Steam Regeneration of Amine Impregnated Silica Based Sorbents for Post Combustion CO_2 Capture

by

Navjot Kaur Sandhu

A thesis submitted in partial fulfillment of the requirements for the degree of

Master of Science

in
Chemical Engineering

Department of Chemical and Materials Engineering
University of Alberta

ABSTRACT

In this study, an experimental investigation of CO_2 capture using amine functionalized mesoporous silica based sorbents was carried out. Polyethyleneimine (PEI) impregnated silica sorbents were synthesized and tested in TGA under different adsorption temperatures and partial pressures of CO_2. Sorbent characterization was carried out using N_2 adsorption-desorption isotherms, FTIR, SEM and elemental analysis. Multiple cycles study was conducted to examine the effect of presence of O_2 (0-5%) in flue gas on CO_2 adsorption performance of sorbent. A separate packed bed study was conducted to study the effect of different concentrations of moisture (5.27–14.74%) in flue gas on CO_2 adsorption and energy requirements for sorbent regeneration. A major study that was undertaken was to test the performance and stability of sorbent under steam stripping conditions. Steam was used for sorbent regeneration in a multiple cycle study and characterization of used sample was carried out to study any change in sorbent properties. Steam at different temperatures was used to study CO_2 desorption. Desorption kinetics for steam and inert gas stripping was compared. It was observed that the sorbent performance was stable under steam environment along with improved desorption kinetics over inert gas stripping. No steam condensation or amine leaching was observed in this study.

ACKNOWLEDGEMENT

Foremost, I would like to express my sincere gratitude and thankfulness to my research supervisor, Dr. Rajender Gupta, for providing me this valuable research opportunity. Also, his continuous guidance and support throughout my program facilitated me to the success of this research work. I would like to thank Dr. Partha Sarkar for his guidance and permitting me to share their facility at Alberta Innovates Technology Futures (AITF).

I am grateful to Dr. Arun Kumar Samanta and Dr. Deepak Pudasainee for their valuable suggestions and assistance at various stages of this work. I would also like to thank Dr. Arvind Rajendran for his valuable comments and suggestions on the packed bed study. I would like to thank Mr Juan Segura and Mr Luis Yamarte for their assistance in AITF.

I am also thankful to all members of the C5MPT lab for their kind cooperation throughout my program. I must thank my colleague An Zhao for his encouragement and technical assistance throughout my research work. I would like to acknowledge the financial assistance from Carbon Management Canada (CMC) and C5MPT.

Last but not the least; I am grateful to my parents and brother for their unconditional support and encouragement and I dedicate this work to them.

Table of Contents

List of figures

List of Tables

Chapter 1

INTRODUCTION

1.1. Motivation for CO_2 capture and sequestration

According to the International Energy Agency (IEA) Energy Technology Perspectives 2012[1], a 6 °C average rise in global temperature is projected under the business-as-usual approach with total CO_2 emissions reaching 58 x 10^9 t (where t refers to a metric tonne) in 2050. In 2011, total CO_2 emissions of 31.2 x 10^9 t were reported, which was 3.2% more than 2010[2] and it further increased to 34.5 x 10^9 t in 2012[3]. Over 40% of these emissions were reported to be associated with electricity generation and 20% from large manufacturing and construction industries, including petrochemicals, cement, iron and steel manufacturing[4]. If not controlled, the increasing trends in CO_2, one of the major greenhouse gas, can lead to severe consequences which include rise in sea levels, causing dislocation of human establishments, extreme weather events, including higher incidents of heat waves, catastrophic storms, and changes to rainfall patterns; resulting in droughts and floods affecting food production, increased human diseases and mortality[5].

This makes Carbon Capture and Sequestration (CCS) a critical solution to greenhouse gas emission reduction. According to IEA[1], CCS will contribute to 1/6th of CO_2 emission reductions required in 2050, and 14% of the cumulative emissions reductions between 2015 and 2050.

1.1. CO_2 capture technologies

Fossil fuels are and will continue to be, for at least next 50 years, the major energy resources. This makes CCS a critical greenhouse gas emission reduction solution, which has been acknowledged by industries as well as governments. As per the IEA report in 2013[6], almost USD 10.2 billion have been spent between 2007 and 2012 on projects that demonstrate CCS - or component technologies in the CCS chain.

A CCS project can be divided into four stages: a) CO_2 capture from large point sources, b) Compression of CO_2 gas, c) Transportation to a storage site and d) Storage (includes injection into a geological formation, use in Enhanced Oil Recovery).Currently, most of the researches are focussed on three types of CO_2 capture technologies: Pre-combustion CO_2 capture, Post combustion CO_2 capture and Oxy-fuel CO_2 capture. Figure 1-1 illustrates an overview of these capture technologies processes for a coal based power system[7].

The principle of pre-combustion CO_2 capture is to first convert the fuel (coal, natural gas or biomass) into syngas (composed of mainly H_2 and CO), followed by steam reforming of syngas to produce a mixture of H_2 and CO_2. The CO_2 is then separated and stored, while H_2 is used as a fuel. The gas for separation is a high pressure (up to 4MPa) mixture, which contains 15-40% CO_2[8]. Oxy-fuel combustion is the combustion of fuel in a pure stream of O_2 to produce flue gas composed of mainly CO_2 and H_2O. Absence of N_2 in the feed stream leads to reduction in formation of NO_x (any NO_x formed would be due to nitrogen present in the fuel). But there is a huge energy penalty associated with the separation of air into pure components of O_2 and N_2, when using standard technique like air separation unit (ASU). This technology is still in the demonstration phase with research focussed on improvements in ASU (includes molecular sieves, membranes) and chemical looping combustion (CLC).

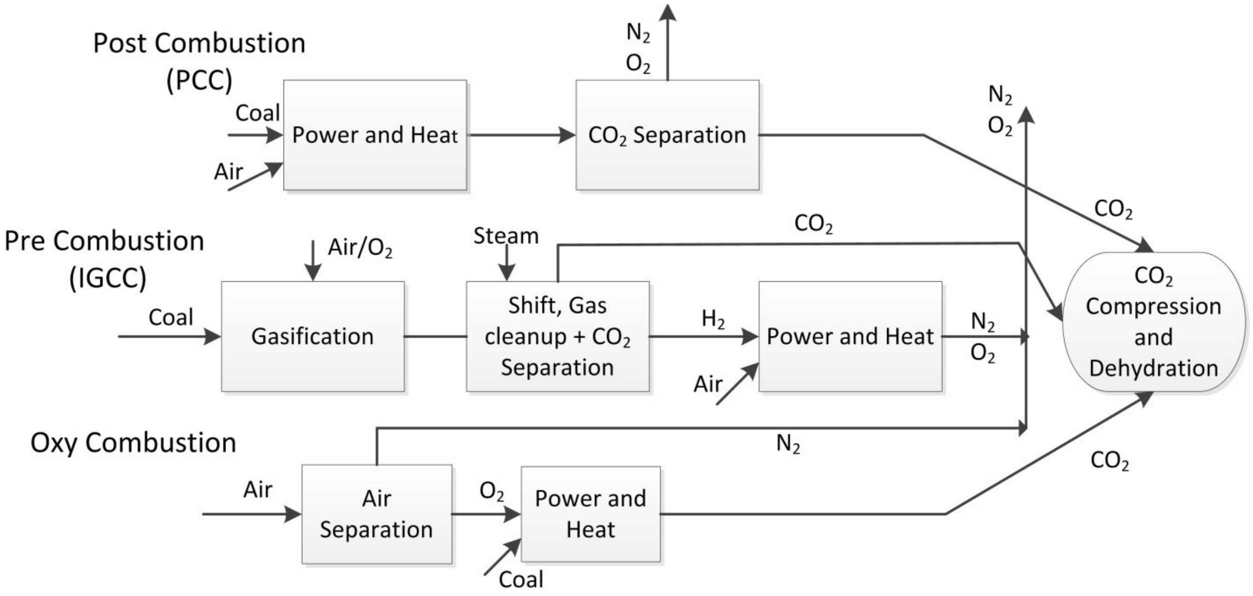


Figure 1-1. Overview of CO_2 capture technologies for a coal based power system[7]

Post-combustion capture involves separation of CO_2 from flue gas produced by fuel combustion. The typical concentration of CO_2 in flue gas produced in a coal-fired plant varies between 12-15%, with the other components being mainly N_2, O_2, H_2O and impurities like SO_x, NO_x. One of the major disadvantages of this process is the large volume of flue gas to be handled at atmospheric pressure. Whereas, in case of pre-combustion capture, high pressure of gas allows the use of physical solvents for CO_2 capture and would reduce the energy penalty. But this technology is only applicable to new power plants because of the significant number of changes required in a combustion process. As discussed in the previous paragraphs, air separation makes oxy-fuel a highly energy intensive process. Table 1-1 discusses the advantages and challenges faced in each of the capture technology[7]. At this stage, post-combustion capture of CO_2 is more economically favored for existing power plants because of ease of installation of PCC units in existing plants and a relatively lesser cost[9].

Table 1-1. Advantages and challenges of CO_2 capture technologies[7]

Technology	**Advantages**	**Challenges**
Post combustion Capture	• Can be retrofitted to the existing plants • Enables deployment of well-established pulverized coal technology • R&D on improved sorbents and capture equipment may reduce the energy penalty of PCC capture • Sub-scale demonstration of PCC is proceeding, such as 110MW Boundary dam project of Saskatchewan power, Canada	• Considerable re-engineering and scale up of existing commercially available amine processes • Significant plot space requirement • Most sorbents efficient under pure flue gas (<10ppm of SO_2+NO_2). Needs optimization before application in flue gas from commercial plants • Loss of net power output of about 30% and 11% reduction in efficiency with addition of current amine technologies
Pre combustion Capture	• Capture using the water-gas shift reaction and removal of the CO_2 with acid gas removal processes already practiced commercially • Incurs less of an energy penalty (~20%) than current PCC technology (~30%) at 90% CO_2 capture • R&D on improved CO shift catalysts, higher temperature gas clean up and membrane separation technology can lead to reduction in the energy penalty of capture	• Energy losses with facility addition less than PCC, but still significant • Commercial demonstration of gas turbines firing H_2 has yet to be demonstrated in an IGCC plant with capture • Additional purification may be needed in case of need to vent the CO_2 • Much higher capital costs of IGCC without capture than Sub-critical pulverized coal without capture
Oxy-fuel Combustion	• Should be able to deploy conventional, well-developed, high efficiency steam cycles without the need to remove significant quantities of steam from the cycle for CO_2 capture • No chemical operations or significant on-site chemical inventory involved in set-up • Ultra low emissions of conventional pollutants can be achieved at no additional cost • Possibility of higher efficiency than air fired power plants	• Expensive technology development than other technologies – requires commitment of whole power plant • Cryogenic ASU and CO_2 compression in capture unit can reduce net plant output by 25% compared to an air fired plant with same capacity • Relaxation in purity requirements of stored CO_2 could lead to reduced operational costs • Air fired combustion during start-ups lead to added flue gas quality controls and hence additional cost

1.2. Technologies for post-combustion CO_2 capture

As already mentioned in Table 1-1, the ease of integrating a post combustion CO_2 capture facility into an existing plant, makes it a highly economically favorable option. Also, the energy demand of the power plant can be controlled by adjusting the extent of CO_2 capture, or by bypassing the CO_2 capture step at the times of peak load[10]. These plants include but are not limited to pulverized coal fired plants, oil and gas fired plants, IGCC and cement kilns and steel and iron production plants.

However, the technology still has some challenges[11], which are discussed as follows:

1) *Scale of CO_2 emissions*: A 500 MW power plant normally produces very large amount flue gas flow rate of more than 2.04×10^6 m^3/h. As evident from Table 1-2, the composition of flue gas changes depending on the source of emission. The scale of emissions puts a limitation on potential of capture technologies and the beneficial use of CO_2.
2) *Energy for separation*: CO_2 Capture represents 70-80% of the energy needed for CCS, while compression represents only about 20-30%, at least for near-term CCS technologies[12]. As 100% selectivity for CO_2 is never attainable, it adds additional cost for supplement method required to purify CO_2 to standards required for transport and storage.
3) *Level of impurities*: Levels of SO_x, NO_x, and other impurities vary depending on flue gas emission source (Table 1-2). The process should be capable of tolerating these levels or additional flue gas pre-treatment equipment would be required.

4) *Other*: This includes plant specific issues which will influence the type and size of capture equipment required. Space for CCS facility can be another limitation as some power plants might not have space available or require large changes in infrastructure to accommodate it.

Table 1-2. Flue gas composition and pressure for various industrial processes[9,13]

Process	**Pressure of gas stream (MPa)**	**CO_2 (dry) vol%**	**Impurities**
Natural gas turbine exhaust	0.1	3-4	Low SO_x and NO_x levels, O_2: 12-15%
Coal/Oil fired boiler	0.1	11-14	High SO_x and NO_x levels, O_2: 2-5%
Blast furnace gas (after combustion)	0.1	27	SO_X and NO_x present
Cement kiln off-gas	0.1	14-33	SO_2 and NO_x, trace elements, particulates

Post combustion capture generally consists of these four main approaches: a) Cryogenic distillation, b) Membrane separation, c) Absorption with liquids, and d) Adsorption using solids. Cryogenic distillation is highly energy intensive while membrane separation is suitable for separation of gases at higher pressure or large concentration which is not the case for CO_2 in flue gas from industries. Absorption and adsorption have been discussed in detail in the next section.

1.2.1. Absorption

Absorption for removal of CO_2 by chemical solvents is a well-established process. It is one of the preferred options for post combustion CO_2 capture and is used as a benchmark for evaluating new technologies. A typical chemical absorption process consists of an absorber for CO_2 removal and a stripper for regeneration of spent solvent. Flue gas enters from the bottom of a packed bed reactor and comes in contact with the solvent counter-currently. CO_2 free gas exits the absorber while the CO_2 rich solvent is sent to the stripper for thermal regeneration (steam stripping) and is then pumped back to the absorber column. 25-30 wt% aqueous amine is used as a solvent, of which, Monoethanolamine (MEA)[14] is the most widely used and studied chemical solvent. Typically, an almost pure (>99%) CO_2 product stream is produced using this technology by capturing about 75-90% of CO_2 .The proposed mechanism for reaction between CO_2 and amines has been shown in Figure 1-2[15]. As per the mechanism, maximum CO_2 absorption is attained when all of the absorbed CO_2 exists in bicarbonate form. This is because one mole of amine is required to form one mole of bicarbonate whereas the requirement is 2 moles for carbamate and carbonate formation.

But the absorption process has its own shortcomings, which are listed below.

1) The solvent causes corrosion of equipment and has high heat of regeneration.
2) Large volume of solvent are required because of the thermal and oxidative degradation of the solvents.
3) Impurities present in flue gas from coal combustion like SO_x, NO_x and fly ash further deteriorate the solvent.

As suggested by a techno-economic study[16], the cost of electricity would increase by 80% in case 30 wt% aqueous MEA absorption process is used in a coal fired power plant for CO_2 capture. Process and solvent improvements need to be made before using this technology in coal fired power plants. Meanwhile, a lot of research is being conducted on other alternative technologies. Among which, there is a growing interest in using adsorption for CO_2 capture.

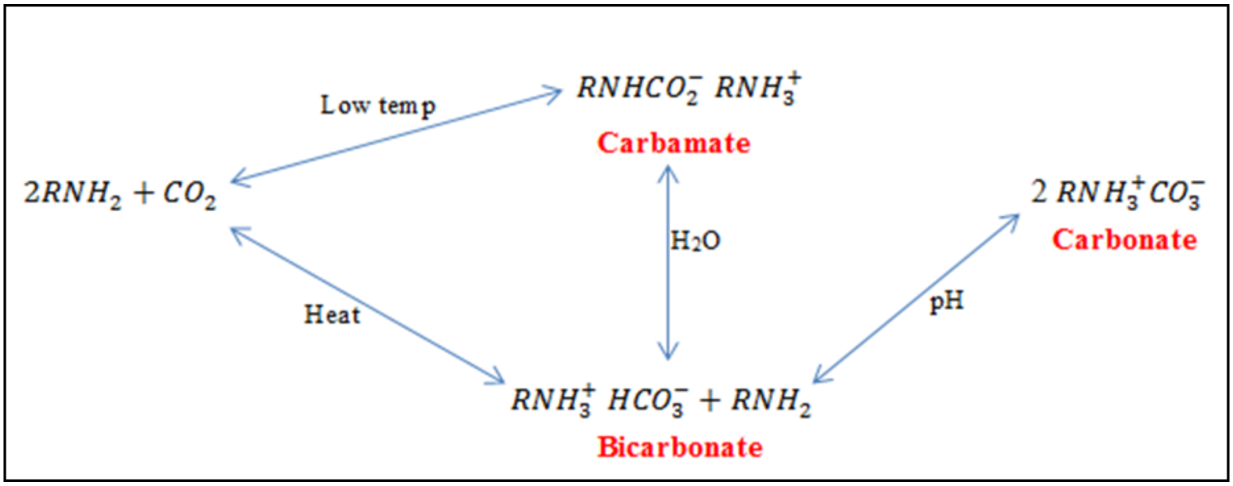


Figure 1-2. Reaction mechanism

(Reprinted with permission from Copyright (2005) Elsevier[15])

1.2.2. Adsorption

One of the key reasons of growing interest in solid sorbents for CO_2 capture is their low heat of regeneration due to higher CO_2 loading, lower material heat capacity and/or lower heat of reaction[17]. They can be used over a wider range of temperature from ambient to 700 °C and generate no liquid wastes[18]. Many different types of solid materials are currently being investigated for CO_2 capture and broadly they can be classified into two categories: a) Physisorbents and b) Chemisorbents.

Physisorbents include porous carbonaceous materials, zeolites, silica gels, alumina and metal-organic frameworks. On other hand, chemisorbents mostly contain some functional groups incorporated into a solid support. These functional groups are generally basic sites that can interact strongly with an acidic CO_2 molecule and hence increase the CO_2 adsorption capacity. These adsorbents have been discussed in detail in chapter 2.

A CO_2 capture adsorption cycle can be classified on the basis of methodology used to regenerate the material. Several regeneration techniques, which include pressure swing adsorption (PSA), temperature swing adsorption (TSA), electrothermal swing adsorption (ESA), vacuum swing adsorption (VSA) and hybrids (VPSA, TVSA) have been studied for these materials. The technique is selected on the basis of type of adsorbent, its CO_2/N_2 selectivity, and change in adsorption capacity with temperature and pressure, among other parameters.

In the past few years, a lot of new materials have been developed for CO_2 capture. As a result, efforts on screening and evaluation of these sorbents are underway[17,19,20]. The key criteria for selection of an adsorbent for CO_2 capture have been listed below:

- *High adsorption capacity of CO_2:* The equilibrium capacity of the adsorbent under conditions relevant to flue gas treatment, i.e. less than 0.4 bar CO_2 partial pressure with a total gas pressure of 1-2 bar and temperature about 70-80 °C[20], is one of the key deciding factors. Higher the adsorption capacity, lesser is the amount of adsorbent needed which then reduces the volume of adsorption vessels. As, it takes a long time for any material to attain equilibrium, working capacity is preferred and used in practical situations. It is the difference in the breakthrough capacity and the amount of CO_2 that remains in the bed after it has been regenerated. Basically, it is the net amount of CO_2 adsorbed in each cycle of an adsorption process. In order to be competitive with the conventional amine scrubbing process, an optimum CO_2 adsorption capacity of 3-4 mmol of CO_2/g-sorbent has been suggested in the literature[21].
- *High selectivity for CO_2:* The adsorbent should possess high selectivity for CO_2 over other components present in the flue gas, primarily N_2. This has a direct impact on the purity of CO_2 product stream.

- *Fast adsorption/desorption kinetics:* Kinetics of an adsorption-desorption cycle, has direct effect on the duration and working capacity of a cycle. Fast adsorption and desorption allows for shorter cycles. Rate of adsorption is governed by mass transfer or diffusional resistance of gas phase through the sorbent and the reaction kinetics of CO_2 with the functional groups present.
- *Mechanical strength/ multiple cycle stability:* An adsorbent should be able to adsorb and desorb CO_2 for several continuous cycles, without losing its adsorption capacity or any degradation in kinetics. Operating conditions, such as high flow rates of flue gas, vibration, changes in temperature should not cause any degradation or leaching of the functional groups (in case of chemisorbents) or any morphological changes in the support. This is crucial in order to keep the sorbent makeup minimal and hence make the whole process cost effective. Resistance to crushing and abrasion is important in case of fluidized bed reactors.
- *Tolerance to impurities:* Flue gas contains impurities like SO_x, NO_x, O_2, moisture, heavy metals and fly ash. The concentrations of those can vary depending on the source (mentioned in Table 1-2). Degree of tolerance and affinity to these components has a direct relation to CO_2 adsorption capacity and selectivity and any upstream flue gas treatment required. This can have a huge impact on the overall economics of the plant. Physisorbents (especially zeolites) have a strong affinity to moisture which drastically reduces their CO_2 adsorption capacity. But on the other hand, most of the amine functionalized sorbents have shown tolerance and increased CO_2 adsorption capacity in presence of moisture. But the impact of O_2 and SO_x, NO_x has not yet been studied in that detail.

- *Regeneration:* As a rule of thumb, the heat of regeneration should be substantially low as this is also one of the major drawbacks of amine scrubbing process. The heat of regeneration is generally -25 to -50 kJ/mole of CO_2 for physisorption and -60 to -90 kJ/mole CO_2 in case of chemisorption[13]. Heat of adsorption is an indirect measure of regeneration energy requirement. High heat of adsorption means strong bonding of CO_2 molecules to adsorption sites, which is good from adsorption perspective but has a negative impact on ease of regeneration of the material.
- *Cost of the material*: As most of the materials are still in the development phase, very little information is available on their techno-economic assessment for large scale plants. Tarka et. al.[22], used a baseline cost of $10/kg of sorbent in their sensitivity analysis for economic performance. According them, $5/kg is favorable for a process whereas $15/kg would be uneconomical.

However, it should be noted that it is difficult to find an adsorbent having all the above mentioned attributes. In reality, all adsorbents have some trade-offs and in the next chapter some of the known CO_2 adsorbents have been reviewed along with adsorption technologies being used for post combustion CO_2 capture.

Chapter 2

LITERATURE REVIEW

2.1. Background

Synthesis of amine functionalized solid sorbents for post combustion CO_2 capture; testing of those and optimization have been carried out in our group previously. The broad focus of the present work is to study the stability of amine impregnated silica based adsorbents in steam atmosphere. In view of the objectives of the present study, literature has been reviewed in two broad aspects: a) amine functionalized adsorbents and b) classification of adsorption separation processes, based on regeneration techniques used.

Most of the conventional physisorbents such as carbonaceous materials (carbon nanotubes (CNTs), activated carbon (AC)), zeolites and metal organic frameworks (MOF) suffer from low CO_2 adsorption capacities at relatively low CO_2 partial pressures, high selectivity towards moisture and low CO_2 selectivity and adsorption capacity, respectively[20]. On the other hand, amine based chemisorbents have demonstrated high adsorption capacities at temperatures in range of actual flue gas temperatures (50-80 °C) and are stable in presence of moisture (in fact moisture enhances the CO_2 adsorption capacity in some cases). Because of this, these materials were the focus of current research work and are discussed in detail in next section.

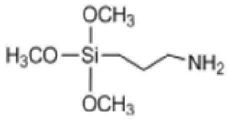
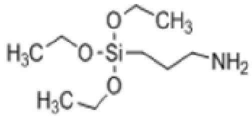
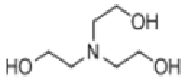
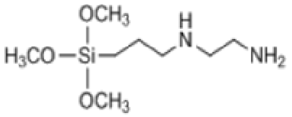
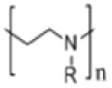
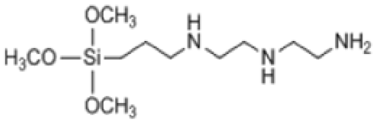
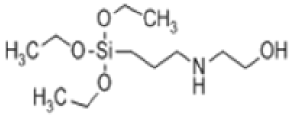
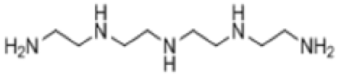
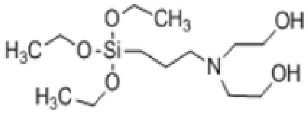
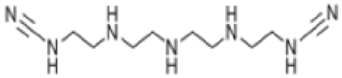
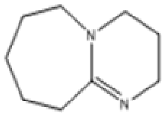
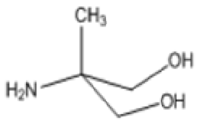
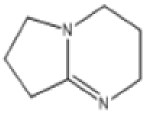
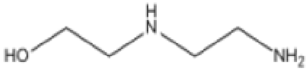
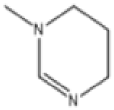
2.2. Amine functionalized adsorbents

As described in previous chapter, aqueous amines such as MEA have been widely used for removing CO_2 from flue gas. The acidic CO_2 easily binds to the basic amine sites. Due to inherent problems of this process as discussed in Chapter 1, a lot of new materials are being developed based on same principles but with solid supports, by immobilizing amines (listed in Table 2-1[13].) on certain support materials. In comparison to physisorbents, these materials have higher adsorption capacity at relatively lower CO_2 pressures and higher selectivity for CO_2.

Three aspects have been primarily focused upon in research activities to improve the CO_2 capture properties of amine-based solid adsorbents[23]: (1) solid supports that are able to accommodate high amine-loading, (2) amines that can generate high amine density, and (3) effective methods for binding amines to the support. Basically, the supports should have a good affinity for the amine molecules; possess high surface area and porosity, good mechanical and hydrothermal stability. Three classes of amine based solid materials have been discussed in literature: a) impregnated adsorbents, b) grafted amine adsorbents and c) hybrid of first two classes.

