THERMODYNAMIC ANALYSIS AND COMPARISON FOR “COP” IN SALT-METAL CLORIDE PACKED BED SYSTEMS

Submitted by:

JITENDRA KUMAR
(**Roll No. : 2K11/THE/10**)
Mechanical Engineering Department

In partial fulfilment of the requirement of the degree of

MASTERS OF TECHNOLOGY

IN

Thermal Engineering

Under the guidance of

Mr. NAUSHAD.A.ANSARI

Asst. Professor

Department of Mechanical Engineering

Department of Mechanical Engineering

DELHI TECHNOLOGICAL UNIVERSITY

(Formerly Delhi College of Engineering)

JULY 2013

CERTIFICATE

DELHI TECHNOLOGICAL UNIVERSITY
(Formerly DELHI COLLEGE OF ENGINEERING)

Date:-__________

This is to certify that report entitled **"THERMODYNAMIC ANALYSIS AND COMPARISON FOR "COP" IN SALT-METAL CLORIDE PACKED BED SYSTEMS "** by **MR. JITENDRA KUMAR** is the requirement of the partial fulfilment for the award of Degree of **Master of Technology (M.Tech)** in **Thermal Engineering** at **Delhi Technological University**. This work was completed under my supervision and guidance. He has completed his work with utmost sincerity and diligence. The work embodied in this project has not been submitted for the award of any other degree to the best of my knowledge.

Mr. NAUSHAD.A ANSARI

Asst. Professor
Department of Mechanical Engineering
DELHI TECHNOLOGICAL UNIVERSITY

ABSTRACT

Solid absorption refrigeration systems are environment friendly as they use low grade thermal energy and the refrigerants used have zero ozone depletion potential and very low global warming potential. However heat powered sorption units require thermal energy, which in most cases is provided by natural gas, solar energy or fuel combustion also resulting in CO_2 emission. Therefore care must be taken that the efficiency of the solid sorption units is high enough to cause as little global warming as possible. Though lot of efforts have been made in this field, COP of the solid sorption refrigeration system is still quite low compared to vapour compression refrigeration systems, thus there is a need for further research to make these systems a viable alternative to vapour compression systems. In this study solid $BaCl_2$ &$SrCl_2$ are used as solid absorbent and ammonia as refrigerant .The technical feasibility of the system is studied using a simple thermodynamic model assuming ideal material kinetics. In this thesis it shown that the variation of the COP & second law COP_C with the variations of evaporator temperature and maximum desorption temperature .The main results showed that the generation temperature is very low for the $BaCl_2$ - NH_3 system, as shown by a comparative study of $SrCl_2$ - NH_3 system and $BaCl_2$ - NH_3 systems.

ACKNOWLEDGEMENT

First of all, I would like to express my gratitude to God for giving me ideas and strengths to make my dreams true and accomplish this thesis. I ask God that this thesis and the published works to be a useful guide to help other researchers towards a green world that is utilised by sustainable energy systems.

To achieve success in any work, guidance plays an important role. It makes us put right amount of energy in the right direction and at right time to obtain the desired result. Express my sincere gratitude to my guide, **Mr. NAUSHAD.A. ANSARI,** Professor, Mechanical Engineering Department for giving valuable guidance during the course of this work, for his ever encouraging and timely moral support. His enormous knowledge always helped me unconditionally to solve various problems.

I am greatly thankful to **Dr. NAVEEN KUMAR**, Professor and Head, Mechanical Engineering Department, Delhi Technological University, for his encouragement and inspiration for execution of the this work. I express my feelings of thanks to the entire faculty and staff, Department of Mechanical Engineering, Delhi Technological University, and Delhi for their help, inspiration and moral support, which went a long way in the successful completion of my report work.

JITENDRA KUMAR

(Roll No- 2K11/THE/10)

TABLE OF CONTENTS

Title **Page no.**

LIST OF FIGURES

Si. No. **Title of figure** **Page no.**

LIST OF TABLES

NOMENCLATURE

Symbol	Quantity	Si.unit
P_C	Condenser pressure	bar
P_E	Evaporator pressure	bar
C_{REA}	Specific heat of reactor material	kJ/kg K
C_X	Specific heat of $SrCl_2$-$8NH_3$,	kJ/kg K
C_Y	Specific heat of $SrCl_2$-$1NH_3$,	kJ/kg K
M_X	Mass of $SrCl_2$-$8NH_3$,	kg
M_Y	Mass of $SrCl_2$-$1NH_3$	kg
COP	Coefficient of performance	
COP_C	Carnot COP	
C_i	Specific heat of all the elements of the reactor bed,	kJ/kg K
ΔH	Heat of reaction,	kJ/mol of NH3
h_1	Enthalpy of refrigerant at inlet to the evaporator	kJ/Kg
h_2	Enthalpy of refrigerant at outlet of the evaporator	kJ/kg
m_i	Mass of all the elements of the reactor bed,	kg
m_r	Ratio of mass of reactor material to that of absorbent bed	kg
Q_G	Heat of generation,	kJ
Q_A	Heat of absorption	kJ
Q_C	Heat of condensation,	kJ
Q_E	Heat of evaporation	kJ
M_{NH_3}	Mass of ammonia transferred	Kg
M_{BaCl_2}	Molecular weight of $BaCl_2$ salt	kg/k mol.
M_{REA}	Mass of the reactor	kg
C_{NH_3}	Specific heat of ammonia vapour	kJ/kg K
C_{BaCl_2}	Specific heat of the salt $BaCl_2$	kJ/kg K
M_{SrCl_2}	Molecular weight of strontium chloride salt	kg/k mol.
C_{NH_3}	Specific heat of ammonia,	kJ/kg K

CHAPTER 1: INTRODUCTION

1.1 Introduction

Refrigeration systems are required for food and vaccines transportation, comfort cooling, cold storage applications, supermarket display and retails. Industry market research for business leaders, January 2011, statistically stated that the global demand for commercial refrigeration equipment is projected to rise 5.2% per year through 2014 to $29.7 billion [1]. The global industry analysts announced that the global market of air conditioning is expected to reach 78.8 million units in volume sales by 2015 and this global demand is significant in areas of warm climate and high capita income. Currently, most of the above demand is met by mechanical vapour compression systems driven by high grade electrical power input and utilises environmentally harmful refrigerants [2]. Refrigeration and air conditioning systems consume around 30% of total worldwide energy consumption [3]. Based on the new environmental regulations (Kyoto protocol, Vienna Convention and Montreal Protocol) CFCs and HCFCs phase-out have been agreed. Moreover, HFCs were one of the six addressed greenhouse gases by Kyoto protocol and countries may seek to limit its use to meet its legally binding greenhouse gas emissions targets. So to accomplish this simple refrigeration units are required which can operates with thermal energy, when electric supply is faulty and/or expansive. The adapted thermal refrigeration cycles are those of absorption, adsorption and the thermo-chemical (solid- gas) absorption.

Adsorption (also called “solid sorption”) refrigeration systems use solid sorption material such as silica gel and zeolite to produce cooling effect. These systems are attracting increasing attention because they can be activated by low-grade thermal energy and use refrigerants having zero ozone depletion potential and low global warming potential. The adsorption refrigeration system has several advantages compared to the absorption refrigeration system.

1.1.1 Absorption System:

The basic absorption cycle employs two fluids, the refrigerant and the absorbent. The refrigerant vapour from the evaporator is absorbed into the absorbent releasing heat. The liquid refrigerant/absorbent solution is pumped to a high pressure generator. This pumping uses a lot less energy that the compressor used in a heat pump. The heat from the waste heat source causes the refrigerant to desorb from the absorbent. The refrigerant-depleted solution then returns to the absorber via a throttling device (labelled as weak in the diagram). The two most common refrigerant/ absorbent mixtures used in absorption chillers are water/lithium bromide and ammonia/water. Kerosene and LPG power refrigerators used in caravans are a common example and use an ammonia/water mix.

The refrigerant vapours flow to a condenser and condense to a high-pressure liquid. The liquid is then throttled though an expansion valve to the lower pressure in the evaporator where it evaporates and takes up heat which produces the cooling effect. The low-pressure refrigerant vapours return to the absorber where they are combined with the absorbent so the cycle can be repeated.

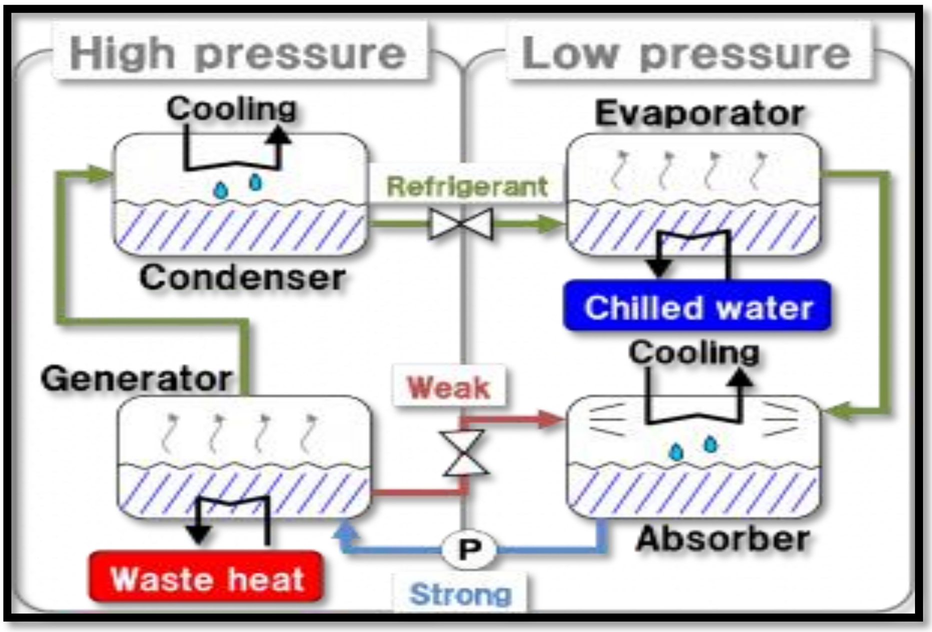


Figure 1-1 Absorption cycle

1.1.2 Adsorption System:

The process is very similar in adsorption chillers, the difference is that adsorption used a solid instead of a liquid and the refrigerant is bound to the surface of the adsorbent rather than absorbed into a liquid in the case of absorption. The solid in the case of the emission less adsorbent chiller shown below is a proprietary permanent silica gel. The silica gel in its neutral state has adsorbed the refrigerant which in this case is water. When heated, the solid desorbs (releases) refrigerant vapour which subsequently is cooled and liquefied. This liquid refrigerant then provides its cooling effect at the evaporator, by absorbing external heat and turning back into a vapour. In the final stage the refrigerant vapour is (re)adsorbed into the solid.

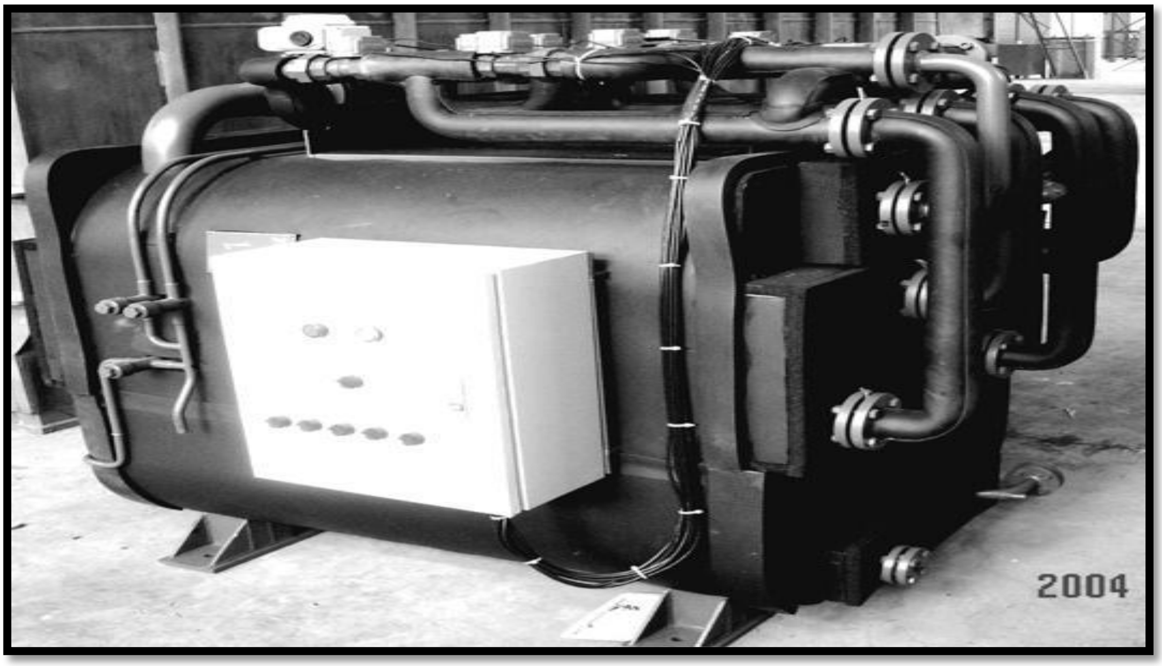


Figure 1-2 Adsorption Chiller

Adsorption chillers are simpler and require less maintenance primarily because they avoid the use of lithium bromide which is toxic and can crystallise in the system. The technology is also being used in conjunction with solar thermal systems for solar powered air-conditioning. An example is the system installed at the Echuca Hospital. While less efficient that heat pumps adsorbent and absorbent chillers can deliver significant cost savings because they derive their energy (except for a small amount of electricity for pumping) from waste heat.

1.1.3 Process

Blue spheres are solute molecules Adsorption and absorption are both sorption processes. Absorption occurs when atoms pass through or enter a bulky material. During absorption, the molecules are entirely dissolved or diffused in the absorbent to form a solution. Once dissolved, the molecules cannot be separated easily from the absorbent.

Adsorption is generally classified into physisorption (weak Vander Waal’s forces) and chemisorptions (covalent bonding). It may also occur due to electrostatic attraction. The molecules are held loosely on the surface of the adsorbent and can be easily removed.

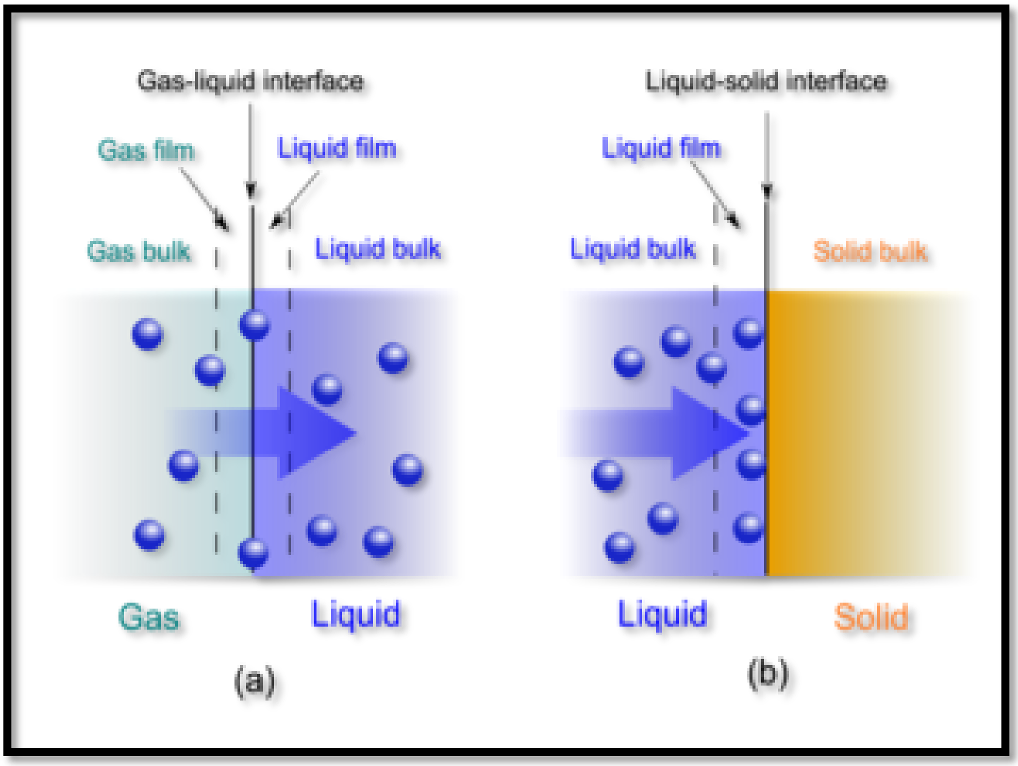


Figure 1-3 (a) Gas-liquid absorption, (b) liquid-solid adsorption mechanism.

1.1.4 Uses of absorption and adsorption

Absorption: The common commercial uses of absorption cycle are absorption chillers for space cooling applications, ice production, cold storage, turbine inlet cooling. High efficiency operation, environmentally friendly refrigerants, clean-burning fuels and few moving parts that require maintenance make absorption a very good choice for consumers. The process of gas absorption by a liquid is used in hydrogenation of oils and carbonation of beverages.

Adsorption: Some of the industrial applications for adsorption are air-conditioning, adsorption chillers, synthetic resin and water purification. An adsorption chiller does not require moving parts and hence is quiet. In pharmaceutical industry applications, adsorption is used as a means to prolong neurological exposure to specific drugs or parts thereof. Adsorption of molecules onto polymer surfaces is used in various applications such as in the development of non-stick coatings and in various biomedical devices.

1.1.5 Principle of adsorption cycles for refrigeration.

Let us just remind that adsorption is a reversible process by which a fluid molecule is fixed onto a solid matrix, typically a surface or a porous material. When the molecule is fixed, it loses some energy adsorption is exothermic. Moreover, the thermodynamic equilibrium is divariant. This divariant equilibrium can be described by the set of isosters in the Clapeyron diagram (LnP vs. -1/T).

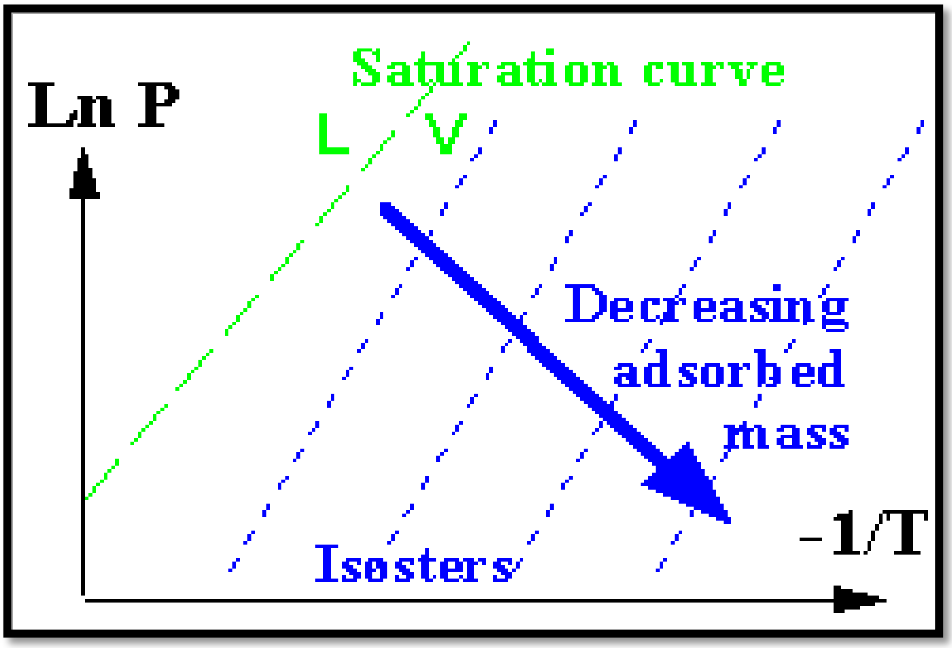


Figure 1-4 Isosters in the Clapeyron diagram (LnP vs. -1/T).

