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Development of an Adsorbent for CO_2 Based on Amine-Impregnated Porous Supports

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Robert S. Franchi

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Abstract

Carbon dioxide is a ubiquitous species that has received much attention particularly because of its greenhouse gas effect. Whether because of environmental constraints or technical reasons, various industries are faced with the task of removing CO_2 from gas mixtures containing a wide range of species in different concentrations. The most commonly employed technologies for this separation are gas-liquid absorption with aqueous solutions of alkanolamines and gas-solid adsorption with zeolites. To benefit from the advantages of each of these separation technologies, a porous solid support was impregnated with an alkanolamine to develop a high capacity, water tolerant adsorbent for CO_2.

During the course of the developmental study, several amines were considered for impregnation, and it was decided to use diethanolamine (DEA) for further studies. Supports that were examined were activated carbon, silica gel, MCM-41 and pore-expanded MCM-41 (PE-MCM-41) silicas. Due to its large pore volume, PE-MCM-41 was capable of accommodating the largest amount of DEA and hence resulted in the highest adsorption capacity. The DEA impregnated PE-MCM-41 was selected for further investigation.

The synthesis procedure for the PE-MCM-41 support was scaled-up, and evaluation of the characteristics of the obtained material revealed that the scaled-up procedure did not result in a significant loss in support quality. The scaled-up procedure also showed good reproducibility.

Further studies with DEA impregnated PE-MCM-41 silica were carried out to improve the performance of the adsorbent, evaluate the stability, determine the effects of gas phase moisture and the presence of methane, and compare the performance to that of a common industrially employed adsorbent, zeolite 13X. These studies revealed that the best performance was obtained from the impregnated material when the DEA content exceeded that required for pore saturation. Improvements in performance were achieved by using ethanol as the impregnation solvent instead of water. The stability of the impregnated adsorbent was comparable to that of a similar material reported in the literature, but still required improvement. Gas phase moisture did not hinder the performance of the impregnated material, unlike zeolite 13X, and the capacity of the impregnated material for methane was low. The adsorption capacity of the impregnated material was higher than that of zeolite 13X for CO_2 partial pressures below 0.15 atm, and the material could be regenerated at a significantly lower temperature than the zeolite.

Agglomeration of the impregnated adsorbent was also examined for the purpose of testing the material in a bench-scale fixed-bed adsorption system. Extrusion of the material with polyvinyl alcohol as the binder was found to be the only suitable method available in the lab. The performance of the resulting agglomerates in the fixed-bed configuration was compared to the performance of commercial zeolite 13X agglomerates under the same experimental conditions. The testing suggested that the performance of the impregnated adsorbent was hindered by the characteristics of the agglomerates and the high heat of adsorption. In addition, the results of the tests suggested that the amine impregnated adsorbent was best suited to applications involving gases with a low CO_2 partial pressure. The performance of the fixed-bed system filled with the impregnated material would likely exceed that of the system filled with the zeolite if the materials were tested at lower CO_2 partial pressures.

Résumé

Le dioxyde de carbone est une espèce omniprésente recevant une grande attention, plus particulièrement à cause des gaz à effet de serre. Dû à des contraintes environnementales ou pour des raisons techniques, plusieurs industries doivent faire faces à la tâche de séparer le CO_2 des mélanges gazeux contenant plusieurs espèces en concentrations différentes. La technologie la plus communément utilisée pour la séparation est l'adsorption complétée à l'aide d'une solution aqueuse d'alkanolamines et l'adsorption gaz-solide complétée à l'aide de zéolites. Pour bénéficier des avantages de chacune de ces technologies de séparation, un support consistant en un solide poreux a été imprégné d'un alkanolamine pour développer un adsorbant pour le CO_2 ayant une haute capacité et tolérant l'eau.

Tout au long de l'étude de développement, plusieurs amines ont été considérés pour l'imprégnation, mais il fut décidé de poursuivre l'étude avec de la diéthanolamine (DEA). Les supports qui ont été examinés sont le carbone activé, le gel de silice et les silices MCM-41 et MCM-41 avec pore expansée (PE-MCM-41). Dû au large volume des pores, PE-MCM-41 était capable d'accommoder un montant plus important de DEA et d'accomplir une plus haute capacité d'adsorption. Le PE-MCM-41 imprégné de DEA fut sélectionné pour la suite de l'étude.

La procédure de synthèse du support de la silice PE-MCM-41 fut complétée à une plus grande échelle et l'évaluation obtenue des caractéristiques du matériel a démontrée que la procédure à grande échelle ne provoque pas de pertes significatives de la qualité du matériel de support.

Des études plus poussées de la silice PE-MCM-41 imprégnée de DEA ont été complétées pour améliorer la performance de l'adsorbant, pour évaluer la stabilité, pour déterminer les effets en phase gazeuse humide et la présence de méthane, et pour comparer la performance du matériel à la performance du zéolite 13X, adsorbant industriel communément utilisé. Ces études révèlent qu'une performance supérieure est atteinte lorsque le matériel imprégné de DEA excède la quantité requise pour saturer les pores. Une amélioration de la performance a été obtenue en utilisant de l'éthanol comme solvant d'imprégnation en remplacement de l'eau. La stabilité de l'adsorbant imprégné était comparable à celle publiée dans la littérature, mais requérait encore de l'amélioration. La phase gazeuse humide n'a pas entravée la performance du matériel imprégné, à l'opposé du zéolite 13X, et la capacité du matériel imprégné pour le méthane était basse. La capacité d'adsorption du matériel imprégné était plus haute que le zéolite 13X pour le CO_2 à des pressions partielles sous 0.15 atm, et le matériel pouvait être régénéré à une température significativement moindre que le zéolite.

L'agglomération de l'adsorbant imprégné a aussi été examinée dans le but de compléter l'essai du matériel dans un système d'adsorption à lit fixe et à l'échelle du laboratoire. Il a été découvert que l'extrusion du matériel en utilisant de l'alcool de polyvinyle comme matière liante était la seule méthode convenable et disponible en laboratoire. La performance des agglomérats résultants de la configuration du lit fixe a été comparée à la performance du zéolite commercial 13X aggloméré sous des conditions expérimentales similaires. Les essais suggèrent que la performance de l'adsorbant imprégné est entravée par les caractéristiques des agglomérats et la haute chaleur d'adsorption. Aussi, les résultats des essais suggèrent que l'adsorbant imprégné d'amine a de meilleures aptitudes pour les applications impliquant des gaz avec des pressions partielles de CO_2 basses. La performance dans un système de lit fixe remplit de matériel imprégné excéderait vraisemblablement la performance d'un système remplit de zéolite si le matériel était testé à des pressions partielles de CO_2 basses.

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Abbreviations

AEAE	2-[(2-aminoethyl)amino]-ethanol or aminoethylaminoethanol
AFC	Alkaline fuel cell
APTES	3-aminopropyltriethoxysilane
Avg.	Average
BET	Based on the method developed by Brunauer, Emmett, and Teller
Break.	Breakthrough
CSA	Concentration swing adsorption
CTAB	Cetyltrimethylammonium bromide
CV	Data obtained using a constant volume system
DAQ	Data acquisition
DEA	Diethanolamine
DGA	Diglycolamine
DMDA	N,N-dimethyldecylamine
EGA	Evolved gas analysis
EOR	Enhanced oil recovery
Eq'm.	Equilibrium
Et	Ethanol
FT-IR	Fourrier-Transform Infrared
g_{ads}	Measured on the basis of one gram of adsorbent
$g_{support}$	Measured on the basis of one gram of support
HPLC	High performance liquid chromatography
IEA WPFF	International Energy Agency Working Party on Fossil Fuels
Impreg.	Impregnated
KJS	Based on the method developed by Kruk, Jaroniec, and Sayari
MCC	Microcrystalline cellulose
MDEA	Methyl-diethanolamine
MEA	Monoethanolamine
MFC	Mass flow controller

MFM	Mass flow meter
MPV	Multiposition valve
MS	Mass spectrometer
NDIR	Non-dispersive infrared
NIOSH	National Institute for Occupational Safety and Health
PEG	Polyethylene glycol
PEI	Polyethyleneimine
PE-MCM-41	Pore-expanded MCM-41
PSA	Pressure swing adsorption
PVOH	Polyvinyl alcohol
R	Alkanol functional group (i.e. -CH_2OH)
rep.	Repeat
req.	Required
SCBA	Self-contained breathing apparatus
STP	Standard temperature and pressure
TEM	Transmission electron micrograph
TEPAN	The product of a reaction between tetraethylenepentamine and acrylonitrile
TGA	Thermogravimetric analyzer
TMAOH	Tetramethylammonium hydroxide
TSA	Thermal swing adsorption
UHP	Ultra-high purity
VOC	Volatile organic compound
(vol.)	Volumetric basis including moisture
(vol. dry)	Volumetric basis neglecting moisture
VSA	Vacuum swing adsorption
wt%	Percentage based on weight
XRD	X-ray diffraction
X-Y-Z(Support)	Sample designation where X represents the amine content in mmol amine/g_{ads}, Y represents the amine, Z represents the impregnation solvent, and Support represents the type of support

Nomenclature

C/C_o	Outlet concentration relative to the inlet concentration
D	Pore diameter of porous supports (nm)
D_a	Diameter of agglomerate (mm)
D_{KJS}	Average pore diameter calculated using the KJS method (nm)
$F_{o_{CO_2}}$	Inlet flow rate of CO_2 (L(STP)/min)
L_a	Length of agglomerate (mm)
P/P_o	Relative pressure
P_x	Pressure, subscript (x = 1 or 2) represents the system condition
PY	Position along the column (Y = 1 - column inlet,......,Y = 10 - column outlet)
S_{BET}	Specific surface area calculated using the BET method (m^2/g)
t	Time (min)
t_b	Breakthrough time (min)
t_e	Equilibrium time (min)
T_x	Temperature, subscript (x = 1 or 2) represents the system condition
V	Pore volume (cm^3/g)
ε_b	External void fraction of the adsorption bed
ρ_a	Agglomerate density (g/cm^3)
ρ_b	Adsorption bed density (g/cm^3)
σ	Standard deviation

1. Introduction

Carbon dioxide (CO_2) is a ubiquitous species that has been the subject of intense research. Most recently, the interest in CO_2 has resulted from concerns of global warming, believed to be caused primarily by emissions of CO_2 into the atmosphere (Allen, 2002). According to Song (2002), the major source of these atmospheric emissions is the combustion of fossil fuels for energy production. This has led to a global research effort examining the capture of CO_2 from power plant flue gas. Storage of the captured CO_2, often referred to as *sequestration*, has also become an issue since the current and anticipated commercial demand for CO_2 cannot make use of the additional supply that would result from large scale capture of CO_2 from flue gas (Song, 2002). This imbalance of supply and demand has in turn resulted in the exploration of novel applications of CO_2 as a chemical feedstock to produce value-added products such as formic acid (Link and Taylor, 2002), methanol (Aresta et al., 2002), ethanol, and others (Inui, 2002).

Besides research on the capture, storage, and use of CO_2 resulting from the environmental concerns, several other industries have applications requiring the removal of CO_2 from gas streams. Some of these applications include: cryogenic separation of air, emergency life support systems for hazardous environments, life support systems for enclosed habitable environments, natural gas purification, and fuel cell feed gas purification.

Currently, the most common method for removing CO_2 from gas streams is absorption with liquid solvents. Considering that this process is both costly and limited in applicability due to the inherent nature of the process, there is a need to develop alternate separation technologies for removing CO_2 from gas streams.

1.1. Research Objectives

The research described herein is aimed at developing a solid adsorbent for the removal of CO_2 from gas streams. The benefits of liquid absorption and solid adsorption processes will be combined by impregnating a solid support with a liquid amine to develop an adsorbent with a high CO_2 adsorption capacity and adsorption rate. In doing so, a material will be produced that is capable of adsorbing CO_2 in the presence of moisture and will have high CO_2 adsorption capacity even at a low CO_2 gas phase partial pressure. A preliminary evaluation to examine different supports and amines will be carried out. The most suitable material will be selected in order to improve its performance with regards to adsorption capacity, regenerability, and cyclic stability. The resulting adsorbent will be compared under the same test conditions to zeolite 13X; another material commonly used in industry to remove CO_2 from gas streams. The adsorbent will then be formed into agglomerates and the performance will be evaluated in a larger fixed-bed configuration.

2. Background

A review of the pertinent literature was conducted to determine the current state of the art related to CO_2 removal from gases. The following summary focuses on CO_2 sources and separation applications, the available separation technologies, MCM-41 porous silica, and solid supported amine adsorbents.

2.1. Carbon Dioxide Sources and Separation Applications

2.1.1. CO_2 emissions from power generation facilities

As described by the International Energy Agency Working Party on Fossil Fuels (IEA WPFF), fossil fuels supply more than 85% of the world's energy needs and are estimated to be responsible for the annual emission of 25 billion tons of CO_2 into the atmosphere (IEA WPFF, 2002). Though it would be economically impossible to capture all of these emissions, it is widely believed that capturing CO_2 from large industrial point-sources represents a feasible method for reducing CO_2 emissions to the environment. Since fossil fuel-fired power generation facilities are responsible for one third of global CO_2 emissions to the atmosphere (IEA WPFF, 2003), the capture of CO_2 emissions from these sources has become the major focus of reducing point-source emissions.

