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Investigation on non-equilibrium performance of composite adsorbent for resorption refrigeration

L. Jiang *, L.W. Wang, Z.S. Zhou, F.Q. Zhu, R.Z. Wang

Institute of Refrigeration and Cryogenics, Key Laboratory of Power Machinery and Engineering of Ministry of Education, Shanghai Jiao Tong University, Shanghai 200240, China

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ABSTRACT

The aims of this paper is to indicate that the non-equilibrium adsorption testing results is more suitable for prediction of real refrigeration performance than equilibrium data. Therefore, a test unit is constructed to test the non-equilibrium performance of different composite adsorbents. The adsorption and desorption quantity are measured and calculated by smart differential pressure transmitter. The non-equilibrium adsorption performances of working pair of Manganese chloride–ammonia, Calcium chloride–ammonia and Ammonium chloride–ammonia are investigated respectively. Results show that hysteresis phenomena happens obviously in non-equilibrium desorption process, which is related with dual variables rather than single variable. Based on the testing results, resorption refrigeration performance is analyzed, in which Manganese chloride is used as high temperature salt (HTS), and Calcium chloride, Ammonium chloride are selected as low temperature salt (LTS) for comparison. Results show that the highest COP and SCP for resorption refrigeration are about 0.272 and 45.6 W/kg, respectively. Performance of Manganese chloride–Calcium chloride and Manganese chloride–Ammonium chloride working pairs are much lower when compared with theoretical data.

1. Introduction

Adsorption refrigeration has played an important role in utilizing the renewable energy since it has no risk of Ozone Depletion Potential (ODP) and Global Warming Potential (GWP) [1]. Both physical and chemical adsorption refrigeration are gathering the momentum. Chemical adsorption takes advantage of larger adsorption capacity than physical adsorption [2], and it is more likely to be applied in the freezing condition [3]. However, there will be two disadvantages of chemisorption refrigeration if ammonia is used as the refrigerant. One disadvantage is the safety problem caused by the liquid ammonia when facing bumpy environment. The other disadvantage is that environmental temperature will have a great influence on the refrigeration performance. Refrigeration performance for solar energy application will decrease greatly when cooling temperature is higher than 35–40 °C in summer time [4]. Compared with typical adsorption refrigeration, resorption refrigeration has flexibility to adapt different heat source temperature by employing different alkali metal halides [5]. The resorption refrigeration utilizes the desorption heat in the refrigeration process, which contributes to performance improvement comparing with adsorption refrigeration [6]. Various researchers analyzed adsorption and resorption refrigeration by using equilibrium line in Clapeyron diagram i.e. the equilibrium solid–gas chemisorption process changes with temperature or pressure. For instance, Lu et al. [7] selected working pair of Manganese chloride ($MnCl_2$) as high temperature salts (HTS) and Barium chloride ($BaCl_2$) as low temperature salts (LTS) to analyze the equilibrium performance of resorption system for refrigeration and power cogeneration. Results showed that coefficient of performance (COP) would be improved by 38%, which is much higher than experimental results. Li et al. [8] proposed a combined double-way thermochemical sorption refrigeration cycle, and maximum COP of the cycle was about 1.24 through theoretical analysis. Desorption temperature was about 180 °C with heat sink temperature of 25 °C and evaporation temperature of 10 °C. Nonetheless, experimental results were quite lower than the performance by equilibrium Clapeyron diagrams analysis. The feasibility and working performance of a double-effect and double-way thermochemical sorption refrigeration system was investigated. Although the highest COP of the experiment was about 1.0, heat source temperature was as high as 260 °C and the chilled temperature of 15 °C [9]. One main reason to explain the great difference between the theoretical and experimental result is that real adsorption refrigeration process is non-equilibrium

* Corresponding author.
E-mail address: maomaojianglong@126.com (L. Jiang).

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Nomenclature

A	area of ammonia vessel
c	specific heat (J/(g K))
COP	coefficient of performance
HTS	high temperature salt
g	gravity acceleration (m/s^2)
LTS	low temperature salt
m	mass (kg)
P	pressure (Pa)
Q	heat (J)
R	gas constant (J/(mol K))
SCP	specific cooling power (W/kg)
t	cycle time (s)
T	temperature (K)
V	volume of liquid ammonia(m^3)
x	adsorption quantities (kg/kg)
Greek letters	
ΔH	enthalpy difference (kJ/mol)
ΔS	entropy difference (J/K)
$v'(T_e)$	specific volume of saturated liquid ammonia m^3/kg
Subscripts	
ad	adsorption bed
cycle	resorption cycle
cool	cooling
des	desorption
eg	ENG-TSA
HTS	high temperature salt
h	heat
i	ideal condition
in	in
NH_3	ammonia
re	reaction heat
s	sensible heat
salt	chloride
tot	total