An adsorption cycle for refrigeration -or heat pumping- does not use any mechanical energy, but only heat energy. Moreover, this type of cycle basically is a four temperatures continuous cycle. An adsorption unit consists of one or several adsorbers plus a condenser plus an evaporator, connected to heat sources. The adsorber or system consisting of the adsorbers- exchanges heat with a heating system at high temperature **-HS-** and a cooling system at intermediate temperature **-CS-,** while the system consisting of the condenser plus evaporator exchanges heat with another heat sink at intermediate temperature (not necessarily the same temperature as the CS), and a heat source at low temperature. Vapour is transported between the adsorber(s) and the condenser, evaporator. The cycle consists of four periods which is shown below in the figure 1.6.

A: Heating and Pressurisation

B: Heating and Desorption + Condensation

C: Cooling and Depressurisation

D: Cooling and Adsorption + Evaporation

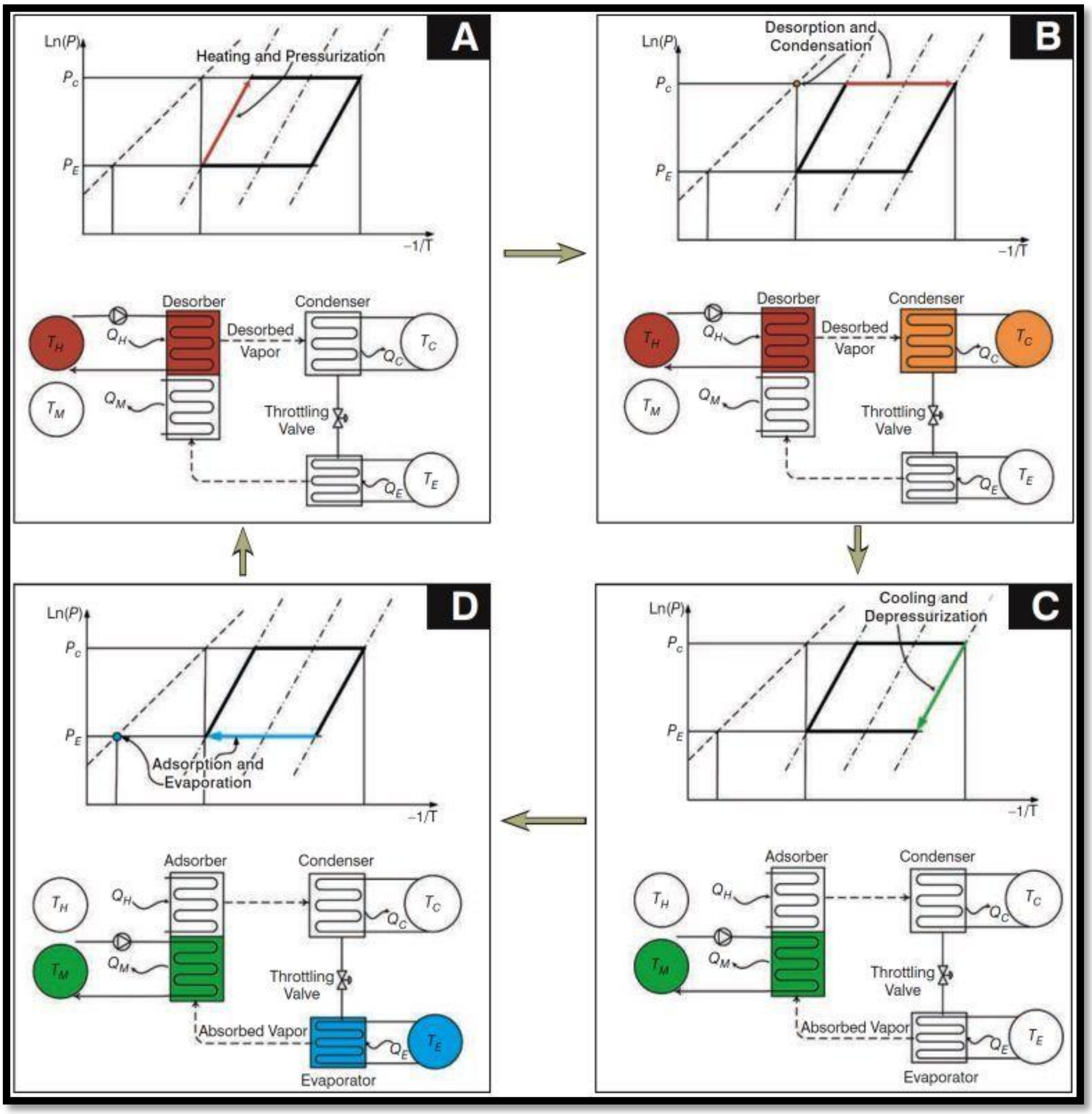


Figure 1-6 A basic adsorption cycle consists of four steps

A: Heating and Pressurisation

During this period, the adsorber receives heat while being closed. The adsorbent temperature increases, which induces a pressure increase, from the evaporation pressure up to the condensation pressure. This period is equivalent to the "compression" in compression cycles.

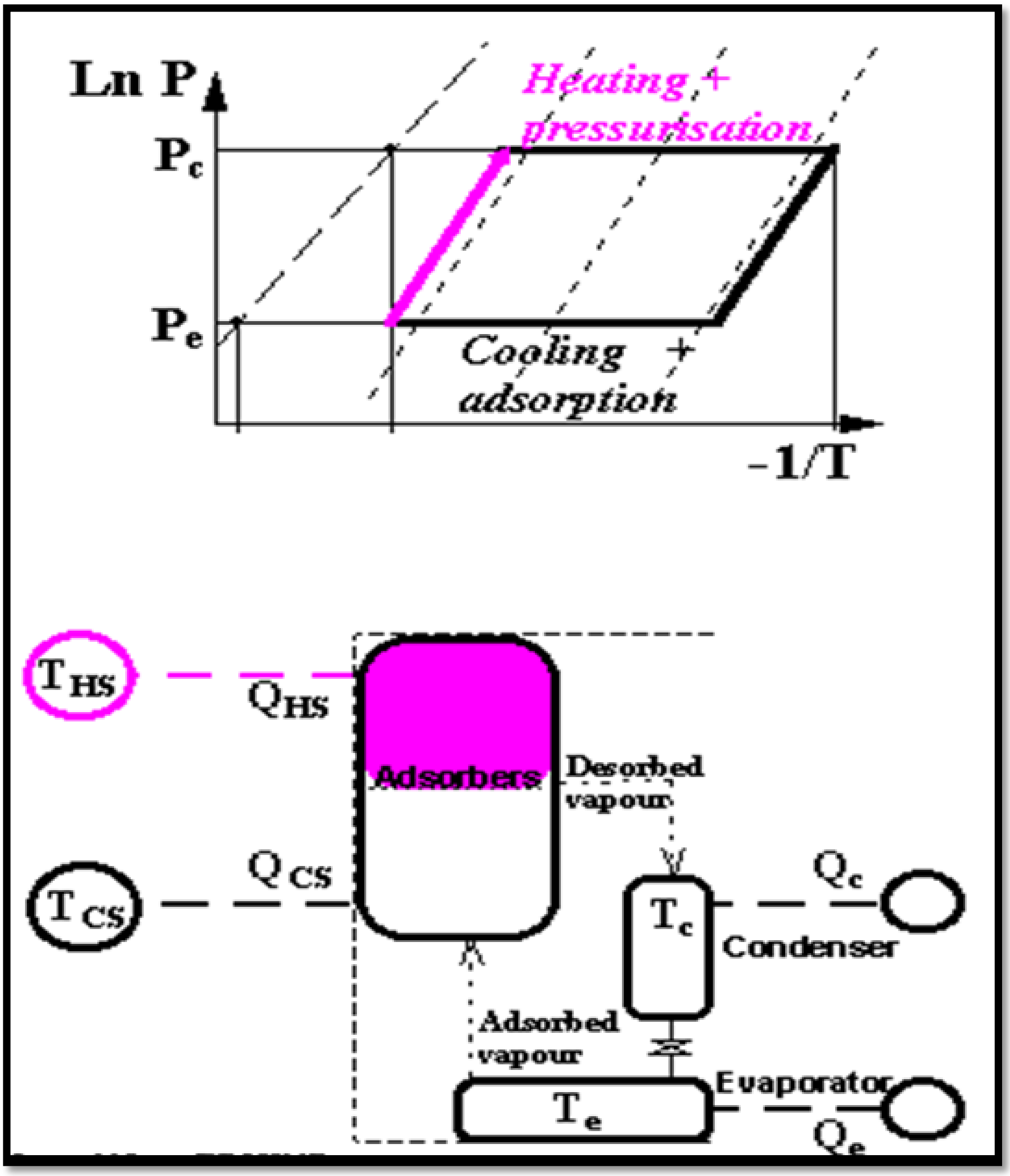


Figure 1-7 heating and pressurisation

B: Heating and Desorption + Condensation

During this period, the adsorber continues receiving heat while being connected to the condenser, which now superimposes its pressure. The adsorbent temperature continues increasing, which induces desorption of vapour. This desorbed vapour is liquefied in the condenser. The condensation heat is released to the second heat sink at intermediate temperature. This period is equivalent to the "condensation" in compression cycles.

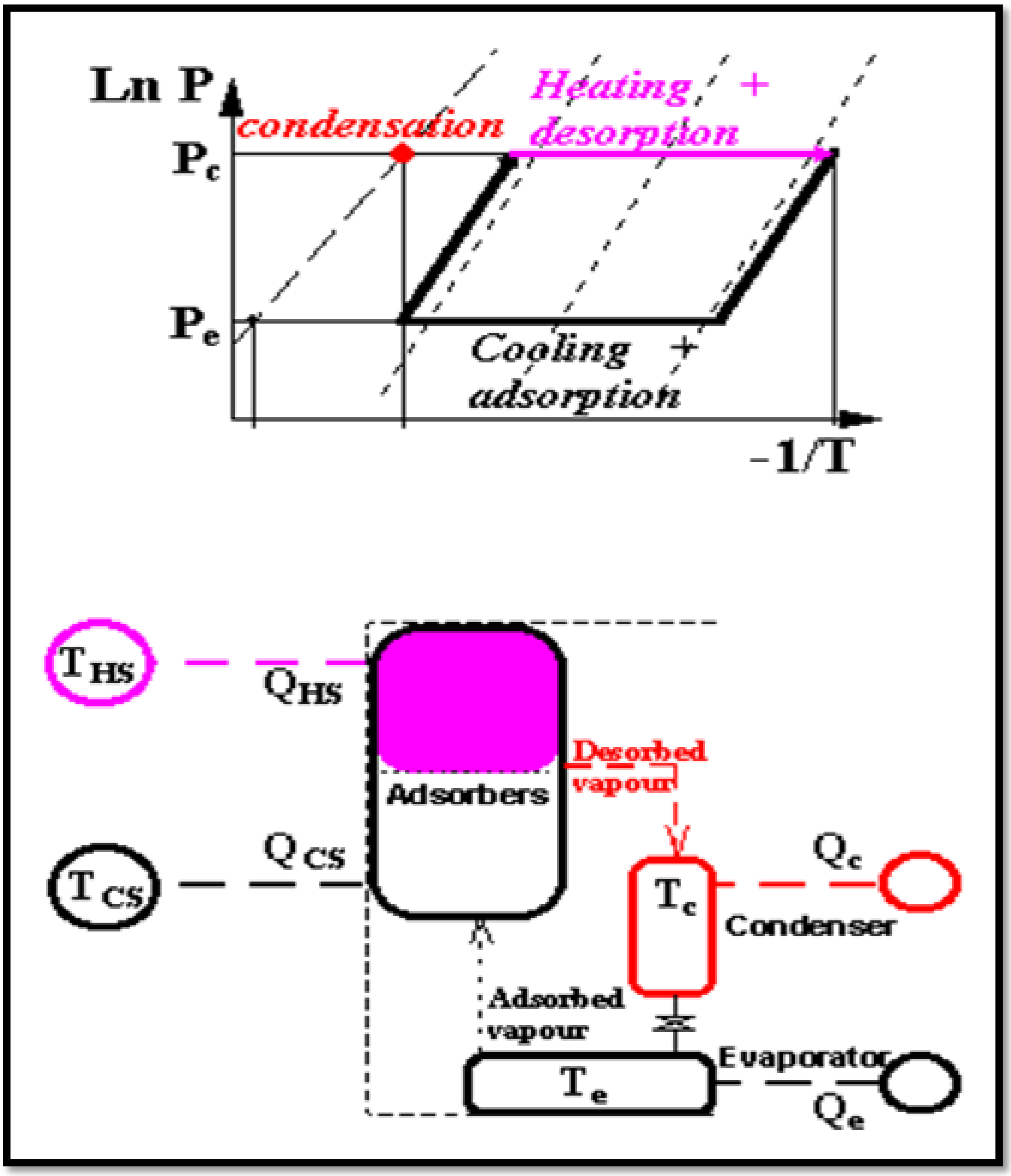


Figure 1-8 Heating and desorption + condensation

C: Cooling and Depressurisation

During this period, the adsorber releases heat while being closed. The adsorbent temperature decreases, which induces the pressure decrease from the condensation pressure down to the evaporation pressure. This period is equivalent to the "expansion" in compression cycles.

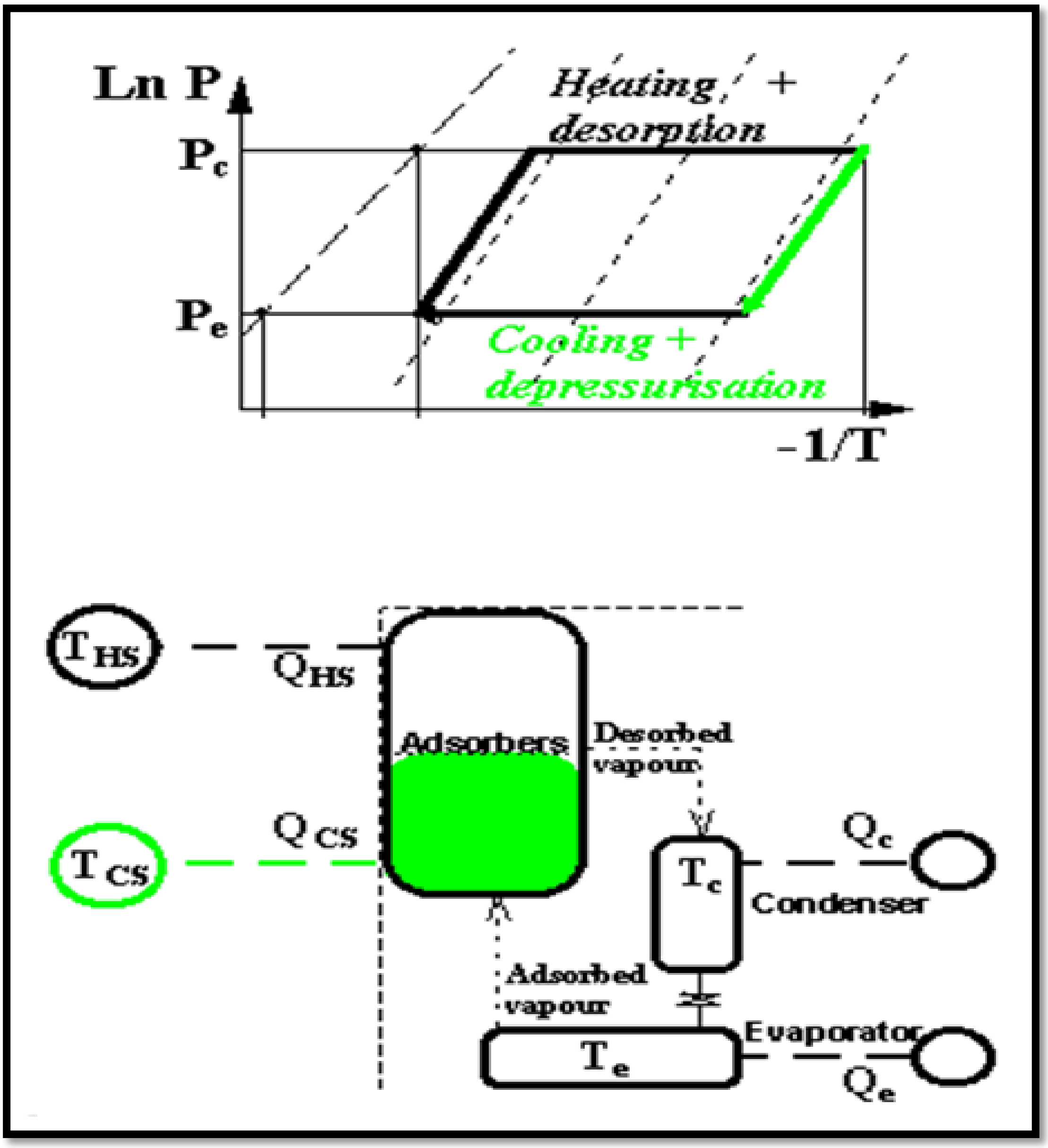


Figure 1-9 Cooling and Depressurisation

D: Cooling and Adsorption + Evaporation

During this period, the adsorber continues releasing heat while being connected to the evaporator, which now superimposes its pressure. The adsorbent temperature continues decreasing, which induces adsorption of vapour. This adsorbed vapour is vaporised in the evaporator. The evaporation heat is supplied by the heat source at low temperature. This period is equivalent to the "evaporation" in compression cycles.

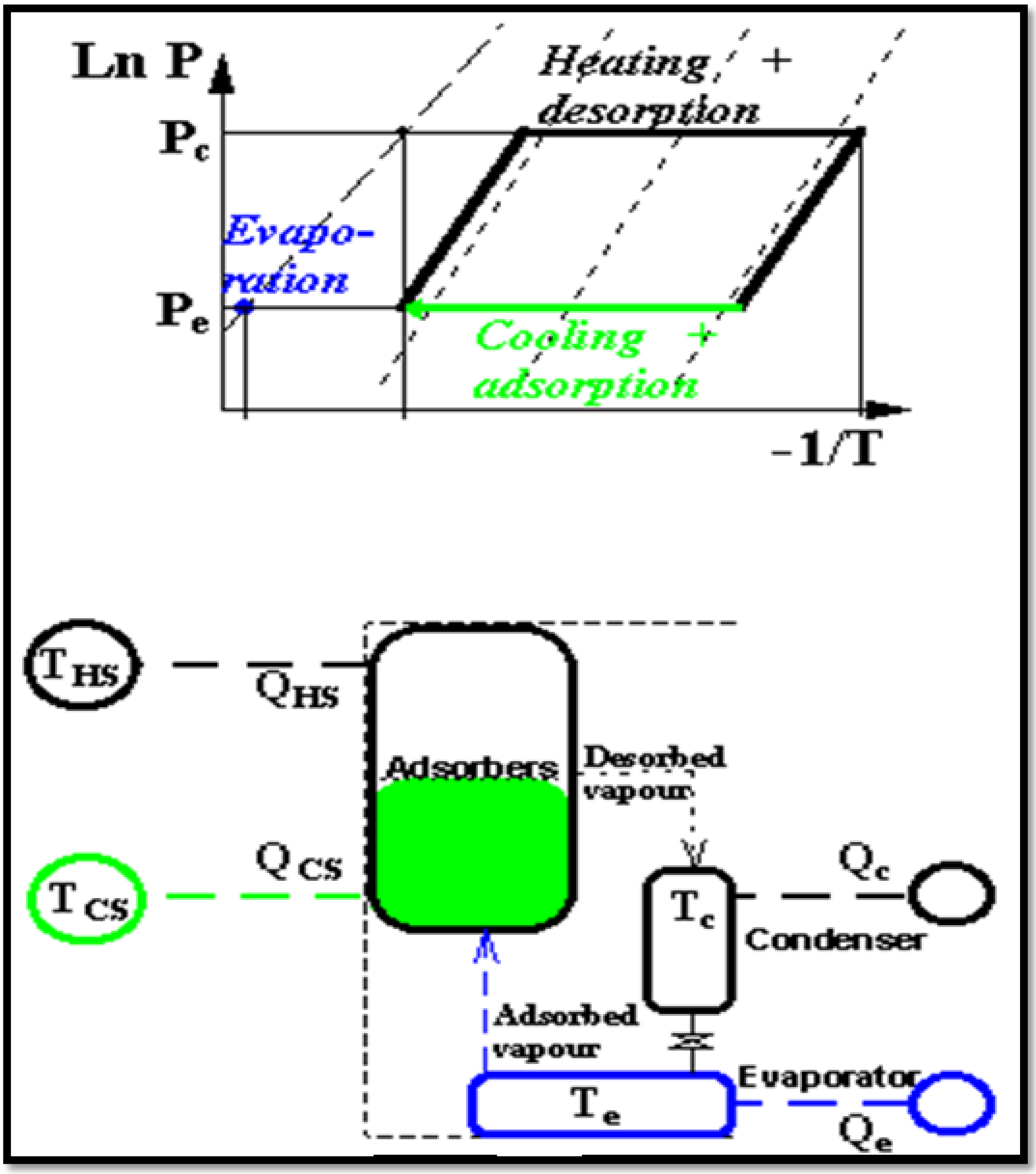


Figure 1-10 Cooling and adsorption + evaporation

Basically, the cycle is intermittent because cold production is not continuous: cold production proceeds only during part of the cycle. When there are two adsorbers in the unit, they can be operated out of phase and the cold production is quasi-continuous. When all the energy required for heating the adsorber(s) is supplied by the heat source, the cycle is termed single effect cycle. Typically, for domestic refrigeration conditions, the coefficient of performance (COP) of single effect adsorption cycles lies around 0.3-0.4.When there are two adsorbers or more, other types of cycles can be processed. In double effect cycles or in cycles with heat regeneration**,** some heat is internally recovered between the adsorbers, which enhance the cycle performance.

