Investigation on non-equilibrium performance of composite adsorbent for resorption refrigeration

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Abstract: The aims of this paper is to indicate that the non-equilibrium adsorption testing results is more suitable for prediction of the real refrigeration performance than equilibrium data. Therefore, a test unit is constructed to test the non-equilibrium performance of different composite adsorbents. The adsorption and desorption quantity are measured and calculated by smart differential pressure transmitter. The non-equilibrium adsorption performances of working pair of Manganese chloride-ammonia, Calcium chloride-ammonia and Ammonium chloride-ammonia are investigated respectively. Results show that hysteresis phenomena happens obviously in non-equilibrium desorption process, which is related with dual variables rather than single variable. Based on the testing results, resorption refrigeration performance is analyzed, in which Manganese chloride is used as high temperature salt (HTS), and Calcium chloride, Ammonium chloride are selected as low temperature salt (LTS) for comparison. Results show that the highest COP and SCP for resorption refrigeration are about 0.272 and 45.6 W/kg, respectively. Performance of Manganese chloride-Calcium chloride and Manganese chloride-Ammonium chloride working pairs are much lower when compared with theoretical data.

Keywords: Resorption; Working pairs; Composite adsorbent; Non-equilibrium

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1 Introduction

Adsorption refrigeration has played an important role in utilizing the renewable energy since it has no risk of Ozone Depletion Potential (ODP) and Global Warming Potential (GWP)[1]. Both physical and chemical adsorption refrigeration are gathering the momentum. Chemical adsorption takes advantage of larger adsorption capacity than physical adsorption[2], and it is more likely to be applied in the freezing condition[3]. However, there will be two disadvantages of chemisorption refrigeration if ammonia is used as the refrigerant. One disadvantage is the safety problem caused by the liquid ammonia when facing bumpy environment. The other disadvantage is that environmental temperature will have a great influence on the refrigeration performance. Refrigeration performance for solar energy application will decrease greatly when cooling temperature is higher than 35-40 °C in summer time[4]. Compared with typical adsorption refrigeration, resorption refrigeration has flexibility to adapt different heat source temperature by employing different alkali metal halides[5]. The resorption refrigeration utilizes the desorption heat in the refrigeration process, which contributes to performance improvement comparing with adsorption refrigeration[6]. Various researchers analyzed adsorption and resorption refrigeration by using equilibrium line in Clapeyron diagram i.e. the equilibrium solid-gas chemisorption process changes with temperature or pressure. For instance, Lu et al.[7] selected working pair of Manganese chloride (MnCl_2) as high temperature salts (HTS) and Barium chloride (BaCl_2) as low temperature salts (LTS) to analyze the equilibrium performance of resorption system for refrigeration and power cogeneration. Results showed that the coefficient of performance (COP) would be improved by 38%, which is much higher than experimental results. Li et al.[8] proposed a combined double-way thermochemical sorption refrigeration cycle, and maximum COP of the cycle was about 1.24 through theoretical analysis. Desorption temperature was about 180 °C with heat sink temperature of 25 °C and evaporation temperature of 10 °C. Nonetheless, experimental results were quite lower than the performance by equilibrium Clapeyron diagrams

