A NUMERICAL ANALYSIS OF THE EFFECT OF HOT WATER TEMPERATURE ON TWO STAGE ADSORPTION CHILLER WITH FIXED CHILLED OUTLET TEMPERATURE

By
Dilip Kumar Das

MASTER OF PHILOSOPHY
In
MATHEMATICS

Department Of Mathematics
BANGLADESH UNIVERSITY OF ENGINEERING AND TECHNOLOGY (BUET)
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A NUMERICAL ANALYSIS OF THE EFFECT OF HOT WATER TEMPERATURE ON TWO STAGE ADSORPTION CHILLER WITH FIXED CHILLED OUTLET TEMPERATURE

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In
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By

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Student No. 100709009P, Session: October 2007

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The Thesis Entitled

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DEDICATION

This work is dedicated
To
My dearest parents
CANDIDATE’S DECLARATION

I am hereby declaring that the work in the dissertation is being carried out in accordance with the regulation of Bangladesh University of Engineering and Technology (BUET), Dhaka, Bangladesh. The work is also original except where indicated by and attached with special reference in the context and no part of it has been submitted for any attempt to get others degrees or diplomas.

All views expressed in the dissertation are those of the author and in no way or by no means represent those of Bangladesh University of Engineering and Technology (BUET), Dhaka. This dissertation has not been submitted to any other university for examination either in home or abroad.

Date 27.03.2019

Dilip Kumar Das
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I must acknowledge the support from my wife, daughter and son for their encouragement during the period of M. Phil degree.
Abstract

This thesis deals with the numerical results of re-heat two-stage adsorption chiller with different mass flow rate along with the variation of cycle time and also compared with the conventional two-stage chiller. The heat source temperature is considered 60°C to 80°C for the innovative chiller along with the coolant temperature 30°C and the chilled water inlet temperature is 14°C. Silica gel-water is chosen as adsorbent and refrigerant pair. Outlet temperature of chilled water also considered by controlling the mass flow rate and subsequently better results are obtained. In all the four beds of the chiller with mass recovery are taken as uniform in size. To analyze all the things the governing equations are solved by finite difference approximation method. A cycle simulation computer program is used to analyze the influence of operating conditions (hot and cooling water temperature, flow rate) on COP (coefficient of performance), CC (cooling capacity) and chilled water outlet temperature. The cooling capacity (CC) is better for the 1300s cycle time and Coefficient of Performance (COP) is gradually increasing for the longer cycle time. Also it is found that the CC and COP both are improved if the mass flow rate of chilled water and cooling water is increased.
NOMENCLATURE

A  area
E\textsubscript{a}  activation energy (JK\textsuperscript{-1}g\textsuperscript{-1})
L  latent heat of vaporization (JK\textsuperscript{-1}g\textsuperscript{-1})
m  mass flow rate (kg s\textsuperscript{-1})
q  concentration (Kg refrigerant/Kg adsorbent)
q\textsuperscript{*}  concentration at equilibrium (Kg refrigerant/Kg adsorbent)
Q  isosteric heat of adsorption (Jkg\textsuperscript{-1})
P  pressure (pa)
P\textsubscript{c}  condensing pressure (Pa)
P\textsubscript{E}  evaporation pressure (pa)
P\textsubscript{s}  saturated vapor pressure (pa)
R\textsubscript{gas}  gas constant (J K\textsuperscript{-1}g\textsuperscript{-1})
R\textsubscript{p}  Average radius of particle (m)
T  temperature (K)
t  time(s)
U  Overall heat transfer coefficient (Wm\textsuperscript{-2}K\textsuperscript{-1})
W  weight (Kg)
C  specific heat (JK\textsuperscript{-1}g\textsuperscript{-1})
D\textsubscript{so}  pre-exponential constant (m\textsuperscript{2}s\textsuperscript{-1})

Subscripts

Ads  adsorber/adsorptions
cond  condenser
chill  chilled water
cw  cooling water
des  desorber/desorption
eva  evaporator
hex  heat exchanger
hw  hot water
in  inlet
out  outlet
s  silica gel
sc  sorption elements
w  water

Greek symbol

β  affinity coefficient
δ  variance
θ  fractional loading
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CHAPTER ONE

INTRODUCTION

1.1 Introduction

To protect the environment the international and environment agencies have lead to the intensification of research efforts on development of ozone and global warming safe heat pump technology. Many technologies are being reassessed for refrigeration and heat pump application. This includes absorption, adsorption, thermoelectric and starling cycle. Along with a consideration for energy efficiency, increasing attention is being given also to the use of waste heat and solar and solar energy. Absorption technologies using lithium bromide-water are fairly well developed and have already been in use for many years but water-ammonia systems have considerable scope for improvement and applications in many countries, in Europe including the United Kingdom. Adsorption technologies have been extensively for separation and purification of gases for the past few decades but their exploitation for refrigeration and heating purposes is rather recent. This paper is aimed at studying the implication of silica gel/ water as adsorbent and adsorbate pairs.

1.2 Background of the study

In the promotion of environment friendly energy utilization systems, one major goal is to develop CFC-free refrigeration/heat pump systems that utilize waste heat or renewable energy sources. Heat driven sorption (adsorption/desorption) cycle is one of the promising candidates to utilize waste heat at near environment temperature. So that waste heat below 100º C can be recovered. In the moment absorption (liquid-vapor) is the most promising technology in the area of heat driven heat pump/refrigeration technologies, however, adsorption (solid-vapor) cycles have some distinct advances over the other systems in view of their ability to be driven by relatively low temperature heat source[1]. In the last three decades, extensive investigations on the performance of the adsorption heat pump refrigeration have been conducted considering various adsorbent /adsorbate pairs. The following are the representative examples: zeolite/
water[ 2], active carbon ammonia[3], active carbon/methanol [4] and silica gel/water[5]. Conceptually, the desorbed vapor is equal to the amount of adsorbed vapor by

1.3 Objective of the study

(i) To determine the effect of hot water temperature in a two-stage adsorption chiller when chilled water outlet temperature is fixed.
(ii) Coefficient of Performance (COP) and Cooling Capacity (CC) with fixed chilled water outlet temperature.
(iii) The effect on Coefficient Of Performance (COP) and Cooling Capacity (CC) for a long cycle time

1.4 Methodology

The present analysis, a cycle simulation computer program will be developed to predict the performance of the innovative two-stage chiller using re-heat. The system of the differential equation will be solved by the finite difference approximation with a time step 1 sec. The data will be obtained from the solution process are taken from the cyclic steady state conditions of the chiller. A real chiller starts its operation with unbalanced conditions. Therefore, iteration process will be employed in solution procedure to fix all the initial values for the cyclical steady state conditions. In the beginning of the solution process, initial values will be assumed and finally those will be adjusted by the iteration process. When two beds are connected with evaporator or condenser, the vapor pressure is unknown that can be calculated through the Antonie’s equation as the vapor temperature can be calculated from the energy balance equation of evaporator or condenser. It is however, difficult to calculate the saturated vapor pressure when two beds are connected with each other, which are essential for the calculation of adsorption/desorption rate inside the adsorbent beds. In this state, the pressure will be assumed and the amounts of vapor adsorbed/desorbed beds are calculated. Conceptually, the desorbed vapor is equal to the amount of adsorbed vapor by the other beds. If this amounts are not equal then vapor pressure will be adjusted for next iteration. Once the satisfactory convergence is achieved, then process goes for the next time step. The convergence criterion for all cases of present study will be taken as $10^{-3}$. 
CHAPTER TWO

PRINCIPLES OF ADSORPTION

2.1 Introduction

Adsorption occurs at the surface interface of two phases, in which cohesive forces including electrostatic forces and hydrogen bonding, act between the molecules of all substances irrespective of their state of aggregation. Unbalanced surface forces at the phase boundary cause changes in the concentration of molecules at the solid/fluid interface. The process of adsorption involves separation of substances from one phase accompanied by its accumulation or concentration at the surface of another. The adsorbing phase is the adsorbent, and the material concentrated or adsorbed at the surface of that phase is the adsorbate. Adsorption process can be classified

(i) Physical
(ii) Chemical, depending on the forces causing the adsorption process.

(i) Physical adsorption (physisorption) occurs the solid phase, these intermolecular forces are as same as ones that bond molecules to the surface of liquid. Molecules that are physically adsorbed to a solid can be released by applying heat; therefore, the process is reversible.

(ii) Chemical adsorption (chemisorptions) occurs when covalent or ionic bonds are formed between the adsorbing molecules and the solid substances. The bonding forces of chemical adsorption are much greater than that of physical adsorption. Thus, more heat is liberated. This bonding leads to change in the chemical form of the adsorbed compounds and hence, it is irreversible. For this particular reason, most of the adsorption process applicable to the thermal system or cooling machine mainly involves physical adsorption.

Adsorption is an exothermic process accompanied by evolution of heat; the quantity of heat release depends upon the magnitude of the electrostatic forces involved, latent heat,
electrostatic and chemical bond energies. The heat of adsorption is usually 30-100% higher than the heat of the condensation of the adsorbate. In general adsorption is stronger than the condensation to liquid phase. Hence, if a fresh adsorbent and adsorbate in liquid form co-exist separately in a closed vessel, transport of adsorbate from the liquid phase to the adsorbent occurs in the form of vapor. The liquid temperature becomes lower while the adsorbent temperature rises. Air conditioning and refrigeration utilize this phenomenon to obtain a cooling effect. Heat of adsorption is either derived from adsorption isotherms, generally referred to as either the isosteric heat (the energy released in the adsorption process), or, as the differential heat of adsorption heat determined experimentally using a calorimetric method. The performance of adsorbents used in physisorption is governed by surface properties, such as surface area, micro-pores and macro-pores, size of granules in powder crystals or in pellets. Adsorbents having special affinity with polar substances like water are termed ‘hydrophilic’. These include silica gel, zeolites and porous or active alumina. Non-polar adsorbents, termed ‘hydrophobic’, have more affinity for oils and gases than for water. These substances include activated carbons, polymer adsorbents and silicalites. The general term ‘sorption’ is used when both adsorption and absorption occurs simultaneously. ‘Desiccants’ are type of adsorbents having special affinity for water and have been extensively for dehumidification or drying in air processing applications.

Adsorbents are characterized by surface properties such as surface area and polarity. A large specific surface area is preferable for providing large adsorption capacity, but the creation of a large internal surface area in a limited volume inevitably gives rise to large numbers of small sized pores between adsorption surfaces. The pore size distribution of micro pores which determines the accessibility of adsorbate molecules to the internal adsorption surface is important for characterizing adsorptivity of adsorbents. Materials such as zeolite and carbon molecular sieves can be engineered specifically for precise pore size distribution and hence ‘tuned’ for a particular separation.

2.2. Commercial hydrophilic solid adsorbents

2.2.1. Silica gel

Silica gel (SiO₂·H₂O) is prepared from pure silica and retains chemically bonded traces of water (about 5%). If it is overheated and loses this water, it’s adsorption capacity is
lost and therefore it is generally used in temperature applications under 200\(^{\circ}\) C. It is available in various pore sizes and the smaller the pore size the greater is the surface area per unit mass, which is typically 650\(m^{2}\cdot g^{-1}\). Silica gel grades with the finest pores have a large molecular sieve effect similar to those of zeolites. Silica gel has a large capacity for adsorbing water, especially at high vapor pressure. And therefore it is widely used as a desiccant for dehumidification purposes. It is also used in the separation of gases and liquids. Silica gel, ranging from pore sizes 2 to 3 nm (type A) at about 0.7 nm (type B) are mostly used in commercial applications. Specifically Type A is used for general drying and Type B for relative humidities greater than 50%. Heat of adsorption of water vapor on silica gel is predominantly due the heat of condensation of water.

