figure 5 that the required constraining temperatures are different due to the different sorption characteristics. Whereas, these different sorbents also have different dynamical equilibrium temperatures dur-

ing the adsorption refrigeration phase at the same evaporation pressure. In addition, the synthesis temperature is usually limited by the heat sink temperature in the case of lower evaporation temperature.

The sorption working pairs should be selected according to the available heat source temperature and the working evaporation temperature in the thermochemical sorption refrigeration systems. For the sorption machines using the metal chlorides-ammonia sorption working pairs, they can utilize effectively the low-grade heat source temperatures between 60°C and 500°C , and the lowest evaporation temperature could reach -70°C . The detailed reaction parameters of chemisorption working pairs were presented in the references [20, 21].

2 Heat and mass recovery thermochemical sorption refrigeration cycle

Low system performance is the serious drawback for solid sorption refrigeration technology, and this could be attributed to the loss of the large amount of thermal energy during the interchanging process between the heating desorption and the cooling adsorption phases^[22]. To improve system performance of the sorption machine, some better energy management strategies were proposed and investigated to reduce the heat consumption by employing the heat recovery process. The previous studies on heat recovery technique were mainly focused on the physical sorption machines, in which the sensible heat of the sorption bed and the partial adsorption heat were recovered from the high-temperature bed to the

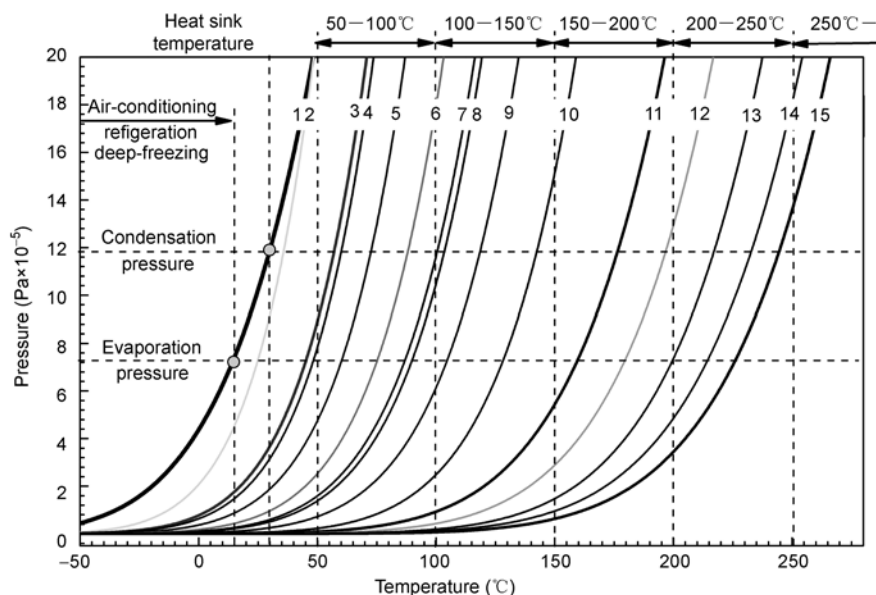


Figure 5 Reaction equilibrium lines of the conventional sorption working pairs using metal chlorides-ammonia. 1-NH₃; 2-PbCl₂ (8/3.25); 3-BaCl₂ (8/0); 4-LiCl (4/3); 5-AgCl (3/1.5); 6-CaCl₂ (8/4); 7-SrCl₂ (8/1); 8-CaCl₂ (4/2); 9-CdCl₂ (6/2); 10-ZnCl₂ (6/2); 11-MnCl₂ (6/2); 12-FeCl₂ (6/2); 13-CoCl₂ (6/2); 14-MgCl₂ (6/2); 15-NiCl₂ (6/2).

low-temperature bed due to the temperature difference during the switching process^[13–15,23]. The decrease in heat consumption enhanced the working performance of sorption refrigerator.

Another possibility to improve the sorption performance is the utilization of mass recovery technique^[16,24–27]. During the mass recovery process, the refrigerant gas is transferred from the high-pressure bed to the low-pressure bed due to the pressure difference. The cycle mass of the refrigerant could be enlarged by the mass recovery process, and thus the sorption cooling capacity was also improved. Especially, a combined physical sorption refrigeration cycle was developed by the research team in Shanghai Jiao Tong University by combining the heat and mass recovery processes, and the results showed that the combination of both heat and mass recovery processes could improve the system performances obviously^[17].

Due to the monovariant characteristics of chemical reaction, the mass recovery can not enlarge the cycle mass of the refrigerant for the chemisorption machine based on the single chemical plateau reaction between the sorbent and the refrigerant. However, for the chemisorption machine based on the two- or multi-chemical plateau reactions such as the calcium chloride-ammonia working pair (Figure 6), the research results showed that the mass recovery is effective to improve the cycle mass by changing the driving pressure drop^[28]. To enhance the cooling capacity, a mass recovery sorption thermodynamic cycle was investigated in the thermochemical sorption system using calcium chloride-ammonia working pair^[28,29]. Later, both mass recovery and heat recovery were employed to improve sorption per-

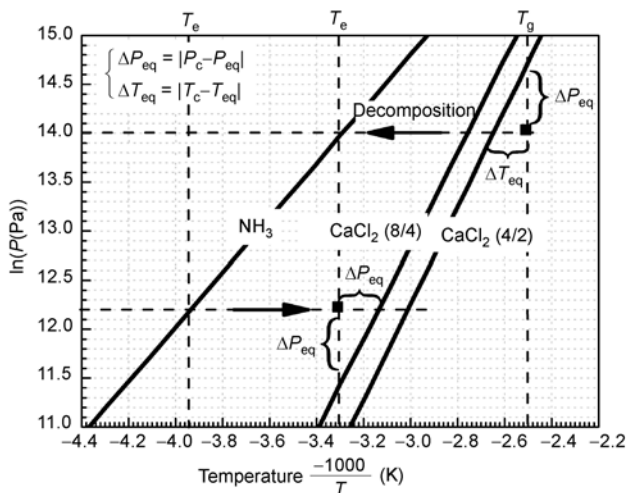


Figure 6 Thermodynamic equilibrium lines for the chemical reaction between calcium chloride and ammonia.

formance in the heat and mass recovery thermochemical sorption refrigeration cycle, in which the function of heat recovery is to recover the thermal energy due to the temperature difference between the two reactors, while mass recovery, due to the pressure difference between the two reactors, can increase the cycle mass of the refrigerant^[30]. The effect of the different mass recovery strategies on system performance of the sorption machine was also investigated by optimization analysis^[31].

The working principle of the heat and mass recovery thermochemical sorption cycle is shown in Figure 7. In comparison with the basic sorption refrigeration cycle, the heat and mass recovery sorption cycle has a larger working area, which means that the heat and mass recovery cycle has a better thermal dynamic performance. For the basic sorption cycle (A–B–C–D), the working modes of different reactors are directly interchanged to the next cycle when the high-temperature reactor finishes the decomposition reaction and the low-temperature reactor completes the synthesis reaction. However, some reactive sorbents inside the reactors could not take part in the chemical reaction due to the limitation of the heat and mass transfer in sorption refrigeration machine, and this could have a negative influence on system performance.

For the conventional heat and mass recovery sorption cycle (A–b–c–B–m–C–e–f–D–n–A), the mass recovery and heat recovery processes are employed to reduce the heat consumption and enlarge the cycle mass respectively during the switching phase. The increase in the driving equilibrium drop promotes the chemical reaction

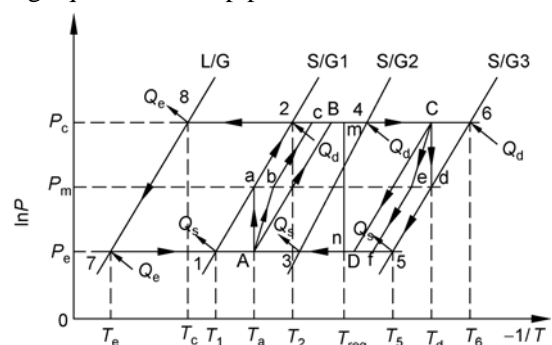


Figure 7 The working principle of the heat and mass recovery thermochemical sorption cycle. L/G: liquid /gas phase. S/G: solid/ gas reaction; 1–2: for equilibrium reaction $\text{CaCl}_2 \cdot 4\text{NH}_3 \leftrightarrow \text{CaCl}_2 \cdot 8\text{NH}_3$, 3–4: for equilibrium reaction $\text{CaCl}_2 \cdot 2\text{NH}_3 \leftrightarrow \text{CaCl}_2 \cdot 4\text{NH}_3$, 5–6: for equilibrium reaction $\text{CaCl}_2 \leftrightarrow \text{CaCl}_2 \cdot 2\text{NH}_3$. A–B–C–D–A: basic cycle; A–B–C–D: conventional heat and mass recovery cycle; A–a–2–B–m–C–d–5–D–n–A: novel heat and mass recovery cycle. A–b, C–e: adiabatic mass recovery process; A–a, C–d: isothermal mass recovery process.

rate between the sorbent and the refrigerant. Thus, system performance could be improved in the heat and mass recovery sorption cycle when compared with the basic sorption cycle.

However, there are no heating and cooling processes during the mass recovery phase in the conventional heat and mass recovery sorption cycle. At the end process of the mass recovery phase, the transferred rate of the refrigerant gas would decrease because the decomposition heat consumed by the high-pressure reactor can not be supplied and the synthesis heat released by the low-pressure reactor can not be removed^[24]. In order to further improve the cooling power, it is necessary to supply the decomposition heat continuously by the heat source and remove the synthesis heat continuously by the heat sink during the mass recovery phase.

In comparison with the conventional heat and mass recovery sorption cycle, the cycle mass can be improved in the novel heat and mass recovery sorption cycle (A-a-2-B-m-C-d-5-D-n-A), in which the mass recovery process is carried out before the heat recovery process, and the desorber is heated and adsorber is cooled during the mass recovery phase, and thus the synthesis and decomposition processes would be more completed. Moreover, the additional heat consumption during the mass recovery phase can be recovered timely by the subsequent heat recovery process. Thus, the novel heat and mass recovery sorption cycle is more beneficial to improving system performance of the thermochemical sorption machine when compared with the conventional heat and mass recovery sorption cycle.