1.2 Aims and objectives

The main aim of this M.Tech project is to investigate the various means of improving the coefficient of performance of two solid adsorption cooling systems utilized with low grade heat recovery schemes.

To achieve the above mentioned research aim, the project objectives are set out below.

- Review of theoretical and experimental research work on adsorption refrigeration cycles.
- Review of various adsorbents to understand their advantages and disadvantages and the parameters that are used in evaluating of new materials.
- Done the theoretical analysis for both solid absorbent systems $BaCl_2$ and $SrCl_2$ with ammonia as refrigerant to obtain the optimum results.
- Use an optimisation tool that enables selecting the optimum operating conditions corresponding to the best performance.
- Study the capability of new species of adsorbent materials to replace the currently used silica gel.

1.3 Thesis outline

This thesis consists of five chapters.

Chapter one: introduces the research topic covered by this thesis. It includes project aims, objectives and thesis outline.

Chapter two: reviews the up to date research progress on adsorption refrigeration cycle improvement techniques. It statistically presents the increasing demand for the refrigeration systems and the ability of adsorption refrigeration system to cover this demand and cope with the recent environmental restrictions.

Chapter three: presents the thermodynamic analysis of solid adsorption system pairs that will be used as a coefficient of performance evaluation to study the effect of various physical and operating conditions. The validation of the model was based on experimental data for a commercialised 450 kW silica gel/water adsorption chiller.

Chapter four: presents the design of a test facility that will be used to investigate the effect of operating conditions on the coefficient of performance and the second law COP_C of scaled down adsorbent bed reactor chiller theoretically. These operating conditions are evaporator temperature, condenser temperature, desorption temperature, generation temperature and ratio of mass of reactor material to that of absorbent bed $m_{r.}$ In this results also compared of both the systems to achieve the best chiller performance

Chapter five: presents the study of adsorption chiller for improvement in the COP using ammonia as refrigerant will be concluded in chapter five. The major findings from the study are summarized and possible future research topics are suggested.

CHAPTER 2: LITERATURE REVIEW

2.1 Introduction

Adsorption refrigeration system is an environmentally friendly alternative for the vapour compression refrigeration system and it has to be enhanced to overcome the problem of its low efficiency. This chapter presents a comprehensive review of different adsorption cooling systems and their development techniques. The adsorption refrigeration system is developed by changing the working materials, the heat exchangers design to improve its heat and mass transfer performance and / or changing the operating cycle. The parameters that affect the system performance and limit the system enhancement are investigated. Each of the above mentioned points are extensively reviewed to conclude the optimum enhancement techniques for the adsorption refrigeration systems.

2.2 Sorption refrigeration systems

There is an increasing need to evolve the refrigeration technology by looking for new alternative technologies [4]. Sorption refrigeration systems appear to be an alternative to the vapour compression refrigeration systems, named green refrigeration technology [5]. Sorption refrigeration integrated with combined heating and power plants to produce cooling, heating and power (CCHP) as a trigeneration system can be employed in many industrial and commercial applications [6] and sustainable building acclimatisation using solar energy as heat source. Sorption cooling technology is a promising solution for more environmentally friendly system in terms of refrigerant used and energy demand.

2.2.1 Sorption phenomena

The sorption phenomena could be absorption or adsorption, where absorption is the incorporation of a substance in one state in another of different state by dissolution of the molecules within a phase. The adsorption is a surface phenomenon based on the physical adherence of molecules onto the surface of another phase mainly by Vander Waals force [7].

2.2.2 Sorption refrigeration cycle

The sorption refrigeration cycle is a thermodynamic cycle with two sources and two sinks, which operates using three temperature levels [8]. Two of them are used to drive the thermal compressor “Reactor” that replaces the mechanical compressor in a vapour compression refrigeration cycle, Figure 2-1. The sorption refrigeration cycle operates between two pressures and two refrigerant / sorbent concentration levels as shown in Figure 2-2. The sorption systems are classified into Adsorption and Absorption system, where table 2-1 compares between them. Due to the favourable features of adsorption refrigeration system over absorption refrigeration system, it makes the former system more preferable [9].

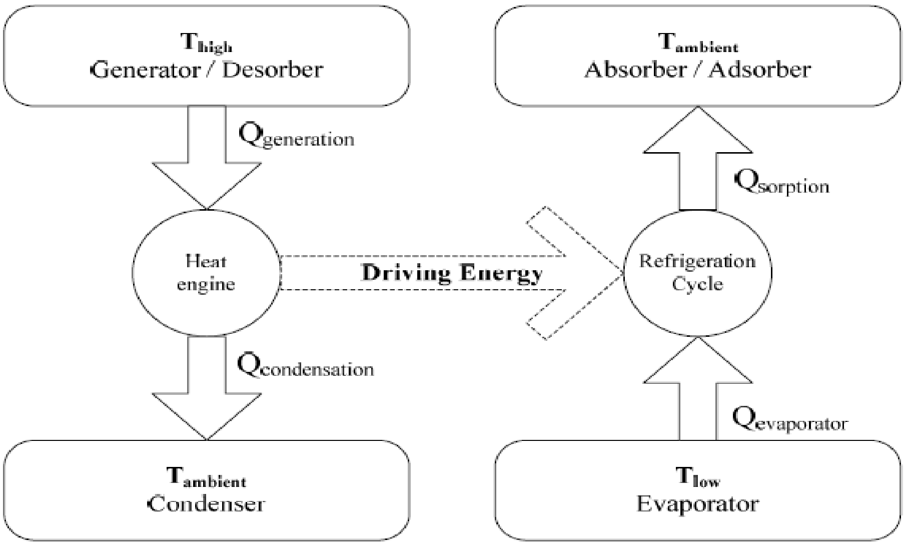


Figure 2-1, Sorption thermodynamic cycle

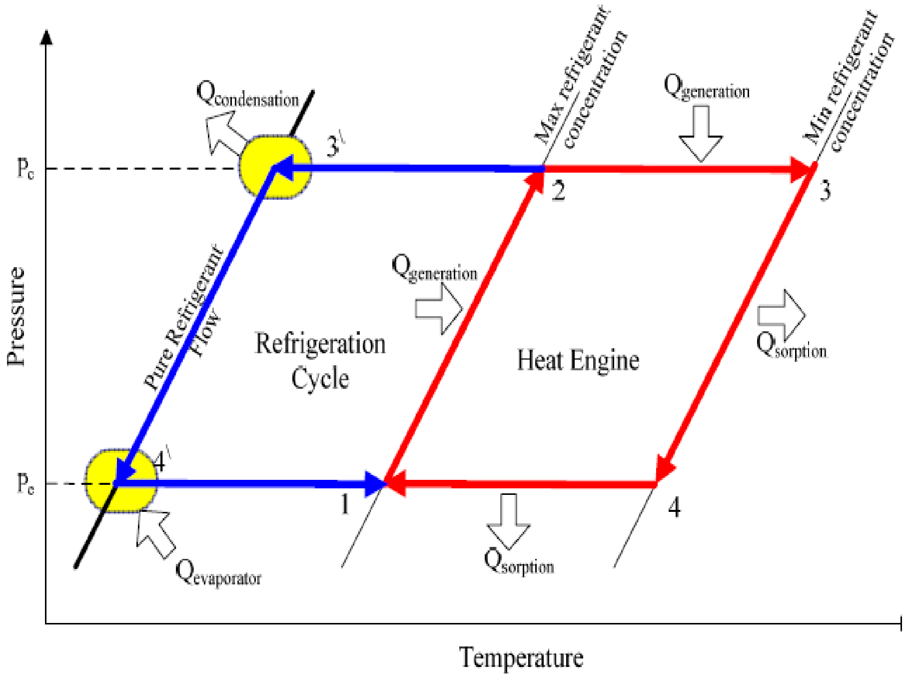


Figure 2-2, Sorption Clapeyron diagram

Table 2-1, The advantages of adsorption over absorption refrigeration systems [10]

Attribute	**Adsorption**	**Absorption**
Heat source	• It is powered by sources of wide temperature range. • Temperature as low as 50˚C can be used as heat source, while heat sources with temperature close to 500˚C can be used directly without producing any kind of corrosion problem. • There is no limitation for the low temperature reservoir.	• Very sensitive against source temperature and the variation must be tightly controlled between 82˚C and 100˚C. • Heat source must be higher than 70˚C to avoid the crystallization problem, even in two-stage cycle. • Severe corrosion would start to occur for temperatures above 200˚. • Low temperature reservoir must be 18-29˚C
Operating consideration	• It is utilized by solid sorbents and hence it is suitable for conditions with serious vibration, such as in fishing boats and locomotives. • It is almost noiseless system, where there are not many moving parts. • Operation possibility over 8000hr per year.	• It is utilized by liquid sorbent and hence it is suitable for stationary units only, where unfavourable absorbent flow from the generator / absorber to the evaporator / condenser. • Daily shutdown due to the dilution of sorbent solution
Maintenance	• There are no special requirements for maintenance, where few used moving parts (vacuum pump). • Annual cleaning of condenser tubes is required. • Simple control system is required	• It needs regular monitoring and maintenance for: − Liquid analysis - pumps − Control system − Air leakage − Sorbent exchange − Heat exchanger replacement due to salt corrosion.
Lifetime	• It has relatively very long lifetime.	• The maximum life time is 7-9 years, due to the problem of salt corrosion.

2.3 Adsorption historical background

The adsorption phenomenon was applied at ancient times, where charcoal was the dominant adsorbent. It was used to reduce copper, zinc and tin ores for bronze manufacturing by Egyptians and Sumerians 3750BC [11]. The first quantitative observations were carried out by Scheele 1773 and Fontana 1777, where they experimentally reported some gases adsorption by charcoal and clays. Saussure 1814 reported that all gases can be taken up by porous materials (sea foam, cork, charcoal and asbestos) exothermally. The first invention of an adsorption cooling system happened in 1848, when Faraday demonstrated an adsorption refrigeration system utilising ammonia and silver chloride as working pair. In 1929, Hulse and Miller described an adsorption system for the air conditioning of railway carriages using silica gel and sulphur dioxide as the working pair [12]. Due to the low performance of adsorption cooling systems compared to the vapour compression systems, research and development of adsorption cooling systems was slowed down. In the last three decades, the adsorption cooling systems are laboratory and commercially developed to be applied in different applications [13]. The adsorption cooling development is due to the need of replacing the conventional vapour compression systems to meet the new environmental regulations.

2.4 Environmental regulations

The environmental regulations were adopted to solve the problems of ozone depletion and global warming, which are the major problems nowadays. The thinning of ozone layer that absorbs 98% of the sun’s high frequency ultraviolet lights has been confirmed in 1980s [14]. In 1985, Vienna convention provided a framework for Montreal protocol that ratified ozone depleting substances in 1987. The original protocol has been amended several times for developed and developing countries between 1990 (London) – 2007 (Montreal) [15]. Conventional vapour compression refrigeration cycles are utilized ozone depleting refrigerants such as CFCs and HCFCs. The Montreal protocol ratified to stop the production of CFCs in developed countries in 1995 and planned to phase-out HCFCs completely by 2030 [16], Figure 2-3.

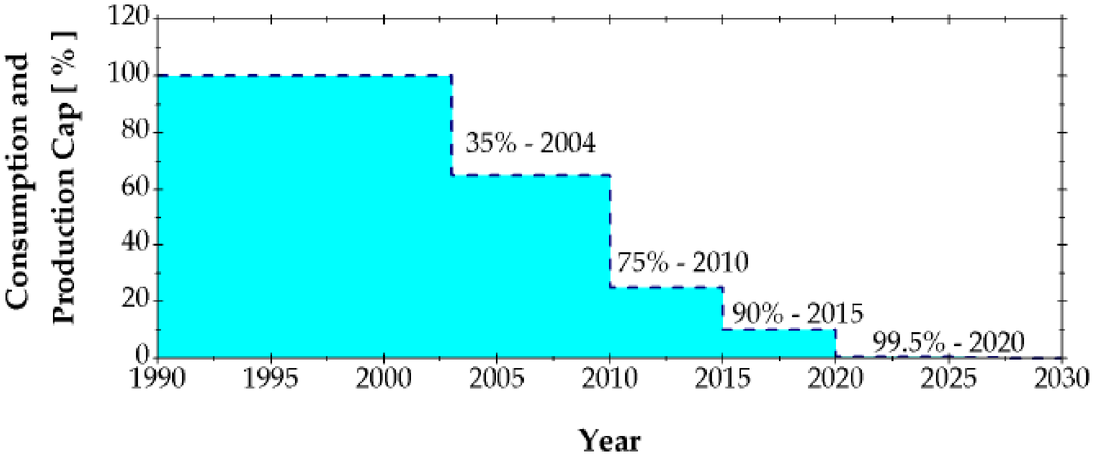


Figure 2-3, Montreal protocol HCFCs phase-out plan

The global warming is the phenomenon of increasing the Earth's average temperature due to the trapping of energy emitted from the Earth. This amount of energy is about 1/3 of the incoming solar radiation and is trapped by means of greenhouse gases (GHG). Some trapping of heat is desired, but excess trapping will affect the natural environment balance by melting polar ice caps and more evaporation of ocean water. Polar ice caps melting causes unusual floods and ocean water evaporation causes more clouds cover and hence reduces the incoming solar radiation to offset the greenhouse effect. In 1997, the Kyoto protocol was initially adopted in Japan to stabilise greenhouse gas concentrations in the atmosphere at a level that would prevent dangerous anthropogenic interface with climate system. The protocol cue into force in 2005, and 191 states have ratified the protocol in September 2011. The protocol addressed six greenhouse gases namely; carbon dioxide (CO_2), Methane (CH_4), Nitrous oxide (N_2O), Hydrofluorocarbon (HFC), Perfluorocarbons (CxFy) and Sulphur hexafluoride (SF_8). It is statistically predicted that the equivalent CO_2 level will be doubled by 2050, tripled by 2100 and quadruple by 2150, even if Kyoto protocol is adopted [17].

Many vapour compression refrigeration systems utilize HFCs, but the direct effect of the released HFCs to the atmosphere is negligible. HFCs contributed about 3% during time period 2000-2100 of the total contributed by all the greenhouse gases. However, electrically driven vapour compression refrigeration systems contribute about 15% of the world man made CO_2 output, and hence contribute more significantly to carbon footprint and global warming compared with refrigerant contribution. Industrial countries that ratified Kyoto protocol have legally bound targets and timetables for mandatory cutting greenhouse gas emissions [18].

2.5 Adsorption refrigeration cycles

2.5.1 Simple two-bed adsorption refrigeration cycle

A simple two-bed adsorption refrigeration cycle of separated heat exchangers consists of four main parts namely: reactors (adsorber or desorber based on operating mode), evaporator, and condenser [19]. The reactors are packed with adsorbent material which has the capability of adsorbing or desorbing the adsorbate / refrigerant during the adsorption or desorption process. Interconnecting valves are used to control the refrigerant flow as shown in the flow diagram, Figure 2-4. Adsorption is an exothermic process, so the heat of adsorption needs to be removed by means of continuous cooling. On the other hand, during the desorption process heating is required to release the refrigerant from the adsorbent pores.

The aforementioned components are controlled to work sequentially through four modes Figure 2-2 namely; isosteric heating (preheating switching) (1-2), isobaric desorption / condensation (2-3 / 2-3`), isosteric cooling (precooling switching) (3-4) and isobaric adsorption / evaporation (4-1 / 4`-1). In the isosteric heating/cooling also named switching periods, the refrigerant amount in the reactor chambers remains constant. During the switching modes all interconnected valves are closed to keep the amount of refrigerant in the reactors constant during preheating / precooling. As a result, during the preheating mode the reactor pressure increases from the evaporation pressure to the condensation pressure and vice versa during the precooling. During the isobaric cooling, one of the reactors is connected to the evaporator to suck the refrigerant vapor from the evaporator producing the cooling effect. During the isobaric heating the other reactor is connected to the condenser to deliver the refrigerant to be condensed and then flow to the evaporator through the liquid line. Using two adsorption reactors is necessary to obtain continuous cooling by making both of them work in parallel, while one reactor is in adsorption phase, the other one will be in desorption mode. Table 2-2 and Figure 2-5 present the cyclic operating modes and valving system for a simple two-bed adsorption refrigeration cycle.

