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Experimental study on composite silica gel supported $CaCl_2$ sorbent for low grade heat storage

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Abstract

A composite sorbent was prepared by utilising a mesoporous silica gel impregnated with the hygroscopic salt $CaCl_2$ to improve the specific thermal energy storage (TES) capacity in low grade heat storage. The properties of water sorption on the composite sorbent were measured in an open environment. A much larger sorption amount of up to 0.73 g water per gram composite sorbent was obtained at the temperature of 30 °C and the relative vapor pressure of 0.8, which conformed a high increase in the specific capacity compared 0.15 $\text{g}\,\text{g}^{-1}$ for the silica gel. The TES performance of the composite sorbent was investigated in an open-type TES setup equipped with 40 kg composite sorbent pellets. The experimental results show that the heat discharging temperature of the composite sorbent varied from 30 °C and 45 °C and the TES system was charged efficiently below 90 °C. At the preset heat supply temperature of 30 °C and the charging temperature below 90 °C, the specific TES capacity of approximately 1 $\text{kJ}\,\text{g}^{-1}$ and the storage efficiency of 0.78 for the composite sorbent were obtained. The sorption stability of the composite sorbent was also studied through over 500 repeated sorption/desorption cycles. The composite sorbent showed an approximately stable 0.95 $\text{kJ}\,\text{g}^{-1}$ in the specific TES capacity. A comparison of the composite sorbent and the other TES materials was made and it was found that the composite sorbent provides great potential to obtain the TES system of small size and high storage density for low grade heat storage.

Keywords: Silica gel; Composite sorbent; Water sorption; Thermal energy storage; Low grade heat

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1. Introduction

As an advanced energy technology, thermal energy storage (TES) has attracted increasing interest for thermal applications, such as space heating, hot water and air conditioning [1]. TES systems are used for correcting the mismatch between the supply of and demand for energy. Increasing societal energy demands, shortage of fossil fuels, and concerns over environmental impact are providing impetus to the development of the storage and use of low grade heat such as solar energy and industrial waste heat [2]. Sensible heat storage and latent heat storage are the two major techniques for TES for different applications. Sensible heat storage using water or rocks is at an advanced stage of development. It has been widely used in large scale seasonal district heating systems. Latent heat storage is a developing technology and has been found very promising on small scale single-family dwellings for its operational advantage of a nearly constant storage-cycle temperature. In the latent heat storage technology, much research is underway in latent TES materials, including phase change materials (PCMs) based on solid–liquid or solid–solid transition and adsorbents based on hygroscopic action [3].

On account of being friendly environment, solid sorption technologies have been developed in recent years [4–7]. Latent heat storage based on sorption/desorption of water on porous materials appears to be suitable for the application of low grade TES [8]. Close et al. [9] first designed a sorption TES apparatus to make use of solar energy in the 1970s. Zeolite–water and silica gel–water combinations are the two most interesting working pairs for sorption TES systems [10–14]. Zhang and

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Nomenclature

A	air moisture content	$\mathrm{g\,g^{-1}}$
A_{in}	inlet air moisture content	$\mathrm{g\,g^{-1}}$
A_{out}	outlet air moisture content	$\mathrm{g\,g^{-1}}$
c_{ES}	specific energy storage capacity	$\mathrm{J\,g^{-1}}$
$C_{p,a}$	specific heat of air	$\mathrm{J\,g^{-1}\,K^{-1}}$
COP	coefficient of performance	
$\dot{m}_a$	air mass rate	$\mathrm{g\,s^{-1}}$
$m_{\mathrm{CaCl_2}}$	calcium chloride mass	g
$m_{\mathrm{H_2O}}$	water mass	g
m_S	sorbent mass	g
$m_{S,\mathrm{dry}}$	dry sorbent mass	g
n	water amount adsorbed	$\mathrm{mol\,mol^{-1}}$
P	pressure	Pa
$P_{\mathrm{H_2O}}$	water vapor partial pressure	Pa
P_r	relative vapor pressure	
P_S	saturated vapor pressure	Pa
P_0	atmospheric pressure	Pa
q_{in}	heat power input	W
Q	heat	J
Q_{in}	heat input	J
Q_{out}	heat output	J
R	universal gas constant	$\mathrm{J\,mol^{-1}\,K^{-1}}$
S	BET surface area	$\mathrm{m^2\,g^{-1}}$
T	temperature	°C
T_C	temperature at core position of adsorber	°C
T_{in}	inlet air temperature	°C
T_{out}	outlet air temperature	°C
T_{HS}	preset heat supply temperature	°C
$w_{\mathrm{CaCl_2}}$	calcium chloride content	wt.%
x	water amount adsorbed	$\mathrm{g\,g^{-1}}$
x_e	water amount adsorbed at the end of sorption process	$\mathrm{g\,g^{-1}}$
x_0	water amount adsorbed at the start of sorption process	$\mathrm{g\,g^{-1}}$
$\dot{x}$	sorption rate	$\mathrm{g\,h^{-1}}$

Greek symbols

ΔH_{evp}	heat of evaporation of water	$\mathrm{J\,g^{-1}}$
ΔH_S	differential heat of sorption	$\mathrm{J\,g^{-1}}$
Δx	water amount adsorbed difference	$\mathrm{g\,g^{-1}}$
χ	dimensionless differential amount of water adsorbed	

Wang [15,16] adopted a zeolite 13X-water pair for automobile waste heat recovery with temperatures above 100 °C. Miltkau and Dawoud [17] studied the combined heat and mass transfer during desorption of water vapor from a zeolite layer at about 160 °C. Compared to zeolites, silica gel can be dehydrated and regenerated at a relatively low temperature (below 100 °C, and typically about 85 °C). Liu et al. [18] tested a developed silica gel adsorption water chiller to utilize low heat sources from 70 °C to 95 °C. Tahat [19] studied theoretically and experimentally a thermo-chemical energy-store using silica gel and water as a reversible pair. The potential for silica gel–water adsorption technologies were evaluated to utilise low grade thermal energy. However, the cycling water amount adsorbed on silica gel is still low. It results in the low specific energy storage capacity of adsorbent and consequently the large weight and volume of the TES apparatus [20].