Figure 8 shows the photograph of the heat and mass recovery sorption machine based on the multifunctional heat pipe technology. It consists mainly of two solid-gas reactors, a water cooler, a condenser, a refrigerant vessel, an ice-making (evaporator), waste heat source equipment, and multifunctional heat pipes. An electrical-powered heater was used to simulate the low-grade waste heat source/exhaust gas. The calcium chloride-activated carbon composite sorbent was utilized as the reactant and ammonia was used as the refrigerant.

The schematic diagram of the heat recovery processes between the two reactors is shown in Figure 9. During the first heat recovery process (Figure 9(a)), reactor B will be interchanged from the decomposition to the synthesis mode and reactor A will be interchanged from the synthesis to the decomposition state. The sensible heat and the partial reaction heat of reactor B are recovered

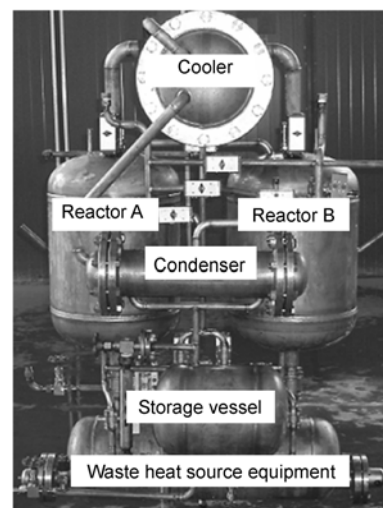


Figure 8 Photograph of the heat and mass recovery sorption machine based on the multifunctional heat pipe.

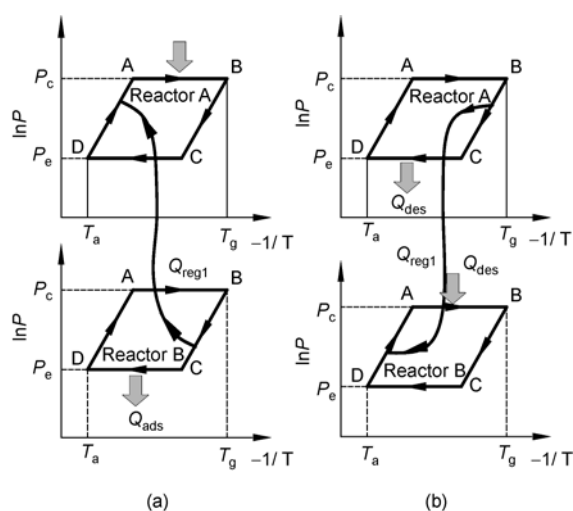


Figure 9 Schematic diagram of heat recovery processes between the two solid-gas reactors.

from the high-temperature reactor B to the low-temperature reactor A due to the temperature difference between the two reactors during the switching process. In the similar approach, the sensible thermal energy and the partial reaction heat are recovered from the high-temperature reactor A to the low-temperature reactor B during the second heat recovery process (Figure 9(b)).

To avoid the corrosion between the reactor and the low-grade thermally energy (such as waste heat, exhaust gas) and the corrosion between the reactor and the cooling working fluid (such as seawater), multifunctional heat pipe was employed to improve the reliability of the sorption machine, and water was used as the heat pipe working fluid^[32]. The research results showed that the multifunctional heat pipe could enhance the heat transfer

performance, and thus heightening energy utilization efficiency and improving cooling power^[33,34].

The working principle of the multifunctional heat pipe is shown in Figure 10. For the test unit, the heating, cooling and heat recovery processes between the two reactors are performed by the multifunctional heat pipe. During the heating process, the reactor is heated by the heat pipe in which the waste heat source serves as an evaporator and the desorber heat exchanger (DHE) serves as a condenser. During the cooling process, the reactor is cooled by the heat pipe in which the adsorber heat exchanger (AHE) serves as an evaporator and the water cooler serves as a condenser. During the heat recovery process, the cold bed is pre-heated and the hot bed is pre-cooled by the heat pipe in which the high-temperature DHE serves as an evaporator and the low-temperature AHE serves as a condenser. The detailed operation was described in the reference [31].

In comparison with the conventional sorption machine, the heat pipe type sorption machine has many advantages^[35]. Firstly, the heat recovery efficiency can be improved by the heat pipe technology; Secondly, multifunctional heat pipe can simplify the configuration of the sorption machine because the heat transfer fluid can share one heat exchanger coil during the heating, cooling and heat recovery processes, and thus it can reduce the proportion of thermal capacity of the metallic

part of the reactor; Thirdly, the corrosion of the reactor by the low-grade waste heat and the corrosion of the reactor by seawater can be avoided by employing the heat pipe technology. Moreover, it can reduce the moving parts and improve the reliability of the sorption machine.

The working performance of the heat and mass recovery thermochemical sorption machine is shown in Table 1. It can be seen that the thermochemical sorption cycle with heat and mass recovery processes could improve the ice production, specific cooling power (SCP) and coefficient of performance (COP) when compared with the basic sorption cycle, and the improvements in all values were more than 11 %. At the optimal mass recovery time of 40 s, the COP improvements in the conventional and novel heat and mass recovery cycles were 43.8 % and 68.7 % respectively in comparison with the basic sorption cycle. Moreover, the novel heat and mass recovery sorption cycle can further improve the ice production, SCP and COP when compared with the conventional heat and mass recovery sorption cycle, and the SCP and COP improvements were higher than 17 %. The additional heat consumption during the mass recovery phase was recovered effectively by the subsequent heat recovery process.

It can be concluded that novel heat and mass recovery processes are more beneficial to improving the per-

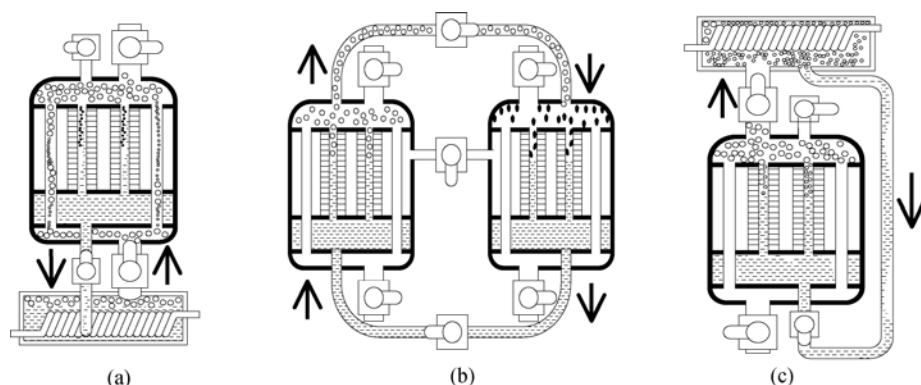


Figure 10 The working principle of the multifunctional heat pipe for the sorption machine with heat and mass recovery processes^[30]. (a) Heat pipe type heating process; (b) heat pipe type heat recovery process; (c) heat pipe type cooling process.

Table 1 The working performance of the heat and mass recovery thermochemical sorption machine^[31]

Time t (s)	Heat and mass recovery	Ice production Q_i /(kg/h)	SCP/(W/kg)	SCP improvement Δ (%)	COP	COP improvement Δ (%)
0	Basic cycle	16.58	329.1	–	0.16	–
20	Conventional heat and mass recovery cycle	18.71	367.5	11.7	0.21	31.3
	Novel heat and mass recovery cycle	22.59	442.8	34.6	0.25	56.3
40	Conventional heat and mass recovery cycle	20.82	409.1	24.3	0.23	43.8
	Novel heat and mass recovery cycle	24.81	486.5	47.8	0.27	68.7

formance of the sorption refrigeration system compared with the conventional heat and mass recovery processes.

3 Double- and multi-effect thermochemical sorption refrigeration cycle with internal heat recovery

3.1 Double-effect thermochemical sorption cycle

In the above-mentioned heat and mass recovery thermochemical sorption cycle, the reactors are filled with the same reactive sorbent. The most amount of the reclaimable thermal energy is the sensible heat of the metallic part of the reactor, and only small partial reaction heat of the sorbent can be reutilized during the heat recovery process due to the limitation of heat transfer in the sorption machine.

To order to further improve the energy reutilization efficiency, Neveu and Castaing^[36] proposed a double-effect thermochemical sorption refrigeration cycle using two different reactive sorbents. In this case, an internal heat recovery process was used to reclaim the reaction heat of one sorbent for the regeneration of the other sorbent.

The operation principle and Clapeyron diagram of the double-effect thermochemical sorption refrigeration cycle with internal heat recovery process is shown in Figure 11. The component of the basic system consists of two solid-gas reactors, a condenser and an evaporator. Two different reactive sorbents are filled with solid-gas reactor 1 (R1) and reactor 2 (R2). S/G1 is the equilibrium line of the high-temperature sorbent (HTS) inside R1 and S/G2 is the equilibrium line of the middle-temperature sorbent (MTS) inside R2. The HTS has a higher equilibrium temperature than the MTS at the same con-

straint pressure.

During the regeneration process of the HTS reactor, the decomposition heat consumed by the HTS is supplied by an external heat source. At the same time, the MTS reactor is cooled by a heat sink to adsorb the refrigerant from the evaporator. Secondly, the working modes of the two reactors are interchanged. An internal heat recovery process is employed between the two reactors to improve the energy utilization efficiency, in which the reaction heat released by the HTS during the synthesis phase is used to regenerate the MTS reactor. During the regeneration process of the MTS, the additional heat consumption from the external heat source is not required because the synthesis heat released by the HTS is usually higher than the decomposition heat consumed by the MTS.

During one double-effect sorption cycle, two useful cold produced by the evaporation heat of the refrigerant could be obtained at the expense of only one high-temperature heat input for HTS reactor. Thus, the double-effect sorption cycle with internal heat recovery process can improve the system performance in comparison with the conventional heat recovery sorption cycle. Later, Sorin et al.^[37] developed a new heat recovery method where both the reaction heat of the reactant and the condensation heat of the refrigerant were reclaimed to regenerate the second reactant, but the operating pressure was very high, which caused large proportion of the thermal capacity of the metallic part of the reactor and reduced the reliability of the sorption machine.