Table 2-1. Structure of amines used for functionalization

(Reprinted with permission from Copyright (2012) American Chemical Society[13])

Name	Structure	Name	Structure
Amines		Silanes	
Monoethanolamine (MEA)		3-aminopropyltrimethoxysilane (APTS)	
Diethanolamine (DEA)		3-aminopropyltriethoxysilane (APTES)	
Triethanolamine (TEA)		N-[3-(trimethoxysilyl)propyl]-ethylenediamine (AEAPTS)	
Polyethyleneimine (PEI)	 (R=H for linear, R=H or CHx for branched)	N-[3-(trimethoxysilyl)propyl]-diethylenetriamine (DAEAPTS)	
Diethylenetriamine (DETA)		Ethylhydroxyl-aminopropyl-trimethoxyslane (EHAPTS)	
Tetraethylenepentamine (TEPA)		Diethylhydroxyl-aminopropyl-trimethoxyslane (DEHAPTS)	
		Cyclic	
Tetraethylenepentamine-acrylonitrile (TEPAN)		Aziridine	
Pentaethylenehexamine (PEHA)		1,8-diazabicyclo[5.4.0]undec-7-ene (DBU)	
2-Amino-2-methyl-1,3-propanediol (AMPD)		1,5-diazobicyclo [4.3.0]non-5-ene (DBN)	
2-(2-Aminoethylamino)ethanol (AEAE)		N-methyltetrahydropyrimidine (MTHP)	

2.2.1. Amine impregnated adsorbents

The first amine impregnated adsorbents were synthesized by Xu et al.[24] and were based on silica support. Wet impregnation of hydrothermally synthesized MCM-41 was done with Polyethyleneimine (PEI) to create an adsorbent termed as "molecular basket". In this technique, the amine is physically loaded into or onto the solid porous support. It was shown that MCM-41 had a synergetic effect on adsorption of CO_2 on PEI and that the adsorption capacity was 24 times greater than that of only MCM-41 and 2 times than that for pure PEI. In 2003[25], the group reported highest adsorption capacity of 3.02 mmol CO_2/g sorbent for 50 wt% PEI loading at 75 °C adsorption temperature. It was reported that the uniform dispersion of PEI into the support pores was critical for the sorbent preparation.

Since then, a lot of solid supports (mainly silica, carbon based) and amines have been tested for impregnation and CO_2 adsorption capacity. Ordered mesoporous silica supports, namely, MCM-41, MCM-48, SBA-15, SBA-16 and KIT-6 were synthesized and impregnated with 50 wt% PEI by Ahn and co-workers[26], to study their CO_2 adsorption properties. The adsorption capacities of all these materials were much higher than that of pure PEI and were in the order of: KIT-6 > SBA-16 ≈ SBA-15 > MCM-48 > MCM-41. Reversible CO_2 adsorption-desorption behavior was exhibited by the materials, with 99% CO_2 recovery. Adsorbent performance was proposed to be influenced by the pore size and pore arrangement of the support material (KIT-6 with largest pore diameter of 6.5 nm had the highest adsorption capacity).

Qi et al.[27] developed a novel high efficiency nanocomposite sorbent for CO_2 capture, based on PEI and TEPA (Tetraethylenepentamine) functionalized mesoporous silica capsules. The material exhibited adsorption capacity up to 7.9 mmol/g under humidified 10% CO_2 flue gas. It was observed that the adsorption capacity was improved by larger particle size, higher interior void volume and thinner mesoporous shell thickness. PEI impregnated sorbents showed better stability and reversibility in comparison to TEPA, when tested for 50 adsorption-desorption cycles.

Some of the other supports that have been explored for amine impregnation include high surface area polymeric supports, mainly Polymethylmethacrylate[28,29] (PMMA), Polystyrene[30] (Maronet), silicon dioxide[30,31] (CARiACT), zeolites (13X[32], beta zeolite[33]) and carbon based materials[34]. Overall, it has been seen that supports with large pore diameter (d_p) have higher adsorption capacities. Sayari et al.,[20] summarized in their review on solid adsorbents that high amine loadings lead to enhanced adsorption capacities, but it resulted in a decrease in rate of adsorption and CO_2/N ratio. High amine content adsorbents are generally inappropriate for low temperature application as their optimum adsorption capacity might occur at a high temperature. Moreover, because of weak interaction between the amine and the support, the adsorbents can be unstable due to amine leaching. This makes regeneration conditions of such adsorbents a critical part and sometimes a limitation in their application.

Drage et al.,[35] investigated the possible regeneration strategies for PEI based adsorbents. TSA was performed under pure CO_2 atmosphere and it was observed that at temperatures higher than 135 °C, CO_2 bonded with PEI linkages to form stable urea compounds. PSA was carried out in N_2 atmosphere at an elevated temperature (TPSA) and from the efficiency of the process it was proposed that steam could be viable regeneration technique for CO_2 capture process. The technique would overcome the problem of thermal degradation as seen in a TSA in CO_2 atmosphere. Sayari and co-workers[36] studied the thermal, oxidative and CO_2 induced degradation of supported PEI based adsorbents. Their findings can be summarized as follows: a) high thermal stability of the material at moderate temperatures, b) highly stable CO_2 uptake in presence of moisture (66 cycles study), c) extensive degradation in presence of dry CO_2 due to urea formation, especially at high temperature, d) fast degradation upon exposure to Carbon free air even at moderate temperatures (due to a combination of material loss and oxidative reactions) and e) stability in presence of humidified gas containing both CO_2 and O_2.

To summarize, amine impregnated adsorbents show good adsorption capacity and uptake kinetics even at lower CO_2 partial pressures. The adsorbent performance is generally enhanced under humid conditions, which is highly favorable, given that flue gas contains significant amount of moisture. Desorption kinetics is still slower[13] and steam regeneration can be promising in this aspect (as will be discussed in section 2.3.3.2).

2.2.2. Amine grafted adsorbents

In this category, the amine, mainly amine-containing silane, is covalently bonded to a solid support. This is performed by binding amines to oxides via use of silane chemistry or preparation of polymeric supports with amine-containing side chains[13]. Choi et al.[19] have pictorially depicted this reaction mechanism, as shown Figure 2-1. The amine is covalently bonded to support, which provides an advantage over impregnation as amine doesn’t leach unless the conditions are strong enough to break the covalent bonds[19].

Figure 2-1. Scheme for reaction of silane with silica

Where, R^1 can either be an alkyl or amino-alkyl group and R^2 is generally a methyl or ethyl group. (Reprinted with permission from Copyright (2009) Wiley-VCH[19])

Leal et al.[37] were the first to report chemisorption of CO_2 on amine (APTES) grafted silica gel at room temperature. It was observed that adsorption process was due to carbamate formation, where two amino groups reacted with each molecule of CO_2 adsorbed. But in presence of moisture, the carbamate ion transformed into two adsorbed bicarbonate molecules. The sorbent exhibited an adsorption capacity of 0.41mmol/g in dry atmosphere, whereas the capacity doubled to 0.89mmol/g in presence of moisture. But in overall, the capacity was very less for industrial application.

Novel SBA-15 based aminosilane grafted adsorbents were prepared by Hiyoshi et al.[38,39] for CO_2 adsorption in presence of moisture. It was observed that although grafting lead to decrease in surface area, the surface area of amine grafted SBA-15 was much higher than that of impregnated sample. CO_2 adsorption capacities of amine grafted SBA-15 increased with increasing amine content but the relationship was not linear. Subsequently, they found out that for APTES, AEAPTS and DAEAPTS grafted SBA-15, the order of CO_2 adsorption capacity was: DAEAPTS > AEAPTS > APTES in both dry and humid gas. Whereas, the amine efficiency order for same amine loading was determined to be reverse of above order. The reason for such behaviour is presence of 3 amino groups in DAEAPTS, 2 in AEAPTS and 1 in APTES. Although, the efficiency of each amino group of the former amine is not as good as the latter ones, however in general, the amine is good enough to give higher adsorption capacity than other two amines.

A lot of work has been done on grafting of sorbents by Sayari's group. They used post synthesis pore expansion method[40] to generate PE-MCM-41 with pore size and pore volume up to 20nm and 3.5cm^3/g, without any change in surface area of parent MCM-41[41]. The group also worked on improving the grafting conditions, leading to improvement in amine loading and adsorption properties[42]. Conventionally, grafting is done under reflux, in a dry solvent with large excess of silane. Harlick and Sayari[41] found that the optimum conditions for grafting 3-[2-(2-aminoethylamino)ethylamino]propyltrimethoxysilane (TRI) on PE-MCM-41 were as: T = 85 °C, water added: 0.3ml/g of support and aminosilane added: 3ml/g of support. This lead to increase in amine content by 30% (7.98 vs. 6.11mmol/g for conventional drying) and a 70% increase in CO_2 adsorption capacity under 5% CO_2/N_2 at 25 °C (1.55 mmol/g vs 2.65 mmol/g). Overall, the combination of pore expansion and optimization of grafting technique lead to a 300% increase in adsorption capacity along with significant increase in the rate of adsorption[20].

Class 3 sorbents are a mixture of first two classes and are prepared by in-situ polymerization of amino polymers with porous solid supports[43]. The sorbent was first synthesized by Jones et al.[44] and was called Hyperbranched Aminosilica (HAS). It was synthesized by one step reaction, i.e. spontaneous aziridine (highly reactive and toxic) ring-opening polymerization off of surface silanols. Next the resulting material was washed extensively to remove physisorbed aziridine. A 32 wt.% organic/inorganic hybrid material was synthesized and CO_2 adsorption capacity of ~ 3 mmol/g was reported.

To conclude, grafting does minimize the leaching of amine to a much greater extent. No thermal degrading of grafted amines has been reported at temperatures as high as 250 °C in presence of air[45]. But the adsorbents have lower adsorption capacities in comparison to impregnated sorbents. Moreover, the synthesis process is complex and adds to the cost of material production. The impregnation technique is much simpler. Amine impregnated adsorbents are potential candidates for industrial application, given that a proper regeneration technique can be developed which overcomes amine leaching problem and is suitable for multiple cycles.

2.3. Adsorption separation processes on the basis of regeneration methods

As already discussed in previous section, selection of a suitable regeneration technique is critical to overall energy efficiency of the process. In case of solid adsorbents, PSA, VSA, VPSA, TSA, hybrid temperature-vacuum swing adsorption (VTSA), electric swing adsorption (ESA) and microwave heating for regeneration have been considered. Table 2-2 gives a list of some solid adsorbents along with regeneration technique specifications used in that specific study. In this section we have discussed these techniques and their application in CO_2 capture.

Table 2-2. List of solid adsorbents along with description of regeneration methodology used

Adsorbent (Amine content, wt. %)	**PCO_2 (bar)**	**CO_2 adsorbed (mmol/g)**	**Desorption methodology**	**References**
N-DETA (27)	1	1.66 (25 °C)	VSA- Regeneration under vacuum for 30 min	Plaza et al.[46]
N-PEI (30)	1	1.11 (25 °C)	VSA- Regeneration under vacuum for 30 min	Plaza et al.[46]
Si-PEI (45)	0.1	3-3.5 (45-60 °C)	TSA- Steam sweep used at 105 °C	Hoffman et al.[47]
VP OC1065[a]	0.1	1.85-1.15 (30-70 °C)	PSA for 20 min under N_2 sweep at adsorption temperature followed by TSA at T ramp rate of 3°C/min	Hallenbeck et al.[48]
F-PEI[b] (80)	0.1	2.5 (75 °C)	Concentration sweep at 75 °C under N_2, TSA at 100 °C under N_2	Qi et al.[49]
HP20/PEI-50[c]	0.15	2.95 (75 °C)	TSA using N_2 and heating the sorbent to 100 °C at a rate of 10 °C/min	Chen et al.[50]
G-10/PEI (40)	0.145	2.25 (80 °C)	PSA at 80 °C for $PCO_2 > 10$kPa	Ebner et al.[51]
SBA-15/T60	0.10	3.48 (75 °C)	TSA at 105°C under N_2	Zhao et al.[52]
K promoted HTlc	0.15	1.72 (302 °C)	PSA (Vacuum) - 3 stripping PSA cycles with a High reflux step gave best performance	Reynolds et al.[53]
AEAPDMS-NFC[d]	400-530 ppm	0.9 (30 °C)	TVSA at 90 °C and 30mbar	Gebald et al.[54]
γ-Alumina/PEI	400 ppm	1.71 (30 °C)	TSA- steam stripping at 110 °C	Sakwa-Novak et al.[55]
Zeolite 5A	0.10	3.39 (25 °C)	TSA- Indirect heating using an internal heat exchanger	Meral et al.[56]
Zeolite 13X	0.10	3.43 (25 °C)	TSA- Indirect heating using an internal heat exchanger	Meral et al.[56]
13X-AC hybrid	0.076	0.83 (25 °C)	ESA- ~50W for electrification in each cycle	Ribeiro et al.[57]
13X – APG	0.15	_	TVSA - Indirect thermal swing at 170 °C and 3kPa vacuum	Wang et al.[58]

a: Ion exchange resin, b: F is Mesoporous Foam, c: Amine loaded resin, d: Amine based cellulose

2.3.1. Pressure/vacuum swing adsorption

This technology is based on reducing the total pressure of the system to carry out regeneration. The mechanism is based on difference in the adsorption capacity of adsorbent at higher pressure of feed and lower pressure applied during regeneration stage. The difference is called cyclic capacity and has been represented in Figure 2-2. In case of VSA, adsorption is carried out at atmospheric pressure followed by regeneration at below atmospheric pressures. Over the years, PSA has been widely used in a large variety of applications: H_2 purification[59,60], air separation[61,62] , Isosiv process for separation of linear and branched hydrocarbons[63,64], CH_4 upgrading[65,66] and so on.

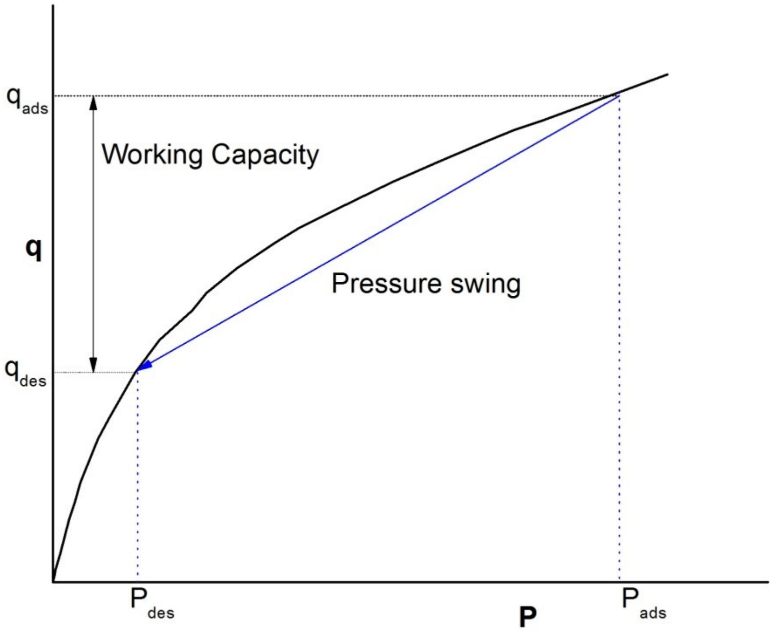


Figure 2-2. Principle of operation for a PSA process

Skarstrom cycle[67] is the most popular configuration for a PSA/VSA cycle. This cycle includes two beds which are subjected to a) pressurization, b) adsorption, c) forward blow down and d) reverse evacuation, in a manner that produces continuous stream of product. The process has been described by Haghpanah et al.,[68] as shown in Figure 2-3 along with a pressure profile for each step. Example of CO_2-N_2 mixture separation has been depicted here where CO_2 is the strongly adsorbed species (Extract) and N_2 the weakly adsorbed one (Raffinate). In step 1 and 2, feed gas is fed to the system through feed end. Next, bed is depressurized to an intermediate pressure (P_I) during blow down through light-product end. The feed end is closed and the bed gets rid of N_2 while retaining CO_2. During evacuation, light product end is closed and the feed inlet is opened to reduce the pressure to P_L. This would produce a high purity CO_2 rich stream.

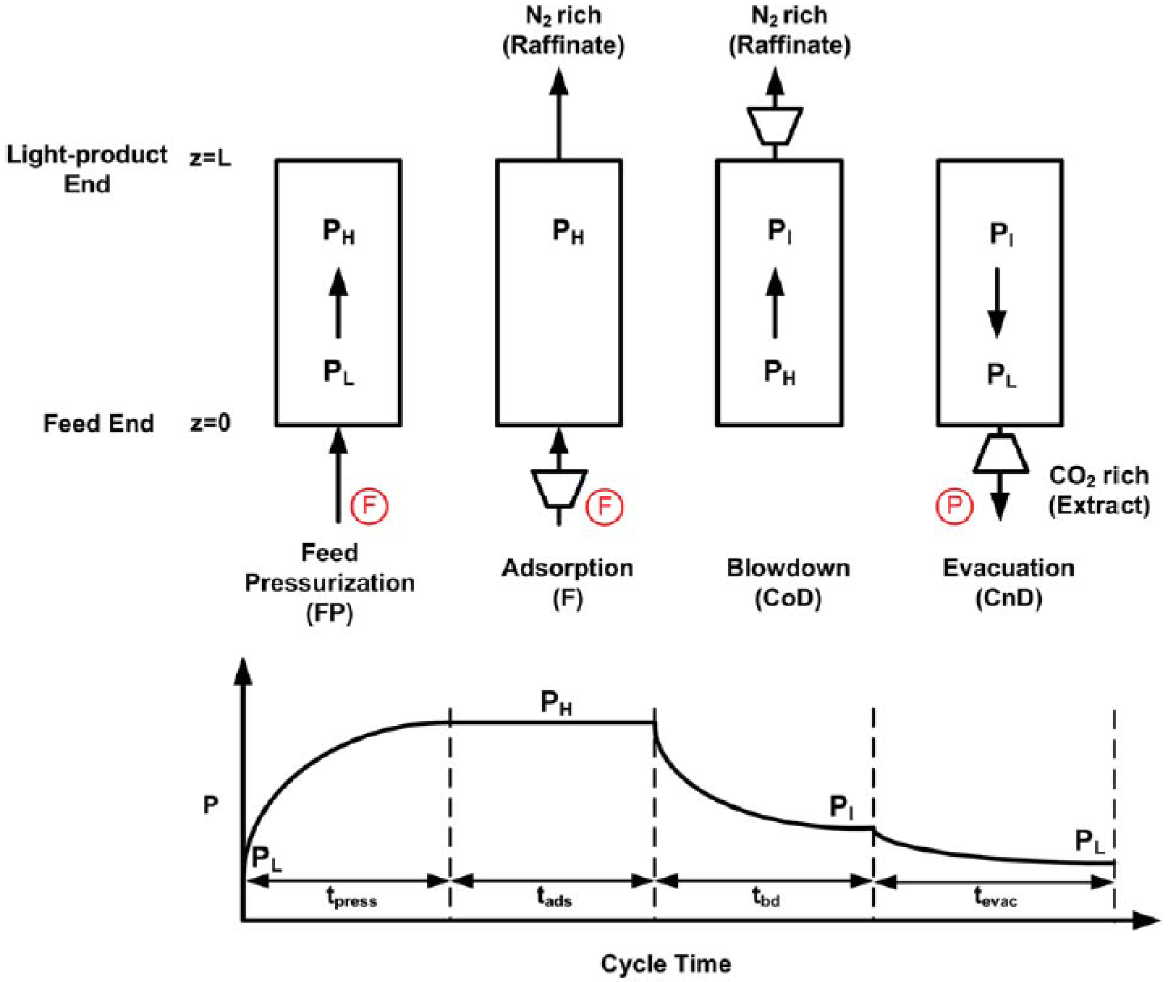


Figure 2-3. 4-step PSA/VSA cycle along with pressure profile

(Reprinted with permission from Copyright (2013) American Institute of Chemical Engineers[68])

The material used in PSA should be easily regenerable. In case of PSA, high vacuum has to be applied on materials that have high adsorption capacity at low pressures to get a good "cyclic capacity" value. This increases the power consumption and hence the operating cost of the unit. Materials that have rectangular adsorption isotherms fall in this category: very steep at low pressures and almost flat curve after a certain pressure[69]. So, PSA is adopted for materials with linear or slightly non-linear isotherms.

Applications in CO_2 capture

Given the fast regeneration and high purity of raffinate, PSA/VSA is an attractive option. But there are several challenges in implementing conventional PSA for CO_2 capture[70]:

1) *Low purity of recovered CO_2*: One of the important aspects of this process is that the weakly adsorbed species can be recovered at high purity but relatively low recovery whereas the strongly adsorbed species is recovered in low purity. This makes the process more suitable for applications where less strongly adsorbed species is the major product. But this is not the case in post combustion capture of CO_2, where CO_2 adsorbs strongly in comparison to N_2 due to its larger electric quadrupolar moment.
2) *Handling large volumes of flue gas*: A 500MW coal-fired power plant produces approximately 10,000 tonne CO_2 per day, which requires large sized equipment for post combustion CO_2 separation. By reducing the cycle time, the plant size (required for CO_2 capture) can be reduced. So, methods utilizing rapid pressure swing adsorption (RPSA) in CO_2 capture are currently under development[71], working on achieving 1/10th volume reduction through increased working capacity of adsorbent and operation at 1/10th cycle time.

3) *Variable composition of flue gas*: The flue gas composition varies depending on the source: 11-14 vol% CO_2 in flue gas from coal-fired plants, 3-4 % in natural gas turbine exhaust and 14-33% in cement kiln off gas[72]. In addition to this, the levels of impurities like SO_x, NO_x, O_2 and moisture also vary. In a cost based comparison study conducted by Hasan et al.,[73], it has been reported that least cost is incurred in MEA based chemical absorption for feed CO_2 composition less than 15-20%. VSA should be preferred for higher CO_2 compositions. They have also emphasized on the need of considering several technology options, depending on CO_2 emission scenarios in different industries.

However, there is an extensive literature on optimization and variation of PSA/VSA to overcome these challenges, which will be discussed in the following paragraphs.

In terms of CO_2 purity, achievement of 90% purity-recovery requirements for CO_2 have been reported by various research groups[68,74,75]. Most of this work has been done using zeolites like 13X, where moisture acts as a major impurity and significantly lowers the CO_2 adsorption capacity. Recently, Li et al.[75], studied the influence of moisture on CO_2 adsorption in a VSA process using single and multilayer columns of alumina and zeolite 13X. It was reported that key factors controlling the performance of H_2O/CO_2 process were volumetric purge to feed (P/F) ratio and layering strategy of the sorbents. Moreover, below a certain P/F ratio penetration of water to lower layer was observed leading to risk of process failure. An axial working capacity model was developed to predict penetration depth of water in feed column and used to calculate sorbent layering ratio. At high moisture content of > 8.5%, a triple layer strategy for adsorbent was proposed: first layer for water removal, second layer for water and CO_2 and third layer for CO_2 removal only.

Since, solid amine sorbents have proven to be water tolerant along with good CO_2 adsorption capacity; they are being considered for PSA technology[51,76]. Ritter et. al.,[51] studied the feasibility of using CARiACT G-10 silica immobilized with PEI for applications in PSA operations. The behavior of material was studied under wide range of industrially relevant conditions, using thermogravimetric analysis. The optimum operating temperature for PSA were reported to be around 80 °C for CO_2 partial pressures > 10kPa and 60-70 °C for partial pressures < 10kPa.

Another field that has attracted much attention is VPSA. Possible low energy requirement, low capital investment cost and easy to achieve automated operation makes it a favorable option for CO_2 capture[77-80]. A 4-step Skarstrom type VPSA was evaluated by Shen et al.,[81] for coal tar pitch based AC beads. Purity of 93.7% with 78.23% recovery was reported for feed with 15% CO_2, at 202.65kPa pressure and 303K temperature. Another, theoretical and experimental study using AC beads was performed by the same group[82] with a 2-stage VPSA process. For a total specific power consumption of 723.6kJ/kg-CO_2, unit productivity of 0.85mol-CO_2/kg h with a CO_2 purity of 95.3% and 74.4% recovery was reported.

In summary, PSA is a good choice due to its simplicity of operation and fast regeneration. But the main drawback is cooling and drying of flue gas in post combustion CO_2 capture[10]. As already discussed, handling of large volume of flue gas released at atmospheric pressure is another challenge. In case of strong CO_2 adsorption, very low pressure requirement for regeneration can increase the operation cost and mechanical energy is more expensive than heat (TSA).[83]

2.3.2. Electrothermal swing adsorption (ESA)

Instead of using an external heating medium (as in conventional TSA), heat is generated inside the adsorbent particles by passing electric current through it, i.e. heating by Joule effect. Based on mode of electric current generation, there are two types of ESA[84] operations: a) Direct ESA, where the adsorbent itself is the electric conductor and b) Indirect ESA, which uses an ancillary conductor. Because of this, electrical conductivity of the materials plays a very crucial role in case of direct ESA. ESA is a cyclic process with a number of different steps involved. A single specific operation guideline is not available for this technique and different configurations can lead to similar results[85].

Some of the advantages of ESA are[86,87]:

1) It is simpler and easier to apply than indirect heating in conventional TSA. Flow rate of carrier gas and heating rate can be controlled independently. Lower flow rates allow for higher purity of products.
2) It enables use of different design solutions and smaller equipment.
3) Larger heating rates (the electrification step) can be applied in comparison to conventional TSA. It is not limited by the heat capacity of heating medium/carrier gas or the heat transfer coefficient between the medium and adsorbent.
4) Heat and mass transfer during desorption will take place in same direction, i.e. from center to surface and then to the fluid. The thermal and diffusion effects provide better desorption kinetics.

Applications in CO_2 capture

ESA has been widely studied for removal of volatile organic contaminants (VOC's)[88-92] but relatively very few studies are available in CO_2 capture. VOCs removal was the first application where ESA was implemented as an alternative to TSA.

Apart from CO_2 adsorption capacity, electrical conductivity of adsorbent becomes an important feature in material selection in ESA. Most of the studies till date are based on AC as adsorbent because of its electrical conductivity properties. The drawback in this case is the low adsorption capacity of AC at low partial pressures of CO_2 (mostly true for all flue gas compositions). Materials like zeolites, which have high CO_2 adsorption capacity, don't conduct electricity and cannot be used for direct ESA[57].

