Experimental investigation on a $\text{MnCl}_2\text{-CaCl}_2\text{-NH}_3$ resorption system for heat and refrigeration cogeneration

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Abstract

Sorption thermal energy storage (STES) is perceived as one prospective way of thermal energy storage (TES) owing to the advantages of high energy density, negligible heat loss, flexible working modes and long-term storage capability. Based on STES, this paper exhibits an innovative resorption thermal energy storage (RTES) system, and the experimental prototype is established for heat and refrigeration cogeneration. Working pair of $\text{MnCl}_2\text{-CaCl}_2\text{-NH}_3$ is chosen, 4.8 kg MnCl_2 and 3.9 kg CaCl_2 impregnated in expanded natural graphite treated with sulfuric acid are filled in two sorption beds respectively. Experimental results indicate that the largest energy storage density reaches 1706 kJ/kg when charging and discharging temperature are 160°C and 30°C, respectively. The maximum average cooling power achieves 1.07 kW during discharging phase and corresponding SCP is 27.33 W/kg within the overall cycle period. When charging temperature increases from 135°C to 160°C, the energy efficiency of the resorption system for heat and refrigeration cogeneration augments steadily from 0.72 to 0.87 while the exergy efficiency rises slowly from 0.29 to 0.35.

Keywords

Resorption; Heat and refrigeration cogeneration; Renewable energy; Energy storage

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Nomenclature

c	Specific heat (kJ/(kg•K))
COP	Coefficient of performance
E	Exergy (kJ/kg)
HTS	High temperature salt
h	Enthalpy (kJ/kg)
LTS	Low temperature salt
MTS	Middle temperature salt
m	Mass flow rate (kg/s)
P	Pressure(Pa)
Q	Heat input/output quantity(kJ)
SCP	Specific cooling power (W/Kg)

Subscripts

sor-M	Sorption of MTS
des-M	Desorption of MTS
sor-H	Sorption of HTS
des-H	Desorption of HTS
H	High equilibrium pressure
L	Low equilibrium pressure
c,out	Cold output
HTS 1	The first vessel of HTS Bed
HTS 2	The second vessel of HTS Bed
HTS 3	The third vessel of HTS Bed
out	Outlet

in	Inlet
coo	Cooling
wat	Water
h,lat	Latent heat
h,sen	Sensible heat
h,in	Heat input
h,out	Heat output
h,rel	Heat releasing
ene	Energy
exe	Exergy

1. Introduction

The increasing scarcity and cost of fossil fuels and incentives to mitigate the deterioration of environment have given rise to a growing interest in renewable energy [1], while its unavoidable characteristic of intermittency and variability remains further research to address. Thermal energy storage (TES) technology provides one promising method for the recovery and utilization of low-grade heat such as solar energy, geothermal resource and industrial exhaust [2,3] owing to its capability of diminishing the contradiction between energy supply and demand [4,5].

Methods of TES are generally divided into three categories: sensible, latent and thermochemical [6-8]. Sensible and latent heat storage are the most studied technologies in recent decades. For sensible storage, the energy is stored by varying the temperature of storage materials such as water, aquifer, rock, bricks and so on. The amount of stored heat is proportional to the mass, specific heat and temperature difference of storage medium [9]. Latent storage relies on the phase change process of phase change materials (PCMs) such as nitrate, paraffin, fatty acids etc. at a constant temperature to achieve the releasing and charging of thermal energy [10]. Compared with sensible heat storage, latent heat storage features more compact dimension and higher storage density with a much smaller temperature interval [11] while sensible heat storage is characterized as more economical with its mature technology and convenient operation. Nevertheless, both sensible and latent thermal energy storage inevitably encounters the drawbacks of relatively low storage density, incompetent for cross-regional and cross-seasonal storage and unacceptable energy losses [12]. Sensible thermal energy storage involves temperature fluctuation during heat releasing process which makes it challenging to meet the demands of end users. PCMs widely applied in latent thermal energy storage have the imperfection of phase segregation and subcooling phenomenon during phase change process, besides PCMs can hardly avoid the

disadvantage of low thermal conductivity [13] and severe performance deterioration over repeatedly heating-cooling cycles [14]. Comparably, thermochemical storage provides a feasible scenario to surmount the aforementioned shortcomings by adjusting the space-time discrepancy and weakening the mismatch between energy supply and demand [15, 16].