Moreover, based on the basic thermochemical resorption refrigeration cycle^[38–41], double-effect thermochemical resorption refrigeration systems can also benefit from the internal heat recovery as proposed by Spin-

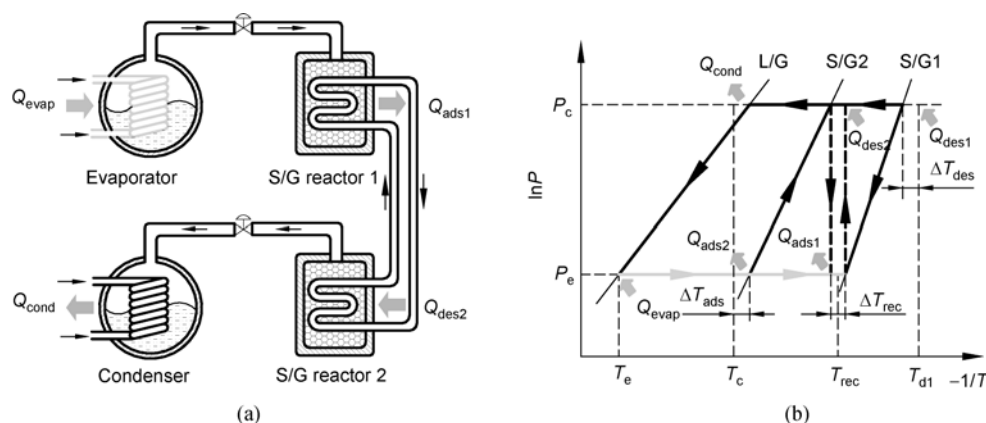


Figure 11 The operation principle and Clapeyron diagram of the double-effect thermochemical sorption refrigeration cycle with internal heat recovery processes. (a) Working principle; (b) Clapeyron diagram.

ner^[42] and Goetz^[43]. To accomplish such a task, four reactors and three different reactive sorbents were used. The reaction heat of the reactor filled with a high-temperature sorbent was utilized in the regeneration process of the reactor filled with a middle-temperature sorbent. The operation principle and Clapeyron diagram of the double-effect thermochemical resorption refrigeration cycle with internal heat recovery process is shown in Figure 12.

Different from the double-effect sorption cycle, it can be seen that the condenser and evaporator are replaced by two low-temperature reactors in the double-effect resorption cycle. To produce the cold continuously, three different reactive sorbents are filled with four solid-gas reactors. Reactor 1 (R1) is filled with a high-temperature sorbent (HTS) and reactor 2 (R2) is filled with a middle-temperature sorbent (MTS). Reactor 3 (R3) and reactor 4 (R4) are filled with low-temperature sorbents (LTS). S/G1 is the equilibrium line of the high-temperature sorbent (HTS) inside R1, S/G2 is the equilibrium line of the middle-temperature sorbent (MTS) inside R2 and S/G3 is the equilibrium line of the low-temperature sorbent (LTS) inside R3 and R4. The HTS has the highest equilibrium temperature and the LTS has the lowest equilibrium temperature at the same constraint pressure among these different reactive sorbents.

During the first phase, the HTS reactor is heated by an external heat source to desorb the refrigerant to LTS reactor 3. At the same time, a resorption refrigeration process occurs between the MTS reactor and the LTS reactor 4, and the decomposition heat consumed by the LTS during the regeneration process is used to produce the first cooling-effect. During the second phase, the working modes of the different reactors are interchanged.

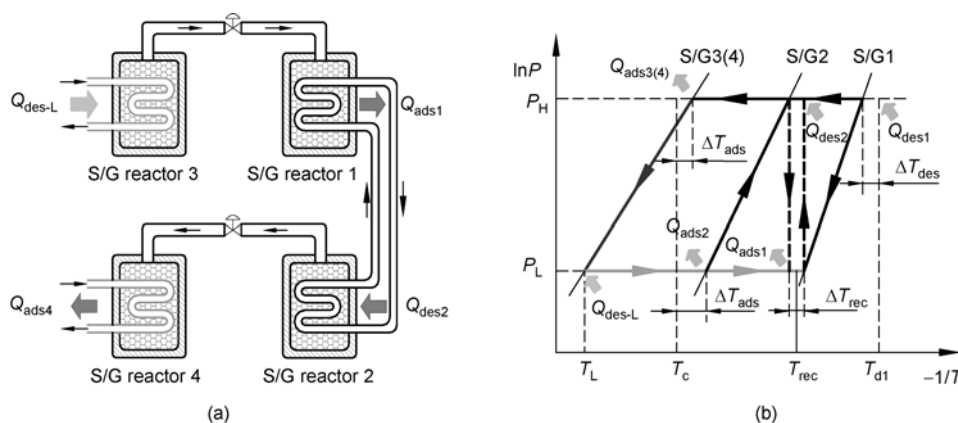


Figure 12 The operation principle and Clapeyron diagram of the double-effect thermochemical resorption refrigeration cycle with internal heat recovery process. (a) Working principle; (b) Clapeyron diagram.

A resorption refrigeration process occurs between the HTS reactor and the LTS reactor 3 in which the second cooling-effect is produced by the reaction heat consumed by the LTS. Simultaneously, the reaction heat released by the HTS reactor is recovered to regenerate the MTS reactor during the internal heat recovery process. The decomposition heat consumed by the MTS can be supplied completely by the synthesis heat released by the HTS. The refrigerant desorbed from the MTS reactor flows into LTS reactor 4.

Thus, two cold productions can also be obtained at the expense of only one high-temperature heat input for HTS reactor during one double-effect resorption cycle. However, in such double-effect resorption cycle, the cooling-effects are produced by the reaction heat consumed by the LTS during the decomposition phase. The double-effect resorption cycle with internal heat recovery process can improve the system performance in comparison with the conventional heat recovery sorption cycle.

For the double-effect thermochemical cycle, the internal heat recovery is mainly dependent on the thermodynamic characteristic of different reactive sorbents. The internal heat recovery is only possible if the total amount of heat released by one reactor during the synthesis phase is equal or higher than the total heat input required during the regeneration phase of the other reactor. To achieve the heat recovery process between the different reactors, the working temperature and the amount of energy released or consumed by the sorbents must be matched during the chemical reaction process. The synthesis heat released by the high-temperature sorbent should be higher than the decomposition heat consumed by the middle-temperature sorbent, and the

adsorption temperature of the HTS should be higher than the regeneration temperature of the MTS.

The feasibility of the internal heat recovery processes between different reactors was evaluated. During the internal heat recovery process, the heat production and the heat consumption with different mass ratio (R) for the double-effect thermochemical cycle is showed in Figure 13. The ratio (R) is defined as the mass ratio between the metallic part of the reactor and the reactive sorbent. If R is equal to 0, it means that the effect of the metallic part of the reactor on the working performance would not be considered in the sorption system, and this is the ideal working condition. In addition, parameter R can be used to evaluate the optimization design of the reactor. The lower the mass ratio R , the smaller is the proportion of thermal capacity of the metallic part, which indicates that the additional heat consumption of the metal would become low.

For both groups of the sorption working pairs ($\text{MnCl}_2\text{-SrCl}_2\text{-NH}_3$, $\text{NiCl}_2\text{-SrCl}_2\text{-NH}_3$) analyzed, MnCl_2 and NiCl_2 is the high-temperature sorbent (HTS), and SrCl_2 is used as the middle-temperature sorbent (MTS). The decomposition heat consumed by the HTS is supplied by an external heat source during the regeneration process of the HTS, and the decomposition heat consumed by the MTS is supplied by employing the thermal energy recovery technology.

It can be seen that the amount of the reaction heat produced by the HTS is higher than the reaction heat consumed by the MTS at different mass ratio R during the internal heat recovery process. Such a result suggests that the internal heat recovery process is feasible and the decomposition reaction heat consumed by the MTS

during the regeneration phase can fully be supplied from the reaction heat released by the HTS.

3.2 Multi-effect thermochemical sorption cycle

Multi-effect thermochemical sorption refrigeration cycle was proposed to further improve system performance by employing two internal heat recovery processes. In such multi-effect cycle, three cold productions could be obtained at the expense of only one high-temperature heat input during one cycle. The operation principle and Clapeyron diagram of the multi-effect thermochemical sorption refrigeration cycle with two internal heat recovery processes is shown in Figure 14.

It mainly consists of three solid-gas reactors, a condenser and an evaporator. In order to implement the two internal heat recovery processes among the reactors, three kinds of reactive sorbents are utilized in the multi-effect sorption cycle. One reactor is filled with a high-temperature sorbent (HTS), the second reactor is filled with a middle-temperature sorbent (MTS), and the third reactor is filled a low-temperature sorbent (LTS). The operating mode of the multi-effect sorption cycle can be divided into two phases:

In the first phase, decomposition reaction of the HTS in reactor 1 occurs by supplying a heat input from an external heat source at a high temperature, and the desorbed refrigerant flows into the evaporator. At the same time, the MTS in reactor 2 is cooled by a heat sink to adsorb the refrigerant from the evaporator, and the evaporation heat of the adsorbed refrigerant produces the first cooling-effect. During this phase, an internal heat recovery process between the MTS and the LTS occurs, where the reaction heat released during the syn-

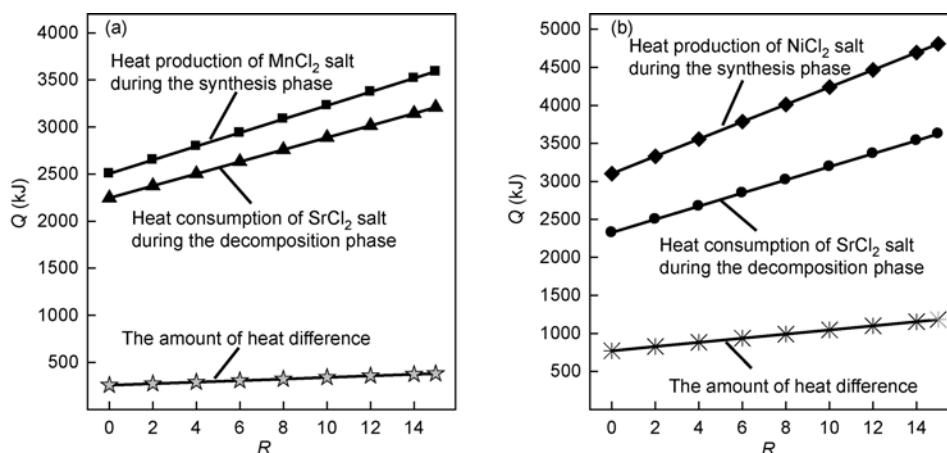


Figure 13 Heat production and heat consumption for double-effect thermochemical cycle during the internal heat recovery process. (a) Working pair: $\text{MnCl}_2\text{-SrCl}_2\text{-NH}_3$; (b) working pair: $\text{NiCl}_2\text{-SrCl}_2\text{-NH}_3$.