Although power generation can be achieved by nuclear, and hydro or other renewable means, most power generation facilities use oil, gas, or coal due to their relatively low costs. These facilities typically vent the combustion products to the atmosphere as a gaseous stream close to atmospheric pressure and temperatures approaching 150 °C (Xu et al., 2002). The stack gas flow rates are reportedly as high as 3 x 10^6 m^3(STP)/h for a 1000 MW coal fired power plant (Suzuki et al., 1997). The CO_2 content can range from less than 4% (vol. dry) for natural gas fired plants to greater than 14% (vol. dry) for coal fired plants (IEA WPFF, 2003). The stack gas also contains an appreciable amount of water vapour, often upwards of 8% (vol.) for gas fired plants (De Wit, 2002) and higher for coal fired plants. Other compounds are also present such as nitrogen (N_2), oxygen (O_2), carbon monoxide (CO), oxides of nitrogen (NO_x), sulphur dioxide (SO_2), and hydrogen sulphide (H_2S), where the proportions depend on the fuel source. The emission of the latter four is currently regulated due to the harmful nature of these compounds.

2.1.1.1. Emissions control options

Technology dictates that the most likely method of reducing the emissions of CO_2 from power generation facilities in the near future is by capturing the CO_2 from the flue gas (IEA WPFF, 2003; Herzog, 1999). This is due to the fact that flue gas CO_2 capture facilities can be retrofitted to power plants as *end of pipe* solutions. There are, however, several problems preventing the widespread implementation of flue gas capture technology such as: the presence of undesirable contaminants in the flue gas, the volume of gas requiring treatment, the low concentration of CO_2, the disposal of the captured CO_2, and the cost of the separation process.

Besides capturing CO_2 from flue gases, several other options have been examined for the purpose of reducing CO_2 emissions to the atmosphere. As discussed in IEA WPFF (2002), some of these options include: increasing overall plant efficiency, the use of fuels with a lower carbon content (i.e. methane instead of coal), combustion using concentrated O_2 with flue gas recycle for flame temperature control, the hydrogen/syngas approach, development of new power cycles, CO_2 fixation using algae fed with flue gas, and the use of fuel cells as the primary power-generating device. Although these may be promising technologies for the future, they can not currently supplant CO_2 removal from flue gas since they can not be easily retrofitted to existing power plants.

2.1.1.2. Disposal of captured CO_2

Regardless of the technology chosen, there still exists the question of what can be done with the large amount of CO_2 produced. The current market for CO_2 is relatively small, and is restricted mostly to the production of dry ice for the food refrigeration industry, beverage carbonation, use in fire extinguishers, enhanced oil recovery (EOR), and urea production (Pierantozzi, 2003). All but the latter eventually result in the CO_2 being released back to the atmosphere, so there is a need for the development of a market which involves converting CO_2 to a permanently stable form. An example of such a market is the use of CO_2 as a chemical feedstock to produce value added products. Barring the rapid development of such a market, the captured CO_2 will have to be sequestered in a manner that prevents its release to the atmosphere.

The options for CO_2 sequestration that have received the most attention in the literature are storage in the following reservoirs: oceans, deep saline formations, depleted oil and gas reservoirs (EOR operations), deep unminable coal beds, terrestrial ecosystems, mineral deposits, and excavated salt domes (IEA WPFF, 2002; Herzog and Golomb, 2004).

Some field trials have been conducted to examine the suitability of these reservoirs for CO_2 storage. For example, Brewer et al. (1999) conducted experiments examining the fate of CO_2 injected into the ocean at varying depths. Researchers at The Petroleum Technology Research Centre in conjunction with several other Canadian organizations and the

International Energy Agency have carried out large scale injections and sequestration of CO_2 by EOR operations (IEA WPFF, 2002; Herzog and Golomb, 2004). Researchers at Statoil in conjunction with the International Energy Agency successfully sequestered large volumes of CO_2 in a deep saline aquifer located below the floor of the North Sea (IEA WPFF, 2002; Herzog and Golomb, 2004). The success of the latter two projects demonstrates the technical feasibility of CO_2 sequestration under certain conditions.

For CO_2 to be sequestered, it must be of relatively high purity (> 95%), and it should be in liquid form. These two requirements ensure that the reservoir is used in an efficient manner by reducing the quantity of impurities sequestered along with the CO_2 and reducing the volume of the stored material. Further, transportation costs for the CO_2 are decreased when the concentration and density is increased. The presence of certain compounds (sulphurous compounds, water, and oxygen) must also be controlled to prevent corrosion of the pipeline used for transportation and to minimize any adverse reactions with the reservoir walls (Herzog, 1999).

2.1.2. Cryogenic separation of air

Cryogenic separation of air is the most commonly employed and cost effective method of producing large quantities of high purity oxygen and nitrogen (Hardenburger and Ennis, 1996). This process uses ambient air as the process feed, with typical flow rates between 140-140 000 m^3(STP)/h (Sherman and Ross, 1975). The separation takes place in a dual column distillation system, where one column operates at high pressure (550 kPa), and the other operates close to ambient pressure (Agrawal et al., 2003).

The ambient air employed as the process feed is pressurized and eventually cooled to approximately -176 °C. Prior to cooling the pressurized air, the removal of certain components from the air stream is required to prevent freezing of these components and subsequent flow restrictions in the distillation columns. Of primary concern are CO_2 and H_2O, which have ambient concentrations of 350 ppm and 1000-28 000 ppm, respectively (Hansel, 1996). According to Kanazirev and Latus (2003), the concentration of these compounds should be kept below 1 ppm. To achieve these low concentrations, some of the water is removed using a condenser, while the CO_2 and remaining water are removed by passing the compressed air through adsorption columns containing molecular sieves.

During the cryogenic separation of air, CO_2 is viewed as an impurity (i.e. a component with a very low concentration). For this reason, the recovery of CO_2 in a relatively high concentration is not required, and the gas is simply vented to the atmosphere. Although this practice is not ideal when considering the concerns over global warming, it results in no net emissions of CO_2 to the atmosphere since the source of the CO_2 is the atmosphere itself.

2.1.3. Emergency life support for hazardous environments

During emergencies in environments where the air supply is restricted such as methane gas explosions or the collapse of a mine shaft, personnel and rescuers must rely on a portable self-contained breathing apparatus (SCBA) to escape or rescue others. The units must perform three main functions: prevent the inhalation of toxic compounds by isolating the breathing air from the ambient atmosphere, provide a supply of fresh oxygen, and remove excess CO_2 and moisture from the inhaled air.

To accomplish these tasks, a typical SCBA contains a breathing bag to recycle the exhaled air, a canister containing a material to remove CO_2 and moisture, a pressure regulated oxygen source, a face mask, and tubing to connect the various components. An example of such a device appears in Figure 1. SCBA units weigh 7-18 kg, with even smaller units designed for very short duration use (< 1h) that weigh 4-8 kg (Kyriazi, 1999a).

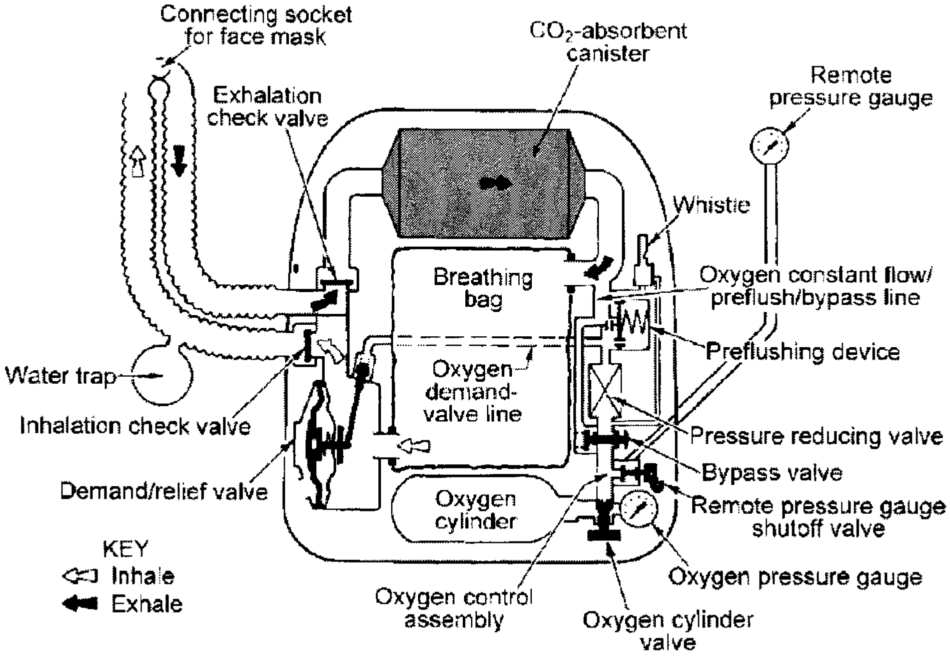

Figure 1: Schematic diagram of a typical SCBA – the Dreager BG-174A (Kyriazi, 1999a).

The air must be recycled through a breathing bag to prevent the inhalation of toxic compounds from the ambient air. This would cause the concentration of CO_2 and moisture to increase rapidly if these compounds were not removed from the closed system. For rescuers and personnel to maintain normal physiological functioning, researchers at the National Institute for Occupational Safety and Health (NIOSH) report that for short term exposures (< 1h), the average level of inhaled CO_2 must be limited to a maximum of 40 000 ppm (Kyriazi, 1999b). While moisture inhaled in the vapour form is generally not harmful, it can cause discomfort for those using the SCBA, resulting in premature removal of the equipment.

The CO_2 canister of SCBAs operates under pulsating flow conditions where the inlet flow rate, pressure, and temperature change periodically depending on the respiratory rate of the user. According to proposed NIOSH testing standards (Kyriazi, 1999b), the flow rate into the canister can be 20-65 L(STP)/min during exhalation, with average CO_2 production rates of 0.4-3.2 L(STP)/min. The maximum pressure that is permitted by the design of the SCBA is 26.7 kPa above atmospheric pressure. Temperatures routinely reach 25-37 °C.

Currently, only adsorption on solids has been shown to be efficient at removing the CO_2 and moisture due the small size of the adsorbent canisters and the simplicity of employing the canisters in these systems. Chemisorbents (materials that react chemically with gaseous species) such as lithium hydroxide and soda lime, are usually used in these systems, and the adsorbents are not regenerated once they become saturated with CO_2 and moisture. Using non-regenerable adsorbents adds to the cost of the process because the saturated adsorbent must be replaced with fresh material.

2.1.4. Life support systems for enclosed habitable environments

Closed habitable environments are found primarily in military and research submarines, spacecrafts, space stations and space suits. These environments are similar to those described in section 2.1.3., but differ because they are designed to support life for periods of several days to several months as opposed to a few hours. Under these circumstances of extended life support, the performance requirements of the environmental control systems are much more stringent. The concentration of CO_2 must be kept below 10 000 ppm, and the moisture content should be accurately controlled to prevent long term negative effects on the personnel and equipment. Also, the CO_2 removal system must process a larger amount of air since there are usually several crew members living in these environments. Given that these environments are found in confined spaces which are isolated from outside sources of energy, it is important that the size and energy requirements of the environmental control systems be kept to a minimum.

A typical application is described by Birbara et al. (2002) and Satyapal et al. (2001). The CO_2 control system operates on the NASA space shuttle and provides life support for a crew of seven astronauts. CO_2 is removed at a rate of 7 kg/day with an inlet CO_2 concentration of 6000 ppm, an inlet H_2O concentration of at least 7000 ppm, and an inlet temperature of 21 °C. These specifications suggest a flow rate of approximately 410 L(STP)/min. Due to a sophisticated heat transfer mechanism, the system consumes only 65 W of power.

CO_2 removal in submarines was initially carried out by absorption using aqueous amine solutions. This was possible for submarines because the space, weight, and energy limitations are not as stringent compared to those for space travel. Since large military submarines have many crew members, the CO_2 removal systems must be capable of purifying large amounts of air, and due to the abundance of energy on nuclear submarines, absorption is still frequently used. The removed CO_2 is simply accumulated, pressurized, and vented to the atmosphere.

Small submarines adopted adsorption with chemisorbents, and according to a report by Frew and Eaton (1992), these chemisorbent based systems are still in use. The spent chemisorbent is disposed of and fresh material must be added to the canister manually.

2.1.5. Natural gas purification

Natural gas is used as an energy source for residential, commercial, and industrial purposes. It is ranked third as a primary energy source behind petroleum derived fuels and coal (Energy Information Administration, 2003). Natural gas use is expected to have the highest growth rate of all primary energy sources (Woodcock and Gottlieb, 2004). This projected growth in demand will result in a greater rate of production of natural gas, accompanied by the need for improved processing technologies.

Natural gas is obtained from subterranean reservoirs. The primary component of natural gas is methane and minor quantities of other light hydrocarbons (ethane, propane, butane, etc.). Unprocessed natural gas can contain large quantities of other compounds such as sulphurous gases, water, carbon dioxide, nitrogen, oxygen, hydrogen, helium, and several others (Woodcock and Gottlieb, 2004). The composition of natural gas varies widely depending on the reservoir.

Contaminants of particular concern are the *acid gases* (H_2S and CO_2) since they result in corrosion of equipment and piping, especially in the presence of moisture. Raw natural gas is usually saturated with water vapour and contains H_2S in the ppm range. Occasionally the H_2S concentration can approach 40%. CO_2 is often present at elevated concentrations in the 10-30% range (Woodcock and Gottlieb, 2004; Keith, 2002). When the concentrations of these components are high, the natural gas is far too corrosive to be transported in carbon steel pipelines and is actually toxic due to the H_2S. In addition to the corrosion problems, high concentrations of these components are also a concern because they reduce the energy content and increase the storage and transportation costs. The specifications for the sale of natural gas to consumers are as follows: $H_2O < 140$ ppm, $H_2S < 4$ ppm, $CO_2 < 20\,000$ ppm (Bhide et al., 1998; Woodcock and Gottlieb, 2004). When the untreated natural gas contains large amounts of inert compounds such as helium and nitrogen, it is also processed cryogenically to remove these materials. In this case, the gas must be further dried, and the concentration of CO_2 must be reduced below 100 ppm (Woodcock and Gottlieb, 2004).

