

**“REMOVAL OF CARBON DIOXIDE FROM FLUE GAS
BY
PRESSURE SWING ADSORPTION”**

A Major Project Report

*Submitted in Partial Fulfillment of the Requirements
For the Degree of*

**MASTER OF TECHNOLOGY
IN
CHEMICAL ENGINEERING
(ENVIRONMENTAL PROCESS DESIGN)**

**By
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Certificate

This is to certify that the Major Project Report entitled “**Removal of Carbon dioxide from Flue Gases By Pressure Swing Adsorption**” submitted by Mr. Devang P.Trivedi Student Name (Roll No. 06MCH015), towards the partial fulfillment of the requirements for the award of Degree of Master of Technology in Chemical Engineering (EPD) of **Nirma University of Science and Technology, Ahmedabad** is the record of work carried out by him at **Central Salt and Marine Chemicals Research Institute, Bhavnagar** under my supervision and guidance. The work submitted has in my opinion reached a level required for being accepted for examination. The results embodied in this major project work to the best of my knowledge have not been submitted to any other University or Institution for award of any degree or diploma.

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Candidate's Statement

I here declare that the work incorporated in the thesis entitled “Removal of CO₂ from Flue gas by Pressure Swing Adsorption” is original and has not been submitted to any university/institution for the award of any diploma/degree.

I further declare that the results presented in the thesis and the considerations made therein, contribute in general to the advancement of knowledge in Chemical Engineering and in particular to adsorption of carbon dioxide on activated carbon.

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*Dedicated to my
Family*

Abstract

The increased emission of greenhouse gases to the atmosphere are causing global warming which leads to the unwanted climate change with consequent risk of extreme weather and adverse effect on biodiversity. Under Kyoto Protocol, 1997 industrialized countries have agreed to limit or reduce their emissions of these greenhouse gases by at least 5% below 1990 levels during the period 2008 to 2012. Carbon dioxide makes greatest contribution to greenhouse gas effect due to large amount of CO₂ emitted to the atmosphere by human activity. Approximately one third of all CO₂ emissions due to human activity come from fossil fuels used for generating electricity, with each power plant capable of emitting several million tonnes of CO₂ annually. These emissions could be reduced substantially, without major changes to the basic process, by capturing and storing the CO₂. Among the carbon dioxide capturing technologies, chemical absorption is presently practiced in the industry. Pressure swing adsorption process is also a potential technology for the removal of carbon dioxide from the flue gas due to its proven record in other gas separation processes. However, the use of PSA process for the removal and recovery of carbon dioxide from hot fuel gas streams at high temperature, the first and most important issue is to find appropriate adsorbent.

This work focuses on the optimization of cyclic adsorption processes to improve the performance of CO₂ capture from flue gas, consisting of nitrogen and carbon dioxide. The adopted processes are the VPSA (Vacuum Pressure Swing Adsorption) process. The main goal of this study is to improve the purity and recovery of carbon dioxide.

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Nomenclature

Sr.No.	Terms	Specification
1	C	Concentration in the gas phase
2	t	Time
3	z	Bed axial distance
4	v	Interstitial fluid velocity
5	D_L	Dispersion coefficient
6	ε	Bed voidage
7	q_i	Concentration of component ' i ' in the solid
8	q_i^*	Equilibrium concentration of component i

Chapter-1

Introduction

Chapter 1

Introduction

1.1 Global Warming and Climate Change

Global warming is referred to as a recent rise in the average global temperature due to enhanced greenhouse effect and is one of the most important contemporary environmental issues which leads to unwanted climate change, with consequent risks of extreme weather, rising sea level and adverse effects on agriculture and biodiversity. Increasing concentrations of carbon dioxide and other green house gases (GHG) like methane (CH_4), nitrous oxide (N_2O), fluorocarbons etc., in the earth's atmosphere are aggravating the natural greenhouse effect and causes global warming.

1.1.1 Green House Effect

The greenhouse effect is the process in which the emission of infrared radiation by the atmosphere warms a planet's surface. The name comes from an incorrect analogy with the warming of air inside a greenhouse compared to the air outside the greenhouse. Around 31% solar radiation coming to earth is directly reflected back to the space and the remaining 69% of the solar radiation is absorbed and warming the land, atmosphere and oceans. In order to keep the thermodynamic equilibrium, earth reflects back the energy in the long wavelength infrared radiation and part of this radiation is absorbed by greenhouse gases and causes a rise in the atmospheric temperature. Figure 1.1 shows the schematic representation of greenhouse effect. Many gases present in the earth's atmosphere exhibit the greenhouse properties. Some of them occur in nature like water vapor, carbon dioxide, methane and nitrous oxide, while others are exclusively human-made like fluorocarbons used for aerosols and other applications.

1.1.2 Greenhouse Gases

Many chemical compounds found in the earth's atmosphere act as greenhouse gases. Carbon dioxide (CO_2), methane (CH_4), nitrous oxide (N_2O), and three fluorinated

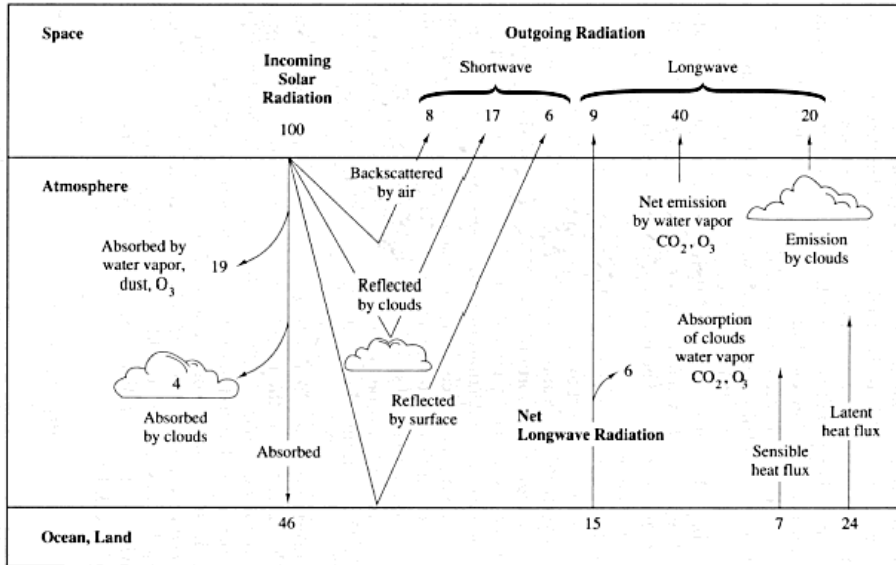


Figure 1.1. Schematic representation of greenhouse effect [1]

industrial gases: hydrofluorocarbons (HFCs), perfluorocarbons (PFCs), and sulfur hexafluoride (SF_6) are considered as major greenhouse gases present in the atmosphere. Water vapor is also considered a greenhouse gas. The global warming potential (GWP) of fluorocarbons ($>10,000$), N_2O (298) and CH_4 (25) are much higher than that of CO_2 (1), but CO_2 makes the greatest contribution to greenhouse gas effect due large amount of CO_2 emitted to the atmosphere by human activity (IEA GHG R&D, 1999).[6] Figure 1.2 shows the distribution of greenhouse gases in the earth's atmosphere. Table 1.1 describes the major sources of greenhouse gases into earth's atmosphere.

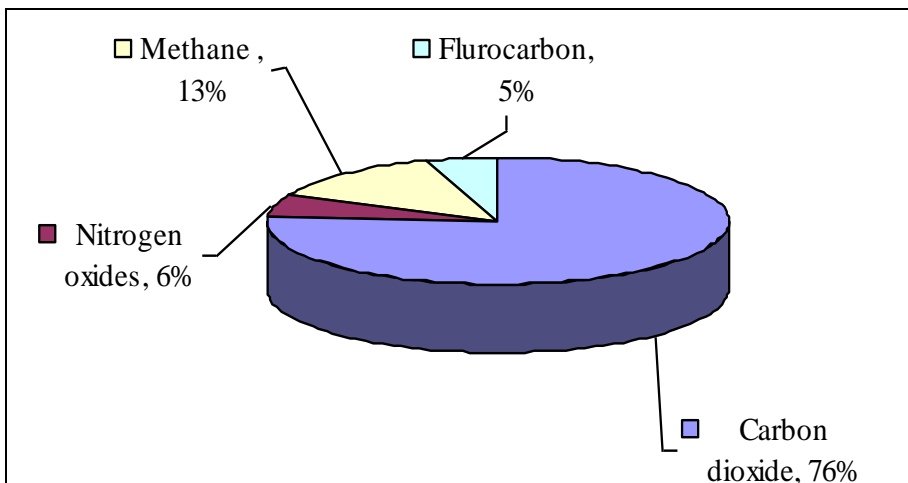


Figure 1.2. Distribution of greenhouse gases in earth's atmosphere. [2]

Table 1.1. Major sources of greenhouse gases [6]

Gas	Sources
Carbon dioxide (CO ₂)	<ul style="list-style-type: none"> • Energy production <ul style="list-style-type: none"> - combustion of coal, oil, gas and other fuels. • Industry <ul style="list-style-type: none"> - production of cement and other processes. • Transport <ul style="list-style-type: none"> - fossil fuel combustion. • Deforestation and land use change
Chlorofluorocarbons (freons) and related gases	<ul style="list-style-type: none"> • Industrial applications <ul style="list-style-type: none"> - aerosols - cooling agents - foam solvents
Methane (CH ₄)	<ul style="list-style-type: none"> • Industrial applications <ul style="list-style-type: none"> - aerosols - cooling agents - foam solvents. • Industry <ul style="list-style-type: none"> - production waste. • Agricultural <ul style="list-style-type: none"> - livestock breeding - rice fields - biomass combustion (humus degradation, peat combustion)
Nitrous oxide	<ul style="list-style-type: none"> • Energy production <ul style="list-style-type: none"> - combustion of coal, oil, gas and other fuels. • Agricultural <ul style="list-style-type: none"> - fertilizer applications - biomass combustion • Deforestation and land use change

1.2 Flue Gas

Flue gas is gas that exits to the atmosphere via a flue, which is a pipe or channel for conveying exhaust gases from a fireplace, oven, furnace, boiler or steam generator. Quite often, it refers to the combustion exhaust gas produced at power plants. Its composition depends on what is being burned, but it will usually consist of mostly nitrogen (typically more than two-thirds) derived from the air used for the combustion, carbon dioxide (CO₂) and water vapor as well as excess oxygen (also derived from the air used for the combustion). It also contains a small percentage of pollutants such as particulate matter, carbon monoxide, nitrogen oxides and sulfur oxides. Table 1.2 shows a typical concentration of flue gases from both coal-fired as well as natural gas fired power plants on dry basis.

Table 1.2 Typical characteristics of power plant flue gas [3]

Composition	Volume percentage(dry basis)	
	Coal-fired	Natural gas
Carbon dioxide	14	4
Oxygen	5	15
Nitrogen	81	81
Contaminants (ppm)		
SO _x	300-3000	1
NO _x	100-1000	100-500
Particulates (mg/m ³)	1000-10000	10

1.3 Carbon Dioxide Emissions

Approximately one third of all CO₂ emissions due to human activity come from fossil fuels used for generating electricity, with each power plant capable of emitting several million tonnes of CO₂ annually. These fossil fuels provides >80 % energy needs all over

the world and will continue to do so for the foreseeable future. Typical CO₂ emission from coal fired power plant is 800 kg CO₂/MWh of electricity produced [3]. A variety of other industrial processes also emit large amounts of CO₂ from each plant, for example oil refineries, cement works, and iron and steel production. Table 1.3 shows the approximate amount of CO₂ emissions per year from power generation and other major industries [3]. From the table, it can be seen that around 78% of CO₂ emissions are coming from power generation using fossil fuels. Table 1.4 describes the worldwide energy usage and carbon dioxide emissions from different regions of the world. It is projected that the increase in the carbon dioxide emission from Asian region is very high at year 2025 compared to industrialized nations.

Table 1.3. Amount of CO₂ emissions per year from various industries [4].

Process	Number of Sources	Emission Mt. CO ₂ yr. ⁻¹
Fossil Fuel		
Power	4,942	10,539
Cement Production	1,175	932
Refineries	638	798
Iron and Steel Industry	269	646
Petrochemical Industry	470	379
Oil and Gas Processing	N / A	50
Other sources	90	33
Biomass		
Bioethanol and Bioenergy	303	91
Total	7,887	13,466

Table 1.4. World energy consumption and carbon dioxide (CO₂) emissions at different Years [5]

Region	Energy consumption (quadrillion btu)				Carbon dioxide emissions (million metric tons)			
	1990	2001	2010	2025	1990	2001	2010	2025
Industrialized nations	182.8	211.5	236.3	281.4	10,462	11,634	12,938	15,643
Eastern Europe/Former Soviet Union	76.3	53.3	59.0	75.6	4,902	3,148	3,397	4,313
Developing nations								
Asia	52.5	85.0	110.6	173.4	3,994	6,012	7,647	11,801
Middle East	13.1	20.8	25.0	34.1	846	1,299	1,566	2,110
Africa	9.3	12.4	14.6	21.5	656	843	971	1,413
Central and South America	14.4	20.9	25.4	36.9	703	964	1,194	1,845
Total developing	89.3	139.2	175.5	265.9	6,200	9,118	11,379	17,168
Total world	348.4	403.9	470.8	622.9	21,563	23,899	27,715	37,124

These emissions could be reduced substantially, without major changes to the basic process, by capturing and storing the CO₂. The ultimate objective of the CO₂ capture is the stabilization of greenhouse gas concentrations in the atmosphere at a level that prevents dangerous anthropogenic interference with the climate system.

1.4 Objectives

The main objective of this project is to develop a pressure/vacuum swing adsorption (P/VSA) process for the separation of CO₂ from flue gas using activated carbon as the carbon dioxide selective adsorbent. For this purpose it is proposed to study the equilibrium adsorption isotherms of carbon dioxide and nitrogen on activated carbon and also the dynamic adsorption measurements of carbon dioxide on activated carbon from a model mixture of carbon dioxide in nitrogen gas in which the later is the major component present in the flue gas.