Table 2-2, two bed cyclic operation and valving

Mode/component	**Bed-A**	**Bed-A**	**V1**	**V2**	**V3**	**V4**
Mode-A Switching	Heating	Cooling	X	X	X	X
Mode-B Ads/Des	Heating	Cooling	O	X	O	X
Mode-C Switching	Cooling	Heating	X	X	X	X
Mode-D Ads/Des	Cooling	Heating	X	O	X	O

X=OPEN, O= CLOSED

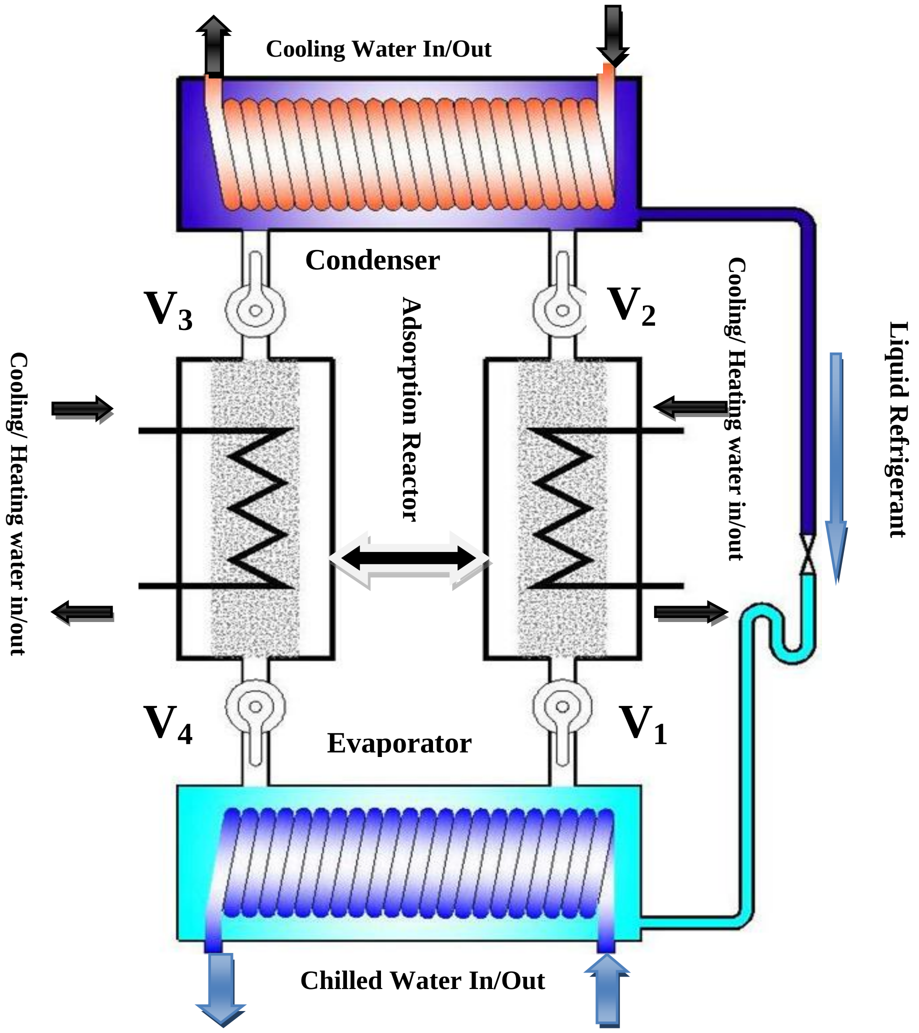
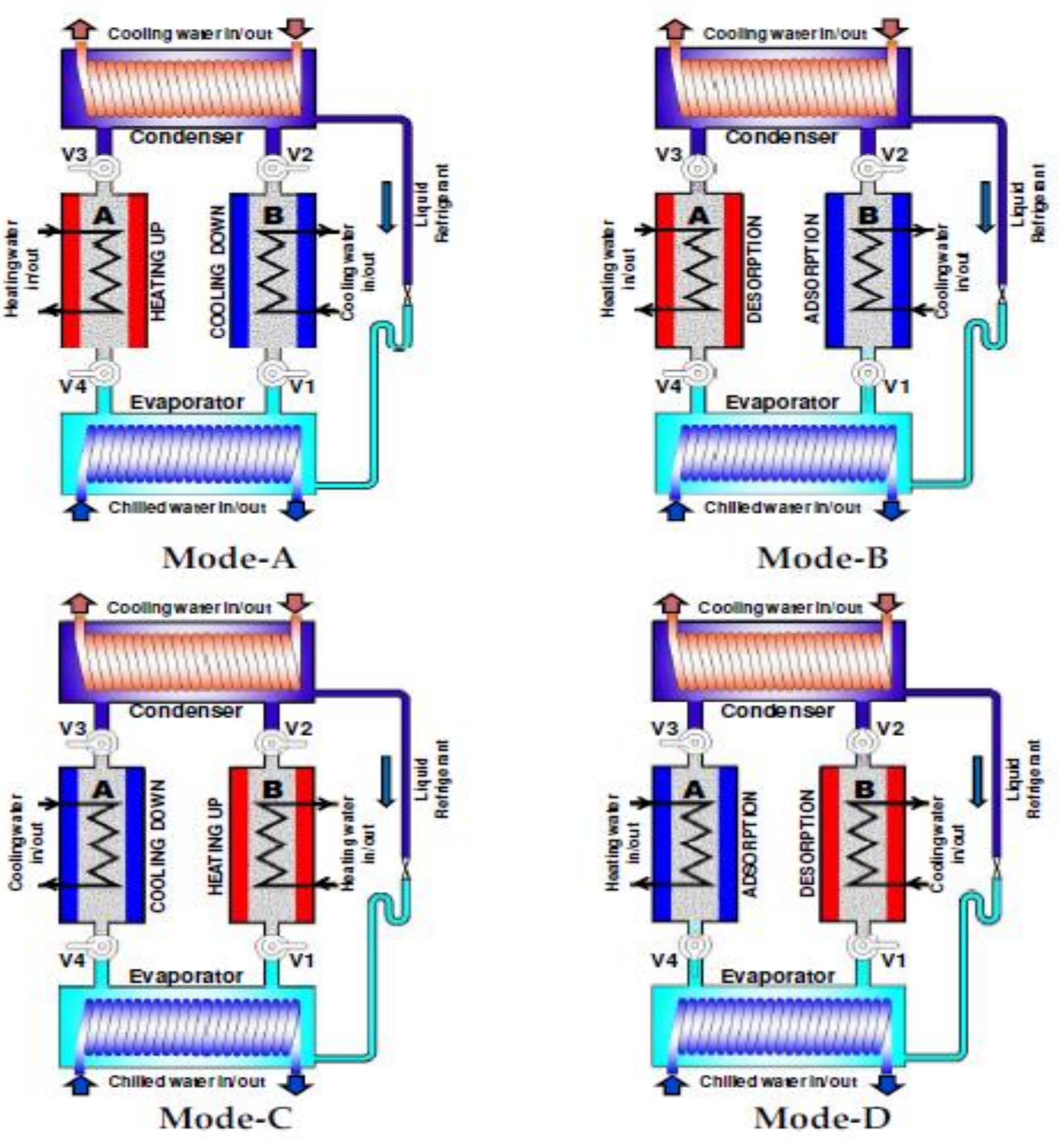


Figure 2-4, Flow diagram of simple two-bed adsorption refrigeration cycle

During the switching mode heat and/or mass recovery can be used [20]. During mass recovery, the adsorber and desorber are connected to speed up the pressure reduction of the hot bed and pressure increase of the cold bed and hence the mechanical equilibrium by means of pressure swings [21]. During the heat recovery period, the cooling water flows through the hot bed and then to the cold bed, which reduces the heat required for regenerating the refrigerant and hence improve the cycle performance [22]. Based on the review of literature the COP of two-bed adsorption refrigeration cycle of different operating schemes is usually between 0.60-0.70.



Mode-A

Mode-B

Mode-C

Mode-D

Figure 2-5, two bed adsorption cycle operating modes

2.5.2 Integrated adsorption refrigeration cycle

The integrated adsorption refrigeration cycle consists of two units where each one consists of adsorbent bed, condenser and evaporator [23], Figure 2-6. The major difference between this cycle and the simple two-bed adsorption refrigeration cycle is the absence of switching mode, which makes it more reliable [24]. The cycle operation is based on two modes; adsorption / evaporation and desorption / condensation where each unit alternatively works in different modes. There is a group of control valves used to control the flow of secondary fluid to each unit.

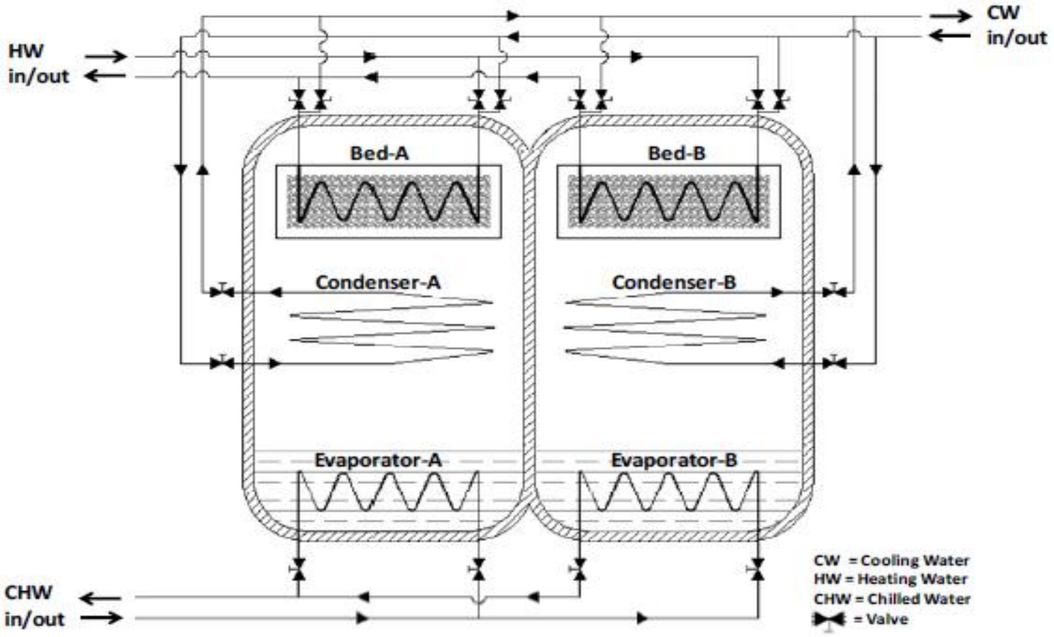


Figure 2-6, Schematic diagram of integrated adsorption refrigeration cycle

This cycle in Figure 2-7 was modified to reduce the number of heat exchangers, where each unit consists of one adsorbent bed and one coil that is working as condenser or evaporator depending on the operating mode [25]. The integrated cycle was also enhanced by combining it with a third chamber of a different refrigerant which acts as a heat pipe [26], as shown in Figure 2-8. The integrated adsorption cycle can also be enhanced by including heat and mass recovery methods. Based on the review of literature the reported COP of the integrated adsorption refrigeration cycle using different operating schemes is 0.15-0.49 (average 0.32) and by applying the heat pipe its value is 0.32-0.45 (average 0.39).

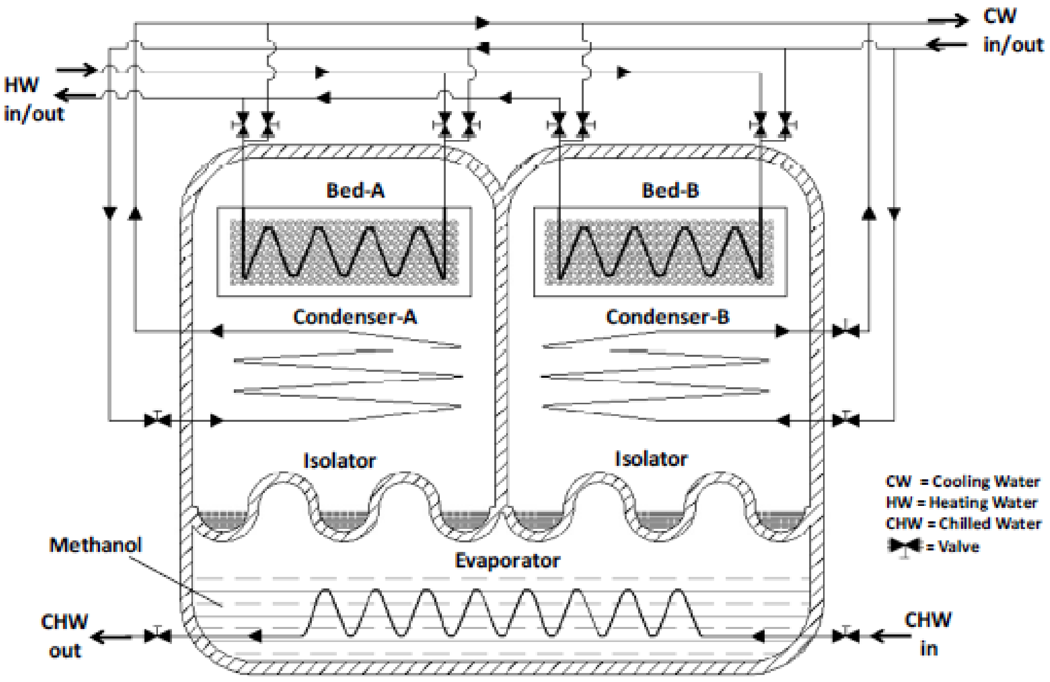


Figure 2-7, Schematic diagram for the integrated adsorption refrigeration cycle combined with heat pipe

Every cycle has some features that make it more compatible with applied resources. Table 2-3 presents the main features of the reviewed cycle and the reported COP using different operating schemes.

Table 2-3, The features of different adsorption refrigeration cycles

Cycle name	**Main features**
Simple two-bed cycle	• Simple and commonly commercially applied
Integrated cycle	• Simple design • Compact • Reliable • COP=0.15-0.49
Three-bed cycle	• More continuity in cooling compared by two-bed
Three-bed with dual evaporator	• Brings more cooling with the same Operating temperature • COP=0.3-0.7
Multi-stages cycle	• Utilise low driving heat sources • COP=0.08-0.25

2.6 Adsorbents

The adsorbents are classified based on the adsorption process as: physical adsorbents, chemical adsorbents and composite adsorbents. This section presents in details the characteristics of each type of these adsorbents.

2.6.1 Physical adsorbents

Physical adsorbents are usually porous materials with different pore sizes, Figure 2-11. It adsorbs the adsorbate (refrigerant) by an intermolecular force called (Vander Waals force). The physical adsorbent can retain its original properties after removing the refrigerant by adding heat during the desorption process as explained previously. This advantage lets the physical adsorbent be commonly used in practical application. The performance of adsorption refrigeration cycle increases when the amount of cycled refrigerant increases [27]. Most of the physical adsorbents suffer from low adsorption kinetics and hence low cyclic refrigerant flow rate. The main physical adsorbent classes are mesoporous silicates, zeolites metalaluminophosphates, porous carbons and metal organic frameworks [28].

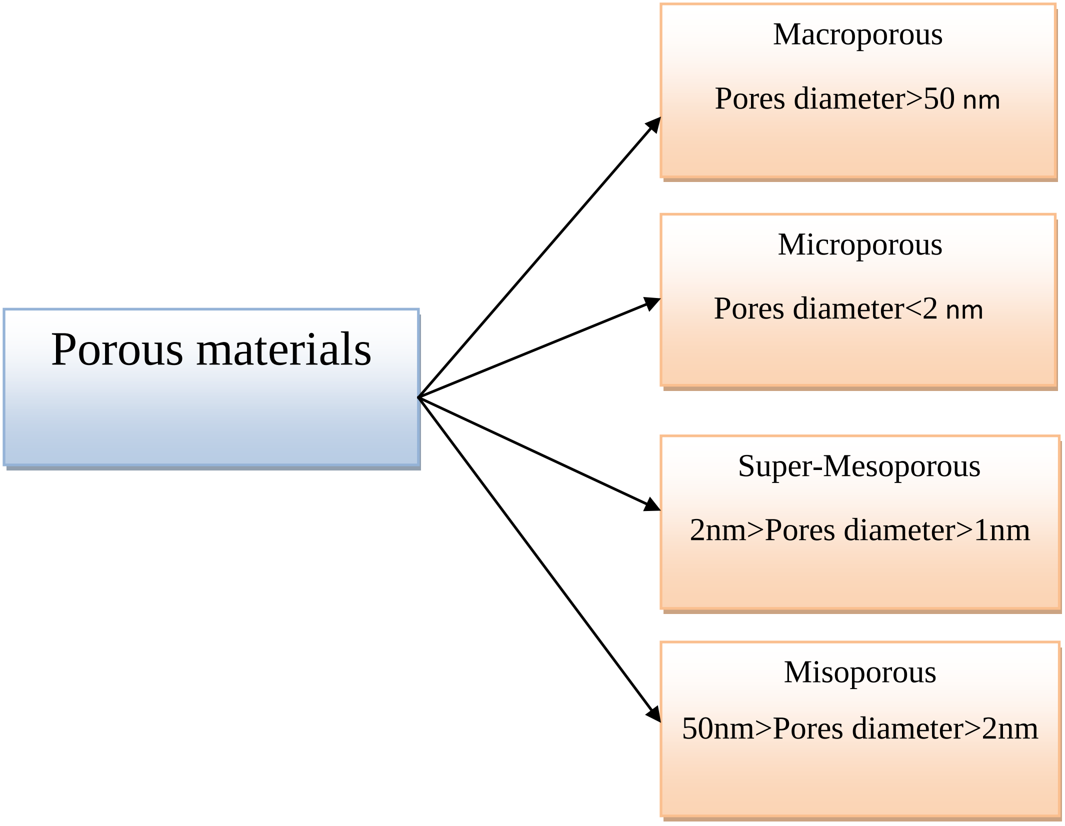


Figure 2-8, Porous materials classification

2.6.1.1 Porous carbons

Activated carbon (AC) is a joint name of porous carbons with high degree of porosity (500-1500 m2/g). It is obtained by gasifying the char using an oxidizing agent and the raw material of wood, peat, coal, fossil oil, char, bone, coconut shell or nut stone. It is usually applied in gas separation and liquid purification, and the potential of using it in adsorption refrigeration systems is promising too [29]. The adsorption heat of the activated carbon pairs is relatively low among the other types of physical adsorbent pairs (1800-2000 kJ/kg_{ads}). Its adsorption capacity is low (0.3-0.4 kg_{ref}/kg_{ads}) and has a weak polarity because the whole surface of activated carbon is also covered by an oxide matrix and some inorganic materials. There are many types of activated carbon, where Critoph et al studied the adsorption performance of 26 types of activated carbon with ammonia [30]. Activated carbon fibre (ACF) is a fibre form of activated carbon that has many advantages over activated carbon in terms of mass and heat transfer performance. Compared to activated carbon, ACF has a larger surface area and its pores are more uniform. The disadvantages of the activated carbon fibre are anisotropic thermal conductivity and high thermal resistance between the fibres and adsorbent-bed heat exchanger surface compared to activated carbon.

2.6.1.2 Mesoporous silicates

The most commonly used mesoporous silicates are the synthetic amorphous silica gel which consists of rigid and continuous net of colloidal silica connected to very small grains of hydrated SiO4. It retains chemically bonded traces of water (about 5%) and loses its adsorbitivity by overheating (above 120°C) due to loss of this bond . Silica gel porosity level is lower than activated carbon (100-1000 m2/g), but the adsorption heat is higher (2500- 2800 kJ/kg) [31]. Based on pore dimension there are two types of silica gel named; regular density (silica gel RD) of 2 nm pore diameter and low density (silica gel LD) 15-20 nm pore diameter. Silica gel has large adsorption ability and can be regenerated using low temperature sources (50-100°C), despite its low porosity level.

There are two types of porous materials in the same family of silica gel named; supermicroporous silica and silica aerogel [32]. Super-microporous or high density (HD) silica gel is a porous material of pore size 1-2nm. It steeply adsorbs water vapour at pressure ratio lower than 0.3 with negligible hysteresis, where it can be driven using lower generation temperature. Its maximum equilibrium uptake is 2.75 time of silica gel RD [33]. Silica aerogel is an exceptionally porous material with high porosity (1000 m2/g), low density

(0.003-0.35 g/cm3) and low thermal conductivity (0.014 W/mK). It is derived from a gel in which a liquid component of the gel has been replaced with a gas. Silica aerogel is unstable for long time application due to their fragility.

2.6.1.3 Zeolites

Zeolites are a crystalline microporous alumina silicate minerals and well known physical adsorbents. There are more than 180 types of zeolite frameworks and most of them adsorb water vapour with different capacity [34]. Zeolites hydrophilicity is related to the silicon / aluminium ratio, where the lower this ratio is the higher hydrophilicity is the zeolite. It adsorbs most of water vapor at low partial pressure. Zeolites have heat of adsorption of 3300-200kJ/kg, the regeneration temperature of 250-300˚C and can withstand high temperature treatment (up to 800˚C). Based on the aforementioned characteristics, zeolite is only applicable for systems where high generation temperature sources are available, but cannot be applied in low generation temperature applications.

2.6.1.4 Metalaluminophosphates

Examples of metalaluminophosphates are Silica-aluminophosphates (SAPOs) and aluminophosphates (AlPOs) have a pore system with three-dimensional networks similar to zeolites. These adsorbents have good water vapour adsorption and perform better than silica gel and zeolite. Many of the aluminophosphates exhibit good thermal stability against high temperature treatment as they undergo up to 400-600˚C during synthesis. These attractive features invited researchers to study the ability to be applied in adsorption refrigeration application, Henninger et al [35].

2.6.1.5 Metal organic framework

Metal organic frameworks (MOFs) are new micro-porous materials with exceptional high porosity, uniform pore size, well-defined molecular adsorption sites and large surface area (up to 5500m2/g) [36]. MOFs have two main components: the organic linkers considered as organic secondary building unit, act as struts that bridge metal centres known as inorganic primary building units and act as joints in the resulting MOF architecture. The two main components are connected to each other by coordination bonds, together with other intermolecular interactions, form a network with defined topology. MOFs are less hydrophilic than silica gel or zeolite and thus can release more water vapour at the same partial pressure [37]. The capability of using MOFs in adsorption refrigeration systems will be discussed in this thesis (chapter 7), where the adsorption characteristics of MOFs are studied.