Sorption storage is one prospective method of thermochemical storage for the large chemical potential between different solid-gas working pairs during sorption and desorption processes [7]. Energy is stored by breaking the binding force between the sorbate and the sorbent in terms of chemical potential in a sorption process. Moreover, sorption storage has been proved to be one of the most efficient TES technologies by energy and exergy analysis of various researches, and it is also regarded as competent for seasonal storage with negligible energy loss. Under this scenario, sorption storage which exhibits high energy density as well as feasibility for long-term energy storage starts to draw a burgeoning attention [17]. Korhammer [18] et al. presented the design criteria as well as thermal and sorption characterizations of composite materials based on CaCl_2 for thermochemical energy storage. Yu [6] et al. summarized different sorption storage technologies driven by the solar energy and compared the strengths and weaknesses of different solid-gas working pairs. Yan [19] et al. summed up the promising candidate reversible reactions and gave the selection criteria of chemical reactions for thermochemical storage. Li [20] et al. analyzed sorption thermal battery for solar cooling and heating energy storage and heat transformer based on solid-gas reaction process of working pairs. Results indicated that the highest heat and cold energy storage density can reach 1600 and 720 kJ/kg respectively using working pair of $\text{SrCl}_2\text{-NH}_3$. Haije [21] et al. investigated the property of a $\text{LiCl-MgCl}_2\text{-NH}_3$ sorption energy storage system and experimentally achieved an energy density of 222 W/kg and a

coefficient of performance (COP) of 0.11 respectively. The research on sorption energy storage mainly focuses on new sorbents, optimized configuration of heat-exchange reactor, advanced charging and discharging cycles [22].

Solid sorption process has been extensively researched for refrigeration in recent decades benefiting from its character of energy saving and environmental benign due to the recovery of low-grade thermal energy and utilization of green refrigerants. Solid sorption chiller has partly achieved industrial application under air-conditioning and ice-making conditions. Kaushik [23] et al. provided detailed analysis of materials and collectors for solar sorption cooling in the second decade of 21st century. Lu [24] et al. experimentally studied a solar powered solid sorption cooling system with new compound parabolic concentrator collectors which had an average solar COP of 0.16. Wang [25] et al analyzed the performance of the cogeneration of electricity and refrigeration of a resorption system and it achieves an electricity generation exergy of up to 0.69 and a refrigeration COP of up to 0.77 with a heat source temperature higher than 100°C theoretically. Resorption refrigeration has a higher refrigeration capacity and coefficient of performance when compared with sorption [26] due to that the refrigerating capacity is generated by reaction heat [27] rather than the latent heat of evaporation of refrigerants, and it also has the superiority of safety and simple structure since there is little liquid ammonia in the system.

With specific regard to the working pair of $\text{MnCl}_2\text{-CaCl}_2\text{-NH}_3$, some studies about this very working pair have been reported. Jiang [28] et al comprehensively investigated the energy storage properties of the working pair under different working conditions. Results revealed that the highest thermal storage density was 1836 kJ/kg when heat charging and discharging temperature was 155°C and 55°C, respectively. Gao [29] et al validated the feasibility of a refrigerated truck

driven by exhaust gas of engine to provide refrigerating capacity. The experimental results showed that the maximum refrigerating capacity of 1.25 kW and COP of 0.143 were obtained when the hot air and refrigerating temperatures were 230°C and -5°C, respectively. Nevertheless, little research on the cogeneration of heat and cold of this sorption material has been launched. In this paper a novel resorption system using the working pair of $\text{MnCl}_2\text{-CaCl}_2\text{-NH}_3$ is established to investigate the performance of heat and refrigeration cogeneration. Performance analysis is introduced for a comprehensive perception of the system.