The process was first developed by Oak Ridge National Laboratory[93] for separation of CO_2 and CH_4 by Carbon fiber composite molecular sieve (CFCMS). Low voltage was applied on the novel monolith along with heating to temperatures below 100 °C. Rapid desorption of CO_2 was observed on application of 4-5 Ampere current flowing under a DC voltage of 1V. Grande et al.,[94] studied ESA for CO_2 capture from Natural Gas combined cycle (NGCC) power stations with low concentration of CO_2 in exit stream (4.51%). A ESA comprising of 4 stages: a) Feed – CO_2 rich gas was passed through the bed to perform separation, b) Electrification – feed was stopped and electric current was passed through the column to heat the adsorbent along with inert gas introduction in a counter current direction to that of feed, c) Desorption – desorbed CO_2 was carried away and removed by the inert gas and d) Purge - amount of inert gas was increased to cool the bed for next cycle, was studied experimentally along with mathematical modelling. CO_2 recoveries higher than 89% were obtained with purity of 16%.

Recently in 2013, Ribeiro et al.[57], tested a hybrid adsorption bed comprising of AC and zeolite 13X (82% to 18% ratio) for ESA. This led to an increased adsorption of CO_2, which was double than employing only AC. Using a six step ESA, CO_2 purity of 46.6% and capture of 81.6% were reported. But the process had a lot of shortcomings. Firstly, the energy consumption summed up to be 33.2 GJ/tonne CO_2 which is about 10 times higher than the value for amine scrubbing process[95]. Secondly, due to non-homogeneous packing of zeolite inside the Carbon monolith, a large mass transfer zone was observed. A significant part of the energy went into heating the adsorbent bed but all of the material couldn't be utilized for CO_2 adsorption during feed step. This implies that the configuration of hybrid adsorbent and its non-homogeneity has to be resolved in order to decrease the energy intensity and adsorption capacity of the process. Using microwaves for heating adsorbent is another technology that is being investigated. Microwaves refer to high frequency range of radio waves in electromagnetic spectrum with frequency between 300MHz and 300GHz. In this technique, heat is generated directly inside the adsorbent bed. It has been observed that microwaves heat the adsorbent internally by dielectric heating, without any thermal or mechanical degradation of the adsorbent[96,97].

In conclusion, ESA is still being studied in research phase and there are certain drawbacks of ESA in CO_2 capture, which still need to be resolved. Some of the major drawbacks are:

- Major drawback is that a part of energy being generated in a power plant will be consumed during the electrification step of ESA[84]. Consequently, design and configuration of the ESA equipment becomes extremely important for reducing the energy penalty. The properties of electrodes (density, volume, resistance, heat capacity) and adsorption column configuration (size, adsorbent and its packing) will have a major role to play in contribution to energy penalty.

- Traditional morphologies of AC such as granular and powdered form cannot be used in ESA[98]. Uniform distribution of temperature is not obtained during Joule heating because of the non-homogeneity of contact between particles.

2.3.3. Temperature swing adsorption

This method is based on difference in adsorption capacity of a material at two different temperatures. The bed is regenerated by raising its temperature while maintaining almost constant pressure. Figure 2-4 shows principle of operation of a TSA process. This application generally consists of at least two adsorbent beds, one adsorbing while other desorbing at a higher temperature[69]. It is generally used for removal of small amounts of gas components that are strongly adsorbed. Typical applications include drying of gases, solvent recovery, removal of volatile organic compounds and natural gas sweetening.

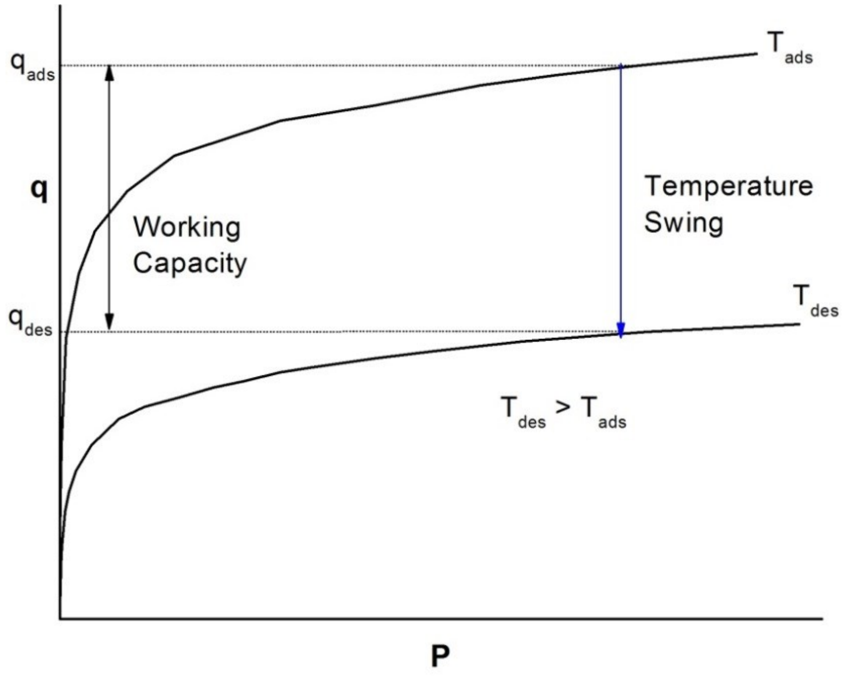


Figure 2-4. Principle of operation of a temperature swing adsorption process

Applications in CO_2 capture

TSA has been investigated by various research groups for amine loaded sorbents[99], metal organic frameworks[100] and circulating fluidized bed arrangement[101]. For post-combustion CO_2 capture, the adsorbents must respond strongly to temperature changes in the range of 30 °C-150 °C in a TSA process[102]. Because this is the temperature range at which heat is available at a power plant in the form of flue gas waste heat and low pressure turbine etc. This makes amine and imide hybrid chemisorbents, with heat of adsorption in the range 40-70 kJ/mol CO_2, most suitable for TSA application[52,102].

This section can be divided into two sections: TSA driven by a) Indirect heating and b) direct heating (using inert purge gas).

2.3.3.1. *TSA driven by indirect heating*

The idea behind this process is to tackle two main drawbacks of TSA in general: large amount of adsorbent required due to low productivity of process and dilution of product due to regeneration with hot purge gas[103]. Most of the work done with this technique is using zeolites as adsorbent and using internal heat exchanger for indirect heating in regeneration step[56,103,104].

Merel et al.,[56] reported use of two-phase heat transfer mode in a heat exchanger for regeneration. Steam at 150 °C was condensed for preheating the bed and no purge gas was used during this step. This allowed for high heat transfer coefficients, which reduced the regeneration time. Only when the flow rate of the desorbed CO_2 became lower than 1.2Ndm^3/min, N_2 purge was introduced to complete regeneration step. In another study by the same group[103], choosing minimum energy consumption for 95% CO_2 purity, following operating parameters were obtained: T_{des} = 160 °C and a purge at 0.3Ndm^3/min. Moreover to enhance the performance of process, use of a hybrid VTSA was recommended. It is to be noted that these results are for zeolites and the desorption temperature for amine sorbents is generally in the range of 100-130 °C. To my knowledge, no work has been reported on amine based sorbents using indirect heating.

2.3.3.2. *TSA driven by direct heating*

This methodology uses a hot inert purge gas or steam for direct heating of sorbent and displacement of adsorbate. As the focus of current research is on steam stripping for CO_2 capture, these two heating methodologies have been discussed separately.

a) Hot inert gas for direct heating

In many TSA processes, the bed is heated by passing a hot gas purge (N_2 in most of the cases) through the bed. Hot inert gas provides the concentration swing for desorption of CO_2. This is the most common method used for testing of new synthesized sorbents for CO_2 capture and suitability of those materials for multiple cycles. But the recovered CO_2 is always diluted in the purge gas, which is because[105]:

- Due to low volumetric heat capacity of hot purge gas, the temperature rise and hence the isotherm decrease occurs slowly. This results in low quantities of desorbed component.
- Hot purge gas plays the role of a carrier gas which leads to dispersive type of desorption front, i.e. progressive decrease in concentration of desorbed component.

Another important issue is thermal stability of amines under dry inert gas atmosphere at elevated temperatures. Thermal stability of different molecular weight PEI and TEPA was investigated by Zhao et al.[31] under N_2 atmosphere at temperatures that are most commonly used for TSA of amine based adsorbents under inert gas atmosphere. It was observed that TEPA loaded silica started losing weight because of amine evaporation at 110 °C and reached a maximum weight loss rate of 2.2 wt%/min at 200 °C. On the other hand, PEI based adsorbents showed a good thermal stability at temperatures below 150 °C. To study stability under more robust conditions, the sorbents were kept under N_2 atmosphere at 140 °C for 5h and 2.5 wt% loss was observed for MW~600 PEI, whereas the higher molecular weight PEI's were highly stable. Drage et al.,[35] conducted similar experiments for CO_2 stripping using pure CO_2 at elevated temperatures. It was observed that stable urea compounds were formed under CO_2 atmosphere; hence steam stripping was suggested as a viable regeneration technique. It was reported that use of steam would overcome problems related to adsorbent degradation in presence of CO_2.

b) Steam for direct heating

Recently, steam stripping has been strongly proposed for CO_2 capture[35,43,55]. Firstly, low temperature steam in easily available in plants as waste heat. This would eliminate the requirement of external equipment, such as vacuum pumps. Secondly, it provides thermal driving force along with concentration gradient for desorption of adsorbed CO_2 (only concentration swing is provided by inert gas). A concentrated CO_2 product stream can be obtained by compressing the CO_2/steam mixture and condensing out the moisture.

The methodology has been traditionally used for VOC's separation[106] but very few studies have been conducted on its application in CO_2 capture. One of the very first studies of steam application in CO_2 capture was done by Dutcher et. al.[107]. The group studied the impact of direct steam heating, VSA and steam aided vacuum-swing adsorption (SA-VSA) for CO_2 capture, in a Carbon filter process. It was observed that except for a minor fraction that had composition similar to flue gas, rest of the effluent stream contained pure CO_2 in case of direct steam heating. Moreover, desorption was rapid. However, it was observed that steam condensed on the surface and in the voids of the adsorbent bed. It was reported that if the water was allowed to accumulate from cycle to cycle, the capacity of adsorbent decreased from 1.7 wt% in 1st cycle to 0.7wt% in 4th cycle. Almost 2/3rd of the desorbed gas had purity > 95% in water free VSA, but it required vacuum below 30 Torr, to achieve substantial CO_2 yield. Finally a hybrid approach of SA-VSA was proposed in this study, to alleviate the problem of condensation in steam stripping and very low vacuum requirement in VSA. In this case, vacuum was pulled in desorption stage and as soon as it reached 30 Torr, steam was admitted in to maintain this pressure[108]. Nearly, 98% pure CO_2 was recovered in a field test of 100 cycles. However, the adsorbent used was coal derived AC and had low CO_2 adsorption capacity and low CO_2 selectivity in presence of moisture. Amine based adsorbents have proven to be better performing in both these cases and recent investigations on their behavior in steam environment have been done, which are discussed next.

Jones's group looked into stability of various amine functionalized commercial silica[43], mesoporous alumina[109] and mesocellular foam[110] based adsorbents. Cyclic runs were performed for commercial silica based adsorbents and steam at 105 °C was used for desorption. Table 2-3 provides information on materials and their performance in these experiments[43]. Further, testing of materials was done under prolonged hours of steam exposure, to study the effect on solid support and amine stability[110]. It was observed that MCF support collapsed almost completely in steam/air environment at 180 °C, which can be attributed to its inherent structure, i.e. high BET surface area and relatively thin walls. For amine functionalized support, the stability trend was reported as:

$$\text{MCF-HAS} > \text{MCF-PEI} > \text{MCF-Mono} > \text{MCF-DMA}$$

Where, MCF-HAS stands for silica polymerized with Aziridine, MCF-Mono and MCF-DMA are functionalized using APTMS and AEAPTMS. Loss in CO_2 adsorption capacity after exposure to steam for 24h was associated with: structural collapse of MCF and amine degradation due to steam and/or O_2.

Table 2-3. Performance of amine functionalized silica based adsorbents in multiple cycle steam regeneration experiments[43]

Adsorbent	Functionalization technique, Amine loading (wt %)	Performance over 3 cycles
PEI-Si	Impregnation, 35	Capacity loss by 2%
3-Aminopropylsilyl-Si	Grafting, 13	Capacity loss by 17%
In-situ Aziridine polymerized Si (MCF)	Hyperbranching, 19	Capacity increase by 3%

New amine functionalized materials, based on mesoporous γ-Alumina support were evaluated against silica based counterparts (SBA-15 in this case) for CO_2 adsorption capacity, amine efficiency and their stability under steam environment[109]. It was observed that PEI impregnated alumina based sorbents performed better than SBA-15 based material in all respects. After steam treatment, capacity of the former decreased by 16.3% while the decrease was 67.1% for the latter.

But most of these studies were in a batch reactor and for static 24h exposure to steam. In actual capture facility, the materials are going to be exposed to environment of flowing steam and the nature of the process would be cyclic. Hammache et al.,[111] conducted a multiple cycle (8 cycle) steam regeneration study for PEI functionalized silica (G-10) based adsorbent in a packed bed reactor. The observations were in contradiction to previous findings reported by Jones group. The silica support was found to be quite stable under steam and loss in CO_2 adsorption capacity over 8 cycles was attributed to likely re-agglomeration of the amine, which resulted in blockage of pores and decrease in number of available sites. Replacement of Helium with steam for regeneration, resulted in faster desorption kinetics.

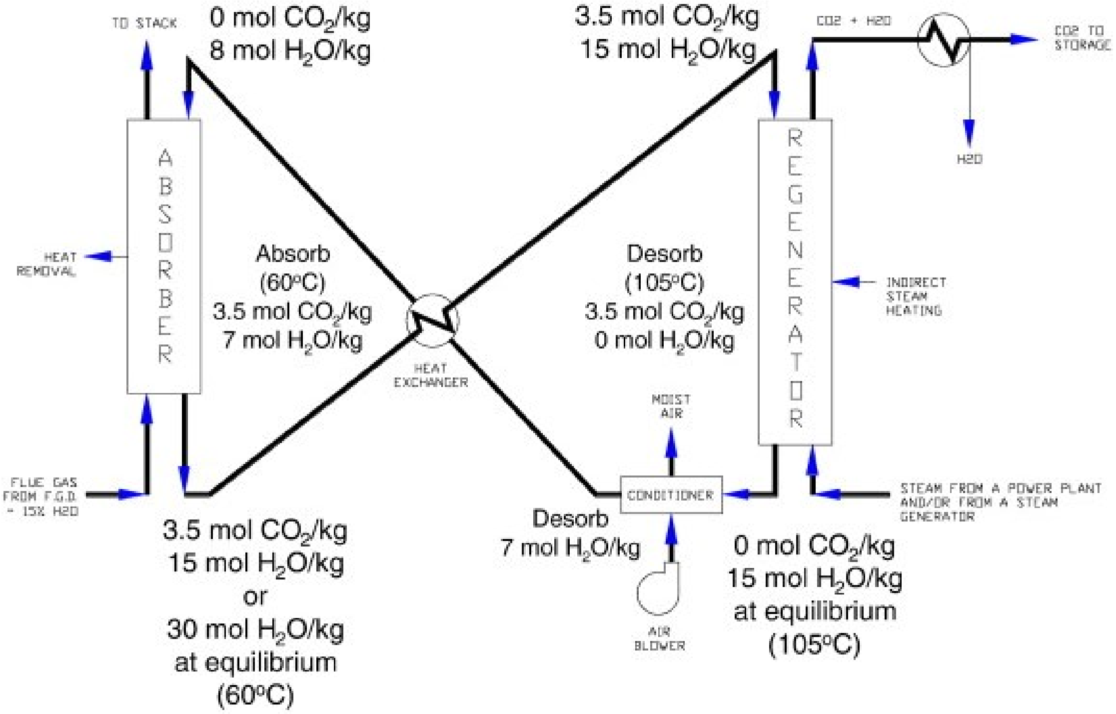


Figure 2-5. Basic Immobilized Amine Sorbent (BIAS) process for steam stripping of PEI/Si (Reprinted with permission from Copyright (2014) Elsevier[47])

Recently, a conceptualized CO_2 removal process – Basic Immobilized Amine Sorbent (BIAS) process (shown in Figure 2-5) has been proposed by Hoffmann et. al.,[47] for PEI/Si based adsorbent. The sorbent continuously flowed between the adsorber and the regenerator and during this flow in circulation loop, the level of moisture was manipulated or controlled to minimize its effect on regeneration heat duty. Steam sweep was used for sorbent regeneration, which lead to equilibrium moisture loading of about 15 mmol H_2O/g of sorbent. The idea was to minimize/avoid moisture desorption in regenerator; hence decreasing its impact on increase in regenerator heat duty. The adsorber was designed in such a way that the sorbent adsorbed roughly 3.5 mmol CO_2/g and 7 mmol H_2O/g from flue gas. An air blower was placed at exit of regenerator which desorbed 7 mmol H_2O/g. On being fed to the adsorber, the sorbent adsorbed 7mmol H_2O/g from humid flue gas. Hence, the adsorbent exiting the adsorber and entering the regenerator was saturated with 15 mmol/g H_2O and this kept the moisture level constant across the regenerator.

Overall, it can be concluded that research on application of steam stripping in CO_2 capture is still in preliminary phase and further investigation needs to be done to understand the desorption kinetics, behavior of adsorbent and its suitability for multiple cycles. The rapidness of the process and the ease of separation of steam and CO_2 by condensation, make this process attractive. But most importantly, low temperature steam is generally available in all plants; especially the coal fired power plants as waste heat.

2.4. Motivation and Objectives

In view of above discussion, it is clear that amine functionalized adsorbents possess high CO_2 adsorption capacity, are highly selective to CO_2 and are stable under humid atmosphere. As amine impregnated sorbents are easy to synthesize and have higher adsorption capacity they have been selected over grafted adsorbents. Thermal stability and performance in multiple cycles are important aspects of sorbent screening and are highly influenced by regeneration methodology used. Low grade steam is generally available as waste heat in coal-fired plants and CO_2-H_2O can be easily separated by compression and condensation. The preliminary tests for using steam stripping for regeneration of amine based sorbents look promising and it would be worthwhile to look into desorption kinetics and its suitability for multiple cycles.

So, the focus of this study was to study the stability of amine impregnated silica based adsorbents in steam atmosphere. The aim was to study the suitability of adsorbent for multiple cycles under steam regeneration, study the effect of steam on amine content and surface morphology of the material. Moreover, as already known, flue gas (e.g. from coal fired power plants) contains moisture and 2-5% O_2. So, effect of moisture and O_2 was studied on CO_2 adsorption and performance of material was evaluated for multiple cycles. The objectives can be specified as below:

1) To synthesize amine impregnated silica sorbents and characterize them.
2) To study the effect of different concentrations of moisture in flue gas on CO_2 adsorption.
3) Study the effect of O_2 on CO_2 adsorption over multiple cycles and to evaluate its impact on amine content.
4) Performing steam stripping of the adsorbent and evaluating its suitability for multiple adsorption and desorption cycles.
5) Compare steam regeneration with inert gas stripping and to study the desorption performance at different steam temperatures.

Chapter 3

MATERIALS AND METHODS

3.1. Materials

Commercial grade silica from Fuji Silysia Chemical Ltd. was used as a solid support for amine impregnation. It was grade Q-10 silica with particle size distribution 75-150µm. Methanol (Fisher Chemical, 99.9%) and branched PEI (Sigma Aldrich, average M_w~800) were used as received for the preparation of adsorbent. Deionized water was obtained from a Milli-Q integral pure and ultrapure water purification system. Pure CO_2 (99.99%), ultra high pure nitrogen (99.999%) and a calibrated CO_2–N_2 mixture (1:9 volume ratio) gases were obtained from Praxair for the CO_2 adsorption/desorption measurements.

3.1.1. Synthesis of amine functionalized adsorbent

Impregnation of PEI amine over silica was done using wet impregnation technique[25]. Firstly, desired amount of PEI amine was mixed for 15 min in 8 g of methanol. 2g of silica was then mixed with the above solution. The slurry formed was mixed for 0.5 h with stirring at room temperature. The resultant mixture was finally dried at 80 °C for 2 h under vacuum. The synthesis was done for 50% and 40 wt% PEI. It was observed that for 50% PEI, all of the amine didn't get into the silica pores as the sorbent was sticky after synthesis with amine clearly visible on surface. Finally, 40 wt% was found to be the optimum PEI loading that the sorbent could hold. The procedure was scaled up to synthesise a batch of 100g amine impregnated sample.

This single batch was used for all the TGA as well as packed bed reactor experiments. The schematic of amine impregnation mechanism has been described in Figure 3-1[112].

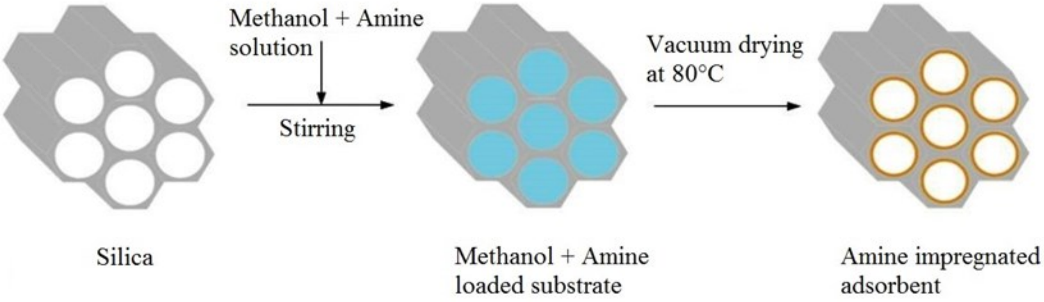


Figure 3-1. Pictorial depiction of amine impregnation mechanism on silica substrate[112]

3.2. Characterization

N_2 adsorption-desorption, Thermo-gravimetric analysis (TGA), Elemental analysis (CHNS) Fourier transform infrared analysis (FTIR), Scanning electron microscopy (SEM) techniques were used for the characterization of silica and amine impregnated sorbents. The same tests were also conducted on samples used in multi-cyclic steam stripping experiments to study any impact on their characteristics.

3.2.1. N_2 adsorption/desorption

Nitrogen adsorption isotherms were measured with Autosorb I (Quantachrome, USA) at a relative pressure range of 0–0.997. The samples were degassed in a vacuum for 8 h at 250 °C before analysis (N_2 adsorption measurement). In case of amine impregnated sorbents, the outgassing was done at 105 °C for 3 h. The total pore volume measurement was done at a relative pressure of 0.997. The surface area was measured based on multi-point Brunauer-Emmett-Teller (BET) method at a relative pressure of 0.05–0.30. The pore size distribution of samples was collected by the BJH method, using the data for the N_2 desorption branch.

3.2.2. Thermo-gravimetric and elemental analysis

Amine loading of the functionalized sample was verified using TGA (TGA/DSC TA Instruments Q500 SDT). The sample temperature was ramped up to 105 °C and kept isothermal for 60 min to remove any moisture and CO_2 adsorbed from atmosphere. After this, the temperature was ramped up to 650 °C at a rate of 10 °C/min. This whole experiment was performed under N_2 atmosphere. The amine loading results were calculated by taking mass of activated amine functionalized adsorbent sample as basis. Elemental analysis was also performed on amine impregnated sorbents for nitrogen content using Elemental analyzer (Model: Vario Micro, USA). From the elemental analysis results, the nitrogen (N) wt% and hence amine loading of the impregnated samples was calculated.

Preliminary CO_2 adsorption capacity tests were also performed on the TGA. Firstly, the sorbent was purged in N_2 atmosphere at 105 °C for 60 min. The temperature was then decreased to desired adsorption temperature and 10% CO_2- N_2 mixture was used for adsorption study. The gas was switched to pure N_2 after 60 min and the temperature was ramped up to 105 °C. Desorption was performed for 60min.

3.2.3. Scanning electron microscopy (SEM)

SEM images were obtained using a JEOL 6301F field emission SEM. It was used to study the surface morphology of samples used in steam regeneration and compare it to that of fresh sample. Samples were placed on carbon tape and then coated with gold. Different resolution and magnification images were collected at 5.00kV for analysis and comparison.

3.2.4. Fourier transform infrared analysis (FTIR)

FTIR analyses were performed using a Nicolet 8700 (thermal) Spectrometer. Smart collector for DRIFTS (Diffused Reflectance Infrared Fourier Transform Spectroscopy) was used for analysis.

KBr was used as a blank and each time a small amount of sample was mixed and grinded with KBr for analysis. Each sample was scanned 64 times at a resolution of $4cm^{-1}$ over the frequency range $4000\text{-}500cm^{-1}$. The analysis was used to compare fresh and used amine impregnated samples in case of steam stripping.

3.3. Experimental

3.3.1. Effect of O_2 on CO_2 adsorption

This study was carried out in a TGA and a pure O_2 (Grade 2.6 extra dry), N_2 (grade 5) and CO_2 (Grade 4.8) cylinder from Praxair were used. A set of 20 cycles was performed for each experiment. The sample was activated by heating it at 105 °C for 1h under N_2 atmosphere. Next, adsorption was performed at 75 °C for a fixed interval of time (30, 20, 10min). Desired amount of O_2 (0, 2.5, 5cc/min) was mixed with 10cc/min of CO_2 and accordingly N_2 was added to attain a total gas flow rate of 100cc/min. After adsorption, the gas was switched to pure N_2, temperature ramped up to 105 °C and kept isothermal for 30min. For humid gas study, the gas mixture was passed through a bubbler at room temperature before adsorption step.

3.3.2. Packed bed reactor set-up

This section gives a detailed description of lab-scale packed bed reactor set-up (shown in Figure 3-2) that was used in moisture effect and steam stripping study. Table 3-1 provides information on instrumentation used in this set-up and their specifications.