1.5 Outline of the Report

This report is organized into five chapters including this introductory chapter, which describes briefly about the greenhouse gas effect, global warming and sources of greenhouse gases especially CO₂. Chapter 2 describes briefly about various technologies for CO₂ capture and storage. Chapter 3 describes about various potential adsorbents for the separation of CO₂ from flue gas especially activated carbon. Various types of adsorption process used for gas separation especially PSA process in detail, are discussed in chapter 4. In chapter 5, experimental measurements of equilibrium adsorption isotherms of CO₂ and N₂, and also the breakthrough measurements of CO₂ in activated carbons are discussed. In chapter 6, detailed description of the PSA system used for the removal of CO₂ from its gaseous mixture with N₂ as well as the PSA experimental results are given.

1.6 Reference

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- [5]. Kristin Jordal, Marie Anheden¹, Jinying Yan¹, Lars Strömberg; “Oxyfuel Combustion for Coal-Fired Power Generation with CO₂ Capture – Opportunities and Challenges”
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Chapter-2

CO₂ Capture and Storage

Chapter 2

CO₂ Capture and Storage

2.1 Scenarios for CO₂ Capture

The three main possibilities for CO₂ reduction/removal from power generation are:

- i) Decarbonization of the fuel prior to combustion (Pre Combustion Capture)
- ii) Combustion in O₂/CO₂ atmospheres and condensation of CO₂ (Oxyfuel Combustion)
- iii) Tail-end capture solution (Post Combustion Capture)

2.1.1 Pre Combustion Capture

This method involves reaction of the fuel with steam and air or oxygen to release an exhaust that consists of carbon monoxide and hydrogen. The carbon monoxide can be reacted with steam in a catalytic reactor, called a shift converter, to give CO₂ and more hydrogen. The CO₂ is then separated out and the hydrogen used as fuel in a gas turbine combined-cycle plant. The process is, in principle, the same for coal, oil or natural gas. The advantage of this process is that, we can have CO₂ at concentration (15-60%) from shift converter at moderate pressure, thus reducing the compression costs for separation. The main disadvantage of this process is that, it requires major modification of existing power plants in order accommodate syngas reactor, shift converter and gas turbine.

2.1.2 Oxyfuel Combustion

These systems use oxygen instead of air for combustion of primary fuel to produce a flue gas that is mainly water vapor and CO₂. This results in a flue gas with high CO₂ concentrations (< 80% by volume). The water vapor is then removed by cooling and

compressing the gas stream. Oxyfuel combustion requires the upstream separation of oxygen from air, with a purity of 95-99% oxygen assumed in the most current designs. Further treatment of the flue gas may be needed to remove air pollutants and non condensed gases (such as nitrogen) from the flue gas before the CO₂ is sent to storage. As a method of CO₂ capture in boilers, oxyfuel combustion systems are in the demonstration phase [1].

2.1.3 Post Combustion Capture

These systems separate CO₂ from the flue gases produced by the combustion of the primary fuel in air. CO₂ represents only a small part of the flue gas stream emitted to the atmosphere by a power station. CO₂ content varies from 4% in the exhaust of a gas-fired combined cycle power plant to around 14% in that of a pulverized coal fired plant. Other gases in the exhaust include nitrogen, oxygen, water vapor and small quantities of SO_x and NO_x. There are a number of existing technologies, including chemical absorption, adsorption, cryogenic processes and membranes, which can separate CO₂ from the flue gases emitted during power plant operation [2]. Some of the existing and potential separation technologies for CO₂ separation are briefly discussed below:

2.2 Chemical Absorption. Currently, all commercial power plants for CO₂ capture use chemical absorption using solvents like mono ethanol amine (MEA). Figure 2.1 shows the schematic diagram of a typical chemical absorption system for CO₂ separation. The flue gas from a fossil fuel power plant is passed through a column in which MEA selectively absorbs CO₂. This CO₂-rich solution is then pumped to a tower in which thermodynamic conditions are manipulated to release the CO₂. High pressure and low temperature favor absorption, while low pressure and high temperature result in regeneration of the solvent. The pressure in absorption systems can be atmospheric or can be manipulated to enhance absorption/desorption. It requires significant amount of heat for solvent regeneration. Temperature manipulation (specifically, to release the CO₂ and regenerate the MEA) makes up 70–80% of operating cost. The current major drawback for this process is the loss of solvent due to the reaction with SO_x and other contaminants. Further more, waste disposal is an issue, as the spent solvent stream cannot be sent to publicly owned treatment works without further treatment.

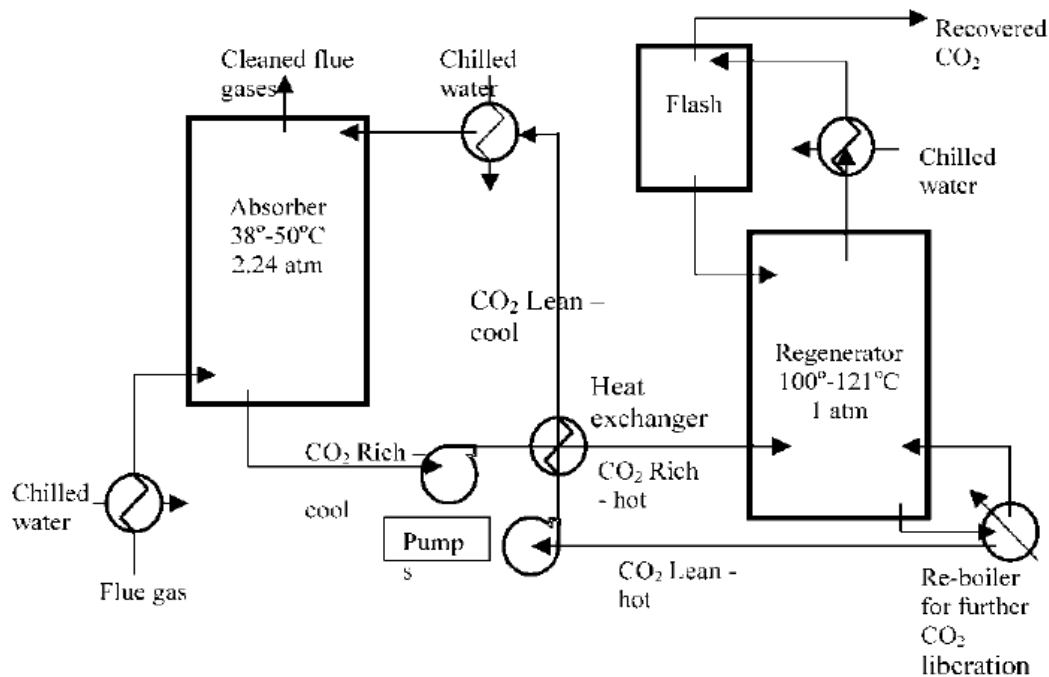


Figure 2.1. Schematic representation of CO₂ chemical absorption system [3]

2.3Cryogenic Distillation. CO₂ can be separated from other gases by cooling and condensation. Cryogenic separation is widely used commercially for streams that already have high CO₂ concentrations (typically >90%) but it is not used for more dilute CO₂ streams. A major disadvantage of cryogenic separation of CO₂ is the amount of energy required to provide the refrigeration necessary for the process, particularly for dilute gas streams. Another disadvantage is that some components, such as water, have to be removed before the gas stream is cooled, to avoid blockages. Cryogenic separation has the advantage that it enables direct production of liquid CO₂, which is needed for certain transport options, such as transport by ship. Cryogenics would normally only be applied to high concentration, high pressure gases, such as in pre-combustion capture processes or oxygen fired combustion. Figure 2.2 shows a simple distillation tower. The whole apparatus is kept in a cold room. Flue gases, after having NO_x, SO_x, and H₂O removed, enter the compressor. The flow then proceeds through the heat exchanger, where the N₂ exiting the tower picks up heat from the entering flow. The CO₂ liquefies or solidifies in the tower [4].

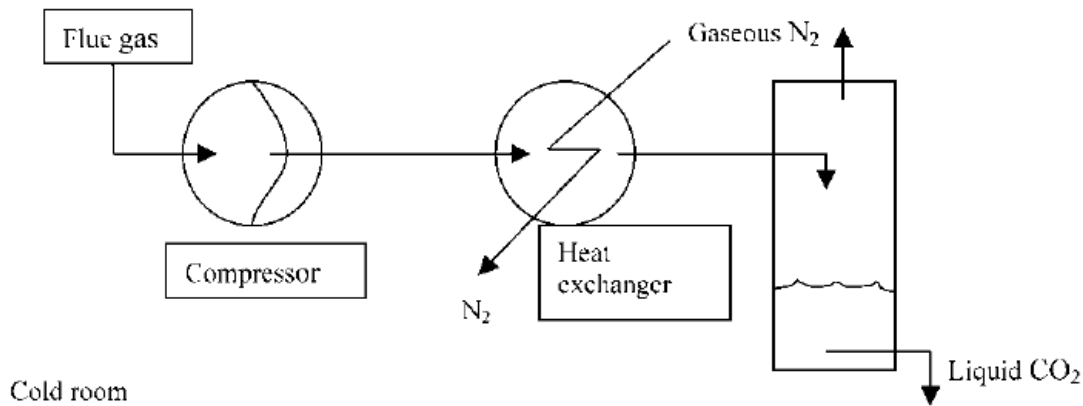


Figure 2.2. Cryogenic separation (after removal of SO_x, NO_x, H₂O, etc.) [4].

2.4 Membrane Separation. Gas separation membranes allow one component in a gas stream to pass through faster than the others. There are many different types of gas separation membrane, including porous inorganic membranes, palladium membranes, polymeric membranes and zeolites. Membranes cannot usually achieve high degrees of separation, so multiple stages and/or recycle of one of the streams is necessary. This leads to increased complexity, energy consumption and costs. Several membranes with different characteristics may be required to separate high-purity CO₂. Solvent assisted membranes are being developed to combine the best features of membranes and solvent scrubbing. Much development is required before membranes could be used on a large scale for capture in power stations. Figure 2.3 shows the schematic representation of a simple membrane system for CO₂ separation. Here, the flue gases simply enter the separation tank, and the CO₂ diffuses across the membrane. The pressure on the permeate side is approximately 10% of the feed side; this pressure difference, once initiated by a vacuum, will continually pull CO₂ across the membrane. The separated CO₂ is blown to a collection tank, and the flue gases exit for further treatment, such as oxidation of NO_x and SO_x, recycling of O₂ for combustion, and condensation of water vapour. Sometimes these gases are separated prior to entering the separation tank because they can harm the membrane. If this is the case, the membrane just has to separate CO₂ from N₂ [5].

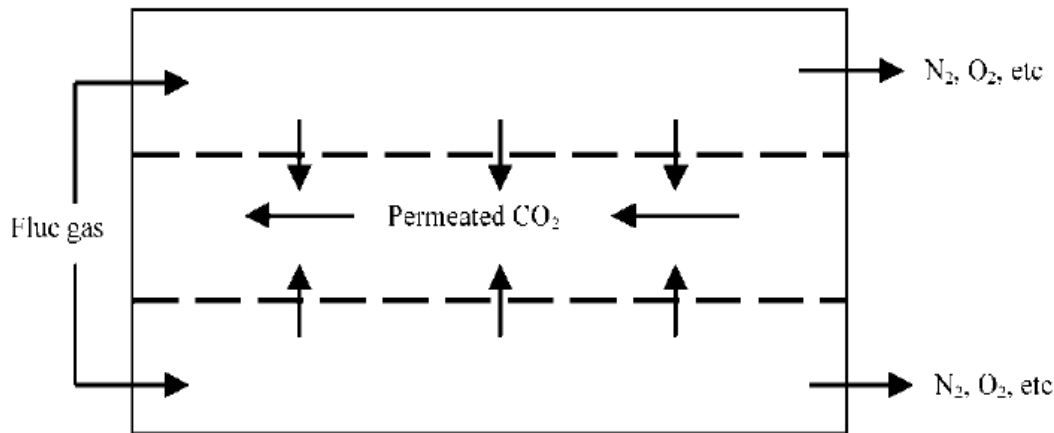


Figure 2.3. Schematic diagram of simple membrane system for CO₂ separation [5].

2.5 Adsorption. Adsorption is commercially established process as a Pressure Swing Adsorption (PSA) or Vacuum Swing Adsorption (VSA) for gas separation. Some of the major separation processes commercially used include oxygen and nitrogen production from air, hydrogen recovery from various gas streams like steam reformer gas, refinery off gas, coke oven gas, ethylene off gas etc. and carbon- methane separation from landfill gas. The development of adsorbent is central to the adsorption process to be envisaged for CO₂ recovery from flue gas as adsorbent's capacity and selectivity for one of the component along with regenerability is likely to determine the process cycle and required capital cost for the separation unit. Chapter 3 and chapter 4 discuss about the adsorbents and PSA process in detail respectively.

2.6 CO₂ Storage

For CO₂ storage to be an effective way of avoiding climate change, the CO₂ must be stored for several hundreds or thousands of years. CO₂ storage also needs to have low environmental impact, low cost and conform to national and international laws. The main options for storing CO₂ are geological storage, ocean storage, and mineralization and industrial uses (IPCC, 2005) [1].

2.6.1 Geological Storage. The main options for geological storages are in depleted oil and gas reservoirs, deep saline reservoirs and unminable coal seams, as shown in

Figure1.1. In each case, geological storage of CO₂ is accomplished by injecting it in dense form into a rock formation below earth's surface. In depleted oil and gas reservoirs, the injected CO₂ can be used for enhanced oil recovery (EOR), which is an established technique. In the deep saline aquifer, CO₂ would partially dissolve in the water and in some formations it would slowly react with minerals to form carbonates, which would lock up the CO₂ essentially permanently. Suitable aquifers would have a cap rock of low permeability to minimize CO₂ leakage. Another potential storage medium is unminable coal. CO₂ can be injected into suitable coal seams where it will be adsorbed onto the coal, locking it up permanently provided the coal is never mined. Moreover, it preferentially displaces methane that exists in the coal. Methane is already extracted from coal seams by depressurization but this typically recovers only about 50% of the gas in place. Injection of CO₂ enables more methane to be extracted, while at the same time sequestering CO₂. Coal can adsorb about twice as much CO₂ by volume as methane, so even if the recovered methane is burned and the resulting CO₂ is reinjected, the coal bed can still provide net storage of CO₂.