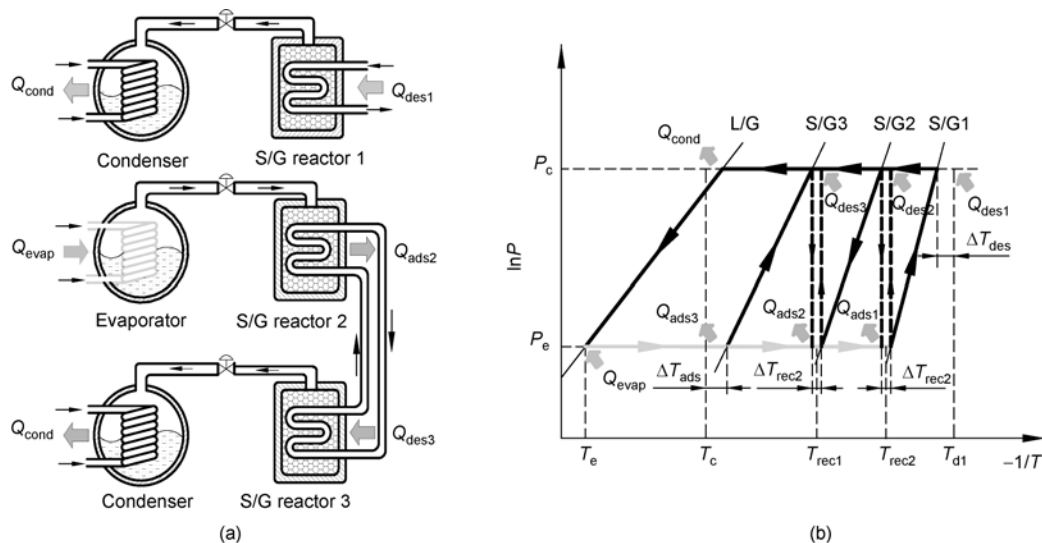


Figure 14 The operation principle and Clapeyron diagram of the multi-effect thermochemical sorption refrigeration cycle with two internal heat recovery processes. (a) Working principle; (b) Clapeyron diagram.

thesis reaction of the MTS is used to regenerate the LTS in reactor 3.

During the second phase, the working modes of the reactors are interchanged. Both the HTS and the LTS reactors perform adsorption while the MTS reactor undergoes desorption. The LTS in reactor 3 adsorbs the refrigerant from the evaporator and produces the second cooling-effect. At the same time, another cooling-effect is obtained during the adsorption process of the HTS in reactor 1. The reaction heat released during the synthesis reaction of the HTS is transferred for the utilization in the regeneration process of the MTS. During the two internal heat recovery processes, the LTS and the MTS reactors are heated by using the recovered thermal energy, and no additional external heat inputs are required

during the desorption processes of the LTS and the MTS.

In comparison with the double-effect sorption cycle, the multi-effect sorption cycle has a more rigorous match between different sorption working pairs due to the implementation of the two internal heat recovery processes. Figure 15 shows the heat production and heat consumption with different mass ratio (R) in the multi-effect sorption cycle during the internal heat recovery processes. During the first internal heat recovery process (Figure 15(a)), the heat produced by the HTS sorbent (NiCl_2) during the synthesis phase is recovered for use in the regeneration process of the MTS sorbent (MnCl_2). During the second internal heat recovery process (Figure 15b), the adsorption heat released by the MTS sorbent

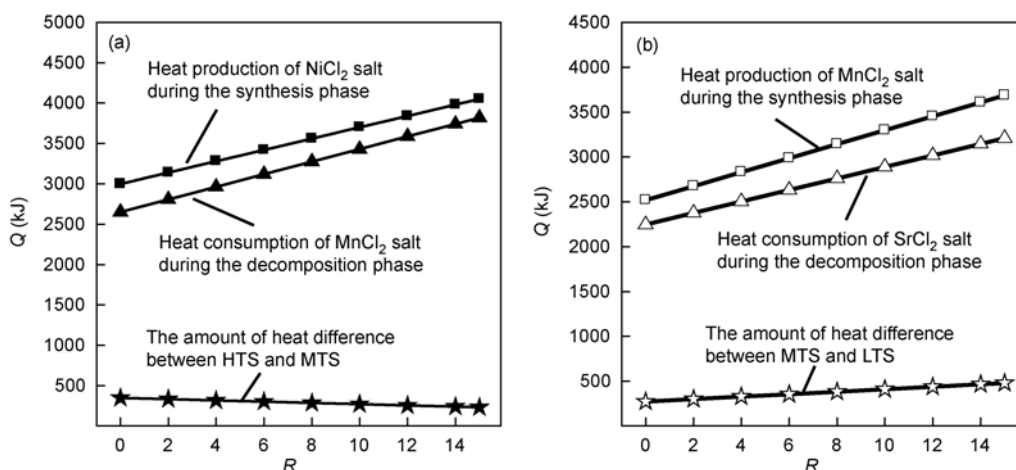


Figure 15 Heat production and heat consumption for multi-effect sorption cycle during the internal heat recovery process. (a) The first internal heat recovery; (b) the second internal heat recovery.

(MnCl_2) during the synthesis phase is recovered and used to regenerate the LTS sorbent (SrCl_2). It was observed that the amounts of heat difference during the two internal heat recovery processes were higher than 250 kJ, which implies that the two internal heat recovery processes between different sorbents are feasible. However, it is necessary to take some measures to keep the energy balance, and the extra heat released must be eliminated by a heat sink to ensure proper operation of the proposed system.

In the multi-effect thermochemical sorption refrigeration cycle, only the HTS in reactor 1 requires a high-temperature heat supply from an external heat source due to the two internal heat recovery strategies. In comparison with conventional sorption refrigeration cycle, the multi-effect sorption cycle has the distinct advantage of larger cooling capacity. This is because the multi-effect system could have three cold productions at the expense of only one heat input at a high temperature.

The performance of the single-effect, double-effect and multi-effect thermochemical sorption refrigeration cycle was evaluated. The ideal COP_i of the single-effect cycle, the double-effect cycle, and the multi-effect cycle is shown in Figure 16(a). It can be seen that the double-effect sorption cycle had a higher COP_i compared with the single-effect sorption cycle, and the multi-effect sorption refrigeration cycle had the highest COP_i among the three kinds of cycles. The improvement in the ideal COP_i obtained with the multi-effect cycle varied between 23%–50%, and 146%–200% compared with the double-effect and the single-effect cycles, respectively.

When the sensible heats of the reactive sorbents, the refrigerant and the metallic part of the reactors were

considered, the COP variation for different mass ratio (R) between the metallic part of the reactor and the reactive sorbent is shown in Figure 16(b). It can be seen that the mass ratio R had a strong influence on system performance. The COP decreased significantly as the mass ratio R increased. In the range of mass ratio R from 0 to 15, the COP of the multi-effect cycle varied between 0.97 and 0.75. The system performance can be significantly improved by the application of the multi-effect cycle as compared with the conventional single- and double-effect sorption cycles.

4 Combined double-way thermochemical sorption refrigeration cycle based on the adsorption and resorption process

In comparison with the conventional single-effect sorption cycle and the heat and mass recovery sorption cycle, the above-mentioned double- and multi-effect sorption cycles can improve significantly the system performance due to the implementation of internal heat recovery. However, these advanced sorption cycles usually have high thermal capacity of the metal and they are complicated because the additional heat exchanger coil is required for the internal heat recovery process.

An innovative combined double-way thermochemical sorption cycle was proposed to improve the sorption performance^[44], in which both adsorption refrigeration and resorption refrigeration processes were combined to improve the cooling capacity. The operation principle and Clapeyron diagram of the combined double-way thermochemical sorption refrigeration cycle based on the adsorption and resorption process is shown in Figure 17. It mainly consists of a solid-gas reactor 1 operating

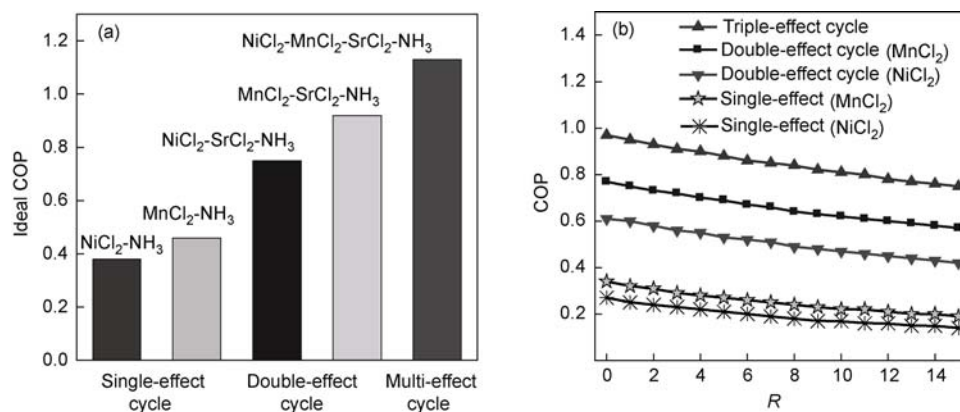


Figure 16 The performance of the single-effect, double-effect and multi-effect thermochemical sorption refrigeration cycle. (a) Ideal COP_i ; (b) effect of metallic part of the reactor.