Recently, composite sorbents have been prepared by impregnating hygroscopic salt inside a porous adsorbent matrix to improve the specific water sorption capacity [21–27]. The new composite sorbents have been developed for various applications including gas drying, fresh water production from the atmosphere [22], ice making on fishing boats [23], sorption refrigeration [24] as well as thermal energy storage from low grade heat sources [20,25–27]. Aristov et al. [24] presented a family of new composite sorbents, namely selective water sorbents (SWSs), and measured the water sorption equilibrium and specific heat of the composite sorbents. Dawoud and Aristov [25] investigated the kinetics of water vapor sorption on composite sorbents under typical operating conditions of sorption heat pumps. The presentation of sorption properties allowed an estimation of the thermodynamic performance of the composite sorbents for thermal energy storage. On the basis of their experimental investigation on sorption properties, Tokarev et al. [27] calculated the specific capacity for the energy storage of the composite sorbents with $\mathrm{CaCl_2}$ confined to mesoporous MCM-41. The composite sorbents showed high sorptivity and low generation temperature compared to common adsorbents, and should be considered as a good candidate for thermal applications driven by low temperature heat sources. Recent studies of composite sorbents have mostly focused on sorption properties, and the TES performance of composite sorbents was usually obtained through thermodynamic calculations. However, the experimental verification of thermal performance of composite sorbents in a TES setup is very important for investigating their potential in practical use for thermal storage from low grade heat sources. Jänchen et al. [20] tested the storage capacity of composite adsorbents on a closed storage apparatus. Unfortunately, besides the literature [20] little wok has been done on the experimental study of the TES property of composite sorbent.

This paper presents the tests of the sorption properties of the composite silica gel supported $\mathrm{CaCl_2}$ sorbent in an open sorption system. It intends to provide some useful experimental results for the application of the composite sorbent of high water sorption capacity in an open sorption storage system to improve the TES density. For this purpose, the TES performance of the composite sorbent was investigated experimentally on an open-cycle sorption TES apparatus equipped with 40 kg of dry composite sorbent.

Table 1
Thermo-physical properties of silica gel and composite sorbent

Property	Silica gel	Composite sorbent
Average pore diameter [nm]	4.61	6.12
Porous volume [$cm^3\ g^{-1}$ silica gel]	0.806	0.529
BET/N_2 surface area [$m^2\ g^{-1}$ silica gel]	575	256
Salt content [wt.%]	–	35

2. Materials and experimental setup

2.1. Composite sorbent

A composite sorbent was obtained from the combination of mesoporous silica gel and hygroscopic salt $CaCl_2$ as follows. The mesoporous silica gel was first dried at 120 °C and cooled down in a vacuum desiccator. The dry silica gel was then impregnated with an aqueous solution of calcium chloride (mass concentration 40%) at 25 °C for 8 hours until all the pores were filled. Finally the composite sample was dried at 120 °C in a vacuum drier until the sample weight remained constant.

The sorption properties of sorbents are influenced by operational parameters as well as thermo-physical properties such as the surface area, pore size and pore volume [28,29]. The standard nitrogen gas adsorption/desorption measurements on the silica gel and composite sorbent were determined on the micrometric gas adsorption analyser machine (ASAP 2010). The thermo-physical properties of silica gel and composite sorbent are summarized in Table 1. It can be observed that the average pore diameters increased from 4.61 nm for the silica gel to 6.12 nm for the composite sorbent. It was caused by the interposition of the hygroscopic salt in the silica gel pores of small diameter. The specific surface area of silica gel matrix decreased from 575 to 256 m^2 per g silica gel after the interposition of the hygroscopic salt $CaCl_2$. It indicates that the confined salt partially blocks the access to the internal volume of the matrix pores.

2.2. Measurement of water sorption properties

As the TES setup is open-type, the water sorption properties were measured in an open environment. Before the measurements of water sorption process, a sample of about 2 g was dried at 120 °C in a vacuum desiccator until the sample weight remained constant. The properties of water adsorbed on silica gel and composite sorbent were investigated by the weight method in a variable-temperature variable-humidity apparatus (Type 302, Shanghai Experimental Apparatus Ltd.). The temperature regulation accuracy of the apparatus was ±0.5 °C, and that of relatively humidity was ±3%. The weight of the sorbent (m_S) was recorded along with the sorption time at a constant temperature and constant relative vapor pressure (P_r).

$$P_r = P_{H_2O}/P_0 \tag{1}$$

where P_{H_2O} and P_0 are the partial pressure of water vapor and the atmospheric pressure, respectively.

The water amount adsorbed on the sorbent (x) is given as:

$$x = \frac{m_S - m_{S,\mathrm{dry}}}{m_{S,\mathrm{dry}}} \tag{2}$$

where m_S and $m_{S,\mathrm{dry}}$ are the mass of the sorbent and dry sorbent respectively. When no change in mass was detected, the water amount adsorbed was the equilibrium amount. The mass of the adsorbent was determined by an analytical balance to an accuracy of ±0.2 mg.