The removal of H_2S and CO_2 is usually achieved by gas-liquid absorption processes (Bhide et al., 1998; Woodcock and Gottlieb, 2004). Typical flow rates for these plants are on the order of 1×10^6 m^3(STP)/day (Bhide et al., 1998; Spears et al., 1996). The temperature is usually close to ambient, and the pressure is in the range of 2000-7000 kPa.

The separated CO_2 can often be used for EOR operations if the concentration of H_2S in the product stream is low. If the H_2S concentration is high, the stream is first processed via the Claus process to yield elemental sulphur and a more pure CO_2 stream, which can then be used for EOR. According to Keith (2002), however, the use of the separated CO_2 for EOR is rare, and usually the CO_2 is simply emitted to the atmosphere.

2.1.6. Feed gas purification for fuel cells

Alkaline fuel cells (AFCs) operate at the highest electrical efficiency of all types of fuel cells (Carrette et al., 2001). This makes them an attractive source of power for many applications. One of the major problems with AFCs is the high purity requirements of both the oxidizing gas and the fuel gas. Since AFCs operate with potassium hydroxide or sodium hydroxide as the electrolyte, the presence of even small amounts of CO_2 can quickly degrade the performance of the fuel cell. This occurs by the formation of carbonates, resulting in the following (Larminie, 2002):

- a decrease in the hydroxyl ion concentration and associated anode reaction rate

- precipitation of the carbonate resulting in electrode pore blockage
- reduced oxygen solubility increasing activation losses at the cathode
- reduced electrolyte conductivity causing increased ohmic losses

Although it is advantageous to operate the fuel cells using air as the source of oxygen, this requires removal of CO_2 from the air stream. To prolong the life of the fuel cell, the concentration of CO_2 should be kept as low as possible, however, advancements in fuel cell design allow for less than complete removal of CO_2 (Kordesch et al., 1999).

As described by Kordesch et al. (1999), an AFC was successfully used to power a commuter car using air as the source of oxygen. The CO_2 removal system employed adsorption with a non-regenerable chemisorbent. The feed conditions were typical of AFC operation, that is to say, ambient conditions with a slightly elevated pressure.

For larger stationary fuel cell applications, both adsorption and absorption can be used to remove CO_2. These applications may also require the removal of CO_2 from the fuel gas since it may be supplied from a methane reformer or other impure source.

2.2. CO_2 Separation Technologies

Removal of CO_2 from gas streams can be carried out by absorption, chemical conversion, cryogenic separation, membranes, biological fixation, and adsorption. Chemical conversion and biological fixation are still developing technologies, while membranes have not had widespread industrial application for the removal of CO_2. Cryogenic separation of CO_2 is only used for applications with high CO_2 concentrations (at least 50-70%) due to the energy requirements (IEA WPFF, 2002). As reflected by section 2.1., by far the most commonly used separation technologies are gas-liquid absorption and gas-solid adsorption.

2.2.1. Gas-liquid absorption

The use of absorption to remove CO_2 from gas streams has been practiced for several decades. The most widespread application of this technology is for the removal of acid gases from natural gas streams. A number of physical and chemical absorption processes have been developed due to the varying characteristics of raw natural gas.

2.2.1.1. Physical absorption

Physical absorption processes include absorption by methanol, propylene carbonate, dimethyl ether of polyethylene glycol, N-methyl-2-pyrrolidinone, and others (Laso and von Stockar, 2003). These compounds are used primarily with very high feed pressures and acid gas contents since the amount of absorption is directly proportional to the partial pressure of CO_2 (Capone, 1997). This phenomenon results in a lower solvent circulation rate than when using chemical absorbents and makes it possible to regenerate the solvent by reducing the pressure (flashing). These two main advantages of physical absorption processes result in lower processing costs for the applicable feed conditions.

2.2.1.2. Chemical absorption

Chemical absorption is the more widely employed method of the two since very high feed pressures and acid gas partial pressures are not required. Also, a variety of chemical absorbents are available that provide excellent selectivity, resulting in high purity natural gas. Some chemical absorbents that are commonly used for removing CO_2 are aqueous solutions of alkanolamines, potassium carbonate, sodium carbonate, sodium hydroxide, and mixtures of these solutions (Woodcock and Gottlieb, 2004; Eggeman, 2001).

Aqueous solutions of alkanolamines are the most commonly used of these chemical absorbents. The reaction of acid gases with alkanolamines has been studied since monoethanolamine (MEA) was first introduced in 1930. Many studies were concerned with determining the precise reaction mechanisms and developing expressions for the reaction rates. From this early work, it was determined that the main factors influencing the reaction mechanisms are the type of amine and the presence of other compounds capable of behaving as bases. The most commonly cited reaction mechanism is the zwitterion mechanism initially proposed by Caplow (1968). This mechanism involves the formation of an intermediate zwitterion (locally ionic, net neutral molecule) during the reaction to form a carbamate. For example, primary alkanolamines (amines bonded to only one alkanol group (R)) react with CO_2 by the reaction scheme appearing in Figure 2 (Hook, 1997).

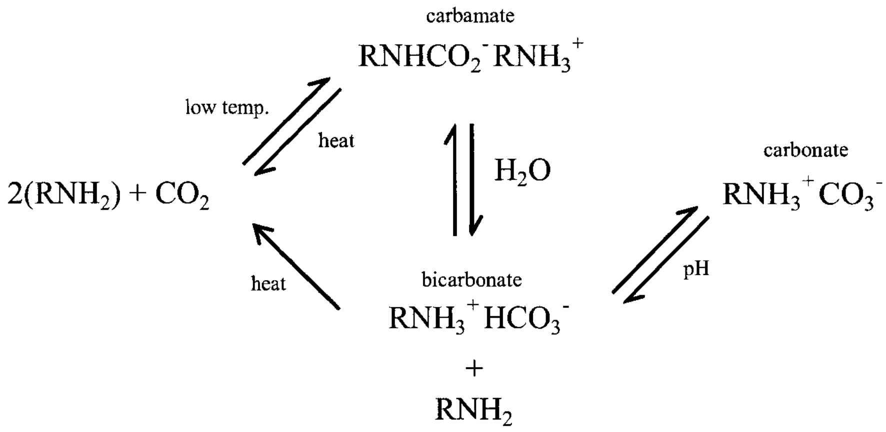

Figure 2: Reaction scheme of CO_2 with primary alkanolamines based on the zwitterion mechanism.

As shown, in the absence of water, two alkanolamines are required to bind CO_2 in the form of a carbamate. When water is present it may hydrolyze the carbamate resulting in the formation of a bicarbonate, thereby liberating the other alkanolamine molecule. Secondary alkanolamines react by a similar method, however, as the carbamate is less stable than that formed with the primary amines, the heat of absorption is lower for secondary amines. The dominant reaction for both primary and secondary alkanolamines is the formation of the carbamate since this species is more stable than the bicarbonate, and the rate of the hydrolysis reaction is slow (Kohl and Riesenfeld, 1985).

Tertiary alkanolamines can not form a carbamate with CO_2, but form a bicarbonate in the presence of water. The reaction proceeds as follows (Littel et al., 1992):

$$CO_2 + R_3N + H_2O \rightleftharpoons R_3NH^+HCO_3^-$$

Although only one alkanolamine molecule is required to bind CO_2, the reaction proceeds very slowly, hence tertiary amines are rarely used alone for the absorption of CO_2.

Commercial absorption units for the removal of CO_2 from natural gas using alkanolamines typically operate under the following conditions (Kohl and Riesenfeld, 1985; Herzog, 2004; Polasek and Bullin, 1985; Spears et al., 1996):

- feed gas flow: 30 000-118 000 m^3(STP)/h,
- feed gas concentration: 0.4-15% CO_2
- absorber configuration: 15-30 trays
- absorber pressure: 2000-7000 kPa
- absorber temperature: 20-55 °C
- liquid flow: 22-340 m^3/h, 10-30% alkanolamine (0.95-2.86 mmol amine/$g_{solvent}$)
- regenerator configuration: 12-25 trays
- regenerator pressure: 170-280 kPa
- regenerator temperature: 100-140 °C
- absorber outlet concentration : 0-2% CO_2

Commonly used alkanolamines are monoethanolamine (MEA), diethanolamine (DEA), methyl-diethanolamine (MDEA), diglycolamine (DGA), and mixtures of these compounds. MEA was first used to absorb acid gases in 1930, and it is still one of the most commonly used alkanolamines (Herzog, 1999; IEA WPFF, 2002). It is non-selective towards H_2S and CO_2, which often results in the over design of absorption columns to ensure that H_2S specifications are met. Solutions of MEA have a very high pH (12.5 for a 20% solution at 21 °C), which results in high acid gas capacities, however, there are several problems that occur when using MEA. Due to the high heat of absorption of acid gases with MEA, the energy required to break the bonds between the gas molecules and MEA is large. This high energy requirement often leads to incomplete regeneration of the solvent and increases processing costs. Incomplete regeneration is a problem since it lowers the capacity of the plant and results in a higher concentration of dissolved acid gas in the circulating fluid, leading to higher corrosion rates. To prevent corrosion, the concentration of MEA must be kept below 20%, and the amount of acid gas absorbed must be kept below 0.4 moles acid gas per mole of amine. If these conditions are exceeded, the high amount of acid gas in solution forms a very corrosive mixture that rapidly corrodes carbon steel. The limitation on the solution concentration means that a large amount of water is present, which not only increases pumping costs, but also increases the energy requirements since extra energy is needed to heat the water. Further, MEA is highly susceptible to degradation by oxygen and other compounds often present in the feed gas such as COS and CS_2. Degradation leads to a loss of capacity, increased solution viscosity, and corrosive byproducts (Stazisar et al, 2003).

DEA is the most commonly used alkanolamine for removal of acid gases (Capone, 1997; Polasek and Bullin, 1985), and it offers several advantages over MEA. Since it forms less corrosive mixtures, it can be used at higher concentrations (up to 35%). Also, the heat of absorption is 20% lower. A higher liquid phase concentration and a lower heat of absorption result in a lower energy consumption. The use of DEA results in lower amine losses since it is less susceptible to degradation, and it is less volatile than MEA. Further, corrosion problems are less severe due to the lower degradation rate, and the decreased corrosivity of the degradation byproducts.

MDEA was developed to provide a means of selectively removing H_2S from streams also containing CO_2. As described by Spears et al. (1996), the advantages of MDEA are: higher solution concentrations (up to 50%), lower corrosivity, lower heat of absorption, higher resistance to degradation, lower vapour pressure, and better selectivity towards H_2S. Although there are advantages to using MDEA, it is seldom used on its own since the reaction with CO_2 is very slow.

DGA has the high reactivity of MEA, but lower vapour pressure. It can be used in concentrations up to 60% with less corrosion problems than other alkanolamines. It is not very susceptible to degradation, but the high heat of reaction (similar to that of MEA) results in high energy consumption. DGA also preferentially absorbs CO_2 over H_2S, further discouraging its use for feeds with both compounds present.

The numerous operational problems associated with this technology result in high processing and capital costs. This limits its use to processes with large economic incentives. Although the absorption process can be adapted to operate under milder conditions, the large size and energy requirements make it completely impractical for some of the applications discussed earlier. Further, since the flow of liquids depends partly on gravity, absorption is precluded from most mobile applications.

2.2.2. Gas-solid adsorption

Removal of CO_2 by adsorption on solids has been practiced for several decades, and it is the preferred separation technology for certain applications, namely pre-purification of air prior to cryogenic distillation and purification of breathable air. It is also used for the removal of CO_2 from natural gas, although it is less popular than absorption.

2.2.2.1. Adsorption mechanisms

For a molecule to adsorb onto a solid, it must transfer from the gas phase to the adsorption site, where it must then interact with the site in order to be retained on the solid. When applied in industry, adsorbents are not used as powders, rather they are formed into agglomerates such as spheres, cylindrical extrudes, or other convenient shapes. This reduces the pressure drop in the system and prevents loss of material, but adds resistance to mass transfer since it introduces an additional network of disordered pores (LeVan et al., 1997). A concentration gradient exists for unsaturated adsorbents, where the concentration of the adsorbate in the bulk gas is greater than the concentration at the solid surface. This induces diffusion of the gas molecules through the agglomerate to the adsorption site. As depicted in Figure 3, gas molecules must flow between the agglomerates (1) to the external film of gas surrounding each agglomerate (2). The gas molecules diffuse through this film to the pores of the agglomerate (3), where they diffuse to the actual adsorbent particles (4). From the exterior of the adsorbent particles, the molecules must then diffuse to the adsorption sites (5), where interaction with the surface may occur.