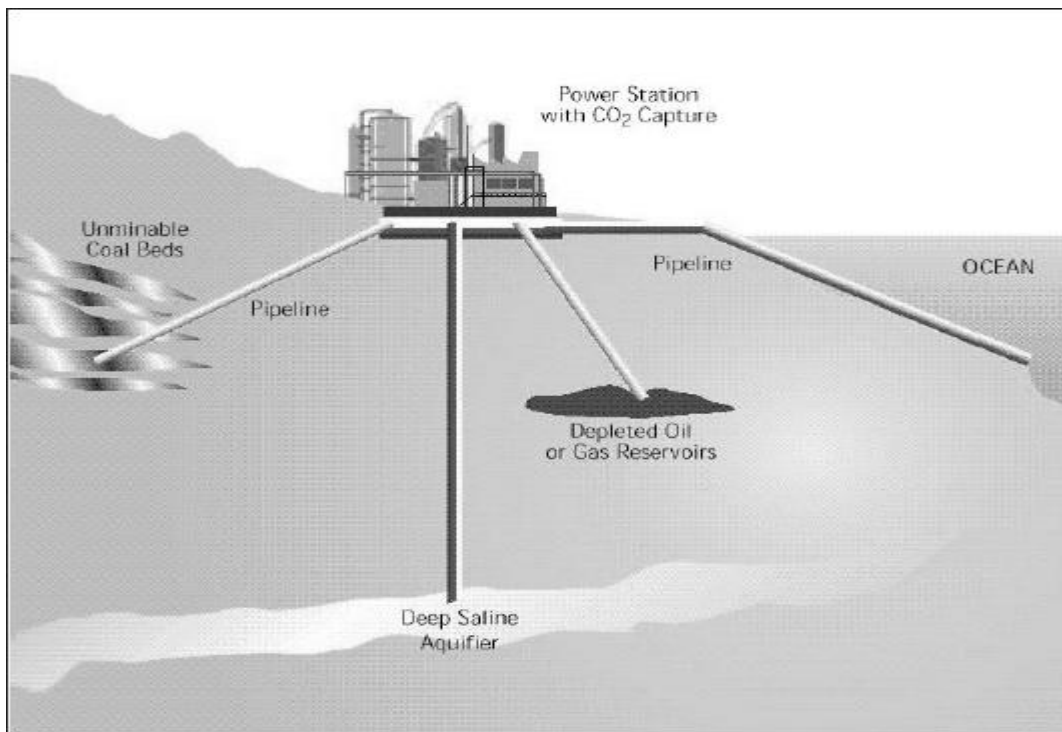


Figure2.4 Options for storage of CO₂ [6].

2.6.2 Ocean Storage. A potential CO₂ storage option is to inject captured CO₂ directly into the deep ocean (at depths greater than 1,000 m), where most of it would be isolated from the atmosphere for centuries. This can be achieved by transporting CO₂ via pipelines or ships to an ocean storage site, where it is injected into the water column of the ocean or at the sea floor. The dissolved and dispersed CO₂ would subsequently become part of the global carbon cycle. Ocean storage has not yet been deployed or demonstrated at a pilot scale, and is still in the research phase.

2.7 Mineral Carbonation and Industrial Uses. Mineral carbonation refers to the fixation of CO₂ using alkaline and alkaline-earth oxides, such as magnesium oxide (MgO) and calcium oxide (CaO), which are present in naturally occurring silicate rocks such as serpentine and olivine. Chemical reactions between these materials and CO₂ produces compounds such as magnesium carbonate (MgCO₃) and calcium carbonate (CaCO₃, commonly known as limestone). The quantity of metal oxides in the silicate rocks that can be found in the earth's crust exceeds the amounts needed to fix all the CO₂ that would be produced by the combustion of all available fossil fuel reserves. These oxides are also present in small quantities in some industrial wastes, such as stainless steel slags and ashes. Mineral carbonation produces silica and carbonates that are stable over long time scales and can therefore be disposed of in areas such as silicate mines, or re-used for construction purposes, although such re-use is likely to be small relative to the amounts produced. After carbonation, CO₂ would not be released to the atmosphere. As a consequence, there would be little need to monitor the disposal sites and the associated risks would be very low.

Industrial uses of CO₂ include chemical and biological processes where CO₂ is a reactant, such as those used in urea and methanol production, as well as various technological applications that use CO₂ directly, for example in the horticulture industry, refrigeration, food packaging, welding, beverages and fire extinguishers. Currently, CO₂ is used at a rate of approximately 120 MtCO₂ per year worldwide, excluding use for EOR. Two thirds of this total CO₂ is used to produce urea, which is used in the manufacture of fertilizers and other products. Some of the CO₂ is extracted from natural wells, and some originates from industrial sources – mainly high-concentration sources such as ammonia and hydrogen production plants – that capture CO₂ as part of the

production process. Industrial uses of CO₂ can, in principle, contribute to keeping CO₂ out of the atmosphere by storing it in the 'carbon chemical pool' (i.e., the stock of carbon-bearing manufactured products). However, as a measure for mitigating climate change, this option is meaningful only if the quantity and duration of CO₂ stored are significant, and if there is a real net reduction of CO₂ emissions.

2.8 Reference

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Chapter-3

Adsorbent for CO₂ Separation

Chapter 3

Adsorbents for CO₂ Separation

3.1 Introduction

Currently, the large-scale separation of carbon dioxide from flue gas is done commercially through chemical absorption, among other processes discussed in chapter 2. Pressure Swing Adsorption (PSA) or Vacuum Swing Adsorption (VSA) process is one of the potential candidate for flue gas separation for CO₂ capture, due to its proven record in other industrial gas separations including, oxygen and nitrogen production from air; hydrogen recovery from various gas streams like steam reformer gas, refinery off gas, coke oven gas, ethylene off gas etc.; and paraffin-olefin separation (Yang, 1997; Ruthven et al., 1994). However, the use of PSA process for the removal and recovery of carbon dioxide from hot fuel gas streams at high temperatures, the first and most important issue is to find the appropriate adsorbent. The adsorbent must have (1) high selectivity and adsorption capacity for carbon dioxide at high temperature; (2) adequate adsorption/desorption kinetics for carbon dioxide at operating conditions; (3) stable adsorption capacity of carbon dioxide after repeated adsorption/desorption cycles; (4) adequate mechanical strength of adsorbent particles after cyclic exposure to high pressure streams. This chapter discuss briefly about various potential adsorbents for the separation of CO₂ include, zeolites; hydrotalcites; metal organic frameworks (MOF); mesoporous molecular baskets; metal oxides; and also discuss in detail about activated carbon as a carbon dioxide selective adsorbent.

3.2 Zeolites

Zeolites are crystalline aluminosilicates with lattice composing of $[\text{SiO}_4]^{4-}$ and $[\text{AlO}_4]^{3-}$ tetrahedra that are so arranged that zeolite crystals contain well defined networks of channels and cavities [1]. The framework is anionic, with a net negative charge equal to the number of aluminium atoms in the framework tetrahedral positions. A corresponding number of non-framework cations are required for charge compensation. Adsorbed phase can be librated or extracted without destroying the structural integrity of framework.

Zeolites are classified into various types according to the framework structures, and zeolite X, A and modernite are some of the commercially important zeolites. Figure 3.1 shows the framework structure of zeolite X.

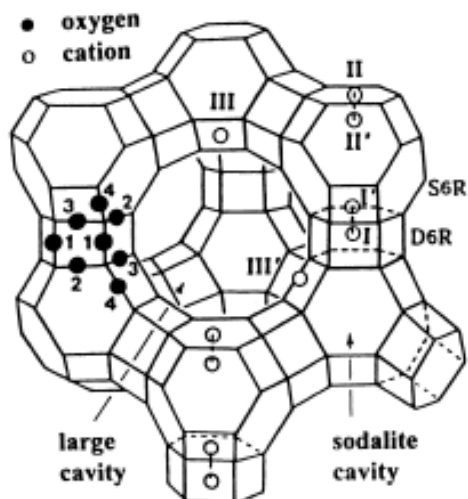


Figure 3.1 Framework structure of Zeolite X [2].

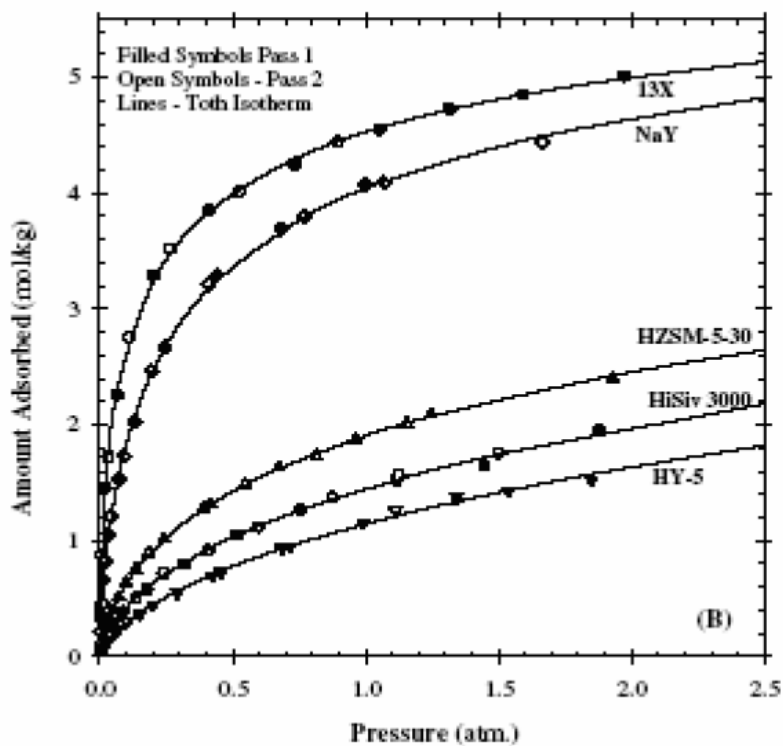


Figure 3.2. Adsorption isotherms of CO₂ on various zeolites [3].

Ahn et al. (2004) have studied the diffusion mechanism of carbon dioxide in zeolite A and calcium exchanged zeolite X at different temperature ranges. Harlick et al. (2004) have done an experimental adsorbent screening study for CO₂ removal from N₂. Figure 3.2 shows the equilibrium adsorption isotherms of CO₂ on various zeolites X at 295 K.

3.3 Hydrotalcites

Hydrotalcites belong to a large class of anionic and basic clays, also known as layered double hydroxides. They are composed of positively charged brucite-like (Mg(OH)₂) layers with trivalent cations substituting for divalent cations at the centers of octahedral sites of hydroxide sheet whose vertex contain hydroxide ions, and each -OH group is shared by three octahedral cations and points to the interlayer regions. The excess positive charge of hydrotalcites is compensated by anions and water molecules present in the interstitial position. A typical structure of hydrotalcite is shown in figure 3.3.

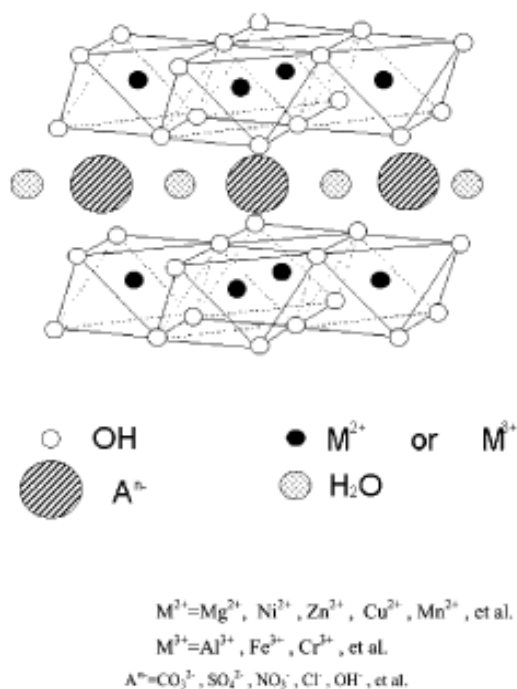


Figure 3.3. Layered structure of hydrotalcite [5]

Hydrotalcites as adsorbents in literature, particularly adsorbents for carbon dioxide are presented only in recent year (Ding and Alpay, 2000; Yong and Rodrigues, 2002; Yong et al, 2002). Yong et al (2001b) have studied the equilibrium adsorption isotherms of CO₂ in different hydrotalcite at higher temperatures and shown that, the adsorption capacity for CO₂ first decreases with temperature and then increases as temperature increases. Figure 3.4 shows the adsorption isotherms of CO₂ in hydrotalcite at different temperatures.