2.3. Investigation on TES using composite sorbent

To study the composite sorbent applied in TES, the composite sorbent was pelleted using some binder and special additives. Approximately 40 kg dry composite sorbent was placed in an open TES setup to investigate the energy storage performance. The schematic diagram of the open-type TES setup is shown in Fig. 1. The TES setup consists mainly of three subsystems. The first compartment is the adsorber/desorber with the dimensions of 0.8 × 0.3 × 0.4 m ($L \times D \times H$). The adsorber is structured as a fixed bed, and there are totally 8 adsorber units (i.e. 1#–8#) in the adsorber. In order to enhance the heat transfer in the TES process, a plate-fin heat exchanger is used in the adsorber. There are 2 heating plates with the dimensions of 0.12 × 0.15 × 0.01 ($L \times D \times H$) to be plated flatly in each adsorber unit. In the heat charging process, the heating plate was used to heat the adsorbent utilizing electric power or other heat sources.

The second subsystem is the air-side system consisting of the air tank, centrifugal fan, humidifier, air pipes and air valves (V1–V4). The ambient air is introduced by the fan and humidified into the humidifier. The humid air, as the medium of water vapor, flows through the adsorber. The air is heated by the heat of sorption. Hot air from the adsorber can be used as a heat source for space heating or other purposes.

The third subsystem is the water-side system consisting of the condenser, water sink, vapor valve (V5) and water valve (V6&V7). In the desorption process, the water vapor condenses and liquid water flows into the water tank.

The data collection in the experimental study was achieved using the data acquisition system equipped with thermocouples, pressure sensors and flow meters located at the desired measurement points. The heat power was measured by a dynamometer ammeter. The temperatures were measured by thermocouples connected to an Agilent multi-channel data recorder. The measuring errors of thermocouples for temperatures are ±0.1 °C. The air humidity was measured by a Vasala dew-point sensor with the measuring errors of ±3%. All the above measurements were collected by a computer. The operation of the experimental setup was controlled by a PLC (Programmable Language Controller).

In a TES cycle, two main processes, i.e., desorption process-thermal energy storage and adsorption process-thermal energy release are included as described below.

2.3.1. Desorption process—heat charging

In order to activate the adsorbent for the first use or regenerate the moist sorbent, the adsorber is heated for desorption.

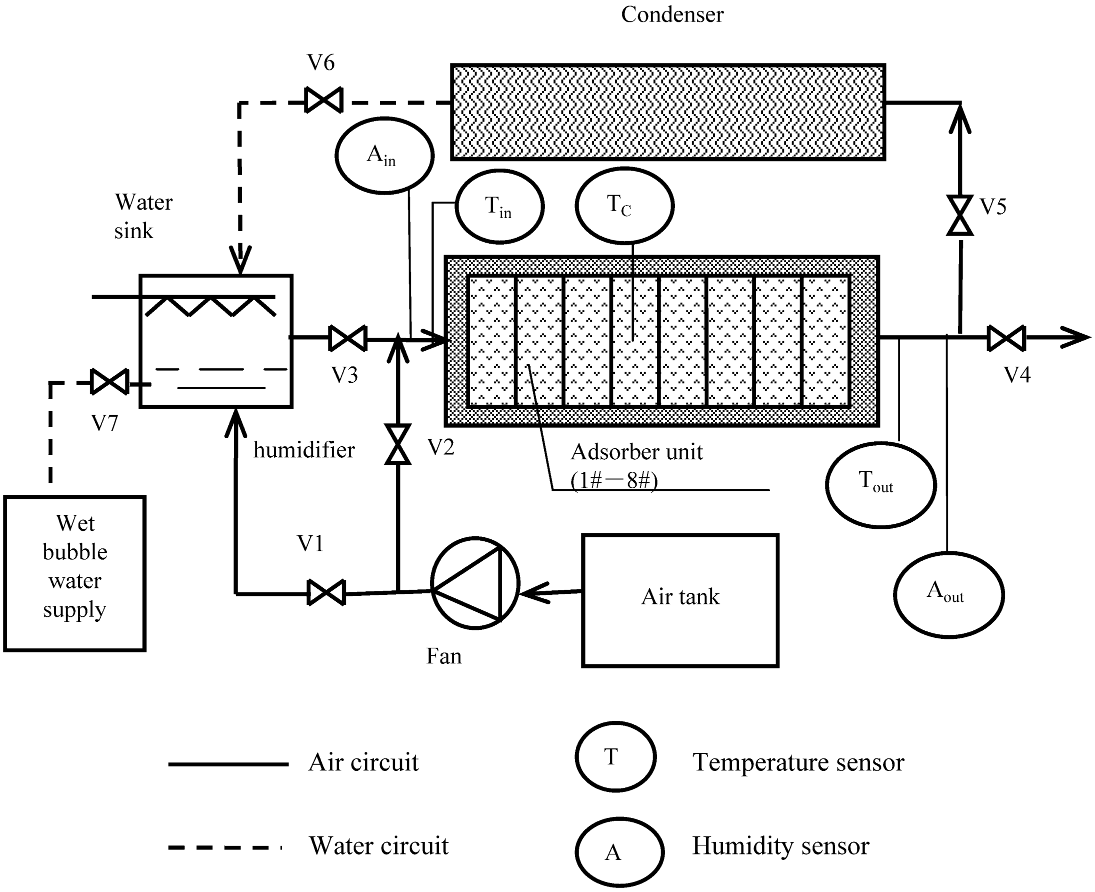

Fig. 1. Schematic of the open-type adsorption TES apparatus.

In the desorption process, the regeneration temperature is controlled at approximately 90 °C. To regenerate the sorbent, the vapor valve V5 and water valve V6 need to be opened, while the regulating air valves V1–V4 remain closed. During the desorption process, the water vapor is desorbed from composite sorbent and condensed in the condenser. The condensed water flows into the water sink. The flow rate of the condensed water was obtained from the observed liquid height. When there is no more condensed water in the water sink, desorption process ends. The vapor valve (V5) and water valve (V6) are then closed for the next adsorption process. During the desorption process, low grade heat is accumulated as the thermochemical energy between the composite sorbent-water pair.

