Applied Thermal Engineering 111 (2017) 580–585

Contents lists available at ScienceDirect

Applied Thermal Engineering

journal homepage: www.elsevier.com/locate/apthermeng

Research Paper

Solution to the sorption hysteresis by novel compact composite multi-salt sorbents

J. Gao, L.W. Wang *, R.Z. Wang, Z.S. Zhou

Institute of Refrigeration and Cryogenic, Key Laboratory of Power Machinery and Engineering of MOE, Shanghai Jiao Tong University, Shanghai 200240, China

HIGHLIGHTS

- Novel composite sorbents of bi-salt and tri-salt are developed by matrix.
- Clapeyron curves and isobaric sorption/desorption performances are studied.
- Multi-salt sorbents show the combining properties of each salt they contain.
- Tri-salt sorbent makes the sorption hysteresis of chemisorption disappear.

ARTICLE INFO

Article history:
Received 23 July 2016
Revised 26 September 2016
Accepted 26 September 2016
Available online 28 September 2016

Keywords:
Consolidated composite sorbent
Multi-salt
Non-equilibrium
Sorption hysteresis

ABSTRACT

Two novel types of consolidated composite sorbents of $NH_4Cl/CaCl_2/MnCl_2$ and $NH_4Cl/CaCl_2$ are developed by the matrix of expanded natural graphite treated with sulfuric acid (ENG-TSA). The Clapeyron curves and sorption/desorption properties of different sorbents are tested and compared under non-equilibrium conditions. Compared with single-salt sorbent, the multi-salt/ENG-TSA sorbents show the combining properties of each kind of metal chloride they contain. One novel phenomenon is discovered in the study is that the sorption hysteresis of single salts, which is regarded as one common phenomenon for chemisorption, can be changed by the composite sorbents of multi-salt. For the composite bi-salt sorbent of $NH_4Cl/CaCl_2$ the sorption hysteresis is much less significant than the single metal chlorides of NH_4Cl and $CaCl_2$. For the tri-salt composite sorbent of $NH_4Cl/CaCl_2/MnCl_2$ the sorption hysteresis disappears. The reason is analyzed and it may be related to the resorption between the metal chlorides they contain, which leads to a reduction of reaction heat that is believed to be a typical reason for sorption hysteresis.

1. Introduction

The solid sorption refrigeration technology, with zero ODP (ozone depletion potential) and GWP (global warming potential), is a type of environmental benign and energy saving technology and attracted more and more attention in recent years. Compared with the vapor compression refrigeration system, it is believed that solid sorption refrigeration system has a simpler structure, less initial investment, lower operating costs and less noise [1,2]. Solid sorption refrigeration had been investigated intensively for the recovery of solar energy and waste heat [3,4].

The traditional intermittent solid sorption refrigeration system generally involves a sorption bed, an evaporator, and a condenser. The sorption bed desorbs in the heating and desorption process and the desorbed refrigerant condenses in a condenser, and the refrigeration effect is output by the evaporation of the refrigerant in an evaporator in sorption and refrigeration phase [5]. Two kinds of sorption technology are involved in the solid sorption, which are physical solid sorption termed as adsorption [6], and chemisorption for which sorption happens both on the surface and inside of sorbents, i.e. has both features of absorption and adsorption [7].

Studies on the solid sorption, both adsorption and chemisorption, mainly focus on the sorption materials, working pairs, and cycles. For example, T. Miyazaki et al. studied the adsorption system with the working pair of silica gel-water, and two kinds of silica gels were compared [8]. The new type of solid sorbent of zeolite $13X/CaCl_2$ was developed by Alireza Sadeghlu for a two-bed system and it was proved with a better performance [9]. Dakkama et al. investigated the performance of various solid sorption working pairs with wide range of applications in sorption refrigeration systems [10]. Tamainot-Telto and Critoph tried to design and develop a low cost rotary regenerative adsorption air conditioning system [11].

* Corresponding author.
E-mail address: lwwang@sjtu.edu.cn (L.W. Wang).

http://dx.doi.org/10.1016/j.applthermaleng.2016.09.152

The metal halide-ammonia working pairs are the common working pairs for chemisorption refrigeration because ammonia complex can be formed easily with a wide range of driving heat source and works under positive pressure. On the research of the metal halide-ammonia working pairs, the sorption hysteresis was early found by Goetz and Marty [12]. After that some academics discussed the sorption hysteresis and it is recognized as a typical phenomenon for the chemisorption. Trudel et al. observed pseudo-equilibrium hysteresis behavior and they thought the width of the hysteresis loop was a function of heating rate [13]. The stability of $CoCl_2{\cdot}xNH_3$ salt was found to be a function of temperature and pressure [14]. Furthermore, the synthesis and decomposition reactions were controlled by different phenomena [15], which may probably cause the sorption hysteresis. Zhong et al. did the research on the isothermal sorption characteristics of $BaCl_2$-NH_3 pair and used the van't Hoff diagram to describe the termination of synthesis and decomposition [16]. Recently Zhou and Wang had studied the non-equilibrium performance of NH_4Cl, $CaCl_2$ and $MnCl_2$, and established the models especially for the desorption hysteresis [17]. It is recognized extensively that the sorption hysteresis is a common phenomenon and should be considered for the desorption process.