analysis. The feasibility and working performance of a double-effect and double-way thermochemical sorption refrigeration system was investigated. Although the highest COP of the experiment was about 1.0, heat source temperature was as high as 260 °C and the chilled temperature of 15 °C[9]. One main reason to explain the great difference between the theoretical and experimental result is that real adsorption refrigeration process is non-equilibrium processes, and it will cause the inaccuracy if refrigeration performances are analyzed based on the equilibrium conditions[10]. Under this scenario, non-equilibrium characteristic of different working pairs was investigated for accurate thermal analysis. Calcium chloride(CaCl_2) with multi-walled carbon nanotubes composite adsorbent was investigated and found different chemical reaction steps between Calcium chloride(CaCl_2) and ammonia (NH_3), and adsorption capacities of the composite adsorbent at different working conditions were evaluated[11]. Characteristic of Cobalt chloride and ammonia working pair proved to be more complicated than a single equilibrium line. Non-equilibrium hysteresis phenomena would cause adsorption process into a bivariate process, which need both temperature and pressure to determine the reaction process[12]. For further research about bivariate characteristic of Cobalt chloride and ammonia working pair, Aidoun et al. investigated and identified the regions of pseudo-stable transitions and instabilities and its application for chemisorption heat pump with carbon fibre and chloride salts composite materials, respectively[13]. Take all investigations above into consideration, compared with the various investigations on equilibrium adsorption performance, there is relatively few experimental investigation about the non-equilibrium performance of composite adsorbent. Recent research has been demonstrated that for different working pairs such as $\text{MnCl}_2\text{-NH}_3$ and $\text{NH}_4\text{Cl-NH}_3$ there will be significant difference between equilibrium and non-equilibrium performance analysis[14]. However, the non-equilibrium performance analysis has not been applied for resorption refrigeration. Techno-economy and energy efficiency should be evaluated as the novel energy conversion technology[15].

In this paper, non-equilibrium reaction line of three different working pairs are investigated and applied for the analysis of resorption refrigeration. Properties such as heat and mass transfer performance are tested for the comprehensive understanding of novel composite adsorbent. Expanded natural graphite treated with sulfuric acid (ENG-TSA) is chosen as the matrix of adsorbent, which is made from natural graphite soaked in sulfuric acid, intercalated in the layered structure of the graphite. ENG-TSA enjoy much lower density than normal expanded natural graphite. Properties such as heat and mass transfer performance of adsorbent are greatly improved through the matrix.

2 Material characterization

2.1 Materials

For different chlorides, Manganese chloride (MnCl_2) is used as high temperature salt (HTS) whereas Calcium chloride (CaCl_2), Ammonium chloride (NH_4Cl) are selected as low temperature salt (LTS). The reaction process of these salts with ammonia can follow the Equation 1-3. The details of composite adsorbent in manufacturing process can be referred to the reference[16]. First, ENG-TSA is dried in the oven with controlled temperature 120 °C. Then mix chloride, ENG-TSA and water together to develop the composite adsorbent. Afterwards, composite adsorbent is dried in the oven with controlled temperature 120 °C to remove the water. To remove the crystal water of some chlorides, the temperature of oven is elevated to 240 °C for drying the composite adsorbents. Finally composite adsorbent is compressed into block by the pressing machine.

Mass ratio of salt and density of composite adsorbent are two major factors when developing the composite adsorbent. The cracks will easily happen if the mass ratio of the adsorbent is too low, which causes SCP (specific cooling power per kilogram adsorbent) become too small. Density of composite adsorbent also ought to be reasonable. The higher density of adsorbent is, the lower permeability and the higher thermal conductivity becomes. The anisotropic characteristics of thermal conductivity and permeability of consolidated ENG-TSA[17] and activated carbon/ENG-TSA composite adsorbent[18] have already been studied, and results indicate that

direction for best heat and mass transfer performance is perpendicular to the compressing direction of composite adsorbent. In the experiment, only plate samples are utilized, and density is selected as 400 kg/m³ with different mass ratio of salt ranging from 50%-83% for comparison.