Table 3-1. Specification of instrumentation used in packed bed reactor set-up

Instrumentation	**Specifications**
Packed bed column	Stainless steel column: ½" O.D., 4cm height
Temperature controllers	Omron E5CK with accuracy of ± 0.6 °C
Thermocouples (TC)	K-type from Omega
Surface TC to heat packed bed column	SA1XL-K-SRTC from Omega
Heating tapes for packed bed column and all other stainless steel heating lines	HTS/Amptek heavy Amox insulated duo-tape
Bubbler for steam formation	Savillex PFA jar with closure (has two 1/4" outlets for gas inlet and outlet, another 1/8" outlet for thermocouple)
Bubbler heating accessory	HTS/Amptek standard Amox insulated duo tape
Hygrometer	Control Company, USA
Gas mass flow controllers	Brooks Instrument 4800 series, flow accuracy ± 3%, flow repeatability ± 0.15%
Mass spectrometer	Pfieffer Vacuum Omnistar GSD 320

The reactor consisted of a stainless steel column with a porous frit at bottom to hold the sample. A heating jacket was placed around the reactor using a heating tape controlled by a temperature controller. This controller worked on feedback provided by a surface thermocouple (TC) mounted on outer surface of reactor column. The tape was insulated uniformly to form a heating jacket type arrangement. A separate K-type TC was placed in the adsorbent material and used to record temperature profiles of sorbent during adsorption and desorption. For a set value of temperature for surface TC during an adsorption study, the adsorbent temperature remained within a range of ± 1 °C. The flue gas and steam lines were all wrapped in heating tapes and maintained at desired temperatures using various temperature controllers controlled by their respective K-type TCs. Separate N_2 connection was also provided for studies that required inert gas for stripping and using a 3-way valve, steam or N_2 could be used for regeneration. Another separate N_2 line bypassing the reactor was provided. This was used during Mass Spectrometer (MS) calibration.

Moisture study**:** In case of moisture effect study, the flue gas was passed through bubbler that was maintained at a constant temperature to achieve desired moisture concentration in flue gas (details in Table 3-2). In case of steam stripping experiments same bubbler was used for steam formation (described below). But for humid flue gas experiments in this study, a separate bubbler maintained at room temperature was used. 95% relative humidity (measured by hygrometer) was obtained for an exit moisture content of 2.71%.

Steam formation**:** In this case, 10cc/min N_2 was passed through the bubbler gas inlet. A heating jacket was formed for the bubbler, using heating tape and insulation covering. The heating power of tape was controlled by a temperature controller. A portable transformer (Staco Inc., Type 3PN1010) was placed between the controller and heating tape to prevent over heating of bubbler and have a slow uniform heating of water in bubbler. A K-type TC was used to measure water temperature and provide feedback to the controller. The target temperature for bubbler was set at 97 °C to get water vapor pressure of 0.89 atm[113]. This led to 90% saturation of inlet gas and hence the exit bubbler gas composition was 10% N_2 and 90% H_2O (henceforth mentioned at steam). N_2 is an inert gas which doesn't get adsorbed by the sorbent. So, it acted as a trace gas in the whole process and was used in quantification of amount of CO_2 desorbed and moisture adsorbed during steam stripping. The exit line from bubbler was heated to desired steam temperature using a heating tape controlled by a K-type TC attached to a temperature controller.

MS calibration**:** Calibrated gas cylinders from Praxair of composition 15:85 volume ratio mixture of CO_2 and He and 15:85 volume ratio mixture of He and N_2 were used for MS calibration of simulated dry flue gas. For moisture calibration, N_2 was passed through bubbler at room temperature and on basis of 95% RH, this composition was used for MS calibration. The bubbler was heated to various temperatures and the MS reading was then compared to values on a water vapor chart[114]. Both the values were in a good agreement. At 97 °C, the theoretical value was expected to be 90%. The MS reading was in a fair agreement with moisture content fluctuating within 88-91% moisture range. These values were accepted for steam stripping experiments.

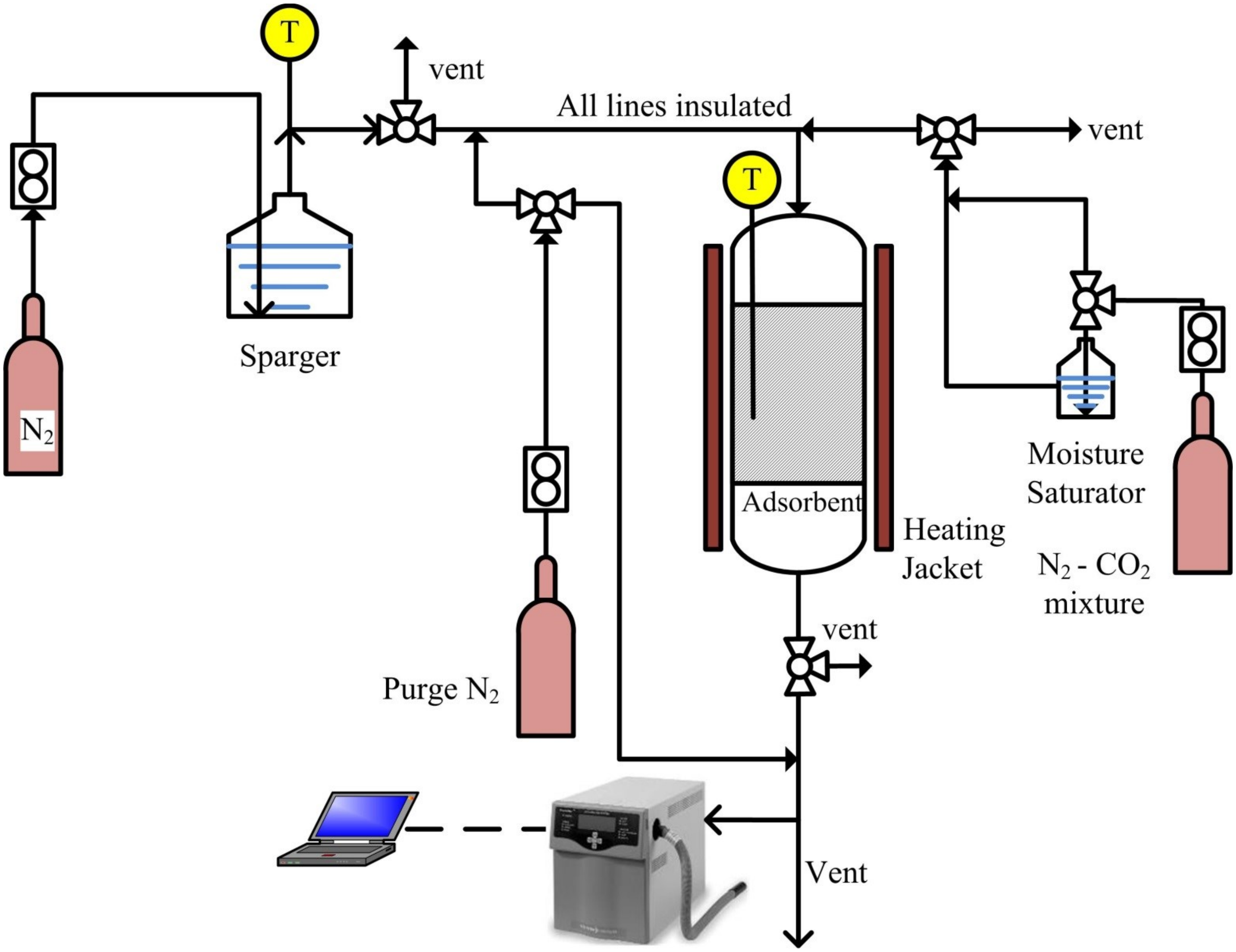


Figure 3-2. A schematic of packed bed reactor set-up used for moisture effect and steam regeneration study

3.3.3. Effect of moisture on CO_2 adsorption

This study was performed on a packed bed reactor set up, shown in Figure 3-2. The set-up has been already described in detail in section 3.3.1. 1g of sorbent was loaded into the packed bed reactor for study. 10% CO_2-N_2 gas mixture was passed through a bubbler maintained at a specific temperature, to attain desired moisture concentration. Relative humidity (RH) of the humid gas was measured using a hygrometer (Control Company, USA) and was observed to be around 95%. Table 3-2 provides details regarding the set temperature of bubbler and exit simulated flue gas composition.

Adsorption was carried out at 75 °C for 1h. The gas was switched to pure N_2 at this point and isothermal desorption was carried out at 75 °C. When the CO_2 exit concentration reached below 1%, the packed bed temperature was ramped up to 110 °C under N_2 atmosphere to carry out desorption of remaining strongly adsorbed CO_2.

Table 3-2. Exit simulated flue gas composition of a bubbler used for moisture effect study

Sparger temperature (°C)	**Exit flue gas composition (vol %)**		
	H_2O	**CO_2**	**N_2**
35	5.27	9.41	85.32
40	7.72	9.16	83.12
52	11.56	8.78	79.66
55	14.74	8.47	76.79

3.3.4. Steam stripping of amine impregnated adsorbent

1g adsorbent was loaded into the packed bed column described above. The temperature was ramped up to 110 °C, to activate the sorbent. As soon as any adsorbed CO_2 and moisture got removed from the sample (as seen through exit gas stream composition in MS), the temperature was cooled down to 75 °C. 100cc/min simulated flue gas was injected through the sample at this point for 10min. After this, the temperature was ramped up to 110 °C under flue gas environment. As the temperature stabilized at 110 °C, steam from the bubbler was sent to the column for 10min. Dry N_2 was passed after this through the sorbent at 110 °C to strip off the moisture adsorbed by the sorbent. Under N_2 environment, the temperature was then cooled to 75 °C for next run. A set of 20 runs was performed in similar manner. From preliminary runs it was observed that the CO_2 adsorption breakthrough occurred at around 4min after flue gas injection. So, a 10min adsorption time was fixed to attain the inlet gas CO_2 concentration. Similarly, in case of steam stripping, the exit CO_2 concentration was in ppm at the end of 10 min interval. Hence, both the adsorption and desorption were fixed at for 10min interval.

Chapter 4

SORBENT CHARACTERIZATION & STUDY THE EFFECT OF OXYGEN IN TGA

This chapter contains two sections as described below:

- The first section contains details regarding characterization and CO_2 adsorption/desorption performance of sorbent in TGA at various temperatures.
- In the second section, results from a TGA study that were carried out to study the influence of presence of O_2 in simulated flue gas on CO_2 capture performance of the sorbent are presented.

4.1. Characterization

4.1.1. N_2 adsorption-desorption

A N_2 adsorption-desorption isotherm for silica support and PEI impregnated silica has been shown in Figure 4-1. Silica displays a typical type IV isotherm, which is a characteristic of mesoporous materials. It has a H_1-type hysteresis loop due to capillary condensation occurring in the 0.7-1.0 relative pressure range and is an indication of narrow pore distribution. The total pore volume and surface area are 1.23cm^3/g, 283.3m^2/g, respectively. The corresponding values for PEI-Si are 0.34cm^3/g and 49.16m^2/g, respectively. The reduction is due to introduction of amine functionalities in the silica support. The pore radius for both materials was calculated to be 6.6nm.

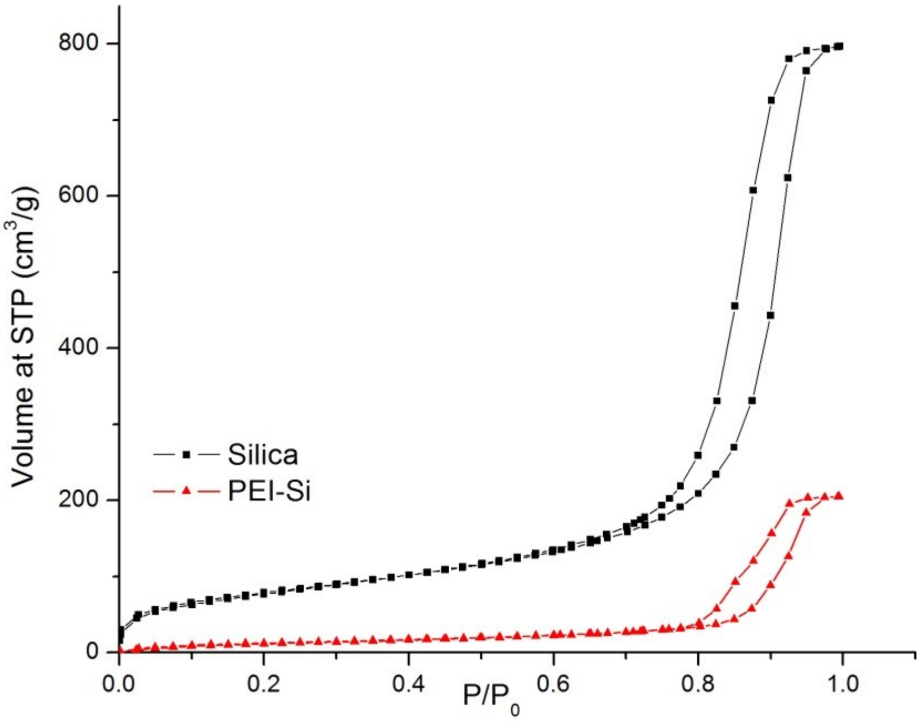


Figure 4-1. N_2 adsorption-desorption isotherm for silica support and PEI/Si

4.1.2. Amine loading using TGA and elemental analysis

After synthesis of adsorbent, a TGA study was carried out to calculate the amount of amine that was actually impregnated in the sorbent (Figure 4-2). Dry sorbent was heated up to 650 °C at a rate of 10 °C/min in N_2 atmosphere. There were two major step changes observed in the weight% vs temperature curve. The first step was observed at around 100 °C due to release of moisture and CO_2 adsorbed from atmosphere. The amine was quite stable till 150 °C after which the amine loss rate increased with temperature, reaching a maximum loss rate of 5.55 wt%/min at 373.81 °C. The presence of single peak during this time indicates that the amine loss took place in a single step. The final residue left behind was around 56.7% of original weight of sorbent. Based on this and the amount of CO_2 and H_2O desorbed, it was calculated that the actual amine loading was 40.8wt% on dry basis. Elemental analysis was conducted to cross check this value. Assuming that PEI contains 33 wt% Nitrogen[19], the amine content was calculated to be 39.71wt%, which is in a good agreement with TGA results.

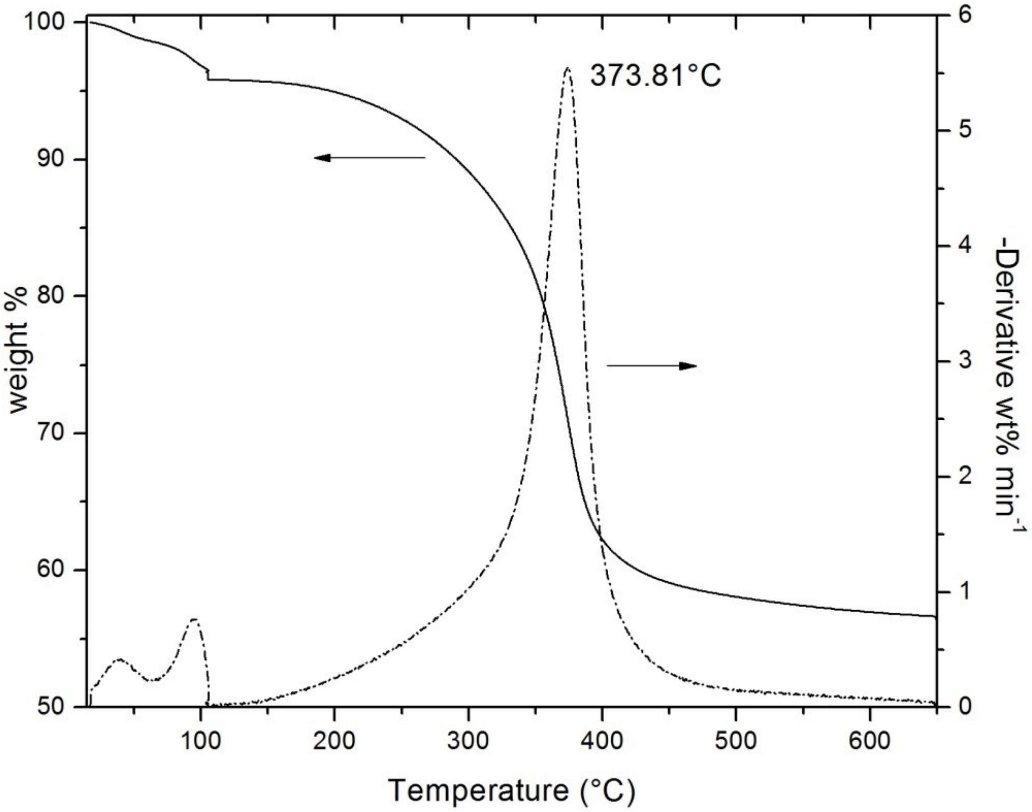


Figure 4-2. Thermal behaviour of PEI/Si under N_2 atmosphere

4.1.3. FTIR analysis

FTIR analysis of silica support and the PEI/Si adsorbent was done to determine the surface functional groups as shown in Figure 4-3. The broad intense peak at ~1103cm^{-1} is associated to asymmetric Si-O stretching in siloxane bonds (Si-O-Si) structure and is a feature of silica framework. Peaks at 3190, 1640cm^{-1} are due to presence of adsorbed moisture in silica[115]. FTIR provides a clear evidence of amine impregnation. PEI/Si shows several distinctive peaks at 3286 and 1579cm^{-1}, which have been assigned to N–H vibration[116]. Peaks appearing at 2933 and

2815cm^{-1} are due to the C–H stretch and 1463 cm^{-1} as a result of CH_3 deformation[116]. These peaks are absent in silica. A more detailed peak assignment has been shown in the Figure 4-3.

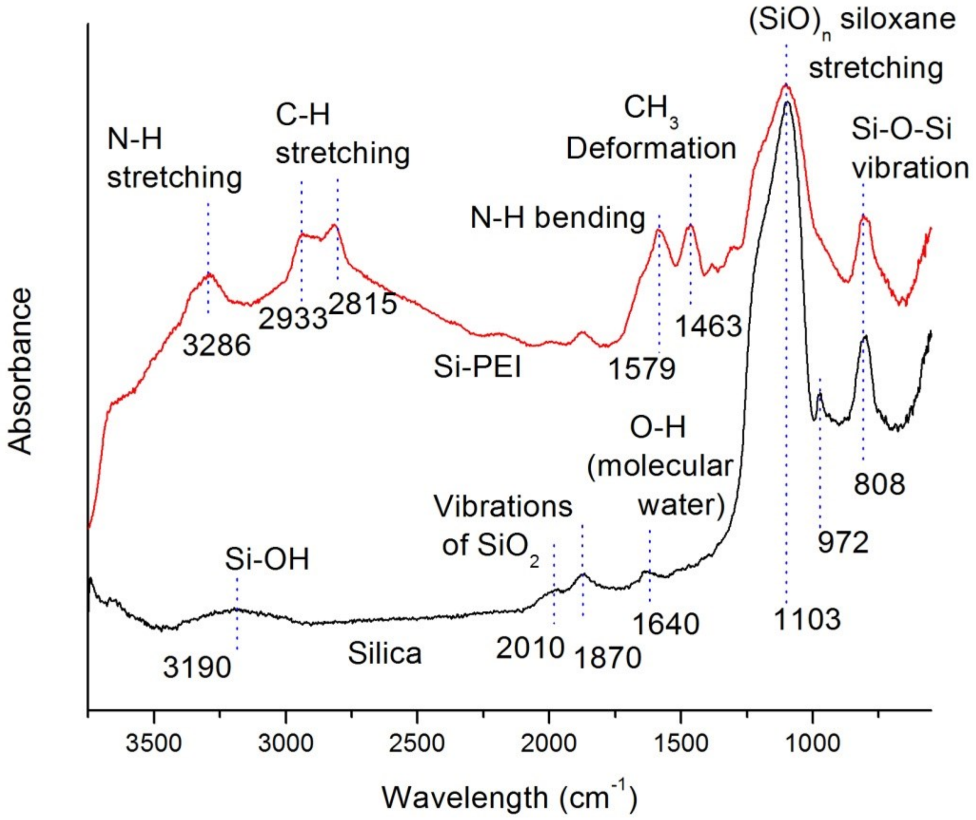


Figure 4-3. FTIR analysis of silica support and PEI/Si

4.1.4. Adsorption performance

40 wt% PEI loaded silica was tested in a TGA to study the effect of different adsorption temperatures and CO_2 partial pressures on CO_2 adsorption capacity of the material. For temperature effect study, the experiments were carried out in a simulated flue gas atmosphere (10% CO_2 and 90% N_2)) at five different temperatures (50, 60, 75, 90, 110 °C). Effect of CO_2 partial pressure was studied at 75 °C for CO_2 concentration of 400ppm, 10, 20, 40, 60, 80 and 100%. In each case before studying adsorption, the temperature was ramped up to 105 °C and

kept isothermal for 1h in N_2 atmosphere to remove any moisture and CO_2 adsorbed by the sorbent from air. As shown in Figure 4-4, the sorbent capacity increased with temperature, reached a maximum of 2.31 mmol/g at 75 °C and decreased with any further increase in temperature. Such behaviour is due to the adsorption being kinetically controlled at lower temperatures[24]. The overall process is diffusion controlled due to which the adsorption capacity is less at lower temperatures. Diffusional resistance decreases with increase in temperature which leads to a higher adsorption rate. But beyond a certain temperature (75 °C), the process becomes thermodynamically controlled and diffusional resistance is no longer a controlling factor[117]. This is consistent with exothermic behaviour of adsorption as well. Overall, the adsorption on PEI impregnated adsorbents is a balance between kinetic and thermodynamic limitations, for which the optimum value was observed at 75 °C.

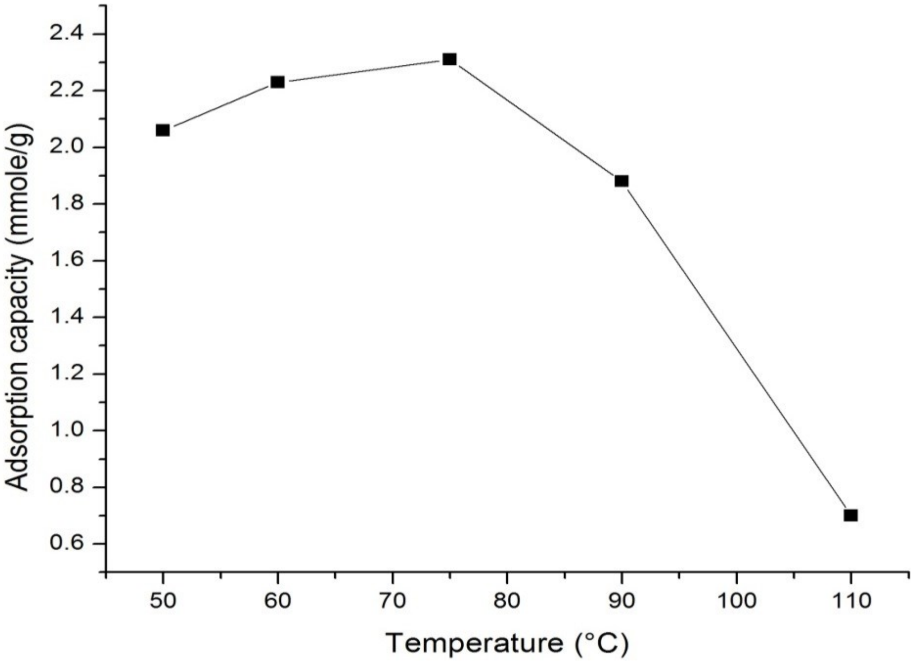


Figure 4-4. Change in adsorption capacity of PEI/Si with increase in temperature

From the effect of partial pressure study, it was observed that the adsorbent had very low CO_2 adsorption capacity in presence of air. It increased dramatically to 2.31 mmol/g when the CO_2 partial pressure was increased to 10 kPa (Figure 4-5). Beyond that, the increase was not as significant and the capacity was calculated to be 2.59 mmol/g under pure CO_2 (100kPa).

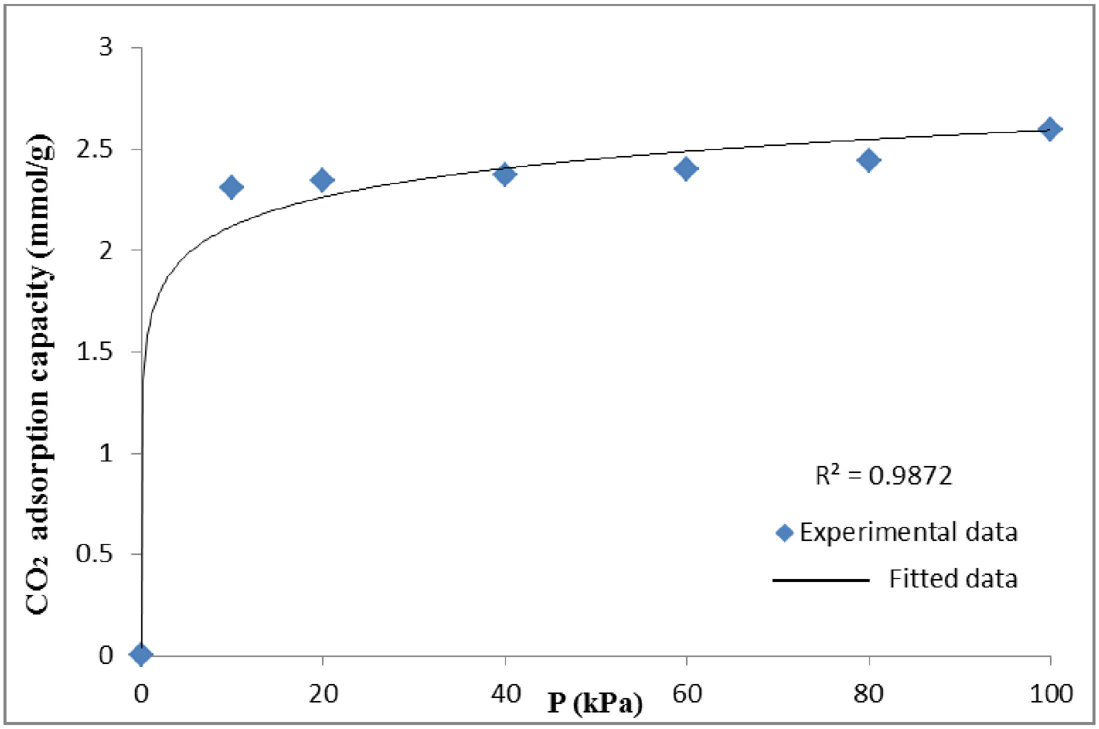


Figure 4-5. Change in CO_2 adsorption capacity with increase in CO_2 partial pressure

4.2. Effect of O_2 on CO_2 adsorption

4.2.1. Influence of O_2 concentration on CO_2 adsorption

Flue gas from a coal fired boiler generally contains 2-5% O_2, due to which the concentrations of O_2 to be studied were chosen as 5% and 2.5%. The results were compared to 10% CO_2 and 90% N_2 case (0% O_2) for 30 min adsorption, as shown in Figure 4-6. The adsorption capacity for 1st cycle was calculated to be 2.03, 1.95 and 1.93 mmol/g for 0, 2.5 and 5% O_2, respectively. After

20 cycles, the drop in capacity was calculated to be 3.53, 3.35 and 4.17% respectively. The values are acceptable but in presence of O_2, slight degradation of amine was observed.

