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Investigation on performance of multi-salt composite sorbents for multilevel sorption thermal energy storage

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Abstract: Novel bi-salt and tri-salt composite sorbents are developed, and expanded natural graphite treated with sulfuric acid (ENG-TSA) is integrated as the matrix with different mass ratios for heat transfer intensification. Tri-salt composite sorbent is mainly composed of Manganese chloride (MnCl_2), Calcium chloride (CaCl_2) and Ammonium chloride (NH_4Cl) whereas bi-salt composite sorbent comprises Calcium chloride (CaCl_2) and Ammonium chloride (NH_4Cl). Sorption characteristics under non-equilibrium condition are investigated and compared with that under equilibrium condition. Results show that the sorption hysteresis can be alleviated by bi-salt composite sorbent and even eliminated by tri-salt composite sorbent. Based on testing results, multilevel sorption thermal energy storage (STES) is analyzed, which can greatly enhance the versatility and working reliability. It is also worth noting that the highest energy storage density of reaction heat is 1802 kJ/kg and 1949 kJ/kg for tri-salt and bi-salt composite sorbents, respectively. Performance of bi-salt composite sorbent is relatively close to the theoretical data, which indicates three main stages. Comparably, performance of tri-salt composite sorbent shows continuous variation with the increment of reaction temperature. The promising multilevel STES reveals the great potential for energy utilization of variable heat source such as solar power when compared with conventional heat storage methods.

Keywords: Multi-salt, Non-equilibrium, Multilevel, Sorption thermal energy storage (STES)

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22 Nomenclature

A	The effective area of ammonia in the evaporator/condenser (m^2)
Bi-salt	Two kinds of sorbents
c	Specific heat ($\text{J}/(\text{g.K})$)
g	Gravity acceleration (m/s^2)
HTS	High temperature salts
LTS	Low temperature salts
MTS	Middle temperature salts
m	Mass (kg)
P	Pressure (Pa)
PCM	Phase change materials
Q	Heat (J)
R	Gas constant ($\text{J}/(\text{mol.K})$)
STES	Sorption thermal energy storage
Tri-salt	Three kinds of sorbents
T	Temperature (K)
TES	Thermal energy storage
V	Volume of liquid ammonia (m^3)
x	Sorption quantities (mol/mol)

23

24 Greek letters

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

25 Subscripts

c	Cross section
de	Desorption

eg	ENG-TSA
eq	Equilibrium
h	Heat
ideal	Ideal condition
in	Input
m	Metal
NH ₃	Ammonia
out	Output
R	Reaction
s	Sorbent
s,s	Stainless steel
salt	Chloride

26

27 1. Introduction

28 Utilization of low grade heat is one of the main options to overcome the developing constraints with ever
 29 rising energy demands[1]. It is extensively acknowledged that thermal energy storage (TES) has played the
 30 leading role in efficient utilization of renewable energy such as solar energy, geothermal and industrial waste
 31 heat [2]. TES technology is able to overcome the disadvantages of time discrepancy, distance discrepancy and
 32 instability of renewable energy by adjusting mismatch between energy supply and demand[3]. Generally
 33 speaking, TES can be divided into three aspects, i.e. sensible heat storage by using concrete and pebbles etc.,
 34 latent heat storage by means of phase change materials (PCM) and thermochemical energy storage[4].

35 The aim of advanced TES system technologies is to seek for the high energy storage density which will
 36 result in the storage system more compact. Under this scenario, various researchers have made great efforts to
 37 investigate the efficient approaches for TES [5]. Sorption process, characterized as one common thermochemical
 38 process, has been extensively studied for refrigeration and heat pump system[6]. Likewise, sorption working
 39 process has been investigated for the possibility to be applied for TES in recent decades[7]. Since low grade heat
 40 is able to be stored in form of chemical bonds with thermochemical sorption process, the higher energy density
 41 can be obtained in comparison with conventional sensible heat and latent heat storage. Theoretically, owing to

the monovariant characteristic of equilibrium performance, sorption thermal energy storage (STES) has good adaptability to one stable heat source temperature [8]. Furthermore, based on a wide range of chemical sorbents[9], STES has the capacity of different working modes such as direct energy supply, energy upgrade, and combined cooling and heating supply, which could meet different needs of end users[10].

