Experimental investigation on a MnCl$_2$−CaCl$_2$−NH$_3$ thermal energy storage system

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ABSTRACT

Thermal energy storage (TES) is regarded as one promising technology for renewable energy and waste heat recovery. Among TES technologies, sorption thermal energy storage (STES) has drawn burgeoning attention due to high energy storage density, long-term heat storage capability and flexible working modes. Originating from STES system, resorption thermal energy storage (RTES) system is established and investigated for recovering the heat in this paper. The system is mainly composed of three high temperature salt (HTS) unit beds; three low temperature salt (LTS) unit beds, valves and heat exchange pipes. Working pair of MnCl$_2$−CaCl$_2$−NH$_3$ is selected for the RTES system. 4.8 kg and 3.9 kg MnCl$_2$ and CaCl$_2$ composite adsorbents are filled in the adsorption bed. Results indicate that the highest thermal storage density is about 1836 kJ/kg when the heat charging and discharging temperature is 155 °C and 55 °C, respectively. Volume density of heat storage ranges from 144 to 304 kWh/m^3. The highest ratio of latent heat to sensible heat is about 1.145 when the discharging temperature is 55 °C. The energy efficiency decreases from 97% to 73% when the discharging temperature increases from 55 to 75 °C.

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1. Introduction

Thermal energy storage (TES) is considered as one paramount technology to utilize the renewable energy by weakening the mismatch between supply and demand. Reasonable utilization of renewable energy such as solar energy and geothermal heat inseparably depends on the development of sustainable and economically feasible TES systems. Under this scenario, an increasing number of attentions have been drawn to seek for the possible and suitable solutions to boost TES technology recently [1].

Generally speaking, common TES technology can be divided into three categories, and they are sensible heat storage, latent heat storage and thermochemical energy storage [2,3]. Sensible heat storage is based on the heat exchanging process between energy storage materials such as pebble, concrete and heat exchange fluid such as water and oil [4,5]. Latent heat storage relies on the heat charging or discharging during phase change process of the materials such as paraffin, nitrate, etc. [6]. However, both sensible and latent heat storage take disadvantages of low energy density, long-term and long-time storage and unacceptable energy loss [7,8].

Comparably, thermochemical energy storage can overcome these shortcomings, which can make up time-discrepancy, space-discrepancy as well as balancing supply and demand [9].

As one common thermochemical process, adsorption process has been extensively studied for refrigeration and heat pump system [10—12]. Similarly, adsorption working process has also been investigated for the possibility to be applied for TES system in recent decades. As for adsorption refrigeration, working pair including adsorbent and adsorbate can also be selected for the application of adsorption thermal energy storage (ATES) systems, and adsorbent means the materials which have the ability to adsorb and adsorbate means working fluid which can be adsorbed. Compared with only heat transfer in conventional sensible and latent heat storage systems, both heat and mass transfer processes should be considered in ATES systems. Research results indicate that working performance of ATES system is not only dependent on selected materials and system design, but also on its thermodynamic cycle. For materials part, zeolite/H$_2$O, silica gel/H$_2$O and chloride/H$_2$O working pairs have been widely studied. Hauer [13] reported an successful large-scale open sorption system with zeolite/H$_2$O working pair, which was installed in a school and connected with the local district heating network in Munich, achieving a heat storage density of 124 kWh/m^3. Jae et al. [14]

Nomenclature

ATES	adsorption thermal energy storage
c	specific heat (kJ/(kg ^{o}C))
cha	charging
COP_h	coefficient of performance for heat storage
discha	discharging
ENG-TSA	expanded natural graphite treated with sulfuric acid
HSD	heat storage density
HTS	high temperature salt
LTS	low temperature salt
m	mass flowrate (kg/s)
M	mass (kg)
Q	heat (J)
RTES	resorption thermal energy storage
TES	thermal energy storage
V	volume (m^3)

