

# REVIEW: USE of COMPOSITE ADSORBENTS in ADSORPTION REFRIGERATION

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## Abstract

The urbanization across the world has resulted in increased demand for refrigeration and air conditioning. The main disadvantage with the conventional method i.e. vapor compression system is environment pollution. Another problem faced during urbanization is energy crisis. The adsorption refrigeration system is one of the solutions to this problem. The advantages of this system are environment friendly, less noise, use of waste heat or solar energy. But the disadvantage with adsorption system is low coefficient of performance (COP) and bulkiness. Researchers across the world are working on this issue to make adsorption system a viable alternative to the compression systems. Since the last two decades considerable work is being done on the use of composite adsorbents to improve the heat and mass transfer performance. This kind of adsorbent is usually obtained by the combination of a chemical adsorbents and physical adsorbents.

Keywords: Refrigeration, Compression System, Adsorption System, Composite Adsorbents, Coefficient of performance (COP).

## I. INTRODUCTION

There are two refrigeration systems that are benign to the environment. They are absorption systems and adsorption systems. Both of them use refrigerants having zero ozone depletion potential and zero global warming potential. Out of these two systems absorption systems are used on a large scale. Researchers have started working on adsorption systems in the last two decades because they have following advantages over absorption refrigeration systems:

- 1) They can be powered by a large range of heat source temperatures from 50°C to 500°C.

- 2) They do not need a liquid pump or the rectifier for refrigerant.
- 3) They do not present corrosion problems due to the working pairs normally used.
- 4) They are less sensitive to shocks and to the installation position.

Although adsorption systems present all the benefits listed above they have drawbacks such as very less coefficient of performance, low specific cooling power and they are bulky. Many researchers are working to reduce the size of the adsorption system and to improve its performance by using composite or consolidated adsorbent for better heat and mass transfer. There is still potential scope in the enhancement of heat and mass transfer properties in the adsorber by increasing the adsorption properties of working pairs and by better heat management during the adsorption cycle. The study may involve the evaluation of the adsorption phenomenon and the physical chemical properties of the working pairs.

## II. REVIEW OF RECENT STUDY

Adsorption refrigeration is one of the most attractive technologies for refrigeration applications, because it is quite benign to the environment: zero ozone depletion potential, zero global warming potential, simple control, low operating cost, less noise, high performance to avoid extra primary energy consumption [1–4]. Ammonia is widely used as a refrigerant in adsorption refrigeration systems [5]. The advantages include high enthalpy of evaporation, stability, wide temperature range and low freezing temperature. One of the most commonly used adsorbents for ammonia sorption reported is alkaline-earth metal chlorides, such as MgCl<sub>2</sub> [6], CaCl<sub>2</sub> [7,8], SrCl<sub>2</sub> [9] and

BaCl<sub>2</sub> [10], which have large adsorption capacity as well as low evaporating temperature.

However, the poor heat and mass transfer performance caused by the phenomena of agglomeration and swelling during the reaction with ammonia make the choice of proper compound adsorbents become vital important. Hybrid materials, which are composed of chemical adsorbents and porous medium, can improve the heat and mass transfer performances of chemical or physical adsorbents effectively [11, 12]. So far, composites for ammonia sorption have been synthesized with CaCl<sub>2</sub> impregnated into various porous mediums, such as activated carbon [13], the synthetic carbon, etc. [14–16]. However, the researches on the basic adsorption equilibrium data are still insufficient to provide comprehensive understanding about the chemical adsorption refrigeration process.

The conventional adsorption cycle mainly includes two phases:

- 1) Adsorbent cooling with adsorption process which results in refrigerant evaporation inside evaporator and thus in the desired refrigeration effect. In this phase the sensible heat and adsorption heat are consumed by a cooling medium.

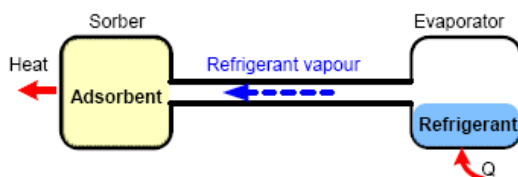


Fig.1: Adsorption (Refrigeration) process

- 2) Adsorbent heating with desorption process also called generation which results in refrigerant condensation at the condenser and heat release to the environment. The heat necessary for the generation process can be supplied by a low grade heat source such as waste heat or solar energy, etc.