Nonetheless, with a variety of forms, energy sometimes varies with the time and place randomly. Solar energy is one good example of variable heat source[11]. It is quite difficult to store the heat with variable temperature through one certain kind of material within a large temperature slide. To deal with that, various researchers have investigated the cascaded energy storage materials as far as PCM technology is concerned. Peiro et al. [12] evaluated the advantages of using the multiple PCM instead of the single PCM configuration in TES systems. Results demonstrated an average enhancement of 19.36% could be obtained for multiple PCM in comparison with the single PCM configuration on the heat transfer fluid (HTF) temperature difference. Xu and Zhao [13, 14] investigated both steady and unsteady cascaded thermal storage system with multiple PCMs of different phase-change temperatures. It was indicated that the optimization of cascaded PCM enjoyed the higher exergy efficiency of heat utilization. Compared with multiple PCM technology, concept of the cascading STES just starts, which take the advantages of relatively less heat loss and higher efficiency. Li et al.[15] proposed a novel cascaded solar thermal battery on basis of the solid-gas thermochemical sorption materials. Results revealed that heat storage density was higher than 1200 kJ/kg through the novel energy storage method. However, the limited selections of reaction working pairs will restrict the further application of this cascading STES technology. It is noted that equilibrium reaction lines of the different sorbents are often used to analyze the performance of STES. The equilibrium sorption process is regarded as monovariant characteristic, which varies with temperature or pressure. Comparably, real sorption process is the non-equilibrium process, and it will cause the inaccuracy and limitation if performance of STES is analyzed based on the equilibrium condition. Researches have verified that the sorption hysteresis occurs on the non-equilibrium condition[16]. Non-equilibrium hysteresis phenomena would cause sorption process into a bivariate process, which require both temperature and pressure to determine the reaction process [17, 18]. Moreover, for multilevel STES, different kinds of sorbents will be mixed together to realize the low grade heat utilization with a large temperature range. Therefore, it is not suitable to analyze the performance of multilevel STES by the equilibrium reaction line of each sorbent because the mixture of several sorbents probably lead to some novel characteristics, which will either improve or hinder its application.

There is less report about the multilevel STES technology which is regard as potential solution to the

problem of solar power storage and utilization. In this paper, multi-salt composite sorbent is developed, and desorption and sorption process are both investigated to analyze the sorption hysteresis phenomenon. Expanded natural graphite treated with sulfuric acid (ENG-TSA) is chosen as the matrix of sorbent, which has proved to enhance the heat and mass transfer performance [19]. On basis of the testing results, multilevel STES is developed and further analyzed to enhance the versatility and working reliability by widening the working temperature scope.

2. Material characterization

2.1. Development of multi-salt composite sorbents

For multi-salt composite sorbent, MnCl_2 , CaCl_2 , NH_4Cl are selected from high temperature salts (HTS), middle temperature salts (MTS), and low temperature salts (LTS). The thermochemical reaction process of these salts with ammonia can be referred to the Equations 1-5. To the simplified the description of thermochemical reaction process of different sorbents, phrases of MnCl_2 6/2, CaCl_2 8/4, CaCl_2 4/2 and NH_4Cl 3/0 are used in the paper. For example, MnCl_2 6/2 represents the process in which MnCl_2 ammoniate reacts with ammonia from 2 moles to 6 moles. Details of multi-salt composite sorbents in developing process can be referred to the reference[20]. First, ENG-TSA is dried in the oven with controlled temperature of 120 °C. The different chlorides of MnCl_2 , CaCl_2 and NH_4Cl are dissolved in the water, sequentially. Afterwards, ENG-TSA is mixed in the salt solution. As the composite sorbent is mixed thoroughly, the mixture is transferred into an oven and dried 7-8 h at the temperature of 160 °C. Finally multi-salt composite sorbent is compressed into block by the pressing machine for testing.