2.2 Characterization methods

Thermal conductivity is investigated by the Laser flash measuring method, and type of the instrument is LFA447 produced by Netzsch Company. The Laser flash measuring method is explained as follows. For a certain setting temperature T, a beam of light pulses is emitted instantaneously by the a xenon flash lamp and uniformly illuminating in the sample surface, so that the temperature transient increases as the hot end of the one-dimensional heat conducts to the cold end propagation. The trend of the temperature can be measured by using an infrared detector. By analyzing the curves of temperature-versus-time and concerning calculation, thermal conductivity can be determined. The random error of the equipment is less than 0.1%, and the largest relative error is 5%. The sample which is perpendicular to the compression direction is prepared in advance. Permeability is measured by the testing unit which is specially designed, and testing method can be referred to reference[19]. The error of pressure difference transducer is $\pm 0.1\%$ and the error of flow meter is $\pm 4\%$. In the testing process, pressure difference is 210.12 kPa as well as flow rate is 1.5 L/min for the minimum permeability, correspondingly the largest relative error of testing unit is 15.1%, and the average relative error of the test unit is 14.7%.

For the non-equilibrium adsorption/desorption testing, the experimental unit is shown in Fig.1. As Fig.1a shows, the experimental unit is composed of a refrigerant vessel, a pressure transmitter, valves and two adsorption beds. Only one adsorption bed is used for the experiments. The vessel acts as condenser or evaporator, depending on the operation conditions. Temperature of adsorption bed and the vessel is controlled by three thermostat baths. Fig. 1b shows photo of the test unit.

The testing processes of isobaric adsorption/desorption lines are as follows:

Adsorption process: Open the valves V1 and V3 in Fig.1. Keep the refrigerant vessel at a constant pressure through thermostat bath, and control the temperature of adsorption bed 1 decreasing from high temperature to environmental temperature slightly. For each test point with predetermined refrigerant temperature and adsorption temperature the fluid level in the refrigerant vessel is recorded by the smart pressure transmitter when the data doesn't change for at least 5 minutes.

Desorption process: By the similar way the bed is heated from environmental temperature to desorption temperature slowly, and the data of the refrigerant level in the refrigerant vessel is recorded. The adsorption quantity of adsorbent is calculated by the refrigerant level in the vessel.

Cycle adsorption quantities are calculated as follows:

$$\Delta x = \frac{1}{m_{salt}} \cdot \Delta \left\{ \left(1 - \frac{v'(T_e)}{v'(T_c)} \right) \cdot \frac{A_c}{g} \cdot \Delta P \right\} \quad (4)$$

where ΔP is the pressure difference for the condensation and evaporation process (Pa), m_{salt} is the adsorbent mass (kg), V is the liquid ammonia volume in the refrigerant vessel (m^3), g is the gravity acceleration (9.80 m/s^2), $v'(T_e)$ is specific volume of saturated liquid ammonia (m^3/kg).

(a)

(b)

Fig.1. Test unit of adsorption performance, (a) Scheme of testing unit; (b) Photo of testing unit.

The adsorbent mass is measured by the balance (BS2202S) with a measuring error of 0.01 g. The pressure difference between the vapor end and liquid end of the evaporator/condenser is tested by the smart pressure transmitter, whose testing error is 0.2%. According to Equation 5, the relative error of adsorption/desorption quantity of calcium chloride is 5.6%.

$$\left| \frac{d\Delta x}{\Delta x} \right| \leq \left| \frac{dm_{salt}}{m_{salt}} \right| + \left[\frac{d\left((1-\nu'(T_e)/\nu''(T_e)) \cdot (A_c/g) \cdot \Delta(\Delta p)\right)}{\Delta\left((1-\nu'(T_e)/\nu''(T_e)) \cdot (A_c/g) \cdot \Delta(\Delta p) + V/\nu''(T_e)\right)} \right] \quad (5)$$

3 Experimental results and discussion

3.1 Thermal conductivity and permeability

Fig.2 shows thermal conductivity of different consolidated composite adsorbents. Results indicate that thermal conductivity increases with decrease of mass ratio of salt under the same density of 400 kg/m³. For different composite adsorbent, when mass ratio of salt is higher than 75%, thermal conductivity of different composite adsorbent is similar to each other. This is mainly because the thermal conductivity improvement caused by the additive of ENG-TSA is not high enough to discriminate that of different composite adsorbent. When mass ratio of salt is lower than 75%, NH₄Cl shows the better performance while CaCl₂ shows the lower performance. The highest thermal conductivity is about 36.5 W/(m.K) for the composite NH₄Cl with 50% mass ratio, which is 120 time higher than granular NH₄Cl. The lowest thermal conductivity of composite MnCl₂ with 83% mass ratio is still 40 times higher than that of granular MnCl₂. For different composite adsorbent, thermal conductivity ranges from 11.9 to 36.5 W/(m.K) with mass ratio of salt from 50% to 75%.