2.2.2. Activated (or porous) Alumina

Activated alumina is aluminium oxide in a porous form prepared by dehydration of aluminium hydrates (mostly \(Al_{2}O_{3}.3H_{2}O\)) to about 6% moisture level and having surface area ranging between 150 and 500\(m^{2}\cdot g^{-1}\) with pore sizes ranging from 1.5 to 6 nm. It is generally useful as a dying agent adsorbent for polar organic substance.

2.2.3. Zeolites

Zeolites including crystalline zeolites, also called molecular sieves, are aluminosilicate minerals and are naturally occurring. Many types of synthetic zeolites have been developed for special application. For example, molecular sieves, using types 4A, 5A, 10X, 13X, which have been developed by the Linde Co. USA. These substances have cavity volumes in the range of 0.05 to 0.30\(cm^{3}\cdot g^{-1}\). However, they may be heated to about 500\(^{\circ}\)C without damage occurring to their adsorption and regeneration properties. Type 4A (also termed as NaA by other manufacturers), is used for drying and separation by hydrocarbon mixtures. For example, type 5A (or CaA) is used to separate paraffin and, some cyclic hydrocarbon mixtures. For example, type 10X (or CaX) and 13X (NaX) adsorb quite a wide range of adsorbates because of their larger diameter of inlet necks of their pores.
2.2.4. Calcium chloride

Calcium chloride is a very widely available adsorbent that remains solid until saturated, beyond which it dissolves in water but can still be used as a low temperature liquid desiccant. It also has good potential for use as a solid chemical adsorbent for methanol and ethanol vapours.

2.3. Commercial hydrophobic solid adsorbent

2.3.1. Activated carbons

Activated carbons are made by pyrolyzing and carbonizing source material, such as coal, Lignite, wood, nutshells and synthetic polymers, at high temperatures (700°C to 800°C). Activated carbons are available in many forms including powders, micro-porous, granulated, molecular sieves and carbon fibers. Generally, the activated carbons in the powdered form (15 to 25 \( \mu m \) particles) is used for adsorption of liquids and in granulated (sieved granules of 4 to 20 mesh or about 0.3 mm to 0.8 mm diameter) or pellet (extruded pellets of 4 to 6 mm in length) forms for air purification and gas separation. Activated carbon in micro porous forms has molecular sieving ability and is widely used for separation of nitrogen and Oxygen in air. Activated carbon fibers (fiber diameter of 7 to 15 \( \mu m \)) made by carbonizing synthetic fibers is available in forms of mats, cloth and fiber chips and is used for air and water purification.

2.3.2. Metal oxides

Metal oxides including titanium oxide, zirconium oxide and magnesium oxide, has been used as adsorbents for special uses involving chemisorptions, For example cerium oxide is used for adsorption of fluoride in waste water.

2.3.3. Specially developed porous metal hydrides

Specially developed porous metal hydrides (PMH) or Mish Metal (Mm) matrix alloys, containing Ni, Fe, La, Al, H have very high rates of sorption and heat of adsorption with hydrogen as adsorbate and have promising uses in development of metal hydride refrigeration and heat pump systems.
2.3.4. Composite adsorbents

Composite adsorbents made from metallic foams, zeolites and natural graphite have good prospects in improving the heat transfer rates in the adsorbent beds, consequently increasing the refrigeration or heat pump system performance[6].

2.4. Adsorbents and adsorbates used in the heat pump system

Although, early efforts to use solid adsorbents for heat pump applications were made decades ago, it was only after the oil crisis during the 1970s that more attention was given to exploit their full potential. In the investigations on solid adsorption heat pump systems, the following adsorbent and adsorbate combination have been used:

(i) Zeolite and water
(ii) Zeolite composites and water
(iii) Activated carbon and ammonia
(iv) Calcium chloride and methanol
(v) Metal hydrides and methanol
(vi) Complex compounds/salts and ammonia or water

Other combination of adsorbents and adsorbates, including silica gel-water, activated carbon-ammonia and calcium chloride-ammonia have been in adsorption refrigeration only systems utilizing solar energy for refrigeration of adsorbent beds [7].

2.4.1. Zeolite –water systems

Zeolite –water combination has been used extensively for open type desiccant cooling systems [7].

2.4.2. Zeolite composites and water systems

Guilleminot et al. [8] In their very promising investigation used the composite adsorbent made from highly conductive carbon (graphite) and metallic foams with zeolite (typically 65% zeolite+35% metallic foam and 70% zeolite+30% graphite). The
thermal conductivities of this composite were improved by about 100 times using this approach. Adsorption systems using this composites yielded cooling capacity of 1500 Wkg\(^{-1}\) of adsorbent and an adsorption heating rate of 2800 Wkg\(^{-1}\) as compared to respective values of 31 Wkg\(^{-1}\) and 200 Wkg\(^{-1}\) for a non-composite systems.

2.4.3. Activated carbon –ammonia systems

Investigation into the use of charcoal ammonia are apparently more recent and mainly during the current decades using a novel carbon moulding technique and incorporating a thermal wave regeneration concept, used in the drying of gas streams [8], a small unit using 0.51 kg of charcoal, developed by Jones [9] at the California institute of Technology, produced 293 watts of cooling with an adsorbent heating and cooling cycle of 6 min with ammonia as adsorbate. With R-22 and r-134 as adsorbates, cooling rates of 113 and 99 watts were reported. Many other recent investigation using charcoal-ammonia involve efforts on performance enhancement.

2.4.4. Metal hydrides-hydrogen systems

Many metals and alloys adsorb or desorb hydrogen and form chemical hydrides depending upon temperature and pressure. The forces of adsorption or hydriding is exothermic and the dehydriding process is endothermic. Specially developed porous metal hydrides (PMH) or misch metal (Mm) matrix alloys, containing Ni, Fe, la, Al, H have very high rates of sorption heats of adsorption when hydrogen is used as the adsorbate. Experimental results are promising in development of metal hydride refrigeration and heat pump systems.

2.4.5. Complex compound /salts and ammonia or water

Beijer and Horsman [10] have developed an interesting Na\(_2\)S-H\(_2\)O adsorption heat pump storage system which have called Salt Water Energy Accumulation and Transformation (SWEAT). SWEAT modules are of tabular construction of 0.2 m diameter and 1.7 m in height. These modules have been developed to store 5 kWh of heat and 3 kWh of cold, which can be combined in various capacities. Bougard et al. (11) has investigated the use of gas-salt reactions (e.g. ammonia-chloride ) for thermo transformation designs. They used the salt couple CaCl\(_2\). (8-4)NH\(_3\).ZnCl\(_2\).(4-2)NH\(_3\). Which could upgrade part
of the high temperature heat source at 90°C to a temperature of 160°C? Using a low temperature heat sink 30°C. With pressure range of 0.5 to 12 bar.

2.5 Adsorption Equilibria

To understand the adsorption process, the adsorption equilibria are introduced to describe the adsorption process and several state equations known as isotherms of adsorption. Several basic theories have been proposed and used to define the main isotherms of an adsorption process and are listed below:

**Henry's law.** For an adsorption process on a uniform surface at sufficiently low concentrations (such that all molecules are isolated from their nearest neighbors), where the equilibrium relationship between fluid phase and adsorbed phase concentrations will always be linear [12].

**Langmuir's approach.** In order to understand the monolayer surface adsorption on an ideal surface, Langmuir's approach is used and this approach is based on kinetic equilibrium; that is, the rate of adsorption of the molecules is assumed to be equal to the rate of desorption from the surface [13].

**Gibbs' theory.** This is based on the ideal gas law, in which the adsorbate is treated in microscopic and bidimensional form and provides a general relation between spreading pressure and adsorbed phase concentration. In this concept, volume in the bulk phase is replaced by the area and the pressure is replaced by the so-called 'spreading pressure'. By assuming some forms of thermal equation of state relating the number of moles of adsorbate, the area and the spreading pressure and using them in the Gibbs equation a member of fundamental equations can be derived, such as the linear isotherm, the Volmer isotherm, etc.

**Adsorption potential theory.** It is purely a thermodynamic approach, suitable for adsorption in microporous materials which was based on a model originally proposed by Polanyi and further developed by Dubinin by the end of the 1920s. Recent equations for ideal solids are introduced by Nitta and his co-workers [14] are based on statistical thermodynamics with features similar to the Langmuir theory and encompasses the Langmuir equation as a special case.
Due to the complexity in structure of practical solids, the above fundamental desorption isotherm cannot completely describe the process. Hence, the analysis of ideal solids are initially used as a basis for the development of equilibria theory for practical solids, and a number of empirical as well as semi-empirical equations to describe adsorption equilibria have been developed.

In order to describe adsorption of gases and vapors below the capillary condensation region, equations such as Freundlich, Langmuir-Freundlich (Sips), Toth, Unilan, and Dubinin-Radushkevich (DR) have been used. Similarly, to describe equilibrium data in the region of multilayering adsorption, the classical equation of Brunauer, Emmett and Teller (BET) is used. To account for the various features inherent with real solids, BET equation is further modified and is listed in the reference [14]. The above-discussed empirical relations are applicable to both subcritical as well as the wider range of supercritical vapors.

To analyze more critically the adsorption process due to the presence of subcritical vapors in the micropores solids, the semi-empirical DR equation was developed by Dubinin et al [15].

\[ w = w_0 \exp\left(-\frac{\Delta A^2}{R T}\right) \]  

(2.1)

In the above equation, \( \Delta A \) is the adsorption potential and is defined as \( \Delta A = R S T \ln\left(\frac{p_0}{p}\right) \); \( E; \) is the interaction energy between solid and adsorbing molecule. The DR equation has been widely used to describe adsorption isotherms of subcritical vapor in microporous solids such as activated carbon and zeolite.

The DR equation describes fairly well many carbonaceous solids with low degree of burned-out. For carbonaceous solids resulting from a high degree of burn-out during activation, the degree of heterogeneity increases because of a wider pore size distribution, and for such cases the DR equation does not describe well the equilibrium data. To take into account of this surface heterogeneity, Dubinin and Astakhov [14] proposed another equation (DA) of the following form:
\[ w = w_0 \exp \left[ -\left( \frac{A}{E_0} \right)^n \right] \]  
(2.2)

where, the exponent n describes the surface heterogeneity. Rewriting the above equation in terms of the characteristic energy of the reference vapor, the expression becomes:

\[ w = w_0 \exp \left[ -\left( \frac{A}{BE_0} \right)^n \right] \]  
(2.3)

where, the parameter \( \beta \) represents the affinity coefficient, which is the ratio of the liquid molar volume to that of the reference vapor. With the additional exponent n in the adsorption isotherm equation, the DA equation provides flexibility in the description of adsorption data of many microporous solids ranging from a narrow to wide micropore size distribution.

Adsorption isotherms of many microporous solids do not usually conform to the simple DR equation. Even with the inclusion of adjustable exponent in the DA equation, in situations. This inability to fit the data is attributed to the cannot reflect experimental data corresponding to different heterogeneity of the system, in which the characteristic energy varies with the different regions in the solid. Since adsorption of many adsorbates in micropores of carbonaceous solids is due to the dispersion force, the micropore size is therefore playing a major role in the attraction of adsorbate molecules. In this sense, distribution of the micropore size dictates the heterogeneity of the solid surface than the distribution in characteristic energy.