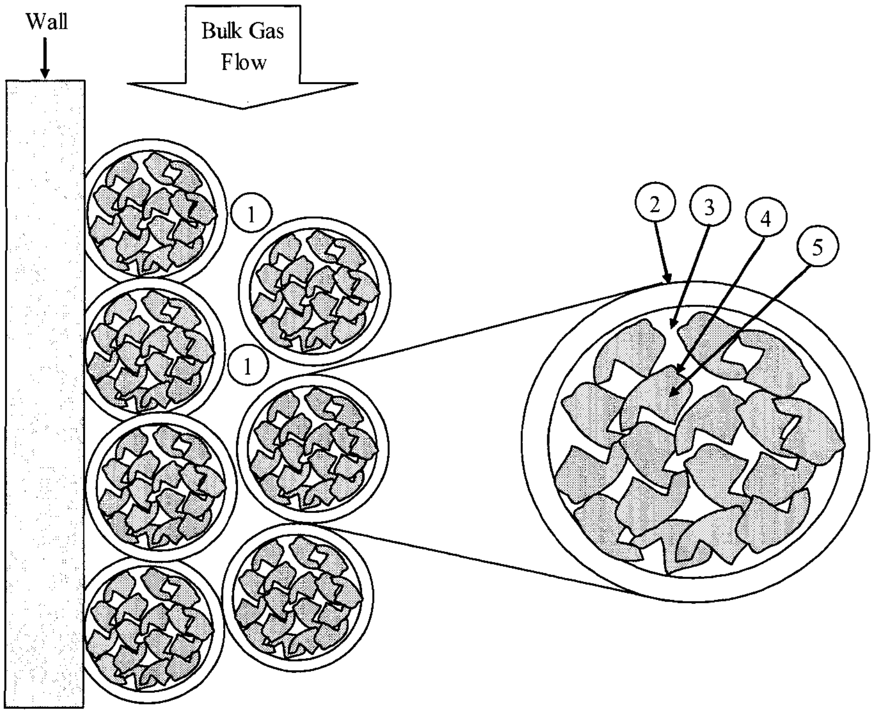

Figure 3: Schematic diagram of mass transfer in a packed bed of adsorbent.

Interaction with the surface occurs by either physical or chemical bonds with the solid. Physical adsorption is the result of relatively weak electrostatic interactions (van der Waal's forces) between the solid and the adsorbate. Physical adsorbents are used in the majority of industrial applications because the weak interactions facilitate regeneration of the material.

Chemical adsorption on the other hand is the result of strong chemical interactions between the solid and gas molecules. A chemical bond is formed between a surface species and the gas molecule, which is often irreversible. For the case of reversible interactions, substantial amounts of energy can be required to break this bond and regenerate the material.

2.2.2.2. Adsorption cycles

The classification of adsorption processes is generally based on the mode of regeneration. Although some adsorbents are not regenerated, the majority of adsorption processes operate under cyclic conditions of adsorption followed by in-situ regeneration. Steady product flow is achieved by employing two or more beds, each of which is at a different stage of the cycle, but one of which is always operating in the adsorption mode.

During adsorption, the effluent is monitored for adsorbate *breakthrough*, indicated by the presence of the adsorbate in the effluent stream. The breakthrough profile may be very abrupt, as is the case for adsorbents with a high rate of adsorption, or the concentration may increase slowly, as is the case for adsorbents with a low rate of adsorption. More abrupt breakthrough profiles are preferred since they permit a larger portion of the adsorbent to become saturated prior to regenerating the bed. Adsorption is ended and regeneration is commenced when the adsorbate concentration in the effluent reaches a predetermined level, known as the *breakthrough concentration*. This value is typically some small fraction (0.01-0.05) of the feed concentration, the magnitude of which is dependent on the desired purity of the product stream.

Regeneration is achieved by reducing the pressure of the adsorbate in the gas phase, applying heat to the adsorbent, or a combination of these methods. Reducing the adsorbate pressure exploits the fact that the adsorption capacity generally decreases with decreasing pressure. This is achieved by reducing the total pressure of the system (pressure swing adsorption - PSA, vacuum swing adsorption - VSA) or by introducing a gas with low adsorbate concentration (concentration swing adsorption - CSA). Heating the adsorbent (thermal swing adsorption - TSA) exploits the fact that the adsorption capacity generally decreases with increasing temperature. Figure 4 demonstrates the desorption step for each mode of operation. The partially saturated adsorbent at condition 1 (T_1 or P_1) is subjected to process changes resulting in a regenerated adsorbent at condition 2 (T_2 or P_2).

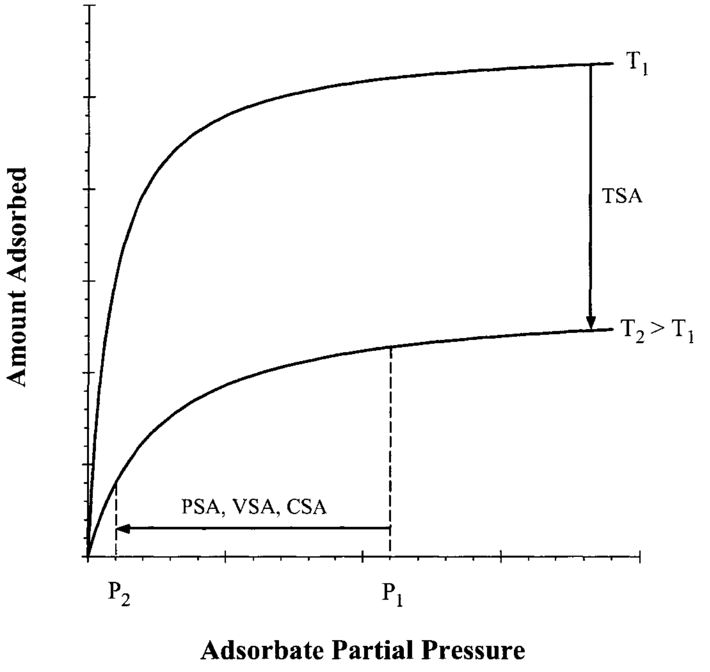

Figure 4: Schematic representation of the principle of regeneration for different adsorption cycles.

2.2.2.3. Adsorbents

Several materials have been developed to adsorb CO_2. These include both regenerable and non-regenerable adsorbents. For large scale industrial applications such as pre-purification of air for cryogenic distillation and purification of natural gas, the adsorbents are almost invariably regenerable since it would be too costly to replace the spent material with new material.

The most widely used adsorbents for CO_2 removal are zeolites, with 4A, 5A, and 13X being the most popular from this class (Yon and Sherman, 2003), although activated alumina is also popular for PSA applications (Kanazirev and Latus, 2003). The sodium form of X zeolites (13X) has been used extensively in TSA processes for the removal of CO_2 from ambient air prior to cryogenic distillation. This material is capable of adsorbing a significant amount of CO_2 under conditions of low temperature (< 5°C) and high feed pressure (Ojo et al., 1996), however, the capacity decreases significantly as the temperature increases or if moisture is present. Regeneration usually takes place at 200 °C under dry conditions, but can require heating to 400 °C if the material has been exposed to moisture (Sircar and Kratz, 1981; Brandani and Ruthven, 2004).

Improved performance of the zeolites in the presence of moisture has been achieved by cation exchange of 13X to produce a barium form of X zeolite (Sherman and Ross, 1975). Other work has focused on improving the capacity of X zeolites when operating in the ambient temperature range (Ojo et al., 1996), while improving the capacity of X zeolites in the very low partial pressure range was the subject of investigations by Gittleman et al. (2001).

Non-regenerable chemisorbents have been used for small scale applications such as SCBAs, privately operated submarines, the first space exploration missions, and mobile fuel cell applications (Kordesch et al., 1999). These adsorbents are used when they can be obtained at low cost, the application makes it impractical to regenerate the adsorbent, regeneration would require the input of too much energy, or the material would be damaged by the regeneration procedure. The most widely used chemisorbents for the removal of CO_2 are LiOH, soda lime (a mixture of CaOH and NaOH or KOH), and potassium superoxide (KO_2) (Kyriazi, 1999a; Frew and Eaton, 1995). The advantages of these materials are that they have a very high selectivity towards CO_2 over O_2 and N_2, and they have adsorption capacities theoretically approaching 46-92 wt% (Frew and Eaton, 1995).

2.2.2.4. Factors affecting adsorption performance

The removal of CO_2 from gas streams is typically achieved using packed-beds or columns, which consist of randomly packed agglomerates of adsorbent particles. The separation performance of packed-beds depends on a number of factors.

The flow rate, temperature, and concentration of the feed gas are important parameters that affect the performance of any process. Premature breakthrough of the adsorbate can occur if the gas flow rate is excessive since convective transport of the adsorbate through the column could exceed the rate of capture by the adsorbent. The feed temperature will affect the amount of adsorbate retained in the column since the capacity of typical adsorbents decreases with increasing temperature. The adsorbate feed concentration affects not only the capacity of the adsorbent, but also the rate of mass transfer since a larger concentration driving force improves mass transfer.

If the rate of reaction with the surface species is fast, which is usually the case for industrial adsorbents, mass transfer between the gas phase and the solid phase can limit the performance of the column (Crittenden and Thomas, 1998). Mass transfer is affected not only by the gas flow rate and inlet concentration, but also by bed porosity, agglomerate porosity, adsorbent particle porosity, and agglomerate size. Bed porosity, which is linked to agglomerate shape and size, has major effects on the hydrodynamics of columns. If bed porosity is too high, channelling will occur, which is undesirable since it can lead to premature breakthrough of adsorbate (Crittenden and Thomas, 1998). Excessively low bed porosity increases the interstitial velocity, which would have similar effects as increasing the inlet flow rate. Agglomerate porosity should be maximized to allow easy access of the adsorbate into the agglomerate; of course bed density must also be considered to keep the equipment size reasonable. The same is true in regards to the adsorbent particle porosity. Agglomerate size should be kept as small as possible to decrease mass transfer resistance into the agglomerate without causing excessive pressure drop across the column (Crittenden and Thomas, 1998). A large pressure drop across a column increases compression costs and can result in crushing of the agglomerates if they are not sufficiently strong to support the added forces. Since the agglomerate characteristics can affect the performance of the column in several ways, agglomeration is further discussed in sections 2.2.2.5. and 2.2.2.6..

Heat transfer is an important consideration not only for TSA, but all adsorption cycles. Since adsorption processes used for industrial separations are exothermic (Crittenden and Thomas, 1998), the heat that is generated can have deleterious effects on the performance of the column. As described by Harlick and Tezel (2004), to avoid these effects, an adsorbent with a low heat of adsorption is preferred. When considering regeneration of the column for TSA applications, the heat capacity of both the vessel and the adsorbent should be as low as possible to minimize the amount of energy consumed and the regeneration time. Also, the method of heat transfer (hot gas or heated coils) must be chosen to minimize regeneration time and provide a uniform bed temperature.

The adsorption capacity of the material at the process conditions generally affects the required size of the bed. All else remaining equal, a higher adsorption capacity results in a smaller bed, which reduces capital costs as well as processing costs. Further, the adsorption capacity for other undesirable components should be as low as possible to increase the selectivity of the separation (i.e. the ability of the adsorbent to separate different molecules) and decrease the likelihood of adsorbent deactivation.

The performance of the adsorbent should not degrade with time. A decrease in capacity may occur for several reasons such as: adsorption of other feed components, adsorption site deactivation, pore blocking or structure degradation, adsorbent coking (carbon formation), and thermal degradation. Decreasing capacity leads to loss of process throughput, process downtime, and increased costs due to adsorbent replacement.

2.2.2.5. Agglomeration

The formation of agglomerates is necessary for most industrial adsorption processes to reduce pressure drop across the column and prevent the loss of adsorbent. According to Snow et al. (1997), agglomeration techniques generally fall into two main categories: granulation and compression. In each category, agglomeration can be carried out in the presence or absence of a binder, which is an additive used to provide bonding strength between particles.

Granulation usually involves mixing the particles with any required additives followed by the addition of an atomized wetting agent to induce agglomeration. This is carried out in a device that continually agitates the material, which promotes the growth of the agglomerate and shapes the material into a suitable form. Examples of such devices are drum, disk, and mixer granulators.

In compression agglomeration, the particles are mixed with additives and fed to a compression device that causes agglomeration due to pressure forces. Common additives include binders, extrusion aids (lubricants), and water for wet extrusion methods. Examples of compression agglomerating devices are screw or ram extruders, roll presses, and tableting machines.

Agglomerates are often dried by heating, especially if wetting agents are used. For thermally stable materials, sintering or calcining is used to further increase the strength of the agglomerate. This can result in the formation of solid bridges or chemical bonds between particles. It is generally agreed that sintering or calcining agglomerates provides the strongest bonding (Snow et al., 1997).

The bond strength is important because it influences the amount of agglomerate attrition. Attrition is caused by the movement of agglomerates resulting in abrasion and eventually fragmentation, which is undesirable because it increases the pressure drop across the bed. Agglomerate strength is a combination of both bond strength and flaw distribution in the agglomerate. Voids in the agglomerate are the most common flaws, and they have a major impact on agglomerate strength. Increasing the pressure exerted on the agglomerate during formation increases the agglomerate density, which decreases the amount of voids, increases the number of inter-particle bonds, and hence greatly increases overall agglomerate strength (Snow et al., 1997).

Elevated agglomerate density also decreases the size of the bed as long as the decrease in agglomerate voidage does not greatly hinder mass transfer to the adsorption sites. Further, agglomerates with higher densities can accommodate higher gas flow rates since they are less likely to undergo fluidization (Crittenden and Thomas, 1998).

2.2.2.6. Industrial agglomerates

Adsorbent manufacturers provide industrial adsorbents primarily in granules (irregular shapes), cylindrical extrudes, and spheroid agglomerates. Due to the challenges involved in producing high quality agglomerates and the major effects the agglomerates have on the separation process, details of agglomeration procedures are usually proprietary. A fairly comprehensive discussion of industrial practices is given by Pietsch (2002), and patent literature gives more detailed descriptions applicable to adsorbent manufacture (Kanazirev and Latus, 2003; Golden et al., 2003).