2. Establishment of the heat and refrigeration cogeneration cycle

For equilibrium pressure of 1.5 MPa, the salts driven by the temperature higher than 150°C, between 90°C and 150°C, and lower than 90°C, were termed as high temperature salts (HTSs such as MnCl_2 , NiCl_2 , FeCl_3), middle temperature salts (MTSs such as CaCl_2 , SrCl_2), and low temperature salts (LTSs such as NH_4Cl , BaCl_2 , NaBr), respectively [30]. In consideration of cycle sorption quantity and matching with the temperature of heat source, MnCl_2 and CaCl_2 are selected as HTS and MTS for the RTES system according to the aforementioned criterion.

The operation procedures of the resorption system for heat and refrigeration cogeneration are based on energy conversion between thermal energy and bond energy of sorption potential during the solid-gas sorption process. The Clapeyron diagram of thermodynamic cycle is presented in Fig.1a, which mainly involves energy storage as well as heat and cold cogeneration processes. The thermodynamic cycle can be broadly divided into two processes: charging (energy storage) and discharging (cold and heat cogeneration) process (Fig.1b and 1c). During charging (A-B) process which consists of desorption (also known as decomposition) in HTS reactor and sorption (also referred to as synthesis process) in MTS reactor (Fig.1b). HTS stores thermal energy in the form

of bond energy deriving from the desorption process at a high temperature. When HTS reactor is heated by the oil tank to a certain temperature (point A in Fig.1a), ammonia which clings to MnCl_2 sorbent begins to escape. Then the gaseous ammonia flows through a pipe under the influence of pressure difference and sorbed by MTS reactor at a lower temperature (point B in Fig.1a). Simultaneously, sorption heat $Q_{\text{sor-M}}$ is released to the ambient through water thermostat. It is worth emphasizing that some extra sensible heat has been introduced into the system to heat the metal, solid sorbent and other components. After the energy storage phase, the ammonia valve between HTS and MTS reactors is closed so as to avoid chemical reaction by separating the sorbents and sorbate (Fig.1b and 1c). Once heating or cooling demand needed, the discharging process occurs by connecting HTS and MTS reactors (Fig.1c). During this process (C-D), system releases stored energy in the form of cold and heat energy by performing desorption process in MTS reactor (point C in Fig.1a) and sorption process in HTS reactor (point D in Fig.1a) at a lower pressure simultaneously. HTS reactor provides a heating effect $Q_{\text{sor-H}}$ at point D and MTS reactor offers a cooling effect $Q_{\text{des-M}}$ at point C based on different demands of end users respectively. Both sensible and sorption heat are utilized to supply the useful heat output.

Fig.1 Schematic diagram of resorption system: (a) Clapeyron diagram of the cycle; (b) charging process; (c) discharging process.

Fig.2a manifests the body section of resorption system. As shown in the photo, six

shell-and-tube containers form two sorption reactors, i.e. HTS and MTS reactor. 4.8 kg MnCl_2 and 3.9 kg CaCl_2 compounded with expanded natural graphite treated with sulfuric acid (ENG-TSA) are compressed among the fin gaps of finned pipes inside HTS and MTS reactors, respectively. There are two PCM energy storage tanks in the resorption system marked with “1” in Fig.2a. The upper tank filled with ternary mixed molten nitrate salt (HITEC molten salt) which consists of 53% KNO_3 , 40% NaNO_2 and 7% NaNO_3 is used to storage the excess heat of heating oil during charging phase, the other filled with tetrabutyl ammonium bromide (TBAB) is utilized to storage cold thus achieving a goal of sustained refrigeration. Fig.3 shows the structure of HTS/MTS reactors in detail. The length, outer diameter and fin height of each finned tube are 1 m, 25 mm and 32 mm, respectively. After the compound sorbents are squeezed into the fin gaps of finned pipes to a certain packed density, a stainless steel mesh is utilized to coat the surface of finned tube to prevent agglomeration phenomenon of sorbent during sorption process effectively. Each container of HTS/MTS reactor involves six such finned tubes. Fig.4 denotes the flow diagram of the RTES system which contains an ammonia valve V_5 , four water valves V_1 , V_2 , V_3 , V_4 and four oil valves V_6 , V_7 , V_8 , V_9 . For the development of sorption material [31], firstly the granular ENG-TSA is dried in the oven at the temperature of 150°C for 2h to eliminate the mass error caused by moisture and impure gas; secondly mix the alkali halides with water to form homogeneous solution; thirdly put the dried ENG-TSA into the solution and stir the mixture thoroughly. The ratio among halide, ENG-TSA, and water is 5:1:15. After that the prepared mixture is put into the oven at the temperature of 120°C for 12h. Due to the existence of crystal water in some alkali halides, put them in the oven at a higher temperature of 220°C for another 12h to eliminate the crystal water.