Fig.3 shows that permeability of consolidated adsorbent with different mass ratio of salts. It demonstrates that for different composite adsorbents, permeability ranges from 10⁻¹¹ to 10⁻¹⁴ m² with mass ratio of salt from 50% to 75%. Permeability increases when mass ratio of salt increases. When mass ratio of salt is higher than 80%, the permeability changes slightly. For different composite adsorbent, MnCl₂ shows the better performance while NH₄Cl appears to be the lower one.

Fig.2 Thermal conductivity of consolidated adsorbent with different mass ratio of salts

Fig.3 Permeability of consolidated adsorbent with different mass ratio of salts

3.2 The Clapeyron line of composite adsorbent under non-equilibrium conditions

As it is shown in Fig.1, thickness of the composite adsorbent in the adsorption bed is 14 mm. Since both non-equilibrium heat and mass transfer process will happen under this condition, it will have a great influence on the refrigeration performance. The temperature testing positions are at the middle of adsorbent, and it is at the thickness of 6.5 and 7.5 mm. This temperature is taken as the average temperature with this thickness. The procedures shown in Fig.4 is utilized to test Clapeyron lines, which is greatly different from the equilibrium theoretical line[20].

According to the procedures of Fig.4, adsorption bed is controlled at 150 °C through thermostat bath. Meanwhile the vessel is controlled at 25 °C as the condenser. The temperature difference can drive the

adsorption bed to desorb completely. When the liquid level in the condenser becomes stable, the desorption process finishes. The vessel is controlled at 0 °C as the evaporator. Decrease the temperature of adsorption bed for constant adsorption. Then stop decreasing when the adsorption quantities reach the set level e.g. 2 mol NH₃/mol MnCl₂, 4 mol NH₃/mol CaCl₂. After that the adsorption bed is disconnected from the vessel as the condenser/evaporator. The adsorption bed is heated and cooled, and data of temperature and pressure is recorded for analysis. The bulk adsorption molar quantity of 3, 4, 5 and 6 of MnCl₂ and 5, 6, 7 and 8 of CaCl₂ are similar to the procedures above. For NH₄Cl, the bulk adsorption molar quantity start from 0, 1, 2 and 3.

Fig.4 The procedure for testing the Clapeyron lines

Since Clapeyron diagram of different working pairs under the non-equilibrium conditions are similar to each other, MnCl₂-NH₃ is taken as the example for illustration which is shown in Fig.5. It indicates that the reaction lines for different bulk molar adsorption quantities are different. Only the bulk adsorption quantity of 2 mol NH₃/mol MnCl₂ is same with the theoretical equilibrium line, the others all have the equilibrium reaction temperature lower than that of the theoretical line if the pressure is kept at the same level. Such a phenomena shows that the chemisorption under the non-equilibrium heat and mass transfer conditions is controlled by two variables rather than one variable.

Fig.5 The Clapeyron diagram under the non-equilibrium conditions of $\text{MnCl}_2\text{-NH}_3$ working pair

3.3 The isobaric adsorption/desorption lines of chlorides-ammonia

In order to verify if the adsorption and desorption processes are the same as the experimental Clapeyron lines in the procedure of Fig.4, $\text{MnCl}_2\text{-NH}_3$ working pair is tested under the condition of 30 °C condensing/evaporation temperature while $\text{CaCl}_2\text{-NH}_3$ and $\text{NH}_4\text{Cl-NH}_3$ working pairs are tested under the condition of 0 °C condensing/evaporation temperature. The testing temperature of different working pair is selected for analyzing the resorption refrigeration later since MnCl_2 is selected as HTS and $\text{CaCl}_2, \text{NH}_4\text{Cl}$ are LTS.