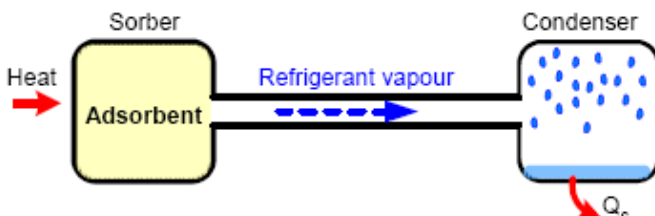


Fig.2: Desorption (Regeneration) process

In comparison with mechanical vapor compression systems, adsorption systems have the benefits of energy saving if powered by waste heat or solar energy, simpler control, no vibration and lower operation costs.

Adsorption systems can be much simpler than absorption systems. For example, in the NH<sub>3</sub>-H<sub>2</sub>O absorption system, dephlegmator equipments must be coupled to the system because the boiling point of water is similar to that of ammonia.

### III. ADSORBENTS

The adsorption process is divided into physical adsorption [17–19] and chemical adsorption [20–22]. The adsorbents can be broadly classified in to three types: a) physical adsorbents b) Chemical adsorbents and c) Composite adsorbents.

#### A. Physical Adsorbents

Physical adsorption is caused by Vander Waals force between the molecules [23] of the adsorbent and the adsorbate. Physical adsorbents with mesopores can adsorb consecutive layers of adsorbate, while those with micropores have the volume of the pores filled with the adsorbate. Physical adsorbents develop the selectivity to the adsorbate after the former undergo specific treatments, like react under a gas stream or with certain agents. The kind of treatment will depend on the type of sorbents [24].

The common physical adsorbents for adsorption refrigeration are activated carbon, activated carbon fibre, silica gel and zeolite.

#### B. Chemical adsorbents

Chemical adsorption is caused by the reaction between adsorbates and the surface molecules of adsorbents. Electron transfer, atom rearrangement and fracture or formation of chemical bond always occurs in the process of chemical adsorption [25]. Only one layer of adsorbate reacts with the surface molecules of chemical adsorbent. The adsorbate and adsorbent molecules after adsorption never keep their original state, e.g., complexation occurs between chlorides and ammonia. Moreover, there are the phenomena of salt swelling and agglomeration, which are critical to heat and mass transfer performance.

Chemical adsorbents mainly include metal chlorides, metal hydrides and metal oxides.

### C. Composite adsorbents

Composite adsorbents [26–28] started to be studied about twenty years ago [29], and they aimed to improve the heat and mass transfer performance of the original chemical adsorbents [27, 30, 31]. This kind of adsorbent is usually obtained by the combination of a chemical adsorbent and a porous medium, that can be or not a physical adsorbent, such as activated carbon, graphite, carbon fibre, etc. [27, 32, 33].

Composite adsorbents are developed and studied with mainly two goals:

(1) Improve heat and mass transfer performance of chemical adsorbents [34], specially due to the swelling and agglomeration phenomena. Salt swelling reduces the heat transfer, and salt agglomeration reduces the mass transfer.

Therefore, the additive for chemical adsorbents must have a porous structure and high thermal conductivity, such as expanded graphite, to help avoiding the above-mentioned problems [35, 36].

(2) Increase the adsorption quantity of physical adsorbents [37]. The addition of chemical sorbents in the physical sorbents increases the adsorption capacity of the latter, without resulting in the problems found in the former.

The composite adsorbents made from porous media and chemical sorbents are commonly a combination of metal chlorides and activated carbon, or activated carbon fibre, or expanded graphite, or silica gel or zeolite.

Increasing popularity of consolidated sorbents can be explained by simplicity of its production and application. The type of consolidated sorbent is determined by application, which influences the type of chosen material [39]:

- 1) Consolidated sorbents using porous metal hydrides or metal matrix alloys containing Ni, Fe, La, Al, H, with or without subsequent sintering;
- 2) Consolidated sorbents using metal foams as porous matrices;
- 3) Consolidated materials using carbon-based materials as inert binder.