For a micropore volume, \( w_0 \int_0^l f(x) \, dx \), \( f(x) \) represents the micropore size distribution, having micropore size between 1 and 1 +dl; the volume of micropore occupied by adsorbate at a given adsorption potential \( \Lambda \) is:

\[ w = \int_{l_{\min}}^{l_{\max}} \theta \left( \frac{A}{\beta E_0} \right)^n f(l) \, dl \]  
(2.4)

Where \( \theta \) is the fraction of the micropore volume occupied by the adsorbate, which is a function of \( \left( \frac{A}{\beta E_0} \right)^n \) [14]. \( l \) is the micropore half width, with \( l_{\min} \) and \( l_{\max} \) are its
minimum and maximum, respectively. However, for mathematical convenience, those limits are usually replaced by 0 and 1, respectively, to facilitate the analytical integration the above integral.

To evaluate the integral Eq. (2.4), the parameters of the local isotherm must be expressed in terms of the micropore half width, 1: The parameter n is usually regarded as a constant. The parameter $E_0$, is the characteristic energy of the reference vapor, which follows the following relationship with the micropore half width, as:

$$E_0 = \frac{k}{l} \quad (2.5)$$

The micropore size distribution can then be assumed to take the following Gaussian distribution:

$$\frac{dw_0}{dx} = \frac{w_0}{\delta \sqrt{2\pi}} \exp\left[ -\frac{(l-l_0)^2}{2\delta^2} \right] = w_0 f(l) \quad (2.6)$$

Where, $dw$ is the total micropore volume, $l_0$ is the half-width of a slit shaped micropore which corresponds to the maximum of the distribution curve, and $\delta$ is the variance.

Using the relationship between the characteristic energy and the micropore half width, the DR equation can be written in terms of this half width $l$ as:

$$w = w_0 \exp\left[ -ml^2 A^2 \right] \quad (2.7)$$

where $m = 1/(\beta k)^2$

In order to obtain an equation for a heterogeneous solid, the above adsorption equation is differentiated to obtain micropore volume element $dw$:

$$\frac{dw}{dx} = \frac{dw_0}{dx} \exp(-ml^2 A^2) \quad (2.8)$$

Combining Eqs. (2.6) and (2.8), yields the volume occupied by
the adsorbate (W):

Evaluation of the above integral results:

\[ w = \frac{w_0^0}{\delta/\sqrt{2\pi}} \exp \left( -\frac{(l-l_0)^2}{2\delta^2} \right) e^x \left[ -ml^2 A^2 \right] dx \]

(2.9)

\[ w = \frac{w_0^0}{2N1+2m^2\delta^2A^2} \exp \left( -\frac{ml^2 A^2}{1+2m^2\delta^2A^2} \right) \times \left[ 1 + \text{erf} \left( \frac{l_0}{\delta/\sqrt{2\pi}1+\text{m}_0^2A^2} \right) \right] \]

(2.10)

This equation was first obtained by Dubinin and Stoeckli [16], and hence referred as DS equation. In this equation, ‘erf’ represents the error function. Using the above equation to fit experimental data, three parameters can be extracted from this fitting process, namely \( w_0^0, l_0, \delta \). Knowing these parameters, the micropore size distribution in terms of volume can then be calculated from Eq. (2.6).

Thermodynamic analysis suggests that an adsorption isotherm must exhibit the Henry law behavior when pressure is very low. Unfortunately, the DA as well as the DR equations do not follow the perfect Henry law when the pressure is approaching zero. The above DR, DA, DS equations, however, suffer from the disadvantage of zero Henry constant at zero pressure.

2.6 Refrigerants and Adsorbents

There are several working pairs for solid adsorption. For the successful operation of a solid adsorption system, careful selection of the working medium is essential. It is because; the performance of the system varies over a wide range using different working pairs at different temperatures. The advantages and disadvantages of different working media and their properties are listed and discussed in this section. For any refrigerating application, the adsorbent must have high adsorptive capacity at ambient temperatures and low pressures but less adsorptive capacity at high temperatures and high pressures. Thus, adsorbents are first characterized by surface properties such as surface area and polarity. A large specific surface area is preferable for providing large adsorption capacity, and hence an increase in internal surface area in a limited volume
inevitably gives rise to large number of small sized pores between adsorption surfaces. The size of the micropores determines the effectiveness of adsorptivity and therefore distribution of micropores is yet another important property for characterizing adsorptivity of adsorbents. Based on the above discussion, the choice of the adsorbent will depend mainly on the following factors:

(i) High adsorption and desorption capacity, to attain high cooling effect;
(ii) Good thermal conductivity, in order to shorten the cycle time;
(iii) Low specific heat capacity;
(iv) Chemically compatible with the chosen refrigerant;
(v) Low cost and widely available.

The selected adsorbate (working fluid) must have most of the following desirable thermodynamics and heat transfer properties:

(i) High latent heat per unit volume;
(ii) Molecular dimensions should be small enough to allow easy adsorption;
(iii) High thermal conductivity;
(iv) Good thermal stability;
(v) Low viscosity;
(vi) Low specific heat;
(vii) Non-toxic, non-inflammable, non-corrosive; and
(viii) Chemically stable in the working temperature range.

Based on the above criteria, some of the appropriate working pairs are zeolite-water, zeolite-organic refrigerants, silica gel-water, zeolite-water and activated carbon-methanol in solid adsorption systems. Several refrigeration applications have been studied using various adsorbent and adsorbate pairs. The recent new development of activated carbon fibre - ACF, shows the possibility for applications in adsorption
One good example is the development in Byelorussia of a refrigerator prototype using ACF-ethanol and ACF-acetone pairs has been reported [17]. New experiments have also been shown to use a heat pipe for heating/cooling ACF adsorbers for the ACF-NH3 pair [18]. In China, several studies had been carried out on solar powered refrigerators using different adsorption pairs such as zeolite-water and activated carbon-methanol., Tamainot and Critoph [19] investigated the thermophysical properties of two types of monolithic activated carbons with an intention to design and fabricate a high performance generator for sorption refrigeration systems and heat pumps using ammonia as refrigerant. It was found that, reduction in volume from granular bed to monolithic bed was up to 50%, which could lead to a substantial economic gain.

2.7 Heat of Adsorption

All absorption processes are accompanied by heat release, i.e. they are, exothermic processes. Since in adsorbed phase, adsorbate molecules are in more ordered configuration, entropy decreases; and from \( \Delta G = \Delta H - T \Delta S \); exothermic character of the process is obvious. The three terms which are often used in adsorption process are:

(i) Integral heat of adsorption which is the total heat released from initial state to final state of adsorbate loading, at constant temperature;

(ii) Differential heat of adsorption is the change in integral heat of adsorption with change in loading;

(iii) Isosteric heat of adsorption is defined by using adsorption isosters and

(iv) Clausius-Clapeyron relationship.

In practice, the difference between differential heat of adsorption and isosteric heat of adsorption is so small that it can easily be neglected, as well as, these two can be considered as identical. At constant loading, \((dc_\mu = 0)\) using the DA Eq. (2.3) and the filling Clapeyron equation,

\[
\frac{\Delta H}{R_\mu T^2} = \left( \frac{\partial \ln \mu}{\partial T} \right)_{c_\mu}
\]

(2.11)
an expression for the isosteric heat can be obtained.

\[-\Delta H = A + \Delta H_{vap} + \frac{(\beta E_0)^n \delta T}{n A^{n-1}}\]  

(2.12)

Thus, the isosteric heat is a summation of three terms. The first term is due to the adsorption potential, the second is the heat of vaporization and the third corresponds due the change in maximum capacity with temperature.

To express the isosteric heat of adsorption in terms of adsorption rate, the above expression can be rewritten as:

\[\Delta H_{vap} + \beta E_0 \left( \ln \frac{1}{\theta} \right) + \frac{(\beta E_0)^n \delta T}{n} \left( \ln \frac{1}{\theta} \right)^{(n-1)/n}\]  

(2.13)

where the fractional loading \(\theta\) can be expressed as \(C_\mu / C_{\mu,s}\)
CHAPTER THREE
Thermodynamics of Adsorption Cycles

Introduction

The environment-friendly adsorption cooling system is an attractive alternative to the traditional CFC based vapour-compression cooling system as it employs safe and natural refrigerants. Another advantage of such adsorption cooling systems is that they can be driven by low-grade energy such as waste heat or solar energy. As a result, adsorption cooling systems have attracted considerable attentions in recent years, adsorption cooling systems is a noiseless, non-corrosive and environment-friendly energy conversion system. So, many researchers around the world have made significant efforts to study such typical adsorption refrigeration cycles.

(i) Basic cycle,
(ii) Continuous heat recovery cycle,
(iii) Mass recovery cycle, thermal wave cycle,
(iv) Convective thermal wave cycle,
(v) Cascade multi effect cycle,
(vi) Hybrid heating and cooling cycle etc.

3.1 Basic adsorption cycle
A basic adsorption cycle consists of four thermodynamic steps, which can be well represented with the aid of the Clapeyron diagram, as shown in Fig. 3.1.
The idealized cycle begins at a point (point A in Fig. 3.1) where the adsorbent is at low temperature \( T_A \) and at low-pressure \( P_E \) (evaporating pressure). A-B represents the heating of adsorbent, along with adsorbate. The collector is connected with the condenser and the progressive heating of the adsorbent from B to D causes some adsorbate to be desorbed and its vapor to be condensed (point C). When the adsorbent reaches its maximum temperature \( T_D \); desorption ceases. Then the liquid adsorbate is transferred into the evaporator from C to E and the collector is closed and cooled. The decrease in temperature D to F induces the decrease in pressure from \( P_C \) to \( P_E \): Then the collector is connected to the evaporator and adsorption and evaporation occur while the adsorbent is cooled from F to A. During this cooling period heat is withdrawn to decrease the temperature of the adsorbant.

### 3.2 Heat recovery adsorption refrigeration cycle

The semi-continuous heat recovery cycle is usually operated with two adsorption beds. The adsorber to be cooled will transfer its heat to the adsorber to be heated, which includes sensible heat as well as heat of adsorption. This heat recovery process will lead to a higher system COP. Multi-beds could be also adopted to get more heat recovery and thereby to attain higher COP, but the operation of a practical system will be complicated.

![Schematics of heat recovery two-bed adsorption refrigeration system](image)
Aqua-continuous adsorption refrigeration system with heat recovery was investigated by Wang et al. [20] and the flow path is shown in Fig. 3.2. While adsorber 1 is cooled connected to the evaporator to realize adsorption refrigeration in evaporator, the absorber 2 connected to the condenser is heated to obtain heating-desorption-condensation. The condensed refrigerant liquid flows into evaporator via a flow control valve. The operation phase can be changed, and the go-between will be a short time heat recovery process. Two pumps are used to drive the thermal fluid in the circuit between two absorbers (the connection to the heater and cooler are blocked during this process). Jones [21] suggested an improvement to the process by installing more than two absorbers into the system.