(a)

(b)

(1) PCM energy storage tanks; (2) HTS reactor; (3) heat exchanger between oil and water for cooling the oil tank; (4) MTS reactor; (5) cooling tower; (6) safety valve; (7) pressure gauge; (8) inlet ammonia valve for power generation; (9) main valve between HTS and MTS reactor; (10) outlet ammonia valve for power generation

Fig.2 Picture of cogeneration system: (a) resorption refrigeration part; (b) auxiliary equipment.

(a)

(b)

Figure.3 Structure of HTS/MTS reactors: (a) finned-tube: 1-bare finned tube; 2-finned tube with sorbent; 3-finned tube covered with coated screen; (b) containers of HTS/MTS reactors.

ENG-TSA can enhance the performance of heat transfer and sorption process due to its porous structure; besides it can also elevate the mass transfer by preventing agglomeration phenomenon significantly [32]. Temperature of HTS reactor is controlled by the oil tank and the cooling tower while the temperature of MTS reactor is regulated by the water thermostat. Fig.2b shows the picture of RTES system with auxiliary equipment, namely data collector, cooling tower, thermostat, oil tank and RTES part. Pt100 temperature sensors (full scale from -20 - 350°C with accuracy of $\pm 0.5\%$) and pressure sensors (full scale from 0 to 2.5 MPa with tolerance of $\pm 0.1\%$)

are placed at different part of HTS and MTS reactor. The experimental data are monitored and recorded by an Agilent 34972A.

Fig.4 Flow diagram of the RTES system

In order to obtain an overall understanding of the resorption system, different charging, cooling and discharging temperature are investigated and compared in this paper. The heat charging temperature of oil ranges from 130°C to 160°C. The heat discharging temperature covers the span of 30°C to 50°C with an increment of 5°C. Cooling temperature is controlled at 5°C, 10°C and 15°C respectively to simulate air-conditioning conditions.

3. Performance analysis

For comprehensive perception sake, some parameters are given to evaluate the performance of the resorption system.

The heat input during charging phase is calculated by:

$$Q_{h,in} = \int_0^{t_{h,in}} c_o \cdot m_o \cdot (T_{HTS,i} - T_{HTS,o}) dt \quad (1)$$

where $Q_{h,in}$ is the charging heat provided by heating oil. $t_{h,in}$ is the charging time. c_o and m_o are specific heat and mass flow rate of heating oil, respectively. $T_{HTS,i}$ and $T_{HTS,o}$ are inlet and outlet temperature of HTS reactor.

$$Q_{h, \text{sen}} = \int_0^{t_{\text{coo}}} c_o \cdot m_o \cdot (T_{\text{HTS}, o} - T_{\text{HTS}, i}) dt \quad (2)$$

where $Q_{h, \text{sen}}$ is the sensible heat output of HTS reactor during cooling phase and t_{coo} is the cooling time.

The heat output during discharging phase is calculated by:

$$Q_{h, \text{rel}} = \int_0^{t_{h, \text{rel}}} c_o \cdot m_o \cdot (T_{\text{HTS}, o} - T_{\text{HTS}, i}) dt \quad (3)$$

where $Q_{h, \text{rel}}$, $t_{h, \text{rel}}$ are the discharging heat and time respectively.

$$Q_{h, \text{out}} = Q_{h, \text{sen}} + Q_{h, \text{rel}} \quad (4)$$

Heat storage density is defined as:

$$\text{HSD} = \frac{Q_{h, \text{out}}}{m_{\text{so}}} \quad (5)$$

where m_{so} is the total mass of sorbents i.e. MnCl_2 and CaCl_2 .