Mass ratio of salt and compressing density are two major factors in the process of developing the multi-salt composite sorbent. The higher density and lower mass ratio of salt are, the lower permeability and the higher thermal conductivity become. It has been proved that ENG-TSA enjoys the desirable thermal conductivity with the reasonable permeability[21]. In this study, density of the multi-salt composite sorbents are all selected as 400

kg/m³ for testing. For bi-salt composite sorbent of NH₄Cl and CaCl₂, the mass ratio among NH₄Cl, CaCl₂ and ENG-TSA is 2:2:1. For tri-salt composite sorbent, the mass ratio among NH₄Cl, CaCl₂, MnCl₂ and ENG-TSA is 4:4:4:3.

2.2. Characterization methods

For the non-equilibrium sorption/desorption testing, the experimental rig is shown in Fig.1. Fig.1a indicates the schematic of testing rig. As Fig.1a shows, the experimental rig is mainly composed of a refrigerant vessel, a sorption reactor, a differential pressure transmitter and several valves. The vessel plays the role of condenser or evaporator with ammonia as the refrigerant, which depends on the operation conditions. Temperature and pressure of sorption reactor and the vessel are controlled by three thermostat baths. Fig. 1b shows photo of the test rig. Although there are two sorption reactors in the real testing rig, only one sorption reactor is used for the testing. The Clapeyron lines and isobaric sorption/desorption lines are tested, separately.

The testing procedures of Clapeyron lines are as follows:

Sorption reactor is controlled at 180 °C by high-temperature thermostat bath, i.e. thermostat 2. Meanwhile the vessel is controlled at 25 °C. The large temperature difference can drive the sorption reactor to desorb completely. When the liquid level in the condenser becomes constant, the desorption process finishes. The vessel is controlled at 0 °C as the evaporator. The temperature of sorption reactor is slowly decreased for constant sorption. Then stop decreasing when the sorption quantities reach the set level. After that the sorption reactor is separated by the ammonia valves V1 and V3 from the vessel as the condenser/evaporator. The sorption reactor is heated and cooled alternately. The suitable decrease/increase rate of temperature for the sorption reactor keep 1K/min, which have no influence on the Clapeyron lines. Data of temperature and pressure are recorded for analysis. The above procedures are repeatable and all the Clapeyron lines under different conditions can be

obtained.

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

Sorption process: Open the valves V1 and V3 in Fig.1a. Keep the refrigerant vessel at a constant pressure by low-temperature thermostat bath i.e. thermostat 1, and control the temperature of sorption reactor decreasing from high temperature to environmental temperature slowly. The decrease/increase rate of temperature also keep 1 K/min, and it will be further reduced to 0.5 K/min for some important temperature ranges when the sorption quantity changes fast. This is because too fast decrease/increase rate of the reactor temperature will miss some variation points of the sorption quantity. For each test point with predetermined refrigerant temperature and sorption temperature the fluid level in the refrigerant vessel is recorded by the smart pressure transmitter when the data doesn't change for at least 6 minutes.

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

Cycle sorption quantities are calculated as Equation 6.

$$\Delta x = \frac{1}{m_{salt}} \cdot \Delta \left\{ \left(1 - \frac{v'(T_e)}{v'(T_c)} \right) \cdot \frac{A_c}{g} \cdot \Delta P \right\} \quad (6)$$

where ΔP is the pressure difference for the condensation and evaporation process (Pa), m_{salt} is the sorbent 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_c is the effective area of cross section of ammonia in the evaporator / condenser (m^2).

(a)

(b)

Fig.1. Test rig for sorption performance (a) schematic of testing rig; (b) photo of testing rig.