There are several kinds of composites proposed in the literature.

One of the most popular is IMPEX (IMPregnated blocks of recompressed EXpanded graphite) e an expanded graphite (EXG) composite developed by Mauran and his coworkers [38, 40, 41], patented and manufactured

by La Carbone Lorraine. It is characterized by strong anisotropic (radial) heat and mass transfer capabilities. The layered structure of compressed EXG improves gas diffusion in direction perpendicular to that of compression [40, 42]. Experimentally obtained values of heat transfer coefficients are  $\lambda = 0.2\text{-}40$  W/mK [43]. Mazet et al. [44] analyzed heat transfer coefficient of IMPEX blocks with apparent density  $200$  kg/m<sup>3</sup> and obtained  $\lambda = 16$  W/mK.

Han and Lee measured effective heat transfer of a composite based on calcium chloride, barium chloride and manganese chloride. The results were  $\lambda = 10\text{-}49$  W/mK and showed that effective thermal conductivity strongly depends on the bulk density, weight fraction of graphite and the ammoniated state of salt [45]. Han et al. [46] has analyzed the influence of acid treatment (intercalation with sulfuric acid at different temperatures) on the porosity and chemical composition of expanded graphite, obtaining higher values (range  $10^{-12}\text{-}10^{-15}$  m<sup>2</sup>) at lower treatment temperatures. Radial thermal conductivity was in range  $4.6\text{-}42.3$  W/mK.

Bou et al. [47] introduced layered, foliated graphite blocks, where each sheet is characterized by different apparent density, and the active agent is dispersed in it. This solution leads to noticeably increased reaction rates (for  $t \leq 40$  min). Lee et al. [48] introduced non-uniform reaction blocks, where apparent density changes with radius direction  $165, 222, 279, 337, 394$  kg/m<sup>3</sup> gradually), which lead to increased transfer capabilities and reaction rates.

### IV. COMPOSITE ADSORBENTS OF SILICA GEL AND CHLORIDES

They are mainly developed by impregnation process [50-53], where the silica gel is immersed in a salt solution, and then dried. According to Aristov et al. [54], the adsorption characteristics of silica gel composite adsorbents can be modified by:

- (1) changing the silica gel pore structure;
- (2) changing the type of salt and
- (3) changing the proportion between salt and silica gel.

The adsorption isotherms of silica gel/CaCl<sub>2</sub>/water pair with different mass ratio of CaCl<sub>2</sub> is shown in Fig. 3 [49]. The letter S in the legend, followed by a number, represents the concentration of the salt solution used to make the composite adsorbent. For example, S0 represents silica gel with no salt, and S40 represents the composite adsorbent made with a 40% CaCl<sub>2</sub> solution. Fig. 3 shows that the increment in the equilibrium adsorption quantity with the solution

concentration decreases when the solution concentration is higher than 40%.

As the salt can easily liquefy during the adsorption process when the compound is prepared with a high concentration solution, the best concentration to avoid such a problem and ensure high adsorption capacity would be around 40%.

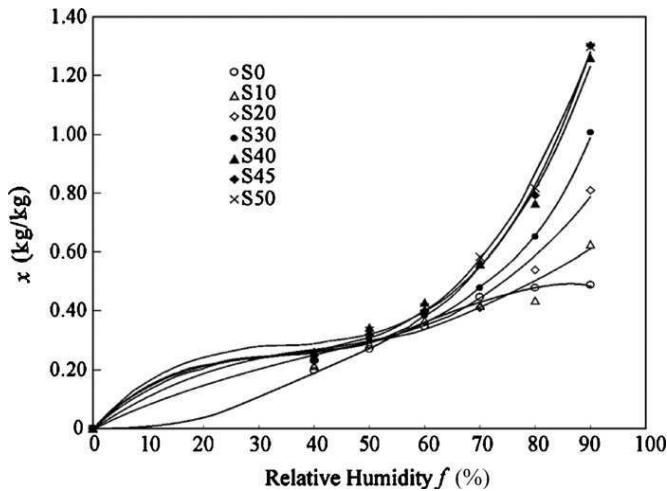


Fig. 3. Isotherms at 40°C [49].