2.6.2 Chemical adsorbents

Chemical adsorbent sorbs the adsorbate (refrigerant) chemically by Valence force, where one layer of refrigerant reacts with the surface molecules of the adsorbent. Chemical adsorbent sorbs more adsorbate at higher rate compared to physical adsorbent. Its stability is lower than a physical adsorbent, where chemical pair molecules never keep their original state which limits its practical applications. Chemical adsorbents suffer from swelling and agglomeration which negatively affect the heat and mass transfer performance, especially in Cycles those operate under low pressure [38]. Chemical adsorbents mainly include metal chlorides, metal hydrides and metal oxides.

2.6.2.1 Metal chlorides

Metal chlorides that are applied for adsorption refrigeration are calcium chloride, strontium chloride, barium chloride and magnesium chloride. Metal chlorides have high adsorption capacity (up to 1 kgref/kgads), but swelling and agglomeration are the main problems of metal chlorides. Calcium chloride has a good potential for use as solid chemical adsorbent for methanol and ethanol vapours, however ammonia is the usual refrigerant used with metal chlorides [29].

2.6.2.2 Salt and metal hydrides

Salt and metal hydrides used in adsorption refrigeration systems are lithium hydrides, calcium hydrides, covalent high polymerized hydrides and non-metal molecular hydrides. Salt and metal hydrides perform promisingly with hydrogen refrigerant. The cycle based on this pair is sensitive to the driving temperature where the COP changed from 0.2 to 0.45 with Increasing the heat source temperature from 120 to 160˚C [29].

2.6.2.3 Metal oxides

The metal oxides are usually employed as catalyst for oxidation and deoxidation reactions. Oxygen is the suitable refrigerant when the metal oxides are used as adsorbents. Metal oxides / oxygen pair is suitable for heat pumps with temperature below 120K because of the large enthalpy of reaction between oxides and oxygen [29]. Similar to most chemical adsorbents, metal oxides suffer from the swelling and agglomeration problems.

2.6.3 Chemical / Physical adsorbent composites

Adsorption and desorption are respectively exothermic and endothermic processes and the chemi-sorption heat is higher than the physi-sorption heat. Higher adsorption rate (kinetics) means more refrigerant flow rate and hence better cooling capacity. A chemical adsorbent using salt of poor heat and mass transfer due to low thermal conductivity and with agglomeration phenomenon is not practical especially in low pressure systems [17]. The aim of using composite adsorbents is to enhance the performance of physical adsorbents (increase the adsorption capacity) and avoid the aforementioned drawbacks of the chemical adsorbents (swelling, agglomeration and poor conductivity) [29]. Examples of composite adsorbents, the combination between metal chloride and activated carbon fibres, expanded graphite, silica gel or zeolite.

2.6.3.1 Hygroscopic salts/silica gel composites

Adding hygroscopic salts ($LiCl_2$, $LiBr_2$, $MgCl_2$, etc) to silica gel increases its water vapour adsorbitivity and avoids the problem of poor mass transfer due to swelling and agglomeration [39]. The adsorption characteristics of the silica gel composite adsorbents (selective water sorbents SWS) can be modified by changing the salt type and changing the percentage of salt in silica gel [40]. Higher salt amount increases the agglomeration possibility and decreases composite porosity; however it enhances the heat transfer in the bed and the adsorption capacity [41]. Using calcium chloride as a hygroscopic salt approximately doubles silica gel adsorption capacity and hence the adsorption refrigeration cycle [42].

2.6.3.2 Chlorides / porous media composite adsorbents

Adding chloride salts to expandable graphite, activated carbon, activated carbon fibre, zeolite and vermiculite is used to enhance these materials adsorbitivity. Chloride salts / expandable graphite composite showed enhanced heat and mass transfer performance without expansion during adsorption [43]. Impregnating activated carbon and activated carbon fibres with chloride salts enhanced the adsorption capacity (up to 95 kg_{ref}/kg_{ads}), but activated carbon performs better than activated carbon fibres in term of not separating from the salt [44]. The above mentioned composites utilized ammonia refrigerant. However, impregnation of zeolite with chloride salt showed unexpected low performance of water vapour adsorption [45].

2.7 Refrigerants

There are many refrigerants utilized in adsorption refrigeration systems, but the appropriate refrigerant need to be selected based on a number of considerations such as;

- Latent heat of vaporization: where the higher the refrigerant latent heats of vaporization, the better the performance of the cycle.
- Thermal stability: stable refrigerant thermophysical properties mean stable cycle over the operating temperature range.
- Environmental friendly: most of adsorption refrigeration cycles utilize environmentally friendly refrigerants with no ozone depletion and low global warming potential. Natural refrigerants such as water, ammonia are most commonly used ones.
- Flammability: some of the refrigerants utilized in adsorption refrigeration systems are flammable within certain concentration. The flammability issue should be taken into account especially when high generation temperature is used in the cycle.
- Toxicity: some of the refrigerants applied in adsorption refrigeration cycle are toxic and hence stringent safety measures should be implemented which may limit their application.
- Explosion: hydrogen refrigerant utilized with salts hydrides, it is an explosive one. This means more consideration and initial cost during manufacturing of such type of cycle.
- Compatibility: some refrigerants are corrosive and need special material of relatively high cost. Thus the machines cost increases limiting its market potential.

The optimum refrigerant is the one that satisfies the maximum number of consideration with high grade. The commonly applied refrigerants in adsorption cycles are water, ammonia, methanol and ethanol. Some other refrigerants are used in the adsorption technology, but not commercially applied such as hydrogen, oxygen, methyl alcohol, R134a, R22, R732 and R407.

2.8 Adsorption pairs

Evaluating adsorbent or adsorbate (refrigerant) independently is not sufficient, where adsorption characteristics vary based on adsorption pairs. Table 2-4 presents the characteristics of the most commonly used adsorption pairs based on the practical cyclic operating conditions [46-47].

The best adsorption pair is the one that satisfies the important requirements which differs depending on the application. Herein, a comparison has been made for the commonly used and applied adsorption pairs based on 16 criteria, Table 2-5. For each criterion the best adsorption pair is marked by 5 and the worst is marked by 1. The same weight is used for each criterion due to their equal importance. For example, complex manufacturing techniques influence the capital cost and hence the commercialization of the system. On the other hand, the temperature and quantity of energy required for adsorption influences the energy savings and the range of industries that can benefit from such systems. Therefore they should be equally weighted.

Table 2-4, Characteristics of commonly used adsorption pairs

Refrigerant characteristics		AC, ACF/ Ammonia	AC, ACF/ Methanol	AC, ACF/ Ethanol	AC, ACF/ 134a	Silica gel/ water	Zeolite/ water
Operating pressure		+Ve	Vacuum	Vacuum	+Ve	Vacuum	Vacuum
Generating temperature ˚C		80-200	80-100	80-120	80-100	50-100	250-300
Adsorption capacity kg$_{ref}$/kg$_{ads}$		0.29	0.45	0.19	0.36	0.30	0.17
Refrigerant boiling point ˚C		-34	65	79	-48	100	100
Refrigerant latent Heat of vaporization kJ/kg		1368	1102	842	217	2258	2258
Adsorption heat kJ/kg		1800-200	1800-2000	1200-1400	1830-2300	2500-2800	3200-4200
Cooling density	Cooling power	2000W/kg	140-500W/kg	--	--	190W/kg	90-150W/kg
	Cooling effect	--	--	118-159kJ/kg	57kJ/kg	--	--

Table 2-5, Evaluation of commonly used adsorption pairs

Criteria	AC, ACF/ Ammonia	AC, ACF/ Methanol	AC, ACF/ Ethanol	AC, ACF/ R134a	Silica-gel/ Water	Zeolites / Water
Adsorption rate	2.7	5	3.3	3.7	2.9	1
Adsorption heat	4	4	5	3.8	2.8	1
Desorption temperature	2.4	4	4	4.4	5	1
Maximum recovered temp.	5	1	2.4	4.7	3.2	3.2
Vaporization Latent heat	3.3	2.7	2.2	1	5	5
Manufacturing complexes	5	2.9	1.6	4.8	1	1
Thermal stability	5	1	5	5	5	5
ODP	5	5	5	5	5	5
GWP	5	5	5	1	5	5
Non-toxicity	1	4	4	5	5	5
Non-flammability	1	1	1	5	5	5
Non-explosive	2.2	1	1	1.9	5	5
Refrigerant compatibility	1	4	4	5	4	4
Refrigerant solidification	4.1	5	2.6	4.8	1	1
Average COP and SCE	1	3.9	4.4	1.2	5	5
Cost	3	3	3	3	5	4
Sum	50.7	52.5	53.5	59.3	62.7	56.2

Solid absorption refrigeration system has wide range of applications. A large body of experiments and numerical works on the various aspects of the intermittent system. Some of these are reviewed here.

2.9 Research papers review

Chinnapa et al. [48] [1961] a systematic investigation is attempted in this paper of the intermittent vapour absorption refrigeration cycle employing the refrigerant-absorbent combinations of ammonia water and ammonia-lithium nitrate. A description is given of the actual cycle, and the differences between the actual and theoretical cycles are traced together with the effects of these differences on the values of the coefficient of performance and the effective cooling per 1b of initial mass of the solution. A simplified approximate expression is given for the theoretical coefficient of performance of the ammonia-water system, as also expressions for the theoretical coefficient of performance of the ammonia-lithium nitrate system suitable for use with the corresponding data charts. Some comments are made regarding condenser performance and evaporator design.

Nielson et al. [49] [1981] made a critical survey of intermittent absorption system based on NH_3 -H_2 O, NH_3 –$LiNO_3$, NH_3 -$CaCl_2$ and NH_3 - $SrCl_2$ combinations. He concludes that the solid absorbents like $CaCl_2$ or $SrCl_2$ should be used for solar refrigeration. $CaCl_2$ exhibits the swelling during absorption and problem of particle migration.

A.V.Kuznetsov et al. [50] [1995] has developed a mathematical model of transport process in a metal hydride packed bed along with an analytical quantification of frequently used assumptions. The complete model takes into account heat transfer by conduction, convection, mass transfer, as well as reaction kinetics and convective interaction between fluid and the solid phase. By analyzing several frequently used assumptions, a system of useful and practical criteria is obtained. The criteria reveals when simplification of the model is possible. Specifically, criteria for validity of local thermal equilibrium, steady state approximation, negligible convective heat transfer compared to conductive heat transfer are established analytically.

M.Pons et al.[51] [1999] has carried out the comparison of thermodynamic performance of different types of sorption systems (liquid absorption, adsorption, ammonia salts and metal hydrides) for typical applications (deep-freezing, ice making air-conditioning and heat pumping) with either air cooled or water cooled heat sink. The results are given in terms of cooling coefficient of performance (COP), heating COP or coefficient of amplification (COA) for the heat pump, cooling (heating) power versus reactor volume or weight and thermodynamic efficiency. $LiBr_2$-water systems show the best result for air conditioning except when small units are required (metal hydride system leads to more compact unit) chemical reaction with ammonia salt show better result for deep freezing and adsorption for heat pumping. In the majority of the cases considered here, the liquid sorption systems have the best performance, in terms of COP, cooling/heating power or reduced volume. The exceptions correspond to the highest temperature rises when adsorption or Chemical reaction systems are advantageous or in the case of compact units where metal Hydride systems are suitable.

Kashiwagi et al. [52] [1999] has carried out both experimental and simulation analysis of the silica gel-water adsorption process in fin plate heat exchanger. It is not easy to estimate the concentration profile by experiment in adsorption cooling systems. Therefore a simulation model has been proposed to analyze the influence of combined heat and mass transfer during the adsorption process. Temperature profiles of adsorber have been calculated by using numerical method. A good agreement has been seen between experimental results and simulation data. Finally, concentration profiles have been calculated by using simulation method to analyze the mass transfer in the adsorbent heat exchangers and a performance comparison is made between the two heat exchangers. The work would provide fundamental understanding of silica gel-water adsorption process and this gives useful guidelines in the design of adsorption reactors.

A.Freni et al. [53] [2001] has investigated the heat and mass transfer properties of a new zeolite coated adsorbent bed to be employed in sorption air conditioning systems by a modelling approach. It consists of a dynamic model which allows calculating the exchanged energy, the cycle time and thus the specific power of the bed. In fact the global heat transfer coefficient of the adsorber was very low because of the low thermal conductivity of the porous material employed and also because of the poor thermal contact among the adsorbent grains and between the particles and the surface of heat exchanger. For the above mentioned reason in this study a different original solution developed at CNR-ITAE is presented; it consists of an adsorbent coating (zeolite-based) firmly bound to the metal of the heat exchanger. The preparation process consists of several steps. Initially, an aqueous solution of zeolite powder and an inorganic binder (alumina gel precipitated in situ) are homogenized. After wards, the slurry is layered on the metal support, properly pre-treated, in order to obtain a homogeneous coating of the desired thickness. A final thermal treatment in air allows the stabilization of the adsorbent. This configuration of the adsorbent bed allow to obtain a slight increase of the thermal conductivity of the adsorbent and a strong rise of the metal/adsorbent wall heat transfer coefficient .To demonstrate these features, a mathematical model for the study of the heat and mass transfer in dynamic condition is developed. The results of the simulations of different types of adsorbent bed, show that the new bed proposed allows to obtain the highest

Specific power of the adsorption cooling device.

Li Yong et al. [54] [2006] the adsorption refrigeration is based on the evaporation and condensation of a refrigerant combined with adsorption or chemical reaction. The soaring fossil fuel price and the awareness of environmental problems offer many potential applications to thermal powered adsorption cooling. However, the adsorption cooling machines still have some disadvantages that hinder their wide application. This paper reviews more than 100 patents filed mainly since year 2000 that propose technologies to improve adsorption system and make it become a realistic alternative. The patents surveyed are classified into four main groups: adsorption system development, adsorbent bed innovation, adsorbent/adsorbate material development and novel application of adsorption cooling system. The various technology options are discussed and evaluated. “Hot spots” and key inventors/applicants are identified. An assessment is made about current and future development of adsorption refrigeration technologies.

Zbigniew Królicki, et al. [**55] [2006]** the concept of using solar energy as a power source of a refrigeration system arose 40 years ago. There are conventional refrigerators powered by photovoltaic cells, as well as heat powered machines, which work either in a liquid or solid sorption cycle. Recently feasibility of solar radiation utilization is the solid adsorption system has been discovered. This paper presents the description and operation of a solar-powered refrigeration and heat pump system based on phenomena of alternate adsorption and desorption. It may be put into effect in the special construction solar collector. Various devices using solid adsorption pair of activated carbon / methanol and zeolite / water have been analyzed. The performance of an adsorption refrigeration and heat pump system is controlled by many parameters such as refrigerant, adsorbent thermophysical properties, system design and operating conditions. Based on the results of thermodynamic analysis the performances as well as the amount of useful heat for activated carbon / methanol and zeolite / water have been presented.

C. Rivera, et al. [56] [2007] an experimental intermittent thermochemical refrigeration system operating with barium chloride–ammonia reaction is described. The barium chloride is used as solid absorbent and ammonia as refrigerant. The equipment components and the experimental preliminary results are also presented. The temperature range of the heating fluid from 70 to 95°C was established. The main results showed that the generation temperature was 53°C for a condensation temperature of 23°C. In the evaporation–absorption process, the evaporating temperature was between −10 and 0°C. The results showed the technical feasibility to operate this refrigeration system with low cost solar flat plate collectors in remote areas.

Y. Zhong et al. [57] [2007] Chemisorptions could be useful in adsorption systems due to the large concentration change compared with physisorption. Equilibrium concentration characteristics of ammonia with a composite adsorbent material ($BaCl_2$ impregnated into a vermiculite matrix) are investigated: the maximum concentration is about 0.4 kg ammonia/kg adsorbent. Hysteresis was observed between the synthesis and the decomposition reactions. The analysis of the data suggests that the hysteresis could be due to the dimensional changes of the solid during the reactions. The bi-variant behaviour observed was contrary to the mono-variant behaviour anticipated and the reasons are discussed. The COP of a basic adsorption cycle for typical ice-making and air-conditioning applications utilizing ammonia and the composite material were calculated. The results show that the material could be used for air-conditioning or other refrigeration applications. The COP could reach up to 0.6 at typical conditions (Tev = 15°C, Tcon = 35°C).

L.W. Wang et al. [58] [2007] Solid sorption refrigeration is a type of environmental benign and energy saving technology and the sorbents utilized can be divided into physical, chemical and composite sorbents, according to the nature of the forces involved in the adsorption process. The types, characteristics, advantages and disadvantages of different adsorbents, refrigerants and working pairs are summarized in this paper, together with the models that describe the adsorption equilibrium. Moreover, some of the procedures to prepare composite adsorbents are presented. The application of different working pairs for different situations is related with the adsorption heat, the adaptability to the driving temperature and to the desired working pressure. The methods to measure the adsorption quantity of different working pairs are compared, and future research directions of adsorption working pairs are also analyzed.

Z.Tamainot-Telto et al. [59] [2009] has carried out a study on carbon-ammonia pairs for adsorption refrigeration to select an optimum adsorbent and refrigerant pair in respect of chosen figure of merit that could be the cooling production (MJ m^{-3}), the heating production (MJ m^{-3}) or the coefficient of performance (COP). The simulation results of 26 various activated carbon-ammonia pairs for three cycles (single-bed, two-bed and infinite number of beds) are presented at typical conditions for ice making, air conditioning and heat pumping applications. The driving temperature varies from 80°C to 200°C .The carbon adsorbents investigated are mainly coconut shell and coal based types in multiple forms: monolithic, granular, compacted granular, fiber, compacted fiber, cloth, compacted cloth and powder. Considering a two-bed cycle, the best performances based on power density are obtained with the monolithic carbon KOH-AC, with driving temperature of 100°C; the cooling production is about 66 MJ m^{-3} (COP=0.45) and 151 MJ m^{-3} (COP=0.61) for ice making and air conditioning respectively. The heating production is about 236 MJ m^{-3} (COP=1.50).

J.V. Veselovskaya et al. [60] [2010] a composite adsorbent composed of BaCl2 impregnated into expanded vermiculite has been synthesized and tested in a laboratory scale adsorption chiller. Previous work has established the promising theoretical performance of this adsorbent with ammonia as a refrigerant, in terms of equilibrium uptake, suitable equilibrium temperatures for use in air conditioning applications and good reaction dynamics. Analysis of the adsorption phase revealed a simple exponential approach to equilibrium uptake which was not previously observed in larger scale experiments. It was demonstrated that this material can provide effective operation of the chiller using a low potential heat source (80–90 C) giving COP as high as 0.54 ± 0.01 and SCP ranging from 300 to 680 W/kg. The specific cooling power depends strongly on the driving temperature difference and the cycle duration.

Alessio Sapienza et al. [61] [2012] this paper aims to present a new composite sorbent, specifically developed at BIC-RAS to operate at low regeneration temperature (<70°C), and its testing by a lab-scale adsorption chiller installed at ITAE-CNR. Adsorption equilibrium measurements demonstrated that the new composite, $LiNO_3$/vermiculite, named SWS-9V, exchanges app. 0.4 g H_2O/g in an exceptionally narrow temperature range, 33-36°C (adsorption at 12.6 mbar) and 62-65°C (desorption at 56.2 mbar), corresponding to a remarkable heat storage capacity (0.9 MJ/kg). The new sorbent, embedded into an adsorber, was tested at ITAE with the aim to optimize the cycle taking into account both the thermodynamic and kinetic properties of SWS-9V. The results demonstrated that the optimal cycle performance, for given operating conditions, are strongly dependent on the cycle time (s) and the relative duration (R) of the isobaric adsorption and desorption steps. Indeed, at Tc = 35°C, Te = 10°C and high driving temperature (T_d = 90°C), the system provided the best performance at s ¼ 20 min delivering about 230 W/kg of specific cooling power (SCP) with a coefficient of performance (COP) equal to 0.66 when the adsorption duration is 7 times longer than the desorption one (R = 7). Differently, at low driving temperature (T_d = 68°C), the best performance (COP = 0.59 and SCP =96 W/kg) were obtained at Ts = 30 min, protracting the duration of the desorption step at the expenses of the adsorption one (R = 0.75).