The operating principle of the cycle remains the same, relying on heat transfer flowing between the absorbers and the desorbers. As compared to the basic cycle, heat recovery in this process is only effective if the heat transfer fluid temperature leaving the absorbers is sufficiently high. Simulation results have shown that the maximum value of the COP depends on the number of absorbers and desorbers installed. The analysis was further extended to a system containing six absorbers and six desorbers at the same test temperature conditions (evaporation at 5°C and condensation at 35 °C)

### 3.3 Mass recovery adsorption refrigeration cycle

Apart from the above discussed heat recovery operation, it had been proved that mass recovery is also very effective for heat recovery adsorption heat pump operation. In this process, at the end of each half cycle, one absorber is cold and the other one is hot. Meanwhile, the former one, which is at low pressure, $P_e$ must be pressurized up to the condenser pressure, and similarly, the other one, which is at high pressure, must be depressurized down to the evaporator pressure. With just one tube between the absorbers and a vapor valve, part of this pressurization-depressurization can be achieved by transferring vapor from the latter absorber to the former one. This process can also be called as an ‘internal vapor recovery process’, and is reported to enhance the cooling power of the unit without reducing the COP by more than 10%.
The above explained process involves only mass transfer and hence the process is rapid. To obtain a ‘double effect’, mass recovery could be initiated followed by heat recovery. An ideal heat and mass recovery cycle is shown in Fig. 3.3, in which the heat recovery state for a two bed system is shown by the state points e-e’

Fig. 3.3. Diagram of heat and mass recovery cycle

The mass recovery cycle \( (a_2, - a_3, g_1' - g_1 - g_2 - g_3 - a'_1 - a_1, - a_2) \) is an extended form of a two bed basic cycle or two-bed heat recovery cycle \( (a_2 - g_1 - g_2 - a_1 - a_2) \) shown in Fig. 3.3, and the cycled mass is increased from \( \Delta x \) to \( \Delta x + \Delta x' \), which causes the refrigeration effect to increase. The principle of these cycles can be described using Fig. 3.3. The very first part of each half cycle is the mass recovery process (path \( g_2 - g_3, a_2, - a_3 \)). Then the heat recovery process proceeds: heat is transferred from the hot absorber to the cold one (path \( g_2 - e' \)). As a consequence, the hot absorber is first depressurized (path \( g_3' - a_3' \)), it then adsorbs vapor from the evaporator (path). Meanwhile, the cold absorber is first pressurized (path \( a_3 - a_1' \)), and then vapor that is desorbed passes into the condenser (path \( g_1' - e \)). Theoretically, the heat recovery process develops until the adorers reach the same temperature. Actually, there still remains a temperature difference between the adorers at the end of this period. Then, for closing each half cycle, the adorers are, respectively, connected to the heat source and heat sink (path e-g_2 and (e'-a_2). The second half-cycle is performed the same way except that the adorers now exchange their roles. Due to this process, about 35% of the total energy transmitted to each absorber can be internally recovered, including part of the latent heat of sorption.
3.4 Thermal wave cycle

To further improve the heat regenerative ratio, Shelton [22] had proposed an attractive cycle called 'thermal wave cycle'. In this process, it is assumed that a large temperature gradient exists along an adsorption bed. Heating and cooling of the adsorbent beds is achieved via a heat transfer fluid such as high temperature oil. The system consists of two absorber beds and two heat exchangers connected in series (Fig.3.4) to effect semi continuous process. The function of the bed and heat exchanger is to combine a large area of heat transfer surface with a low oil flow rate.

A typical thermal wave cycle is shown in Fig.3.4. The cycle consists of two phases: In the first phase, the oil recovers heat from bed 2 (hot), has a further heat addition from the heat exchanger and then proceeds to heat bed - 1 (cold). As the heating of the bed proceeds, bed 1 desorbs refrigerant which passes to the condenser (giving a useful heat output in the case of a heat pump) and bed 2 adsorbs gas from the evaporator, which provides cooling. In the following phase (second phase) of the cycle the pump is reversed, and hence, bed 1 is cooled (adsorbing) and bed 2 is heated (desorbing) in a similar fashion until the original conditions are reached and the pump can again be reversed. Though the procedure is simple, significant heat recovery can be achieved. Further, the system would achieve much better performance due to the combination of the special nature of the internal bed heat exchangers and the low flow rate.

Although many researchers have studied the cycle, up to now, there is no report of a successful prototype adopting thermal wave cycle. Also, some experimental reports had shown that the performance of the thermal wave cycle is not very good.
The efficiency of the thermal wave regenerative system depends on a relatively large number of parameters: for example, rates of various heat transfer processes, the flow rate of the circulating fluid, the cycle time, the adsorber configuration, etc. A numerical analysis of adsorptive heat pumps with thermal wave heat regeneration had been presented by Sun et al. [23]. They had derived two time constants, which can be used directly to quantify the relative importance of the two heat transfer processes. This allows ready determination of which of the two processes is rate limiting and needs to be improved. The work has also confirmed that the performance of an adsorptive heat pump system using a traditional packed-bed would be too low, even with heat regeneration, and therefore a significant enhancement of heat transfer properties inside the adsorber is necessary. Similar to the above numerical study, the effect of various operating parameters on the performance of an adsorptive thermal wave regenerative heat pump had been studied by Ben Amar et al. [24], theoretically.

They had developed a two-dimensional model which simultaneously considers heat and mass transfer in the bed. The results have shown that under ideal conditions, the performance of a thermal wave regenerative heat pump is considerably better than that of a basic 'uniform temperature' heat pump. The study showed that a COP greater than 1 and a power of cold production of near 200 W per kg of adsorbent could be obtained.

### 3.5 Convective thermal wave cycles

Thermal wave cycles normally suffer from low power density because of poor heat transfer through the adsorbent bed. Rather than attempting to heat the bed directly, it is possible to heat the refrigerant gas outside the bed and to circulate it through the bed in order to heat the sorbent. The high surface area of the grains leads to very effective heat transfer with only low levels of parasitic power needed for pumping. Hence, Critoph [25] has presented a modified version of a thermal wave cycle, known as 'convective thermal wave cycle'. The concept is the same as thermal wave cycle, however, the thermal fluid for heating and cooling to the beds is initiated by the refrigerant itself and thus the heat transfer between thermal fluid and adsorption bed is a direct contact heat transfer, which is incorporated with mass transfer in the system. A practical schematic of the proposed system is shown in Fig. 3.5. The two 'active' beds are packed with
activated carbon and the two 'inert' beds are packed with non-reactive particles such as steel balls. The diagram shows the first half of the cycle, during which Active bed 1 is heated and desorbs ammonia while Active bed 2 is cooled, adsorbing ammonia.

In the fluid circulation loop shown on the left, a low power pump circulates ammonia steam through inert bed 1 which is initially hot. The gas stream is heated by the bed and a 'cold wave passes through the bed from right to left. Having been preheated by the inert bed, the ammonia stream is heated to the maximum cycle temperature (150–200 °C) in a heat exchanger. The ammonia gas then passes to active bed 1 where it heats the carbon. A 'hot' thermal wave passes from left to right through the active bed. As the temperature of the active bed rises it desorbs ammonia which first increases the pressure in the left handloop and then condenses in the condenser, rejecting heat to the environment.

The mass flow rate of circulating ammonia is typically ten times that of the condensing stream of ammonia and it may take about ten minutes for the two thermal waves to travel the length of their respective beds. In similar fashion the circulating flow might be ten times the adsorption flow from the evaporator.
Fig. 3.5. Adsorption refrigeration system with convective thermal wave cycle

The advantages of this system are:

(i) The four packed beds are in effect heat exchangers of very high surface areas but at minimal cost. They are not only cheap but very compact.

(ii) There are only four conventional heat exchangers and this is the minimum number allowed by thermodynamics. These are the evaporator and condenser, a gas heater whereby high-grade heat is input and a gas cooler whereby the low grade heat of adsorption is rejected to the environment.

(iii) The cycle is highly regenerative since the packed beds act like large counter flow heat exchangers. This results in good energy efficiency (i.e. high COP).
3.6 Multi-stage and cascading cycles

The adsorption cycles discussed in previous sections are applicable only to a single stage cycle. The single stage cycle systems have certain limitations, that is, they cannot effectively utilize high temperature heat source, as well as do not perform well at very low temperatures. Hence, to improve the system performance under such situations, adsorptive processes may be adapted for advanced cycles, such as, multi-stage and cascading cycle. The basic idea of a multi-stage cycle is to perform the desorption-condensation processes and evaporation-adsorption processes at different temperature/pressure levels by using the 'same working pair'. The internal re-use of heat of condensation or adsorption can increase the system performance significantly. Another practical cycle that can make good use of high temperature heat source is the 'cascading cycle', which operates with different working pairs' (either liquid/liquid or solid/liquid), such as zeolite-water/activated carbon-methanol, or zeolite-water/silica gel-water, etc. These cascading cycles are applied to situations especially, when there exists a large temperature difference between the heat source/ambient and the temperature in the evaporator/refrigeration space. For such situations, it may not be practical to use single stage cycle. Hence, one way of dealing with such situations is to perform the evaporation/refrigeration process in stages, that is, to have two or more cycles that operate in series at different temperature levels (cascading). A high temperature heat source (e.g. boiler) is used to drive the high temperature stage adsorption refrigeration cycle. The low temperature stage adsorption refrigeration is driven by sensible heat and heat of adsorption obtained from high temperature stage. To minimize the contribution of sensible heat, special care has been attached to the heat management of the adsorbers.

n-adsorber cycles operating with a single evaporator and a single condenser have been proposed with sequences of heat recovery between adsorbers. Such cycles offer some advantages: for example, a single condenser is used and pressure in the n-adsorber unit is not higher than that in the unit operating an intermittent cycle; moreover, adsorption heat at high temperature is used as desorption heat at low temperature. Counteracting heat transfer fluid circuits between adsorbers reduces entropy generation in comparison with what happens in intermittent cycles. The driving heat supplied to the cycle is at high temperature level (Fig. 3.6) so that the entropy generation due to the inadaptation
between the temperature levels of the source and of the adsorber is much less in an n-adsorber cycle than in an intermittent cycle.

The same thing happens for the rejected heat: the rejection temperature is much closer from the utility temperature with an n-adsorber cycle than with an intermittent cycle.

Fig. 3.6. n-Adsorber cascading cycle

Very similar conclusions to that drawn by Scharfe et al. [26] have been presented by Meunier [27] in the case of heat recovery between adsorbers. In a particular case, Meunier has shown that using an infinite number of adsorbers with ideal heat recovery between adsorbers, the maximum achievable with given conditions of operating temperatures would be a cooling COP equal to 1.85 corresponding to 68% of ideal Carnot COP. Another cascading cycle which includes a triple effect machine operating a cascade between a water zeolite heat pump and a single stage LiBr-H₂O refrigerator has been tested.
3.7 Continuous adsorption systems

Continuous solar adsorption refrigeration systems are being reported widely because of their higher system performance over intermittent alternatives and for their timely coincidence with the requirement of the cooling and refrigeration demand. Continuous adsorption cycles depending on their technologies, can be grouped as:

(i) Multi-stage and cascading systems;

(ii) Thermal wave adsorption systems;

(iii) Convective thermal wave adsorption systems; and

(iv) Hybrid systems.

In general, thermal wave and convective thermal wave adsorption systems are also called as ‘heat regenerative systems’ owing to its heat recovery properties.