Results of $\text{MnCl}_2\text{-NH}_3$ working pair under the pressure of 11.6 bar is shown in Fig.6. 11.6 bar is corresponding to 30 °C saturation temperature of ammonia. Fig.6 indicates that the actual isobaric adsorption data of $\text{MnCl}_2\text{-NH}_3$ working pair fits the experimental Clapeyron line well, but the isobaric desorption line is much different from experimental Clapeyron line. This phenomenon demonstrates if theoretical Clapeyron line is used for simulating the refrigeration performance, the data will have a big deviation because the actual desorption process has the significant hysteresis phenomenon. Fig.6 also indicates that the hysteresis happens for $\text{MnCl}_2\text{-4NH}_3$, and the corresponding heat source temperature is about 131 °C. Such a result is higher than the equilibrium desorption temperature of 110 °C. The hysteresis phenomenon is weaker when ammonia in the ammoniate MnCl_2 becomes less. It almost disappears when the adsorption quantity is nearly 2 mol $\text{NH}_3/\text{mol MnCl}_2$.

Fig.6 The isobaric adsorption/desorption lines of $\text{MnCl}_2\text{-NH}_3$ working pair under 11.6 bar

Similarly, Fig.7 and Fig.8 show the isobaric adsorption/desorption lines of $\text{CaCl}_2\text{-NH}_3$ and $\text{NH}_4\text{Cl-NH}_3$ under the condition of 4.3 bar, which is corresponding to 0 °C saturation temperature of ammonia. Results show that the isobaric adsorption line is very close to experimental Clapeyron line, but the desorption line is much deviated from that. The significant hysteresis phenomenon happens for the $\text{CaCl}_2\text{-7NH}_3$. Comparing the results with experimental Clapeyron line, the serious desorption hysteresis of CaCl_2 happens. The hysteresis happens for $\text{NH}_4\text{Cl-NH}_3$ working pair as well. Although both the isobaric adsorption and desorption line of $\text{NH}_4\text{Cl-NH}_3$ are relatively close to the experimental Clapeyron line, the hysteresis phenomenon still happens to the working pair.

Fig.7 The isobaric adsorption/desorption lines of $\text{CaCl}_2\text{-NH}_3$ working pair under the condition of 4.3 bar

Fig.8 The isobaric adsorption/desorption lines of $\text{NH}_4\text{Cl-NH}_3$ working pair under the condition of 4.3 bar

4 Resorption refrigeration evaluation

4.1 Cycle description

Schematic diagram of the resorption refrigeration cycle is presented in Fig.9a, which mainly includes HTS and LTS adsorption beds. Those two adsorption beds interact through mass transfer in gaseous phase and they interact cyclically throughout two processes of the resorption refrigeration cycle. This process is analogous to conventional adsorption process. Evaporator and condenser is replaced with LTS adsorption bed in the role of heat extraction for cold production. Fig.9b presents thermal dynamic process. Working processes are as follows:

(1) Desorption process of HTS bed. In this process ammonia valve connected between HTS and LTS beds are open. HTS bed is heated by low grade heat $Q_{\text{des-H}}$ and subjected to the temperature $T_{\text{des-H}}$. LTS bed is cooled by environmental heat sink which is subjected to the temperature $T_{\text{ads-L}}$. The desorbed ammonia of HTS bed will be adsorbed by LTS bed. For thermodynamic process in Fig.1b, Point A is the isothermal and isobaric desorbing process of $\text{MnCl}_2 \cdot 6\text{NH}_3$ to $\text{MnCl}_2 \cdot 2\text{NH}_3$ at desorption temperature of HTS, and the isobaric and isothermal adsorption processes for the ammoniate LTSs take place at B.