The sorbent 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 differential pressure transmitter, whose testing error is 0.2%. According to Equation 7, the relative error of sorption/desorption quantity and cycle sorption quantity of different sorbent are 0.37% and 0.56%, respectively.

$$\left| \frac{d\Delta x}{\Delta x} \right| \leq \left| \frac{dm_{salt}}{m_{salt}} \right| + \left[\frac{d\left((1-\nu'(T_e)/\nu''(T_e)) \cdot (A_c/g) \cdot \Delta(\Delta p)\right)}{\Delta\left((1-\nu'(T_e)/\nu''(T_e)) \cdot (A_c/g) \cdot \Delta(\Delta p) + V/\nu''(T_e)\right)} \right] \quad (7)$$

3. Experimental results and discussion

3.1. Sorption characteristic of single salt composite sorbent

The Clapeyron lines and isobaric sorption/desorption lines of composite NH_4Cl , CaCl_2 and MnCl_2 are shown in Fig. 2, which can be referred to our previous work[22]. Fig. 2a shows that the Clapeyron lines of three different composite sorbents whereas Fig.2b indicates the isobaric sorption/desorption lines. According to Fig.2a, it is indicated that the experimental non-equilibrium Clapeyron lines for MnCl_2 , CaCl_2 and NH_4Cl composite sorbent are parallel to theoretical line, but much different from the theoretical value. The more ammonia sorbed, the larger difference between the theoretical and experimental results. Such a result indicates that the experimental sorption/ desorption performance of different halides has binary variables of pressure and temperature other than single variable of pressure or temperature. As it is shown in Fig.2b, the sorption hysteresis phenomena is significant in the isobaric sorption/desorption processes of three different kinds of $\text{MnCl}_2\text{-NH}_3$, $\text{CaCl}_2\text{-NH}_3$ and $\text{NH}_4\text{Cl -NH}_3$ working pair.

(a)

(b)

Fig. 2. Performance of single salt composite sorbent under non-equilibrium conditions (a) Clapeyron lines; (b) isobaric sorption/desorption lines.

3.2. Sorption characteristic of bi-salt composite sorbent

Considering for the bi-salt composite sorbent, both temperature and pressure have been tested under the condition of different sorption quantities, and the results are compared with equilibrium Clapeyron lines of CaCl_2 8/4, CaCl_2 4/2 and NH_4Cl 3/0, separately. Fig.3 reveal the Clapeyron lines of bi-salt composite sorbent under non-equilibrium conditions. For bi-salt composite sorbent, when the sorption quantity reaches in the vicinity of 4.6 mol NH_3 /mol salt, the line is close to the theoretical Clapeyron line of NH_4Cl 3/0. That means sorption process of bi-salt proceeds thoroughly. Comparably, when the sorption quantity becomes as low as 0.7 mol NH_3 /mol salt, the line is close to the equilibrium Clapeyron line of CaCl_2 4/2, which means that this sorption process of bi-salt composite sorbent just begins. The bi-salt composite sorbent has the conformity with single salt

from the beginning to the end.

Fig. 3. The Clapeyron lines of bi-salt composite sorbent under non-equilibrium conditions.

Fig. 4 indicates the isobaric sorption/desorption lines of bi-salt composite sorbent under different working pressure. As Fig.4a shows, one worthy noting fact is that one desorption stage begins at 24 °C and ends in 63 °C at 630 kPa pressure which is according to condensing temperature of 10 °C. These desorption temperatures are quite close to the equilibrium values, which demonstrates that both kinds of chlorides, i.e. CaCl₂ and NH₄Cl distribute well in the bi-salts composite sorbent.

Similar conclusions can be obtained from Fig.4b, which show the isobaric sorption/desorption lines under the condition of 1046 kPa (i.e. 25°C condensing temperature). Compared with the performance of the single salt composite sorbent above, sorption hysteresis is much less significant. This phenomenon is mainly because the development of multi-salt composite sorbent can lower reaction heat, which is considered to be relevant with the hysteresis by various researchers[23]. Sorption, desorption and resorption process happen in the bi-salt composite sorbent, leading to the decrease of the reaction heat with their interaction. Therefore, multi-salt composite sorbent maybe a better choice for sorption refrigeration and thermal energy storage because it proceeds a continuous sorption process, which can fit the heat source better than the single salt.

Fig. 4. The isobaric sorption/desorption lines of bi-salt composite sorbent (a) 630 kPa; (b) 1046 kPa.