Heat storage efficiency and the ratio of latent heat to sensible heat are defined as:

$$\text{COP}_h = \frac{Q_{h, \text{out}}}{Q_{h, \text{in}}} \quad \varepsilon = \frac{Q_{h, \text{sen}}}{Q_{h, \text{rel}}} = \frac{Q_{h, \text{sen}}}{Q_{h, \text{lat}}} \quad (6)$$

where $Q_{h, \text{lat}}$ and $Q_{h, \text{sen}}$ are the latent and sensible heat output respectively.

The refrigerating capacity is calculated by:

$$Q_{\text{ref}} = \int_0^{t_{\text{ref}}} c_w \cdot m_w \cdot (T_{\text{MTS}, i} - T_{\text{MTS}, o}) dt \quad (7)$$

where t_{ref} is refrigerating time. c_w , m_w are specific heat and mass flow rate of cooling water. $T_{\text{MTS}, i}$,

$T_{\text{MTS}, o}$ are inlet and outlet temperature of MTS reactor.

Heat and refrigeration exergy are calculated by:

$$E_{h, \text{in}} = Q_{h, \text{in}} \cdot \left(1 - \frac{T_0}{T_{\text{chr}}}\right) \quad (8)$$

$$E_{\text{heat}} = Q_{h, \text{out}} \cdot \left(1 - \frac{T_0}{T_{h, \text{ave}}}\right) \quad (9)$$

$$E_{\text{cold}} = Q_{\text{ref}} \cdot \left(\frac{T_0}{T_{\text{c,ave}}} - 1 \right) \quad (10)$$

where T_0 is the ambient temperature, T_{chr} and $T_{\text{h,ave}}$ are the average charging and discharging temperature (average temperature of inlet and outlet of oil during charging and discharging phase).

$T_{\text{c,ave}}$ is the average temperature of chilled water.

The coefficient of performance and specific cooling power per kilogram sorbent are expressed as:

$$\text{COP}_c = \frac{Q_{\text{ref}}}{Q_{\text{h,in}}} \quad \text{SCP} = \frac{Q_{\text{ref}}}{M_{\text{ad}} \cdot t_{\text{cyc}}} \quad (11)$$

where t_{cyc} is cycle time.

Total energy efficiency and exergy efficiency:

$$\eta_{\text{ene}} = \frac{Q_{\text{h,out}} + Q_{\text{ref}}}{Q_{\text{h,in}}} \quad \eta_{\text{exe}} = \frac{E_{\text{heat}} + E_{\text{cold}}}{E_{\text{h,in}}} \quad (12)$$

4. Results and discussions

4.1 Heat storage performance

4.1.1 Temperature and pressure variations

The temperature and pressure variations of HTS reactor during charging phase share the similar trends under different charging temperature, and a representative working condition is given to interpret. Fig.5a illustrates the temperature fluctuation in different parts of HTS reactor during charging phase with a heat source temperature of 130°C. Fig.5b presents the pressure change of HTS reactor which also signifies the pressure of MTS reactor thus further characterizes the pressure of the system since the valve between HTS and MTS reactors remains open during energy storage phase.

Fig.5 Temperature and pressure variations of HTS reactor during charging phase under the temperature 130°C: (a) temperature; (b) pressure.