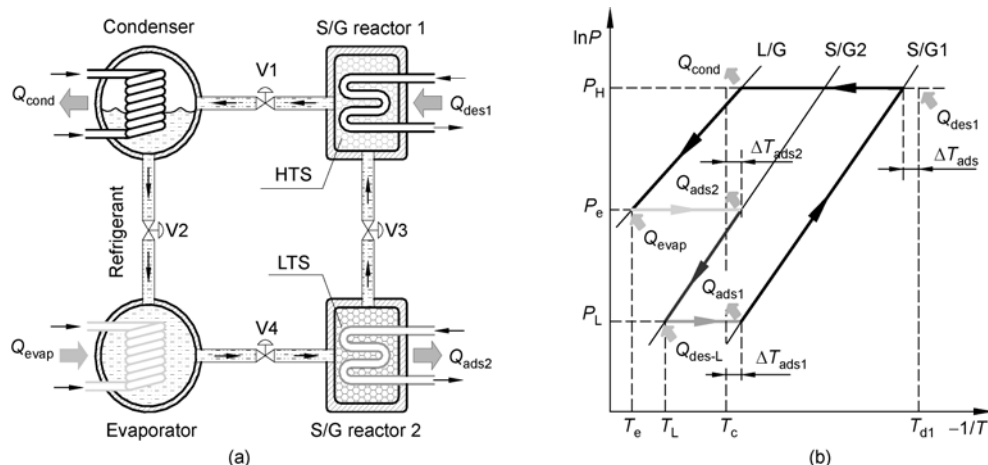


Figure 17 The operation principle and Clapeyron diagram of the combined double-way thermochemical sorption refrigeration cycle based on the adsorption and desorption process. (a) Working principle; (b) Clapeyron diagram.

at a high temperature (R1), a solid-gas reactor 2 operating at a low temperature (R2), a condenser and an evaporator.

Different from the double- and multi-effect sorption cycle, the internal heat recovery process between the two reactors is not employed and thus the additional heat exchanger coil can be removed in the combined double-way sorption cycle. Thus, the presented advanced sorption cycle can simplify the configuration of the sorption machine and reduce the thermal capacity of the metallic part of the reactor. The working mode of the combined double-way sorption cycle can be divided into two phases.

During the first phase, the high-temperature sorbent (HTS) inside reactor 1 receives a heat input from an external heat source at a high temperature. This heat input causes the HTS to desorb the refrigerant into the condenser at a high-pressure P_H . The refrigerant rejects condensation heat to the environment and then flows into the evaporator. At the same time, the low-temperature sorbent (LTS) inside reactor 2 is cooled by a heat sink, and adsorbs the refrigerant from the evaporator at a middle-pressure P_e . The enthalpy of vaporization of the adsorbed refrigerant produces the first cooling-effect by extracting heat from a chilled medium.

In the second phase, the initial working modes of the two reactors are interchanged. Reactor 1 performs adsorption while reactor 2 undergoes desorption. When the high-temperature reactor 1 is connected to the low-temperature reactor 2, the refrigerant gas is transferred from reactor 2 to reactor 1 due to the driving pressure drop. A resorption process occurs between the HTS and the LTS at a low-pressure P_L . This process produces the

second cooling-effect by absorbing heat from the chilled medium during the decomposition reaction phase of the LTS.

The combined double-way cycle has a distinct advantage of larger cooling capacity per unit of heat input compared with the conventional single-effect sorption or resorption refrigeration cycle. This is because two cooling-effects could be obtained at the expense of only one heat input at a high temperature. The first production occurred during the adsorption process when refrigerant vaporized in the evaporator, and the second production occurred during the resorption process when low-temperature sorbent absorbed heat at a low temperature.

The working pairs were selected in order to carry out the adsorption refrigeration and the resorption refrigeration with a moderately high temperature during the regeneration phase. When BaCl_2 and MnCl_2 were used as the reactive sorbents and ammonia was the refrigerant, the ideal COP of the combined double-way sorption cycle is shown in Figure 18(a). It can be seen that the combined double-way sorption refrigeration cycle based on adsorption and resorption processes had the highest ideal COP of 1.24 among the single-effect sorption and resorption cycles. Thus, the system performance has been significantly improved by the advanced combined double-way cycle in comparison with the conventional adsorption cycle and the resorption cycle.

The performance of the combined double-way sorption cycle was evaluated at the heat source temperature of 180°C , cooling water temperature of 30°C , evaporation temperature of 10°C , and pseudo-evaporation temperature (regeneration temperature of LTS) of 10°C . The theoretical COP of adsorption cycle ($\text{MnCl}_2/\text{NH}_3$), re-

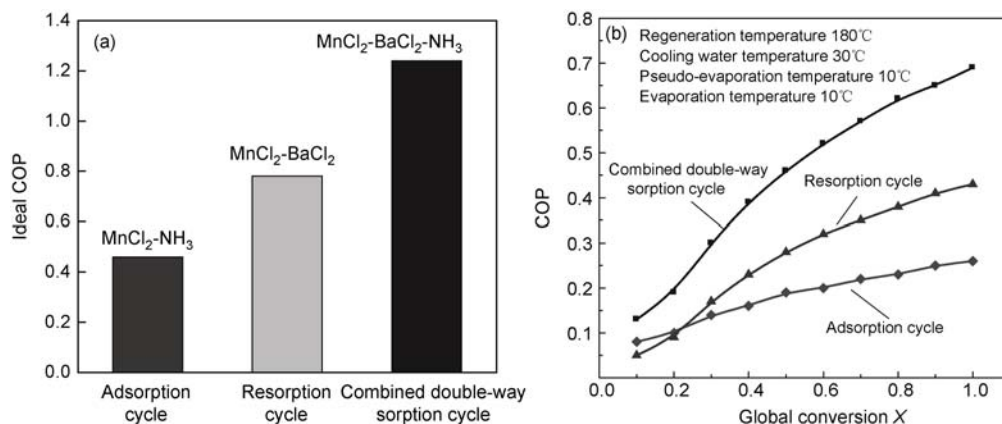


Figure 18 The performance of the combined double-way thermochemical refrigeration cycle based on the adsorption and resorption processes^[44]. (a) Ideal COP; (b) COP with different global conversion.

sorption cycle (MnCl₂/BaCl₂), and combined double-way sorption cycle (MnCl₂/BaCl₂/NH₃) were calculated based on different global conversions, and the result is shown in Figure 18(b).

It was observed that the theoretical COP of three kinds of cycles increased with global conversion. The rate of increase of the combined double-way cycle was higher than those of the other two cycles. Moreover, the combined double-way cycle had the highest COP among the three kinds of cycles, ranging between 0.13 and 0.69 when global conversion X varied from 0.1 to 1. However, the theoretical COP was much lower than the ideal COP of 1.24 mentioned previously. This was due to a large proportion of thermal capacity of the metallic part of the reactor in the simple experimental test unit^[44]. Usually, a high global conversion requires a considerable long cycle time owing to the fact that the reaction rate decreases with the amount of conversion, and the cooling power of the system could be largely reduced. Assuming a more realistic instance where all the reactions were 85 % complete, then the calculated COP of the combined double-way sorption cycle would be as high as 0.64. This value represents an improvement of 167 % and 60 % in the COP when compared with the adsorption cycle and the resorption cycle, respectively.

In the conventional thermochemical sorption or resorption cycle, the operation process is carried out at two levels of pressure: high pressure during the regeneration phase of the reactive sorbent and low pressure during the cold production phase. For the combined double-way thermochemical sorption cycle, the operation process is constrained by three levels of working pressure as shown in Figure 19. The high-pressure P_H during the regeneration phase of the HTS, the middle-

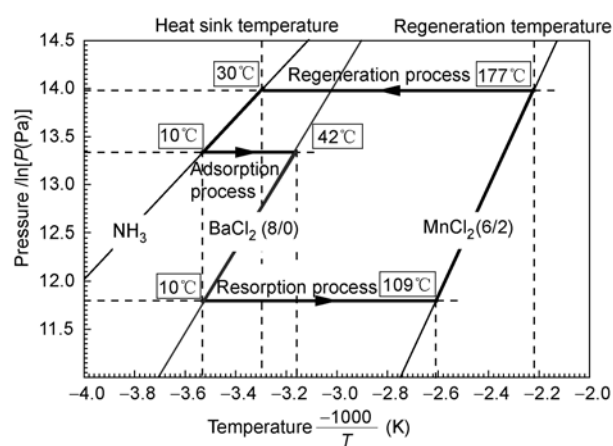


Figure 19 The Clapeyron diagram of the combined double-way thermochemical sorption refrigeration cycle^[45].

pressure P_e during the cold production by evaporation process, and the low-pressure P_L during the second cold production by the desorption heat of LTS.

It can also be seen that the operating pressure during the resorption process was much lower than that during the adsorption process when kept at the same refrigeration temperature. Thus, it suggests that the mass transfer performance inside the reactive materials during the resorption cooling is more important than that during the adsorption cooling due to the low working pressure. The combined double-way cycle would create a vacuum if a low refrigeration temperature was required during the resorption process.

During the resorption process of the combined double-way sorption cycle, synthesis reaction occurs in the HTS reactor, whereas decomposition reaction takes place in the LTS reactor. Different from the conventional physical or thermochemical sorption cycle, the working pressure is strongly influenced by the amount of the gas

simultaneously desorbed by the LTS reactor and adsorbed by the HTS reactor. Figure 20 shows the experimental pressure evolution during the resorption process. It was observed that the working pressure decreased rapidly at the beginning of the resorption process, and then it remained approximately constant as the reaction progressed. Such a pressure evolution suggests that the synthesis rate of the HTS was higher than the decomposition rate of the LTS at the beginning process of the resorption phase. The stabilization of pressure occurred when the amount of ammonia desorbed by the LTS in decomposition reaction was similar to the amount adsorbed by the HTS in synthesis reaction. Thus, in order to avoid the vacuum condition and improve the reliability of sorption machine, it is very important to match the synthesis rate of the HTS, the decomposition rate of the LTS and the sorption capacity of different reactive sor-

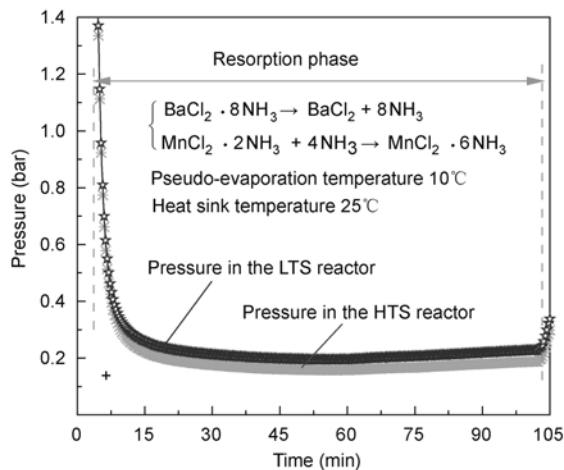


Figure 20 Pressure evolution during the resorption refrigeration phase of the combined double-way sorption cycle^[45].

bents in the combined double-way thermochemical sorption cycle.