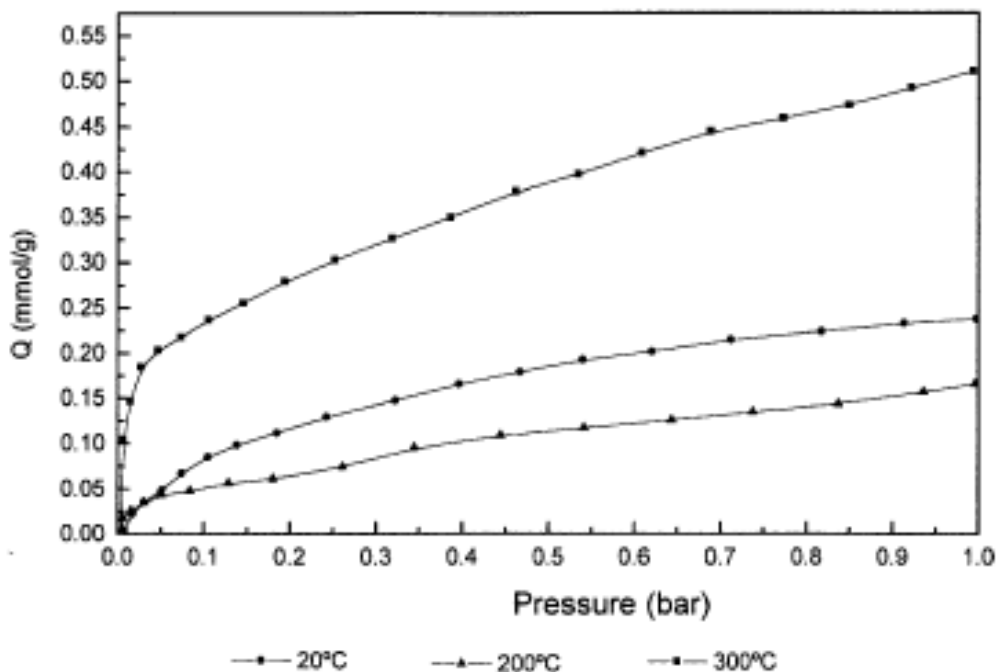


Figure 3.4. Adsorption isotherms of CO₂ on hydrotalcite at different temperatures [4]

3.4 Metal Organic Frameworks (MOFs)

The use of MOF as adsorbent is one of the recent research interest for the separation of CO₂. In MOFs, the coordination of polydentate ligands to metals allows the design of specific framework geometries. This arises from the directed valency of the multidentate ligands and the stereochemistry dictated by the size and electronic configuration of the metal centre. The metal–ligand coordinate bond and the hydrogen bond between donor and acceptor molecules have both been exploited to generate infinite framework structures (Li and Govind, 1994). However, due to lack of sufficient chemical or mechanical rigidity leads to collapse (reversible or irreversible) of the network structures.

But there are some frameworks which are sufficiently robust to display permanent porosity, pore volume and window diameter and have been prepared on pilot plant scale and demonstrated to give useful sorption behaviour with the separation of CO/CO₂, CO₂/CH₄, ethane /ethylene mixtures. One recent example is metal coordination polymer, polymeric copper (II) benzene-1, 3, 5 tricarboxylate, Cu-BTC, [Cu₃(BTC)₂-(H₂O)_x]_n (Wang et al, 2002). Figure 3.5 shows the adsorption isotherms of various gases on Cu-BTC at 22°C. The selectivity and capacity for CO₂ is much greater than nitrogen.

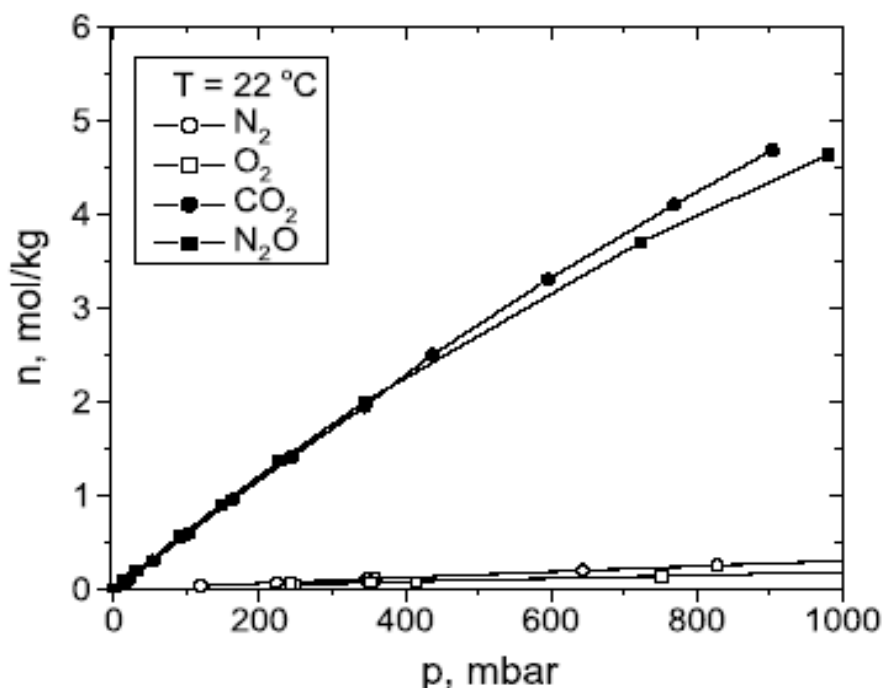


Figure 3.5. Adsorption isotherms of various gases on Cu-BTC at 22°C (Wang et al., 2002).

3.5 Mesoporous Molecular Baskets

Ordered mesoporous materials based on silica or mixed oxides have emerged as potential adsorbents for metal recovery from aqueous effluents due to their large surface area (as high as 1000 m²/g), ease of surface functionalisation for selective metal adsorption and desorption. Recently, the surface of such solids has also been functionalised with basic amino substrates to selectively adsorb acidic carbon dioxide molecules and is termed as molecular baskets. Xu et al. (2002) have presented a novel molecular basket adsorbent

for CO₂, in their work. This adsorbent is based on mesoporous molecular sieve MCM-41 with large pore volume, in which polyethylenimine (PEI) is loaded.

3.6 Metal Oxides

Carbon dioxide, which is an acid gas, is expected to adsorb more strongly on basic sites. Metal oxide adsorbents for CO₂ include alkaline metal oxides (Na₂O, K₂O), alkaline earth metal oxides (CaO, MgO) and alumina. These adsorbents are basic in nature and can be used as high temperature adsorbents for CO₂, as they are stable at flue gas temperatures. Sircar et al. (1995) reported the adsorption isotherms of CO₂ in MgO at temperature ranges from 300 – 500°C. Gaffney et al. (1999) discuss a PSA process for CO₂ separation using alumina adsorbent in their US patent.

3.7 Activated Carbons

Activated Carbon is the most widely used sorbent. Its manufacture and use date back to the 19th century. Its usefulness derives mainly from its large micro pore and meso pore volumes and the resulting high surface area. Activated carbon can be manufactured from carbonaceous material, including coal (bituminous, sub bituminous, and lignite), peat, wood, or nutshells (i.e., coconut). The manufacturing process consists of two phases, carbonization and activation. The carbonization process includes drying and then heating to separate by-products, including tars and other hydrocarbons, from the raw material, as well as to drive off any gases generated. The carbonization process is completed by heating the material at 400–600°C in an oxygen-deficient atmosphere (called Pyrolysis) that cannot support combustion

3.7.1 Manufacture of Activated Carbons

The modern manufacturing processes basically involve the following steps:

- (1). Raw material preparation,
- (2). Low-temperature carbonization, and
- (3). Activation.

The conditions are carefully controlled to achieve the desired pore structure and mechanical strength. The raw materials for activated carbon are carbonaceous matters

such as wood, peat, coals, petroleum coke, bones, coconut shell, and fruit nuts. Anthracite and bituminous coals have been the major sources. Starting with the initial pores present in the raw material, more pores, with desired size distributions, are created by the so called activation processes. Two standard activation methods are used. Gas and Chemical. After initial treatment and palletizing, gas activation first involves carbonization at 400-500 °C to eliminate the bulk of the volatile matter, and then partial gasification at 800-1000 °C to develop the porosity and surface area. A mild oxidizing gas such as CO₂ and steam, or flue gas, is used in the gasification step because the intrinsic surface reaction rate is much slower than the pore diffusion rate, thereby ensuring the uniform development of pores throughout the pellet. The activation process is usually performed in fixed beds, but in recent years fluidized beds have also been used. The activated carbon created by the activation process is primarily for gas and vapour adsorption processes. The other activation process that is also used commercially depends on the action of inorganic additives to degrade and dehydrate the cellulosic materials and, simultaneously, to prevent shrinkage during carbonization. This is called chemical activation. .

Physical Reactivation

The precursor is developed into activated carbons using gases. This is generally done by using one or combining the following processes:

Carbonization: - Material with carbon content is pyrolysed at temperatures in the range 400-600 °C, in absence of air (usually in inert atmosphere with gases like argon)

Activation/Oxidation: - Raw material or carbonized material is exposed to oxidizing atmospheres (carbon dioxide, oxygen, or steam) at temperatures above 250 °C, usually in the temperature range 600-1200 °C.

Chemical activation

Impregnation with chemicals such as acids like phosphoric acid or bases like potassium hydroxide, sodium hydroxide or salts like zinc chloride, followed by carbonization at temperatures in the range 450-900 °C. It is believed that the carbonization / activation step proceeds simultaneously with the chemical activation. This technique can be problematic in some cases because, for example, zinc trace residues may remain in the

end product. However, chemical activation is preferred over physical activation owing to the lower temperatures and shorter time needed for activating material.

Activated carbon includes a wide range of amorphous carbon-based materials prepared to exhibit a high degree of porosity and an extended surface area. Surface Area 300-2500 m²/g largest among all sorbents (except Metal organic frameworks ranging from 390m²/g to 4000m²/g). [6]

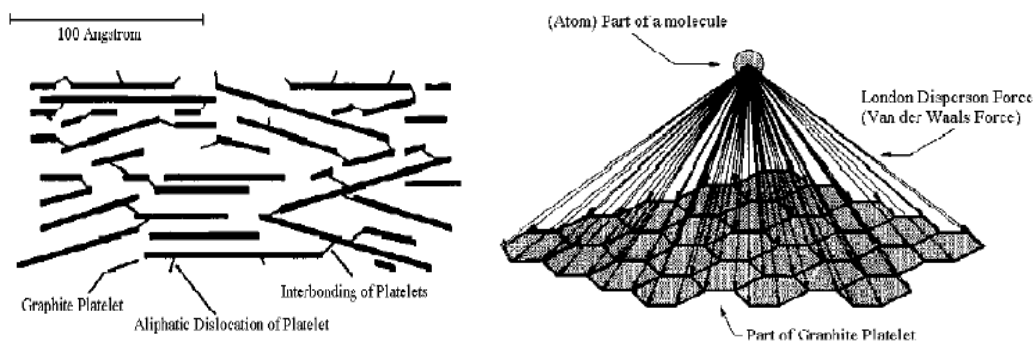


Figure 3.6. Structure of activated carbon

3.7.2 Types of Activated Carbon

Powdered Activated Carbon (PAC)

PAC is made up of crushed or ground carbon particles, 95–100% of which will pass through a designated mesh sieve or sieves. The American Water Works Association Standard (AWWA, 1997) defines GAC as being retained on a 50 - mesh sieve (0.297 mm) and PAC material as finer material, while American Society for Testing and Materials (ASTM D5158) classifies particle sizes corresponding to an 80-mesh sieve (0.177mm) and smaller as PAC. PAC is not commonly used in a dedicated vessel, owing to the high head loss that would occur. PAC is generally added directly to other process units, such as raw water intakes, rapid mix basins, clarifiers, and gravity filters.[7]

Granular Activated Carbon (GAC)

GAC can be either in the granular form or extruded. GAC is designated by sizes such as 8 × 20, 20 × 40, or 8 × 30 for liquid phase applications and 4 × 6, 4 × 8 or 4 × 10 for vapor phase applications. A 20 × 40 carbon is made of particles that will pass through a U.S. Standard Mesh Size No. 20 sieve (0.84 mm) (generally specified as >85% passing) but be

retained on a U.S. Standard Mesh Size No. 40 sieve (0.42 mm) (generally specified as >95% retained). AWWA (1992) B604 uses the 50-mesh sieve (0.297mm) as the minimum GAC size. The most popular aqueous phase carbons are the 12 × 40 and 8× 30 sizes because they have a good balance of size, surface area, and head loss characteristics.[7]

3.8 Reference

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Chapter-4

Gas Separation by Pressure Swing Adsorption Process

Chapter 4

Gas Separation by Pressure Swing Adsorption Process

4.1 Introduction

The surface of a solid represents a discontinuity of its structure. The forces acting at the surface are unsaturated. Hence, when the solid is exposed to a fluid, the fluid molecules will form bonds with it and become attached. The strength of the surface forces depends on the nature of both the solid and the fluid. If the forces are relatively weak, involving only van der Waals interactions supplemented in the case of polar or quadrupolar species by electrostatic forces (dipole or quadrupole interactions), we have what is called “physical adsorption” or “physisorption”. By contrast, if the interaction forces are strong, involving a significant degree of electron transfer, we have “chemisorption”. Chemisorption is limited to a monolayer, whereas, in physisorption, multiple molecular layers can form. Most practical adsorption separation processes depend on physisorption rather than on chemisorption, since, the capacities achievable in chemisorption systems are too small for an economic process. The solid material on which adsorption is taking place is known as adsorbent and the fluid which gets adsorbed is known as adsorbate. Direct exploitation of the adsorption phenomenon remained limited, until the early 1960s, to the purification of air and industrial vent gases. The picture has been drastically changed, however, by two major events: the development of a new adsorbent and the invention of a new process cycle. The first major development was the invention of synthetic zeolites or molecular sieves by Milton (1959) [1] at the Union Carbide Corporation. This class of adsorbents is the only known to adsorb a constituent from air preferentially. It preferentially adsorbs nitrogen over oxygen. The second breakthrough was the invention of efficient pressure swing cycles for the adsorption and regeneration of the adsorbents, concurrently by Skarstrom (1960) and, Guerin de Montgareuil and Domine (1964) [3]. These events were followed by a series of significant developments in the past three decades that have made adsorption a key process for gas separation in the chemical and petrochemical industries.

4.2 Categorization of Adsorptive Separation Processes

The principle of all adsorptive separation processes is the selective retention of one or more components of a feed mixture on a solid adsorbent so that an adsorbed phase having a composition different from that of the feed mixture is formed when the feed is contacted with the adsorbent. This produces a fluid phase enriched in the less selectively adsorbed components of the feed mixture. The adsorbed components are then desorbed by some means to produce a fluid enriched in the more selectively adsorbed components. The adsorption processes can be classified into three categories, based on (1) method of adsorbent regeneration, (2) feed composition, and (3) mechanism of separation.