In this process, the heating power (q_{in}) input was adjusted and measured. Thus the total heat input needed (Q_{in}) is the integration of the heating power input.

$$Q_{\text{in}} = \int_{\text{des}} q_{\text{in}}\,\mathrm{d}t \tag{3}$$

At the end of the regeneration process of sorbent, the adsorber is relatively hot and needs to be cooled down to the preset sorption temperature by the circulating cool water. For the adsorber units with good thermal insulation, the sensible heat can also be used for heating supply through the circulating water medium.

2.3.2. Adsorption process—heat discharging

The sorption process starts once the air valves (V1,V3,V4) and fan are opened. In the open-type TES setup, humid air, as the medium of water vapor, flows through the adsorber. The water vapor is adsorbed by the composite sorbent, and sorption heat is released and removed by the air medium. The hot air can be used for space heating or for other purposes. Along with the progress of sorption, the rate of heat discharge reduces. This results in a reduction of the air temperature at the outlet of the adsorber. The temperature and relative humidity of the air at the inlet and outlet of the adsorber were measured by the data acquisition system. When the outlet temperature falls below the preset heat supply temperature (T_{HS}), the sorption process ends. In the sorption process, the change of the water amount adsorbed on the composite sorbent (Δx) can be calculated according to the air flow rate ($\dot{m}_a$) and moisture content (A) at the inlet and outlet of the adsorber:

$$\Delta x = \frac{\int_{\text{sorp}} (\dot{m}_a A_{\text{in}} - \dot{m}_a A_{\text{out}})\,\mathrm{d}t}{m_{S,\text{dry}}} \tag{4}$$

Stable heat output is necessary in a TES system for real TES application. The outlet air temperature can be regulated by controlling the air flow rate through the composite sorbent. The water amount (x_e) adsorbed on composite sorbent at the end of sorption process is illustrated as

$$x_e = x_0 + \Delta x \tag{5}$$

For a certain sorbent, the sorption rate can be obtained by the differential of the amount of water to the time:

$$\dot{x} = \frac{\mathrm{d}x}{\mathrm{d}t} \tag{6}$$

In order to compare the sorption kinetic characteristics between silica gel and composite sorbent, the dimensionless differential amount of water is introduced. It is defined as the ratio between the instantaneous differential amount of water to the maximum amount of water achievable at each operating condition of the sorption process [25]

$$\chi(t) = \frac{x(t) - x_0}{x_e - x_0} \tag{7}$$

When the humidity of the air from the air tank is very high, the humidifier may not be needed. In this case, the valves V1&V3 can remain closed while the valve V2 remains open. The accumulated heat from the regeneration process is discharged by the air during this sorption process.

According to the practical operation of space heating, it is allowable to consider only the sensible heat for the calculation of heat supply if the indoor air is not too dry (requesting humidification). Therefore, only the sensible heat was considered as the heat output in the paper for the purpose of space heating under the above condition, which is true mostly in the south part of China. Therefore, only the sensible heat was considered as the heat output in this paper. In fact, the heat of condensation is also discharged from the condenser. The usability of the heat of condensation lies on the structure of the sorption storage system and the space heating system. This paper aims at the possibility of the composite sorbent for space heating and thermal energy storage and mainly concerns the heat of sorption during the discharging process. The possible heat of condensation released in the charging process was not considered in the use of space heating. Therefore, the heat output (Q_{out}) by the air during the sorption process is calculated if the preset heat supply temperature of air is set asT_{req}:

$$Q_{\text{out}} = \int\limits_{\text{sorp}} c_{p,a} \cdot \dot{m}_a (T_{\text{out}} - T_{\text{req}})\,\mathrm{d}t \tag{8}$$

The specific energy storage capacity c_{ES} per unit weight of composite sorbent during the sorption process is calculated as

$$c_{\text{ES}} = \frac{Q_{\text{out}}}{m_{S,\text{dry}}} \tag{9}$$

During a TES cycle, the coefficient of performance (COP) of the TES system is calculated:

$$COP = \frac{Q_{\text{out}}}{Q_{\text{in}}} \tag{10}$$

3. Results and analysis

3.1. Water sorption properties on composite sorbent

Figs. 2 and 3 give the kinetic curves of water adsorbed on the silica gel and composite sorbents under different temperatures and relative vapor pressures in an open environment. From these two figures, it can be observed that the maximum amount of water adsorbed on the composite sorbent was much larger than that on the silica gel. Fig. 2 shows a detailed comparison of the water sorption kinetic between the silica gel and composite sorbent at the temperature of 30 °C and the relative vapor pressure of 0.8. The maximum amount of water adsorbed on the pure silica gel was 0.15 g per gram of dry adsorbent, while the maximum amount of water on the composite silica gel supported $CaCl_2$ sorbent reached 0.73 g per gram of dry sorbent. Evidently, the water amount adsorbed by the composite sorbent was much higher than that of the other type of silica gel [29] and other common adsorbents such as zeolites [10]. The large amount of water adsorbed on composite sorbent provides great potential to improve its specific energy storage capacity. The significant increase of the amount of water was caused by the interposition the hygroscopic salt $CaCl_2$ in the silica gel. The confined $CaCl_2$ affected the sorption capacity of water on the composite sorbents in two possible ways i.e. the chemical adsorption of the salt $CaCl_2$ and the absorption of the hydrate $CaCl_2 \cdot nH_2O$. The sorption mechanism of water on the silica gel supported $CaCl_2$ was demonstrated as the combination of the physical adsorption of the silica gel porous structure and the