3.3. Sorption characteristic of tri-salt composite sorbent

Fig.5 indicates that Clapeyron lines of tri-salt composite sorbent under non-equilibrium conditions, which show the similar trends as bi-salt composite sorbent. The sorption quantity range from 1.4 to 4.9 mol ammonia/mol salt in accord with theoretical lines of MnCl_2 6/2 and NH_4Cl 3/0, respectively. The line of about 2.6 mol NH_3 /mol salt conforms to the theoretical Clapeyron line of CaCl_2 8/4. Another striking point is that the sorption and desorption process of one certain sorbent is more than monovariant, i.e. one temperature accords with one pressure.

Fig. 5. The Clapeyron lines of tri-salt composite sorbent under non-equilibrium conditions.

Fig.6 shows the isobaric sorption/desorption lines of tri-salt composite sorbent. Results show that desorption temperature of each stage is quite close to the equilibrium value, which demonstrates that three kinds of chlorides, i.e. $\text{NH}_4\text{Cl}/3-0$, $\text{CaCl}_2/8-4$, $\text{CaCl}_2/4-2$ and $\text{MnCl}_2/6-2$ exist in the tri-salts composite sorbent. Still sorption hysteresis is even less significant than that of bi-salt composite sorbent and almost disappear in other words. As for the results among single salt, bi-salt and tri-salt composite sorbents, the more kinds of salts are mixed, the less sorption hysteresis phenomenon exists. This is mainly because more parts of the desorption heat and sorption heat will be neutralized while more resorption processes may happen and interact with each other. As Fig.6 shows, some parts of sorption and desorption process are almost overlapped due to lower reaction heat.

Fig. 6. The isobaric sorption/desorption lines of tri-salt composite sorbent (a) 630 kPa; (b) 1046 kPa.

4. Multilevel sorption thermal energy storage (STES) evaluation

4.1. Cycle description

Schematic diagram of the multilevel STES cycle is shown in Fig.7, which mainly consists of a reactor, a condenser and an evaporator. Fig.7a and Fig.7b indicate working mode and thermodynamic process of the multilevel sorption energy storage, respectively. Considering for the same condensing and evaporation temperature, different kinds of sorbents with cascading equilibrium reaction temperature from T_1 to T_n ($T_n > \dots > T_2 > T_1$) are filled inside the reactor by means of the developing method of multi-salt composite sorbent. The reactor and evaporator/condenser interact through mass transfer in gas channel. Two theoretical working processes are as follows:

(1) Desorption process of the reactor. In this heat charging process ammonia valve connected between reactor and condenser are open. The reactor is heated by low grade heat Q_{des} . Condenser is cooled by environmental heat sink. Ammonia will be desorbed according to the desorption temperature of each sorbent sequentially, and be condensed in the condenser, releasing the condensing heat Q_{con} to the environment. For thermodynamic process, point A is the isothermal and isobaric desorption process of sorbent with equilibrium temperature T_{d1} while point A' is the isothermal and isobaric desorbing process of sorbent with equilibrium temperature T_{dn} . With the increment of reaction temperature, desorption processes sequentially happen from point A to point A', and condensing processes for the refrigerant all take place at point B.

(2) Sorption process of the reactor. After the desorption process, energy releasing phase starts as shown in Fig.7a. Similar as the desorption process, the reactor will adsorb ammonia from evaporator sequentially when its pressure is lower than that of the evaporator. Sorption processes of multi-salt sorbents release the energy and transport the heat to the heat exchange medium. For thermodynamic process shown in Fig.7b, isobaric and isothermal evaporating processes take place at point C. Point D is the isobaric and isothermal sorption processes of the salt with equilibrium temperature T_{s1} while point D' is the isothermal and isobaric sorption process of salt with equilibrium temperature T_{sn} . Sorption processes happen from point D' to point D sequentially.

(a)

Fig.7. Schematic diagram of multilevel sorption thermal energy storage (a) working mode;
(b) thermodynamic process.

Fig.8 shows the equilibrium isobaric sorption/desorption lines in term of single salt and multi-salt composite sorbents. Fig.8a shows one kind of single salt with three reaction stages. It can be noted that solid-gas reaction of single salt sorbent cannot fit the variable heat source well for efficient utilization. In contrast, if the multi-salt sorbent could be developed with more reaction stages as shown in Fig.8b, the heat source can be matched better, which can further improve the exergy efficiency of heat source. If the reaction stages tend to infinity, it will take the same trend as the heat source.