4.2.1 Based on Method of Adsorbent Regeneration

The adsorbent can be regenerated by a number of methods, some of which are combined in the same process in practice. Three main methods of adsorbent regeneration are as follows:

1. Temperature Swing Adsorption (TSA). In temperature swing adsorption cycles, the adsorbent is primarily regenerated by heating. Heating is usually provided by preheating a purge gas. Each heating-cooling cycle usually requires a few hours to over a day. Thus TSA is used almost exclusively for purification purposes, in which the amounts of adsorptive gases being processed are small.[12]

2. Pressure Swing Adsorption (PSA). In this process adsorption is carried out at higher pressures and the saturated adsorbent is regenerated by reducing the pressure inside the adsorbent column. Some inert purging of a non-adsorbing gas, usually the product itself, is also used along with this to regenerate the adsorbent completely. If the regeneration is carried out at sub-atmospheric pressures, it is known as vacuum swing adsorption (VSA) process. The throughput is high in this process, since rapid cycles, usually in minutes and seconds, are possible. It is a most rapidly growing process in chemical industry [11].

3. Displacement Purge Adsorption (DPA). In this cycle, a purge gas is used which adsorbs as strongly as the adsorbates contained in the mixture to be separated. The purge gas is known as desorbent. This cycle is used when the regeneration is not

feasible by using the above mentioned cycles – for example, when a high temperature in the TSA would damage the products. The desorbent must be separated from the purge stream for reuse.

4.2.2 Based on Feed Composition

Depending on the concentration of the strongly adsorbed component in the feed mixture, the separation processes may also be divided into *bulk separation* and *purification* processes. There is no clear demarcation between the two categories [2]. has defined bulk separation as the point when 10 weight percentage or more of the mixture is adsorbed.

4.2.3 Based on Mechanism of Adsorption

The adsorptive separation is achieved by one of the three mechanisms: steric, kinetic, or equilibrium effect. In the case of steric selectivity, only small and properly shaped molecules can diffuse into the adsorbent, whereas other molecules are totally excluded. Kinetic separation is achieved by virtue of the differences in diffusion rates of different molecules into the pores of the adsorbents. Equilibrium adsorption property is used for the separation of the gases when one of the components interacts strongly with the adsorbent surface than the other components.

4.3 Pressure Swing Adsorption (PSA) Process

Adsorption is a commercially established process as Pressure Swing Adsorption (PSA) or Vacuum Swing Adsorption (VSA) for gas separation. The introduction of PSA processes is commonly attributed to Guerin de Montgareuil, P. and Domine, and D. 1964 [4]. The essential feature of a PSA process is that, during the regeneration step, the preferentially adsorbed species are removed by reducing the total pressure, rather than by raising the temperature or purging with a displacing agent (although a low-pressure purge step is commonly included in the cycle). The process operates under approximately isothermal conditions so that the useful capacity is the difference in loading between two points, corresponding to the feed and regeneration pressures [5]. on the same isotherm as shown in the Figure 4.1. The simple PSA system consists of two adsorber beds for a cyclic operation, but there are poly bed PSA systems in the industry for the separation and purification of other gases like oxygen, nitrogen, hydrogen etc.

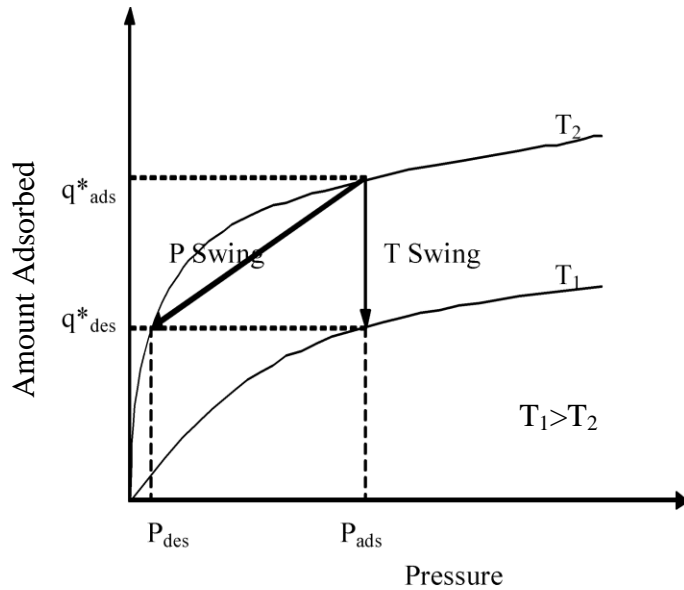


Figure 4.1. Adsorption isotherms showing pressure and temperature swings.[6].

The principle of all adsorptive separation processes is the selective retention of one or more components of a feed mixture on a solid adsorbent so that an adsorbed phase having a composition different from that of the feed mixture, is formed when the feed is contacted with the adsorbent [7]. This produces a fluid phase enriched in the less selectively adsorbed components of the feed mixture. The adsorbed components are then desorbed by some means to produce a fluid enriched in the more selectively adsorbed components of the feed mixture. Desorption process also cleans the adsorbent so that it can be reused. In PSA process the saturated adsorbent is regenerated by reducing the pressure inside the adsorber column and then by a low pressure purge of the product gas. PSA/VSA is a process of substantial interest in CO_2 separation due to its low energy requirements and cost advantages. However, at present this technology is not used at industrial scale for the separation of CO_2 from flue gas. There are a lot of research is going on this technology in order to find its technical and economical feasibility. Takamura et al. (2001) have evaluated the pressure swing adsorption of CO_2 on different layers of adsorbents, zeolite X and A, at pilot plant scale. The simple PSA system consists of two adsorber beds for a cyclic operation, but there are poly bed PSA systems in the industry for the separation and purification of other gases like oxygen, nitrogen, hydrogen etc.

4.3.1 PSA Cycle

The schematic representation of a two bed PSA system is given in Figure 4.2. The main steps in a PSA cycle are (1) pressurization with feed, (2) high pressure adsorption and product withdrawal, (3) Depressurization or blow down, and (4) low pressure purge with product to regenerate the adsorbent column. The simple two bed PSA cycle is shown in Figure 4.3. During step 1, a high pressure feed is supplied continuously to bed 2 in which preferential adsorption of the more strongly adsorbed or faster diffusing species occurs.

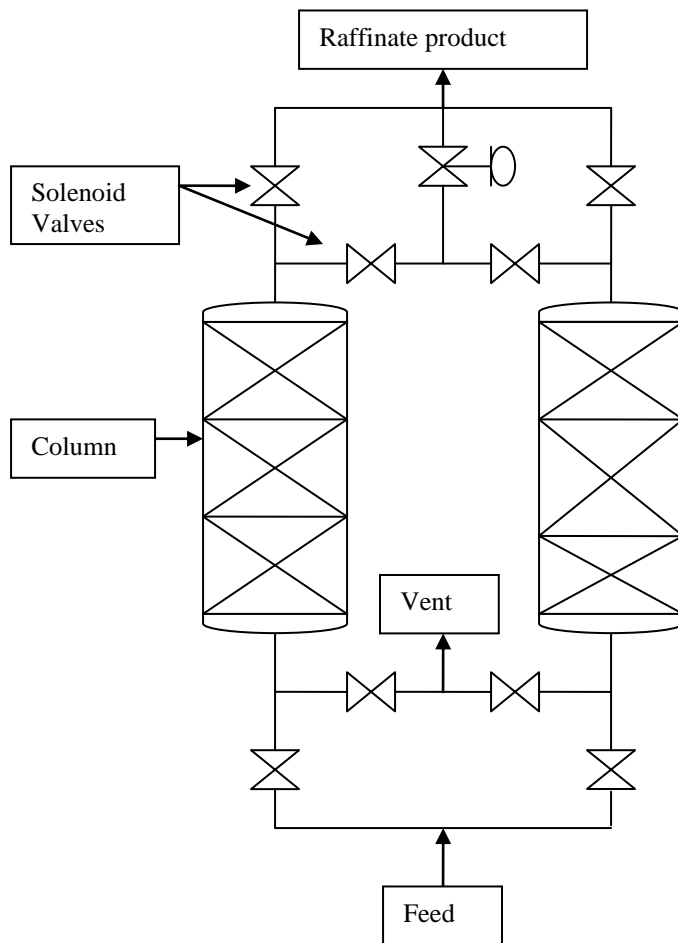


Figure 4.2. Basic two-bed PSA process[6]

The less strongly or slower diffusing species is removed as raffinate product at the bed outlet. A small portion of this stream is expanded to low pressure and is used to purge bed 1. In step 2, bed 1 is pressurized and the contents of bed 2 are blown down in the

reverse flow direction. This completes one half cycle. The other half cycle is accomplished similarly in steps 3 and 4 with adsorption in bed 1 and purge in bed 2, followed by blow down of bed 1 and pressurization of bed 2. A common feature of all PSA processes is that they are dynamic, i.e. they have no steady state. After a sufficiently large number of cycles, each bed in the process reaches a cyclic steady state (CSS), in which the conditions in the bed at the end of a cycle are approximately the same as those at the beginning of the next cycle.

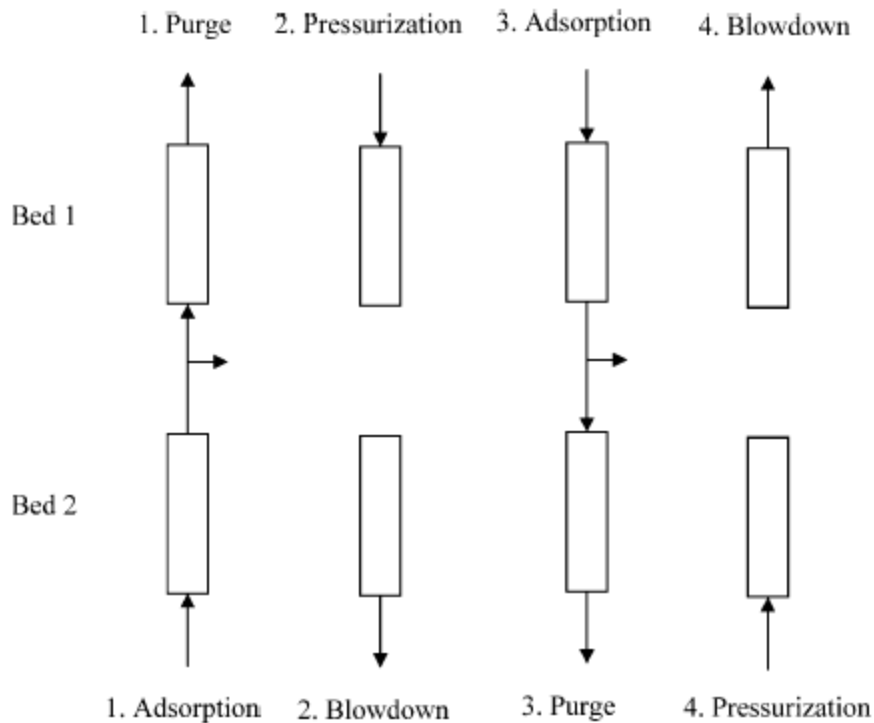


Figure 4.3. Schematic diagram of a two-bed PSA Cycle.[6]

4.3.2 Mathematical Model for PSA process

Simulation provides a method of predicting outlet concentrations and dynamic capacity of PSA, based on basic kinetics and equilibrium data as well as operation parameters, without doing the experiment in the pilot plant scale. To this end, a comprehensive model and a numerical solution method are required. There are a lot of models for the PSA process for purification or bulk separation of the gas mixtures. Some of them are

equilibrium based models [9] and others are linear driving force (LDF) based models [8]. The dynamic behavior of high pressure flow during adsorption and purge (of both bed 1 and 2) for component 'i' is described by the following equations (Jain et al., 2003):

Component mass balance in the gas phase:

$$\frac{\partial C_i}{\partial t} - D_L \frac{\partial^2 C_i}{\partial z^2} + \frac{\partial(vC_i)}{\partial z} + \frac{1-\varepsilon}{\varepsilon} \frac{\partial \bar{q}_i}{\partial t} = 0 \quad (4.1)$$

where C represents concentration in the gas phase; t denotes time; z is bed axial distance; v is interstitial fluid velocity; D_L is dispersion coefficient; ε is bed voidage. The last term in eqn. (4.1) is the mass transfer term between solid and gas, where q_i is the concentration of component 'i' in the solid. This model can be simplified by the following assumptions:

- 1) The system is isothermal with negligible pressure drop through the adsorbent beds.
- 2) The pressure change in the steps of pressurization and blowdown is so rapid that no significant exchange between adsorbed phase and gas phase occurs (frozen solid assumption).
- 3) The ideal gas law is applicable.
- 4) There is no axial or radial dispersion (plug flow).

Now eqn.(4.1) becomes,

$$\frac{\partial C_i}{\partial t} + \frac{\partial(vC_i)}{\partial z} + \frac{1-\varepsilon}{\varepsilon} \frac{\partial \bar{q}_i}{\partial t} = 0 \quad (4.2)$$

For constant pressure steps (adsorption and purge) the total concentration of the fluid remains constant in the bed, thus the total mass balance will be,

$$C \frac{\partial v}{\partial z} + \frac{1-\varepsilon}{\varepsilon} \sum_{i=1}^N \frac{\partial \bar{q}_i}{\partial t} = 0 \quad (4.3)$$

while for pressure changing steps the total mass balance is

$$\frac{\partial v}{\partial z} + \frac{1}{P} \frac{\partial P}{\partial t} = 0 \quad (4.4)$$

where it is assumed that the pressure drop in the bed is negligible. Eqns. (3.2) to (3.4) are applied for the flow from $z = 0$ to L . If the flow is reverse, the term $\partial/\partial z$ will be negative. The mass transfer kinetics is modeled using the LDF approximation, based on the simplification of Fick's second law of diffusion.

$$\frac{\partial \bar{q}_i}{\partial t} = k_i (q_i^* - q_i) \quad (4.5)$$

where q_i^* denotes the equilibrium concentration of component i . It is calculated using either extended Langmuir isotherm,

$$\frac{q_i^*}{q_{Si}} = \frac{b_i C_i}{1 + \sum_{j=1}^{j=n} b_j C_j} \quad (4.6a)$$

or using Henry's law,

$$q_i^* = K_i C_i \quad (4.6b)$$

The boundary condition for adsorption and pressurization steps is;

$$C_{i|z=0} = C_{fi} \quad (4.7)$$

for the purge step it is

$$C_{i|z=L} = \frac{P_L}{P_H} (C_{i|z=L})_{ads} \quad (4.8)$$

and for the depressurization step

$$\left. \frac{\partial C_i}{\partial z} \right|_{z=0} = 0 \quad (4.9)$$

The velocity boundary condition for the pressurization and adsorption step is

$$v \Big|_{z=0} = v_f \quad (4.10)$$

where v_f is the superficial velocity of feed at $z=0$

For the purge step the velocity boundary condition is

$$v \Big|_{z=L} = G v_f \quad (4.11)$$

where G is the purge-to-feed velocity ratio. For the blowdown step the velocity boundary condition is

$$v|_{z=L} = 0 \quad (4.12)$$

In the cyclic operation, the initial condition in the bed is the condition at the end of the previous step. For startup, either a clean bed or a saturated bed can be used. For a clean bed the initial conditions are

$$C_i(z, 0) = 0; \quad q_i(z, 0) = 0 \quad (4.13a)$$

and for a saturated bed they are

$$C_i(z, 0) = C_0; \quad q_i(z, 0) = q_i^* \quad (4.13b)$$

The above set of equation can be solved by numerical methods to get the required solution. The performance of a PSA process is measured on the basis of product purity and product recovery.