5 Double-effect and double-way thermochemical sorption refrigeration cycle with internal heat recovery

In order to further improve system performance of the sorption machine, internal heat recovery is employed in the above-mentioned combined double-way thermochemical sorption cycle. The operation principle and Clapeyron diagram of the double-effect and double-way thermochemical sorption refrigeration cycle with internal heat recovery process is shown in Figure 21^[46].

To accomplish such a task, the system has four solid-gas reactors, a condenser and an evaporator. Three different reactive sorbents are used as the reactants in the double-effect and double-way cycle. One reactor is filled with a high-temperature sorbent (HTS), and another is filled with a middle-temperature sorbent (MTS), while other two reactors have the low-temperature sorbents (LTS). The cycle operation has five thermodynamic processes, including pre-heating, desorption, pre-cooling, adsorption and resorption. The cycle process can be divided into two sub-cycles according to the refrigerant flow.

In the first phase, the decomposition of the HTS inside reactor 1 requires a heat input from an external heat source at a high temperature, and the desorbed refrigerant condenses in the condenser and then flows into the evaporator. Simultaneously, the LTS reactor 4 is cooled by a heat sink to adsorb the refrigerant from the evapo-

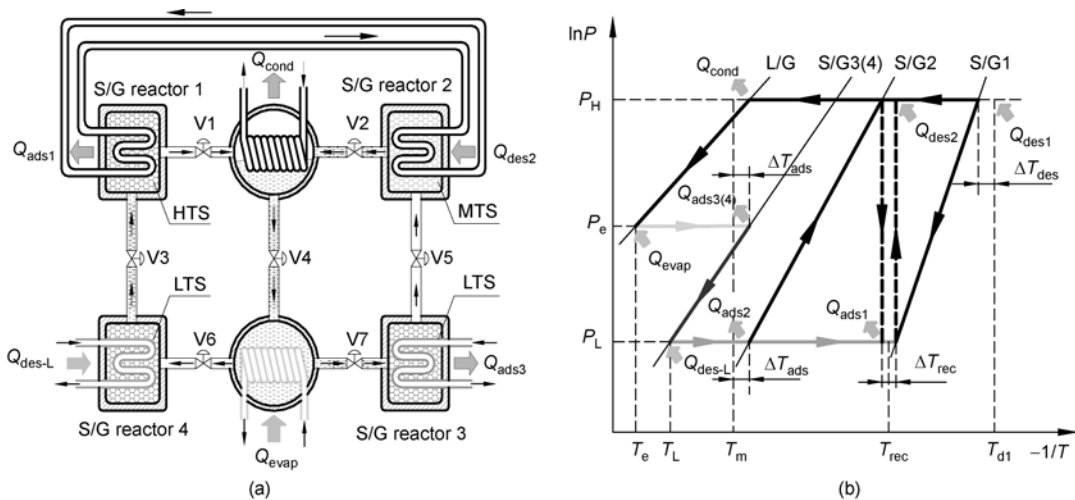


Figure 21 The operation principle and Clapeyron diagram of the double-effect and double-way thermochemical sorption refrigeration cycle with internal heat recovery process. (a) Working principle; (b) Clapeyron diagram.

rator. The refrigerant vaporization produces the first cooling-effect by extracting heat from a chilled medium during the adsorption process. At the same time, the MTS reactor is connected to the LTS reactor 3, and the refrigerant gas is transferred from the LTS reactor to the MTS reactor due to the driving pressure drop. Thus, a resorption process between the MTS reactor and the LTS reactor 3 occurs, and the second cooling-effect is produced by the reaction heat consumed by the LTS at a low temperature during the decomposition process of the LTS reactor 3.

During the second phase, the working modes of the reactors are interchanged. The HTS reactor is in adsorption mode while the MTS reactor is under desorption. The LTS reactor 4 works as a pseudo-evaporator to produce the third cooling-effect during the resorption refrigeration process between the HTS and the LTS. The refrigerant gas flows from the LTS reactor 4 to the HTS reactor and reacts with the high-temperature sorbent. A large amount of adsorption heat is released by the synthesis reaction of the HTS, and this energy is reutilized for the regeneration of the MTS. During the internal heat recovery process, the MTS is heated by the adsorption heat of the HTS. The refrigerant desorbed from the MTS reactor flows to the condenser. In this process, no additional external heat source is required during the regeneration process of MTS. Simultaneously; LTS reactor 3 is cooled by a heat sink to adsorb the refrigerant from the evaporator. The evaporation heat of the refrigerant produces the fourth cooling-effect.

When compared with other kinds of sorption refrigeration cycles, the double-effect and double-way cycle has the distinct advantage of larger cooling capacity per unit of heat input, due to the four cooling-effects obtained at the expense of only one heat input. During every working phase, the cold production consists of the adsorption refrigeration based on the evaporation process and the desorption refrigeration based on the resorption process.

To assess the performance of the double-effect and double-way sorption cycle, a group of working pair NH_3 , BaCl_2 , CaCl_2 , NiCl_2 was studied, in which NiCl_2 is high-temperature sorbent, CaCl_2 is middle-temperature sorbent, and BaCl_2 is low-temperature sorbent. The Clapeyron diagram of the double-effect and double-way sorption cycle with internal heat recovery is shown in Figure 22.

The decomposition heat of NiCl_2 is supplied by an

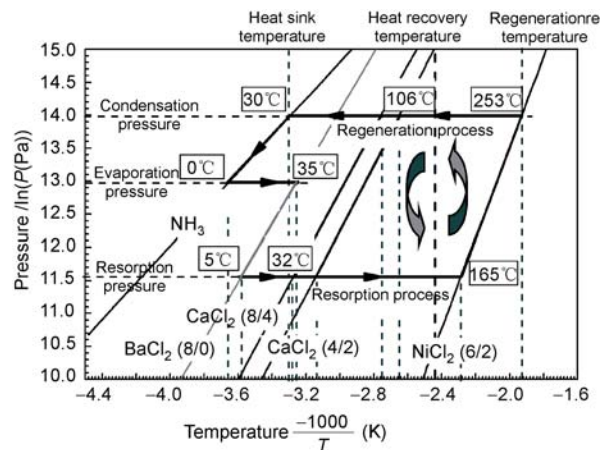


Figure 22 The Clapeyron diagram of the double-effect and double-way thermochemical sorption refrigeration cycle with internal heat recovery process^[46].

external heat source during the regeneration process, and the decomposition heat consumed by the CaCl_2 is supplied by the adsorption heat of NiCl_2 by employing the internal heat recovery strategy between the HTS and the MTS. The useful cold is produced by the evaporation heat of the refrigerant during the adsorption phase of BaCl_2 and the reaction heat consumed by BaCl_2 at a low temperature during the decomposition phase of the LTS.

Although the working cooling temperature (10°C) during the resorption refrigeration process is higher than that (0°C) during the adsorption refrigeration process, it can be seen that the operating pressure during the former process is much lower than that during the latter process. Such a result indicates that the mass transfer performance inside the reactive materials is a major constraining factor during the resorption refrigeration process, and it would have a strong influence on the system performance of the double-effect and double-way thermochemical sorption refrigeration cycle.

The ideal COP of the double-effect and the double-way thermochemical sorption cycle with internal heat recovery process is shown in Figure 23. It can be seen that the double-effect and the double-way sorption refrigeration cycle based on the adsorption and resorption had the highest COP among the three kinds of sorption cycles. In comparison with the double-effect sorption cycle ($\text{FeCl}_2/\text{NiCl}_2\text{-CaCl}_2\text{-NH}_3$) based on the evaporation process and the double-effect resorption cycle ($\text{FeCl}_2/\text{NiCl}_2\text{-CaCl}_2\text{-BaCl}_2$) based on the resorption process, the double-effect and the double-way sorption cycle ($\text{FeCl}_2/\text{NiCl}_2\text{-CaCl}_2\text{-BaCl}_2\text{-NH}_3$) could improve the ideal COP by more than 169% and 59%, re-

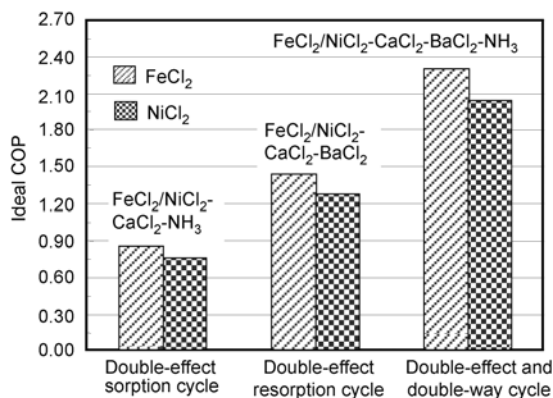


Figure 23 Ideal COP of the double-effect and the double-way sorption cycle with internal heat recovery process^[46].

spectively.

At the heat sink temperature of 30°C, evaporation temperature of 0°C and the pseudo-evaporation temperature (regeneration temperature of LTS) of 10°C, the COP variation with different mass ratio (R) between the metallic part of the reactor and the reactive sorbent is shown in Figure 24, in which the sensible heats of the reactive sorbents, the refrigerant and the metallic part of the reactors were considered in the calculation COP of the double-effect and the double-way thermochemical sorption cycle.

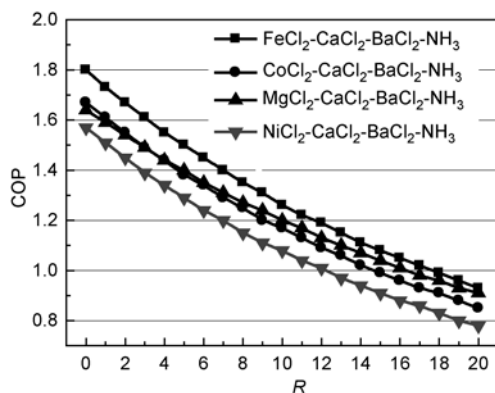


Figure 24 COP variation with the different mass ratio (R) of double-effect and double-way sorption cycle with internal heat recovery process^[46].