(2) Desorption process of LTS bed. After the desorption process, resorption refrigeration phase starts as shown in Fig.1a. HTS bed will adsorb ammonia from LTS bed when its pressure is lower than that of LTS bed. Desorption process of LTS bed generates the refrigeration power and transports the refrigeration power to the heat exchange medium. For thermodynamic process shown in Fig.1b, isobaric and isothermal refrigerating processes take place at point C, and at point D the isobaric and isothermal adsorption processes of the ammoniate HTS compound.

Fig.9 Schematic diagram of resorption refrigeration process. (a) Working mode, (b) Thermal dynamic processes.

4.2 System evaluation

According to the experiment unit as Fig.1, cooling production can be obtained by the energy conversation Equation 6. The heat input in the desorption process can be obtained by the Equation 7.

$$Q_{R,LTS} + Q_{S,LTS} = Q_{Cool,LTS} \quad (6)$$

$$Q_{R,HTS} + Q_{S,HTS} = Q_{in,HTS} \quad (7)$$

where Q_R is chemical reaction heat and Q_S was the sensible heat of all parts of the adsorption bed,

which includes salts, ENG-TSA, ammonia and adsorption bed as Equation 8.

$$Q_s = Q_{salt} + Q_{eg} + Q_{NH_3} + Q_{ad} \quad (8)$$

$$Q_{salt} = m_{salt} \cdot C_{p_{salt}} \cdot \Delta T \quad (9)$$

$$Q_{eg} = m_{eg} \cdot C_{p_{eg}} \cdot \Delta T \quad (10)$$

$$Q_{NH_3} = m_{NH_3} \cdot C_{p_{NH_3}} \cdot \Delta T \quad (11)$$

$$Q_{ad} = m_{ad} \cdot C_{p_{ad}} \cdot \Delta T \quad (12)$$

where Q_{salt} , Q_{eg} , Q_{NH_3} and Q_{ad} is sensible heat of chloride, ENG-TSA, ammonia and adsorption bed.

The reaction heat Q_R is calculated as the Equation 13.

$$Q_R = \Delta x_{NH_3} \cdot \Delta H \quad (13)$$

In the calculation of Q_s , since thickness of the composite adsorbent is small, it is assumed that all the elements of the consolidated block (salt and ENG-TSA) and ammonia inside the adsorption bed have the same temperature. The method of measurement is described as Fig.1 above. Two thermocouples are fixed in different positions of adsorption bed to ensure the temperature uniformity of the adsorbent inside. ΔT indicates the difference between initial and end temperature in either adsorption or desorption process. The coefficient of performance (COP) under non-equilibrium condition and COP under ideal condition can be calculated as equation 14.

$$COP = \frac{Q_{Cool,LTS}}{Q_{in,HTS}} \quad COP_i = \frac{\Delta H_{r,LTS}}{\Delta H_{r,HTS}} \quad (14)$$

The specific cooling power (SCP) can be calculated as equation 9.

$$SCP = \frac{Q_{Cool,LTS}}{t_{cycle} \cdot m_{tot}} \quad (15)$$

where t_{cycle} is cycle time which is defined as 30 minutes. m_{tot} is the total mass of HTS and LTS composite adsorbent.

Table 1 Main parameters used in the calculation of refrigeration performance.