When an adsorption process for separating a gas mixture is determined, a logical sequence of decision steps in design of a PSA process is as follows:

- 1) Selection of proper adsorbent based on its equilibrium and kinetic characteristics.
- 2) Selection of particle size and shape.
- 3) Selection of operating pressure levels for a PSA system.
- 4) PSA cycle configuration and duration of each individual steps.
- 5) Adsorbent Bed dimensions
- 6) Vacuum swing adsorption (VSA) as an alternative.[10]

Table 4.1. Some of major PSA processes used in the industries [11]

Process	Product	Adsorbent	Type of system
H ₂ recovery from fuel gas	Ultra pure H ₂	Activated carbon or zeolite	Multiple bed system
Heatless drier	Dry air (for instrument)	Activated Al ₂ O ₃	Two bed skarstrom cycle
Air seperation	O ₂ (+Ar)	5A zeolite	Two bed skarstrom cycle
Air seperation	N ₂ (+Ar)	Carbon Molecular Sieve (CMS)	Two bed self purging cycle
Air seperation	N ₂ and O ₂	5A Zeolite or CaX	Vacuum swing system
Isosiv	Linear/ Branched hydrocarbon	5A zeolite	Molecular sieve separation with vacuum swing
Landfill gas separation	CO ₂ and CH ₄	Carbon Molecular Sieve (CMS)	Vacuum swing

4.4 Applications of the PSA technology

PSA technology is widely used in various industrial processes. One of the primary applications of PSA is in the removal of carbon dioxide (CO₂) as the final step in the large-scale commercial synthesis of hydrogen (H₂) for use in oil refineries and in the production of ammonia (NH₃). Another application of PSA is the separation of carbon dioxide from biogas to increase the methane (CH₄) content. Through PSA the biogas can be upgraded to a quality similar to natural gas. Research is currently underway for PSA to capture CO₂ in large quantities from coal-fired power plants prior to geosequestration, in order to reduce greenhouse gas production from these plants. PSA is an economic choice for small-scale production of reasonable purity oxygen or nitrogen from air. PSA technology has a major use in the medical industry to produce oxygen, particularly in

remote or inaccessible parts of the world where bulk cryogenic or compressed cylinder storage are not possible. PSA has also been discussed as a future alternative to the non-regenerable sorbent technology used in space suit primary life support systems, in order to save weight and extend the operating time of the suit. Table 4.1 shows some of the major PSA processes used in the industries.

4.5 Reference

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Chapter-5

Equilibrium and Dynamic Adsorption Measurements CO₂ on Activated Carbon

Chapter 5

Equilibrium and Dynamic Adsorption Measurements

CO₂ on Activated Carbon

5.1 Experimental

5.1.1 Materials

Activated carbons AP360 (pellet size 3mm) and AP460 (pellet size 4mm), supplied by Calgon Carbon Corporation, Pittsburgh, USA, were used as such for the equilibrium and dynamic adsorption studies of carbon dioxide and nitrogen. Both samples were having same chemical properties and differ only in the size of the pellets. Carbon dioxide (99.9%) and nitrogen (99.99%) were used for all the adsorption measurements.

5.1.2 Equilibrium adsorption isotherm measurements

The equilibrium adsorption isotherms of carbon dioxide and nitrogen on activated carbons were measured using a static volumetric adsorption system (*Micromeritics Instrument Corporation, USA, Model ASAP 2010*) at 303 K. Prior to adsorption measurements, the samples were activated *in situ* by increasing the temperature (at a heating rate $<1 \text{ K min}^{-1}$) to 473 K under vacuum ($5 \times 10^{-3} \text{ mmHg}$) and the temperature and vacuum was maintained for 8 hours before the adsorption measurements. Adsorption temperature was maintained ($\pm 0.1 \text{ K}$) by circulating water from a constant temperature bath (*Julabo F25, Germany*). Requisite amount of the adsorbate gas was injected into the volumetric set up at volumes required to achieve a targeted set of pressures ranging from 0.1 to 850 mmHg. Three pressure transducers of capacities 1 mmHg (Accuracy within 0.12% of the reading); 10 mmHg (Accuracy within 0.15% of the reading) and 1000 mmHg (Accuracy within 0.073% of full scale) were used for the pressure measurements. A minimum equilibrium interval of 5 seconds with a relative target tolerance of 5.0% of the targeted pressure and an absolute target tolerance of 5.000 mmHg were used to determine equilibrium for each measurement point. The adsorption and desorption was completely reversible and it is possible to remove the adsorbed gases by simple evacuation.

The pure component selectivity of two gases A and B was calculated by using the equation,

$$\alpha_{A/B} = \left[\frac{V_A}{V_B} \right]_{P,T}$$

where V_A and V_B are the volumes of gas A and B respectively adsorbed at any given pressure P and temperature T.

Adsorption isotherms measured were fitted into Langmuir adsorption isotherm model and is given by the equation

$$\frac{q}{q_m} = \frac{bP}{1 + bP}$$

where q = amount of gas adsorbed on the adsorbent at equilibrium, q_m = monolayer or saturated amount adsorbed, b = Langmuir constant, P = equilibrium pressure of the adsorbate. The quantity $q_m b = K$, the Henry's law constant.

5.1.3 Dynamic adsorption measurements or breakthrough measurements

Dynamic adsorption of CO_2 on activated carbon from its gaseous mixture with nitrogen was carried out in a breakthrough measurement set up (in-house modified vapor-liquid plug flow reactor). Figure 5.1 shows the schematic diagram of the break through setup for studying the dynamic adsorption properties of gases in adsorbent column. It consists of an adsorbent column of length 35 cm. and diameter 1.9 cm, made up of stainless steel; a furnace which can be used heat the column upto 873 K. Two mass flow controllers (MFC) are there to control the flow of two different gases at the same time. All gas lines are of stainless tubing ($\frac{1}{4}$ " diameter). Figure 5.2 shows the photograph of break through setup. The column was filled with activated carbon adsorbent pellets and activated at 473 K under nitrogen gas flow for overnight and then cooled to 303 K before the carbon dioxide breakthrough measurements. The feed gas consist of around 15% CO_2 and 85% N_2 , in which N_2 acts as a carrier gas for the dynamic adsorption measurements, was passed through the adsorbent column at a constant flow rate. The feed concentration and the product concentration at the other end of adsorbent column, were measured in a GC

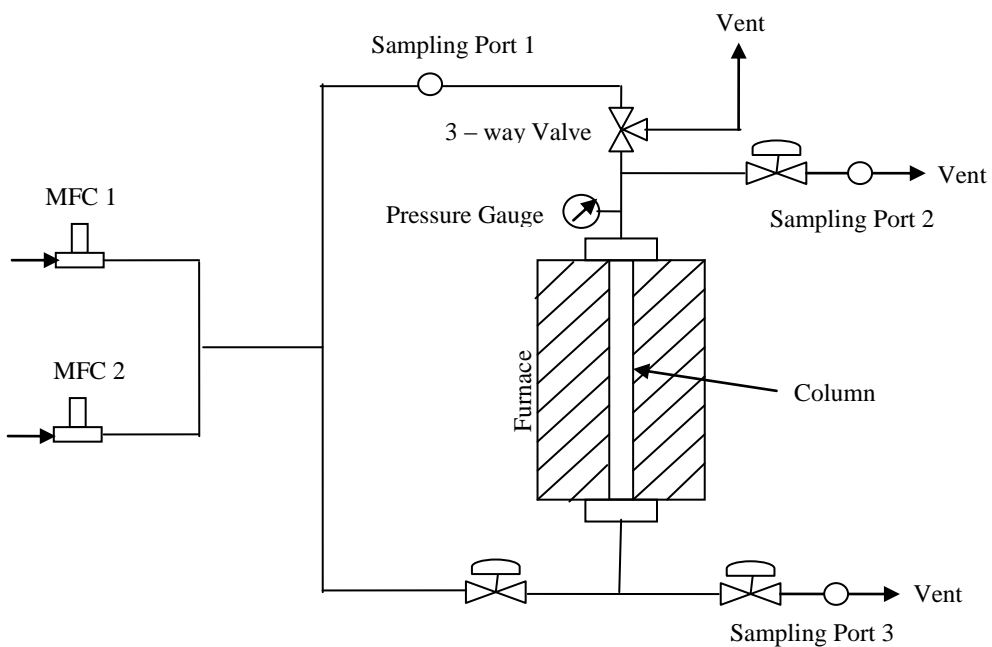


Figure 5.1. Schematic diagram of break through setup.

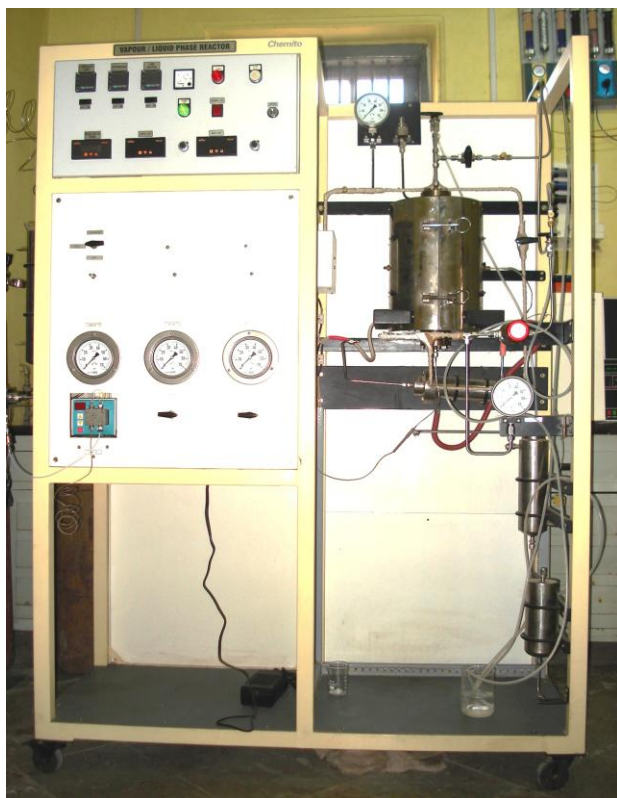


Figure 5.2. Photograph of break through setup.

instrument (GC-7610, Chemito Technologies Pvt. Ltd., Nasik, India) equipped with a TCD detector (TCD 866) using a Porapaq packed column with H₂ gas as a carrier gas at a flow rate of 40ml/min. Around 0.5 ml of the gas samples were taken in a gas tight syringe and analyzed in the GC.

5.2 Results and Discussions

5.2.1 Equilibrium adsorption isotherms

The equilibrium adsorption isotherms of carbon dioxide and nitrogen on activated carbons AP360 and AP460 at 303 K are given in Figure 5.3. The equilibrium adsorption capacities for carbon dioxide and nitrogen at 1 atm pressure were slightly different for both the adsorbent with around 38 cc/g in AP360 and 34 cc/g in AP460 For carbon dioxide and 5 cc/g in AP 360 and 4.8 cc/g in AP460 for nitrogen. The heats of adsorption of CO₂ and N₂ in these adsorbents were around 23 kJ/mol and 15 kJ/mol respectively.

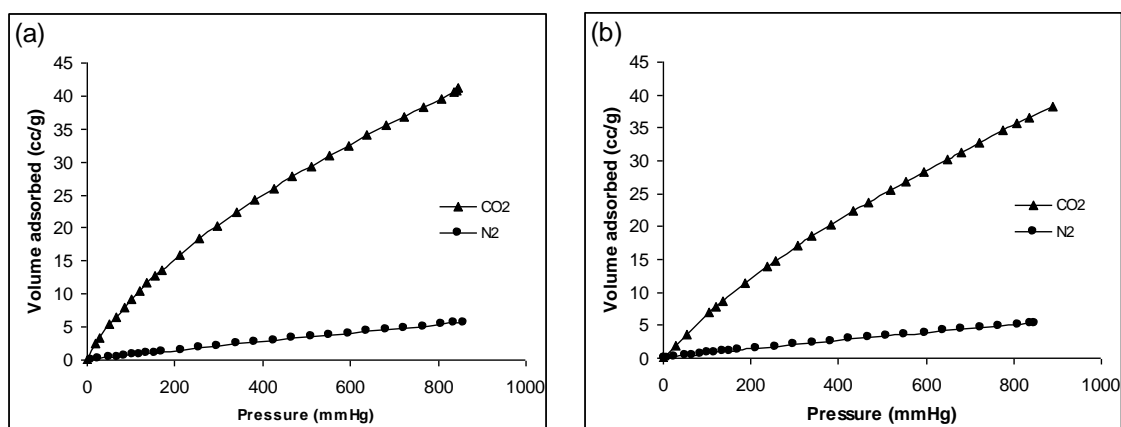


Figure 5.3. Equilibrium adsorption isotherms of CO₂ and N₂ in (a) AP360 and (b) AP460 activated carbons at 303 K.

Table 5.1. Pure component selectivities of CO₂ over N₂ in activated carbons at 303 K

Sample	Selectivity, $\alpha_{\text{CO}_2/\text{N}_2}$		
	100 mm Hg	380 mm Hg	760 mm Hg
AP 360	12.4	8.9	7.6
AP 460	9.7	7.7	7.1

Pure component selectivities for CO₂ over N₂ are given in Table 5.1 at different partial pressures. The selectivity for CO₂ over N₂ was higher for AP360 compared to AP460 at different partial pressures. At lower pressure region the selectivity for CO₂ over N₂ was high in both the samples.