3.7.1 Multi-stage and cascading systems

A lot of theoretical studies exist on the possibilities of cascading cycles while very few experimental data are available. Douss and Meunier [28] had reported the experiments on a cascading adsorptive heat pump. The cycle comprised of a two-adsorber zeolite-water system at high temperature stage and an intermittent active carbon-methanol system at low temperature stage. Driving heat was supplied by a boiler to zeolite adsorbers while active carbon adsorber was heated by heat recovered from zeolite adsorber under adsorption. Evaporators from both basic cycles operated at the same temperature and contributed to the evaporating load. The cycle had adapted well to air conditioning as long as the evaporation temperature lift was less than 45 °C.

A similar study on combined cycle comprising of an adsorption-absorption cascading multi-effect refrigeration cycle was carried out by Shu et al. [29]. The system consists of a high temperature stage of solid adsorption unit working with zeolite water and a low temperature stage of double effect absorption unit working with LiBr-water. The working principle of this multi effect cascading cycle can be explained using Clapeyron diagram shown in Fig. 3.7.
Fig. 3.7. Adsorption-absorption (1) adsorption cycle; (2) High pressure absorption cycle and (3) low pressure absorption cycle. Cascading multi-effect refrigeration cycle:

The single stage cycle with heat source $Q_h$ represents the adsorption cycle using zeolite + water as working medium. The double stage cycle obtains the absorption heat of the single stage cycle as its driving heat ($Q_{ads}$) for its high temperature stage. The heat obtained from the condenser of the single stage cycle is used as the heat source for its low temperature stage. The study has shown that the COP of the cycle can be greatly improved by efficient utilization and recovery of energy within the system.

Also, they had reported that there exists no corrosive problem though the temperature of the working pair is higher than 200 °C in the adsorption unit. Saha et al. [30] has proposed a two-stage nonregenerative adsorption chiller design and experimental
prototype using silica gel-water as the adsorbent refrigerant pair. The main advantage of the two-stage adsorption chiller is its ability to utilize low temperature solar/waste heat (40-75 °C) as the driving heat source in combination with a coolant at 30°C. With a 55°C driving source in combination with a heat sink at 30°C, the COP of the two-stage chiller is 0.36. Wang [31] carried a study on a four-bed adsorption refrigeration system and the multi-stage system configuration is shown in Fig. 3.8

![Fig. 3.8. The system configuration of four-bed cascading adsorption refrigeration cycle](image)

The system consisted of four adsorbers (A1; A2; B1; B2); one condenser (C), and one evaporator (E). The working principle can be explained as follows according to the Clapeyron diagram as shown in Fig. 3.9:
To begin with, $A_1$ and $A_2$ are in the high temperature stage, for which generation (temperature about 200°C) is initiated by heat input. The desorbed water vapor will go through the adsorber $B_1$ or $B_2$ at the low temperature stage to release heat for desorption. The adsorption pressures of the two stages are the same because only one evaporator is used in the system. During phase 1, the desorption process in desorber $B_1$ is furnished by the heat from desorber $A_1$, and adsorber $A_2$ in the high temperature stage. The coordination of adsorption and desorption of the two stages is very important to operate the system properly. By the way, the desorption pressure in desorber $A_1$, must be higher than the desorption pressure of desorber $B_1$, in order to facilitate the vapor desorbed from $A_1$, to pass through desorber $B_1$, effectively. In this multi-stage system, water is the refrigerant and the desorbed vapor flows through the adsorbent bed in desorber $B_1$, to get a triple-effect installation. Here, a double effect is accomplished with sensible and adsorption heat recovery to generate low temperature stage in addition to the heat input to the high temperature stage, a triple effect is accomplished with the heat recovery of the desorbed vapor in the high temperature stage in addition.

The heat used in a double effect arrangement to generate low temperature stage. The maximum energy recovery from high temperature stage can be arranged by a triple effect system, in which the sensible heat of adsorbent bed, heat of adsorption and the latent heat of refrigerant vapor are fully used to drive the low temperature stage system. The simulation work has shown that, the performance of a cascading cycle interve of COP can be triple (COP = 1.56), compared to two independent stage system (COP = 1.0).
0.6). This concept could be used for multi-effect adsorption systems, as well as extended to adsorption-absorption cascading systems [31].

### 3.7.2 Thermal wave adsorption systems

Thermal wave adsorption is the most commonly attempted technology. In a two-bed adsorption system shown in Fig. 4, substantial part of heat from the adsorbent bed is rejected at a temperature greater than the temperature of the bed being heated. Therefore, it was soon recognized that part of this rejected heat could be used for heating the desorbing bed, thus providing gains in efficiency. Fuller et al. [32] design models for this technique, by means of a single heat transfer fluid loop passing through adsorbent beds, a fluid cooler, a fluid heater and a reversible circulation pump. For a two-bed system, high temperature thermal fluid flows into the adsorber, exchanges heat with the bed, and the temperature goes down along the bed rapidly, thus the outlet temperature will be close to ambient. After being cooled by ambient surroundings, the fluid flows into another adsorption bed, absorbs heat from the bed, and the temperature of the fluid goes up. At the exit of this bed, the thermal fluid temperature will be very close to the temperature of heat source. In this case, only less heat is added to the system, and less heat released to the environment. Thus, heat recovery ratio is high and the COP is increased significantly.

Analytical models of square and ramp waveforms predicted that heating COP of up to 1.6 is possible. In a similar effort, Zheng et al. [33], using a charcoal-ammonia pair, found that system performance improves significantly with a reduction of ambient temperature, and is also affected by cycling speed and regeneration temperature.

Wang et al. [34] had developed two heat regenerative adsorption systems, with two different types of heat exchangers:

(i) heat regenerative adsorption refrigerator with a spiral plate heat exchangers adsorbers;

(ii) plate fin heat exchangers or plate fin shell heat exchangers adsorbers.

The activated carbon-methanol adsorption pair was used for the above two adsorption systems. The two adsorbers were independently operated for heating and cooling, along with the intermediate heat recovery process. Fig. 3.4 shows the schematic of the unit. A
receiver was installed for easy observation of refrigerant flow in the system. An ice box was used which was cooled by a salt water cooling heat exchanger. With a heat source temperature of 100°C, the refrigerator achieved a refrigeration power density of more than 2.6 kg per day of ice per kg of activated carbon with a COP of 0.13, and the heat pump achieved 150 W kg\(^{-1}\) activated carbon for air conditioning with a COP of about 0.4.

3.7.3 Convective thermal wave adsorption systems

Critoph et al. [25] suggested the use of a forced convection effect by direct use of refrigerant vapors. During desorption, the refrigerant is heated externally and passes through the adsorber bed, where it heats the adsorbent rapidly because of good heat transfer coefficient and the large surface area of the adsorbent bed. The desorbed vapor is condensed in a condenser in the usual way. During the adsorption process, the flow is reversed and heat of adsorption is removed by the refrigerant, which is cooled externally. This technique enhances performance by virtue of the combined effects of forced convection and thermal wave. Flow of hot gas through the adsorbent gives rise to a thermal wave traveling through the bed during desorption, and vice versa during adsorption process. Based on this theory, a new continuous adsorption refrigeration/heat pump system using a number of simple tubular adsorption modules was developed. Each single module comprised of a generator and a receiver/condenser/evaporator. A complete module was tested in a simple rig, which was subjected to alternating hot and cold air streams, desorbing and adsorbing ammonia.

The performance of a temperature wave regenerative heat pump has been analyzed using a two-dimensional model by Ben Amar et al. [24]. The model simultaneously considers heat and mass transfers in the adsorbent bed. The mathematical model has been solved numerically by use of the ADI finite different method. The consideration of both heat and mass transfer in the model has made it possible to determine the impact of the convective transport of the gaseous adsorbate in the adsorber on the global performance, in addition to that of the heat transfer. It has been shown that with a traditional packed bed, which generally has a low thermal conductivity (0.2 W m\(^{-1}\)k\(^{-1}\)), the performance of the resulting heat pump is very poor. In contrast, with a consolidated adsorbent material, which can have a much improved thermal conductivity but relatively poor mass transfer properties, the heat pump performance could be poor as
well, due to the large mass transfer resistances encountered by low pressure adsorbates like water. A proper design of the adsorber should therefore ensure good properties for both heat and mass transfer, in particular when the adsorbate used has low working pressures.

### 3.8 Conclusion

The development of adsorption system for refrigeration is promising. An overall thermodynamics-based comparison of sorption systems shows that the performance of adsorption systems depend highly on both the adsorption pairs and processes. Of the several kinds of adsorption systems analyzed in this chapter, the intermittent system has been extensively studied both theoretically and experimentally, Owing to its simplicity and cost effectiveness. However, the main disadvantages such as long adsorption/desorption time have become obstacles for commercial production of the system. Hence, to compete with conventional absorption and vapor-compression technologies, more efforts should be made in enhancing the COP and SCP). Heat recovery, mass recovery, multi-bed and multi-stage technologies are promising technologies in improving the COP and SCP. Adsorption technology combined with other technologies for multi-purpose application seems to be a new trend in the research. This will widen the area of applications of adsorption technologies and make the adsorption refrigeration more cost effective. Any method that improves the efficiency even marginally would improve the economic viability of operating such devices. Thus, further studies need to be carried out to validate the potential for possible application in household refrigerators.
CHAPTER FOUR

Multi-stage adsorption chiller using silica gel/water as adsorbent-adsorbate pair

Introduction

With the increasing awareness of global warming and ozone depletion problems, adsorption refrigeration and heat pump systems have received much attention by researchers in many parts of the world; in particular, the low-temperature waste heat sources for cooling energy production. The use of waste heat at near environment temperature is an important contemporary problem. Heat driven sorption (absorption or adsorption) cycle is one of the promising candidates to utilize waste heat at near environment temperature. Though the absorption cycles are predominant in the area of heat driven refrigeration cycles, adsorption cycle has a distinct advantage over absorption systems in their ability to be driven by relatively low-temperature heat source, which cannot effectively regenerate the absorption systems (1). In the last three decades, extensive investigations on the performances of adsorption refrigeration/heat pump systems have been conducted considering various adsorbent/refrigerant pairs, such as zeolite/water [2], activated carbon/ammonia [3], activated carbon/methanol [4] and silica gel/water [5].

It is well known that the performance of adsorption cooling/heating system is lower than that of other heat driven heating/cooling systems specially, absorption system provided that the available heat source temperature is at 75°C or higher. From this context, many authors proposed and/or investigated the adsorption cooling and heating system to improve the performance. To improve the coefficient of performance, Shelton et al. [35] studied thermal wave regenerative adsorption heat pump using zeolite/
ammonia pair. Meunier [36] analyzed the system performance of cascading adsorption cycles in which an active carbon/methanol cycle is used, which is topped by a zeolite/water cycle. Pons and Poyelle [37] studied the influence of mass recovery process in conventional two beds adsorption cycle to improve the cooling power. In a similar effort, Wang [38] investigated the performance of vapor recovery cycle with activated carbon/methanol as adsorbent/adsorbate pair and indicated that mass recovery cycle is effective for low regenerative temperature. Akahira et al. [39] investigated two-bed mass recovery cycle with novel strategy, which shows that mass recovery cycle with heating/cooling improves the cooling power.