As mentioned previously, zeolites are the most commonly employed adsorbents for CO_2. Agglomerate s of these materials are usually formed in a continuous pressure agglomeration process by mixing the dry powder with a binder and moistening the mixture with water. The mixture is then densified by kneading, and the resulting paste is fed to a low pressure extrusion device, typically a basket extruder or a screw extruder. If cylindrical extrudes are desired, the product is first cured to remove the bulk of the moisture and subsequently fired (calcined) to increase the strength of the agglomerate. If the material is to be formed into spheroids, the partially wet (green) extrudes are conveyed from the extruder directly into a spheronizer, which breaks the extrudes into smaller pieces and forms them into spheroids using centrifugal forces exerted by a horizontal plate rotating at high speed. The spheroids then follow the same drying procedure used for cylindrical extrudes.

Binders must be compatible with the primary particles to ensure good agglomerate strength (Snow et al., 1997). Often the binder should have a similar density or structure, and it should be capable of some type of interaction with the primary particles. Examples of binders used for zeolites are clays (kaolin, bentonite), alumina, and colloidal silica. It is not uncommon for agglomerates to contain 20 wt% binder, however, since the binders are generally inert, it is desirable to keep the binder content as low as possible. This decreases the mass and volume of material required for a separation process.

Occasionally, organic compounds are also added as temporary binders to give strength to the green agglomerates. These materials decompose upon firing, and can leave a pore network in the fired agglomerate. Organic binders are frequently used in the ceramics and ore processing industries to aid in transportation and processing of the powdered raw material by providing green agglomerate strength. Polyvinyl alcohol is an example of a commonly used organic binder. These binders are usually used at low contents of 1-4 wt% (Pirtle and Nigro, 2002).

2.3. MCM-41 Mesoporous Silica

MCM-41 designates a porous form of silica (SiO_2) or modified silica such as aluminosilica. Recently there has been significant research involving the use of this material for several potential applications including catalysis, high performance liquid chromatography (HPLC), enzyme encapsulation, and adsorption (Zhao et al., 1996; Selvam et al., 2001). A description of the discovery, manufacture, properties and uses of MCM-41 follows.

2.3.1. Discovery and manufacture of MCM-41

Researchers at Mobil Corporation reported the discovery of ordered mesoporous aluminosilicate materials in 1992 and designated the family of materials as M41S (Kresge et al., 1992; Beck et al., 1992). The synthesized materials were distinct from other mesoporous solids due to the presence of regular arrays of uniform channels, as demonstrated by X-ray diffraction (XRD) data, transmission electron micrographs (TEM), and electron micrographs. According to the researchers, these arrays were the result of the formation of inorganic walls between self-organized surfactant micelles; a process termed *templating*. The method used to manufacture the material was fairly simple and consisted essentially of mixing a basic aqueous emulsion of a quaternary ammonium surfactant with a silica and alumina (Al_2O_3) source, aging the mixture at a moderate temperature for two days, and calcining the recovered product. Pore diameters from 3-10 nm were obtained by varying the length of the surfactant alkyl chain, or by adding various hydrocarbons during synthesis. By varying the ratio of surfactant to silica during synthesis, materials with different pore structures were obtained. Two materials were found to be thermally stable: MCM-41 with a hexagonal array of straight cylindrical channels and MCM-48 with interconnected pores compatible with a cubic structure.

Since the initial discovery, researchers have examined several alternate synthesis methods for MCM-41, as summarized by Zhao et al. (1996) and Selvam et al. (2001). Different sources of silica and alumina have been used, and it was found that the alumina could be completely eliminated from the structure, resulting in increased hydrophobicity. Substitution of the alumina with other metal oxides has produced materials with various metals incorporated into the framework. The synthesis time has been reduced by using microwave heating. Post synthesis modification procedures have also been developed to adjust the pore size.

2.3.2. Properties of MCM-41

The MCM-41 structure is based on a hexagonal array of cylindrical, straight pores or channels. Proof of this arrangement was given by Beck et al. (1992) based on XRD, TEM, and electron micrographs. The walls of pure silica MCM-41 are formed from a combination of siloxane (Si-O-Si) and silanol (Si-OH) bonds (Beck et al, 1992). The Si atom is replaced in varying amounts by metal atoms in other forms of MCM-41.

MCM-41 is unique due to its structural properties such as high surface area, high pore volume, narrow pore size distribution, well defined pore shape, and easily tailored pore size.

The high density of reactive silanol groups in MCM-41 allows for modification of the surface with other compounds, which can be used to impart MCM-41 with desired chemical characteristics useful for a variety of applications (Trong On et al., 2001; Selvam et al. 2001).

Although many of the properties of MCM-41 can be altered, MCM-41 typically has a surface area in the region of 1000 m^2/g, which is very high compared to other mesoporous materials such as silica gels, which usually have one quarter to one half of this value (Waddell and Evans, 1997). The pore volume is in the region of 1.0 cm^3/g, with the majority of this distributed in mesopores. The pore diameter of MCM-41 is highly dependent on the synthesis conditions, but is usually in the low to mid mesopore range (3-20 nm).

As summarized by Sayari et al. (1999), several methods have been developed to control the pore size and pore volume of MCM-41. These include:

- varying the alkyl chain length of the surfactant
- adding auxiliary hydrocarbons during synthesis
- performing synthesis at high temperatures
- using oligomers and polymers as templates
- emulsion templating
- colloidal crystallization
- post synthesis hydrothermal treatment with amine swelling agents

In particular, post synthesis hydrothermal treatment with amine swelling agents has been shown to result in unprecedented pore expansion with negligible effect on the surface area (Sayari, 2000). The method is also easy to implement, and parameters can be modified to achieve various degrees of pore expansion. Under certain conditions, the pore diameter was expanded from 3.2 nm to 25 nm, resulting in an increase in pore volume from 0.9 to 3.3 cm^3/g, while the surface area decreased only slightly from 1316 to 1268 m^2/g.

The thermal and mechanical stability of the MCM-41 structure is generally considered to be high (Kresge et al., 1992; Selvam et al, 2001) except in the presence of moisture and basic compounds (Koyano et al., 2001; Broyer et al., 2002). Water molecules and basic species are capable of reacting with the silanol and siloxane groups, which quickly destroys the wall structure resulting in a loss in pore volume and structural order. Various attempts have been made to improve the stability of MCM-41 by increasing the hydrophobicity, converting the silanol bonds to siloxane bonds (condensation), and otherwise occupying the silanol groups to make them unreactive.

2.3.3. Applications of MCM-41

Since the discovery of MCM-41, research related to potential applications of the material has been extensive. Although pure silica MCM-41 has a fairly neutral framework, functionality can be imparted by many methods, as described by Moller and Bein (1998) and Trong On et al. (2001). These functionalized materials potentially have broad ranging applications, although none have enjoyed widespread industrial use thus far.

Traditional applications of MCM-41 are in the field of catalysis. Some examples of incorporating functionality into the material are by inclusion of metal ions into the framework during synthesis and by post synthesis ion exchange of metals which have been incorporated into the framework. Catalysts have reportedly been produced which are suitable for hydrogenation, hydrocracking, hydrodesulphurization, hydrodenitrogenation, redox reactions including pollution abatement, and other catalytic applications (Selvam et al., 2001).

MCM-41 has also been examined for use in HPLC systems (Grun et al., 1996). The aluminum form of MCM-41 was found to be suitable for separating all types of compounds examined in the study (basic, acid, and neutral), unlike other packing materials such as alumina, amorphous silica, titania, and zirconia, which were only suitable for specific types of compounds.

Enzymes immobilized in solid materials provide numerous advantages over traditional systems that require a liquid phase separation in order to recycle the enzymes. In addition to facilitating reuse of the enzymes, solid supports can also increase the chemical stability of the enzyme, and the pores of the material can be used to restrict access of molecules of a specific size or shape to the enzymes. Immobilization of enzymes in the pores of MCM-41 was examined by Diaz and Balkus (1996) as a method to stabilize enzymes and produce biosensors, biocatalysts, and bio-molecule separation systems. According to the authors, the enzymes can be deposited in the large pores of MCM-41, and the pore opening can then be restricted by reactions with organosilanes (grafting), preventing the enzyme from leaching out of the support.

The high density of surface silanol groups makes MCM-41 well suited for the attachment of organic molecules with specific functionality. For example, Feng et al. (1997) and Liu et al. (1998) developed an adsorbent suitable for removing heavy metals from wastewater by grafting tris-(methoxy)mercaptopropylsilane onto MCM-41. In addition to imparting thiol functionality, the grafting procedure also increased the hydrophobicity of the material, one of the key requirements for MCM-41 to be used in aqueous media.

A novel approach to employing MCM-41 based materials for wastewater clean-up was described by Sayari et al. (2005). In their study, MCM-41 was subjected to post synthesis hydrothermal treatment with amine swelling agents and was used in an un-calcined form to remove hydrocarbons from model wastewater. The un-calcined material contained large amounts of hydrophobic surfactant molecules capable of adsorbing significant quantities of certain hydrocarbons, but still exhibited an open pore structure.

The gas-phase adsorption of hydrocarbons with MCM-41 was one of the first potential applications examined. Early studies by Kresge et al. (1992) reported exceptionally high adsorption capacities (49-67 wt%) for cyclohexane, n-hexane, and benzene even at low partial pressures of 0.05-0.07 atm. The enhanced adsorption capacity was attributed to the large pore volume and high surface area of the material. Given that the pore volume can be easily increased without significantly decreasing the surface area, it is likely that the adsorption capacity of MCM-41 for hydrocarbons and volatile organic compounds (VOCs) can be further increased. Since many VOCs are fairly bulky compounds, the large pore size of MCM-41 should result in increased rates of adsorption in comparison to conventional microporous activated carbons.

2.4. Solid Supported Amine Adsorbents

As discussed earlier, the two most widely employed technologies for separating CO_2 from gas streams are gas-liquid absorption with alkanolamines and gas-solid adsorption with zeolites. Each of these technologies has certain advantages over the other.

Liquid absorption with alkanolamines is a proven method for the removal of CO_2 that has been used for several decades and is capable of achieving very high purity in the product streams. The selectivity of the process can be optimized by choosing the proper combination of amines, and the process can be scaled up to treat fairly large gas flow rates. However, there are several problems associated with liquid absorption namely: high rates of corrosion and amine degradation, low liquid phase amine concentration leading to increased pumping and heating costs, large equipment size, and the difficulty of the using the process for mobile applications.

Under the right conditions, solid adsorption can solve some of these problems. There is little corrosion in adsorption systems, and industrial adsorbents are chemically stable materials. Since the separation medium is usually stationary, it is unnecessary to circulate a large volume of material, and the process can be used in a broad range of mobile applications. However, most of the industrial adsorbents currently employed for the removal of CO_2 suffer from low selectivity or adsorption capacity, intolerance to moisture, and the requirement of high temperature regeneration upon exposure to moisture.

2.4.1. Potential advantages of solid supported amine adsorbents

Combining liquid absorption and solid adsorption by impregnating solid supports with amine-bearing compounds may make it possible to exploit the advantages of both processes. The highly porous supports available such as the pore expanded MCM-41 previously described, should allow for high amine contents to be occluded in the solid adsorbents, thereby potentially decreasing the size of the required vessels and reducing the processing costs. Corrosion could be reduced since the majority of the amine would be contained in the pores of the adsorbent, away from the metal surfaces of the column. Removing liquid water from the system could lower energy requirements by eliminating the need to heat the large amount of inactive material. As regeneration of amine solutions typically requires heating to only 100-140 °C, the lower temperature could also result in energy savings compared to the regeneration of typical adsorbents.

The selectivity of amine impregnated solid supports would likely be higher than that of conventional adsorbents. Unlike adsorption with many conventional adsorbents, which relies on physical interactions, amines interact with CO_2 by forming weak chemical bonds, which generally results in excellent selectivity. Chemical adsorption also implies that the adsorption capacity for CO_2 would be high even at very low adsorbate concentrations, eliminating the need to compress the feed gas to very high pressure in order to realize an elevated adsorption capacity.

Further, adsorption processes are capable of operating in any orientation since they do not depend on gravity for the flow of fluids, hence the amine impregnated solid supports could be used in mobile and zero-gravity applications. Also, as the presence of water is reportedly beneficial to the reaction between amines and CO_2, pre-treatment dehydration of humid streams would not be required, as is the case for conventional adsorbents.

2.4.2. Prior art

The idea of combining amines with solid supports to produce CO_2 adsorbents has been examined by several groups. The materials were prepared either by deposition of amine containing molecules onto the support or by grafting of amine containing alkoxysilanes onto the surface of the support. Common problems encountered when developing amine loaded solid supports are low capacity for CO_2 due to the limited quantity of amine retained by the support, operation in a narrow temperature range, and poor thermal stability.

2.4.2.1. Initial concepts

One of the first to report the use of alkanolamine impregnated solids for the removal of acid gases was Haensel (1957). According to the author, solid materials that were suitable for such a procedure were silica gel, zirconia, magnesia, clay, diatomaceous earth, and activated carbon. These materials could be impregnated with large quantities of high boiling point amines and still retain the properties of the solid. Amines that were found to be particularly suitable were DEA, dipropylamine, dipropanolamine, butylamine and dibutylamine. The preferred embodiment was a continuous process using the impregnated material in the form of agglomerated spheres in a fluidized bed. Adsorption could be carried out between room temperature and 150 °C, while the preferred method of regeneration was to heat the material in a separate vessel in flowing air. Neither the amine content of the material, nor the adsorption capacity for acid gases was mentioned in the patent.