processes, and it will cause the inaccuracy if refrigeration performances are analyzed based on the equilibrium conditions [10]. Under this scenario, non-equilibrium characteristic of different working pairs was investigated for accurate thermal analysis. Calcium chloride ($CaCl_2$) with multi-walled carbon nanotubes composite adsorbent was investigated and found different chemical reaction steps between Calcium chloride ($CaCl_2$) and ammonia (NH_3), and adsorption capacities of the composite adsorbent at different working conditions were evaluated [11]. Characteristic of Cobalt chloride and ammonia working pair proved to be more complicated than a single equilibrium line. Non-equilibrium hysteresis phenomena would cause adsorption process into a bivariate process, which need both temperature and pressure to determine the reaction process [12]. For further research about bivariate characteristic of Cobalt chloride and ammonia working pair, Aidoun et al. investigated and identified the regions of pseudo-stable transitions and instabilities and its application for chemisorption heat pump with carbon fiber and chloride salts composite materials, respectively [13]. Take all investigations above into consideration, compared with the various investigations on equilibrium adsorption performance, there is relatively few experimental investigation about the non-equilibrium performance of composite adsorbent. Recent research has been demonstrated that for different working pairs such as $MnCl_2$–NH_3 and NH_4Cl–NH_3 there will be significant difference between equilibrium and non-equilibrium performance analysis [14]. However, the non-equilibrium performance analysis has not been applied for resorption refrigeration. Techno-economy and energy efficiency should be evaluated as the novel energy conversion technology [15].

In this paper, non-equilibrium reaction line of three different working pairs are investigated and applied for the analysis of resorption refrigeration. Properties such as heat and mass transfer performance are tested for the comprehensive understanding of novel composite adsorbent. Expanded natural graphite treated with sulfuric acid (ENG-TSA) is chosen as the matrix of adsorbent, which is made from natural graphite soaked in sulfuric acid, intercalated in the layered structure of the graphite. ENG-TSA enjoy much lower density than normal expanded natural graphite. Properties such as heat and mass transfer performance of adsorbent are greatly improved through the matrix.

2. Material characterization

2.1. Materials

For different chlorides, Manganese chloride ($MnCl_2$) is used as high temperature salt (HTS) whereas Calcium chloride ($CaCl_2$), Ammonium chloride (NH_4Cl) are selected as low temperature salt (LTS). The reaction process of these salts with ammonia can follow the Eqs. (1)–(3). The details of composite adsorbent in manufacturing process can be referred to the reference [16]. First, ENG-TSA is dried in the oven with controlled temperature 120 °C. Then mix chloride, ENG-TSA and water together to develop the composite adsorbent. Afterwards, composite adsorbent is dried in the oven with controlled temperature 120 °C to remove the water. To remove the crystal water of some chlorides, the temperature of oven is elevated to 240 °C for drying the composite adsorbents. Finally composite adsorbent is compressed into block by the pressing machine.

Mass ratio of salt and density of composite adsorbent are two major factors when developing the composite adsorbent. The cracks will easily happen if the mass ratio of the adsorbent is too low, which causes SCP (specific cooling power per kilogram adsorbent) become too small. Density of composite adsorbent also ought to be reasonable. The higher density of adsorbent is, the lower permeability and the higher thermal conductivity becomes. The anisotropic characteristics of thermal conductivity and permeability of consolidated ENG-TSA [17] and activated carbon/ENG-TSA composite adsorbent [18] have already been studied, and results indicate that direction for best heat and mass transfer performance is perpendicular to the compressing direction of composite adsorbent. In the experiment, only plate samples are utilized, and density is selected as 400 kg/m^3 with different mass ratio of salt ranging from 50% to 83% for comparison.

$$MnCl_2 \cdot 2NH_3 + 4NH_3 \leftrightarrow MnCl_2 \cdot 6NH_3 + 4\Delta H_{MnCl_2} \quad (1)$$

$$CaCl_2 \cdot 4NH_3 + 4NH_3 \leftrightarrow CaCl_2 \cdot 8NH_3 + 4\Delta H_{CaCl_2} \quad (2)$$

$$NH_4Cl + 3NH_3 \leftrightarrow NH_4Cl \cdot 3NH_3 + 3\Delta H_{NH_4Cl} \quad (3)$$