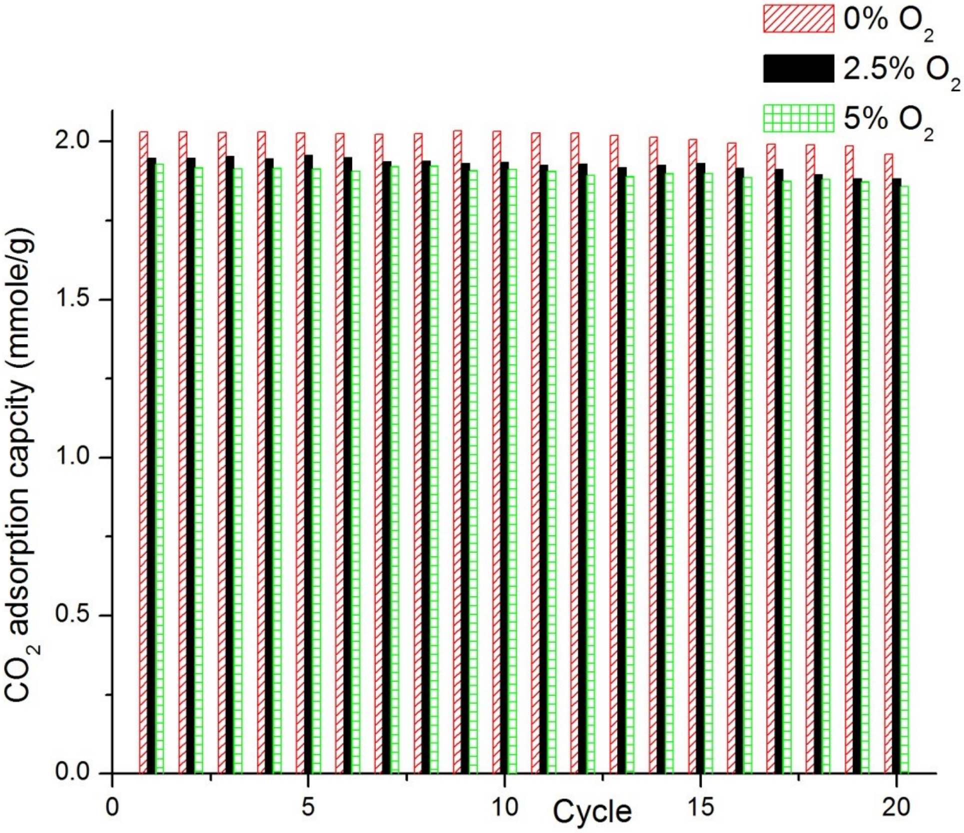


Figure 4-6. Multiple cycle CO_2 adsorption study for different concentrations of O_2 in flue gas (the standard error for this data varied between 0.02-0.08)

Figure 4-7 shows a TGA run for 5% O_2 in which a shift can be seen in the y axis. This drop in baseline is due to loss in amine from the sorbent[118]. To confirm this, elemental analysis was performed for 5% O_2 case and compared with fresh sample. Moreover, to confirm if this loss was because of oxidation under O_2 or due to thermal degradation, a sample was kept under N_2 at 105 °C for 10 h (to replicate desorption conditions in O_2 study). It was observed that the amine content decreased to 35.4 wt% in case of O_2 study, which is 4.6% less than original amine content in fresh sorbent (40%). The value was found to be 33.59% for thermal degradation study performed under N_2. It can be concluded on the basis of these results, that O_2 didn't significantly lead to material degradation. The loss of amine was more due to thermal degradation than oxidation under O_2.

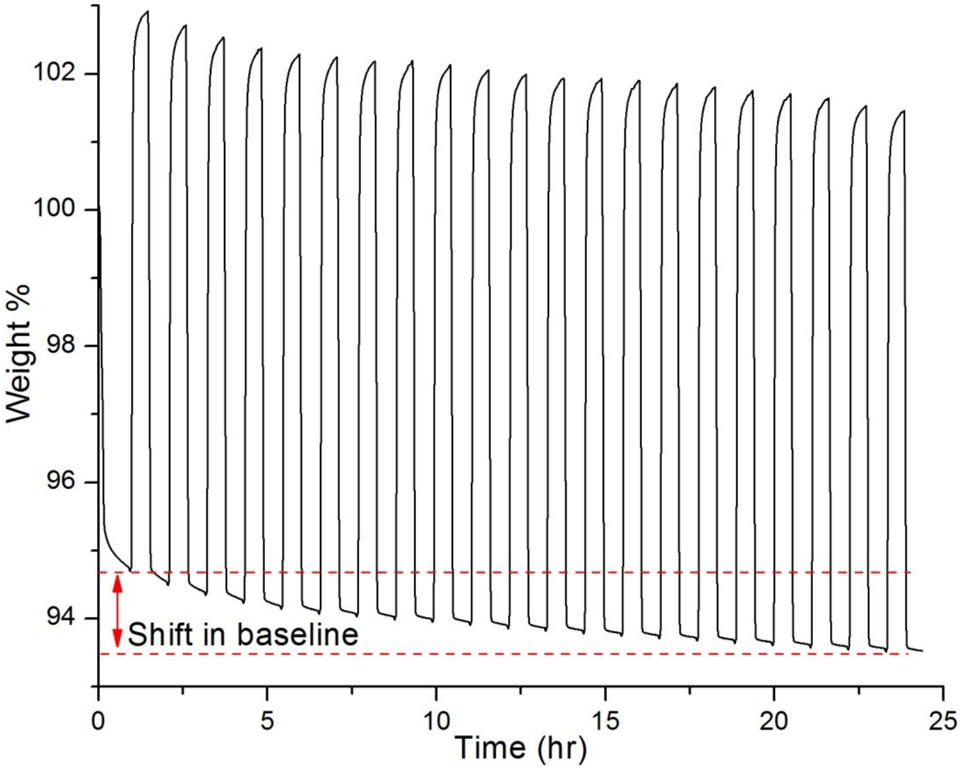


Figure 4-7. Change in weight of sorbent with time during multiple cycle CO_2 adsorption for 5% O_2 in flue gas

4.2.2. Influence of duration of adsorption time

Another set of experiments was conducted, to study the influence of exposure time to O_2. This was conducted for 5% O_2 case and the comparison was done for a multiple cycle study consisting of 10 min, 20 min and 30 min adsorption cycle. So, basically over 20 cycles, the sorbent was getting exposed to O_2 for 3.33, 6.67 and 10 h, respectively. The adsorption capacity remained constant for all the 20 cycles in case of 10 min adsorption cycle, which was calculated to be 1.93 mmol/g. In case of 20 min study, the adsorption was again stable and the average CO_2

adsorption capacity over 20 cycles was 1.94 mmol/g. Figure 4-8 shows drop in baseline as the cycles progress for 10 min adsorption cycles. On comparing with Figure 4-7, it can be observed that the drop is not as significant as in case of 30 min adsorption cycles. Moreover, the adsorption capacity remained constant in this case and is comparable to that with 30 min adsorption cycles. So, keeping the cycles short, degradation of sorbent can be avoided while having a high adsorption capacity at the same time.

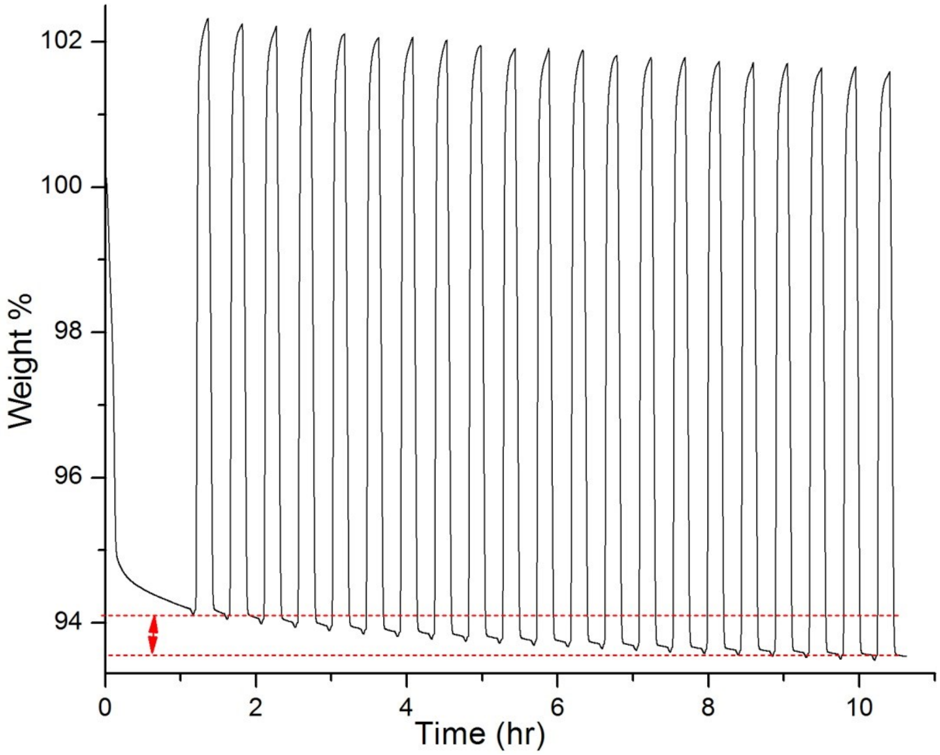


Figure 4-8. Change in weight of sorbent with time during multiple cycle study for 5% O_2 in flue gas and 10min adsorption cycle

4.2.3. Influence of O_2 on CO_2 adsorption in presence of moisture

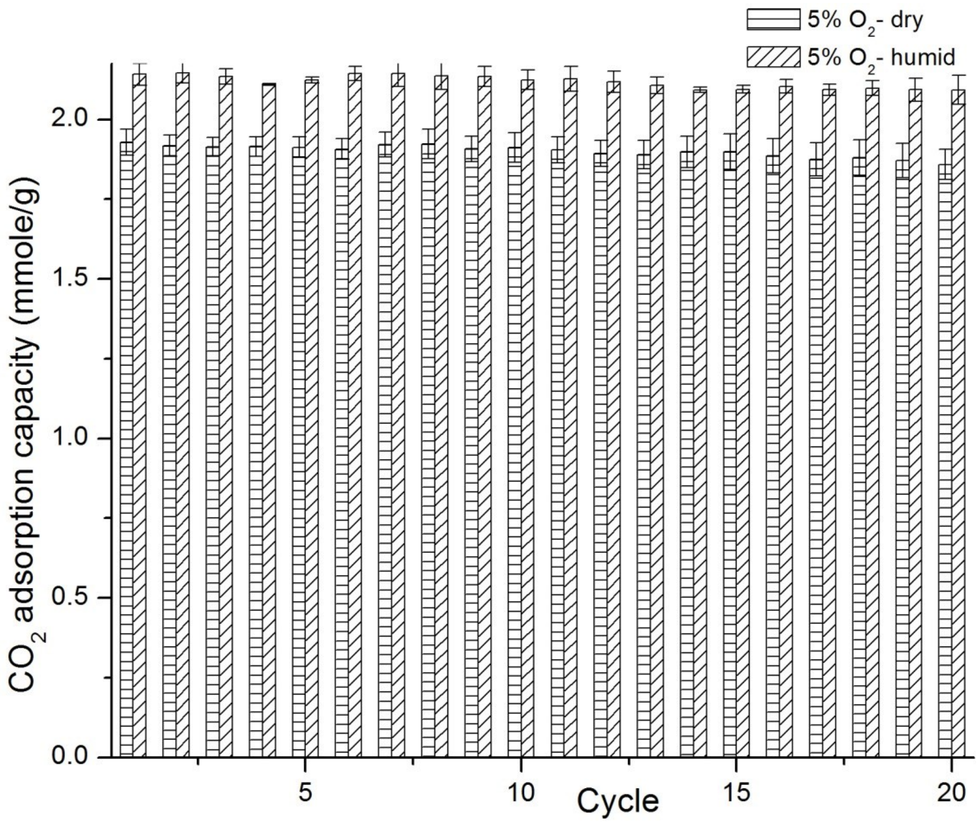


Figure 4-9. Multiple cycle CO_2 adsorption for 5% O_2 containing dry and humid flue gas (standard error bars for CO_2 adsorption capacity measurement)

The experiment was conducted for 30 min adsorption case for 5% O_2 in presence of 1.74% moisture. A given amount of gas was passed through a bubbler at room temperature and then mixed with dry gas to attain 1.74% moisture content by volume. Firstly, the adsorption capacity in 1st cycle increased to 2.15 mmol/g in presence of moisture as compared to 1.93 mmol/g in dry gas case. The adsorption capacity dropped by 2.27% only, over the span of 20 cycles. The results for CO_2 adsorption capacity for dry and humid flue gas containing O_2 have been compared in Figure 4-9. Overall, the adsorbent showed stability in presence of O_2 in flue gas, especially under humid flue gas condition which is the case for flue gas emitted from the industries.

Chapter 5

CO_2 ADSORPTION AND DESORPTION STUDIES IN A PACKED BED REACTOR

This chapter contains the results from packed bed study. The chapter has been divided into 2 sections, as described below:

- First section deals with effect of presence of moisture on CO_2 adsorption. Different moisture concentrations have been studied.
- In second section, performance of sorbent in multi-cyclic experiments has been discussed where steam was used as a CO_2 stripping agent in desorption step.

5.1. Effect of moisture on CO_2 adsorption

5.1.1. Influence of moisture concentration on CO_2 adsorption

The effect of moisture was studied at four different H_2O concentrations: 5.27, 7.72, 11.56 and 14.74% at 75°C. The corresponding relative humidity (RH) values at 75 °C for these concentrations would be 13.68, 17.96, 30.11 and 38.48%, respectively. A breakthrough curve for CO_2 and H_2O has been shown for 7.72% moisture case in Figure 5-1. As seen in the Figure, breakthrough for H_2O occurs before CO_2 and same behaviour was observed for other three concentrations of moisture.

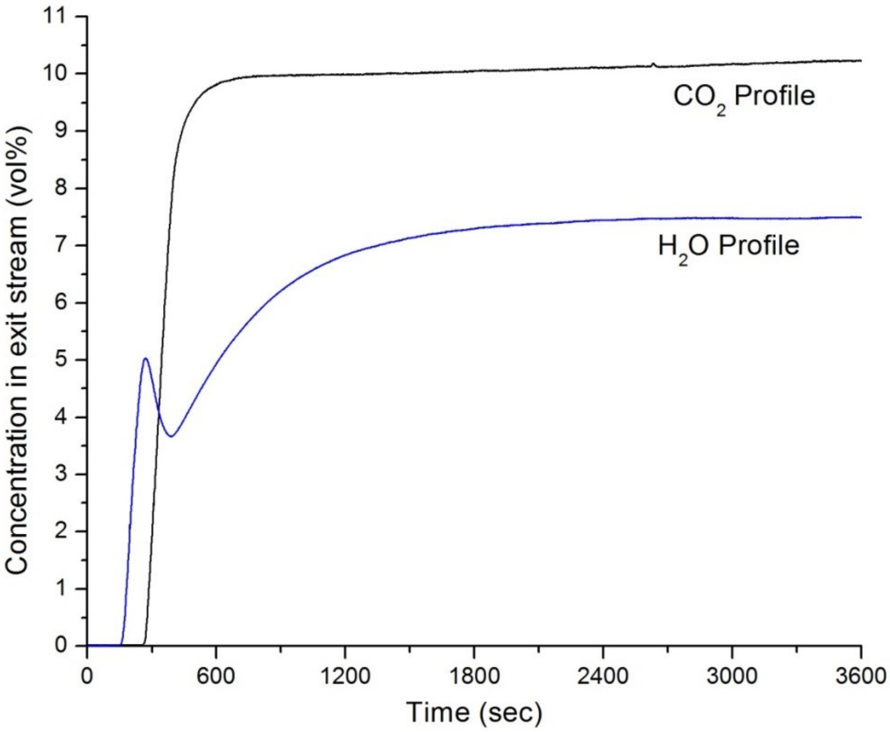


Figure 5-1. Adsorption breakthrough curve for H_2O and CO_2 at 75 °C for 7.72% H_2O content in simulated flue gas

Presence of moisture had a positive effect on amount of CO_2 adsorbed, although the difference was not large. Figure 5-2 shows the relative increase in CO_2 adsorption for all the four cases, in comparison to dry simulated flue gas case. It can be seen that the adsorption capacity increases by 7.03% for moisture content of 5.27%. It slightly increases to 8.74% for 7.72% moisture content. This increase is not as significant as mentioned in some other studies[119,120]. But similar results were reported elsewhere[47,121]. This can be due to the partial production of bicarbonate when humid flue gas comes in contact with PEI/Si. Moreover, it is possible that the increase in CO_2 adsorption capacity in humid conditions is a function of adsorption temperature as well. At H_2O concentrations higher than 7.72% (in other words, when H_2O concentration in feed crossed that of CO_2), the increase in adsorption capacity was significantly less and dropped with further increase in moisture. The values were 6.18 and 3.91% for 11.56 and 14.74% moisture content, respectively. Similar results were reported by Xu et al.[120], where the increase in CO_2 adsorption capacity was less pronounced for moisture concentrations above 10%. The amount of moisture adsorbed increased with increase in H_2O concentration and was calculated to be 2.55, 3.75, 5.37 and 5.86 mmol/g sorbent, respectively.

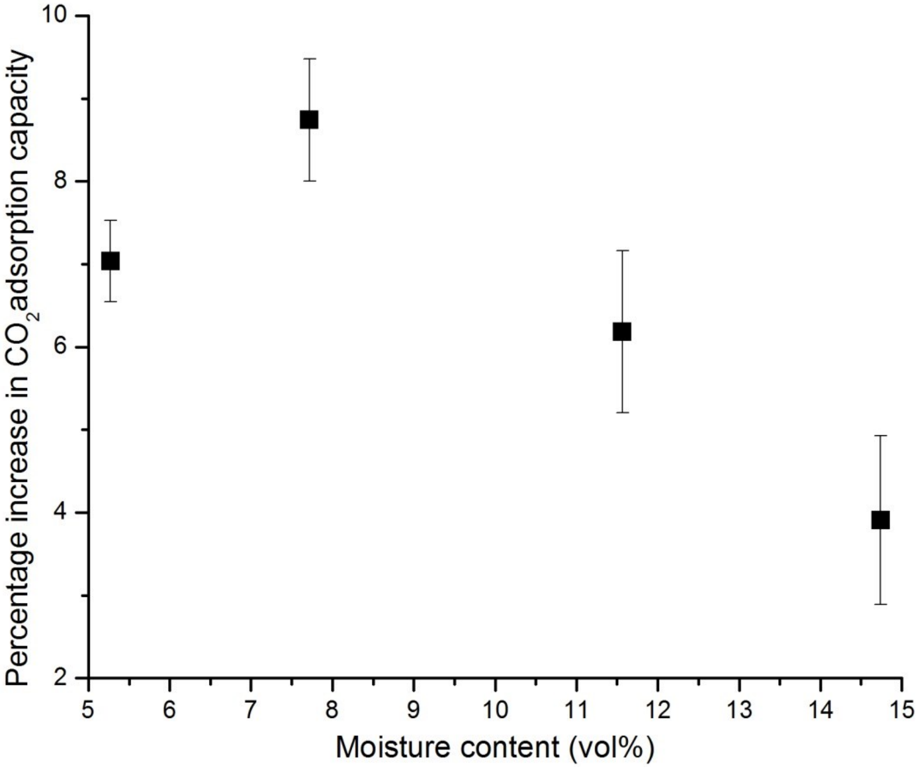


Figure 5-2. Change in CO_2 adsorption capacity at 75 °C with increase in moisture level in simulated flue gas (CO_2 adsorption capacity for dry case taken as basis and standard error bars shown for calculation)

5.1.2. Impact of moisture on energy required for regeneration

Wurzbacher et al.[122] conducted a VTSA study on concurrent separation of CO_2 and H_2O from air. They studied the process for different RH values of air and performed an energy requirement analysis. Similar attempt has been made here to study the effect of moisture content in feed stream, on energy requirement for sorbent regeneration. Sensible heat (energy required to heat the sorbent after adsorption is complete, to desorption temperature) and heat of desorption for CO_2 and H_2O have been considered in the calculation. The values have been calculated on per kg of sorbent basis and the equations for sensible heat (Q_{sens}) and heat of desorption (Q_{des}) are as following[122]:

$$Q_{sens} = \left(c_{P,s} + q_{CO_2} * c_{P,CO_2} + q_{H_2O} * c_{P,H_2O} \right) * (T_{des} - T_{ads})$$

$$Q_{des} = q_{CO_2} * h_{des,CO_2} + q_{H_2O} * h_{des,H_2O}$$

Table 5-1. Assumptions made for calculation of heat of regeneration

Parameter	**Value**	**Reference**
Heat capacity of sorbent, $c_{P,s}$	1.8 kJ/kg.K	Fillerup et al.[118]
Heat capacity of adsorbed CO_2, c_{P,CO_2}	40.5 J/mol.K	Green et al.[123]
Heat capacity of adsorbed H_2O, c_{P,H_2O}	75.6 J/mol.K	Green et al.[123]
Heat of desorption of CO_2, h_{des,CO_2}	90 kJ/mol*	Wurzbacher et al.[122]
Heat of desorption of H_2O, h_{des,H_2O}	47 kJ/mol*	Wurzbacher et al.[122]
Regeneration Temperature, T_{des}	110 °C	This work

*Values taken from data for a PEI based solid sorbent

Table 5-2. Calculated values of heat of regeneration for different moisture concentrations

Moisture content (vol%)	Q_{sens} (kJ/Kg sorbent)	Q_{des} (kJ/Kg sorbent)	$Q = Q_{ses} + Q_{des}$ (kJ/Kg sorbent)
0	66.33	211.5	277.83
5.27	73.31	345.75	419.06
7.72	76.54	405.75	482.29
11.56	80.74	476.49	557.23
14.74	81.96	495.02	576.98

Assumptions for calculations have been summarized in Table 5-1. The results have been shown in Table 5-2 for adsorption at 75 °C. As shown in the table, the energy required increases from

277.83kJ/Kg for dry flue gas to 576.98kJ/Kg for 14.74% moisture, which is 2 times increase in energy demand. This is a huge increase, which predominantly comes from increase in moisture adsorption with increase in RH of flue gas. This has significant impact on sensible heat of the material and increase in heat of desorption. As already discussed, the corresponding increase in CO_2 adsorption capacity is not significant. The highest adsorption capacity was obtained for 7.72% moisture content, for which the increase in energy requirement would be 73.59%.

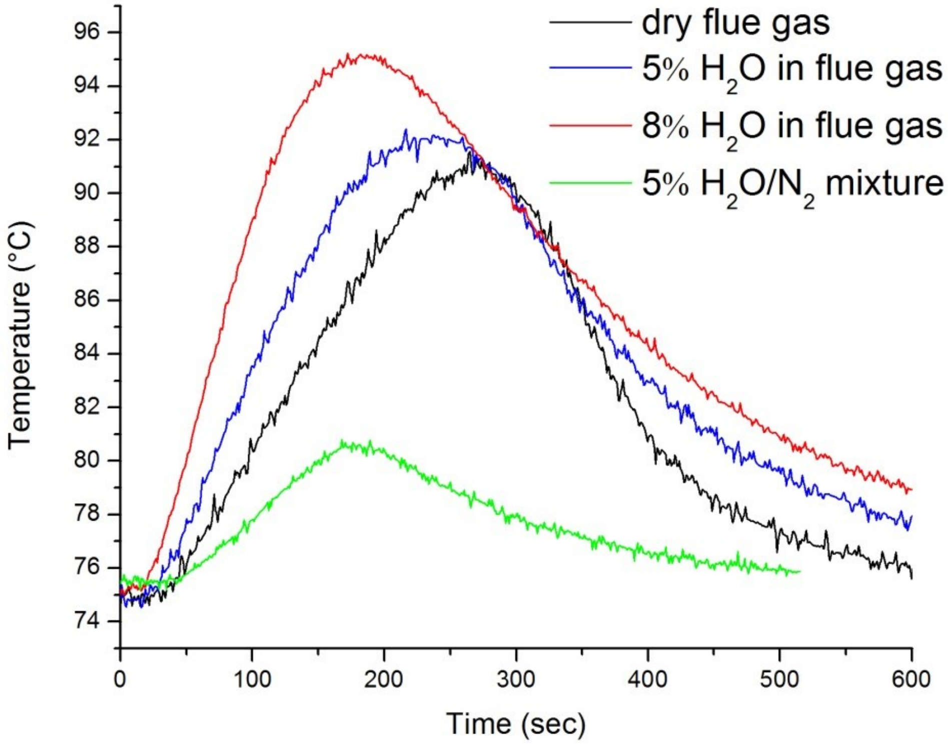


Figure 5-3. Temperature profile recorded in the adsorbent for different moisture content

Figure 5-3 shows adsorption temperature profile for dry flue gas, humid flue gas and only H_2O/N_2 mixture conditions. This doesn't provide quantitative information on heat of adsorption (as discussed above) but it can be seen that area under the curve increases with increase in moisture, which is an indication of increase in heat of regeneration. This validates the assumptions made in above discussion. This makes it important to get rid of moisture before regeneration at elevated temperature (110 °C in this case) to avoid the increase in sensible heat and heat of regeneration of sorbent. In a similar moisture study conducted by Hoffman et al.[47], it was observed that H_2O was weakly bonded to the amine sites and could be swept off using isothermal inert gas swing. Similar behavior was observed here, as shown in Figure 5-4. Isothermal N_2 swing was sufficient to remove all the moisture from the bed whereas, a thermal swing had to be given to get rid of all CO_2 (both in dry and humid flue gas case).