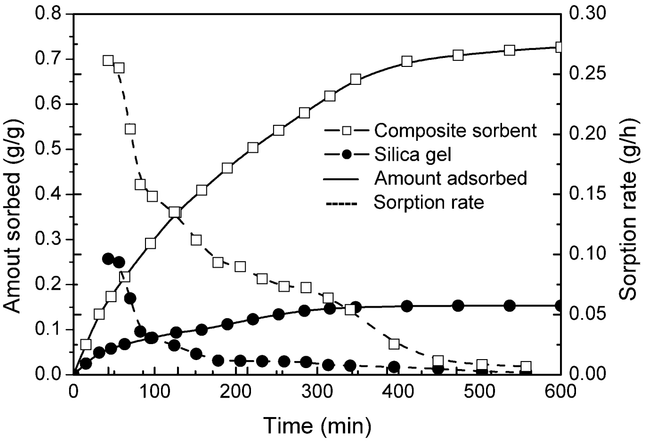

Fig. 2. A comparison of sorption kinetics of water between pure silica gel and composite sorbent at 30 °C and 0.8 relative water pressure.

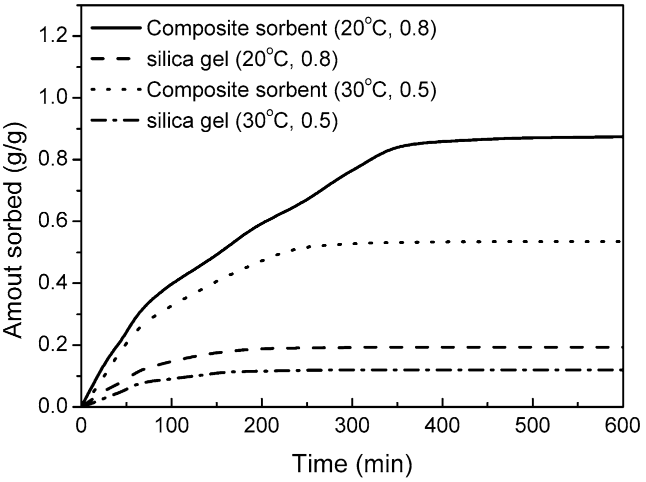

Fig. 3. A comparison of sorption kinetics of water between pure silica gel and composite sorbent at 30 °C, 0.5 and 20 °C, 0.8 of relative water pressure.

Table 2
A comparison of the sorption kinetics characteristics between silica gel and composite sorbent

Sorbent	x_e [g g^{-1}]	Time [min] (at $\chi = 0.5$)	Time [min] (at $\chi = 0.9$)
Silica gel	0.16	78	253
Composite sorbent	0.74	130	346

above two sorptions caused by $CaCl_2$ in the literature [25]. The maximum amount of water adsorbed on the composite sorbent was 4.87 times as much as that on the silica gel at the temperature of 30 °C and the relative water pressure of 0.8. Thus the latter two sorptions caused by $CaCl_2$ were the main sorption behavior in the composite sorbent.

The absolute sorption rate of the composite sorbent ($\dot{x}$) can be obtained from the differential of the sorption amount to time. From Fig. 2 it can be observed that the absolute sorption rate was also significantly larger than that of the pure silica gel. The similar result that the absolute sorption rate increased after impregnating hygroscopic salt was found in the composite sorbent used for water extraction from atmosphere [21]. The larger change of water amount per unit of time results in a higher efficiency of TES. In order to compare the sorption kinetic characteristics between silica gel and composite sorbent, the dimensionless differential amount of water (χ) was calculated as illustrated in Table 2. The initial amount of water adsorbed on sorbent (x_0) was considered zero for the sorbent had been adequately dried primarily. It can be observed that it took shorter time to arrive 90% of the maximum adsorption capacity for the silica gel than the composite sorbent. Thus the presence of the hygroscopic salt impregnated into the silica gel slowed down the dimensionless sorption kinetics of the composite sorbent. The possible effects of the impregnated salt on the mass transfer for water sorption were presented in previous work [25].

Fig. 4 shows an example of the sorption isotherms of water on the composite silica gel supported $CaCl_2$ sorbent at different temperatures from 30 °C to 70 °C. From this figure it can be observed that the water amount adsorbed on composite sorbent was up to 1.06 g g^{-1} at the low temperature of 30 °C and the high relative pressure of 0.9. Due to the high sorption capacity, a large quantity of sorption heat can be accumulated and discharged, which results in a high thermal storage density. With increases of sorption temperature, less water can be adsorbed. At a temperature of 70 °C, only 0.23 g g^{-1} water was adsorbed on the composite sorbent even at the high relative pressure of 0.9. The great change of sorption capacity of the composite sorbent with changes of temperature at relatively low temperature ranges also leads to large amounts of water being handled during the sorption/desorption process, which leads to a high capacity of the TES. Accordingly, it is very suitable for the storage of low grade heat such as solar energy and low temperature building heat.

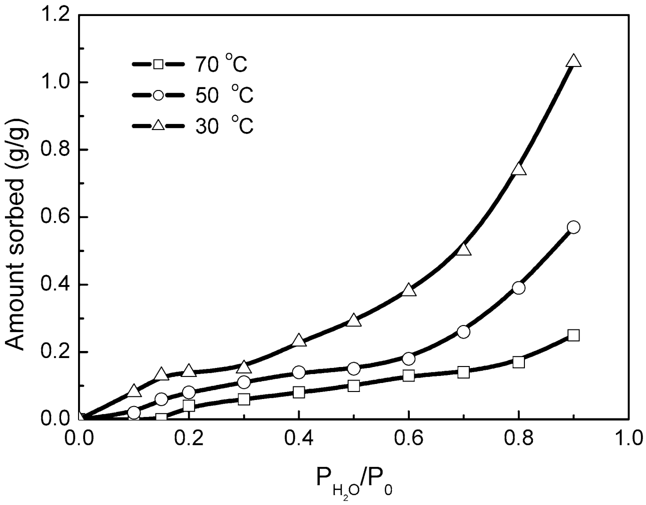

Fig. 4. Sorption isotherms of water on the composite silica gel supported $CaCl_2$ sorbent.