Being low-temperature waste heat driven, the COP of such systems is low, which is classified by Ng [40] in an editorial report. Therefore, there is a need to explore various thermal utilization schemes. To utilize low-temperature waste heat source between 40 and 60°C, Saha et al. [41] proposed and examined experimentally a three-stage adsorption chiller with silica gel/water pair. It is shown that the three-stage chiller can be operated with a driving heat source of temperature 50°C in combination with a coolant 30 °C. Saha et al. [42] also introduced a two-stage adsorption chiller and the required driving heat source temperature is validated experimentally. In the two-stage chiller, it is possible to get effective cooling with driving heat source temperature below 60°C. Alam et al. [43] proposed and analyzed a re-heat two-stage adsorption chiller, which can be operated with driving heat source temperatures between 50 and 90°C along with a coolant at 30°C. The COP of the re-heat two-stage chiller is higher than that of two-stage chiller without reheat. Moreover, the re-heat two-stage chiller produces effective cooling even though heat source temperatures are varied between 50 and 90°C. Recently, Khan et al. [44] studied on a re-heat two-stage adsorption chiller with silica gel/water as adsorbent/adsorbate pair. In the present study, the chiller investigated the effect of heat source temperature along with different flow rate on cooling capacity (CC), co-efficient of performance (COP), chilled water outlet.

4.1 Working principles

4.1.1 Single stage chiller

A single-stage adsorption chiller consists of four heat exchangers, namely, a condenser, an evaporator and one pair adsorbent bed and metallic tubes for heat transfer fluid and refrigerant flows as shown in Fig. 4.1. In an adsorption refrigeration system, adsorbent
beds are operated in a cycle through the four thermodynamic states, namely, pre-heating, desorption, pre-cooling and adsorption period. The chiller can be operated in different strategies. Only one strategy has been described in the present study; The chiller has four modes, A, B, C, D (Table 4.1). To describe the cycle of the system mode-A, it is assumed that Hex-1 is in cooling position at temperature To while Hex-2 is in heating position at temperature Th. At the beginning of the cycle all valves are closed. The desorber Hex-2 heated by hot water while adsorber Hex-1 cooled by cooling water.

During a short intermediate process (30s for this system) no adsorption/desorption occurs. After this short period, valves V2 and V3 are opened to allow refrigerant to flow from Hex-2 to condenser, from evaporator to Hex-1.

![Fig. 4.1 Schematic of Single-stage chiller (Mode-A)](image)

When refrigerant concentrations in the adsorbers and desorbers are at near their equilibrium level, the flows of hot and cooling water are redirected by switching the valves so that the desorber can change its mode into adsorber and adsorber into desorber. The adsorption/desorption process can be continued by changing the direction
of hot and cooling water flow. The standard operational strategy of a single stage chiller is shown in Table 4.1
Fig. 4.1 Schematic of Single-stage chiller (Mode-B)

Fig. 4.1 Schematic of Single-stage chiller (Mode-C)
Fig. 4.1 Schematic of Single-stage chiller (Mode-D)
Fig. 4.2: Conceptual P-T-X diagram for a single-stage chiller

Table 4.1: Operational strategies of a single-stage adsorption chiller
4.1.2 Two-stage adsorbent chiller

Before going to describe working principle of a two-stage chiller employing re-heat scheme it is better to know about basic of two-stage chiller without re-heat and its operational strategy. A conventional silica gel-water adsorption cycle cannot be operational with the driving heat source temperature 50°C, if the heat sink is at 30°C or more. For practical utilization of these temperatures (between 50 and 75°C) to adsorption chiller operation, an advanced two-stage adsorption cycle can be introduced. As can be seen from Fig.4.3 the cycle allows reducing regeneration temperature (pressure) lift of the adsorbent (Tdes-Tads) by dividing the evaporating temperature (pressure) lift (Tcond - Teva) into two smaller lifts. Thus refrigerants (water- vapor) pressure rises into two consecutive steps from evaporation to condensation level; to achieve this objective, an additional pair of adsorber/desorber heat exchangers is necessary to include to the conventional two bed adsorption chiller. An advanced two-stage adsorption chiller consists of six heat exchangers, namely, a condenser, an evaporator and two pairs adsorbent bed heat exchangers as shown in Fig. 4.3. In an adsorption refrigeration system, adsorbent beds are operated in a cycle through the four thermodynamic states, namely, pre-heating, desorption, pre-cooling and adsorption period. To describe the cycle of the system, it is assumed that Hex-1 and Hex-4 are in cooling position at temperature Tc while Hex-2 and Hex-3 are in heating position at temperature Th. At the beginning of the cycle all valves are closed. The desorbers (Hex-1 and Hex-4) are heated by hot water while adsorbers (Hex-2 and Hex-3) are cooled by cooling water. During a short intermediate process (30s for this system) no adsorption/desorption occurs. After this short period, valves 2, 4 and 6 are opened to allow refrigerant to flow from Hex-) to condenser, from evaporator to Hex2. and from Hex-4 to Hex-3.

When refrigerant concentrations in the adsorbers and desorbers are at near their equilibrium level, the flows of hot and cooling water are redirected by switching the valves so that the desorber can change its mode into adsorber and adsorber into desorber. The adsorption/adsorption process can be continued by changing the direction of hot and cooling water flow. The standard operational strategy of two stages without re-heat is shown in Table-4.2
Fig. 4.3 Schematic of two-stage chiller (Mode-A)

Fig. 4.3 Schematic of two-stage chiller (Mode-B)
Fig. 4.3 Schematic of two-stage chiller (Mode-C)

Fig. 4.3 Schematic of two-stage chiller (Mode-D)
Fig. 4.4: Conceptual P-T-X diagram for a two-stage chiller

Table 4.2: Operational strategies of a two-stage adsorption chiller
4.1.3 Two-stage chiller with re-heat scheme

The design criteria of the two-stage adsorption chiller using re-heat is almost similar to that of a two-stage adsorption chiller without re-heat, which is developed by Alam et al. [43]. Operational strategy of the chiller (Table 4.3), however, is completely different from the operational strategy of a conventional two-stage chiller (Table 4.2). In two-stage adsorption chiller, the evaporating pressure lift is divided into two consecutive pressure lifts to exploit low heat source temperature by introducing four adsorbent beds. In the two stage adsorption chiller using re-heat, the evaporating pressure (temperature) lift (Fig.4.6), however, can be divided into different ways from the conventional two-stage chiller (Fig.4.4). If one bed is in the end position of adsorption-evaporation process (Fig. 4.6) and another bed is in the end position of desorption-condensation process (Fig. 4.6), those two beds can be connected with each other by continuing cooling and heating and that can be done in the two bed conventional adsorption chiller which is known as the mass recovery process presented by Akahira et al. [39]. In this time, another two beds are connected with condenser and evaporator to continue cooling effects. To complete one full cycle in reheat scheme, all adsorbent beds pass through six consecutive steps: (i) desorption (ii) mass recovery process with heating (iii) pre-cooling (iv) adsorption (v) mass recovery process with cooling, and (vi) pre-heating. The two-stage adsorption chiller using re-heat comprises with four adsorbent beds, one condenser, one evaporator, and metallic tubes for hot, cooling and chilled water flows as shown in Fig. 4.5 .In a conventional two-stage chiller, lower two beds never interact with the condenser and upper two beds never interact with the evaporator. However, in the two-stage adsorption chiller using re-heat, all beds undergo through all processes and interact with the condenser and evaporator. The chiller can be operated in different strategies. However, only one strategy has been considered in the present study. The chiller has 10 modes, mode A, B, C, D, E, F, G, H, I, and J (Table 4.3)
Fig. 4.5 Schematic of a re-heat two-stage chiller (Mode-A)
Fig. 4.5 Schematic of a re-heat two-stage chiller (Mode-B)
Fig. 4.5 Schematic of a re-heat two-stage chiller (Mode-C)
Fig. 4.5 Schematic of a re-heat two-stage chiller (Mode-D)
Fig. 4.5 Schematic of a re-heat two-stage chiller (Mode-E)
Fig. 4.5 Schematic of a re-heat two-stage chiller (Mode-F)
Fig. 4.5 Schematic of a re-heat two-stage chiller (Mode-G)
Fig. 4.5 Schematic of a re-heat two-stage chiller (Mode-H)
Fig. 4.5 Schematic of a re-heat two-stage chiller (Mode-I)
Fig. 4.5 Schematic of a re-heat two-stage chiller (Mode-J)
Table 4.3. mode A, B, and C, eva-Hex-2 is in adsorption process and cond-Hex-1 is in desorption process. In the desorption-evaporation process, refrigerant (water) in evaporator is evaporated at evaporation temperature, $T_{\text{eva}}$, and seized heat, $Q_{\text{eva}}$ from the chilled water. The evaporated vapor is adsorbed by adsorbent (silica gel), at which cooling water removes the adsorption heat, $Q_{\text{ads}}$. The desorption-condensation process takes place at pressure ($P_{\text{cond}}$). The desorber (Hex-1) is heated up to the temperature ($T_{\text{des}}$) by heat $Q_{\text{des}}$, provided by the driving heat source. The resulting refrigerant is cooled down by temperature ($T_{\text{cond}}$) in the condenser by the cooling water, which removes heat, $Q_{\text{cond}}$. In mode A, adsorber (Hex-4) is connected with desorber (Hex-3) through pipe with continuing cooling water in Hex-4 and hot water in Hex-3. It is noted that, at the beginning of mode A, Hex-4 was in the end position of evaporation-adsorption process and Hex-3 was in the end position of desorption-condensation process. Due to higher pressure difference at Hex-3 and Hex-4 in mode A, the refrigerant mass circulation will be higher than that of conventional two stages. This will lead the chiller to provide better performance. In mode B, adsorber (Hex-4) is heated up by hot water, and the desorber (Hex-3) is cooled down by cooling. Mode B is warm up process for Hex-4 and Hex-3.

![Fig. 4.6: Conceptual P-T-X diagram for a re-heat two-stage chiller](image)
When the pressure of adsorber (Hex-3) and desorber (Hex-4) are nearly equal to the pressure of evaporator and condenser respectively, then Hex-3 and Hex-4 are connected to evaporator and condenser respectively to flow the refrigerant. This mode is denoted as mode C. In mode C, Hex-4 works as desorber and Hex-3 works as adsorber and this process will continue up to mode E. In mode D, Hex-2 (at the end position of adsorption-evaporation process) and Hex-1 (at the end position of desorption-condensation process) are connected with each other continuing cooling water and hot water respectively.

<table>
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<tr>
<th>Mode</th>
<th>A</th>
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<th>C</th>
<th>D</th>
<th>E</th>
<th>F</th>
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<td>Hex 4</td>
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</table>

![Diagram of operational strategy]

Table. 4.3 Operational strategy of there-heat two-stage chiller

When the pressure (temperature) of both Hex-1 and Hex-2 nearly equal, then warm up process will start, called mode E. In mode E, Hex-2 is heated up by hot water, and cooling water-cools down the Hex-1. When the pressure of Hex-1 and Hex-2 are nearly equal to the pressure of evaporator and condenser respectively, then Hex-1 and Hex-2 are connected to evaporator and condenser respectively to flow the refrigerant. This connection will continue up to mode F, G, and H for Hex-1 and Hex-2. In mode F, Hex-3 (at the end position of adsorption-evaporation process) and Hex-4 (at the end position of desorption-condensation process) are connected with each other continuing cooling water and hot water respectively.
When the pressure (temperature) of both Hex-3 and Hex-4 are nearly equal, then warm up process will start, called mode G. In mode G, Hex-3 is heated up by hot water, and cooling water-cools down the Hex-4. When the pressure of Hex4 and Hex3 are nearly equal to the pressure of evaporator and condenser respectively, then Hex4 and Hex3 are connected to evaporator and condenser respectively to flow the refrigerant. This connection will continue up to mode H, J, and I for Hex3 and Hex4. In mode I, Hex1 (at the end position of adsorption-evaporation process) and Hex-2 (at the end position of desorption-condensation process) are connected with each other continuing cooling water and hot water respectively. When the pressure (temperature) of both Hex-1 and Hex-2 are nearly equal, then warm up process will start, called mode J. In mode J, Hex-1 is heated up by hot water, and cooling cools down the Hex-2. The mode J is the last process and after this mode, all return to mode A (Table 1). The values adapted in simulation are presented in Table 3.3 and Table 3.4.