Recently we studied the new types of consolidated composite sorbents of multi-salt, and one interesting phenomenon is found that the sorption hysteresis will disappear with the reasonable combination of different salts. In this paper such a phenomenon is analyzed by the Clapeyron curves and isobaric sorption and desorption performances.

2. Development of compact composite multi-salt sorbents

Two types of the multi-salt composites are studied, which are bi-salt mixture with NH_4Cl and $CaCl_2$ and tri-salt mixture of NH_4Cl, $CaCl_2$ and $MnCl_2$.

According to the temperature of the driving heat source, NH_4Cl, $CaCl_2$ and $MnCl_2$ are classified as low-temperature salt (desorption temperature of 60–90 °C), mid-temperature salt (desorption temperature of 90–150 °C) and high-temperature salt (desorption temperature higher than 130–150 °C) respectively. Chlorides of non-crystalline water are used in the test. The matrix for the sorbents is expanded natural graphite treated by the sulfuric acid (ENG-TSA). ENG-TSA is made from natural graphite that is soaked in sulfuric acid, which become intercalated in the layered structure of the graphite. The sample is exfoliated by heating in a flame, forming expanded graphite with much lower density than normal ENG whilst the intercalated acid is removed. The compact ENG-TSA has been proved with high thermal conductivity and reasonable permeability. The maximum thermal conductivity measured is 337 W/(m·K) at a bulk density of 831 kg/m^3. The permeability perpendicular to the direction of compression vary in the range of 10^{-11}–10^{-16} m^2 as the density increases from 111 to 539 kg/m^3. As a type of heat transfer matrix the thermal diffusivity is about five times higher than that of pure aluminum [18]. The development of the novel composite sorbents involves the following steps.

(1) Different metal chlorides and matrix, such as NH_4Cl, $CaCl_2$, $MnCl_2$ and TNG-TSA are dried in the oven for 3–4 h to dry up the water inside the sorbents and matrix. The temperature of the oven is controlled at 130 °C.
(2) The salts are weighted by the balance with accuracy of 0.01 g, and then they are dissolved in water respectively. After that the ENG-TSA is mixed in the solution. For the bi-salt composite of NH_4Cl and $CaCl_2$, the ratio among NH_4Cl, $CaCl_2$ and ENG-TSA is 2:2:1, and for the tri-salt mixture, the ratio among NH_4Cl, $CaCl_2$, $MnCl_2$ and ENG-TSA is 4:4:4:3. After the composite is uniformly mixed, the mixture is placed in an oven and dried 6–7 h at the temperature of 160 °C.
(3) The dried composite sorbent is compressed into blocks and the density is about 400 kg/m^3.

3. Experimental unit and testing process

The experimental test unit is mainly consisted of one sorption bed, one evaporator/condenser and one differential pressure transmitter. The detailed structure of the test unit is shown in Ref. [17]. The temperature of the sorption bed and evaporator/condenser is controlled by two thermostats.

The testing procedures of Clapeyron curves are as follows:

(1) The condenser is controlled at −10 °C and the highest desorption temperature is set at 180 °C. The refrigerant is desorbed from the sorption bed and condenses in the condenser. When the system reaches the equilibrium state, i.e. the level of the refrigerant inside condenser gets to the pre-set value and changes little, the desorption condensation process is completed. For such a state the NH_3 sorbed by NH_4Cl is desorbed thoroughly. But for $CaCl_2$ and $MnCl_2$, 2 mol NH_3/mol salt cannot be desorbed because the temperature isn't high enough for thoroughly desorption.
(2) Close the valve between the sorption bed and condenser, then the temperature of the high temperature thermostat is slowly decreased, and the sorption quantity, pressure, and temperature are recorded.
(3) When the temperature decreases to the lowest sorption temperature, open the valve between sorption bed and evaporator, and get a new pre-set data for sorption quantity. After that closed the valve, and change the temperature of sorption bed. A new Clapeyron curve can be gotten by recording the data of sorption quantity, temperature and pressure.
(4) The above procedures are repeated and all the Clapeyron curves under different conditions can be gotten.

Taking the evaporating/condensing temperature of −10 °C as one example, the testing procedures of isobaric sorption and desorption performance are as follows:

(1) The evaporating/condensing temperature is set at −10 °C. Open the valve between the evaporator/condenser and sorption bed, and let the sorption bed sorbs the refrigerant to the maximum sorption quantity. Record the initial sorption quantity.
(2) Heat the sorption bed by the step of 5–8 °C. The desorption will happen when the temperature of the sorption bed increases. The temperature inside the sorption bed and sorption data are recorded for each set sorption temperature when the sorption quantity tested by the differential pressure transmitter changes little for five minutes, and the isobaric desorption curve is gotten.
(3) When the desorption temperature gets to the highest desorption temperature, the sorption bed is cooled by the thermostat, and the temperature decreases slowly. The sorption between sorption bed and evaporator will happen and the temperature and sorption data are recorded when the data collected by the differential pressure transmitter changes little for five minutes. The isobaric sorption curve is gotten.
(4) The evaporating/condensing temperature is adjusted from −10 °C to 25 °C by the step of 5 °C, and the steps 1–2 are repeated. Then all isobaric desorption/sorption curves are obtained.