Y. Alyousef et al. [62] [2011] three adsorbers' solar cooler was experimentally investigated. Ammonia was chosen as a working fluid. Two adsorbers (twins) were filled with the same complex compound (activated carbon fiber with $MnCl_2$ microcrystal's on the filament surface). The third low temperature adsorber has second complex compound (activated carbon fiber with $BaCl_2$ microcrystal's on the filament surface). The cycle of physical adsorption and chemical reactions in the sorbent bed of adsorber was followed by condensation/evaporation of ammonia inside the pores. This combination of adsorption/condensation and evaporation/desorption is a novelty of cooler design, which increases the heat and cold generation in adsorber. The specific feature of third adsorber is the time of its cold generation. This time includes the liquid evaporation and desorption/regeneration time of ammonia in the sorbent bed. The cooler thermal management is based on heat pipes. The solar heating is a source of energy for cooler. The sink of the cold is the air flow.

Janna V. Veselovskaya et al. [63] [2012] the dynamics of ammonia sorption was investigated by means of a Large Temperature Jump (LTJ) method for loose grains of "$BaCl_2$/vermiculite" and "$BaCl_2$/$BaBr_2$/vermiculite" composites which are promising materials for adsorption air-conditioning. The influence of the grain size, the adsorbent composition and the adsorbent load was studied. The heat transfer coefficients were calculated for adsorbents with different grain sizes. The results of LTJ experiments were used for modelling the adsorption air-conditioning cycle operating in the cyclic steady state mode. The potential of using a proper ratio of durations for the adsorption and desorption stages of the cycle along with a harmonization of the driving forces for the enhancement the dynamic performance of the adsorption chiller was discussed. Appropriate recommendations on optimization of the adsorbent composition and load were made.

The literature survey reveals the general interest in solid sorption systems for various applications. It also shows the areas that need attention for improving system performance. It is seen that compared to other working materials, studies on solid sorption systems that use NH_3 as refrigerant and either $BaCl_2$ or $SrCl_2$ as absorbents are relatively scarce, even though they exhibit some important advantages over other systems. Hence in the present study analysis of $BaCl_2$-NH_3 and $SrCl_2$-NH_3 systems are carried out.

CHAPTER-3 THERMODYNAMIC ANALYSIS

3.1 Basic principle of operation

Ability of a solid medium to absorb and generate specific vapors depending on its temperature constitutes the basis of the absorption refrigeration system. The solid which absorbs is called absorbent and the vapor which gets absorbed is called absorbate. Some of the important absorbent and absorbate pair are

1. $BaCl_2$-NH_3
2. $SrCl_2$-NH_3
3. $CaCl_2$-NH_3
4. $MnCl_2$-NH_3

The system as shown in Fig 3.1 consists of three components, reactor, condenser, and evaporator. The reactor contains closely packed salt bed. It is an intermittent process. The reactor behaves as generator/absorber alternatively. In the present case solid $BaCl_2$ and $SrCl_2$ are considered as the absorbent and ammonia is the refrigerant (absorbate).

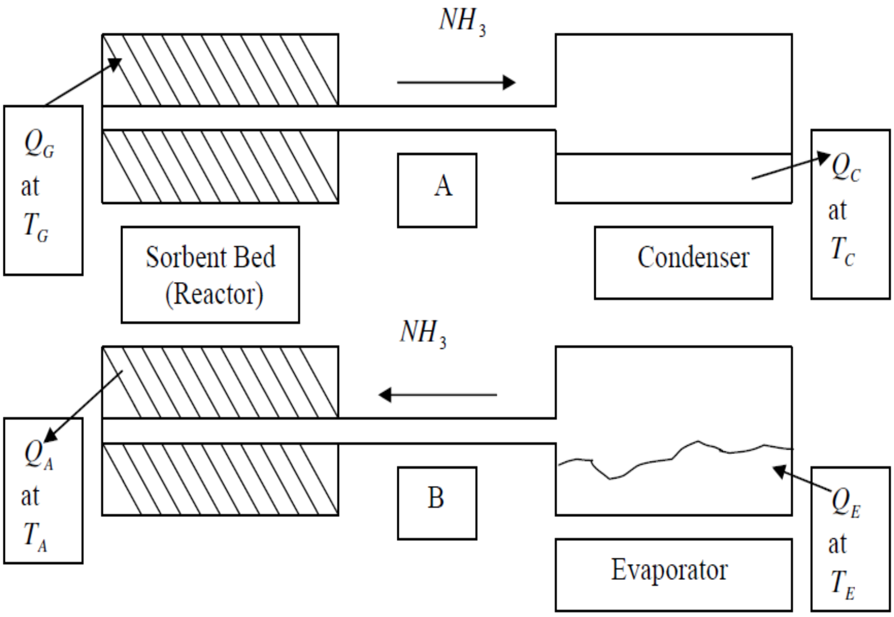


Fig 3.1 System schematic

Imagine initially the reactor contains the salt saturated with ammonia at ambient temperature (say 30° C) and low pressure about 3atm. The condenser is empty. First the reactor is heated sensibly from ambient temperature to T_G (about 80° C) while the condenser is kept at 30° C This cause the pressure to rise to about 12 bars, and ammonia to desorbed from the reactor. After sensible heating to T_G heat is added further to begin release of NH3. This process has been shown by in the schematic and lnP -1/T diagram (Figs. 3.2, 3.3). As both the absorbent bed and condenser are connected by a pipe both are at 12 bar pressure. But Condenser is maintained at 30°C.The saturation temperature corresponding to 12 bar pressure, 30.9°C which is slightly more than T_C. So as soon as the desorbed ammonia goes to condenser it gets condensed at T_C. The condensation heat is released to the sink. To produce refrigeration effect the reactor is now cooled from T_G to T_A. When the sorbent bed is cooled from T_G to T_A, due to reduction in pressure and as some of the ammonia gets evaporated from the condenser taking latent heat of vaporization from the remaining liquid refrigerant. So the temperature of the condenser reduces from T_C to T_E so the pressure reduces to about 3atm and cause the liquid ammonia in the evaporator to boil at T_E taking heat from the refrigerated space. The ammonia vapor is reabsorbed in the reactor. This process has been shown by B both in schematic and lnP-1/T diagram. Since absorption of NH_3 by absorbent is exothermic, heat generated is rejected to the sink. When the liquid ammonia is used up the evaporator returns to ambient temperature and initial state of the system.

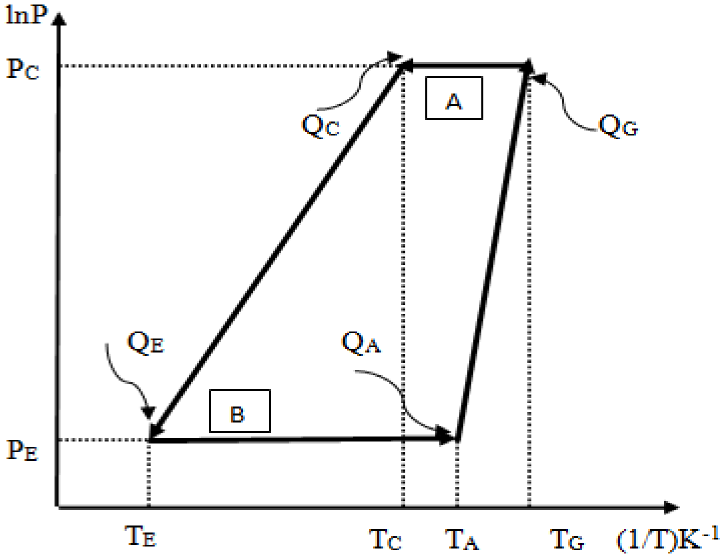


Fig. 3.2: lnP vs.-1/T diagram for $BaCl_2$ - NH_3 system

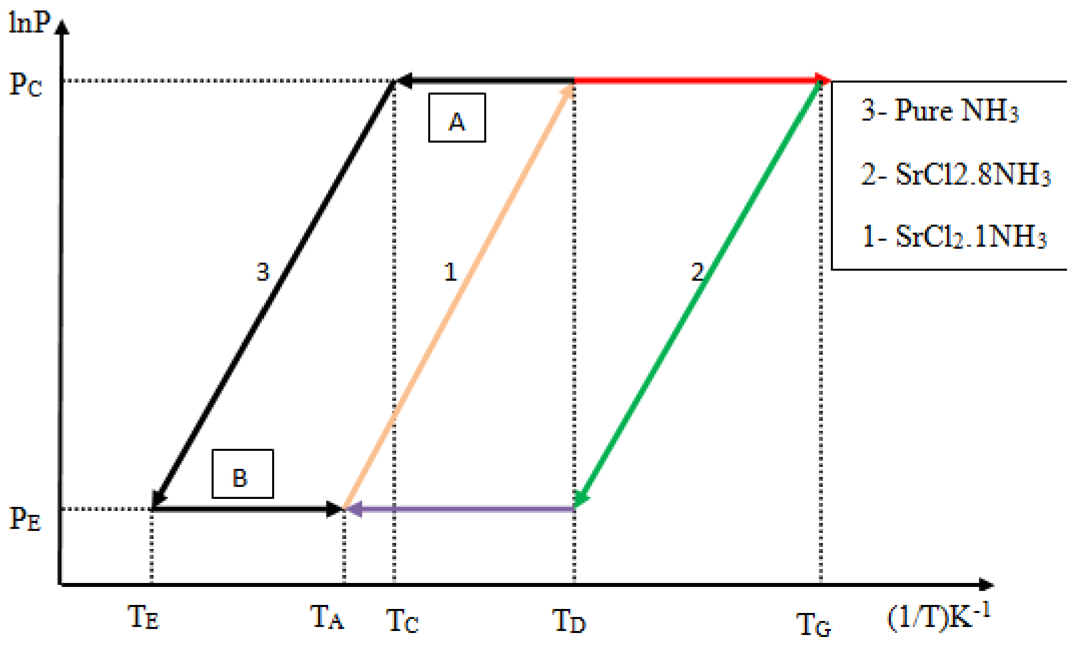


Fig. 3.3: lnP vs.-1/T diagram for $SrCl_2$ -NH_3 system

Referring to the system schematic Fig 3.1 and the lnPvs.-1/T diagram as shown in the figure 3.2 and 3.3 for two different salts, all the processes of the cycle are analyzed here.

3.2 Assumptions

1. Ammonia vapor is assumed to be ideal.
2. Reactor is assumed to be made of stainless steel.
3. Unless otherwise specified the specific heats of different materials like salt, Refrigerant, reactor material etc are assumed to be constant.
4. There is a pressure loss of 0.1bar between different components.

3.3 Calculation of the coefficient of performance (COP):

From the energy balance equations for a single stage solid absorption refrigeration cycle:

$$Q_G+Q_E=Q_C+Q_A \qquad (3.1)$$

Where Q_G, Q_E, Q_C and Q_A are the generation, evaporation, condensation and absorption heats respectively. It is possible to establish a relation that will allow the evaluation of the thermal behaviour of the cycle:

$$COP = \frac{Q_E}{Q_G} \qquad (3.2)$$

$$COP_C = \frac{T_E}{T_C - T_E} \times \frac{T_G - T_C}{T_G} \quad (3.3)$$

In the present study results from thermodynamic analysis are obtained for two systems:

(i) $BaCl_2$ - NH_3

(ii) $SrCl_2$ - NH_3.

3.4 Thermochemical system: barium chloride–ammonia

The chemical reaction between barium chloride and ammonia is represented by following equilibrium relation [56].

$$BaCl_2 .8NH_3 \leftrightarrow BaCl_2 + 8NH_3 \quad (3.4)$$

In this case, during the dissociation period, in stage one, 8 mole of ammonia for each mole of barium chloride can be recuperated. The vapor pressure as a function of temperature is represented by the following relation with pressure in bar and temperature in Kelvin (K) [56].

$$\text{Ln}\,(P \times 10^5) = 29.3 - \frac{5017}{T} \quad (3.5)$$

With the heat of reaction:

$\Delta H = 41.7$ kJ mol^{-1}

NH_3 (liquid) $\leftrightarrow 2NH_3$ (vapour)

For the ammonia equilibrium the vapour pressure is represented by [56].

$$\text{Ln}\,(P) = 11.676 - \frac{2793.3}{T} \quad (3.6)$$

Where the pressure P is expressed in Pa and temperature T in K,

Referring to the figure 1.2 for the process A (desorption).

$Q_G = M_{NH_3} \times \Delta H + \sum m_i C_i \ (T_G - T_A)$ (3.7)

During evaporation.

$Q_E = M_{NH_3} \times (h_2 - h_1) - C_{NH_3} \times (T_C - T_E) - M_{REA} \times C_{REA} \times (T_C - T_E)$ (3.8)

$$\text{COP} = \frac{Q_E}{Q_G} = \frac{M_{NH_3} \times (h_2 - h_1) - C_{NH_3} \times (T_C - T_E) - M_{REA} \times C_{REA} \times (T_C - T_E)}{M_{NH_3} \times \Delta H + \sum m_i C_i (T_G - T_A)} \qquad (3.9)$$

3.5 Thermochemical system: $SrCl_2$-NH_3

The chemical reaction between $SrCl_2$ and ammonia is represented by the following equilibrium relation [57].

$$\underset{(X)}{SrCl_2\,8NH_3} \leftrightarrow \underset{(Y)}{SrCl_2.1NH_3} + \underset{(Z)}{7NH_3} \qquad (3.10)$$

In this case one mole of $SrCl_2$ can absorb 8 moles of NH_3, but generate/desorbs only 7 moles under the design condition of the system. So one mole always remain absorbed in $SrCl_2$. referring to the Fig1.3 the vapor pressure as function of temperature can be represented by the following equation with pressure in bar and temperature in Kelvin (K)[57].

(Equilibrium equation for $SrCl_2$ $8NH_3$)

$$\text{Ln (P)} = 15.6229 - \frac{4692.41371}{T} \qquad (3.11)$$

(Equilibrium equation for $SrCl_2 1NH_3$)

$$\text{Ln (P)} = 17.67.67906 - \frac{5786.85423}{T} \qquad (3.12)$$

Heat of reaction: $\Delta H = (46.2251 - 0.0976(T_G - 273)) \times 58.819$ kJ/kg of NH_3

In the above equation T_G is the generation temperature expressed in Kelvin (K). Specific heat of composition (X) that is $SrCl_2.8NH_3$ and that of composition (Y) that is $SrCl_2.1NH_3$ are presented by the equations (3.13) and (3.14)[57].

$C_X = (576.296 + (3.124 \times (T-273) + 0.07(T-273)^2) + 0.00005(T-273)^3)/1000$ kJ/kg K (3.13)

$C_Y = (649.8 + (3.524 \times (T-273) + 0.021(T-273)^2) + 0.00016(T-273)^3)/1000$ kJ/kg K (3.14)

Referring to the figure 1.3 for the process A (desorption).

$$Q_E = M_{NH3} \times (h_2 - h_1) - C_{NH3} \times (T_C - T_E) - M_{REA} \times C_{REA} \times (T_C - T_E) \quad (3.15)$$

$$Q_G = M_X \times C_X \times (T_D - T_A) + M_Y \times C_Y \times (T_G - T_D) + M_{NH3} \times \Delta H + M_{REA} \times C_{REA} \times (T_G - T_A) \quad (3.16)$$

$$COP = \frac{M_{NH_3} \times (h_2 - h_1) - C_{NH_3} \times (T_C - T_E) - M_{REA} \times C_{REA} \times (T_C - T_E)}{M_X \times C_X \times (T_D - T_A) + M_Y \times C_Y \times (T_G - T_D) + M_{NH_3} \times \Delta H + M_{REA} \times C_{REA} \times (T_G - T_A)} \quad (3.17)$$

3.6 Input data

Input data for both the system is shown by the table1 as follows.

Table 3-1, Input data for $BaCl_2$-NH_3 & $SrCl_2$-NH_3 systems

SI. NO	NAME	SYMBOL	VALUE
1	Mass of ammonia transferred	M_{NH_3}	1 Kg
2	Molecular weight of $BaCl_2$ salt	M_{BaCl_2}	208.2324 kg/k mol.
3	Mass of the reactor	M_{REA}	1.26 kg
4	Ratio of mass of reactor material to that of absorbent bed	m_r	0.5
5	Specific heat of ammonia vapor	C_{NH_3}	4.635 kJ/kg K
6	Specific heat of rector material	C_{REA}	0.46 kJ/kg K
7	Specific heat of the salt $BaCl_2$	C_{BaCl_2}	0.341 kJ/kg K
8	Molecular weight of strontium chloride salt	M_{SrCl_2}	158.62 kg/k mol.
9	The range of the evaporator temperature	T_E	258K-285K

CHAPTER-4 RESULT AND DISCUSSION

4. 1 Result and Discussion:

Figure 4.1 obtained from the result in (APPENDIX A.1&A.2) shows the variation of condenser and generator temperature with evaporator temperature for (m_r = 0.5). As evaporator temperature increases there is increase in evaporator pressure. As evaporator is connected to the absorber, absorber pressure also increases resulting in increase in absorber temperature. As both absorber and condenser are rejecting heat to same heat sink we have taken condenser temperature to be equal to absorber temperature so condenser temperature also increases. As condenser temperature increases, condenser pressure also increases. Condenser is connected to the generator so generator pressure also increases resulting in increase in generator temperature. So from the figure 4.1 it is clear the variation of the condenser temperature and the generator temperature for the different solid adsorbent salt $BaCl_2$ and $SrCl_2$.For the same condenser temperature and the generator temperature of $SrCl_2$ system is more than that of $BaCl_2$ system. In the figure 4.1 it clear that the temperature difference (T_G-T_C) for $SrCl_2$ is greater than the temperature difference for $BaCl_2$. So from this figure we come to know that $BaCl_2$ system requires lower heat source temperature compared to $SrCl_2$ system.

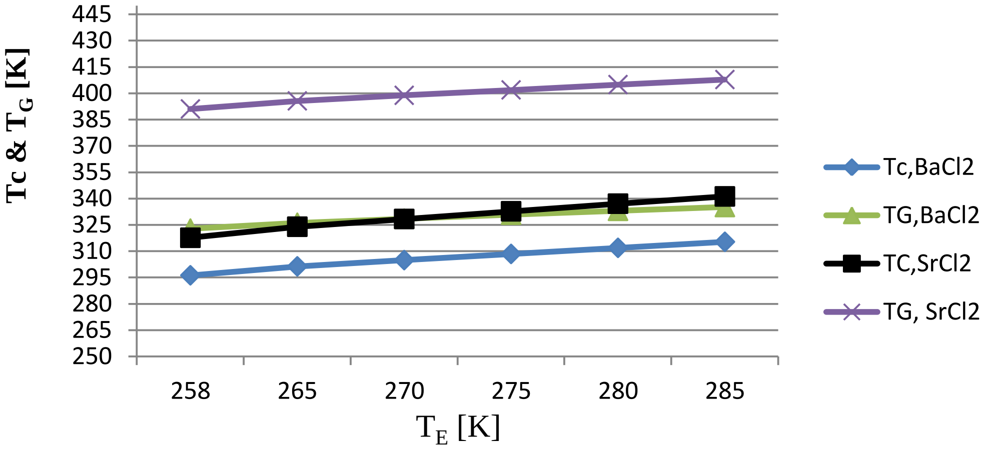


Figure 4.1 Variation of condenser and generator temperature with evaporator temperature

Figure 4.2 obtained from the result in (APPENDIX A.1&A.2) shows the variation of COP with evaporator temperature for m_r =.5. From the figure it is clear that with increase of evaporator temperature there is increase in COP because with increase of evaporator temperature although there is decrease in (T_C - T_E) and (T_G - T_A) but the reduction in Q_E= (h_2-h_1) is more for both the system. From the figure it is clear that for the same evaporator temperature COP of $SrCl_2$ system is more compared to $BaCl_2$ system because for the given range of the evaporator temperature the enthalpy of reaction for $SrCl_2$ system is less than that of $BaCl_2$ system. In case of $BaCl_2$ system COP varies from 0.424788-0.447282 and for $SrCl_2$ it varies from 0.42731-0.449309 for the given range of T_E. It is clear from the figure that $BaCl_2$, salt yields marginally lower COPs compared to $SrCl_2$ system and the required heat sink temperatures are also lower for $BaCl_2$ system compared to $SrCl_2$ system. It is preferable to use $BaCl_2$ salt for solid absorption system because barium chloride salt is cheaper than $SrCl_2$ salt.