Adsorption bed	HTS bed(MnCl ₂)	LTS bed(CaCl ₂)	LTS bed(NH ₄ Cl)
m_{salt} (g)	200	200	200
$m_{e,g}$ (g)	50	50	50
$m_{s,s}$ (kg)	3.42	3.42	3.42
C_{salt} (J/g.K)	0.6	0.64	1.6
$C_{e,g}$ (J/g.K)	0.6	0.6	0.6

C_{NH_3} (J/g.K)	4.59	4.59	4.59
$C_{\text{s,s}}$ (J/g.K)	0.46	0.46	0.46
ΔH (J/mol)	47,416	41,013	29,433

4.3 Calculation results

Under the condition of 0 °C evaporating temperature, 30 °C condensing temperature and different heat source temperature from 115-135 °C, the equilibrium and non-equilibrium refrigeration performance of resorption refrigeration are calculated. Theoretically, COP_i and SCP of $\text{MnCl}_2\text{-CaCl}_2\text{-NH}_3$ working pairs for equilibrium resorption refrigeration is 0.86 and 349.4W/kg while COP_i of $\text{MnCl}_2\text{-NH}_4\text{Cl-NH}_3$ is about 0.62 and 307.3 W/kg. Considering the metal capacity ratio, COP_i of $\text{MnCl}_2\text{-CaCl}_2\text{-NH}_3$ working pairs for equilibrium resorption refrigeration is 0.45 and 182.9 W/kg while COP_i of $\text{MnCl}_2\text{-NH}_4\text{Cl-NH}_3$ is about 0.32 and 160.8 W/kg.

The non-equilibrium refrigeration performance of $\text{MnCl}_2\text{-CaCl}_2\text{-NH}_3$ and $\text{MnCl}_2\text{-NH}_4\text{Cl-NH}_3$ working pair are shown in Fig.10 and Fig.11, respectively. It indicates that COP and SCP of $\text{MnCl}_2\text{-CaCl}_2\text{-NH}_3$ working pair range from 0.272-0.25 and 45.6-57.1 W/kg. COP decreases and SCP increases with the increment of heat source temperature. This is mainly because 115 °C heat source temperature can proceed the desorption process completely. Keeping heating HTS adsorption bed is not able to improve the system performance. Compared with $\text{MnCl}_2\text{-CaCl}_2\text{-NH}_3$ working pair, both COP and SCP of $\text{MnCl}_2\text{-NH}_4\text{Cl-NH}_3$ working pair is a little lower. This is mainly because the adsorption quantity is determined by the composite MnCl_2 , and the same mass of composite adsorbent is filled for testing in the adsorption bed. In the real reaction process of analysis, part of composite NH_4Cl don't proceed adsorption and desorption. Besides, COP and SCP of $\text{MnCl}_2\text{-CaCl}_2\text{-NH}_3$ working pair range from 0.2-0.179 and 34.3-40.9 W/kg. The highest SCP and COP of $\text{MnCl}_2\text{-NH}_4\text{Cl-NH}_3$ are 40.9 W/kg and 0.2, which are much lower than the theoretical values of 160.8 W/kg and 0.32. Results of $\text{MnCl}_2\text{-CaCl}_2\text{-NH}_3$ is

similarly lower than the theoretical values. Such results indicate that the equilibrium theoretical data is not suitable for the prediction of the refrigeration performance.

Fig.10 The refrigeration performance for MnCl₂-CaCl₂ resorption working pair

Fig.11 The refrigeration performance for MnCl₂-NH₄Cl resorption working pair

Based on the resorption refrigeration performance, techno-economic analysis is also evaluated by the method in reference [21]. When cooling capacity of resorption refrigerator is assumed as 3kW based on the results of MnCl₂-CaCl₂ working pair in Fig.10. Considering the initial investment of the resorption refrigerator

and current electricity price, payback period of the resorption refrigerator will be 7.2 years with enough heat source. Comparably, payback period of fuel oil is about 19.8 years while that of natural gas is about 30.1 years.