On account of the formation of the hydrate in the composite sorbent, a clear sorption plateau was reported both in the sorption isotherms by Jänchen et al. [20] and in the sorption isobars by Aristov et al. [25]. A plateau can also be observed approximately at the water sorption amount of 0.15 g g^{-1} in the sorption isotherms of the composite sorbent in an open sorption environment as shown in Fig. 4. However, it should be noted that the sorption plateau obtained in the open sorption environment was not as clear as that in the closed (evacuated) sorption system [20,25]

$$n = \frac{m_{H_2O}/M_{H_2O}}{m_{CaCl_2}/M_{CaCl_2}} = \frac{x}{w_{CaCl_2}} \frac{M_{CaCl_2}}{M_{H_2O}} \tag{11}$$

where M_{H_2O} (= 18 g mol^{-1}) and M_{CaCl_2} (= 111 g mol^{-1}) are the molecular weights of water and calcium chloride, respectively. w_{CaCl_2} is the content (wt.%) of calcium chloride in the composite sorbent. It can be calculated that the plateau in the sorption isotherms was caused by the formation of the dehydrate.

Concerning the experimental sorption data as shown in Fig. 3, the differential heat of sorption on the composite silica gel supported $CaCl_2$ sorbent at the temperature T and vapor pressure P can be calculated:

$$\Delta H_S = \Delta H_{\mathrm{evp}} + RT \ln\left(\frac{P_S}{P}\right) \tag{12}$$

where ΔH_{evp} is the heat of evaporation of water (approximately 2.40 kJ g^{-1} at 30 °C), and P_S is the saturated vapor pressure.

The calculated differential heat of sorption can also be fitted with a polynomial function of the amount of water adsorbed:

$$\Delta H_S = c_4 x^4 + c_3 x^3 + c_2 x^2 + c_1 x + c_0 \tag{13}$$

where, the constants c_i $(i = 0, 1, \ldots, 4)$ can be obtained from fitting the curve of heat of sorption; their values were $c_4 = 1139$, $c_3 = -3307$, $c_2 = 3459$, $c_1 = -1620$, $c_0 = 2727$. The calculated and fitted results are shown in Fig. 5. It was found that the heat of water adsorbed on the composite sorbent was noticeably larger than the heat of water evaporation. The heat of sorption decreased slightly with the increase of the water amount adsorbed on the composite sorbent.

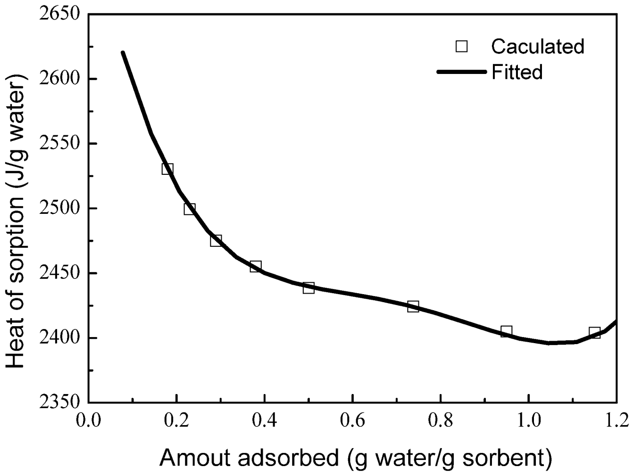

Fig. 5. Differential heat of water sorption *vs* water amount adsorbed.

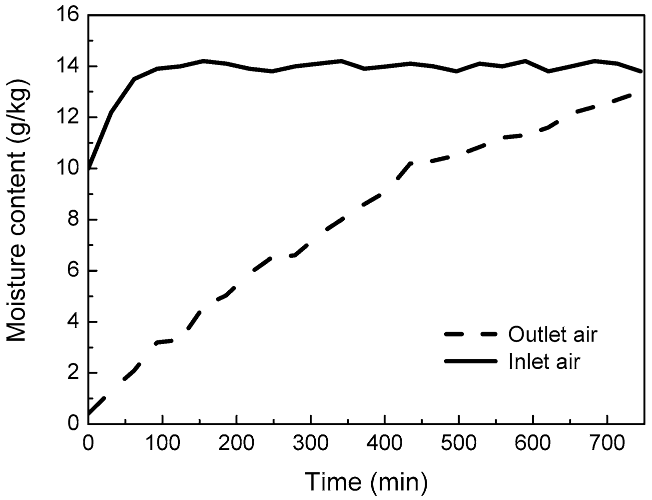

Fig. 6. Moisture content of air during TES sorption process (heat discharging).