The Langmuir fitting parameters are given Table 5.2. The Langmuir parameters for CO₂ and N₂ were higher for AP360 compared to AP460. The Langmuir model showed good fitting with the experimental adsorption isotherm data which can be seen from the R² values given in the table.

Table 5.2. Langmuir parameters for CO₂ and N₂ in activated carbons at 303 K.

Sample	CO ₂			N ₂		
	K	b	R ²	K	b	R ²
	(cc/g .atm ⁻¹)	(atm ⁻¹)		(cc/g .atm ⁻¹)	(atm ⁻¹)	
AP360	70.35	0.85	0.9980	5.69	0.12	0.9996
AP460	50.22	0.47	0.9995	5.55	0.15	1.0000

Table 5.3. Adsorbent column details and flow conditions of CO₂ breakthrough measurements in activated carbons AP360 and AP460 at 303 K.

Adsorbent column details	Adsorbent	
	AP 360	AP 460
Feed concentration	CO ₂ = 15.0 ± 0.5 % N ₂ = 85.0 ± 0.5 %	CO ₂ = 15.0 ± 0.5 % N ₂ = 85.0 ± 0.5 %
Weight of adsorbent (g)	47.4	39.3
Feed flow (ml/min)	120 ± 1	120 ± 1/ 60± 1
Average particle diameter (mm)	3	4
Column length (cm)	35	35
Column diameter (cm)	1.9	1.9

5.2.2 CO₂ breakthrough curves

The breakthrough measurements of CO₂ in activated carbons AP360 and AP460 were carried out at 303 K and the feed conditions are given in Table 5.3. Both dynamic adsorption and desorption curves of CO₂ in activated carbons AP360 and AP460 at 303 K are shown in Figure 5.4. In AP360 sample, the breakthrough of CO₂ happened around 25 minutes and in the case of AP460, the breakthrough happened around 14 minutes. The breakthrough capacity of CO₂ in AP360 was around 10.2 cc/g and in AP460 it was around 6.4 cc/g. This difference in breakthrough capacity could be due to the following reason: due to larger particle size of AP460 (4 mm) compared to AP360 (3 mm), there could be diffusion resistance for CO₂ in AP460 compared to AP360. Figure 5.5 shows the breakthrough curves of CO₂ in AP460 at two different flow rates of 60 ml/min and 120 ml/min. The CO₂ breakthrough times were 35 minutes and 14 minutes respectively for 60 ml/min and 120 ml/min feed flow rates. The breakthrough capacity of CO₂ increased from 6.4 cc/g to 8.0 cc/g in AP460 sample when the flow rate is decreased from 120 ml/min to 60 ml/min. This increase in breakthrough adsorption capacity could be due to the fact that at low flow rate, CO₂ molecules get more residence time and can diffuse further inside into the adsorbent particle than at higher flow rates.

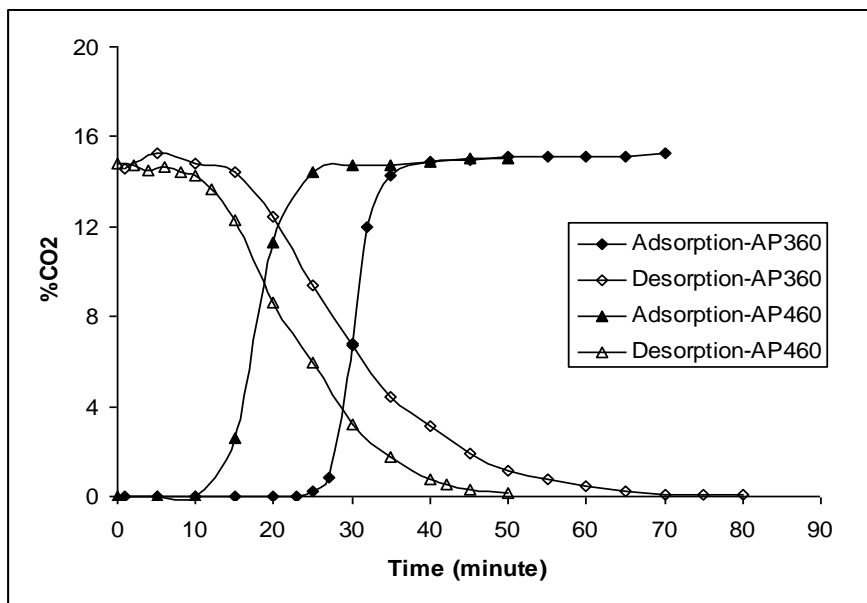


Figure 5.4. CO₂ breakthrough curves at 303 K in activated carbons AP360 and AP460 at a feed flow rate of 120 ± 1 ml/min.

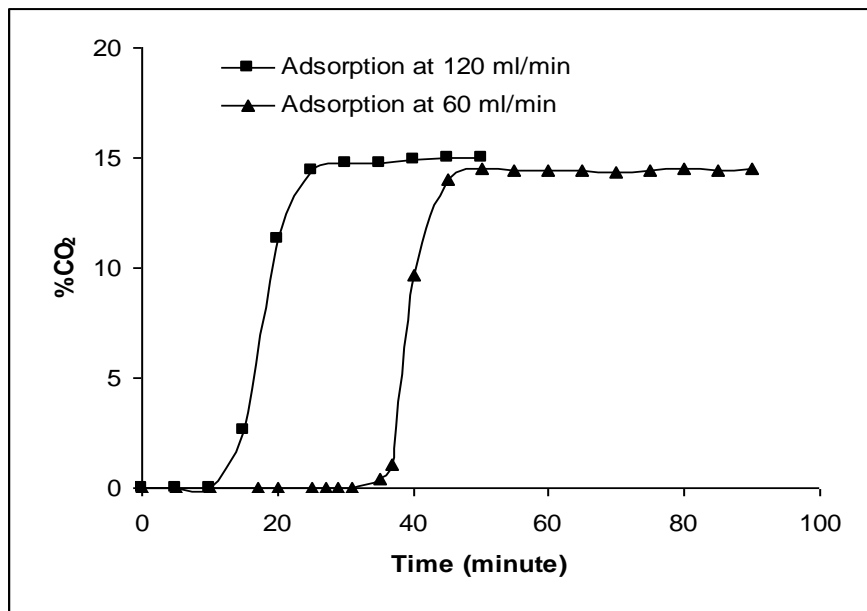


Figure 5.5. CO₂ breakthrough curves at 303 K in activated carbons AP460 at feed flow rates of 60± 1 ml/min and 120 ± 1 ml/min.

5.3 Conclusions

The equilibrium and dynamic adsorption measurements of CO₂ were carried out in two activated carbon samples namely AP360 (3 mm pellets) and AP460 (4 mm pellets). It was found that the equilibrium adsorption capacity for CO₂ was slightly higher in AP360 sample compared to AP460 sample. The breakthrough adsorption capacity of CO₂ was also higher in AP360 compared to AP460. This could be due to the larger particle size of AP460 compared to AP360, so that there would be resistance for the diffusion of CO₂ into the interior of the adsorbent particle. Dynamic adsorption measurements of CO₂ in AP460 were conducted at two different flow rates of 60 ml/min and 120 ml/min. It was found that the breakthrough adsorption capacity for CO₂ was increased at low feed flow rate compared to higher feed flow rate. This could be due to the fact that at low flow rate, CO₂ molecules get more residence time and can diffuse further inside into the adsorbent particle than at higher flow rates.

Chapter-6

Pressure Vacuum Swing Adsorption (PVSA) Process for CO₂ Removal

Chapter 6

Pressure Vacuum Swing Adsorption (PVSA) Process for CO₂ Removal

6.1 Two bed pressure swing adsorption (PSA) setup

Pressure/vacuum swing adsorption studies for the removal of CO₂ from flue gas was conducted in an in-house built two bed PSA setup using a model gas mixture of 15% CO₂ and 85% N₂ at room temperature. Schematic diagram of the two bed PSA setup is given in Figure 6.1. The experimental PSA setup consists of two adsorbent beds made up of aluminum columns and eleven solenoid valves to controls the process cycle sequences. Gas lines were made up of ¼ inch diameter stainless tubes and a back pressure regulator was fitted at the raffinate end to maintain the pressure inside the adsorbent column during

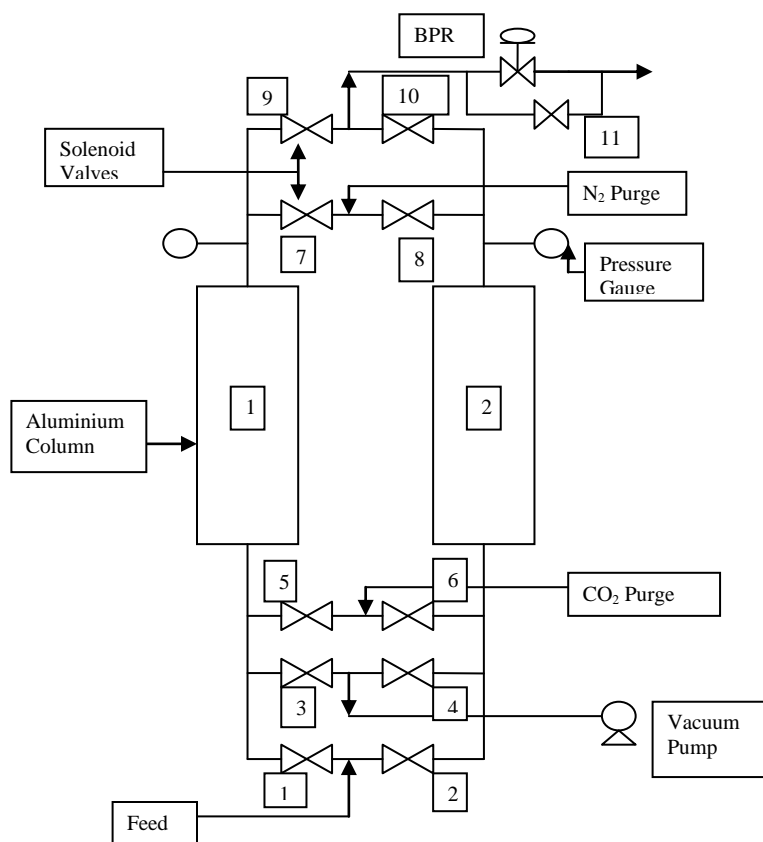


Figure 6.1. Schematic diagram of two bed PSA setup.

process cycles. A vacuum pump was connected to the extract end to collect the carbon dioxide as product from the adsorbent column. The open-close sequence of the solenoid valves were controlled by a programmable logic controller (PLC). The feed, raffinate and extract flow rates were measured using wet test meters. Figure 6.2 shows the photograph of the in-house build two bed PSA setup used for the P/VSA studies for the removal of CO₂ from its gaseous mixture with N₂.

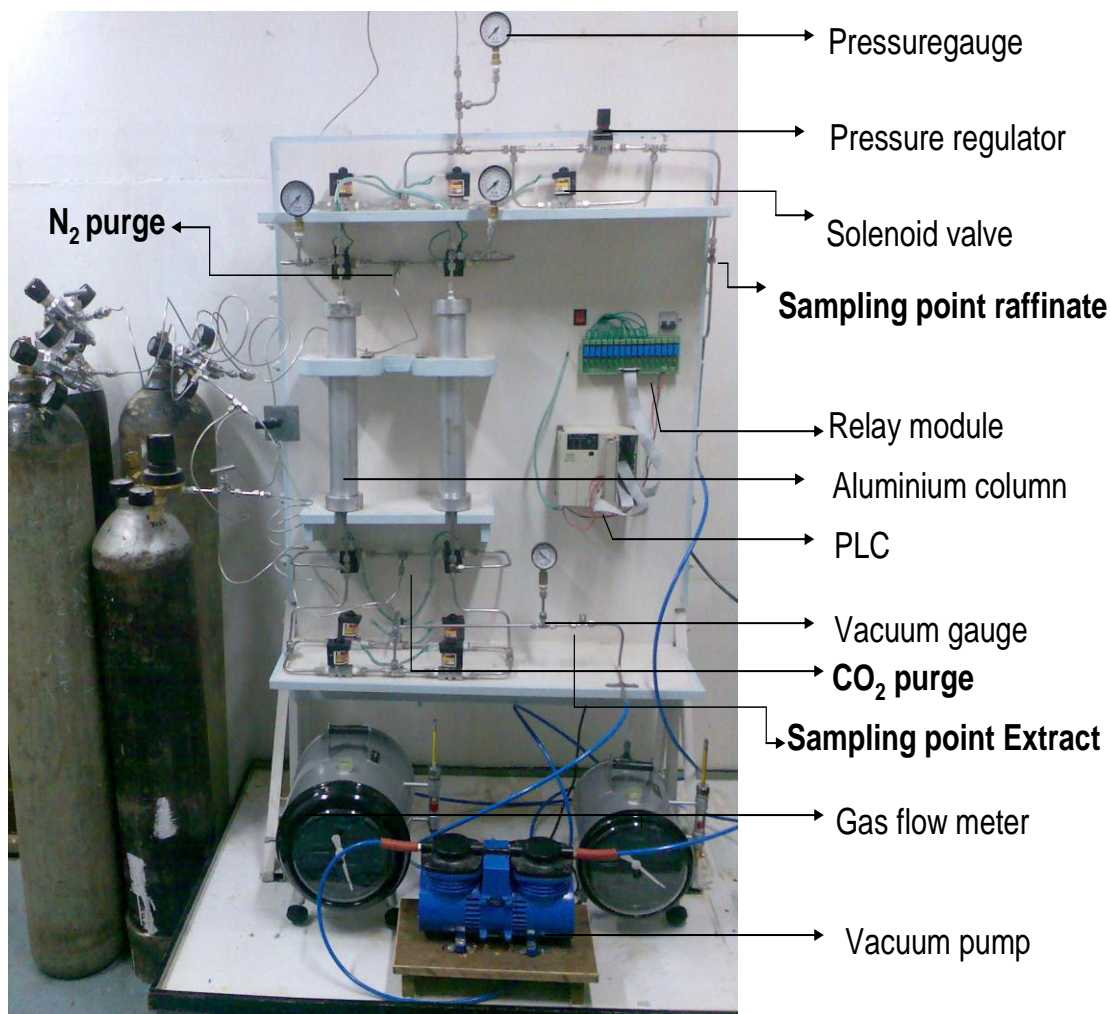


Figure 6.2. Photograph of two bed PSA setup.