It can be seen that mass ratio R had a strong influence on the system performance. The COP decreased significantly as mass ratio R increased. In the range of mass ratio R from 0 to 15, the COP varied between 1.08 and 1.80 for the group of sorbent with NH_3 , BaCl_2 , CaCl_2 and FeCl_2 . For most of the solid-gas sorption systems with optimized design, the mass ratio (R) between the metallic part of the reactor and the reactive sorbent is about 5. The corresponding COP obtained with the double-effect and double-way sorption cycle ranged from 1.50 to 1.26. Thus, system performance can significantly be improved by the presented double-effect and double-way sorption cycle compared with the conventional single- and double-effect sorption cycles.

The performance comparisons for different thermochemical sorption thermodynamic cycles were analyzed by Oliveira et al., and the result is shown in Table 2^[47]. These advanced thermodynamic cycles include the sing-effect sorption cycle ($\text{NiCl}_2\text{-NH}_3$), the sing-effect resorption cycle ($\text{NiCl}_2\text{-BaCl}_2$), the double-effect sorption cycle ($\text{NiCl}_2\text{-MnCl}_2\text{-NH}_3$), the double-effect resorption cycle ($\text{NiCl}_2\text{-MnCl}_2\text{-BaCl}_2$), the combined double-way sorption cycle ($\text{NiCl}_2\text{-BaCl}_2\text{-NH}_3$) and the double-effect and double-way sorption cycle ($\text{NiCl}_2\text{-MnCl}_2\text{-BaCl}_2\text{-NH}_3$).

It can be seen that the combined double-way sorption cycle based on the adsorption and resorption process had higher COP when compared with the sing-effect sorption cycle and the single-effect resorption cycle without internal heat recovery. The COP obtained with the combined double-way sorption cycle, sing-effect resorption cycle and sing-effect sorption cycle were 0.47, 0.32 and 0.16, respectively. In comparison with the sing-effect sorption cycle and sing-effect resorption cycle, the combined double-way sorption cycle could improve the COP by more than 194 % and 47 %, respectively.

When the internal heat recovery process was employed between the different reactive sorbents, the COP and the energy utilization efficiency were improved sig-

Table 2 Performance comparisons for different advanced thermochemical sorption thermodynamic cycles^[47]

Thermochemical thermodynamic refrigeration cycle	Cooling power per volume (kW/m^3)	Coefficient of performance (COP)	Energy utilization efficiency (η)
Sing-effect sorption cycle ($\text{NiCl}_2\text{-NH}_3$)	499	0.16	0.38
Double-effect sorption cycle ($\text{NiCl}_2\text{-MnCl}_2\text{-NH}_3$)	214	0.38	0.51
Sing-effect resorption cycle ($\text{NiCl}_2\text{-BaCl}_2$)	70.2	0.32	0.46
Double-effect resorption cycle ($\text{NiCl}_2\text{-MnCl}_2\text{-BaCl}_2$)	47.2	0.72	0.57
Combined double-way sorption cycle ($\text{NiCl}_2\text{-BaCl}_2\text{-NH}_3$)	37.1	0.47	0.42
Double-effect and double-way sorption cycle ($\text{NiCl}_2\text{-MnCl}_2\text{-BaCl}_2\text{-NH}_3$)	21.5	1.10	0.55

nificantly due to the implementation of the heat recovery process. It can be seen that the double-effect thermodynamic cycles had higher COP than their corresponding single-effect thermodynamic cycles. For example, the COP improvement was about 125 % in the double-effect resorption cycle compared with the single-effect resorption cycle, and it was about 138 % for the double-effect sorption cycle. Moreover, the double-effect and double-way sorption cycle with internal heat recovery process had the highest COP among these thermochemical cycles, and the COP was as high as 1.10. This figure represents seven times of the COP obtained with the conventional single-effect sorption cycle and three times of the COP obtained with the double-effect sorption cycle. However, the double-effect and double-way sorption cycle usually has a long cycle time due to the low driving equilibrium drop, and long cycle time could reduce the cooling power per volume sorbent compared with the other thermodynamic cycles as shown in Table 2. Thus, the heat and mass transfer inside reactors is the key factor to the double-effect and double-way thermochemical sorption cycle.

6 Perspectives of the thermochemical sorption refrigeration

Solid-gas sorption refrigeration systems based on the thermochemical process have been paid a lot of attention due to their efficient cold production based upon the low-grade thermal energy utilization. These heat-powered refrigeration systems have a large energy-saving potential to reduce the primary energy consumption and thus can contribute to the economic and social sustainable development. As one of the promising energy-saving and environment friendly green refrigeration technologies, solid-gas thermochemical sorption refrigeration would play an important role in environment protection and low-grade waste heat reutilization in the future.

Solid sorption refrigeration systems based on the evaporation process have been widely discussed and some silica-gel water sorption machines have now reached the stage of pre-industrial prototype. Many factories have manufactured the commercial sorption chillers such as Mycom Company in Japan, HIJC Company in American, Nishiyodo Kuchouki Company in Japan, and so on. Moreover, a distributed energy system was installed in the Maltese Hospital in Germany, and a solid sorption chiller was utilized to produce useful cold in the

CCHP energy system. Later, a similar distributed energy system was built in the Tokai Photonics Company of Nagoya in Japan^[48]. In China, solar powered silica-gel water sorption air-conditioning machines developed by Shanghai Jiao Tong University have been successfully applied to the green building of Shanghai Research Institute of Building Science^[49], grain storage in Jiangsu Province^[50] and the micro-scale combined cooling, heating and power (MCCHP) distributed energy system driven by a gas engine^[51].

In comparison with the physical sorption working pair, thermochemical sorption working pair has the advantage of the larger sorption capacity per mass of sorbent. Moreover, it has a wider range of working temperature according to the available heat source temperature and the refrigeration temperature. For the sorption refrigeration machines using the metal chlorides-ammonia sorption working pairs, they can utilize effectively the low-grade heat source temperatures between 60°C and 500°C, and the refrigeration temperature can be used as air-conditioning (5°C–10°C), refrigeration (–10°C–0°C) and deep-freezing (–50°C––20°C). In addition, thermochemical sorption working pair is also suitable for the heat pump due to its monovariant characteristic and large energy storage, and the upgrading temperature could reach 100°C in the solid thermochemical transformer.

Due to the above-mentioned advantages, many investigations have been performed on the solid thermochemical sorption refrigeration/heat pump in recent years. For example, a solar-powered thermochemical sorption refrigeration prototype using strontium bromine-water sorption working pair was developed by the PROMES Lab (Processes, Materials and Solar Energy Laboratory) of CNRS (National Center for Scientific Research) in France^[52]. This sorption machine has a heating capacity of 60 kW h and a cooling capacity of 40 kW h, in which several flat-plate solar collectors were used to provide the driving heat energy. The research team in Shanghai Jiao Tong University designed a split heat pipe type high-efficient thermochemical ice-making prototype using calcium chloride-ammonia working pair, and multifunctional heat pipe technology was employed to enhance the heat transfer performance and improve the reliability of the sorption prototype^[30–32]. In addition, solid thermochemical sorption ice-making machines were manufactured for fishing boats in Taishan Group Company in China, and these

sorption machines were driven by exhaust gas from engines. These above-mentioned investigations promote the development of the thermochemical sorption refrigeration technology. However, these thermochemical sorption machines usually have low system performance due to the utilization of the conventional single-effect sorption cycle, and COP was usually lower than 0.3.

However, low system performance is still the drawback for the solid thermochemical sorption refrigeration in comparison with the conventional vapor compression refrigeration and the liquid-gas absorption refrigeration. Low working performance has been limiting the wide application of the solid sorption refrigeration technology. The leading reason could be attributed to the large amount of energy loss during the interchanged process between the heating and the cooling phases in the single-effect sorption cycle.

To improve system performance and accomplish high-efficient sorption refrigeration, several studies on the solid thermochemical sorption refrigeration should be further performed. Firstly, to study the novel composite sorption materials: Sorption working pair is the key element to the sorption machine, and the cooling power can be improved by enhancing the sorption capacity per mass of sorbent. Secondly, to develop the advanced sorption thermodynamic cycles: Sorption cycle has a strong influence on the working performance of the sorption machine, and the cooling power can significantly be improved by designing innovative sorption cycles such as the double-effect cycle, multi-effect cycle, combined double-way cycle, double-effect and double-way cycle, and so on. In order to optimize the energy match between different sorbents in these advanced thermochemical sorption cycles, the investigation on the adsorption and desorption characteristics of different sorbents should be performed at different working conditions. Thirdly, to research the high-efficiency energy reutilization technologies: Low energy utilization effi-

ciency is a serious and usual problem in the sorption refrigeration cycle, thus, the advanced integrated energy technology is the main developing direction to improve working performance of the sorption machine. Fourthly, to enhance the heat and mass transfer inside the reactors: Good heat and mass transfer performance can promote the chemical reaction rate and thus reduce the cycle time. To reduce the thermal capacity of the metallic part of the reactor, the optimization design of the S/G reactor and the enhancement on heat and mass transfer of reactive sorbents is necessary to research further in the future. Finally, to study the sorption mechanism, the chemical reaction dynamics and the transient heat and mass transfer of porous material: Solid thermochemical sorption refrigeration is related to the thermodynamics, chemical reaction dynamics and the heat and mass transfer inside the porous sorption material. Moreover, solid configuration and the refrigerant content inside the sorbent complex are always varying during the chemical reaction process. Therefore, the transient heat and mass transfer property of the sorption material is also variational during the adsorption and desorption processes. It is desirable to further research the effects of the heat and mass transfer of porous material and the chemical reaction dynamics on the working performance of solid thermochemical sorption machine.

In addition, when the advanced sorption thermodynamic cycles with internal heat recovery are employed to improve system performance, solid thermochemical sorption refrigeration system usually requires a high heat source temperature during the regeneration process of the sorbent. The high desorption temperature would limit the application of sorption refrigeration to some locations where the available heat source temperature is relatively low. Thus, it is desirable to develop new desorption technologies to decrease the regeneration temperatures of these advanced high-efficient thermochemical sorption refrigeration cycles.