Greek letters

ε	ratio of latent heat to sensible heat

Subscripts

ad	adsorbent
c	condensing
h	heat
i	inlet
in	input
l	latent heat
m	mass
metal	metal
o	outlet
out	output
sa	salt
s	sensible heat
v	volume
w	mass flowrate

developed several generations of prototype with silica-gel/H_2O working pair in a series of studies and experimentally achieved a material storage density of 50 kWh/m^3. Yu et al. [15] investigated a novel silica gel-$LiCl_2$ composite adsorbent for the application of ATES. The novel composite adsorbent could achieve a cold storage density of 108 kWh/m^3 and a heat storage density of 163.6 kWh/m^3 with 80 °C desorption temperature by simulating adsorption properties. After that, to solve highly hygroscopic problem for silica gel-$LiCl_2$ composite adsorbent as well as to enhance the heat transfer ability, activated carbon (AC) and expanded natural graphite treated with sulfuric acid (ENG-TSA) were added since addition of other elements didn't influence the equilibrium water uptake of LiCl. Results showed that variation of bulk densities from 462 to 820 kg/m^3 displayed thermal conductivities from 2.0 to 2.83 W/(mK), improving that of loose-packed AC-LiCl composite by at least 14 times [16]. For thermodynamic cycle part, Li et al. [17] analyzed different solid–gas reaction TES cycles for application of direct heat supply, heat upgrade and combined heating and cooling. Theoretical TES performances of different modes are compared, and advantages of different modes are pointed out. Lourdudoss et al. [18] evaluated the three phase absorption heat pump process for energy storage, which indicated that three phase absorption process enjoyed a higher TES performance.

Like adsorption process, resorption process has also been investigated for refrigeration system gradually, which begins to be applied in the TES technology. Resorption process involves two different adsorbents such as halides. Compared with ATES system, resorption thermal energy storage (RTES) systems are characterized as safety feature and simple structure since there is no ammonia liquid in the system. Li et al. [19] analyzed working pair $MnCl_2$–$CaCl_2$–NH_3 for energy storage and upgrade, and indicated its feasibility and high energy density. Bao et al. [20] designed and established one resorption system for cold storage and long distance refrigeration. Results pointed out the optimal distance and period for the system.

Nonetheless, there is few research on the experiments for RTES system, especially for that ammonia is rarely investigated for the application of TES in real system. In this paper, a novel RTES system is established and investigated with improved safety. $MnCl_2$–$CaCl_2$–NH_3 work pair is selected and ENG-TSA is used as additive to develop composite adsorbent. In order to have an overall understanding of this novel system, energy analysis is used for investigating the performance, and exergy analysis is not utilized since it is much lower than energy efficiency for energy storage system [21].

2. Working process of RTES cycle

For RTES, there are commonly three modes for different application occasions, which are energy storage, energy upgrade and combined cooling and heating supply. This paper presents direct heat supply of energy storage mode. The working procedures of the RTES cycle can be generally divided into two processes: charging and discharging processes. Fig. 1 shows schematic diagram of thermal energy storage process. Fig. 1a is working mode, and Fig. 1b is thermal dynamic process, in which energy storage is between energy upgrade and combined heating and cooling supply. The charging processes consist of desorption process in HTS reactor and adsorption process in LTS reactor (Fig. 1a). As Fig. 1b shows, when HTS reactor is heated by heat source at point A, ammonia vapor which clings to adsorbent starts to escape as the threshold binding force between the adsorbate and adsorbent is exceeded. Ammonia vapor flows through a pipe and is adsorbed by LTS reactor at a lower temperature level (point B). Adsorption heat Q_{ads-L} is released to the surrounding environmental medium at point B. Compared with sensible and latent heat storage characterized as direct method, RTES cycle is considered as an indirect TES approach. This is mainly because the binding potential is stored in the adsorbent during the charging process. Simultaneously, adsorption heat is released to heat sink. In addition, part of sensible heat has to be brought into the system to heat up the adsorbent and other components. After the charging process, HTS and LTS reactor are separated from each other. When heating or cooling demand is needed, HTS and LTS reactor are connected with each other again. Similarly, discharging process proceeds in a reverse direction: it includes an adsorption process of HTS reactor and desorption process of LTS reactor (Fig. 1a). Depending on practical demands, LTS reactor can produce a cooling effect of Q_{des-L} at point C or HTS reactor can supply a heating effect at point D in Fig. 1b.

Fig. 2a is the photo of RTES system. Six shell-and-tube type vessels are used as two adsorption reactors, i.e. HTS and LTS reactors. Temperature of HTS adsorption reactor is controlled by the oil tank while LTS adsorption reactor is controlled by ethanol water thermostat. 4.9 kg $MnCl_2$ and 3.8 kg $CaCl_2$ are impregnated in ENG-