5 Conclusions

In order to analyze the performance of different working pairs for the resorption refrigeration cycle, heat and mass transfer properties as well as adsorption performance under non-equilibrium condition of different composite adsorbent are studied. Thermal conductivity and permeability are tested by Laser flash measuring method and the principle of Ergun model, respectively. Conclusions are yielded as follows:

- [1] Thermal conductivity increases with decrease of mass ratio of salt. The highest thermal conductivity is about 36.5 W/(m.K) for the composite NH_4Cl , and for different composite adsorbent, thermal conductivity ranges from 11.9 to 36.5 W/(m.K). Permeability of different composite adsorbents ranges from 10^{-11} to 10^{-14} m^2 . For different composite adsorbent, MnCl_2 shows the better performance while NH_4Cl appears to be the lower one.
- [2] The Clapeyron lines for different bulk molar adsorption quantities are different. Only the bulk adsorption quantity of 2 mol NH_3 /mol MnCl_2 is same with the theoretical equilibrium line, the others all have the equilibrium reaction temperature lower than that of the theoretical line if the pressure is kept at the same level. Such phenomenon shows that the chemisorption under the non-equilibrium heat and mass transfer conditions is controlled by two variables rather than one variable.
- [3] The actual isobaric adsorption data of $\text{MnCl}_2\text{-NH}_3$ working pair fits the experimental Clapeyron line well, but the isobaric desorption line is much different from experimental Clapeyron line. The hysteresis phenomenon is weaker when ammonia in the ammoniate MnCl_2 becomes less. The serious desorption hysteresis of CaCl_2 and MnCl_2 happens when compared with their Clapeyron experimental line.
- [4] COP and SCP of $\text{MnCl}_2\text{-CaCl}_2\text{-NH}_3$ working pair range from 0.272-0.25 and 45.6-57.1 W/kg. Compared with $\text{MnCl}_2\text{-CaCl}_2\text{-NH}_3$ working pair, both COP and SCP of $\text{MnCl}_2\text{-NH}_4\text{Cl-NH}_3$ working pair are a little lower. Besides, COP and SCP range of $\text{MnCl}_2\text{-CaCl}_2\text{-NH}_3$ working pair from 0.2-0.179 and 34.3-40.9 W/kg. The highest SCP and COP of $\text{MnCl}_2\text{-NH}_4\text{Cl-NH}_3$ are 40 W/kg and 0.2, which are much lower than the theoretical values of 160.8 W/kg and 0.32. The results of $\text{MnCl}_2\text{-CaCl}_2\text{-NH}_3$ is

similarly lower than the theoretical values.

If compared the similar heating, cooling, and refrigeration in reference[22], for which COP is about 0.3, COP of the resorption refrigerator in the manuscript is about 0.272. The lowest theoretical driving temperature for $\text{MnCl}_2\text{-NH}_4\text{Cl}$ resorption refrigerator is about 103 °C, which is much lower than that of refrigerator developed in this paper. From the reference [23], heat source temperature generally is higher than 130 °C. It shows that the real reaction process for resorption refrigeration is close to the non-equilibrium process, in which lower cycle adsorption quantity proceeds. Besides, heat source temperature can be decreased with limited scope.

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Nomenclature

A	Aera of ammonia vessle
c	Specific heat (J/(g.K))

COP	Coefficient of performance
HTS	High temperature salt
g	gravity acceleration (m/s^2)
LTS	Low temperature salt
m	Mass (kg)
P	Pressure (Pa)
Q	Heat (J)
R	Gas constant ($J/(mol.K)$)
SCP	Specific cooling power (W/kg)
t	Cycle time (s)
T	Temperature (K)
V	Volume of liquid ammonia(m^3)
x	Adsorption quantities (kg/kg)

Greek letters

ΔH	Enthalpy difference (kJ/mol)
ΔS	Entropy difference (J/K)
$v'(T_e)$	Specific volume of saturated liquid ammonia m^3/kg

Subscripts

ad	Adsorption bed
cycle	Resorption cycle
cool	Cooling
des	Desorption
eg	ENG-TSA
HTS	High temperature salt
h	Heat

i	Ideal condition
in	In
NH ₃	Ammonia
re	Reaction heat
s	Sensible heat
salt	Chloride
tot	Total