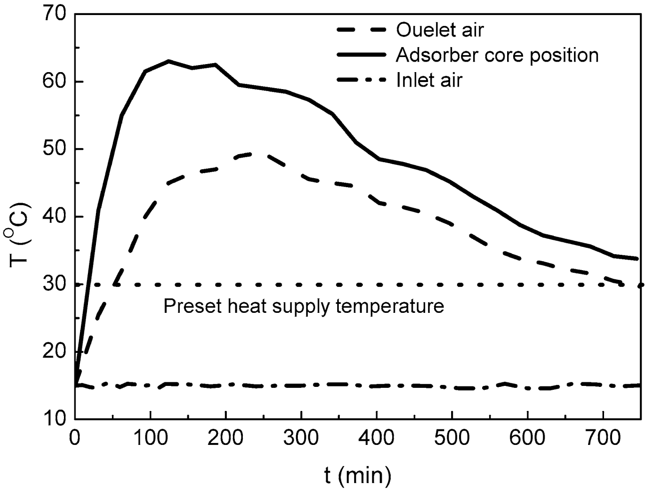

Fig. 7. Temperatures of air and adsorber during TES sorption process (heat discharging).

3.2. Thermal performance of the composite sorbent in TES

Before heat discharging by water sorption on the composite sorbent from the air flow, the ambient air was humidified through the humidifier up to the moisture content of approximately 14 g per kg dry air. The water vapor of humid air was adsorbed by the composite sorbent. The moisture content of air during the heat discharging process is presented in Fig. 6. With the progress of the sorption process, the moisture content of the outlet air increased. On account of the heat discharging the temperatures of both the adsorber and the outlet air increased. Fig. 7 shows the temperature curves of the air at the positions of inlet, core position and outlet of the adsorber during heat discharging process. The temperature of the inlet humid air was preset at approximately 15 °C. The core position temperature of the adsorber increased quickly up to about 63 °C. The temperature of air flowing through the adsorber consequently increased. The outlet air temperature varied between 30 °C (the preset heat supply temperature) and 45 °C (the preset maximum temperature). The air temperature was limited to the preset maximum of 45 °C to allow a large amount of water to be adsorbed on the composite sorbent in order to achieve a high capacity of TES.

According to Eq. (8), a heat output (Q_{out}) of 40276 kJ in the heat discharging period can be obtained. Thus, the specific energy storage capacity of 1.01 kJ per gram dry composite sorbent was obtained. This is a remarkable improvement of TES capacity compared with the reported results of pure silica gel and other zeolites. Concerning Eq. (3) and the recorded input heat power measured by the data collection system, the heat input (Q_{in}) can be calculated as 51636 kJ. Thus the COP of 0.78 was obtained from Eq. (10) at the preset heat supply temperature of 30 °C and the desorption temperature below 90 °C. It should be noted that the COP of TES was affected by operating conditions. The COP increased noticeably with the reduction of the heat supply temperature. A comparison of the TES parameters between the composite sorbent and other typical TES materials is listed in Table 3. The storage efficiency of approximately 0.78 can be comparable with other TES materials (i.e. 0.80 for rock and 0.83 for PCMs). However, the high increase of the specific storage capacity of the composite sorbent can provide a great potential to the TES device of small size and high storage density. Thus less composite sorbent is needed than the common PCMs for the same heat storing. For instance, approximately 1 kg composite sorbent can be used for to storing 1000 kJ heat, while approximately 4 kg paraffin has to be needed. It can be estimated according to the prices that the investment cost of the composite sorbent is approximately half of that of paraffin for the same heat storage charge.

If the outlet air temperature is below the preset heat supply temperature, the heat discharging process ends and the charging process starts. Fig. 8 shows the temperature curve of the adsorber and the mass curve of condensed water in heat charging period. It can be observed that the charging temperatures varied from 30 °C to 90 °C and approximately 24 kg condensed water was obtained. The change of water adsorbed on the composite sorbent in the charging period was 0.6 $\mathrm{g\,g^{-1}}$. Such a great change in sorption capacity of the composite sorbent during the TES cycle at a relatively low temperature range leads to a high capacity of TES. Thus, the composite sorbent can be applied

Table 3
A comparison of the composite sorbent and other TES materials [2,3]

Property	Sensible heat storage material		Phase change materials		Adsorbent	
	Rock	Water	Organic	Inorganic	Silica gel	Composite silica gel supported $CaCl_2$ sorbent
Specific heat [$kJ\,kg^{-1}$]	1.0	4.2	2.0	2.0	0.6	0.9
Density [$kg\,m^{-3}$]	2240	1000	800	1600	480	806
Specific TES capacity [$kJ\,kg^{-1}$]	15	63	189	230	350	1000
Typical storage efficiency	0.80	0.75	0.83	0.83	0.60	0.78

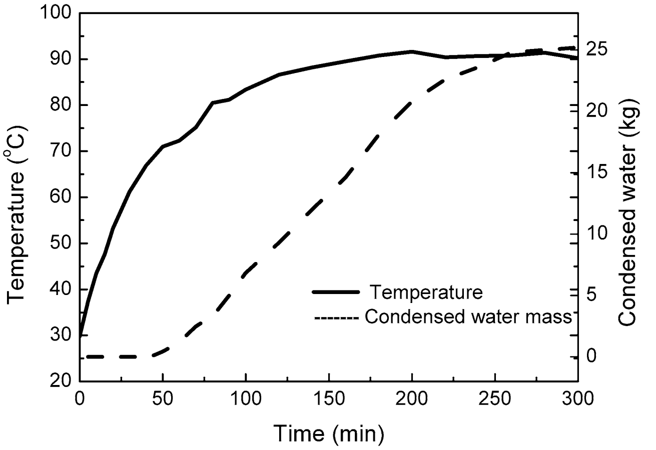

Fig. 8. Air temperature and condensed water mass during TES desorption process (heat charging).