- 1 Jiang Z M. Reflections on energy issues in China. *J Shanghai Jiao Tong Uni* (in Chinese), 2008, 42(3): 345–359
- 2 Wang R Z, Oliveira R G. Adsorption refrigeration—an efficient way to make good use of waste heat and solar energy. *Prog Energ Combust Sci*, 2006, 32: 424–458[DOI]
- 3 Meunier F. Solid sorption heat powered cycles for cooling and heat pumping applications. *Appl Therm Eng*, 1998, 18: 715–729[DOI]
- 4 Lebrun M, Spinner B. Models of heat and mass transfers in solid/gas reactor used as chemical heat pumps. *Chem Eng Sci*, 1990, 45: 1743–1753[DOI]
- 5 Mauran S, Prades P, Haridon F L. Heat and mass transfer in consolidated reacting beds for thermochemical systems. *Heat Recov Syst CHP*, 1993, 13: 315–319[DOI]
- 6 Mazet N, Amouroux M, Spinner B. Analysis and experimental study of the transformation of non-isothermal solid/gas reacting medium. *Chem Eng Commun*, 1991, 99: 155–174[DOI]
- 7 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. *Chem Eng Sci*, 1992, 47: 4445–4454[DOI]
- 8 Dellerio T, Sarneo D, Touzain Ph. A chemical heat pump using carbon fibers as additive. Part I: enhancement of thermal conduction. *Appl*

- Therm Eng, 1999, 19(9): 991–1000[DOI]
- 9 Aidoun Z., Ternan M. Salt impregnated carbon fibres as the reactive medium in a chemical heat pump: the $\text{NH}_3\text{-CoCl}_2$ system. *Appl Therm Eng*, 2002, 22: 1163–1173[DOI]
 - 10 Wang L W, Wang R Z, Wu J Y, et al. Adsorption performances and refrigeration application of adsorption working pair of $\text{CaCl}_2\text{-NH}_3$. *Sci China Ser E-Technol Sci*, 2004, 47(2): 173–185[DOI]
 - 11 Zhong Y, Critoph R E, Thorpe R N, et al. Isothermal sorption characteristics of the $\text{BaCl}_2\text{-NH}_3$ pair in a vermiculite host matrix. *Appl Therm Eng*, 2007, 27: 2455–2462[DOI]
 - 12 Oliveira R G, Wang R Z. A consolidated calcium chloride-expanded graphite compound for use in sorption refrigeration systems. *Carbon*, 2007, 45: 390–396[DOI]
 - 13 Shelton S V, Wepfer J W, Miles D J. Ramp wave analysis of the solid/vapor heat pump. *ASME J Energ Res Technol*, 1990, 112: 69–78[DOI]
 - 14 Critoph R E. Performance estimation of convective thermal wave adsorption cycles. *Appl Therm Eng*, 1996, 16: 429–437[DOI]
 - 15 Meunier F. Theoretical performances of solid adsorbent cascading cycles using the zeolite-water and active carbon-methanol pairs: four case studies. *Heat Recov Syst CHP*, 1986, 6: 491–498[DOI]
 - 16 Pons M, Poyelle F. Adsorptive machines with advantaged cycles for heat pumping or cooling applications. *Int J Refrig*, 1999, 22: 27–37[DOI]
 - 17 Wang R Z. Performance improvement of adsorption cooling by heat and mass recovery operation. *Int J Refrig*, 2001, 24: 602–611[DOI]
 - 18 Saha B B, Koyama S, Kashiwagi T, et al. Waste heat driven dual-mode, multi-stage, multi-bed regenerative adsorption system. *Int J Refrig*, 2003, 26: 749–757[DOI]
 - 19 Wang R Z. Adsorption refrigeration research in Shanghai Jiao Tong University. *Renew Sust Energ Rev*, 2001, 5: 1–37[DOI]
 - 20 Neveu P, Castaing J. Solid-gas chemical heat pumps: field of application and performance of the internal heat recovery. *Heat Recov Syst CHP*, 1993, 13: 233–251[DOI]
 - 21 Touzain Ph. Thermodynamic values of ammonia-salts reactions for chemical sorption heat pumps. In: *Proceedings of the International Sorption Heat Pump Conference*, Germany, 1999, 225–237
 - 22 Wang R Z, Wang L W. Adsorption refrigeration- green cooling driven by low-grade thermal energy. *Chin Sci Bull*, 2005, 50(3): 193–204
 - 23 Tchernev D I, Emerson D T. High-efficiency regenerative zeolite heat pump. *ASHRAE Transactions*, 1988, 14: 2024–2032
 - 24 Akahira A, Alam K C A, Hamamoto Y, et al. Experimental investigation of mass recovery adsorption refrigeration cycle. *Int J Refrig*, 2005, 28: 565–572[DOI]
 - 25 Oliveira R G, Silveira V Jr, Wang R Z. Experimental study of mass recovery adsorption cycles for ice making at low generation temperature. *Appl Therm Eng*, 2006, 26: 303–311[DOI]
 - 26 Wang D C, Wu J Y, Xia Z Z, et al. Study of a novel silica gel-water adsorption chiller. *Int J Refrig*, 2005, 28: 1073–1091[DOI]
 - 27 Yang G Z, Xia Z Z, Wang R Z, et al. Research on a compact adsorption room air conditioner. *Energy Convers Manage*, 2006, 47: 2167–2177[DOI]
 - 28 Wang L W, Wang R Z, Lu Z S, et al. Comparison of the adsorption performance of compound adsorbent in a refrigeration cycle with and without mass recovery. *Chem Eng Sci*, 2006, 61: 3761–3770[DOI]
 - 29 Li T X, Wang R Z, Wang L W, et al. Influence of mass recovery on the performance of a heat pipe type ammonia sorption refrigeration system using CaCl_2 /activated carbon as compound adsorbent *Appl Therm Eng*, 2008, 28: 1638–1646[DOI]
 - 30 Lu Z S, Wang R Z, Li T X, et al. Experimental investigation of a novel multifunction heat pipe solid sorption icemaker for fishing boats using CaCl_2 /activated carbon compound-ammonia. *Int J Refrig*, 2007, 30: 76–85[DOI]
 - 31 Li T X, Wang R Z, Wang L W, et al. Performance study of a high efficient multifunction heat pipe type adsorption ice making system with novel mass and heat recovery processes. *Int J Therm Sci*, 2007, 46: 1267–1274[DOI]
 - 32 Wang L W, Wang R Z, Lu Z S, et al. Split heat pipe type compound adsorption ice making test unit for fishing boats. *Int J Refrig*, 2006, 29: 456–468[DOI]
 - 33 Vasiliev L L. Heat pipes in modern heat exchangers. *Appl Therm Eng*, 2005, 25: 1–19[DOI]
 - 34 Wang R Z. Efficient adsorption refrigerators integrated with heat pipes. *Appl Therm Eng*, 2008, 28: 317–326[DOI]
 - 35 Lu Z S, Wang R Z, Wang L W. A study on multifunction heat pipe high efficient adsorption refrigerator using compound adsorbent-ammonia. *Chin Sci Bull*, 2006, 51(2): 239–242[DOI]
 - 36 Neveu P, Castaing J. Solid-gas chemical heat pumps: field of application and performance of the internal heat recovery. *Heat Recov Syst CHP*, 1993, 13: 233–251[DOI]
 - 37 Sorin M, Spinner B, Stitou D. Thermodynamic techniques for the conceptual design of thermochemical refrigerators using two salt materials. *Chem Eng Sci*, 2002, 57: 4243–4251[DOI]
 - 38 Choi H K, Neveu P, Spinner B. System modeling and parameter effects on design and performance of ammonia based thermochemical transformer. In: *Proceedings of International Absorption Heat Pump Conference*, Montreal, Canada, 1996
 - 39 Castaing J, Neveu P. Equivalent Carnot cycle concept applied to a thermochemical solid/gas resorption system. *Appl Therm Eng*, 1998, 18: 745–754[DOI]
 - 40 Lepinasse E, Marion M, Goetz V. Cooling storage with a resorption process: application to a box temperature control. *Appl Therm Eng*, 2001, 21: 1251–1263[DOI]
 - 41 Vasiliev L L, Mishkinis D A, Antukh A A, et al. Resorption heat pump. *Appl Therm Eng*, 2004 24: 1893–1903[DOI]
 - 42 Spinner B. Ammonia-based thermochemical transformers. *Heat Recov Syst CHP*, 1993, 13: 301–307[DOI]
 - 43 Goetz V, Spinner B, Lepinasse E. A solid-gas thermochemical cooling system using BaCl_2 and NiCl_2 . *Energy*, 1997, 22: 49–58[DOI]
 - 44 Li T X, Wang R Z, Oliveira R G, et al. A combined double-way chemisorption refrigeration cycle based on adsorption and resorption processes. *Int J Refrig*, 2008, 32: 47–57
 - 45 Li T X, Wang R Z, Oliveira R G, et al. Experimental investigation of a combined double-way solid-gas chemisorption refrigeration system using consolidated composite adsorbent. In: *Proceedings of International Sorption Heat Pump Conference*, Seoul, 2008
 - 46 Li T X, Wang R Z, Oliveira R G, et al. Performance analysis of an innovative multimode, multisalt and multieffect chemisorption refrigeration system. *AIChE J*, 2007, 53: 3222–3230[DOI]
 - 47 Oliveira R G, Wang R Z, Li T X. Transient analysis of a chemisorption air conditioning system operating under different kinds of cycle. *Ind Eng Chem Res*, 2008, 47: 1102–1110[DOI]
 - 48 Wang R Z, Wang L W, Wu J Y. Application and theory of adsorption refrigeration (in Chinese). Beijing: Science Press, 2007
 - 49 Zhai X Q, Wang R Z, Wu J Y, et al. Design and performance of a solar-powered air-conditioning system in a green building. *Appl Energy*, 2008, 85: 297–311
 - 50 Luo H L, Wang R Z, Dai Y J, et al. An efficient solar-powered adsorption chiller and its application in low-temperature grain storage. *Sol Energy*, 2007, 81: 607–613[DOI]
 - 51 Kong X Q, Wang R Z, Wu J Y, et al. Experimental investigation of a micro-combined cooling, heating and power system driven by a gas engine. *Int J Refrig*, 2005, 28 (7): 977–987[DOI]
 - 52 Mauraan S, Lahmidi H. Goetz V. Solar heating and cooling by a thermochemical process. First experiments of a prototype storing 60 kW h by a solid/gas reaction. *Sol Energy*, 2008, 82: 623–636[DOI]