Fig.8. The equilibrium isobaric sorption/desorption lines (a) single salt; (b) multi-salt.

Fig.9 indicates schematic diagram for multilevel STES system, which illustrates an example of real application of solar energy. The real multilevel STES system is composed of a reactor, a condenser, an evaporator, water valves, ammonia valves and some auxiliary equipment such as water tank and cooling tower. For energy charging process, the reactor is connected with the hot water tank which is heated by the solar collector with a variable temperature through pump 1, pump 2, V1 and V2. The condenser is cooled by the cooling tower through pump 3, V3 and V4. The refrigerant is desorbed from the reactor and flows to the condenser through AV 1. It will be condensed there, and flows into the evaporator. After that ammonia valve AV1, AV2 and AV3 are closed. For energy releasing process, the refrigerant evaporated from the evaporator will be sorbed by the reactor when opening the AV2. Sorption heat will be exchanged between the reactor and water tank through pump 4, V5 and V6. Finally, the heat will be supplied to the end user with different heat demands. Through multilevel STES system, the variable heat source can be stored to adjust the time and place discrepancy. The system can even realize the seasonal energy storage though the reaction heat of the sorbent if the proportion of reaction heat released to the total heat output is high enough[24].

Fig.9. Diagram of real application for multilevel STES system by utilizing solar energy.

4.2. System evaluation

The equilibrium temperature can be calculated according to Equation 8 as follows:

$$\ln\left(\frac{P_{eq}}{P}\right) = -\frac{\Delta H_R}{RT_{eq}} + \frac{\Delta S}{R} \quad (8)$$

Total heat output is as follow:

$$\begin{aligned} Q_{out} &= Q_R + Q_S + Q_m \\ &= \sum_{k=1}^n \Delta H_k \cdot \Delta x_k + \sum_{k=1}^n \left(\int_{T_{out}}^{T_{in}} c_{sk} m_{sk} dT + \int_{T_{out}}^{T_{in}} c_{egk} m_{egk} dT \right) + \sum_{k=1}^n \int_{T_{out}}^{T_{in}} c_{s,sk} m_{s,sk} dT \end{aligned} \quad (9)$$

where Q_R , Q_S , Q_m represent reaction heat, sensible heat of sorbent and metal. ΔH is the reaction enthalpy of the each sorbent, Δx is the sorption quantity, C_s , C_{eg} , $C_{s,s}$ are specific heat of multi-salt, ENG-TSA and stainless steel, m_s , m_{eg} , $m_{s,s}$ are the mass of multi-salt, ENG-TSA and stainless steel. The ammonia part is included and calculated in the multi-salt part.

When the metal and composite sorbent are cooled from the heat input temperature to output temperature, the sensible heat will be released. The mass of metallic part of the reactor is calculated as 5 times that of the composite sorbent for qualitative analysis[25].

Proportion of the reaction heat released by multi-salt composite sorbent to the total heat output is as follow:

$$\eta = \frac{Q_R}{Q_{out}} \quad (10)$$

Energy storage density of reaction heat for mass density:

$$ESD_{ideal} = \frac{\sum_{k=1}^n \Delta H_k}{\sum_{i=1}^n M_i} \quad (11)$$

where ΔH is the reaction enthalpy of the sorbent, M is the mass of the multi-salt composite sorbent. The symbol i and k are used separately since one kind of sorbent may proceed two reaction processes.