4.2 Formulation of the problem

4.2.1 Energy balance for the adsorber/desorber

Adsorption and desorption heat balances are described by identical equations, where heat transfer fluid (water) temperature term $T_{in}$ and $T_{out}$ denotes cooling water upon adsorption and hot water upon desorption. $T$ denotes bed temperature. The adsorbent bed temperature, pressure and concentration are assumed to be uniform throughout the adsorbent bed. We have taken the specific of refrigerant (water) in liquid phase as our system works in low the concentration range. The heat transfer and energy balance equations for the adsorbent bed can be described as follows:

$$T_{out} = T + (T_{in} - T) \exp \left(- \frac{u_{hex} A_{hex}}{m_w C_w} \right)$$  
\hspace{1cm} (4.1)

$$\frac{d}{dt} \{(W_s C_s + W_g C_w q + W_{hex} C_{hex})T\} = W_s Q_{st} \frac{da}{dt}$$  
$$-\delta W_s C_w \{y(T - T_{eva}) + (1-y)(T - T_{wv})\} \times \frac{da}{dt} + m_w C_w (T_{in} - T_{out})$$  \hspace{1cm} (4.2)

where, 8 is either 0 or 1 depending whether the adsorbent bed is working as desorber or adsorber and y is either 1 or 0 depending on whether the bed is connected with evaporator or another bed.
Equation (4.1) expresses the importance of heat transfer parameters, namely heat transfer area $A_{\text{hex}}$ and heat transfer coefficient $U_{\text{hex}}$. The left hand side of the adsorber/desorber energy balance equations (Eq.4.2) provides the amount of sensible heat required to cool or heat the silica-gel ($s$), the water ($w$) as well as metallic ($\text{hex}$) parts of the heat exchanger during adsorption or desorption. This term accounts for the input/output of sensible heat required by the batched-cycle operation. The first term on the right hand side of Eq. (4.2) represents the release of adsorption heat or the input of desorption heat, while the second and third terms for the sensible heat of the adsorbed vapor. The last term on the right hand side of Eq. (4.2) indicates the total amount of heat released to the cooling water upon adsorption or provided by the hot water for desorption. Equation (4.2) does not account for external heat losses to the environment as all the beds are considered to be well insulated. Also Eq. (4.2) does not account the thermal mass effect of reactor vessel because for a relatively longer cycle time operation like the present case the thermal mass effect of reactor vessel will be lesser in comparison to that of a short cycle time.

### 4.2.2 Energy balance for the evaporator

In the present analysis, it is assumed that the tube bank surface is able to hold a certain maximum amount of condensate and the condensate would flow into the evaporator easily. The heat transfer and energy balance equations for evaporator can be expressed

$$T_{\text{eva, out}} = T_{\text{eva}} + (T_{\text{chill,in}} - T_{\text{eva}}) \exp \left( - \frac{U_{\text{eva}} A_{\text{eva}}}{m_{\text{chill}} C_{\text{chill}}} \right)$$

(4.3)

$$\frac{d}{dt} \left\{ (W_{\text{eva,w}} C_w + W_{\text{eva,hex}} C_{\text{eva,hex}}) T_{\text{eva}} \right\} = -L W_s \frac{dq_{ads}}{dt}$$

$$-W_s C_w (T_{\text{cond}} - T_{\text{eva}}) \frac{dq_{ads}}{dt} + m_{\text{chill}} C_{\text{chill}} (T_{\text{chill,in}} - T_{\text{chill, out}})$$

(4.4)

Where the suffixes chill and eva indicate chilled water and evaporator respectively. The left hand side of Eq. (4.4) represents the sensible heat required by the liquid refrigerant ($w$) and the metal of heat exchanger tubes in the evaporator. On the right hand side, the first term gives the latent heat of evaporation ($L$) for the amount of refrigerant adsorbed ($dq_{ads}/dt$), the second term shows the sensible heat required to cool down the incoming
condensate from the condensation temperature $T_{\text{cond}}$ to vaporation temperature $T_{\text{eva}}$, and the last term represents the total amount of heat given away by the chilled water.

### 4.2.3 Energy balance for the condenser

The heat transfer and energy balance equations for condenser can be expressed as:

$$
T_{\text{cond,out}} = T_{\text{cond}} + (T_{\text{cw,in}} - T_{\text{cond}}) \exp \left( - \frac{U_{\text{cond}} A_{\text{cond}}}{m_{\text{cw}} c_{\text{w}}} \right)
$$

(4.5)

$$
\frac{d}{dt} \left\{ \left( W_{\text{cw},W} C_{\text{w}} + W_{\text{cond,hex}} C_{\text{cond,hex}} \right) T_{\text{cond}} \right\} = -L W_s \frac{dq_{\text{des}}}{dt}
- W_s C_w (T_{\text{des}} - T_{\text{cond}}) \frac{dq_{\text{des}}}{dt} + \dot{m}_{\text{cw}} C_{\text{w}} (T_{\text{cw,in}} - T_{\text{cw,out}})
$$

(4.6)

### 4.2.4 Mass balance

Mass and heat balances are based on the assumption that both the temperature and the amount of refrigerant adsorbed are uniform in the adsorbent beds. Since the temperatures in an adsorption cycle are unsteady state, the energy balance equations (Eqs. 4.2, 4.4, 4.6) must account for sensible heat input and/or output during cycle period. The mass balance for the refrigerant can be expressed by neglecting the gas phase as:

$$
\frac{dW_{\text{eva},W}}{dt} = -W_s \left( \frac{dq_{\text{des-cond}}}{dt} + \frac{dq_{\text{eva-ads}}}{dt} \right)
$$

(4.7)

### 4.2.5 Adsorption rate

The adsorption rate is expressed as

$$
\frac{dq}{dt} = k_s a_p (q^* - q)
$$

(4.8)

where, the overall mass transfer coefficient $(k, qp)$ for adsorption is given by:
\[ k_s a_p = \left( 15D_s \right) / \left( R_p \right)^2 \]  

(4.9)

The adsorption rate is considered to be controlled by surface diffusion inside a gel particle and surface diffusivity \( D_s \) is expressed by Sakoda and Suzuki as a function of temperature by:

\[ D_s = D_{so} \exp \left[ - (E_a) / (RT) \right] \]  

(3.10)

and \( q^* \) is the amount adsorbed in equilibrium with pressure \( P_s(T_w) \) and is derived from the manufacturer property data by the following equation

\[ q^* = \frac{0.06 [P_s(T_w) / P_s(T_s)]}{1 + 0.05 \left[ P_s(T_w) / P_s(T_s) \right]} \]  

(4.11)

where \( P_s(T_w) \) and \( P_s(T_s) \) are the saturation vapor pressure at temperatures \( T_w \) (water vapor) and \( T_s \) (silica gel), respectively. The saturation vapor pressure and temperature are correlated by Antoine's equation, which can be written as:

\[ P_s = 13332 e^{18 - \frac{3.820}{T-46}} \]  

(4.12)
Table 4.4: Baseline parameters

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Value</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_{\text{cond}}$</td>
<td>2.0</td>
<td>m²</td>
</tr>
<tr>
<td>$A_{\text{eva}}$</td>
<td>6.0</td>
<td>m²</td>
</tr>
<tr>
<td>$A_{\text{hex}}$</td>
<td>$0.061 \text{m}^2 \text{kg}^{-1} \times W_s (\text{kg})$</td>
<td>m²</td>
</tr>
<tr>
<td>$C_{\text{chill}}$</td>
<td>$4.20 \times 10^3$</td>
<td>Jkg⁻¹K⁻¹</td>
</tr>
<tr>
<td>$C_s$</td>
<td>924</td>
<td>Jkg⁻¹K⁻¹</td>
</tr>
<tr>
<td>$C_w$</td>
<td>$4.18 \times 10^3$</td>
<td>Jkg⁻¹</td>
</tr>
<tr>
<td>$D_{\text{so}}$</td>
<td>$2.54 \times 10^{-4}$</td>
<td>m²s⁻¹</td>
</tr>
<tr>
<td>$E_a$</td>
<td>$2.33 \times 10^3$</td>
<td>Jkg⁻¹</td>
</tr>
<tr>
<td>$L$</td>
<td>$2.50 \times 10^6$</td>
<td>Jkg⁻¹</td>
</tr>
<tr>
<td>$Q_{st}$</td>
<td>$2.80 \times 10^6$</td>
<td>Jkg⁻¹</td>
</tr>
<tr>
<td>$R$</td>
<td>$4.62 \times 10^2$</td>
<td>Jkg⁻¹K⁻¹</td>
</tr>
<tr>
<td>$R_p$</td>
<td>$0.30 \times 10^{-3}$</td>
<td>m</td>
</tr>
<tr>
<td>$U_{\text{ads}}$</td>
<td>1000</td>
<td>Wm⁻²K⁻¹</td>
</tr>
<tr>
<td>$U_{\text{cond}}$</td>
<td>3900</td>
<td>Wm⁻²K⁻¹</td>
</tr>
<tr>
<td>$U_{\text{des}}$</td>
<td>750</td>
<td>Wm⁻²K⁻¹</td>
</tr>
<tr>
<td>$U_{\text{eva}}$</td>
<td>5800</td>
<td>Wm⁻²K⁻¹</td>
</tr>
<tr>
<td>$W_{\text{cw}}$</td>
<td>5</td>
<td>kg</td>
</tr>
<tr>
<td>$W_{\text{eva},w}$</td>
<td>25</td>
<td>kg</td>
</tr>
<tr>
<td>$W_s$</td>
<td>16</td>
<td>kg</td>
</tr>
</tbody>
</table>
4.2.6 Measurement of system performance

The performance of a two-stage adsorption chiller using re-heat is mainly characterized by cooling capacity (CC), coefficient of performance (COP) and can be measured by the following equations:

\[
\text{Cooling Capacity (CC)} = \frac{m_c w \int_0^{t_{cycle}} (T_{chil.in} - T_{chil.out}) \, dt}{t_{cycle}}
\]

(4.13)

Here \( W_{s, \text{chiller}} \) stands for the total mass of silica gel in the two-stage chiller.

\[
\text{Coefficient of Performance (COP)} = \frac{m_{chil} c_w \int_0^{t_{cycle}} (T_{chil.in} - T_{chil.out}) \, dt}{m_{hot} c_w \int_0^{t_{cycle}} (T_{hot.in} - T_{hot.out}) \, dt}
\]

(4.14)