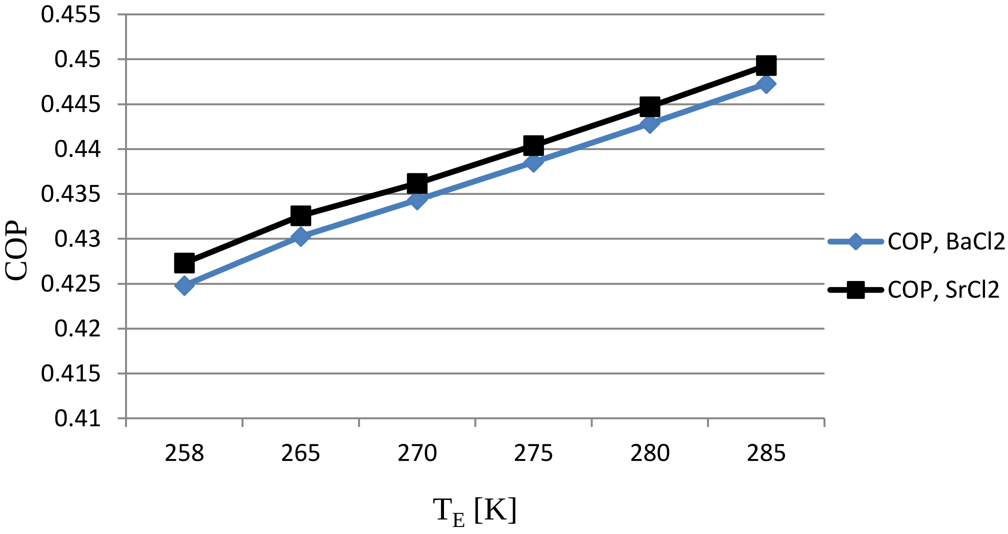


Figure 4.2 variation of COP with evaporator temperature

Figure 4.3 obtained from the result in (APPENDIX A.1&A.2) shows the variation of second law COP with evaporator temperature for m_r =.5. From the figure it is clear that for a given evaporator temperature the Second law COP is less for $SrCl_2$ system as ΔT = (T_G -T_A) is more for the $SrCl_2$ system than that of $BaCl_2$ system. In case of $BaCl_2$ system second law

COP varies from 0.55674-0.5569 and for $SrCl_2$ system it varies from 0.0972-0.111796 when T_E varies from 258K-285K.

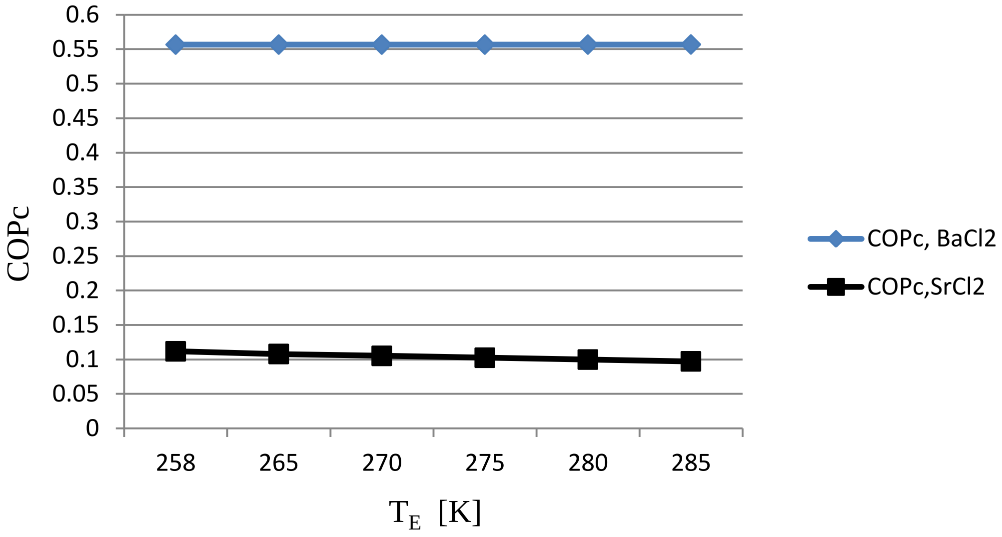


Figure 4.3Variation of second law COP_C with evaporator temperature

For extreme climate conditions in tropical areas with ambient temperatures between 30°C and 40°C and for temperatures for ice formation of -10°C, the COP oscillates between 0.40 and 0.45 with minimum temperatures in the desorber between 50°C and 63°C. Based on the thermodynamic model, coefficient of performance and useful heat for $BaCl_2$ and $SrCl_2$ working pairs has been calculated for different operating conditions and the results are shown in (Appendix A.1&A.2). The COP for both the system will varies same manner .Figure 4.4 &4.5 show that $BaCl_2$ Pair is better than the $SrCl_2$ because $BaCl_2$ decomposed easily at low temperature (T_D= 322.18K) and the $SrCl_2$ starts to decomposed at the higher temperature (T_D= 368.26K) when the evaporator maintains at the (T_E= 258K).while the COP of $BaCl_2$ is near about the COP of $SrCl_2$.

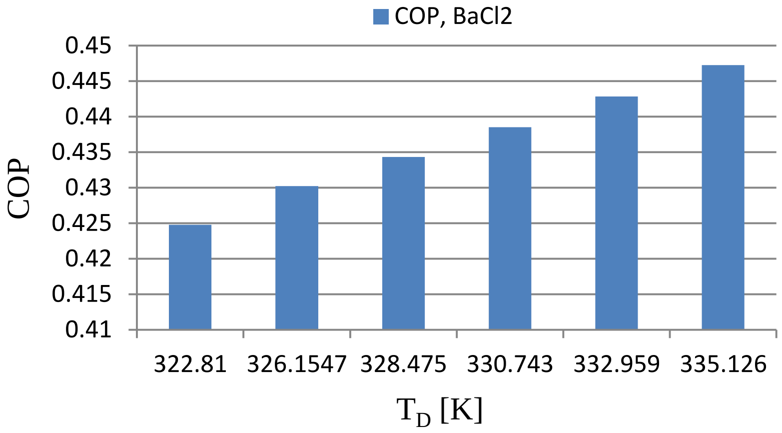


Figure 4.4 influence of the maximum desorption temperature on the COP

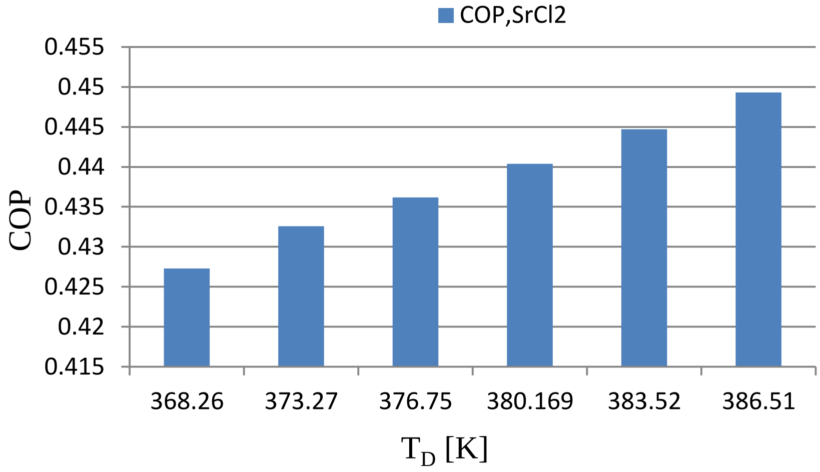


Figure 4.5 influence of the maximum desorption temperature on the COP

Figure 4.6 &4.7 obtained from the result in (APPENDIX A.1&A.2) shows the variation of heat exchanged in evaporator with desorption temperature. it is clear from the figure that the heat exchange for $BaCl_2$ is larger at the small value of the desorption temperature in comparison of $SrCl_2$ .the minimum and maximum value of heat exchanged in evaporator for $BaCl_2$ are 1106.82 and 1148.05 kJ/kg. The minimum and maximum value of heat exchanged in evaporator for $SrCl_2$ is 997.74 and 1015.525 kJ/kg. So the $BaCl_2$ system is better than the $SrCl_2$ system.

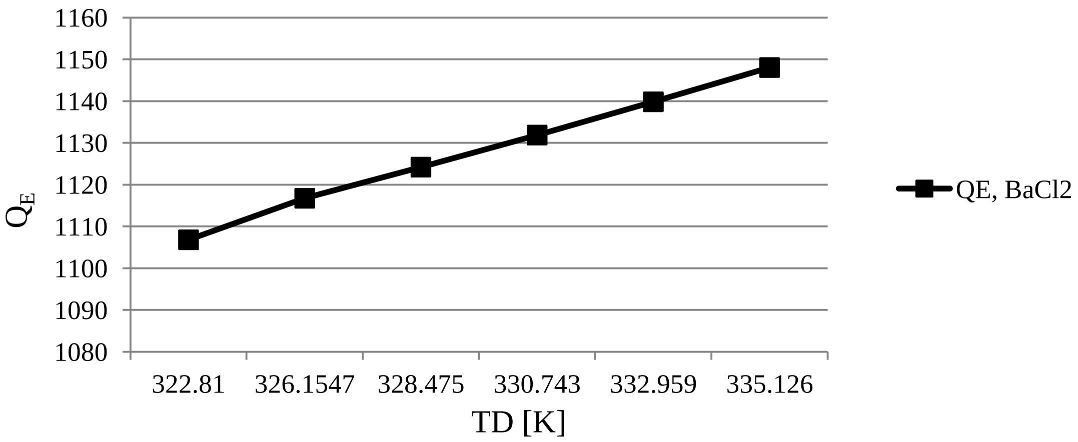


Figure 4.6 variation of heat exchanged in evaporator with desorption temperature for $BaCl_2$

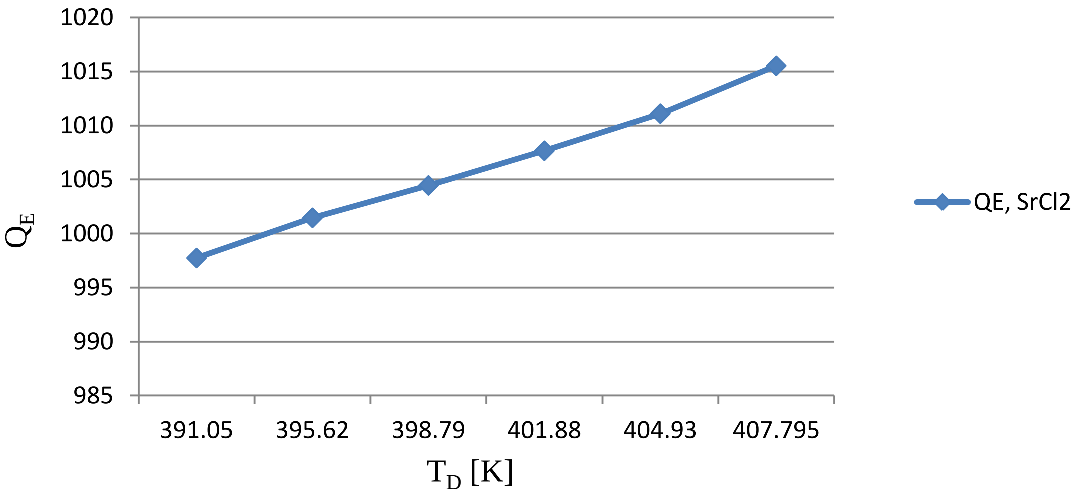


Figure 4.7 variation of heat exchanged in evaporator with desorption temperature for $SrCl_2$

Figure 4.8 and 4.9 obtained from the result shown in (Appendix A.3&A.4) represent the variations of the coefficient of performance in relation to the evaporation and condensation temperature is from 20°C to 40°C, taken every 5°C and the evaporation from -20°C to 10°C, taken every 5°C. For the $BaCl_2$ salt it clear from the figure that the COP of the salt will varies linearly as a straight line corresponding to the different evaporation temperatures. The COP difference for two temperature difference of condenser as 5°C will be almost same from the beginning to the end corresponding to the evaporator temperature from -20°C to 10°C.

In figure 4.8 it can be observed that COP increase when the evaporation temperature rises and the condensation temperature decreases. The maximum value of COP is 0.448 corresponds to T_E of 10°C and to T_C of 20°C. For the dominion of operation temperature, the COP varies from .39 to .448. It is possible that the increase of the COP depends more on T_C than on T_E.

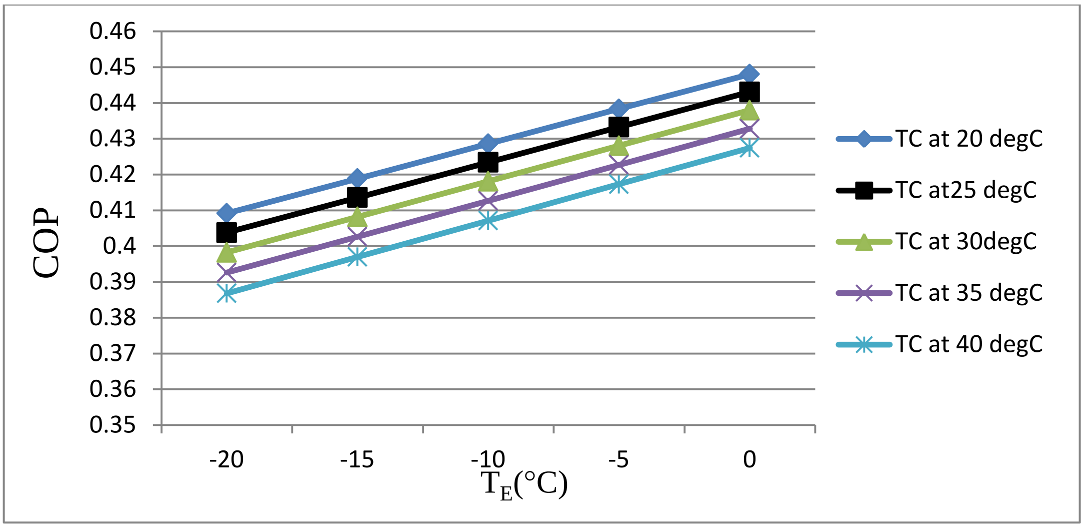


Figure 4.8 Evolution of the COP as a function of the evaporator temperature

Figure 4.9 shows that COP decreases when T_C increase and T_E decreases. In this case COP depends less on T_E. For this specific case, COP varied between 0.38 and .467.

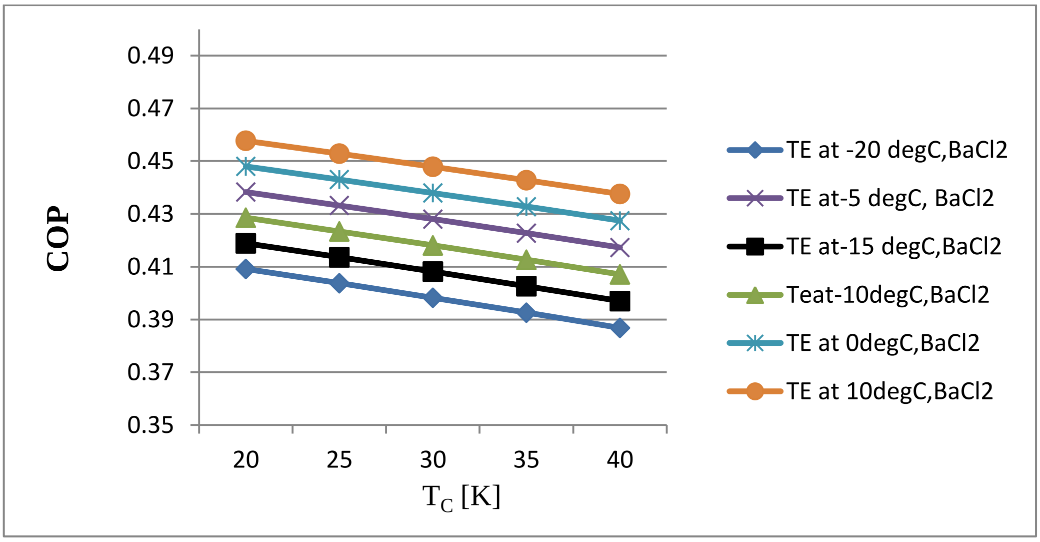


Figure 4.9 Evolution of the COP as a function of the condenser temperature

Figure 4.10 shows the variation of COP with m_r. from the figure it is clear that with increase of m_r there is decrease in COP but it is more sensitive in $SrCl_2$ system because $\Delta T = T_G - T_A$ is more for the $SrCl_2$ system. Figure also shows that the COP difference for both the salt is very close for m_r = .5 and the difference varies when the value of m_r increases. So m_r =.5 is the more suitable value for both the reactors.

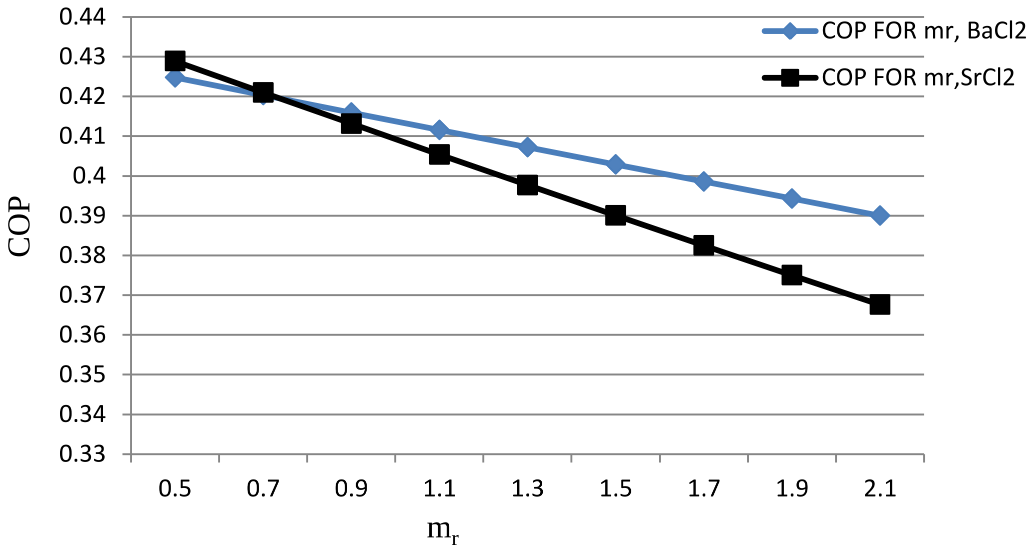


Figure 4.10 variation of COP with m_r

So from the thermodynamic analysis we come to know that $BaCl_2$ system requires lower heat source temperature compared to $SrCl_2$ system. Also it has higher second law COP. The barium chloride salt is cheaper than the $SrCl_2$ salt. Hence it is preferable to use $BaCl_2$ salt for solid absorption system even though it yields marginally lower COPs compared to $SrCl_2$ system and the required heat sink temperatures are also lower for $BaCl_2$ system compared to $SrCl_2$ system. However, in tropical countries where the ambient temperatures are high, and /or when lower refrigeration temperatures are required for a given heat sink temperature, $SrCl_2$ may be preferable to $BaCl_2$.

CHAPTER 5: CONCLUSIONS AND FUTURE WORK

5.1 Introduction

Adsorption cooling systems have received significant interest during the last few decades in order to satisfy the market demand of cooling systems and cope with the current environmental issues. This thesis investigates theoretically the performance of $BaCl_2$ and $SrCl_2$ /ammonia adsorption cooling systems. It also evaluates the effect of various physical parameters on the cooling load and the coefficient of performance of the adsorption cooling systems. The effects of enhancing the adsorber bed through adding metal particles and eliminating contact resistance between the adsorbent beds.