The charging phase persisting roughly 45 minutes as seen in Fig.5a consists of several stages indeed which fail to emerge in the picture. During the first stage of approximately 15 minutes, the temperature of HTS reactor rises gradually since the heat consumed is a prerequisite energy to heat up the reactor to a certain desorption temperature which is subject to the temperature difference, mass ratio between sorbent and auxiliary metal components and heat losses. After that in 15 to 35 minutes, heat absorbed at this stage is primarily applied to provide the desorption heat of composite sorbents inside HTS reactor which accounts for a relatively smooth temperature increment of three containers of HTS reactor. Under the effect of thermal resistance along the route of heating oil, $T_{1,HTS}$ is higher than $T_{2,HTS}$ and $T_{2,HTS}$ is higher than $T_{3,HTS}$, likewise. Simultaneously, MTS reactor undergoes a sorption process and heat released this period explains the temperature fluctuation of cooling water at the outlet of MTS reactor. For the last nearly 10 minutes, temperature of HTS reactor augments slightly and emerges a trend to maintain at a constant magnitude under the presence of heat transfer temperature difference which also signifies the termination of desorption process in HTS reactor. The pressure remains almost unchanged at 0.1 MPa for the first 15 minutes, then increases sharply from 0.1 MPa to 0.7 MPa for the next 15

minutes and declines gradually for the last 15 minutes which depicts the aforementioned several stages indirectly as well. It is worth emphasizing that the desorption process in HTS reactor and sorption process in MTS reactor share the identical reaction rate when system achieves its peak pressure of 0.7 MPa at around 30 minutes. The main ammonia valve is closed in order to avoid the chemical reaction thus achieving an objective of energy storage at the end of charging phase. Subsequently, HTS reactor is cooled to discharging temperature ranging from 30°C to 50°C while MTS reactor is controlled to the predesigned temperature simulating air-conditioning conditions. Once heat or cold needed, HTS reactor is connected to MTS reactor to meet the demands of end users by performing solid sorption and desorption process correspondingly as mentioned before.

4.1.2 Energy density and efficiency

A full cycle consisting of three phases namely charging phase, cooling phase and discharging phase takes almost 90 minutes and each phase accounts for 45, 15 and 30 minutes, respectively. Since a high-power cooling tower is applied to cool the HTS reactor with an oil-water heat exchanger, the cooling phase occupies a relatively smaller share of total cycling time. After cooling phase, the ammonia valve between HTS and MTS reactor is open to release the stored energy while the HTS reactor is adjusted to 30-50°C with an increment of 5°C. When the MTS reactor is 15°C, the corresponding theoretical equilibrium temperature of HTS is 64°C which means the lower the discharging temperature is the more obvious effect we can get, due to a larger driven force. In order to give an intuitive impression of the resorption system during discharging phase, the largest outlet temperature increment of HTS reactor which features the largest temperature difference between outlet temperature of cycling oil and discharging temperature is introduced to qualitatively describe the effect of thermal storage. Table 1 depicts the largest outlet

temperature increment under different charging and discharging temperature at a cooling temperature of 15°C. The outlet temperature increment ranges from 4°C to 20°C under different working conditions. As clearly indicated, the maximum temperature increment increases with the augment of charging temperature and the decrease of discharging temperature. The temperature variation during discharging phase shows the similar trends of which increases sharply at the early period and then decrease gradually. This is mainly because the desorption process in MTS reactor has a faster reaction rate than the sorption process in HTS reactor. Charging temperature plays an important role in determining the performance of heat releasing for a higher charging temperature leads to a faster reaction rate which means that more ammonia will be sorbed by MTS in the same charging time. Similarly, a lower discharging temperature means a larger temperature difference thus a higher outlet temperature increment can be expected.

Table.1 The largest outlet temperature increment of HTS reactor during discharging phase

The largest outlet temperature increment/°C		Charging temperature/°C			
		130	140	150	160
Discharging temperature/°C	50	4	6	9	10
	45	8	10	11	12
	40	13	14	15	16
	35	14	15	16	17
	30	17	18	18	20

Heat storage density is commonly used to evaluate the performance of TES and it is also introduced for the resorption system based on the quantity of filling sorbents as depicted in Fig.6. Fig.6a describes the energy density with different charging and discharging temperature at a cooling temperature of 15°C. Energy density ranges from 912-1706 kJ/kg and the highest energy density is achieved at a charging temperature of 160°C and a discharging temperature of 30°C. As seen from the picture, energy density increases with the increment of charging temperature and the

decrease of discharging temperature which agrees with the trends of outlet temperature increment shown in Table 1. Fig.6b presents the energy density with different charging and cooling temperature when the discharging temperature is 30°C. Energy density ranges from 1159-1629 kJ/kg and the largest energy density attains when charging and cooling temperature are 155°C and 15°C respectively. Energy density increases with the increment of both charging and cooling temperature, as shown in Fig.6b. Incidentally, the corresponding theoretical discharging temperature increases when cooling temperature augments which signifies a higher temperature driven force of heat releasing.