**Table 4.5 Standard operating conditions**

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Flow rate (kg/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hot water</td>
<td>60</td>
</tr>
<tr>
<td>Cooling water</td>
<td>30</td>
</tr>
<tr>
<td>Chilled water</td>
<td>14</td>
</tr>
<tr>
<td>Cycle Time</td>
<td>1300s (=480 for ads/des + 140 for mr + 30 for ph/pc) s×2</td>
</tr>
</tbody>
</table>

ads/des = adsorption/desorption, mr = mass recovery, ph/pc = pre-heat/pre-cool
Elaborate calculations for heat transfer equation (2.2.1) and energy balance equation (2.2.2) for desorber:

For heat transfer equation:

We know the heat transfer equation, \( Q_{\text{water}} = n \dot{m} (T_{wi} - T_{wo}) \)

Again, we know from thermodynamics, Logarithms Mean Temperature difference,

\[
LMTD = \frac{(T_{wo} - T_{ad}) - (T_{wi} - T_{ad})}{\ln \left( \frac{T_{wo} - T_{ad}}{T_{wi} - T_{ad}} \right)}
\]

The heat equation for water is

\[
Q_{\text{water}} = LMTD \times UA
\]

or, \( n \dot{m} (T_{wi} - T_{wo}) = \frac{(T_{wo} - T_{ad}) - (T_{wi} - T_{ad})}{\ln \left( \frac{T_{wo} - T_{ad}}{T_{wi} - T_{ad}} \right)} \times UA \)

or, \( n \dot{m} = \frac{UA}{\ln \left( \frac{T_{wo} - T_{ad}}{T_{wi} - T_{ad}} \right)} \)

or, \( \frac{\dot{m} c_p}{UA} = \frac{1}{\ln \left( \frac{T_{wo} - T_{ad}}{T_{wi} - T_{ad}} \right)} \)

or, \( \frac{UA}{m c_p} = \ln \left( \frac{T_{wo} - T_{ad}}{T_{wi} - T_{ad}} \right) \)

or, \( \exp \left( -\frac{UA}{m c_p} \right) = \frac{T_{wo} - T_{ad}}{T_{wi} - T_{ad}} \)

or, \( (T_{wo} - T_{ad}) = (T_{wi} - T_{ad}) \times \exp \left( -\frac{UA}{m c_p} \right) \)

or, \( T_{wo} = T_{ad} + (T_{wi} - T_{ad}) \times \exp \left( -\frac{UA}{m c_p} \right) \)
For energy balance equation:
\[
\frac{d}{dt} \left\{ (W_c C_s + W_C C_w q_{des} + W_{des} C_{des}) T_{des} \right\} = W_s Q_s \frac{d q_{des}}{dt} + \dot{m}_w C_w (T_{in} - T_{out})
\]
or,
\[
(W_c C_s + W_C C_w q_{des} + W_{des} C_{des}) \frac{d T_{des}}{dt} + W_s C_w \frac{d q_{des}}{dt} T_{des} = W_s Q_s \frac{d q_{des}}{dt}
\]
\[+ \dot{m}_w C_w \left\{ T_{in} - T_{des} - (T_{in} - T_{des}) \exp \left( - \frac{U A}{\dot{m}_w C_w} \right) \right\}
\]
\[(4.15)\]

Let, \( W_c C_s + W_C C_w q_{des} + W_{des} C_{des} = \gamma \)

The Eq. (3.15) becomes,
\[
\gamma \frac{T_i - T_{i-1}}{\Delta t} + W_s C_w \frac{q_{i-1} - q_{i}}{\Delta t} T_i = W_s Q_s \frac{q_{i} - q_{i-1}}{\Delta t}
\]
\[+ \dot{m}_w C_w \left\{ T_{in} - T_{des} - (T_{in} - T_{des}) \exp \left( - \frac{U A}{\dot{m}_w C_w} \right) \right\}
\]
\[(4.16)\]

Let, \( NTU = \frac{U A}{\dot{m}_w C_w} \)

The Eq. (3.16) becomes,
\[
\gamma \frac{T_i - T_{i-1}}{\Delta t} + W_s C_w \frac{q_{i-1} - q_{i}}{\Delta t} T_i = W_s Q_s \frac{q_{i} - q_{i-1}}{\Delta t}
\]
\[+ \dot{m}_w C_w \left\{ T_{in} - T_{des} \right\} \left\{ 1 - \exp \left( -NTU \right) \right\}
\]
or,
\[
\gamma \frac{T_i - T_{i-1}}{\Delta t} + W_s C_w \frac{q_{i-1} - q_{i}}{\Delta t} T_i = W_s Q_s \frac{q_{i} - q_{i-1}}{\Delta t}
\]
\[+ \dot{m}_w C_w \left\{ T_{in} - T_{des} \right\} \left\{ 1 - \exp \left( -NTU \right) \right\}
\]
\[(4.17)\]

Let, \( EXPN = 1 - \exp \left( -NTU \right) \)

The Eq. (3.17) becomes,
\[
T_i \left\{ \gamma + \dot{W}_C C_w (q_i - q_{i-1}) + \Delta t \dot{m}_w C_w EXPN \right\}
\]
\[= \gamma T_{i-1} + \dot{W}_S Q_s (q_i - q_{i-1}) + \Delta t \dot{m}_w C_w T_{in} EXPN
\]
Again let, \( EXPND = \dot{m}_w C_w EXPN \)

Then Eq. (5.17) takes the form,
\[
T_i \left\{ \gamma + \dot{W}_C C_w (q_i - q_{i-1}) + \Delta EXPND \right\}
\]
\[= \gamma T_{i-1} + \dot{W}_S Q_s (q_i - q_{i-1}) + \Delta T_{in} EXPND
\]
\[(4.18)\]
which implies,

\[ T_i = \frac{\gamma T_{i-1} + W_s Q_{st} (q_i - q_{i-1}) + \Delta t \text{in}_{\text{EXPND}}}{\gamma + W_s C_w (q_i - q_{i-1}) + \Delta t \text{EXPND}} \]
4.3 Results and discussion

The effect of hot water on Cooling Capacity (CC) and Coefficient of Performance (COP) were shown in the figure 4.7(a) and 4.7(b). It should be noted that the total amount of silica gel mass are same in the four beds. In this investigation effect of different mass flow rate are considered for the improvement of Cooling Capacity (CC) and Coefficient of Performance (COP) along with the different cycle time. It is observed that the different mass flow rates plays significant role in improving Cooling Capacity (CC) and Coefficient of Performance (COP). In this analysis chilled water outlet temperature is also considered by controlling the mass flow rate.

4.3.1. Effect of heat source temperature on Cooling Capacity (CC) and Coefficient of Performance (COP)

Figure 4.7(a) and 4.7(b) show the Cooling Capacity (CC) and Coefficient of Performance (COP) both are improved with the increased heat source temperature between 60°C to 80°C with cooling water inlet 30°C. This is because the amount of refrigerant circulated increases due to increased refrigerant desorption with higher driving source temperature. Moreover the mass recovery process generates more desorption heat and that is transferred from the desorber through desorbed vapor, so the chiller gives the better performance. The optimum CC and COP values are 6.68 and 0.46 respectively.

![Figure: 4.7(a). Effect of heat source temperature on cooling capacity (CC)](image-url)
Figure 4.7(b). Effect of heat source temperature on coefficient of performance (COP)
4.3.2. Effect of chilled water mass flow rate on Cooling Capacity (CC) and Coefficient of Performance (COP)

Figure 4.8(a) and 4.8(b) show that the Cooling Capacity (CC) and Coefficient of Performance (COP) both are increased with the increase of chilled water mass flow rate between 0.22 kg/s to 0.30 kg/s. The optimum CC value is 6.68 and COP value is 0.46.

Figure: 4.8(a). Effect of chilled water mass flow rate on cooling capacity (CC)
Figure: 4.8(b). Effect of chilled water mass flow rate on Coefficient of Performance (COP)
4.3.3. Effect of hot water mass flow rate on Cooling Capacity (CC) and Coefficient of Performance (COP)

Figure 4.9(a) and 4.9(b) show that the Cooling Capacity (CC) is increased from 6.65 to 6.69 with the increased of hot water mass flow rate between 1.2 kg/s to 2.0 kg/s but Coefficient of Performance (COP) is constant.

Figure: 4.9(a). Effect of hot water mass flow rate on cooling capacity (CC)
Figure: 4.9(b). Effect of hot water mass flow rate on Coefficient of Performance (COP)
4.3.4. **Effect of cooling water mass flow rate on Cooling Capacity (CC) and Coefficient of Performance (COP)**

Figure 4.10(a) and 4.10(b) show that both Cooling Capacity (CC) and Coefficient of Performance are increased as the cooling water mass flow rate is increased. In the present simulation, cooling water mass flow rate in the adsorber and condenser are initially taken 0.8 kg/s and 0.4 kg/s respectively and considered up to 1.2 kg/s and 0.8 kg/s in the adsorber and condenser respectively and it is found that optimum CC and COP are 6.93 and 0.48.

Figure: 4.10(a). Effect of cooling water mass flow rate on Cooling Capacity (CC)
Figure: 4.10(b). Effect of cooling water mass flow rate on Coefficient of Performance (COP)
4.3.5. Effect of cycle time on Cooling Capacity (CC) and Coefficient of Performance (COP)

CC and COP variations with adsorption/desorption cycle time are depicted Figure 4.12(a) and 4.12(b) which show that the Cooling Capacity (CC) is decreased as the cycle time is increased. The sensible heating cooling time is kept 30s. In this simulation cycle time variation is considered from 1300s to 3500s. The results show that CC is maximum for the cycle time between 1300s to 1500s. It is also observed that for the shorter cycle time (1000s) the CC falls drastically as there is not enough time for adsorption and desorption process. CC falls gradually for the higher cycle time as the adsorbent approaches to its equilibrium condition. It is also observed that the COP increases uniformly with longer cycle time. This is because of the lower consumption of driving heat with longer adsorption/desorption cycles.

Figure: 4.11(a). Effect of cycle time on Cooling Capacity (CC)
Figure: 4.11(b). Effect of cycle time on Coefficient of Performance (COP)
4.6 Table for comparison between two-stage and re-heat two-stage adsorption chiller:

Source heat temperature: $70^\circ$C, Coolant $30^\circ$C, Chilled water temperature $14^\circ$C

<table>
<thead>
<tr>
<th></th>
<th>CC</th>
<th>COP</th>
</tr>
</thead>
<tbody>
<tr>
<td>Two-stage chiller</td>
<td>4.74</td>
<td>0.36</td>
</tr>
<tr>
<td>Reheat Two-stage Chiller</td>
<td>4.81</td>
<td>0.43</td>
</tr>
<tr>
<td>Percentage</td>
<td>1.48%</td>
<td>19.44%</td>
</tr>
</tbody>
</table>

So re-heat two-stage adsorbent chiller gives the better performance
Conclusion

In this study the effect of hot water temperature and different flow rate of re-heat two stage adsorption chiller on cooling capacity and COP is investigated numerically. A finite difference approximation method is used in analyzing the solution procedure maintaining different flow rate as it effect the chilled water outlet temperature. The analyze concludes

- As the heat source temperature increases both CC & COP are increases with chilled water outlet temperature decreases.
- Better CC is obtained for the initial cycle time and as the cycle time increases CC decreases but COP increase.
- Both CC and COP increases for the increasing of chilled water mass flow rate and cooling water mass flow rate.
- CC increases with the increase of mass flow rate of hot water but COP is fixed.
- Both CC and COP have given the better result in re-heat two-stage chiller than that of two-stage chiller.
Reference


Saha, B. B., Boelman, E. C., Kashiwagi, T., Computational analysis of an