2.4.2.2. Carbon supported alkanolamines

Two researchers at Pittsburgh Activated Carbon Company (owned by Calgon Corporation) reported the use of MEA impregnated activated carbon for the removal of CO_2 and other acid gases from several sources (Manes, 1970; Stoneburner, 1970). Impregnation was achieved by spraying the activated carbon with MEA, an aqueous solution of MEA, or by exposing the activated carbon to MEA vapours. The impregnated material contained between 5 and 50 wt% MEA and could be used to treat gas streams containing between 5 and 200 000 ppm CO_2, depending on the total volume of gas to be treated. The adsorbent could not be regenerated at temperatures above 80 °C since considerable loss of the amine would result from exposure to higher temperatures. When regenerated at 80 °C, the second cycle capacity was reduced by half, hence Stoneburner developed a regeneration method whereby the material was exposed to hot MEA vapours.

Zinnen et al. (1989) disclosed a method for producing a carbon molecular sieve suitable for use as a support for several alkanolamines, with DEA being preferred. The precursor materials were first shaped into suitable forms, and the agglomerates were subjected to a hydrothermal pore forming procedure. The molecular sieve was impregnated with the amine to a level between 20 and 65 wt%. One such material, containing 50 wt% DEA (4.8 mmol DEA/g_{ads}), achieved CO_2 adsorption capacities between 2.2 and 6.5 wt% (0.5 and 1.48 mmol CO_2/g_{ads}) at a temperature of 23 °C and equilibrium pressures of 0.003 atm and 0.517 atm respectively. The presence of moisture did not affect the adsorption of CO_2. Regeneration was carried out by heating the material to 50-70 °C. Chang (2003), a co-inventor of the material, elaborated on the adsorbent. He stated that the support had a Brunauer, Emmett, and Teller (BET) surface area of between 2000 and 2500 m^2/g, a pore volume between 1.5 and 2.5 cm^3/g, and a pore diameter between 0.5 and 1.2 nm. The author also claimed that the material contained two distinct adsorption sites which allowed it to independently adsorb CO_2 and H_2O. At 25 °C, the reported capacity for H_2O in the presence of CO_2 was 10 to 30 wt% (5.6 to 16.7 mmol H_2O/g_{ads}) at H_2O feed partial pressures between 0.01 and 0.034 atm.

2.4.2.3. Polymer supported amines

Groups at United Technologies Corporation and subsidiary Hamilton Sunstrand have also developed adsorbents for CO_2 by impregnating porous polymeric supports with amines. These materials were used for removal of CO_2 from closed habitable environments found in space applications. Early adsorbents (Birbara and Nalette, 1994; 1996; 1997) consisted of porous supports impregnated with 1-25 wt% amine for the capture of CO_2 and moisture, and 1-25 wt% polyol for viscosity control, improved stability, and improved adsorption rates. The polymeric amine preferably had a molecular weight greater than 1000, with polyethyleneimine (PEI) being the ideal amine. Desirable supports had the following characteristics: surface areas between 50 and 1000 m^2/g, high porosity, and polar surfaces. The preferred support was an acrylic ester polymer such as Amberlite produced by Rohm and Haas. Adsorption required the presence of water either from the inlet gas itself, or if the inlet gas was dry, moisture had to be added to the system. The material could be regenerated by heating to 30-50 °C while lowering the partial pressure of CO_2 to below 1.4×10^{-4} atm using vacuum or a sweep gas. Satyapal et al. (2001) performed detailed studies of the performance of such a material, designated HSC+. Adsorption was carried out at 21 °C using a stream with the following composition: 0.02 atm CO_2, 0.02 atm H_2O, 0.96 atm N_2. Under these conditions, the material had a CO_2 adsorption capacity of 4.0 wt% (0.9 mmol CO_2/g_{ads}) and a H_2O adsorption capacity of 16.8 wt% (9.3 mmol H_2O/g_{ads}). The peak regeneration rate occurred between 60 and 70 °C, and thermogravimetric analysis studies suggested that the adsorbent was stable up to 100 °C.

Further work by the same group reported the development of a material designated HSX (Birbara et al., 1999), which was characterized by a higher amine content of between 35 and 75 wt% and was capable of operating under humid or dry conditions. The adsorbent was based on the same polymeric support, however, the polymeric amine was replaced by alkanolamines, with DEA being preferred. These modifications resulted in a material with a CO_2 adsorption capacity approximately twice that of HSC+ under the same conditions (Satyapal, 2001).

Birbara et al. (2002) then reported the development of an adsorbent with improved cyclic stability. This material was again based on an acrylic ester polymeric support impregnated with an amine. The amine in this case was the product of a reaction between tetraethylenepentamine and acrylonitrile, which they referred to as TEPAN. By adjusting the ratio of the two chemicals, they were able to achieve various concentrations of primary, secondary, and tertiary amines, with the goal being to convert the majority of the amines to secondary amines. The use of TEPAN reportedly reduced the vapour pressure of the amine to immeasurably low levels, decreasing the loss of amine caused by volatilization. The authors did not report either the amine content or the CO_2 adsorption capacity of the TEPAN impregnated adsorbent.

The use of the TEPAN impregnated material was also contemplated for the removal of CO_2 from flue gas and raw natural gas. Nalette et al. (2004), who were involved in the development of the previous amine impregnated polymeric supports, disclosed an adsorption system using multiple beds for the treatment of these gases. A heat transfer coil was installed in the adsorption bed to remove the heat generated during adsorption. Regeneration of the bed was achieved by applying heat and removing the evolved CO_2 with a vacuum source. The specific conditions of the process such as temperature, pressure, and processing capacity were not mentioned in the patent.

2.4.2.4. Alumina supported DEA

Contarini et al. (2003) performed a screening study of several combinations of supports and amines with the goal of producing regenerable adsorbents for the capture of CO_2 from flue gases. They examined silica, silica-zirconia, alumina, and a clay material. Six alkanolamines were examined along with three polyamines. The supports had surface areas between 200 and 712 m^2/g, pore volumes between 0.27 and 1.1 cm^3/g, and pore diameters between 2 and 12.5 nm. In preliminary studies, DEA contents between 24 and 54 wt% were achieved, and the researchers reported that the alumina support resulted in the highest uptake capacities.

Using an alumina support containing 47.5% DEA (4.5 mmol DEA/g_{ads}), a CO_2 adsorption capacity of 8.7 wt% (2.0 mmol CO_2/g_{ads}) was achieved at 25 °C and a CO_2 pressure of 1.0 atm. The support employed for this adsorbent had the highest pore volume of all the supports examined. This adsorbent was also tested for cyclic stability, and the researchers reported that the material showed a minor decrease in performance after 16 cycles, although no quantitative results were included to support the claim. The same alumina support was then impregnated to a level of 49.8 wt% (5.7 mmol N/g_{ads}) with a 50/50 mixture of DEA and 2-((2-[(2-Hydroxyethyl)amino]ethyl)amino)ethanol. This resulted in a further increase in capacity to 9.6 wt% (2.2 mmol CO_2/g_{ads}) under the same conditions.

2.4.2.5. MCM-41 supported polyethyleneimine

Researchers at Pennsylvania State University conducted experiments using MCM-41 as a support for PEI (Xu et al. 2002; 2003). Their goal was to prepare an adsorbent suitable for the removal of CO_2 from flue gases. Adsorbents were prepared by impregnating the support with the amine to obtain contents between 5 and 75 wt%. The MCM-41 support had a surface area of 1 480 m^2/g, a pore volume of 1.0 cm^3/g, and a pore diameter of 2.8 nm. Several parameters believed to affect the performance of the adsorbent were investigated such as: the silicon to aluminum ratio of the support, the amine content, the impregnation solvent, the ratio of the impregnation solution mass to the support mass, the presence of a polyethylene glycol (PEG) additive, the impregnation method, and the operating temperature. Adsorbents were tested for CO_2 capacity by thermogravimetric measurements using pure CO_2 as well as diluted CO_2/N_2 mixtures at atmospheric pressure. Cyclic and thermal stability were also examined by thermogravimetric measurements.

The researchers found that incorporation of aluminum into the support and the addition of PEG improved the performance of the adsorbent. A one step impregnation gave better results than a two step impregnation and mechanical mixing procedures. The cyclic studies demonstrated that the CO_2 capacity was fairly stable when operated at a constant temperature of 75 °C. A CO_2 isotherm obtained for one of the samples indicated that the adsorption capacity dropped sharply below a partial pressure of 0.10 atm.

The highest reported CO_2 adsorption capacity of 13.3 wt% (3.0 mmol CO_2/g_{ads}) was obtained at 75 °C under a CO_2 pressure of 1.0 atm using a sample of pure silica MCM-41 impregnated with 75 wt% amine. The PEI impregnated adsorbents were found to exhibit the best adsorption and desorption performance when operated at 75 °C for both phases, hence regeneration was achieved by flushing the material with pure nitrogen. It was believed that below 75 °C, the high molecular weight polymer formed nano-sized particles, which reduced the rates of adsorption and desorption due to diffusional limitations. At temperatures exceeding 75 °C regeneration was incomplete, although no explanation was given for this phenomenon. The adsorbent eventually decomposed at temperatures approaching 100-125 °C.

2.4.2.6. Grafting of alkoxysilanes onto siliceous supports

Grafting is a procedure whereby a reaction between a surface group and a free species results in the formation of a strong covalent bond. In the context of producing CO_2 adsorbents, grafting is usually carried out in a solution of non-polar solvent and aminoalkoxysilanes. These compounds are formed from a central silicon atom to which are typically attached three alkoxy groups and one alkylamino group of varying length and complexity. Under specific temperature conditions, the oxygen of the alkoxy group will react with the surface hydroxyl groups of the support, resulting in the release of alcohol molecules and the attachment of the silicon atom and associated alkylamino group.

This procedure was apparently first used by Leal et al. (1992; 1995) to produce a commercially viable adsorbent for CO_2. The material was manufactured in both a powdered form and an agglomerated form, and was examined for the removal of CO_2 from enclosed habitable environments as well as a variety of industrial gas streams. The authors described grafting of alkoxysilanes onto mesoporous silica gels with surface areas between 170 and 340 m^2/g, pore volumes between 0.4 and 1.4 cm^3/g, and pore diameters between 6 and 18 nm. Although several alkoxysilanes could be used, the primary focus of the research was on the use of 3-aminopropyltriethoxysilane (APTES). By varying the reaction time between 1.5 and 30 hours, amine contents between 3.3 and 7.4 wt% (0.57 and 1.27 mmol N/g_{ads}) could be obtained. Dry CO_2 adsorption capacities at 23 °C were reportedly between 1.5 and 2.8 wt% (0.34 and 0.64 mmol CO_2/g_{ads}) for CO_2 partial pressures between 0.10 and 1.2 atm. When the CO_2 stream was saturated with water, the CO_2 adsorption capacity reportedly doubled. Desorption of the CO_2 occurred at temperatures between 40 and 140 °C, while the preferred method of regeneration was to heat the material to 100 °C under flowing purge gas.

Huang et al. (2003) examined the use of grafting to produce CO_2 adsorbents for the purification of natural gas. Silica xerogel and mesoporous MCM-48 silica were used as supports, and grafting was done with APTES. The xerogel and MCM-48 supports had surface areas of 816 and 1389 m^2/g respectively, and the resulting adsorbents had amine contents of 9.9 wt% and 13.3 wt% (1.7 and 2.3 mmol N/g_{ads}) respectively. Volumetric adsorption measurements at 25 °C showed that the capacity of the modified MCM-48 increased rapidly between CO_2 partial pressures of 0.0 and 0.10 atm, and subsequently increased gradually to 9.8 wt% (2.2 mmol CO_2/g_{ads}) at a CO_2 partial pressure of 1.0 atm. The CO_2 adsorption capacity of the modified xerogel was approximately half that of the modified MCM-48. Thermogravimetric measurements using a dry mixture of 0.05 atm CO_2 and 0.95 atm He at 25°C resulted in a CO_2 adsorption capacity of 5 wt% (1.1 mmol CO_2/g_{ads}) for the modified MCM-48. Adsorption studies were also conducted at 25 °C with a gas mixture containing 0.05

atm CO_2, 0.02 atm H_2O, and 0.93 atm He. Under these humid conditions, the CO_2 adsorption capacity reportedly doubled. Regeneration of the adsorbents was achieved by heating to 75 °C under purge gas.

Chang et al. (2003) and Gray et al. (2004) described the use of another mesoporous silica, SBA-15, as a support for the attachment of APTES. The SBA-15 used in the study had a surface area of 200-230 m^2/g, and a pore diameter of 21 nm. The amine content of the adsorbent was approximately 7 wt% (1.2 mmol N/g_{ads}), and the CO_2 adsorption capacity at 25 °C was found to be between 0.9 and 1.8 wt% (0.2 and 0.4 mmol CO_2/g_{ads}) when exposed to a stream containing 0.04 atm CO_2, 0.03 atm H_2O, and 0.93 atm He. When exposed to a humid stream of helium containing a CO_2 partial pressure of 0.10 atm at 25 °C, the adsorption capacity increased to 8.8 wt% (2.0 mmol CO_2/g_{ads}) under unspecified humidity conditions. Cyclic studies were carried out using the same gas stream. Three cycles were performed which consisted of adsorption followed by regeneration by heating to 60 °C under a purge flow of humid He. The researchers reported a decreased adsorption capacity of 7.7 wt% (1.8 mmol CO_2/g_{ads}) on the third adsorption cycle.