Total heat output for mass density:

$$q_{out} = \frac{Q_{out}}{\sum_{i=1}^n M_i} \quad (12)$$

4.3. Performance analysis

Table 1 shows theoretical performance analysis of each selected salt for energy storage density. The parameters of m and n in the Table 1 can be referred to the Equation 13. Results show that the equilibrium desorption temperature is calculated when the heat sink temperature is assumed as 25 °C. It can be noted that the equilibrium desorption temperature range from 43.3 °C to 146.4 °C, in which CaCl_2 take two reaction stages in this temperature range. For each selected salt for multilevel STES, the theoretical energy density is higher than 750 kJ/kg, which is about 2-5 times than that obtained with latent heat storage method by using PCM on basis of heat release and mass of the salt [7, 26]. NH_4Cl gains the highest energy storage density which is about 1654 kJ/kg. This is mainly due to its reasonable reaction heat and relatively lower molar mass.

$$\text{salt} \times (n + m) \text{NH}_3 + \Delta H = \text{salt} \times n \text{NH}_3 + m \text{NH}_3 \quad (13)$$

Table 1 Theoretical performance analysis of selected working pairs for thermal energy storage.

Salt	Reaction coefficient m	Reaction coefficient n	Molar mass (g/mol)	Equilibrium desorption temperature(°C)	Energy density(kJ/kg)
MnCl_2 6/2	4	2	308.7	146.4	1509
CaCl_2 4/2	2	2	110.8	95	763
CaCl_2 8/4	4	4	110.8	83	1481
NH_4Cl 3/0	3	0	53.4	43.3	1654

Fig.10 indicates the energy storage density of bi-salt and tri-salt composite sorbents based on the reaction heat. As the Fig.10a shows, the energy storage density of bi-salt composite sorbent under non-equilibrium condition still has some similarities with that of equilibrium condition when the temperature is higher than 60 °C.

Under equilibrium condition, performance of the bi-salt composite sorbent displays three stages i.e. 827 kJ/kg, 1567.5 kJ/kg and 1949 kJ/kg. For non-equilibrium condition, when the temperature is higher than 95 °C, the highest energy storage density of bi-salt composite adsorbent could reach 1949 kJ/kg. With temperature increasing from 83 °C to 95 °C, the energy storage density is in the vicinity of 1550 kJ/kg. When temperature below 83 °C, the results almost show the trend of continuous variation. Compared with equilibrium and non-equilibrium condition, it is indicated that the optimal application temperature range is from 60 °C to 83 °C, in which the novel multilevel STES technology with multi-salt composite sorbent will lead to the increment of energy density from 0 to 81%.

For energy storage density of tri-salt composite sorbent as shown in Fig.10b, the results are much different from that of bi-salt composite sorbent. For equilibrium condition, it will proceed four stages i.e. 551.3 kJ/kg, 1045 kJ/kg, 1299.3 kJ/kg and 1823.3 kJ/kg. For non-equilibrium condition, the highest energy storage density of tri-salt composite sorbent is 1823.3 kJ/kg, and it happens when the temperature is higher than 146.4 °C. One striking point is that with temperature increasing, there are no obvious stage of tri-salt composite sorbent under the non-equilibrium condition compared with that the equilibrium condition. This good phenomena is because the multi-salt composite sorbent shows the continuous variation of sorption quantity with the temperature increment. Also another reason is that sorption hysteresis is almost disappear for the tri-salt composite sorbent whereas there is still slight sorption hysteresis for bi-salt composite sorbent. In comparison with the performance of bi-salt composite sorbents under equilibrium and non-equilibrium conditions, it is demonstrated that temperature from 60 °C to 80 °C, 83 °C to 95 °C and 97 °C to 152 °C show the energy density increment from 0 to 86%, 0 to 24% and 0 to 37%, respectively. This manifest the advantages of the multilevel STES with multi-salt composite sorbent, which will lead to the good capability for adaption to the variable heat source such as solar power in real application as shown Fig.9.

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Fig.10. Energy storage density based on reaction heat (a) bi-salt, (b) tri-salt.

The global conversion rate (X) is defined as the percentage of composite sorbent that reacted with the refrigerant, which is a key parameter to assess the working performance of STES system[27]. The overall heat output of bi-salt and tri-salt composite sorbent with different global conversion rate X is shown in Fig.11. Results show that overall heat output is very sensitive to the global conversion rate, which increases remarkably with the increment of conversion rate. Also heat output of tri-salt composite sorbent is a little better than that of bi-salt composite sorbent. This is mainly because the sensible heat output of the tri-salt composite sorbent is higher than that of the bi-salt composite sorbent. The high global conversion rate is desirable for achieving the good performance of multilevel STES. When the conversion rate reach 0.8, the energy output of bi-salt and tri-salt composite sorbent could reach 1814 kJ/kg and 1913 kJ/kg, respectively.