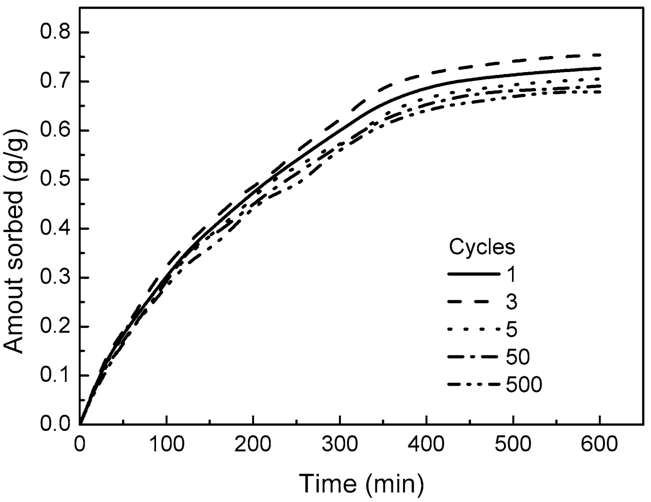

Fig. 9. Sorption kinetics of the composite sorbent for multiple repeated cycles.

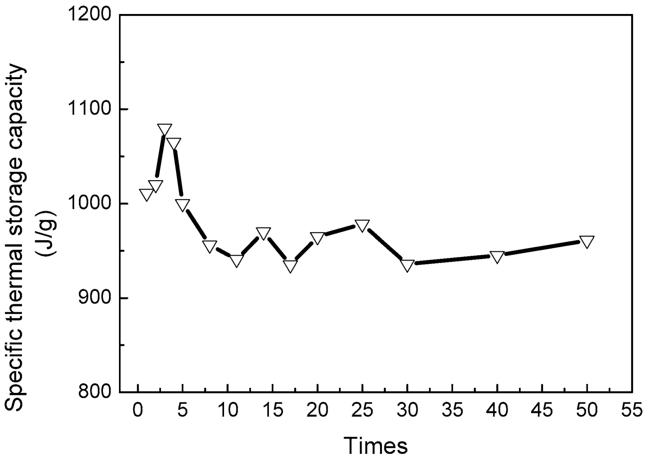

Fig. 10. Specific TES capacity of the composite sorbent for multiple repeated cycles.

for storing low grade heat sources such as solar energy and low temperature building heat.

Concerning the experimental results of TES as shown in Figs. 6 and 7 for heat discharging and Fig. 8 for heat charging at the condensing temperature of approximately 15 °C, the storage periods of the composite sorbent used in an open TES cycle can be evaluated. It can be observed that the open-type TES had a long duration including the heat discharging period of approximately 12 h and the heat charging period of approximately 5 h. Both the two periods can be controlled and regulated by adjusting the ratio of the air flow rate to the mass of the composite sorbent according to the given space heating need. On account of the adsorbate being apart from the composite sorbent, there is no heat loss during the thermal storing period. Thus the open-type TES setup is very suitable for a long storage period.

Fig. 9 gives an example of the sorption stability of the composite sorbent for the repeated TES uses in an open environment. The repeated experimental results show that the sorption kinetics of the composite sorbent changed noticeably in the starting several times and then kept approximately stable in the subsequent hundreds of cycles. Fig. 10 gives some experimental results of the specific TES capacity of the composite sorbent obtained in the open TES system. From Fig. 10 it can be observed that the specific TES capacity of the composite sorbent increases noticeably from the first to forth TES cycle. After the sixth cycle, the TES capacity reduced slightly and remained constant. It can be observed that the specific TES capacity behaved a peak at approximately the third or forth cycle. The possible reason for the former increase of the TES capacity is that the pores of the sorbent change more suitable to water sorption after the first and second sorption/desorption cycle. The latter decrease of the TES capacity results from little loss of the hygroscopic salt from the composite sorbent, which is related to the lyolysis of the composite sorbent. But the loss of the hygroscopic from the composite sorbent is in such a small amount that the TES capacity of the composite sorbent can keep stably at a high value of 0.95 kJ g^{-1} over 500 repeated sorption/desorption cycles. However, it is known that the long repeated use of sorbent even over thousands of sorption/desorption cycles is one of the sorbent's greatest strengths as a thermal energy medium. It should be noted that 500 cycles is not enough if it aims to evaluate the longevity of the composite sorbent used in a real TES system. Therefore, more investigations will be tested in our further work to evaluate the longevity of the composite sorbent as a TES medium for real use.

4. Conclusions

The water sorption measurements on the pure silica gel and the composite silica gel supported $CaCl_2$ sorbent in an open sorption system show that the sorption capacity of water on silica gel increased significantly after its impregnation with the hygroscopic salt $CaCl_2$. The water amount of 0.73 g adsorbed on per gram composite sorbent was 4.9 times as much as 0.15 g g^{-1} for the silica gel. The differential heat of sorption calculated concerning the sorption isotherms varies from 2.62 to 2.41 kJ g^{-1}, which decreases as the amount of water adsorbed on the composite sorbent increases. The high increase in the water sorption capacity provides great potential to improve the specific TES capacity.

The TES tests on an open-type TES setup equipped with 40 kg composite sorbent pellets show a high specific TES capacity of approximately 1 kJ g^{-1} and storage efficiency of 0.78 at the preset heat supply temperature of 30 °C and the relatively low charging temperature below 90 °C. A long duration was observed in the open TES cycle including the heat discharging period of approximately 12 h and the heat charging period of approximately 5 h. Concerning the heat can be stored for a long period without heat loss, the open-type TES setup is very suitable for a long storage period. An approximately stable TES density of 0.95 kJ g^{-1} can be obtained from the sorption storage experiments over multiple repeated sorption/desorption cycle.

Thus the composite silica gel supported $CaCl_2$ sorbent shows great competitive for its huge water sorption amount and high specific TES capacity compared to other TES materials. It has great potential in the application in the low grade heat storage to improve the TES density.

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