2.4.3. Potential for improved solid supported amine adsorbents

Examination of the literature regarding existing solid supported amine adsorbents reveals the potential for producing improved adsorbents based on the reaction mechanism between amines and CO_2. As demonstrated by the literature, the highest adsorption capacities were obtained with impregnated materials as opposed to grafted materials. This is due to the fact that the amine content of grafted materials is generally limited by the surface concentration of reactive hydroxyl groups. Impregnated materials, on the other hand, can be loaded with amine to much higher levels, the limit of which is dependent on factors such as accessible pore volume, diffusion rates through pores or the amine itself, and adsorbent texture. It would therefore seem reasonable that the potential for producing the highest capacity adsorbents lies with impregnation of porous supports.

If the support does not repel the amine, and the pores of the support are large enough to accommodate the amine, increasing the pore volume should increase the amount of amine retained in the support. Also, assuming that interactions with the surface of the support aid in retaining the amine, higher specific surface areas should also result in increased amine contents. Therefore, there exists the potential to increase the adsorption capacity by impregnating higher pore volume, higher surface area supports with amines.

The severity of amine losses described by Manes (1970) and Stoneburner (1970) can be decreased by using supports and amines which interact with each other more strongly, or by simply using amines with lower vapour pressures. Although MEA is not highly volatile, there are several amines with lower volatility that have the potential to be used for impregnation such as DEA, DGA, and others.

The work by Xu et al. (2002; 2003) demonstrated the potential of MCM-41 to yield high capacity adsorbents for CO_2, however, the adsorbent operated in a very narrow temperature range (75-100 °C). This thermal restriction is disadvantageous since it is difficult to control the temperature in such a limited range for industrial scale adsorption beds. The disadvantages of operating in a narrow temperature range could be overcome by using amines which do not form the nano-sized particles at lower temperatures as described by the authors.

3. Experimental Procedure

The following section explains the procedures used in developing an adsorbent for the removal of CO_2 from gaseous streams. In particular, the synthesis and characterization of the support, small scale testing of adsorbent samples, agglomerate formation, and bench-scale adsorption column tests are described. The chemicals used during the synthesis procedures were supplied by Sigma-Aldrich, except for the Cab-O-Sil fumed silica, which was supplied by Cabot Corporation. All gases were supplied by Praxair.

3.1. Synthesis of Pore-Expanded MCM-41

Pore-expanded MCM-41 (PE-MCM-41) was prepared in two steps as described by Sayari et al. (1998; 1999), Kruk et al. (1999; 2000; 2002), and Sayari (2000). The first step consisted of preparing a MCM-41 silica mesophase at relatively low temperature (i.e. 70-100 °C). Synthesis of MCM-41 was carried out using Cab-O-Sil M5 fumed silica as the silica source, cetyltrimethylammonium bromide (CTAB) as the surfactant template, and a 25% solution of tetramethylammonium hydroxide in water (TMAOH) for pH adjustment. The molar composition of the gel was based on the recipe described by Sayari (2000) and Sayari and Yang (2000) and was as follows: 1 SiO_2 : 0.32 TMAOH : 0.45 CTAB : 67 H_2O.

The second step consisted of a post-synthesis pore expansion via hydrothermal treatment of uncalcined MCM-41 silica in the presence of an emulsion of N,N-dimethyldecylamine (DMDA) in water.

3.1.1. Small batch synthesis

Small scale batches were synthesized in a Teflon lined cylindrical pressure vessel with an internal volume of 700 mL. TMAOH (57.72 g) was added under magnetic stirring to the synthesis vessel containing 556.5 g of distilled, de-ionized water. CTAB (82 g) was added to the solution and stirred until a homogeneous mixture was obtained. Fumed silica (30 g) was slowly added to this mixture, and stirring was maintained for 30 min following the dissolution of the silica. The vessel was then sealed and placed in an oven at 100 °C with no further stirring for 40 hours. The product was recovered by vacuum filtration and washed repeatedly with distilled, de-ionized water. The obtained filter cake was then broken into small pieces, spread on aluminum foil, and dried in ambient conditions for two days.

Pore expansion of small batches of MCM-41 was carried out in the 700 mL Teflon lined vessel by adding 43.75 g of DMDA to 525 g of distilled, de-ionized water under magnetic stirring. As-synthesized surfactant-containing MCM-41 (35 g) was then added to the emulsion, and the mixture was stirred for 30 min. The vessel was then sealed and placed in an oven at 120 °C with no further stirring for 3 days. The product was recovered by vacuum filtration and washed with distilled, de-ionized water. It was then dried in ambient conditions for two days resulting in 55 g of product. The occluded expander (DMDA) was selectively extracted from the dried product by mixing it with 10 mL of anhydrous ethanol (99%) per gram of material. The suspension was stirred for 30 min in a glass beaker. This procedure was repeated once, and the solid was recovered by vacuum filtration. The expander-free product, which consisted of a large pore, silica-surfactant nanocomposite (Kruk et al., 2002), was then broken into small pieces, spread on aluminum foil, and dried under ambient conditions for one day.

Use of the 700 mL Teflon lined cylindrical pressure vessel produced 43 g of expander-free product based on the recipe described for the first synthesis step. Several of these small batches were produced to perform the preliminary studies, however, it became clear that this scale of production was inadequate for future studies planned for the adsorption column.

3.1.2. Large batch synthesis

A synthesis vessel was designed and built to increase the batch size and reduce the total amount of time required to synthesize the support. A volume scale-up factor of 11 was chosen based both on the estimated amount of support required for testing with the bench-scale adsorption column and the dimensions of the oven available. Figure 5 shows a schematic diagram of the vessel. The synthesis vessel was built from 304 stainless steel and had an

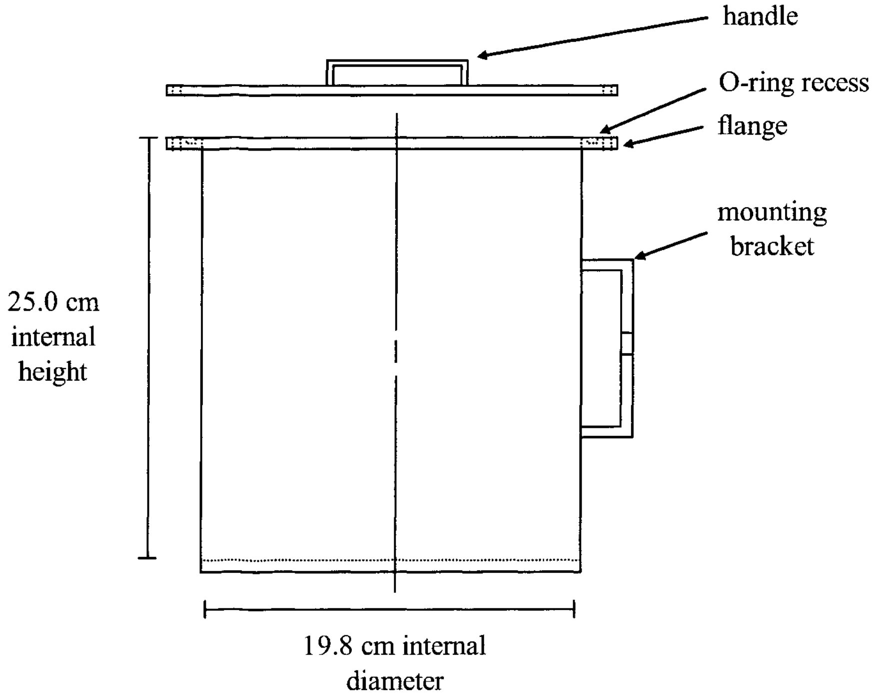

Figure 5: Schematic diagram of the large batch synthesis vessel.

internal diameter of 19.8 cm and a height of 25.0 cm, which resulted in an internal volume of 7.70 L. A Viton O-ring formed the seal between the vessel and the top plate.

Synthesis with the large vessel was carried out with the same recipe used for the small batches. A tenfold increase in the recipe was used regardless of the volume scale-up factor of 11 to ensure adequate room for thermal expansion of the contents. Stirring was achieved using a mechanical agitator. Due to the quantity of material required for the synthesis of large batches, agitation was used during all phases of heating to ensure homogeneity of the mixtures. This was achieved by mounting the vessel to a rotating shaft that spun the vessel at 60 rpm along the transverse axis. Figure 6 demonstrates the agitation method employed while heating the contents of the vessel. Use of the large stainless steel synthesis vessel produced 420 g of expander-free product based on the recipe described for the first synthesis step.

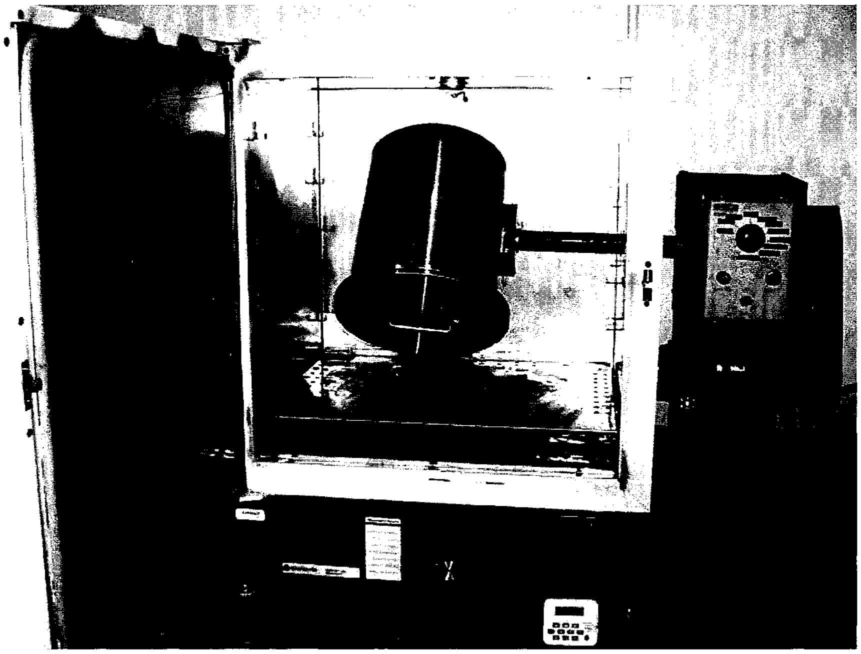

Figure 6: Mounting arrangement of the large batch synthesis vessel while heating in the oven.

3.2. Calcination

Small quantities of calcined PE-MCM-41 were obtained by placing a known amount of silica-surfactant composite in a ceramic calcination boat and heating in a tube furnace. Large scale calcination of the silica-surfactant composite for the final adsorbent synthesis was carried out by placing 100–150 g of the material on aluminum foil and heating in a Lindberg/Blue M laboratory box furnace. For calcinations both in the small tube furnace and the large laboratory box furnace, the temperature was ramped from room temperature to 550 °C at a rate of 133 °C per hour under flowing nitrogen. The gas was then changed to air to remove any carbon residues, and the temperature was held at 550 °C for five hours.

3.3. Impregnation of the support

Impregnation of the supports was carried out by a wet impregnation method. DEA was the amine of primary interest, but some other amines such as MEA and 2-[(2-aminoethyl)amino]-ethanol (AEAE) were also examined.

3.3.1. PE-MCM-41 support

Impregnation of the PE-MCM-41 support with amines was carried out by mixing various quantities of the amine with a solvent, followed by the addition of the desired amount of support. Both distilled, de-ionized water and anhydrous ethanol (99%) were examined as solvents. The slurry was mixed for 30 min, and the excess solvent was evaporated. Drying was carried out in a vented oven at 60 °C. Samples prepared in water were typically dried for 16 h, while those prepared in ethanol were typically dried for 4 h. Samples prepared with higher amine contents required longer drying times. Amine contents ranged from 0.00 mmol

DEA/g_{ads} to 7.70 mmol DEA/g_{ads}. The samples were designated using the following nomenclature system: X-Y-Z(Support), where X represents the amine content in mmol amine/g_{ads}, Y represents the amine, Z represents the impregnation solvent, and Support represents the type of support.

A typical impregnation procedure for the preparation of small batches used for preliminary studies was as follows: 1.25 g of DEA was added to 10 g of distilled, de-ionized water under magnetic stirring. PE-MCM-41 (0.5 g) was added to the solution and stirred for 30 min. The excess solvent was then evaporated by placing the mixture in an oven at 60 °C for 16 hours.

Preparation of the adsorbent for the adsorption column studies was typically carried out as follows: 300 g of DEA was mixed with 900 cm^3 of anhydrous ethanol in a large glass beaker. The PE-MCM-41 (100 g) was separately mixed with 750 cm^3 of anhydrous ethanol. This mixing procedure was chosen to ensure homogeneity of the solvent-DEA-support mixture and to keep the final volumetric ratio of solvent to support approximately the same as for the small batches. The slurry of PE-MCM-41 in ethanol was added to the solution of DEA in ethanol, and 500 cm^3 of ethanol was used to rinse the sides of the beaker. The solution was mixed for 30 min, and placed in an oven at 60 °C under flowing air. The flowing air was used to remove the ethanol vapour and increase the drying rate. Due to the large amount of material, these batches required 12 h of drying time.