In order to evaluate the contributions of sensible heat and reaction heat of reactor with different global conversion rate X , the proportion of reaction heat released to the total heat output for bi-salt and tri-salt composite sorbent is analyzed and compared as shown in Fig.12. This proportion is an important analysis parameter since it is related to the seasonal STES performance. Results indicate that the proportion of reaction

heat released to the total heat output is higher than 60% when global conversion rate X is higher than 0.2, which means the reaction heat of reactor plays a main contribution for multilevel STES. Also noting that proportion of the reaction heat released to the total heat output for bi-salt and tri-salt composite sorbent increases with the increment of the conversion rate. Besides, the proportion of bi-salt composite sorbent is higher than that of the tri-salt composite sorbent with the increment of the conversion rate. When the conversion rate reach 0.7, proportion of the reaction heat released by multi-salt composite sorbent to the total heat output for bi-salt and tri-salt are 83% and 73%, respectively.

Fig.11. Overall heat output for bi-salt and tri-salt.

Fig.12. Proportion of the reaction heat released by multi-salt to the total heat output for bi-salt and tri-salt.

5. Conclusions

In order to analyze the performance of multilevel STES, sorption performance of multi-salt composite sorbent under non-equilibrium condition is investigated for comparison with that under the equilibrium condition. Expanded natural graphite treated with sulfuric acid (ENG-TSA) is integrated as the matrix with different mass ratios for heat transfer intensification. Conclusions are yielded as follows:

- [1] The Clapeyron lines and isobaric sorption/desorption lines of bi-salt and tri-salt composite sorbents show that each kind of salt distributes well in the multi-salt composite sorbent. Sorption hysteresis of bi-salt is much less significant than that of the single salt composite sorbent. Still sorption hysteresis phenomenon is almost disappear for the tri-salt composite sorbent. Multi-salt composite sorbent may be one potential solution to the sorption hysteresis.
- [2] For bi-salt composite sorbent under non-equilibrium conditions, when the temperature is higher than 95 °C, the highest energy storage density for reaction heat of bi-salt composite adsorbent will reach 1949 kJ/kg. With temperature increasing from 83 °C to 95 °C, the energy storage density is in the vicinity of 1550 kJ/kg. When temperature below 83 °C, the results show almost continuous variation. Comparably, for tri-salt composite sorbent under non-equilibrium conditions, the highest energy storage density for reaction heat of tri-salt composite sorbent is 1823.3 kJ/kg when the temperature is higher than 146.4 °C. With temperature increasing, there are no obvious stage of tri-salt composite sorbent for the non-equilibrium condition when compared with that the equilibrium condition.
- [3] The overall heat output is very sensitive to the global conversion rate, which increases remarkably with the increment of conversion rate. Overall heat output of tri-salt composite sorbent is a little better than that of bi-salt composite sorbent. When the conversion rate reach 0.7, the energy output of the bi-salt and tri-salt composite sorbent will be 1667 kJ/kg and 1730 kJ/kg, respectively.
- [4] Proportion of the reaction heat released to the total heat output for bi-salt and tri-salt composite sorbent increases with the increment of the conversion rate. The proportion of bi-salt composite sorbent is higher than that of the tri-salt composite sorbent with the increment of the conversion rate.

When the conversion rate reach 0.7, proportion of the reaction heat released by multi-salt to the total heat output for bi-salt and tri-salt composite sorbent are 83% and 73%, respectively.

With the potentially wide use of TES technology for solar power in the near future, multilevel STES technology of the multi-salt composite sorbent could be considered as a method to solve the problem for solar power storage and utilization. Besides, the sorption results of the testing rig only reflect the relation between sorption quantity, sorption temperature and pressure. Therefore, performance of multi-level STES by using the multi-salt composite sorbent is analyzed based on the testing sorption quality and theoretical reaction heat. Our future study should be emphasized more on the testing method to gain the accurate reaction heat for further analysis of this technology.

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