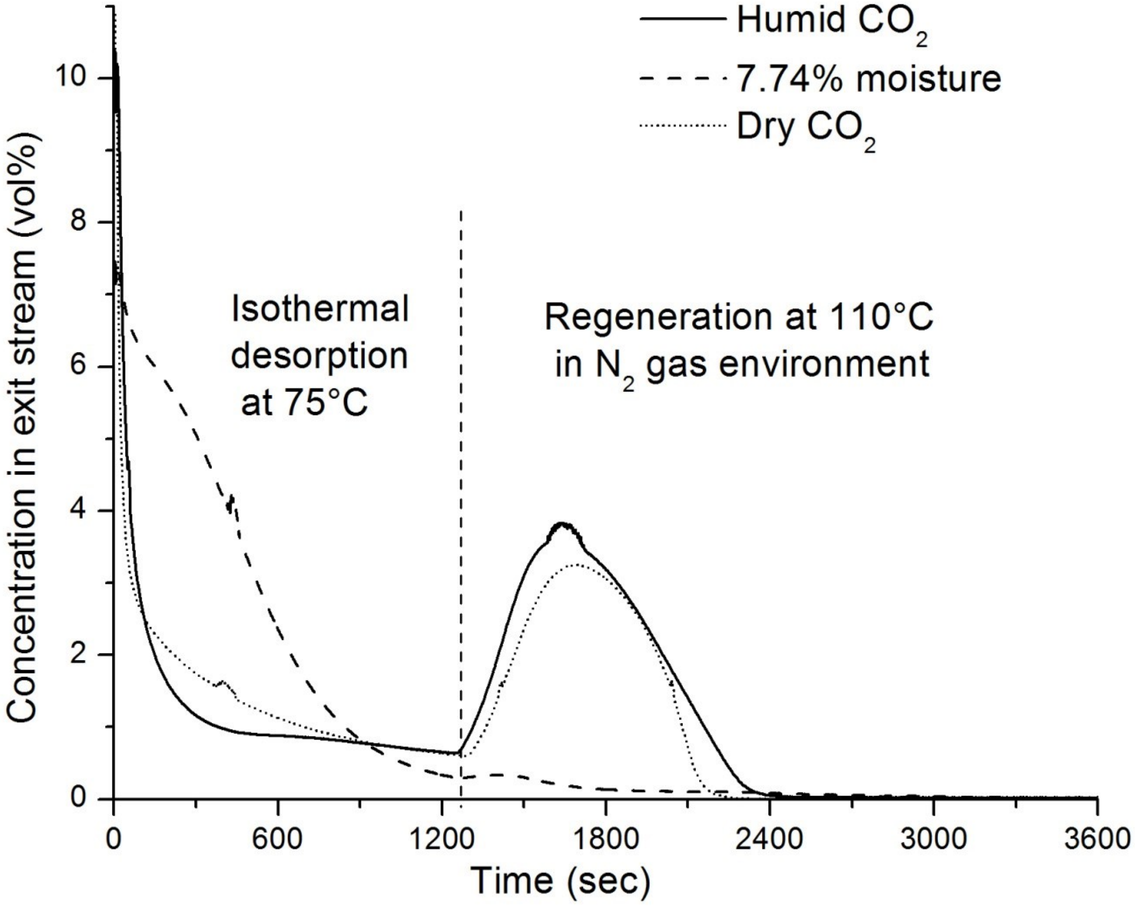


Figure 5-4. Comparison of CO_2 and H_2O desorption for humid and dry flue gas conditions

5.2. Performance of material in a steam regeneration process

5.2.1. Preliminary testing of adsorbent

The sorbent was first tested in a steam environment for 5 h period to check its stability. The testing was done for both the silica support and the amine impregnated sample, individually. It was observed that after 5 h of continuous exposure to steam at 110 °C, there was no degradation of the material. As seen in Table 5-3, the amine content and surface area of adsorbent remains same after the testing. No changes in surface morphology or surface area characteristics of the material were observed in SEM and BET analysis, respectively. TGA analysis was done to measure CO_2 adsorption capacity in 10% CO_2 atmosphere at 75 °C. The value was calculated to be 2.2 mmol/g which is almost similar to capacity of fresh sample, i.e. 2.31 mmol/g.

5.2.2. Desorption using steam

Figure 5-5 is a typical adsorption-desorption cycle for steam regeneration study, which shows CO_2 concentration at exit of packed bed as well as temperature profile in the adsorbent. The temperature profile is important from heat of regeneration of sorbent point of view. As seen from temperature profile, the temperature of sorbent raised by around 12 °C after steam injection. This is because of the exothermic temperature front formed due to moisture adsorption by the sorbent. The amount of moisture adsorbed by sorbent at 110 °C was calculated from H_2O breakthrough curve and the value was around 9-10 mmol/g sorbent. This heat wave rapidly pushes the CO_2 out of the bed, hence a pulse like CO_2 exit concentration profile is observed at the packed bed exit. An experiment was performed on TGA-DSC using humid N_2 to calculate heat of adsorption of moisture at 110 °C. It was calculated from the heat flow curve that 2693.13 Joules of heat was released for each gm of moisture adsorbed. The value is same as specific enthalpy of superheated steam at 110 °C, i.e. 2696.09 J/g[124]. This implies that most of the heat for CO_2 removal comes from moisture condensation during H_2O adsorption (of this total energy, 2256.7 J/g is the energy from specific enthalpy of evaporation). After steam stripping, dry N_2 is passed through the bed to remove the adsorbed moisture. It can be seen that the temperature of bed falls from 110 °C to around 88 °C, which is due to heat of desorption of moisture. One of the recommendations here can be that N_2 stream exiting the adsorption column can be used to dry the sorbent after steam stripping. But depending on the purity of this N_2 stream (which depends on amount of CO_2 present), the working capacity of next adsorption cycle would certainly be affected.

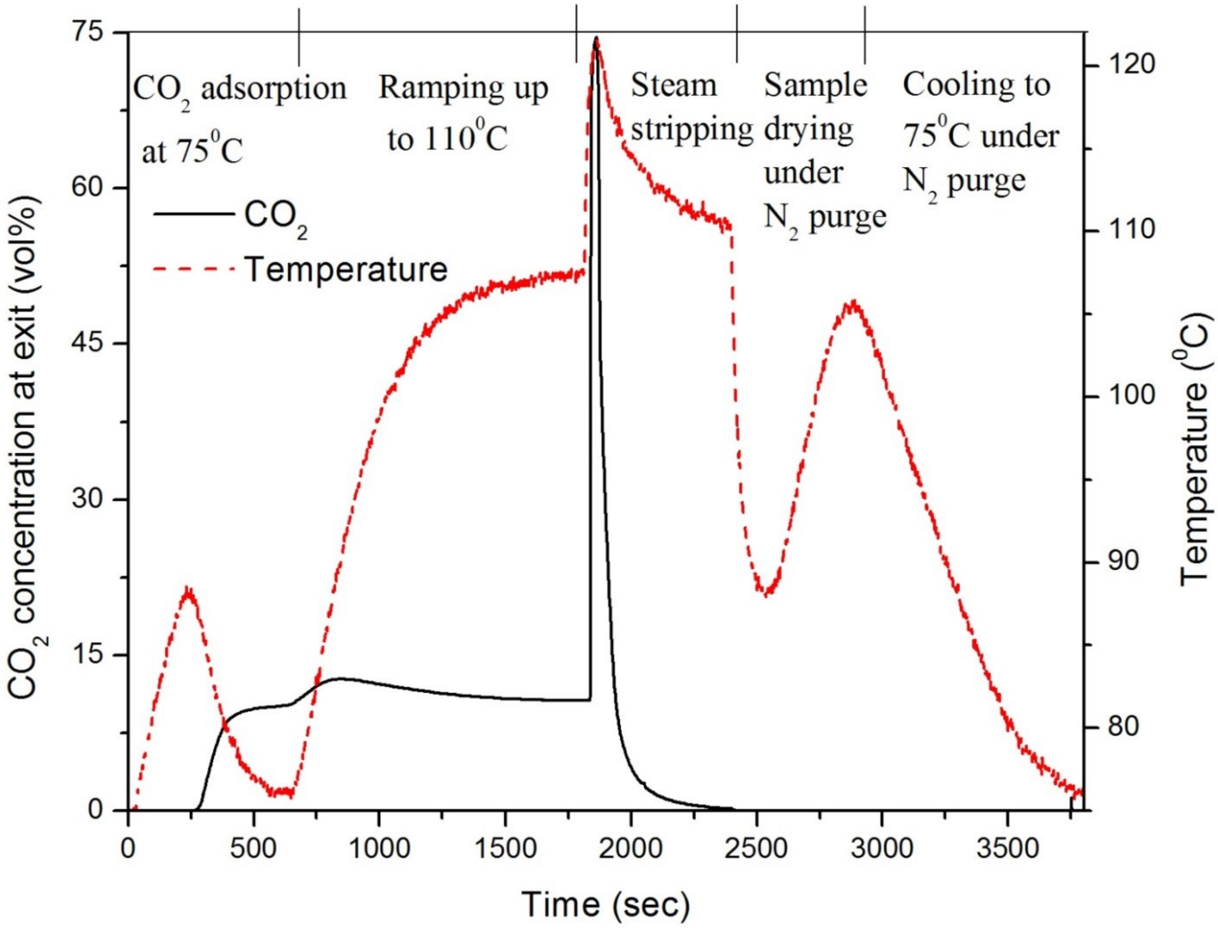


Figure 5-5. Temperature and CO_2 concentration profile in packed bed for a typical adsorption-desorption cycle

5.2.3. Suitability of steam regeneration for multiple cycles

One of the most important aspects of any adsorbent or an adsorption technique is its suitability for multiple cycles of adsorption-desorption. In this case, the material was tested for 20 cycles of adsorption followed by steam stripping. The study was conducted for dry flue gas as well as humid flue gas (2.71% moisture). Adsorption was carried out at 75 °C and steam regeneration at 110 °C. Figure 5-6 presents the CO_2 adsorption capacity for all 20 cycles of dry and humid flue gas study. The capacity observed for 1st and 20th cycle in dry flue gas study was 2.46 mmol/ g and 2.24 mmol/ g, respectively. The corresponding values for humid flue gas were 2.56 mmol/ g and 2.41 mmol/ g. The drop in capacity for dry flue gas over a span of 20 cycles was 8.94% and 5.86% for humid flue gas. The average adsorption capacity for 20 cycles was calculated to be 2.31mmol/ g for dry flue gas and 2.47 mmol/ g for humid flue gas. The results confirm with literature, that amine based sorbents are more stable under humid conditions[36].

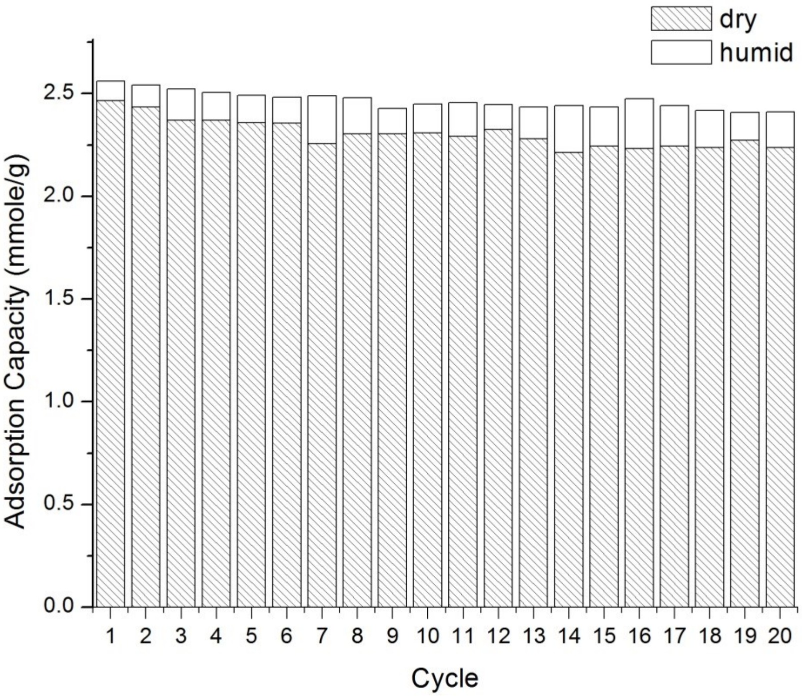


Figure 5-6. CO_2 adsorption capacity for dry and humid flue gas at 75 °C in a multiple cycle study

It is believed that 3% difference in drop in capacity between both conditions might be due to higher extent of amine degradation because of urea formation in presence of dry CO_2 in case of dry flue gas[36,125,126]. Although, no signs of urea linkages were observed in FTIR analysis (as shown in Figure 5-8). Since the only difference in both studies was the composition of simulated flue gas, this seems to be the only possible cause of higher extent of loss in CO_2 adsorption capacity in dry flue gas case. It is possible that at higher number of cycles, the urea formation is significant enough to be detected by FTIR.

5.2.4. Possible causes of loss in CO_2 adsorption capacity

After multiple cycle study, various characterization techniques were used to compare the used sorbent with fresh sorbent and look into possible causes of loss in CO_2 adsorption capacity. Firstly, elemental analysis was carried out to check the amine content of used sorbent. As seen in Table 5-3, the amine content of used samples was similar to that of fresh adsorbent. This indicates that leaching of amine from the sorbent is not a contributor to loss in CO_2 adsorption capacity in this study. The results were also verified by TGA analysis, which also showed similar kind of values.

SEM and BET analysis were also done for the samples. Figure 5-7 shows the images for SEM analysis of all the samples. No significant change in morphology of the sorbents was observed after multiple cycles study and in 5h steam treatment experiment. The possible major cause of attrition in these samples (including fresh sample) can be vigorous stirring during wet impregnation for sorbent synthesis as well as sample handling and loading-unloading. N_2 physisorption isotherms at 77K were used to study BET surface areas of fresh and used samples. As seen in Table 5-3, the surface area as well as pore volume measurements for the both type of sorbents are very much similar. The fluctuations seen in results are within the measurement error of the instrument. Another possible cause of decrease in CO_2 adsorption capacity could be change in nature of amines due to exposure to steam. This possibility was also ruled out, as evident from DRIFTS analysis shown in Figure 5-8.

Table 5-3. Comparison of characteristics of fresh sample and sample used in steam regeneration

Sample	**Amine content*** **(wt. %)**	**BET Analysis**	
		Surface Area (m^2/g)	**Pore Volume (cc/g)**
Fresh sorbent	39.71 ± 0.17	49.16	0.34
20cycle_dry flue gas	40.43 ± 0.18	53.06	0.33
20cycle_humid flue gas	40.15 ± 0.08	-	-
5h_steam treatment	39.18 ± 0.06	49.78	0.32

*Standard error in amine content measurement

As evident from the results discussed above, no significant degradation/changes in the sorbent were observed during exposure to steam. The results are however, in contradiction to Jones et al.[109]'s findings, where they observed 86.4% decrease in surface area and 82.2% decrease in total pore volume for PEI impregnated SBA-15. Moreover, in 10% CO_2 condition the adsorption capacity of the adsorbent decreased by 67.1%. But all these results were for static conditions where the sample was exposed to steam at 105 °C for 24h in a batch reactor. But the results are in good agreement with Hammache et al.[111], who conducted a packed bed study using PEI impregnated silica (G-10) and found the sorbent to be stable under similar conditions of steam stripping for 8 cycles.

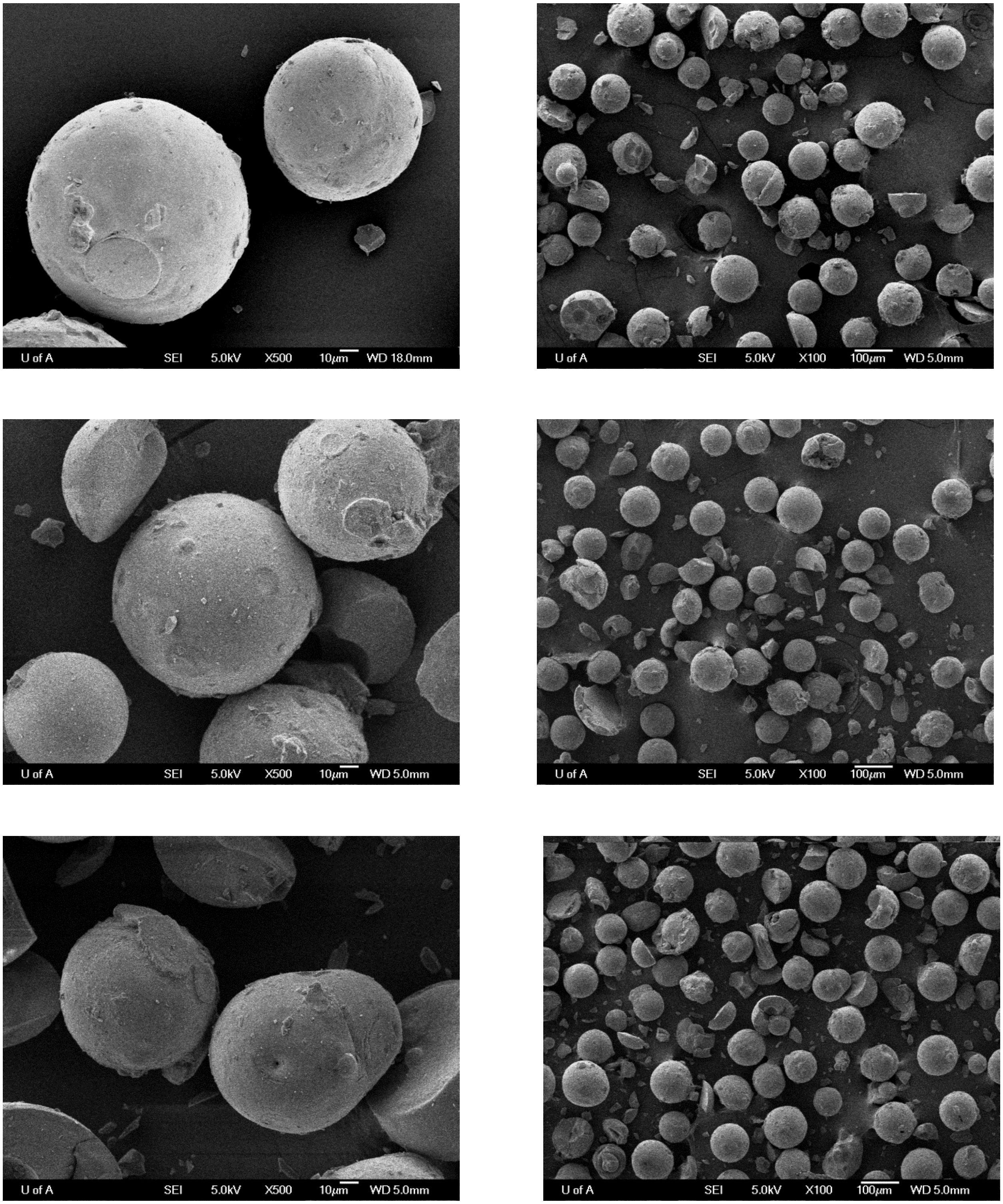


Figure 5-7. SEM images at 500 and 100x resolution for a) 1st row: fresh sorbent, b) 2nd row: sample used in multiple cycle dry flue gas study and c) 3rd row: sample after 5h steam treatment

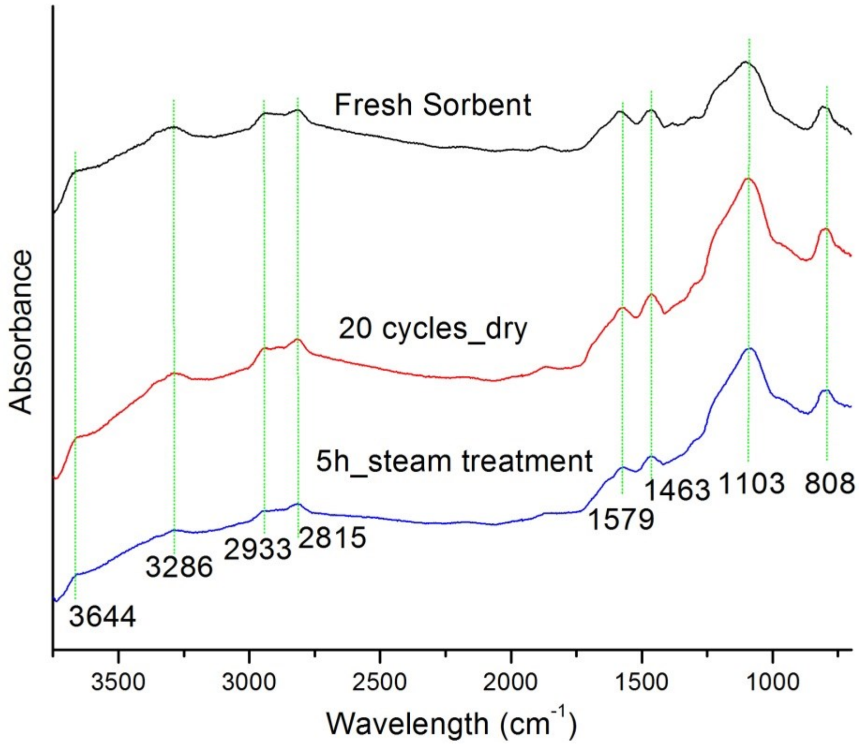


Figure 5-8. Comparison of DRIFTS spectra of fresh PEI/Si sample with samples used in study

As seen from adsorption-desorption cycle in Figure 5-5, a significant amount of time in each cycle is spent in removal of moisture after steam stripping and cooling of sorbent to 75 °C. This is done in the presence of dry N_2. So, in order to eliminate the effect of thermal degradation, adsorption-desorption was done at 110 °C. Multiple cycles study, consisting of 20 cycles was done for both steam stripping and N_2 stripping. Figure 5-9 shows a comparison of CO_2 adsorption capacities for steam and N_2 stripping for all 20 cycles. In this figure, normalized adsorption capacity is adsorption capacity in a given cycle relative to that of the fresh sorbent in 1st cycle. It was observed that while decrease in capacity for steam stripping was 1.6%, it was 6% under N_2 atmosphere. This implies that exposure of adsorbent to dry N_2 for long period of times is a major cause of loss in capacity. In this particular case, steam didn’t lead to deterioration of the amine. But it should be noted that in this study, the adsorbent was exposed to short intervals of (10 min each) steam stripping in a 20 cycle run. In a recent study by Jones et al.[55] on steam stripping of PEI impregnated alumina based samples; effect of steam exposure time (90min, 12h and 24h) was studied. Significant PEI leaching was observed in case of 24h steam exposure which led to loss in CO_2 adsorption capacity, whereas no such PEI loss was observed in other samples.

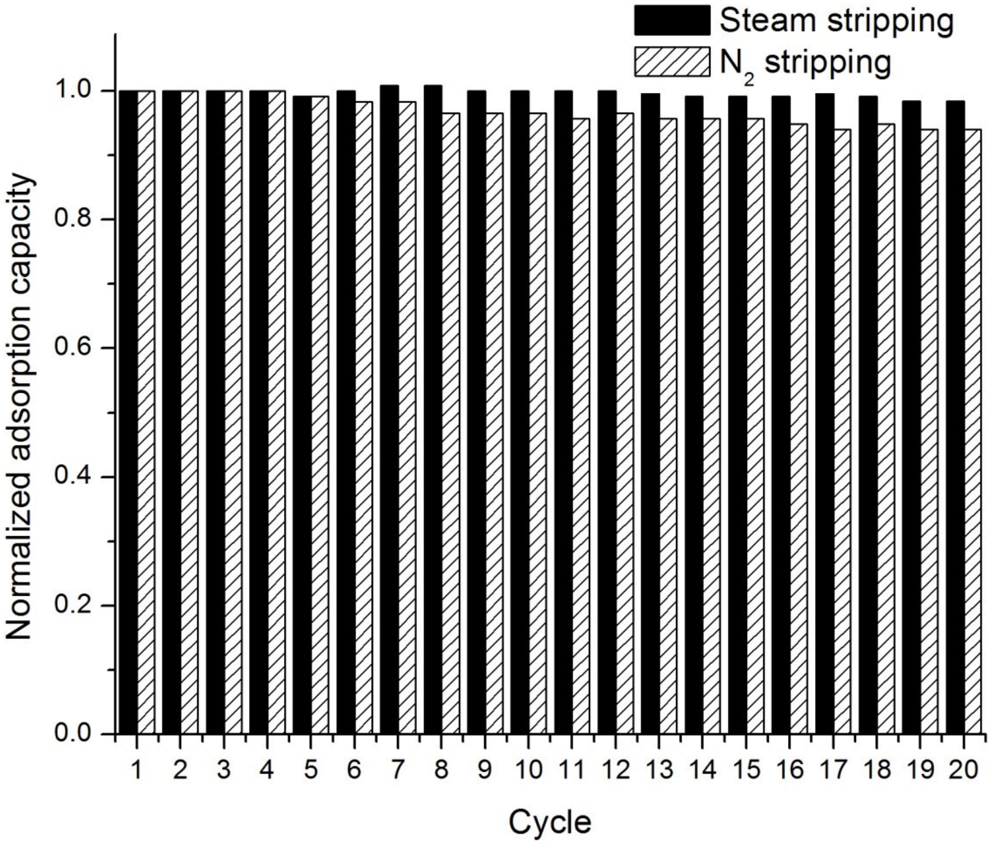


Figure 5-9. Comparison of a multiple cycle steam and N_2 stripping study for adsorption-desorption at 110 °C

5.2.5. Steam stripping vs N_2 stripping

N_2 was used as an inert purge gas for stripping out CO_2 under similar conditions as steam. Figure 5-10 shows a comparison between exit gas CO_2 concentrations for both the cases. Firstly, the rapidness of the steam stripping can be seen from the fact that there are very few data points as the curve approaches maxima of 74.54% CO_2 concentration. Secondly, in N_2 stripping case, the CO_2 is highly diluted in inert gas. Moreover, as the CO_2 concentration starts decreasing in both the cases, the tailing effect (slow drop in CO_2 concentration) is more prominent in case of N_2 stripping. As seen from Figure 5-10, at point of maxima, the concentration of N_2 is 25.23%. It is important to mention here that this N_2 comes from the inert gas present in steam which was used as a tracking agent. For industrial application, pure steam would be used and hence the actual concentration of CO_2 would be higher than 74.54%.