Fig.6 Heat storage density for resorption system: (a) density with discharging temperature; (b) density with cooling temperature.

With the same discharging and cooling temperature of 30°C and 15°C respectively, Figure 6 describes the energy storage efficiency and the ratio of sensible heat to latent heat under different charging temperature ranging from 135-155°C with an increment of 5°C. Results reveal that both energy efficiency and ratio of sensible heat to latent heat increase with the rise of charging temperature. The ratio of sensible heat to latent heat ranges from 0.72 to 0.90 while energy storage efficiency covers the span of 0.67 to 0.79, and the maximum values both achieve at the charging temperature of 155°C. As the charging temperature rises, the increment of sensible heat and latent heat is larger than the heat input during charging phase which accounts for a gradual augment of

energy storage efficiency. For charging temperature lower than 150 °C, ratio of sensible heat to latent heat increases sharply. This is mainly because HTS reactor only desorbs partly during charging phase which leads to little ammonia sorbed by HTS for discharging phase. When charging temperature is higher than 150°C, energy storage efficiency changes very little for cycle sorption quantity determined by charging temperature almost remains unchanged which means HTS can desorb completely during charging phase, and heat input is mainly used for providing sensible heat of mental, salt and auxiliary components. The corresponding exergy efficiency ranges from 0.28 to 0.34 when charging temperature increases from 135°C to 155°C.

Fig.7 Heat storage efficiency and the ratio of sensible heat to latent under different charging temperature

4.2 Performance of resorption refrigeration

Different refrigeration temperature shares the similar trends along with the charging temperature, and air-conditioning condition of 15°C is chosen as an example when the discharging temperature is 30°C. Fig.8 shows the average cooling power under different charging temperature with a refrigeration time of 20 minutes. The average cooling power during discharging phase ranges from 0.59 to 1.07 kW and the largest value achieves at the charging temperature of 160°C. If taking the average cycle time 90 minutes into consideration, the average cooling power falls to

as low as 238 W. SCP and COP of the resorption system under different charging temperature are presented in Fig.9 which cover the range of 15.00 to 27.33 W/kg and 0.05 to 0.07, respectively. As shown in picture, both SCP and COP increase with the increase of charging temperature and the maximum values both occur at charging temperature of 160°C. Since the heat input is quite large, and the large part of cooling power consumed by the sensible heat of MTS reactor, the values of SCP and COP are relatively small.

Fig.8 Average cooling power under different charging temperature during discharging phase

Fig.9 Refrigeration performance of resorption system under different charging temperature

4.3 Heat and refrigeration cogeneration

Table 2 interprets the energy balances of the RTES system at a cooling temperature of 15°C and a discharging temperature of 35°C. Total heat input, sensible heat output, latent heat output and refrigeration capacity output all increase with the increment of charging temperature as shown in the table. The quantities of sensible and latent heat output share the similar magnitude while the value of refrigeration capacity output is much smaller due to the large metal thermal capacity of MTS reactor and relatively short resorption refrigeration time. Energy and exergy efficiency derived from Eq.12 are calculated so as to evaluate the resorption system for heat and refrigeration cogeneration. The discharging temperature and refrigerating temperature are 30°C and 15°C respectively. Fig 10 describes the overall energy and exergy efficiency of the resorption system under different charging temperature. Energy efficiency ranging from 0.72 to 0.87 which achieves its largest value at a charging temperature of 160°C increases with the augment of charging temperature as shown in picture. Comparatively, exergy efficiency raises quite smoothly from 0.29 to 0.35 while charging temperature rises from 135°C to 160°C.