6.2 Adsorbent column activation unit

Prior to the PSA experimental studies the adsorbent column filled with the adsorbent was activated under nitrogen flow in order to remove the adsorbed moisture and other gases inside the adsorbent particles. For this purpose a heating jacket was fabricated with a high

temperature withstanding cloth made up of glass wool fibers. Heating coil was properly wound inside this cloth and thick blanket of glass wool were used for thermal insulation to the outer side of this heating jacket. Figure 6.3 shows photograph of the activation unit.

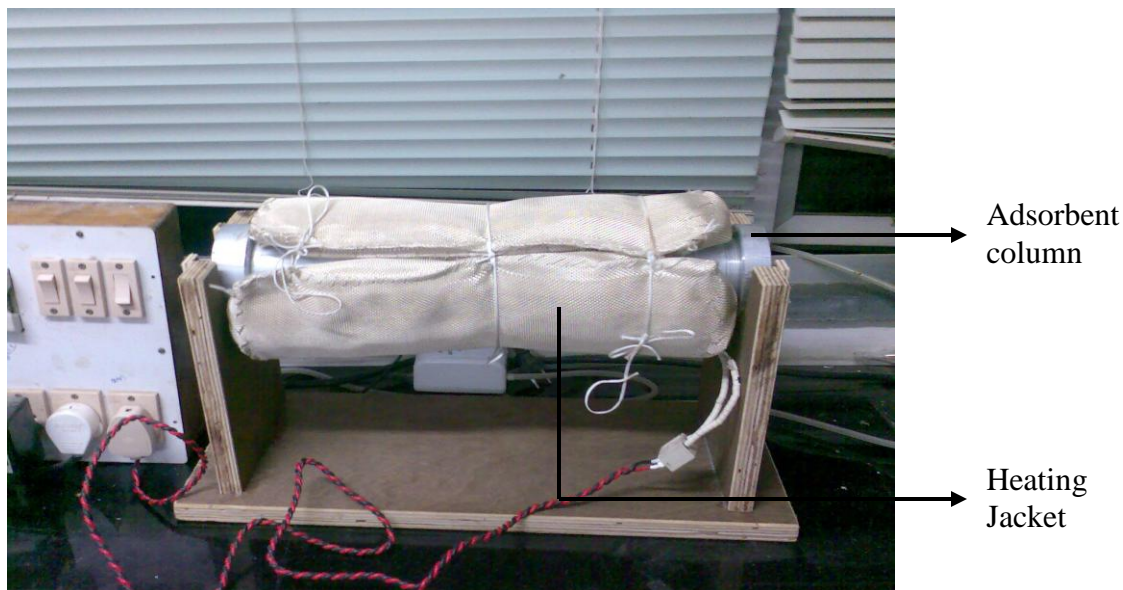


Figure 6.3. Photograph of adsorbent column activation unit.

6.3 PSA experiments

Four runs of PSA experiments were carried in the PSA setup in order to study the effect of cycle sequences, cycle time and feed conditions on the purity and recovery of CO₂ from its gaseous mixture with N₂ as a model gas mixture for flue gas. The adsorbent used for the experiment was AP360 activated carbon which showed higher breakthrough capacity for CO₂ in the dynamic adsorption studies. All experiments were carried out at room temperature.

6.3.1 Six step PSA cycle with N₂ pressurization

The PSA experimental run 1 was conducted according to the cycle steps along with the particular time for each step as given in Table 6.1. The adsorption pressure was 2 atm and the feed flow rate was 1 liter/minute with around 15% CO₂ and 85% N₂ as feed concentration. At step 1, bed 1 undergoes pressurization by feed mixture and bed 2 is purged with CO₂ co-currently to the feed flow at flow rate of 1 liter/minute, in order to remove the nitrogen gas from the void space of the adsorbent column, since the desired

product is CO₂ which is the strongly adsorbing species and has to collect as the extract by vacuum desorption. In step 2, bed 1 is in adsorption mode where CO₂ in the feed gets adsorbed and bed 2 is desorbed counter-currently to collect the adsorbed CO₂ as product.

Table 6.1. PSA cycle sequences with time for experiment run 1.

Steps	Bed-1	Bed-2	Time (minute)
1.	Pressurization	Co-current CO ₂ purge	1
2.	Adsorption	Counter-current desorption by vacuum	6
3.	Co-current depressurization	Counter-current N ₂ pressurization	1
4.	Co-current CO ₂ purge	Pressurization	1
5.	Counter-current desorption by vacuum	Adsorption	6
6.	Counter-current N ₂ pressurization	Co-current depressurization	1

Table 6.2. Solenoid valves open-close sequence in PSA experiment run 1.

Steps	Bed-1					Bed-2					V ₁₁
	V ₁	V ₃	V ₅	V ₇	V ₉	V ₂	V ₄	V ₆	V ₈	V ₁₀	
1	on	off	off	off	off	off	off	on	off	on	on
2	on	off	off	off	on	off	on	off	off	off	off
3	off	off	off	off	on	off	off	off	on	off	on
4	off	off	on	off	on	on	off	off	off	off	on
5	off	on	off	off	off	on	off	off	off	on	off
6	off	off	off	on	off	off	off	off	off	on	on

The maximum vacuum could be achieved during the desorption process was 0.2 atm. During step 3, the bed 1 was depressurized co-currently and bed 2 was pressurized with N₂. In step 4, bed is purged with CO₂ co-currently and bed 2 was pressurized further with feed gas mixture. Bed 1 was evacuated in step 5 to collect the adsorbed CO₂ and bed 2 was in adsorption mode. In step 6, bed 1 is pressurized from vacuum with N₂ and bed 2 is depressurized co-currently. The open-close sequences of solenoid valves are given Table 6.2. The total time for one cycle was 16 minutes. PSA experiment run 2 was conducted with the same cycle sequence but the adsorption/desorption time was 8 minutes and the total of a single cycle was 20 minutes. The feed flow rate was 2 liter/minute with a CO₂ concentration of 15 % and the CO₂ purge flow rate was also 2 liter/minute.

Table 6.3. PSA cycle sequences with time for experiment run 3.

Steps	Bed-1	Bed-2	Time (minute)
1.	Pressurization	Co-current CO ₂ purge	2.0
2.	Adsorption	Counter-current desorption by vacuum	4.0
3.	Co-current depressurization	Counter-current N ₂ purge	1.5
4.	Co-current CO ₂ purge	Pressurization	2.0
5.	Counter-current desorption by vacuum	Adsorption	4.0
6.	Counter-current N ₂ purge	Co-current depressurization	1.5

6.3.2 Six step PSA cycle with N₂ purge

PSA experiment run 3 was conducted with nitrogen purge in step 3 and 6 instead of nitrogen pressurization as in the case of run 1 and 2. This was done to clean the bed so that more CO₂ can be adsorbed during the adsorption step. The pressure during the adsorption step was 1 atm and the feed flow rate was 2 liter/minute. The CO₂ purge rate was 3 liter/minute. Table 6.3 shows the PSA cycle steps with the time for each step. Table 6.4 shows the solenoid valve open-close sequence in experiment run 3. The total time of a single step was 15 minutes.

Table 6.4. Solenoid valves open-close sequence in PSA experiment run 3.

Steps	Bed-1					Bed-2					V ₁₁
	V ₁	V ₃	V ₅	V ₇	V ₉	V ₂	V ₄	V ₆	V ₈	V ₁₀	
1	on	off	off	off	off	off	off	on	off	on	on
2	on	off	off	off	on	off	on	off	off	off	off
3	off	off	off	off	on	off	on	off	on	off	on
4	off	off	on	off	on	on	off	off	off	off	on
5	off	on	off	off	off	on	off	off	off	on	off
6	off	on	off	on	off	off	off	off	off	on	on

Table 6.5. PSA cycle sequences with time for experiment run 4.

Steps	Bed-1	Bed-2	Time (minute)
1.	Counter-current N ₂ pressurization	Co-current CO ₂ purge	2.5
2.	Adsorption	Counter-current desorption by vacuum	5.0
3.	Co-current CO ₂ purge	Counter-current N ₂ pressurization	2.5
4.	Counter-current desorption by vacuum	Adsorption	5.0

6.3.3 Four step PSA cycle

PSA experiment run 4 was conducted in four steps cycle manner. In step 1, bed 1 was pressurized with N₂ and bed 2 was purged with CO₂ at flow rate of 3 liter/minute. During step 2, bed 1 was in adsorption mode while bed 2 is evacuated to collect the adsorbed CO₂ as product. The adsorption pressure was 1 atm with a feed flow rate of 2 liter/minute. Around 25% of CO₂ was contained in the feed along with N₂ gas. In step 3,

bed 1 is purged with CO₂ and bed 2 is pressurized with N₂. Bed 1 was evacuated in step 4 in order to collect adsorbed CO₂ from bed 1 and bed 2 was in adsorption mode. The PSA cycle steps with the time for each step are shown in Table 6.5. The total time for one complete cycle was 15 minutes. Table 6.6 shows the solenoid valve open-close sequence in experiment run 4.

Table 6.6. Solenoid valves open-close sequence in PSA experiment run 4.

Steps	Bed-1					Bed-2					V ₁₁
	V ₁	V ₃	V ₅	V ₇	V ₉	V ₂	V ₄	V ₆	V ₈	V ₁₀	
1	off	off	off	on	off	off	off	on	off	on	on
2	on	off	off	off	on	off	on	off	off	off	off
3	off	off	on	off	on	off	off	off	on	off	on
4	off	on	off	off	off	on	off	off	off	on	off

6.4 Results and discussions

Table 6.7 shows the purity and percentage recovery of CO₂ in the product extract at different process conditions. The percentage recovery was calculated from the ratio of the amount of CO₂ present in the extract and the total amount CO₂ present in both the feed and CO₂ purge streams. From the table it can be seen that the percentage recovery of CO₂

Table 6.7. Percentage purity and recovery of CO₂ in product extract at different process conditions.

Experiment	Feed flow rate (liter/minute)	%CO ₂ in the feed	CO ₂ purge flow rate (liter/minute)	% Purity	% Recovery
Run 1	1	15	1	45.7	94.0
Run 2	2	15	2	70.0	76.4
Run 3	2	15	3	82.4	63.9
Run 4	2	25	3	90.7	72.0

was the maximum in experiment run 1 compared to other experiment runs, but the purity of CO₂ was very low. In experiment run 4 the CO₂ purity was 90.7%, highest among the all the PSA experiment run in the present study, with a recovery of 72%. But, the feed concentration was around 25% CO₂. In experiment run 3, the CO₂ purity and recovery were moderate with values of 82.4 % and 63.9% respectively. The decreased product recovery may be due the fact that the adsorbed CO₂ may not be evacuated completely from the bed and some of the CO₂ is lost in the counter current N₂ purge to clean the adsorbent bed. The CO₂ recovery may be increased if the evacuation as well as the adsorption time is increased in the experiment run 3.

6.4 Conclusions

PSA experimental setup for the removal of CO₂ from its gaseous mixture with N₂ was fabricated and the PSA experiments were conducted using AP360 as the carbon dioxide selective adsorbent. Experiment run 1 showed higher recovery, but the CO₂ purity was very low. Higher CO₂ purity was got in experiment run 4 with moderate recovery. However, it is desired to have a PSA process with more than 95% product purity and recovery for the effective capture and storage of CO₂ from flue gas. Rigorous process simulation study is needed to optimize the CO₂ PSA process, in order to have the desired product purity and recovery.

Chapter-7

Conclusion and Future Work Scope

Chapter 7

Conclusions and Future Scope of Work

7.1 Conclusions

The emission of carbon dioxide into the atmosphere is one of the most serious problems with regards to its greatest contribution towards the greenhouse gas effect. Approximately one third of all CO₂ emissions due to human activity come from fossil fuels used for generating electricity, with each power plant capable of emitting several million tonnes of CO₂ annually. But, these fossil fuels provides >80 % energy needs all over the world and will continue to do so for the foreseeable future. Therefore, it important to capture and store the CO₂ emitted from these source, in order to avoid greenhouse gas effects. Pressure Swing Adsorption (PSA) or Vacuum Swing Adsorption (VSA) process is one of the potential candidates for flue gas separation for CO₂ capture, due to its proven record in other industrial gas separations. However, the use of PSA process for the removal and recovery of carbon dioxide from hot fuel gas streams at high temperatures, the first and most important issue is to find the appropriate adsorbent.

Equilibrium and dynamic adsorption measurements of CO₂ and N₂ were carried out in two activated carbon samples namely AP360 and AP460. AP 360 sample showed higher equilibrium as well as breakthrough adsorption capacity for CO₂ compared to AP460. Activated carbon AP360 was used for CO₂ PSA experiment due to its higher breakthrough capacity for CO₂. At a feed concentration of 15% CO₂, around 82.4 % and 63.9% of CO₂ purity and recovery respectively were got in the PSA experiments of the present study. At higher CO₂ feed concentration, the purity and recovery for CO₂ increased. However, to optimize the CO₂ PSA process for the higher purity and recovery of CO₂, rigorous process simulation study is needed. Poly bed PSA system with more than two adsorbent columns may also required, to increase the product purity and recovery of CO₂,

7.2 Future scope of work

It is desired to get CO₂ with a purity and recovery of more than 95% from the CO₂ PSA process. Therefore to optimize the present study, rigorous process simulation is needed. It can also be investigated the scope of other adsorbents like zeolites for the effective removal of CO₂ from flue gas with a CO₂ purity and recovery of more than 98%. Since the flue gas is coming at a higher temperature, the PSA experiments can be done at elevated temperatures in the experimental PSA setup. Another option for increase the purity and recovery of CO₂ is the use of poly bed PSA systems having more than two adsorbent columns.