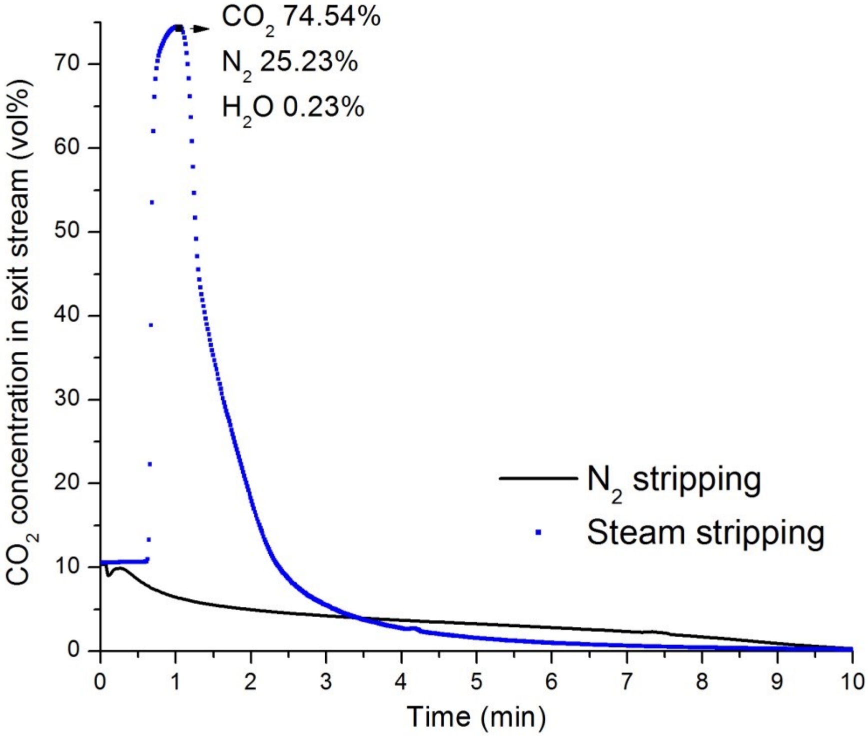


Figure 5-10. CO_2 concentration profile in exit stream during desorption using steam and N_2

A plot comparing fraction of total volume of CO_2 released at a given instant for both cases has been shown in Figure 5-11. It was observed that the initial rate of CO_2 desorption was slow in case of steam stripping. However, after t = 41 sec, the rate was found to be higher for steam stripping case. It was calculated that at t = 2.65 min, 80% of the total CO_2 got released in case of steam in comparison to 50% for N_2 case. Similar results were observed by Hammache et al.,[111] where after approximately 1min the desorption rate was higher for steam stripping. The plot for fraction of CO_2 released per unit of time (min^{-1}) was similar in shape to that of CO_2 concentration profile shown in Figure 5-10. As already discussed, water has affinity for amine sites, unlike inert gases like N_2. Hydrogen bond accepting functionalities of PEI interact with H_2O as per following reaction and lead to a rapid displacement of CO_2[111,127]:

$$R_2NCO_2^- + H_2O \leftrightarrow R_2NH^+CO_2^- + OH^- \leftrightarrow R_2NH + CO_2 + OH^-$$

The initial proton transfer is rapid whereas CO_2 release is the rate limiting step[111,127]. This can be a reason for delay in CO_2 desorption. But being a displacer, ultimately H_2O expels CO_2 more rapidly than N_2[111,128].

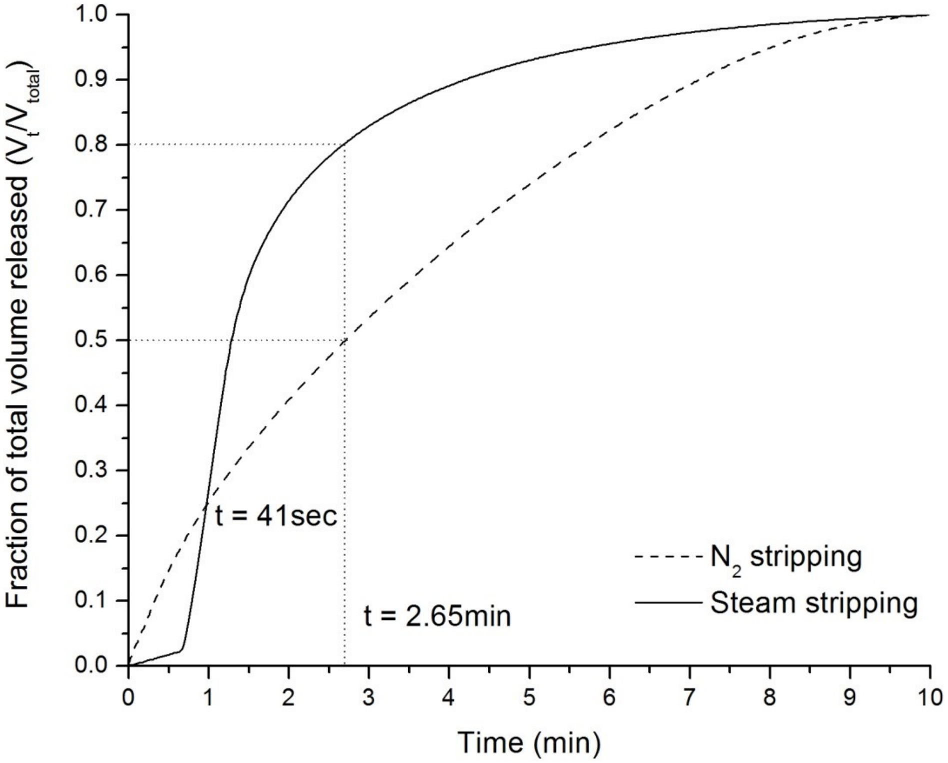


Figure 5-11. Fraction of total CO_2 released vs time during desorption using steam and N_2

5.2.6. Effect of steam temperature on CO_2 desorption

Steam at different temperatures was injected to study its effect on desorption kinetics. Four different temperatures were studied: 100, 110, 120 and 130 °C and in each case desorption was carried out for 10 min. Figure 5-12 shows amount of CO_2 released with time but only first 200 sec of each run have been shown for better comparison. As expected, desorption kinetics improved with increase in temperature. The desorption peak became sharper and less wide as the temperature increased. In each case, there are two peaks. It is to be clarified that the second peak is due to steam stripping. The smaller first peak is due to desorption of weakly bonded CO_2. After adsorption, the sorbent in each case was heated to respective desorption temperature in absence of any purge gas. This lead to desorption of CO_2 weakly bonded to amine sites, which accumulated in the packed bed and got removed as soon as steam was swept over the sorbent.

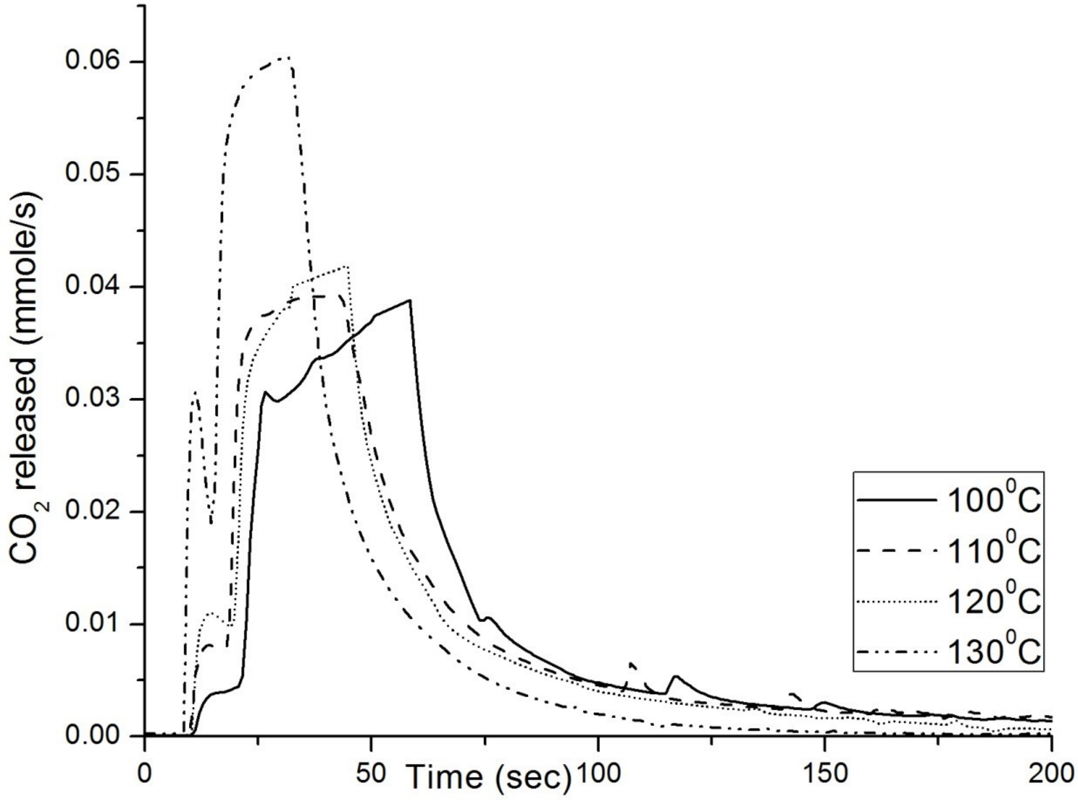


Figure 5-12. Desorption profile for CO_2 at different steam stripping temperatures

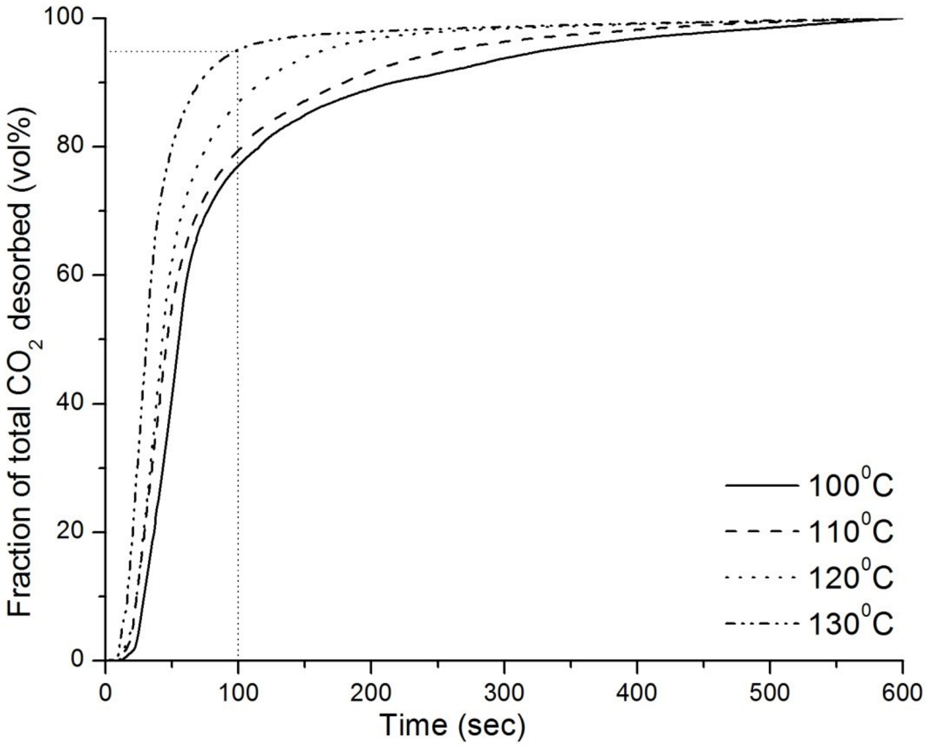


Figure 5-13. Fraction of total CO_2 desorbed vs time for different steam temperatures

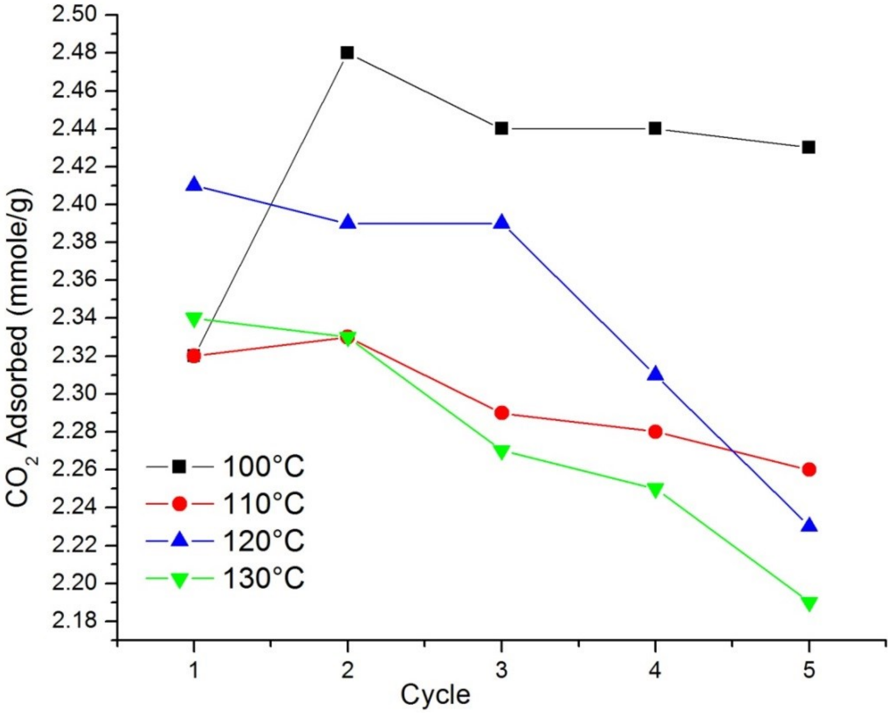


Figure 5-14. Performance of sorbent over 5 cycles of adsorption-desorption for different steam temperatures

Table 5-4. Amount of moisture adsorbed during steam stripping at different inlet steam temperatures

Temperature	**100 °C**	**110 °C**	**120 °C**	**130 °C**
Amount of moisture adsorbed, mmol/g	12.85	9.51	7.97	5.31

Another comparison was done in terms of fraction of CO_2 released with time, as shown in Figure 5-13. The difference was not much pronounced at relatively lower temperatures of 100 and 110 °C. But on comparing the results for 100 and 130 °C it was seen that while only 77% of the CO_2 got released within 100 sec of steam injection in the former case, the value was as high as 95% for the latter. However, it is not recommended going beyond 130 °C, especially for this particular low molecular weight amine as thermal degradation of amine enhances with temperature[31,35]. For this purpose, 5 consecutive adsorption-desorption cycles were done at each of these temperatures and CO_2 adsorption capacities were measured (Figure 5-14). It is important to mention here that ideally the adsorption capacities for 1st cycle in each case should be the same, which is not the case here. But they are in the range of ± 4%, which is acceptable. It was observed that the capacity decreased by 7.5% and 6.5% in case of 120 and 130 °C, respectively. But the actual value is lower for the latter case, i.e. 2.19mmol/g, whereas the value is 2.23 mmol/g for the former. Much of the drop took place after 3rd cycle. The drop was around 2.5% in case of 110 °C, whereas the capacity increased by 4.7% in case of 100 °C. The exact reason for this increase is unknown at this time but one of the possible reasons might be the positive effect of traces of moisture left adsorbed in the sorbent after drying. Firstly, the adsorption values after run 1 are in the range of that in case of humid flue gas. Secondly, mass balance for moisture adsorption during steam stripping was carried out for all cases. 12.85 mmol/g of moisture is adsorbed by the sorbent at 100 °C, which is maximum out of all the given temperatures (Table 5-4).

Chapter 6

CONCLUSION AND RECOMMENDATIONS

6.1. Conclusion

In this work, PEI impregnated silica adsorbent was synthesised and post combustion CO_2 capture performance was evaluated. The objective of this study was to study the suitability of material for steam stripping in a CO_2 capture facility. Along with that, effect of O_2 and presence of moisture on CO_2 adsorption performance of sorbent were also studied. A 40 wt% PEI impregnated sorbent was synthesized and optimum operating conditions in terms of adsorption temperature and CO_2 partial pressure were determined. Experiments were carried out in TGA to examine the effect of O_2 whereas, the effect of moisture and steam studies were conducted in a packed bed. Key findings from this study have been mentioned below:

- The sorbent had a maximum adsorption capacity of 2.31 mmol/g at 75 °C and 1 atm pressure under simulated flue gas conditions of 10% CO_2 in N_2. The adsorption capacity was negligible (0.005 mmol/g) under low CO_2 partial pressure conditions (400 ppm CO_2 in air) and increased significantly to 2.31 mmol/g when the partial pressure of CO_2 was increased to 10 kPa.
- The adsorption capacity of the sorbent decreased by 4.17% in presence of 5% O_2, when tested for 20 cycles where each cycle consisted of 30 min adsorption time. The amine loading decreased from 40% to 35.4% (as confirmed by elemental analysis). But it was determined that most of this loss came from thermal degradation and not from oxidation of amine.

- In the same study mentioned above, the adsorption time of each cycle was reduced to 10 min. It was observed that the sorbent had adsorption capacity similar as 30 min cycle (1.94 mmol/g). Moreover, no significant loss of amine was observed. So, keeping the cycles short, amine loss can be avoided while maintaining the CO_2 adsorption capacity.
- Presence of moisture along with 5% O_2, further enhanced the CO_2 adsorption to 2.15 mmol/g. The sorbent performance was more stable under these conditions as compared to dry flue gas case.
- The effect of different concentrations of moisture on CO_2 adsorption performance of the sorbent was studied. 8.74% increase in adsorption capacity was observed for 7.72% moisture in flue gas but the capacity increase was not as significant for further increase in moisture content.
- The sorbent adsorbed significant amount of moisture along with CO_2. It was calculated that this would increase the sensible heat and overall heat of regeneration of sorbent significantly. It was also observed that H_2O was weakly bonded on the amine sites whereas CO_2 was both weakly and strongly bonded and only inert gas pressure swing was sufficient to get rid of adsorbed moisture.
- The sorbent was observed to be highly stable under steam environment. No changes were observed in amine loading, surface morphology and nature of amine linkages, surface area and pore volume after multiple cycle steam stripping. Similar observation was made when the sorbent was kept continuously under steam environment for 5 h.
- Multiple cycles steam stripping was studied for dry and humid flue gas at 75 °C. It was observed that the drop in adsorption capacity was 8.94 and 5.86%, respectively. Lesser

stability of sorbent in dry case was attributed to possible urea linkages formation in presence of dry flue gas.

- Another multiple cycle study was conducted at 110 °C (both adsorption-desorption) for steam stripping and N_2 stripping. It was observed that at the end of 20 cycles, loss in capacity was more noticed for inert gas case than steam. Desorption kinetics were studied for both these cases, which was much faster for steam stripping. Moreover, the exit stream was highly concentrated in CO_2 in case of steam stripping, whereas it was highly diluted in N_2 for inert gas case.
- Effect of different steam temperatures was studied on CO_2 desorption. As anticipated, the desorption kinetics improved with increase in temperature, whereas the amount of moisture adsorbed decreased.

Overall, a stable performance was shown by the sorbent in presence of both H_2O and O_2 in the simulated flue gas. Steam stripping can be a practical solution for sorbent regeneration. Both adsorption and desorption were found to be exothermic in nature and the heat released can be used for pre heating of flue gas, steam line etc.

6.2. Recommendations

The findings of this research work may provide the basis for the future work in post-combustion CO_2 capture using amine functionalized sorbents, especially for their application in steam stripping. Some of the recommendations based on current study are as follows:

- Scaling up of the packed bed reactor and making the whole system automatic. Automated system would better enable the study of large number of multiple cycles (in range of at least hundreds). Due to manual operation of the system, the present study was limited to 20 cycles.

- Powdered sorbent would cause huge pressure drop in case of scaled up packed beds. Pelletizing the sorbent would be another upgrading option. But synthesis mechanism or binders would have to be carefully chosen so that the CO_2 adsorption capacity and kinetics don't drop drastically. Attrition resistance can be another property, especially for application in fluidized bed reactors.
- Current study only considered change in steam temperature for CO_2 desorption. Looking into different steam pressures would be worthwhile.
- Apart from moisture and O_2, SO_X and NO_X are important industrial pollutants that are emitted along with CO_2. It is crucial from sorbent performance point of view, to study their effect on CO_2 adsorption and amine degradation. Considering the complex nature of the flue gas chemistry emitted from the industries, it is recommended to test the sorbents in flue gas emitted from the industries.
- Steam regeneration has been recommended strongly on the basis that low pressure steam is easily available (sometimes as waste heat) in coal-fired power plants. But an actual techno-economic analysis would be needed to study the feasibility of its application in an actual industrial set-up.

REFERENCES

1. IEA (2012c) Energy Technology Perspectives 2012. *OECD/IEA, Paris* **2012**.
2. IEA (2012a) World Energy Outlook 2012. *OECD/IEA, Paris* **2012**.
3. BP Statistical Review of World Energy 2013, www.bp.com. **2013**.
4. IEA (2012) CO_2 emissions from fuel combustion Highlights. *OECD/IEA,Paris* **2012**.
5. Working Group III, I. Fourth Assessment Report of the IPCC. *Cambridge University Press, UK* **2007**.
6. IEA (2013a) Tracking Clean Energy Progress 2013: IEA Input to the Clean Energy Ministerial. *OECD/IEA, Paris* **2013**.
7. CO_2 capture technologies, technology options for CO_2 capture http://cdn.globalccsinstitute.com/sites/default/files/publications/29701/CO2-capture-technologies.pdf. *Global CCS Institute* **Jan 2012**.
8. Bennaceur, K. *Chapter 26 - CO_2 Capture and Sequestration;* Letcher, T. M., Ed.; Future Energy (Second Edition); Elsevier: Boston, **2014**; pp 583-611.
9. Metz, B.; Davidson, O.; De Coninck, H.; Loos, M.; Meyer, L. Intergovernmental Panel on Climate Change. Special Report on Carbon Dioxide Capture and Storage. *Cambridge University Press, UK* **2005**.
10. Zaman, M.; Lee, J. Carbon capture from stationary power generation sources: A review of the current status of the technologies. *Korean J. Chem. Eng.* **2013**, *30*, 1497-1526.
11. Bhown, A. S.; Freeman, B. C. Analysis and Status of Post-Combustion Carbon Dioxide Capture Technologies. *Environ. Sci. Technol.* **2011**, *45*, 8624-8632.
12. McGlashan, N. R.; Marquis, A. J. Availability analysis of post-combustion carbon capture systems: Minimum work input. *Proc. Inst. Mech. Eng. Part C* **2007**, *221*, 1057-1065.
13. Samanta, A.; Zhao, A.; Shimizu, G. K. H.; Sarkar, P.; Gupta, R. Post-Combustion CO_2 Capture Using Solid Sorbents: A Review. *Ind. Eng. Chem. Res.* **2012**, *51*, 1438-1463.
14. Blauwhoff, P. M. M.; Versteeg, G. F.; Van Swaaij, W. P. M. A study on the reaction between CO_2 and alkanolamines in aqueous solutions. *Chem. Eng. Sci.* **1984**, *39*, 207-225.
15. Gray, M. L.; Soong, Y.; Champagne, K. J.; Pennline, H.; Baltrus, J. P.; Stevens Jr., R. W.; Khatri, R.; Chuang, S. S. C.; Filburn, T. Improved immobilized carbon dioxide capture sorbents. *Fuel Process. Technol.* **2005**, *86*, 1449-1455.

16. Rao, A. B.; Rubin, E. S. A Technical, Economic, and Environmental Assessment of Amine-Based CO_2 Capture Technology for Power Plant Greenhouse Gas Control. *Environ. Sci. Technol.* **2002**, *36*, 4467-4475.

17. Sjostrom, S.; Krutka, H. Evaluation of solid sorbents as a retrofit technology for CO_2 capture. *Fuel* **2010**, *89*, 1298-1306.

18. Harrison, D. P. *The role of solids in CO_2 capture: A mini review;* Rubin, E. S., Keith, D. W., Gilboy, C. F., Wilson, M., Morris, T., Gale, J. and Thambimuthu, K., Eds.; Greenhouse Gas Control Technologies 7; Elsevier Science Ltd: Oxford, **2005**; pp 1101-1106.

19. Choi, S.; Drese, J.; Jones, C. Adsorbent Materials for Carbon Dioxide Capture from Large Anthropogenic Point Sources. *ChemSusChem* **2009**, *2*, 796-854.

20. Sayari, A.; Belmabkhout, Y.; Serna-Guerrero, R. Flue gas treatment via CO_2 adsorption. *Chem. Eng. J.* **2011**, *171*, 760-774.

21. Gray, M. L.; Champagne, K. J.; Fauth, D.; Baltrus, J. P.; Pennline, H. Performance of immobilized tertiary amine solid sorbents for the capture of carbon dioxide. *Int. J. Greenhouse Gas Control* **2008**, *2*, 3-8.

22. Tarka, T. J.; Ciferno, J. P.; Gray, M. L.; Fauth, D. *CO_2 capture systems using amine enhanced solid sorbents;* 5th Annual Conference on Carbon Capture & Sequestration, Paper 152; **2006**.