## V. POROUS MEDIA FOR COMPOSITE ADSORBENTS

Four types of porous media are used to produce composite adsorbents with chlorides: expanded graphite, activated carbon, activated carbon fibre and vermiculite. Expanded graphite is utilized to make composite adsorbents with chlorides, which present enhanced heat transfer and mass transfer properties, and almost no expansion during the adsorption process [55].

The structure of the expandable graphite greatly changes after expansion, and this change can be seen in the scanning electron microscope (SEM) picture shown in Fig. 4 [55].

A composite adsorbent of  $\text{CaCl}_2$  and expanded graphite called IMPEX, for which the solution of 20 wt%  $\text{CaCl}_2$  was utilized to impregnate with the graphite block, was developed by the research group of Mauran [58, 55–57]. The dimension stability of IMPEX was studied, and results showed that the volume expansion rate will null if the density of graphite block used to produce composite adsorbent was  $156 \text{ kg/m}^3$ .

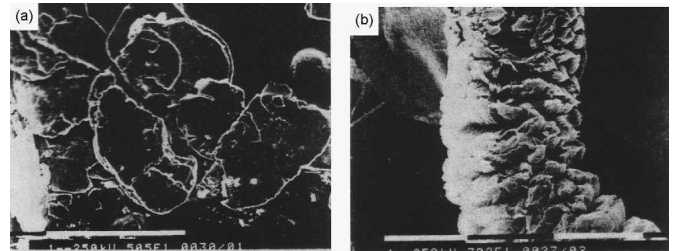


Fig. 4. SEM photo of granular graphite [55]. (a) Before expansion; (b) after expansion.

Shanghai Jiao Tong University [59,60] also researched the adsorption performance of composite adsorbents with  $\text{CaCl}_2$  and expanded graphite, and results showed that SCP as high as  $1000 \text{ W/kg}_{\text{CaCl}_2}$  can be obtained when the mass ratio between expanded graphite and  $\text{CaCl}_2$  is 1:1, evaporation temperature is  $-20$  to  $-10$  °C, and the heat sink temperature is  $20$ – $30$  °C. The overall heat transfer coefficient for this compound was  $787 \text{ W/(m}^2 \text{ °C)}$ .

The advantage of composite adsorbent made with activated carbon, when compared with the composite adsorbent made with activated carbon fibre, is the fact that the salt does not separate from the former and accumulates at the bottom of the adsorber when the compound is prepared as a simple mixture.

Activated carbon fibre is used in combination with chlorides to enhance the heat transfer in the adsorbent bed. Most of the researches are related to impregnated carbon fibres (ICFs) with  $\text{MnCl}_2$  and graphite fibres intercalation compounds (GFICs) [61, 62].

The optimal adsorption performance of ICF–ammonia is similar to the performance of GFIC–ammonia and this value is  $1 \text{ kg/kg}$  for the latter and  $0.95 \text{ kg/kg}$  for the former.

Vasiliev [63,64], also developed a composite adsorbent, which is called Busofit, of activated carbon fibres impregnated with salt, but the solvent was water instead of alcohol. The salt was evenly distributed over the carbon fibre surface as a  $2$ – $3 \text{ mm}$  film. Such a type of adsorbent is mainly utilized for resorption system using ammonia as refrigerant.

## VI. CONCLUSION

The adsorption refrigeration is an alternative refrigeration system that uses refrigerants having zero ozone depletion potential and zero global warming potential. There is a growing need for refrigeration and air-conditioning across the world. At the same time we need to protect our environment. Hence the focus is on greener technologies. Adsorption refrigeration is one of the solutions. But it has very low coefficient of performance. Researchers are working on the techniques to improve the performance of adsorption systems. Various combinations of composite adsorbents are being explored. The use of composite adsorbents in the adsorption refrigeration has resulted in the performance improvement. But, there is still a lot of scope in this field.

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