5.2 Conclusions

This M.Tech project was set out to bridge the gap between the theoretical ideas of enhancing adsorption cooling systems and their practicality. To achieve that, a novel lumped analytical Simulation model for a commercialised $BaCl_2$ adsorption chiller is to be used as performance evaluation tools. Three main objectives have been achieved; (1) the investigation of different operating conditions effect on the adsorbent-bed and chiller performance, theoretically (2) theoretical investigation of the effect of physical parameters on chiller performance .(3) theoretical characterisation of a new species of adsorbents that could replace the $SrCl_2$-NH_3 system. The following points conclude the project contributions.

5.2.1 Based on the literature survey

- Chemical reaction with ammonia salts shows the best result for deep freezing and adsorption for heat pumping. $LiBr_2$-water systems show the best result for air conditioning where as in case of compact units metal hydride systems are suitable.
- Using solid sorption systems based on $BaCl_2$-NH_3, it is possible to generate ammonia vapor at 60°C using hot water at 70°C which allows the use of low cost flat solar collectors.
- Compared to wet absorption and adsorption systems, there is relatively less information available in open literature on systems that use ammonia-salts for refrigeration purposes. Hence, it is necessary to carry out more theoretical and experimental studies on these systems as they show certain advantages compared to other heat operated systems.

5.2.2 Based on thermodynamic analysis

- For $BaCl_2$-NH_3 system generator temperature varies from 323K-335K and condenser temperature varies from 296-315K for the range of evaporator temperature from 258K-285K.
- For $SrCl_2$-NH_3 system generator temperature varies from 391K-407K and condenser temperature varies from 368K-387K for the range of evaporator temperature from 258K-285K.
- For a given condenser temperature as pressure drop increases there is increase in evaporator and generator temperature as a result 2nd law COP of the system decreases.
- For the $BaCl_2$ system COP varies from 0.424788-0.447282 and second law COP varies from 0.55674-0.5569 and generator temperature varies from 323K-335K following condenser temperature varies from 296-315K for the range of evaporator temperature from 258K-285K.
- For $SrCl_2$ system COP varies from 0.42731-0.449309 and second law COP varies from 0.0972-0.111796 generator temperature varies from 391K-407K and desorption temperature varies from 368K-387K with the condenser temperature variation from 318K-341K for the range of evaporator temperature from 258K-285K.
- From the thermodynamic analysis we come to know that $BaCl_2$ system requires lower heat source temperature compared to $SrCl_2$ system. Also it has higher second law COP. The barium chloride salt is cheaper than the $SrCl_2$ salt. Hence it is preferable to use $BaCl_2$ salt for solid absorption system even though it yields marginally lower COPs compared to $SrCl_2$ system and the required heat sink temperatures are also lower for $BaCl_2$ system compared to $SrCl_2$ system. However, in tropical countries where the ambient temperatures are high, and /or when lower refrigeration temperatures are required for a given heat sink temperature, $SrCl_2$ may be preferable to $BaCl_2$.

5.3 Future work

This thesis presented research efforts towards the enhancement of $BaCl_2$-NH_3 adsorption chiller and it can be considered as a strong foundation for further work. The following is a list of the suggested future work.

1. To apply new cycle which can recover more heat?
2. To improve the adsorbent bed by enhancing the heat and mass transfer in the adsorbent.
3. Various heat and mass recovery strategies are proved to be effective on improving the energy performance in terms of COP. However, intensive research is still needed to:
   (i) Enhance the amount of recovered thermal energy, without adding complexity into the design and operation of system;
   (ii) Optimize the recovered mass rate to achieve the best effect. For various multi-bed systems, easy, reliable and efficient switching methods of adsorption/ desorption period must be found out.
4. To develop new adsorbent material.
5. Adsorbent bed is the heart of the adsorption system. The heat and mass in the adsorbent bed as well as heat transfer between the adsorbent material and heat transfer fluid are always the most influential factors on adsorption system performance. Adsorbent bed can be improved by novel coating technology. However, using coated adsorber leads to high ratio between the inert (metal) mass and the adsorbent mass, which might reduce the COP of the system. Hence, optimized coating thickness should be studied according to different coating technology and different adsorbent material used.
6. Finally reducing the cost of the system by inventing low cost adsorption material, new heat and mass recovery approaches and higher performance adsorbent bed are still important research area.

APPENDIX-A

TableaA.1. Theoretical result for the COP of $BaCl_2$-NH_3 system

T_E[k]	$T_C=T_A$	T_G	P_E	P_C	T_G-T_A	T_C-T_E	Q_G	Q_E	COP
258	296.201	322.811	2.337	9.4400	26.611	38.201	2605.584	1106.820	0.424788
265	301.288	326.154	3.112	11.076	24.868	36.288	2595.603	1116.762	0.430251
270	304.862	328.475	3.783	12.348	23.613	34.862	2588.393	1124.209	0.434327
275	308.387	330.743	4.566	13.711	22.356	33.387	2581.183	1131.885	0.438514
280	311.863	332.959	5.474	15.168	21.096	31.863	2573.954	1139.847	0.442839
285	315.291	335.126	6.521	16.721	19.836	30.291	2566.726	1148.050	0.447282

TableA.2. Theoretical result for the COP of $SrCl_2$-NH_3 system

T_E	$T_C=T_A$	T_D	T_G	P_E	Pc	T_C-T_E	T_D-T_A	T_G-T_D	T_G-T_A	ΔH	C_X	C_Y	Q_E	Q_G	COP
258	317.61	368.26	391.05	2.34	17.83	59.61	50.65	22.79	73.44	2041.21	1.55	1.62	997.74	2334.93	0.42731
265	323.89	373.27	395.62	3.12	21.15	58.89	49.38	22.35	71.73	2014.99	1.64	1.69	1001.46	2315.12	0.432573
270	328.31	376.75	398.79	3.78	23.76	58.31	48.44	22.04	70.48	1996.80	1.72	1.74	1004.46	2302.86	0.436178
275	332.69	380.17	401.88	4.57	26.57	57.69	47.48	21.71	69.19	1979.05	1.78	1.79	1007.70	2288.11	0.440393
280	337.03	383.52	404.93	5.47	29.61	57.03	46.50	21.41	67.904	1961.56	1.84	1.85	1011.10	2273.56	0.444721
285	341.17	386.51	407.795	6.52	32.74	56.17	45.34	21.29	66.625	1945.09	1.91	1.90	1015.53	2260.20	0.449309

Table A.3 Theoretical values for Second law efficiency of $BaCl_2$-NH_3

T_E[K]	T_C=T_A[K]	T_G[K]	T_C-T_E[K]	T_G-T_C[K]	COPc
258	296.20	322.81	38.20	26.61	0.556742
265	301.29	326.16	36.29	24.87	0.556772
270	304.86	328.48	34.86	23.613	0.556754
275	308.39	330.74	33.39	22.356	0.556756
280	311.86	332.96	31.86	21.096	0.556776
285	315.29	335.13	30.29	19.836	0.556918

Table A. 4 Theoretical values for Second law efficiency of $SrCl_2$-NH_3

T_E[K]	T_C=T_A[K]	T_D[K]	T_G[K]	T_C-T_E[K]	T_D-T_C[K]	T_G-T_C[K]	COPc
258	317.61	368.26	391.05	59.61	50.65	73.44	0.11179
265	323.89	373.27	395.62	58.89	49.38	71.73	0.10793
270	328.31	376.75	398.79	58.31	48.44	70.48	0.10521
275	332.69	380.16	401.88	57.69	47.48	69.19	0.10249
280	337.03	383.52	404.93	57.03	46.49	67.90	0.09981
285	341.17	386.51	407.79	56.17	45.34	66.63	0.09724

REFERENCES

[1] Industry market research for business, strategists, decision makers, 2010, The Fredonia Group.

[2] Hassan, H.Z., A.A. Mohamad, and R. Bennacer, Simulation of adsorption solar cooling system energy, 2011. 36(1): 530-537

[3] Navarro-Esbr et al., A low data requirement model of a variable-speed vapour compression refrigeration system based on neural networks. International Journal of refrigeration, 2007. 30(8): 1452-1459.

[4] Pons, M., et al., Thermodynamic based comparison of sorption systems for cooling and heat pumping: Comparison des performances thermodynamique des systA¨mes de pompes A chaleur A sorption dans des applications de refroidissement et de chauffage. International Journal of Refrigeration, 1999. 22(1): 5-17.

[5] Xu, L., et al., Experimental study on the performance of double-effect and double-way thermochemical sorption refrigeration cycle. Applied Thermal Engineering, 2011. 31(17-18): 3658-3663.

[6] Li, S. and J.Y. Wu, Theoretical research of a silica gel-water adsorption chiller in a micro combined cooling, heating and power (CCHP) system. Applied Energy, 2009. 86(6): 958- 967.

[7] Wang, L.W., R.Z. Wang, and R.G. Olivera, A review on adsorption working pairs for refrigeration. Renewable & Sustainable Energy Review, 2009. 13: 518 - 534.

[8] Demir, H., M. Mobedi, and S. Ulku, Effect of Factors on Variations of Desorption Pressure of Adsorption Heat Pump, in Heat Powered Cycle Conference 2009: Berline.

[9] Saha, B.B., S. Koyama, and T. Kashiwagi, waste heat driven dual-mode, multi-stage,multi-bed regenerative adsorption system. International Journal of Refrigeration, 2003, 26: 749-757.

[10] Chua, H.T., et al., Multi-bed regenerative adsorption chiller and improving the utilization of waste heat and reducing the chilled water outlet temperature fluctuation. International Journal of Refrigeration, 2001. 24(2): 124-136.

[11] Dabrowski, A., Adsorption from theory to practice. Advances in Colloid and Interface Science, 2001. 93(1-3): 135-224.

[12] Critoph, R.E., Evaluation of alternative refrigerant-adsorbent pairs for refrigeration cycles. Applied Thermal Engineering, 1996. 16: 891-900.

[13] Gordon, J.M., et al., The electro-adsorption chiller: a miniaturized cooling cycle with applications to micro-electronics. International Journal of Refrigeration, 2002. 25(8): 1025-1033.

[14] Guid, M.A., Refrigerants, 2002, McQuay international. 1-66.

[15] United-Nations-Environment-Programme, the Montreal Protocol on Substances that Deplete the Ozone Layer. 8 ed2009: Duncan Brack. 565.

[16] Grof, T., Greening of Industry under the Montreal Protocol, 2009, United Nations industrial development organization: Manila. 1-20.

[17] 2009 Greenhouse Gas Inventory Based on Data from 2000 through 2006, in the University of Texas at Austin2009.

[18] Hasse, V., L. Ederberg, and D. Colbourne, Natural Refrigerants2008, Eschborn: German Technical Cooperation.

[19] Hamamoto, Y., et al., Study on adsorption refrigeration cycle utilizing activated carbon fibers. Part 2. Cycle performance evaluation. International Journal of Refrigeration, 2006.29(2): 315-327.

[20] Taylan, O., D.K. Baker, and B. Kaftano, COP trends for ideal thermal wave adsorption cooling cycles with enhancements. International Journal of Refrigeration, 2010.35(3): p 562-570.

[21] Ng, K.C., et al., Experimental study on performance improvement of a four-bed adsorptionchiller by using heat and mass recovery. International Journal of Heat and Mass Transfer, 2006. 49(19-20): 3343-3348.

[22] Wang, X., H.T. Chua, and K.C. Ng, Experimental investigation of silica gel/water adsorption chillers with and without a passive heat recovery scheme. International Journal of Refrigeration, 2005. 28(5): 756-765.

[23] Liu, Y.L., R.Z. Wang, and Z.Z. Xia, Experimental performance of a silica gel-water adsorption chiller. Applied Thermal Engineering, 2005. 25(2-3): 359-375.

[24] Chen, C.J., et al., Study on a silica gel - water adsorption chiller integrated with a closed wet cooling tower. International Journal of Thermal Sciences, 2010. 49(3): 611-620.

[25] Chang, W.S., C.C. Wang, and C.C. Shieh, Design and performance of a solar-powered heating and cooling system using silica gel/water adsorption chiller. Applied Thermal Engineering, 2009. 29(10): 2100-2105.

[26] Di, J., et al., Theoretical and experimental study on characteristics of a novel silica gel-water chiller under the conditions of variable heat source temperature. International Journal of Refrigeration, 2007. 30(3):515-526.

[27] Maggio, G., et al., Simulation of a solid sorption ice-maker based on the novel composite sorbent "lithium chloride in silica gel pores". Applied Thermal Engineering, 2009. 29:1714-1720.

[28] Yuriy I, A., Challenging offers of material science for adsorption heat transformation: A review. Applied Thermal Engineering, 2011.

[29] Srivastava, N.C. and I.W. Eames, A review of adsorbents and adsorbates in soild-vaporadsorption heat pump system. Applied Thermal Engineering, 1998. 18: 707-714.

[30] Tamainot-Telto, Z., and et al., Carbon-ammonia pairs for adsorption refrigeration application: ice making, air conditioning and heat pump. International Journal of Refrigeration, 2009.In press: 1-18.

[31] Loh, W.S., et al., Adsorption cooling cycles for alternative adsorbent/adsorbate pairs working at partial vacuum and pressurized conditions. Applied Thermal Engineering, 2009, 29:793-798.

[32] Yamada, Y. and K. Yano, Synthesis of monodispersed super-microporous/mesoporous silica spheres with diameters in the low submicron range. Microporous and Mesoporous Materials, 2006, 93(1-3):190-198.

[33] Yano, K. and Y. Fukushima, Synthesis of Hexagonally Ordered Super-Microporous Silicas, Using Conventional Alkyltrimethl ammonium Bromide, as Adsorbents for Water Adsorption Heat-Pump System. The Chemical Society of Japan, 2003, 76: 2103-2109.

[34] McCusker, L. http://www.iza-online.org/. 2011.

[35] Engineer, S.K., et al., Cycle stability of sorption materials and composites for the use in heat pumps and cooling machines. Renewable Energy, 2011, 36(11): 3043-3049.

[36] Saha, D. and S. Deng, Ammonia adsorption and its effects on framework stability of MOF-5 and MOF-177. Journal of Colloid and Interface Science, 2010. 348(2): 615-620.

[37] Henninger, S.K., H.A. Habib, and C. Janiak, MOFs as Adsorbents for Low Temperature Heating and Cooling Applications. Journal of the American Chemical Society, 2009, 2776-2777.

[38] Li, T.X., et al., A combined double-way chemisorptions refrigeration cycle based on adsorption and resorption processes. International Journal of Refrigeration, 2009. 32: 47-57.

[39] Aristov, Y.I., et al., A family of new working materials for solid sorption air conditioning systems. Applied Thermal Engineering, 2002. 22: 191-204.

[40] San, J.-Y. and H.C. Hsu, Performance of a multi-bed adsorption heat pump using SWS-1L composite adsorbent and water as working pair. Applied Thermal Engineering, 2009, 29: 1606-1613.

[41] Restuccia, G., et al., Selective water sorbent for solid sorption chiller: experimental

results and modelling. International Journal of Refrigeration, 2004, 27: 284-293.

[42] Tokarev, M., et al., New composite sorbent CaCl2 in mesopores for sorption cooling/heating. International Journal of Thermal Sciences, 2002, 41(5): 470-474.

[43] Deshmukh, V.N. and S.V. Joshi, Review: Use of composite adsorption in adsorption refrigeration. International journal of innovative technology & creative engineering, 2012, 2:11-16.

[44] Ghorishi, S.B., et al., Development of a Cl-Impregnated activated carbon for entrained flow capture of elemental mercury. Environ. Sci. Technol., 2002, 36: 4454-4459.

[45] Cortes, F.B., et al., Water sorption on silica- and zeolite-supported hygroscopic salts for cooling system applications. Energy Conversion and Management, 2012,53(1): 219-223.

[46] Saha, B.B., et al., Adsorption characteristics and heat of adsorption measurements of R-134a on activated carbon. International Journal of Refrigeration. In Press, Accepted Manuscript.

[47] Chua, H.T., et al., Modeling the performance of two bed, silica gel-water adsorption chiller. International Journal of Refrigeration, 1999. 22: p. 194-204.

[48] Chinnapa J.C.V,eperimental study of the intermittent vapour absorption refrigeration cycle employing the refrigerant-absorbent systems of ammonia lithium nitrate. Solar energy (1961), 5: 1-18.

[49] Nielson P.B, A critical survey of intermittent absorption systems for solar refrigeration, int. Congr. Og refrigeration Moscow, session 1B 2.1, pp. 659-667.

[50] A.V. Kuzentsov, K.Vafai, Analytical comparison and criteria for heat and mass transfer models in metal hydride packed beds. International journals of Heat and Mass transfer 38 (1995) 2873-2884.

[51] M. Pons, F. Meunier, G. Cacciola, R.E. Critoph, M.Groll, L.Puigjaner, B.Spinner, F. Ziegler. Thermodynamic based comparison of sorption systems for cooling and heat pumping. International journals of Refrigeration 22 (1999): 5-17

[52] H.T. Chua, K.C. Ng, A. Malek, T. Kashiwagi, A. Akisawa, B.B. Saha,Modelling the performance of two-bed, sillica gel-water adsorption chillers. International journal of Refrigeration 22(1999) 194-204

[53] G. restuccia, A. Freni , G. Maggio, A zeolite-coated bed for air conditioning adsorption systems: parametric study of heat and mass transfer by dynamic simulation. Applied Thermal Engineering (2001)

[54] Li Yong and Ruzhu Z. Wang Adsorption Refrigeration: A Survey of Novel Technologies Recent Patents on Engineering 2007, 1, 1-21

[55] Zbigniew Królicki, Tomasz Wilk, Bartosz Zajączkowski study on the efficiency of solar adsorption refrigeration and heat pump systems. 61st ATI National Congress – International Session “Solar Heating and Cooling”

[56] C. Rivera, I. Pilatowsky, E. Mendez, W. Rivera Experimental study of a thermo chemical refrigerator using the barium chloride –ammonia reaction. International journal of Hydrogen energy 32 (2007) 3154-3158.

[57] Y. Zhong , R.E. Critoph , R.N. Thorpe , Z. Tamainot-Telto , Yu.I. Aristov Isothermal sorption characteristics of the BaCl2–NH3 pair in a vermiculite host matrix. Applied Thermal Engineering 27 (2007) 2455–2462

[58] L.W. Wang, A review on adsorption working pairs for refrigeration. Renewable and sustainable energy reviews (2009), 13, pp. 518-534.

[59] Z. Tamainot-Telto, S.J. Metcalf, R.E. Critoph , Y. Zhong, R. Thrope, Carbon ammonia pairs for adsorption refrigeration applications: ice making, air conditioning and heat pumping. International Journals of Refrigeration (2009).

[60] J.V. Veselovskaya, R.E. Critoph, R.N. Thorpe, S. Metcalf, M.M. Tokarev, Yu.I. Aristov Novel ammonia sorbents ‘‘porous matrix modified by active salt” for adsorptive heat transformation: 3.Testing of ‘‘BaCl2/vermiculite” composite in a lab-scale adsorption chiller. Applied Thermal Engineering 30 (2010) 1188–1192

[61] Alessio Sapienza, Ivan S. Glaznev, Salvatore Santamaria, Angelo Freni, Yuriy I. Aristov Adsorption chilling driven by low temperature heat: New adsorbent and cycle Optimization. Applied Thermal Engineering 32 (2012) 141-146

[62] Y. Alyousef, A.A. Antukh, A.P. Tsitovich, L.L. Vasiliev Three adsorbers solar cooler with composite sorbent bed and heat pipe thermal control. Applied Thermal Engineering 38 (2012) 124-130

[63] Janna V. Veselovskaya, Mikhail M. Tokarev, Alexandra D. Grekova, Larisa G. Gordeeva Novel ammonia sorbents ‘‘porous matrix modified by active salt” for adsorptive heat transformation: 6. The ways of adsorption dynamics enhancement. Applied Thermal Engineering 37 (2012) 87-94

[64] N.K. Bansal, J.Blumenberg, H.J. Kavasch, T. Roettinger. Performance testing and evaluation of solid absorption solar cooling unit. Solar Energy 61 (1997) 127-140.