Table.2 Energy and exergy balances for RTES system

Cooling temperature=15°C; Discharging temperature=35°C							
Charging temperature (°C)	Total heat input (kJ)	Total exergy input (kJ)	Sensible heat output (kJ)	Latent heat output (kJ)	Refrig. capacity output (kJ)	Total energy loss (kJ)	Total exergy loss (kJ)
135	15710	4426	4419	6158	705	4427	3152
140	16243	4717	4841	6288	773	4341	3333
145	16908	5054	5544	6494	868	4001	3498
150	17574	5399	6248	6998	957	3370	3638
155	18016	5680	6730	7438	1144	2704	3752
160	18458	5965	7213	7628	1284	2332	3888

Fig.10 Energy and exergy efficiency for the resorption system under different charging temperature

Heat storage density and total energy efficiency are two major parameters involved in the performance evaluation of the RTES system, and the relative tolerances are calculated as follows:

$$\left| \frac{dHSD}{HSD} \right| \leq 2 \left| \frac{dm_{so}}{m_{so}} \right| + \left| \frac{dQ_{h,sen}}{Q_{h,sen}} \right| + \left| \frac{dQ_{h,rel}}{Q_{h,rel}} \right| = 2 \left| \frac{dm_{so}}{m_{so}} \right| + 2 \left| \frac{dm_o}{m_o} \right| + 2 \left| \frac{d\Delta T}{\Delta T} \right|$$

$$\left| \frac{d\eta_{ene}}{\eta_{ene}} \right| \leq 3 \left| \frac{dQ_{h,in}}{Q_{h,in}} \right| + \left| \frac{dQ_{h,sen}}{Q_{h,sen}} \right| + \left| \frac{dQ_{h,rel}}{Q_{h,rel}} \right| + \left| \frac{dQ_{ref}}{Q_{ref}} \right| = 5 \left| \frac{dm_o}{m_o} \right| + \left| \frac{dm_w}{m_w} \right| + 6 \left| \frac{d\Delta T}{\Delta T} \right|$$

The maximum relative tolerances of heat storage density and energy efficiency are 4% and 9% respectively.

5. Conclusions

A novel RTES system for heat and refrigeration cogeneration is investigated and analyzed. Working pair of $MnCl_2$ - $CaCl_2$ - NH_3 is selected for the system. Both heat storage and refrigeration performance as well as overall performance are investigated under different charging, cooling and discharging temperature. Conclusions are yielded as follows:

- (1) The energy storage density and largest outlet temperature increment increase with the decrease of discharging temperature. Under the discharging and cooling temperature of 30°C and 15°C respectively, the maximum outlet temperature increment is 20°C at the charging temperature

of 160°C. The energy storage density ranging from 912-1706 kJ/kg also achieves its peak value under that working condition. The ratio of sensible heat to latent heat ranges from 0.72 to 0.90 while the energy storage efficiency covers the span of 0.67 to 0.79 and energy storage efficiency changes little when charging temperature is higher than 150°C.

(2) With a cooling temperature of 15°C, the average cooling power rises from 0.59 kW to 1.07 kW during discharging phase and the refrigeration time is 20 minutes. Corresponding COP and SCP range from 0.05 to 0.07 and 15.00 to 27.33 W/kg, respectively. Taking total cycle time 90 minutes into consideration, the average cooling power falls to as low as 238 W.

(3) Both energy and exergy efficiency of the RTES system for heat and refrigeration cogeneration increase with the augment of charging temperature. Energy efficiency increases from 0.72 to 0.87 while exergy efficiency rises slowly from 0.29 to 0.35.

For the RTES system the TES performance is perspective, while the cooling power for cogeneration phase is too low. Such a result is due to the large mental thermal capacity of MTS reactor, and it consumes large part of the cooling power. Meanwhile the short resorption refrigeration time, which is less than 1/4 of the whole cycle time, indicates the excellent heat and mass transfer performance for resorption refrigeration process. Thus in the future the reasonable design of the MTS bed with big ratio between the sorbent and metal mass, which can balance the heat and mass transfer process and thermal capacity of MTS reactor, would be desirable for the improvement of the refrigeration performance.

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