23. Wang, Q.; Luo, J.; Zhong, Z.; Borgna, A. CO_2 capture by solid adsorbents and their applications: current status and new trends. *Energy Environ. Sci.* **2011**, *4*, 42-55.

24. Xu, X.; Song, C.; Andresen, J. M.; Miller, B. G.; Scaroni, A. W. Novel Polyethylenimine-Modified Mesoporous Molecular Sieve of MCM-41 Type as High-Capacity Adsorbent for CO_2 Capture. *Energy Fuels* **2002**, *16*, 1463-1469.

25. Xu, X.; Song, C.; Andrésen, J. M.; Miller, B. G.; Scaroni, A. W. Preparation and characterization of novel CO_2 "molecular basket" adsorbents based on polymer-modified mesoporous molecular sieve MCM-41. *Microporous Mesoporous Mater.* **2003**, *62*, 29-45.

26. Son, W.; Choi, J.; Ahn, W. Adsorptive removal of carbon dioxide using polyethyleneimine-loaded mesoporous silica materials. *Microporous Mesoporous Mater.* **2008**, *113*, 31-40.

27. Qi, G.; Wang, Y.; Estevez, L.; Duan, X.; Anako, N.; Park, A. A.; Li, W.; Jones, C. W.; Giannelis, E. P. High efficiency nanocomposite sorbents for CO_2 capture based on amine-functionalized mesoporous capsules. *Energy Environ. Sci.* **2011**, *4*, 444-452.

28. Filburn, T.; Helble, J. J.; Weiss, R. A. Development of Supported Ethanolamines and Modified Ethanolamines for CO_2 Capture. *Ind. Eng. Chem. Res.* **2005**, *44*, 1542-1546.

29. Jung, H.; Jo, D. H.; Lee, C. H.; Chung, W.; Shin, D.; Kim, S. H. Carbon Dioxide Capture Using Poly(ethylenimine)-Impregnated Poly(methyl methacrylate)-Supported Sorbents. *Energy Fuels* **2014**, *28*, 3994-4001.

30. Gray, M. L.; Hoffman, J. S.; Hreha, D. C.; Fauth, D. J.; Hedges, S. W.; Champagne, K. J.; Pennline, H. W. Parametric Study of Solid Amine Sorbents for the Capture of Carbon Dioxide. *Energy Fuels* **2009**, *23*, 4840-4844.

31. Zhao, W.; Zhang, Z.; Li, Z.; Cai, N. Investigation of Thermal Stability and Continuous CO_2 Capture from Flue Gases with Supported Amine Sorbent. *Ind. Eng. Chem. Res.* **2013**, *52*, 2084-2093.

32. Jadhav, P. D.; Chatti, R. V.; Biniwale, R. B.; Labhsetwar, N. K.; Devotta, S.; Rayalu, S. S. Monoethanol Amine Modified Zeolite 13X for CO_2 Adsorption at Different Temperatures. *Energy Fuels* **2007**, *21*, 3555-3559.

33. Fisher, J. C.; Tanthana, J.; Chuang, S. S. C. Oxide-supported tetraethylenepentamine for CO_2 capture. *Environ. Prog. Sustainable Energy* **2009**, *28*, 589-598.

34. Plaza, M. G.; Pevida, C.; Arias, B.; Fermoso, J.; Casal, M. D.; Martín, C. F.; Rubiera, F.; Pis, J. J. Development of low-cost biomass-based adsorbents for postcombustion CO_2 capture. *Fuel* **2009**, *88*, 2442-2447.

35. Drage, T. C.; Arenillas, A.; Smith, K. M.; Snape, C. E. Thermal stability of polyethylenimine based carbon dioxide adsorbents and its influence on selection of regeneration strategies. *Microporous Mesoporous Mater.* **2008**, *116*, 504-512.

36. Heydari-Gorji, A.; Sayari, A. Thermal, Oxidative, and CO_2-Induced Degradation of Supported Polyethylenimine Adsorbents. *Ind. Eng. Chem. Res.* **2012**, *51*, 6887-6894.

37. Leal, O.; Bolívar, C.; Ovalles, C.; García, J. J.; Espidel, Y. Reversible adsorption of carbon dioxide on amine surface-bonded silica gel. *Inorg. Chim. Acta* **1995**, *240*, 183-189.

38. Hiyoshi, N.; Yogo, K.; Yashima, T. Adsorption of Carbon Dioxide on Amine Modified SBA-15 in the Presence of Water Vapor. *Chem. Lett.* **2004**, *33*, 510-511.

39. Hiyoshi, N.; Yogo, K.; Yashima, T. Adsorption characteristics of carbon dioxide on organically functionalized SBA-15. *Microporous Mesoporous Mater.* **2005**, *84*, 357-365.

40. Sayari, A. Unprecedented Expansion of the Pore Size and Volume of Periodic Mesoporous Silica. *Angew. Chem.* **2000**, *112*, 3042-3044.

41. Harlick, P. J. E.; Sayari, A. Applications of Pore-Expanded Mesoporous Silica. 5. Triamine Grafted Material with Exceptional CO_2 Dynamic and Equilibrium Adsorption Performance. *Ind. Eng. Chem. Res.* **2007**, *46*, 446-458.

42. Harlick, P. J. E.; Sayari, A. Applications of Pore-Expanded Mesoporous Silicas. 3. Triamine Silane Grafting for Enhanced CO_2 Adsorption. *Ind. Eng. Chem. Res.* **2006**, *45*, 3248-3255.

43. Li, W.; Choi, S.; Drese, J.; Hornbostel, M.; Krishnan, G.; Eisenberger, P.; Jones, C. Steam-Stripping for Regeneration of Supported Amine-Based CO_2 Adsorbents. *ChemSusChem* **2010**, *3*, 899-903.

44. Hicks, J. C.; Drese, J. H.; Fauth, D. J.; Gray, M. L.; Qi, G.; Jones, C. W. Designing Adsorbents for CO_2 Capture from Flue Gas-Hyperbranched Aminosilicas Capable of Capturing CO_2 Reversibly. *J. Am. Chem. Soc.* **2008**, *130*, 2902-2903.

45. Khatri, R. A.; Chuang, S. S. C.; Soong, Y.; Gray, M. Thermal and Chemical Stability of Regenerable Solid Amine Sorbent for CO_2 Capture. *Energy Fuels* **2006**, *20*, 1514-1520.

46. Plaza, M. G.; Pevida, C.; Arenillas, A.; Rubiera, F.; Pis, J. J. CO_2 capture by adsorption with nitrogen enriched carbons. *Fuel* **2007**, *86*, 2204-2212.

47. Hoffman, J. S.; Hammache, S.; Gray, M. L.; Fauth, D. J.; Pennline, H. W. Parametric study for an immobilized amine sorbent in a regenerative carbon dioxide capture process. *Fuel Process. Technol.* **2014**, *126*, 173-187.

48. Hallenbeck, A. P.; Kitchin, J. R. Effects of O_2 and SO_2 on the Capture Capacity of a Primary-Amine Based Polymeric CO_2 Sorbent. *Ind. Eng. Chem. Res.* **2013**, *52*, 10788-10794.

49. Qi, G.; Fu, L.; Choi, B. H.; Giannelis, E. P. Efficient CO_2 sorbents based on silica foam with ultra-large mesopores. *Energy Environ. Sci.* **2012**, *5*, 7368-7375.

50. Chen, Z.; Deng, S.; Wei, H.; Wang, B.; Huang, J.; Yu, G. Polyethylenimine-Impregnated Resin for High CO_2 Adsorption: An Efficient Adsorbent for CO_2 Capture from Simulated Flue Gas and Ambient Air. *ACS Appl. Mater. Interfaces* **2013**, *5*, 6937-6945.

51. Ebner, A. D.; Gray, M. L.; Chisholm, N. G.; Black, Q. T.; Mumford, D. D.; Nicholson, M. A.; Ritter, J. A. Suitability of a Solid Amine Sorbent for CO_2 Capture by Pressure Swing Adsorption. *Ind. Eng. Chem. Res.* **2011**, *50*, 5634-5641.

52. Zhao, A.; Samanta, A.; Sarkar, P.; Gupta, R. Carbon Dioxide Adsorption on Amine-Impregnated Mesoporous SBA-15 Sorbents: Experimental and Kinetics Study. *Ind. Eng. Chem. Res.* **2013**, *52*, 6480-6491.

53. Reynolds, S. P.; Ebner, A. D.; Ritter, J. A. Stripping PSA Cycles for CO_2 Recovery from Flue Gas at High Temperature Using a Hydrotalcite-Like Adsorbent. *Ind. Eng. Chem. Res.* **2006**, *45*, 4278-4294.

54. Gebald, C.; Wurzbacher, J. A.; Tingaut, P.; Steinfeld, A. Stability of Amine-Functionalized Cellulose during Temperature-Vacuum-Swing Cycling for CO_2 Capture from Air. *Environ. Sci. Technol.* **2013**, *47*, 10063-10070.

55. Sakwa-Novak, M.; Jones, C. W. Steam Induced Structural Changes of a Poly(ethylenimine) Impregnated-Alumina Sorbent for CO_2 Extraction from Ambient Air. *ACS Appl. Mater. Interfaces* **2014**.

56. Merel, J.; Clausse, M.; Meunier, F. Experimental Investigation on CO_2 Post-Combustion Capture by Indirect Thermal Swing Adsorption Using 13X and 5A Zeolites. *Ind. Eng. Chem. Res.* **2008***, 47*, 209-215.

57. Ribeiro, R. P. P. L.; Grande, C. A.; Rodrigues, A. E. Activated carbon honeycomb monolith – Zeolite 13X hybrid system to capture CO_2 from flue gases employing Electric Swing Adsorption. *Chem. Eng. Sci.* **2013***, 104*, 304-318.

58. Wang, L.; Liu, Z.; Li, P.; Yu, J.; Rodrigues, A. E. Experimental and modeling investigation on post-combustion carbon dioxide capture using zeolite 13X-APG by hybrid VTSA process. *Chem. Eng. J.* **2012***, 197*, 151-161.

59. Golden, T. C.; Kumar, R.; Kratz, W. C. US Patent 4957514, 1990.

60. Sircar, S. US Patent 4171206, 1979.

61. Ruthven, D. M.; Raghavan, N. S.; Hassan, M. M. Adsorption and diffusion of nitrogen and oxygen in a carbon molecular sieve. *Chem. Eng. Sci.* **1986***, 41*, 1325-1332.

62. Skarstrom, C. W. US Patent 2944627, 1960.

63. IsoSiv Process Operates Commercially. *Chem. Eng. News Archive* **1962***, 40*, 59-63.

64. Holcombe, T. C. US Patent 4176053, 1979.

65. Kapoor, A.; Yang, R. T. Kinetic separation of methane—carbon dioxide mixture by adsorption on molecular sieve carbon. *Chem. Eng. Sci.* **1989***, 44*, 1723-1733.

66. Seery, M. W. WO Patent 1998058726A1, 1998.

67. Skarstrom, C. W. US Patent 2944627 A, 1960.

68. Haghpanah, R.; Nilam, R.; Rajendran, A.; Farooq, S.; Karimi, I. A. Cycle synthesis and optimization of a VSA process for postcombustion CO_2 capture. *AICHE J.* **2013***, 59*, 4735-4748.

69. Cavalcante JR, C. L. Industrial Adsorption Separation Processes: Fundamentals, Modeling and Applications. *Latin Am. App. Res.* **2000***, 30*, 357-364.

70. Hedin, N.; Andersson, L.; Bergström, L.; Yan, J. Adsorbents for the post-combustion capture of CO_2 using rapid temperature swing or vacuum swing adsorption. *Appl. Energy* **2013***, 104*, 418-433.

71. Ritter, J. A. *Bench -Scale Development and Testing of Rapid PSA for CO_2 capture;* 2012 NETL CO2 Capture Technology Meeting; Pittsburgh, PA, **2012**.

72. IPCC, 2005: IPCC Special Report on Carbon Dioxide Capture and Storage. Prepared by Working Group III of the Intergovernmental Panel on Climate Change [Metz, B., O.

Davidson, H. C. de Coninck, M. Loos, and L. A. Meyer (eds.)]. *Cambridge University Press*, Cambridge, United Kingdom and NewYork, NY, USA, 442 pp.

73. Hasan, M. M. F.; Baliban, R. C.; Elia, J. A.; Floudas, C. A. Modeling, Simulation, and Optimization of Postcombustion CO_2 Capture for Variable Feed Concentration and Flow Rate. 2. Pressure Swing Adsorption and Vacuum Swing Adsorption Processes. *Ind. Eng. Chem. Res.* **2012***, 51*, 15665-15682.

74. Reynolds, S.; Mehrotra, A.; Ebner, A.; Ritter, J. Heavy reflux PSA cycles for CO_2 recovery from flue gas: Part I. Performance evaluation. *Adsorption* **2008***, 14*, 399-413.

75. Li, G.; Xiao, P.; Zhang, J.; Webley, P.A.; Xu, D. The role of water on post combustion CO_2 capture by vacuum swing adsorption: Bed layering and purge to feed ratio. *AIChE J.* **2014**, 60, 673-689.

76. Belmabkhout, Y.; Sayari, A. Isothermal versus Non-isothermal Adsorption-Desorption Cycling of Triamine-Grafted Pore-Expanded MCM-41 Mesoporous Silica for CO_2 Capture from Flue Gas. *Energy Fuels* **2010***, 24*, 5273-5280.

77. Aaron, D.; Tsouris, C. Separation of CO_2 from Flue Gas: A Review. *Sep. Sci. Technol.* **2005***, 40*, 321-348.

78. Chaffee, A. L.; Knowles, G. P.; Liang, Z.; Zhang, J.; Xiao, P.; Webley, P. A. CO_2 capture by adsorption: Materials and process development. *Int. J. Greenhouse Gas Control* **2007***, 1*, 11-18.

79. Diagne, D.; Goto, M.; Hirose, T. Parametric Studies on CO_2 Separation and Recovery by a Dual Reflux PSA Process Consisting of Both Rectifying and Stripping Sections. *Ind. Eng. Chem. Res.* **1995***, 34*, 3083-3089.

80. Ho, M. T.; Allinson, G. W.; Wiley, D. E. Reducing the Cost of CO_2 Capture from Flue Gases Using Pressure Swing Adsorption. *Ind. Eng. Chem. Res.* **2008***, 47*, 4883-4890.

81. Shen, C.; Yu, J.; Li, P.; Grande, C.; Rodrigues, A. Capture of CO_2 from flue gas by vacuum pressure swing adsorption using activated carbon beads. *Adsorption* **2011***, 17*, 179-188.

82. Shen, C.; Liu, Z.; Li, P.; Yu, J. Two-Stage VPSA Process for CO_2 Capture from Flue Gas Using Activated Carbon Beads. *Ind. Eng. Chem. Res.* **2012***, 51*, 5011-5021.

83. Ruthven, D. M. *Adsorption (Chemical Engineering);* Meyers, R. A., Ed.; Encyclopedia of Physical Science and Technology (Third Edition); Academic Press: New York, **2003**; pp 251-271.

84. Ribeiro, R. P. P. L.; Grande, C. A.; Rodrigues, A. E. Electrothermal performance of an activated carbon honeycomb monolith. *Chem. Eng. Res. Design* **2012***, 90*, 2013-2022.

85. Grande, C. A.; Ribeiro, R. P. L.; Oliveira, E. L. G.; Rodrigues, A. E. Electric swing adsorption as emerging CO_2 capture technique. *Energy Procedia* **2009***, 1*, 1219-1225.

86. Petkovska, M.; Tondeur, D.; Grevillot, G.; Granger, J.; Mitrovic, M. Temperature-Swing Gas Separation with Electrothermal Desorption Step. *Sep. Sci. Technol.* **1991***, 26*, 425-444.

87. An, H.; Feng, B.; Su, S. CO_2 capture by electrothermal swing adsorption with activated carbon fibre materials. *Int. J. Greenhouse Gas Control* **2011***, 5*, 16-25.

88. Dombrowski, K.; Lehmann, C.; Sullivan, P.; Ramirez, D.; Rood, M.; Hay, K. Organic Vapor Recovery and Energy Efficiency during Electric Regeneration of an Activated Carbon Fiber Cloth Adsorber. *J. Environ. Eng.* **2004***, 130*, 268-275.

89. Luo, L.; Ramirez, D.; Rood, M. J.; Grevillot, G.; Hay, K. J.; Thurston, D. L. Adsorption and electrothermal desorption of organic vapors using activated carbon adsorbents with novel morphologies. *Carbon* **2006***, 44*, 2715-2723.

90. Place, R. N.; Blackburn, A. J.; Tennison, S. R.; Rawlinson, A. P.; Crittenden, B. D. US Patent 6964695 B2, 2005.

91. Yu, F. D.; Luo, L.; Grevillot, G. Electrothermal swing adsorption of toluene on an activated carbon monolith: Experiments and parametric theoretical study. *Chem. Eng. Process. Process Intensif.* **2007***, 46*, 70-81.

92. Le Cloirec, P. Adsorption onto Activated Carbon Fiber Cloth and Electrothermal Desorption of Volatile Organic Compound (VOCs): A Specific Review. *Chin. J. Chem. Eng.* **2012***, 20*, 461-468.

93. Burchell, T. D.; Judkins, R. R.; Rogers, M. R.; Williams, A. M. A novel process and material for the separation of carbon dioxide and hydrogen sulfide gas mixtures. *Carbon* **1997***, 35*, 1279-1294.

94. Grande, C. A.; Rodrigues, A. E. Electric Swing Adsorption for CO_2 removal from flue gases. *Int. J. Greenhouse Gas Control* **2008***, 2*, 194-202.

95. Abu-Zahra, M. R. M.; Niederer, J. P. M.; Feron, P. H. M.; Versteeg, G. F. CO_2 capture from power plants: Part II. A parametric study of the economical performance based on mono-ethanolamine. *Int. J. Greenhouse Gas Control* **2007***, 1*, 135-142.

96. Mao, H.; Zhou, D.; Hashisho, Z.; Wang, S.; Chen, H.; Wang, H. (Constant power and constant temperature microwave regeneration of toluene and acetone loaded on microporous activated carbon from agricultural residue. *J. Ind. Eng. Chem.* **2014**, DOI: 10.1016/j.jiec.2014.03.014.

97. Cherbanski, R.; Komorowska-Durka, M.; Stefanidis, G. D.; Stankiewicz, A. I. Microwave Swing Regeneration vs Temperature Swing Regeneration - Comparison of Desorption Kinetics. *Ind. Eng. Chem. Res.* **2011***, 50*, 8632-8644.

98. Salvador, F.; Martin-Sanchez, N.; Sanchez-Hernandez, R.; Sanchez-Montero, M. J.; Izquierdo, C. Regeneration of carbonaceous adsorbents. Part I: Thermal Regeneration. *Microporous Mesoporous Mater.* **2014**, DOI: 10.1016/j.micromeso.2014.02.045.

99. Sjostrom, S.; Krutka, H.; Starns, T.; Campbell, T. Pilot test results of post-combustion CO_2 capture using solid sorbents. *Energy Procedia* **2011**, *4*, 1584-1592.

100. Mason, J. A.; Sumida, K.; Herm, Z. R.; Krishna, R.; Long, J. R. Evaluating metal-organic frameworks for post-combustion carbon dioxide capture via temperature swing adsorption. *Energy Environ. Sci.* **2011**, *4*, 3030-3040.

101. Zhao, C.; Chen, X.; Anthony, E. J.; Jiang, X.; Duan, L.; Wu, Y.; Dong, W.; Zhao, C. Capturing CO_2 in flue gas from fossil fuel-fired power plants using dry regenerable alkali metal-based sorbent. *Prog. Energy Combust. Sci.* **2013**, *39*, 515-534.

102. Webley, P. A. Adsorption technology for CO_2 separation and capture: a perspective. *Adsorption* **2014**, *20*, 225-231.

103. Clausse, M.; Merel, J.; Meunier, F. Numerical parametric study on CO_2 capture by indirect thermal swing adsorption. *Int. J. Greenhouse Gas Control* **2011**, *5*, 1206-1213.

104. Bonjour, J.; Chalfen, J.; Meunier, F. Temperature Swing Adsorption Process with Indirect Cooling and Heating. *Ind. Eng. Chem. Res.* **2002**, *41*, 5802-5811.

105. Lei, M.; Vallieres, C.; Grevillot, G.; Latifi, M. A. Thermal Swing Adsorption Process for Carbon Dioxide Capture and Recovery: Modeling, Simulation, Parameters Estimability, and Identification. *Ind. Eng. Chem. Res.* **2013**, *52*, 7526-7533.

106. Suri, R.; Crittenden, J.; Hand, D. Removal and Destruction of Organic Compounds in Water Using Adsorption, Steam Regeneration, and Photocatalytic Oxidation Processes. *J. Environ. Eng.* **1999**, *125*, 897-905.

107. Dutcher, B.; Adidharma, H.; Radosz, M. Carbon Filter Process for Flue-Gas Carbon Capture on Carbonaceous Sorbents: Steam-Aided Vacuum Swing Adsorption Option. *Ind. Eng. Chem. Res.* **2011**, *50*, 9696-9703.

108. Dutcher, B.; Krutkramelis, K.; Adidharma, H.; Radosz, M. Carbon Filter Process for Flue-Gas Carbon Capture on Carbonaceous Sorbents: Field Tests of Steam-Aided Vacuum Swing Adsorption. *Energy Fuels* **2012**, *26*, 2539-2545.

109. Chaikittisilp, W.; Kim, H.; Jones, C. W. Mesoporous Alumina-Supported Amines as Potential Steam-Stable Adsorbents for Capturing CO_2 from Simulated Flue Gas and Ambient Air. *Energy Fuels* **2011**, *25*, 5528-5537.

110. Li, W.; Bollini, P.; Didas, S. A.; Choi, S.; Drese, J. H.; Jones, C. W. Structural Changes of Silica Mesocellular Foam Supported Amine-Functionalized CO_2 Adsorbents Upon Exposure to Steam. *ACS Appl. Mater. Interfaces* **2010**, *2*, 3363-3372.

111. Hammache, S.; Hoffman, J. S.; Gray, M. L.; Fauth, D. J.; Howard, B. H.; Pennline, H. W. Comprehensive Study of the Impact of Steam on Polyethyleneimine on Silica for CO_2 Capture. *Energy Fuels* **2013**, *27*, 6899-6905.

112. An, Z. Adsorptive Removal of CO_2 by Amine Functionalized Sorbents: Experimental and Kinetics Study, *University of Alberta, Edmonton, Canada*, **2012**.

113. Hoffman, J. S.; Hammache, S.; Gray, M. L.; Fauth, D. J.; Pennline, H. W. Packed-Bed Reactor Study of NETL Sample 196c for the Removal of Carbon Dioxide from Simulated Flue Gas Mixture. **2012**, *NETL-PUB-336*.

114. Vapor pressure of water. http://intro.chem.okstate.edu/1515sp01/database/vpwater.html2013.

115. Rostami, M.; Mohseni, M.; Ranjbar, Z. Investigating the effect of pH on the surface chemistry of an amino silane treated nano silica. *Pigm. Resin Technol.* **2011**, *40*, 363-373.

116. Khatri, R. A.; Chuang, S. S. C.; Soong, Y.; Gray, M. Carbon Dioxide Capture by Diamine-Grafted SBA-15: A Combined Fourier Transform Infrared and Mass Spectrometry Study. *Ind. Eng. Chem. Res.* **2005**, *44*, 3702-3708.

117. Heydari-Gorji, A.; Yang, Y.; Sayari, A. Effect of the Pore Length on CO_2 Adsorption over Amine-Modified Mesoporous Silicas. *Energy Fuels* **2011**, *25*, 4206-4210.

118. Fillerup, E.; Zhang, Z.; Peduzzi, E.; Wang, D.; Guo, J.; Ma, X.; Wang, X.; Song, C. CO_2 Capture from Flue Gas Using Solid Molecular Basket Sorbents. **November 30th, 2012**, *DOE Project DE-FE0000458*.

119. Sayari, A.; Belmabkhout, Y. Stabilization of Amine-Containing CO_2 Adsorbents: Dramatic Effect of Water Vapor. *J. Am. Chem. Soc.* **2010**, *132*, 6312-6314.

120. Xu, X.; Song, C.; Miller, B. G.; Scaroni, A. W. Influence of Moisture on CO_2 Separation from Gas Mixture by a Nanoporous Adsorbent Based on Polyethylenimine-Modified Molecular Sieve MCM-41. *Ind. Eng. Chem. Res.* **2005**, *44*, 8113-8119.

121. Liu, Y.; Ye, Q.; Shen, M.; Shi, J.; Chen, J.; Pan, H.; Shi, Y. Carbon Dioxide Capture by Functionalized Solid Amine Sorbents with Simulated Flue Gas Conditions. *Environ. Sci. Technol.* **2011**, *45*, 5710-5716.

122. Wurzbacher, J. A.; Gebald, C.; Piatkowski, N.; Steinfeld, A. Concurrent Separation of CO_2 and H2O from Air by a Temperature-Vacuum Swing Adsorption/Desorption Cycle. *Environ. Sci. Technol.* **2012**, *46*, 9191-9198.

123. Green, D. W.; Perry, R. H. *Perry's Chemical Engineers' Handbook (8th Edition);* McGraw-Hill Professional Publishing: Blacklick, OH, USA, **2007**, pp 2703.

124. http://www.spiraxsarco.com/ca/resources/steam-tables/superheated-steam.asp (accessed 06/20, 2014).

125. Sayari, A.; Belmabkhout, Y.; Da’na, E. CO_2 Deactivation of Supported Amines: Does the Nature of Amine Matter? *Langmuir* **2012**, *28*, 4241-4247.

126. Sayari, A.; Heydari-Gorji, A.; Yang, Y. CO_2-Induced Degradation of Amine-Containing Adsorbents: Reaction Products and Pathways. *J. Am. Chem. Soc.* **2012**, *134*, 13834-13842.

127. Gu, T.; Tsai, G.; Tsao, G. T. Some considerations for optimization of desorption chromatography. *Biotechnol. Bioeng.* **1991**, *37*, 65-70.

128. Caplow, M. Kinetics of carbamate formation and breakdown. *J. Am. Chem. Soc.* **1968**, *90*, 6795-6803.