3.3.2. Other supports

Some other supports for DEA were examined as a comparison, namely Norit Darco KB-B activated carbon, Davisil grade 643 silica gel, and conventional MCM-41 silica. Activated carbon and silica gel were examined as supports since they are commonly used for various adsorption applications, and their structural properties are such that both were expected to retain DEA in the porous structure. MCM-41 silica was compared to PE-MCM-41 to study the effect of enhanced pore volume. In all cases, the supports were impregnated with DEA at a level that resulted in pore saturation based on the pore volume measured by nitrogen adsorption experiments. The small batches of adsorbent were prepared with water as the impregnation solvent, as previously described.

3.4. Agglomeration

To perform testing with the bench-scale adsorption column, it was necessary to form agglomerates from the powdered adsorbent. The methods that were examined were granulation, compression, and extrusion.

Several binders were examined. Among these were: kaolin, bentonite, starch, microcrystalline cellulose (MCC), DuPont "Ludox" colloidal silica aqueous solutions, Cabot Cab-O-Sil M5, St. Lawrence Type 10 Normal Portland Cement, and polyvinyl alcohol (PVOH).

3.4.1. Granulation

Granulation was attempted by mixing samples of the powdered adsorbent with various powdered binders or aqueous binder solutions. The binder content was generally varied from 0 wt% to a maximum binder content of 50 wt%. The upper limit was chosen to minimize the effect on the adsorption capacity since the presence of any amount of inert binders would result in a decrease of the adsorption capacity of the agglomerated material. Preliminary trials with small 1.0 g batches were carried out manually. Water was added to the dry mixture of adsorbent and binder, or the aqueous binder solution was added to the dry adsorbent powder until a paste was formed. The resulting pastes were then dried at various temperatures. If the dried material formed a rigid mass, it was cut into smaller agglomerates. This method was also attempted with the calcined PE-MCM-41 support prior to impregnating with the amine.

Trials with larger batches of 10-15 g of adsorbent were carried out in a 500 cm^3 drum that was spun on a Mars Minerals DP-14 “Agglo-miser”. Two methods of adding the binder were investigated. The first method involved adding the binder as a dry powder and mixing the binder with the adsorbent in the drum. Water was then added in the form of a fine mist. The second method involved spraying the binder in the form of an aqueous solution onto the dry adsorbent powder. In both cases, the addition of the moisture caused the formation of spheroid green agglomerates as the contents were spun in the drum. These agglomerates were dried in a vented oven at various temperatures between room temperature and 75 °C.

3.4.2. Compression

Compression trials were carried out using a Carver 12 ton laboratory press and an IR disk die. Samples of approximately 0.5 g were placed in the 1.0 cm diameter die, and the material was compressed to various pressures. When binders were used during the compression trials, they were used as dry powders which were first mixed with the adsorbent.

3.4.3. Extrusion

Extrusion was examined primarily with the PVOH binders since use of these binders resulted in a paste that was suitable for extrusion by the means available in the laboratory. Addition of the PVOH solution to the dry adsorbent powder provided lubricating properties that made it relatively easy to extrude with plastic syringes commonly obtained from suppliers of scientific equipment. Several preliminary trial batches were made to determine the best type of PVOH, a suitable green agglomerate moisture level, a suitable agglomerate PVOH concentration, and the effect of the DEA content of the adsorbent. Agglomerates were first evaluated based on qualitative measurements of strength, then on quantitative measurements of CO_2 capacity. Agglomerates of insufficient strength were not usually tested for CO_2 capacity.

Three different grades of PVOH were examined to cover a wide range of characteristics. The three types of PVOH that were examined were:

1. 80% hydrolyzed PVOH with a molecular mass of 9000 -10 000 (PVOH1)
2. 99%+ hydrolyzed PVOH with a molecular mass of 89 000-98 000 (PVOH2)
3. 99%+ hydrolyzed PVOH with a molecular mass of 124 000-186 000 (PVOH3)

Typical trials were carried out by dissolving the PVOH in boiling distilled, de-ionized water and forming a solution of known concentration. The concentration was verified by evaporating the solvent and recording the mass of residual solids. The required mass of PVOH solution was then placed in a container, and 2.0 g of amine impregnated PE-MCM-41 was slowly added while mixing the paste manually. After forming a homogeneous mixture, the paste was immediately transferred to a 5 cm^3 plastic syringe and extruded onto an aluminum pan. The extrudes were dried in an oven at temperatures between 25 °C and 90 °C for 1 to 3 h.

Green agglomerate moisture content was varied by adjusting the PVOH solution concentration. Agglomerate PVOH content was varied by adjusting the amount of PVOH solution added to the impregnated material. The effect of DEA content was examined by using adsorbent powders prepared with different amine contents.

3.4.4. Final agglomeration procedure

Agglomeration of the adsorbent for the adsorption column studies was carried out by extrusion. The powdered adsorbent selected for agglomeration was PE-MCM-41 impregnated in ethanol with 3.0 g of DEA per gram of support. PVOH3 was used as the binder at a content of 7-8 wt% based on the composition of the final agglomerated product. A PVOH solution concentration of 10.8 wt% was used.

A typical agglomeration was carried out as follows: 150 g of distilled, de-ionized water was brought to a boil in a glass beaker, and 11.0 g of PVOH3 granules was slowly added to the boiling water under vigorous magnetic stirring. Once the PVOH granules were completely dissolved, the beaker and its contents were heated, and the weight was periodically recorded as the excess liquid was evaporated. During this time, two 50.0 g quantities of amine impregnated PE-MCM-41 were measured out and placed in separate containers. When the solution mass reached 101.85 g, two 40.26 g quantities of the solution were measured out and placed in separate containers. The 50 g quantities of adsorbent were slowly added to the containers of PVOH solution while mixing manually until uniform pastes were obtained. The pastes were transferred to 60 cm^3 plastic syringes and extruded onto aluminum pans using modified caulking guns. The extrudes were dried at 75 °C for one hour, and the dried extrudes were then cut with a razor blade into smaller segments.

3.5. Support Characterization

3.5.1. Nitrogen adsorption

Nitrogen adsorption experiments were performed to determine the surface area, pore size distribution, average pore diameter, and pore volume of the various supports. Adsorption was carried out at the normal boiling point of liquid nitrogen (-196 °C) using a Coulter Omnisorp 100 gas analyzer. The sample size varied according to the anticipated surface area, but was typically 30 mg. The default instrument test parameters were used, which were as follows:

- adsorption cut-off relative pressure: 0.9986
- desorption cut-off relative pressure: 0.1316
- adsorbate dose: 4000 Pa
- desorbate dose: 4000 Pa
- equilibrium conditions: 6 consecutive points sampled at 5 second intervals equal to each other within the tolerance
- equilibrium tolerances: for pressures $\leq$ 1333 Pa, tolerance $\leq$ 1.33 Pa
  : for pressures $\geq$ 1333 Pa, tolerance $\leq$ 40 Pa

Before exposure to nitrogen, the samples were heated to 100 °C under high vacuum (10^{-3} Pa). The specific surface area (S_{BET}) was determined from the linear part of the BET plot occurring between relative pressures (P/P_o) of 0.05 – 0.15. The average pore diameter (D_{KJS}) for the MCM-41 based materials was taken as the peak of the pore size distributions as calculated from the adsorption branch using the KJS (Kruk et al., 1997) method. This modified form of the BJH method was used since it was shown to more accurately represent the pore diameter for MCM-41 materials. The total pore volume (V) was determined as the volume of liquid nitrogen adsorbed at a relative pressure of 0.995.

3.5.2. X-ray powder diffraction

XRD patterns were collected for MCM-41 samples to compare the quality of the different batches prepared in the large synthesis vessel. Patterns were obtained using a Scintag X_2 Advanced Diffraction System with the following parameters:

- Cu Kα radiation with 0.15418 nm wavelength
- scan step size of 0.02° 2θ
- scan counting time per step of 4.0 s
- scan range of $0.7° < 2\theta < 8°$

3.5.3. Amine content

The actual amount of amine retained by the supports was measured for each sample by decomposition in ultra-high purity (UHP) nitrogen using a TA Instruments Q500 Thermogravimetric Analyzer (TGA) coupled to a Pfeiffer Thermostar mass spectrometer (MS).

The Q500 had a sample capacity of 1.0 g, however, the 200 mg weight range was used since a higher resolution was possible. This range had a weight resolution of 0.1 μg and an accuracy of 0.1 μg. The temperature control range was from 5 °C above ambient to 1000 °C. The temperature was measured with a Platinel II thermocouple. Platinum sample pans with a 100 μl capacity were used. The Q500 was fitted with a quartz lined evolved gas analysis (EGA) furnace to permit coupling with the Pfeiffer Thermostar mass spectrometer. This furnace was capable of a maximum temperature ramp of 50 °C/min. The Q500 was supplied with Universal Analysis software version 4.1 D, which was used to display and analyze all the data.

The Pfeiffer Thermostar mass spectrometer was coupled to the Q500 for purposes of evolved gas analysis. The capillary line was heated to 175 °C to prevent condensation of gaseous components in the capillary. Only qualitative results were obtained with the mass spectrometer, which were used to identify the presence of various compounds such as CO_2, H_2O, amines, and solvents.

A typical test used a sample of approximately 60 mg. To ensure consistent test results, all powdered samples were loaded on the sample pan using the same procedure. This was necessary since some samples, particularly those impregnated with high levels of amine, formed a clumpy powder that could be pressed onto the sample pan forming a dense layer, resulting in different adsorption behaviour. The samples were placed onto the sample pan, and the pan was tapped on the counter five times to cause the material to settle. Excess adsorbent was scraped off the pan using a straight edge, and any loose particles were removed from the pan to prevent them from falling off during the test. Agglomerated samples required no special loading procedure since they could not form the same dense layer as the powdered materials. The sample pan was then loaded onto the microbalance using the automated loading feature of the Q500. The EGA furnace was raised, and the sample was heated and held at a specified activation temperature for 30 min under a UHP nitrogen purge flow rate of 160 cm^3(STP)/min. This was done to remove any pre-adsorbed compounds. Subsequent to this activation procedure the samples were cooled to 25 °C, and decomposition was carried out by heating the samples to 1000 °C under a UHP nitrogen purge flow rate of 160 cm^3(STP)/min. Typically, a temperature ramp of 50 °C/min was used, however, slower ramps such as 2 °C/min or 10 °C/min were also used to obtain more detailed decomposition profiles.

To calculate the amine content of the powdered samples, an unimpregnated support was first decomposed to determine the mass loss due to dehydroxylation of the support surface. The total mass loss of the impregnated material was corrected to account for the mass loss due to dehydroxylation.

3.6. TGA Adsorption Measurements

Adsorption studies were conducted at atmospheric pressure with the Q500 TGA-MS to determine the adsorption capacity and adsorption rate of the various adsorbent powders and agglomerates.

3.6.1. CO_2 adsorption capacity and rate of amine impregnated materials

The amine impregnated adsorbents were activated by heating the samples to 75 °C for 30 min prior to performing adsorption tests. The furnace was then cooled to 25 °C, and the gas was switched to a dry mixture of CO_2 in UHP nitrogen. Since CO_2 reacts chemically with the amine, the adsorption capacity should be fairly insensitive to the CO_2 partial pressure in the range studied (0.02-1.0 atm), hence the majority of the tests were conducted at a CO_2 partial pressure of 0.05 atm (5% CO_2/N_2 mixture at 1 atm). A gas flow rate of 150 cm^3(STP)/min was used during these tests. Samples were exposed to the gas mixture for 80 min to ensure that the mass stabilized. Adsorption capacities were calculated based on the mass gain after 60 min of exposure to the CO_2 gas mixture since all of the samples except those with the highest amine content reached equilibrium during this time. The adsorption rate, which was a function of the residual CO_2 capacity, was calculated automatically by the Universal Analysis software, and the maximum value was reported as the adsorption rate. An average rate was also calculated based on the average slope of the mass change curve between the initial mass before exposure to the gas mixture, and the mass at 50% of the total adsorption capacity. This value was calculated to attempt minimize any effects caused by inconsistent packing of the sample on the sample pan, but it was found to follow the same pattern as the maximum adsorption rate, hence these data were not reported.

Following 80 min of exposure to the CO_2 mixture, the gas was switched to UHP nitrogen, and the temperature was increased at a ramp rate of 50 °C/min to 1000 °C to obtain the amine content of the sample.

This test procedure was used for the following purposes:

- compare the relative performance of the various supports, i.e. silica gel, activated carbon, MCM-41, and PE-MCM-41
- obtain the relationship of adsorption capacity and adsorption rate to amine loading for the amine impregnated PE-MCM-41
- evaluate the performance of the agglomerated DEA impregnated PE-MCM-41 materials

3.6.2. CO_2 adsorption capacity of zeolite 13X

Zeolite 13X powder (obtained from Sigma-Aldrich) was used to compare the performance of the amine impregnated materials to an industrially employed CO_2 adsorbent. Due to the strong adsorption of H_2O on zeolite 13X, this material was initially heated to 400 °C for complete dehydration prior to adsorption tests. Samples were then cooled to 25 °C and exposed to a dry mixture of CO_2 and nitrogen for a period of one hour, which was sufficient to reach equilibrium. The zeolite 13X samples were then regenerated by heating to 75 °C in dry nitrogen, and adsorption data were collected upon exposure to the same CO_2/N_2 mixture at 25 °C. This was necessary to ensure that the amine impregnated samples and the zeolite 13X samples were compared after being activated at the same temperature (i.e. 75 °C). The adsorption capacity was calculated based on the mass increase measured after one hour of exposure to the gas mixture. The adsorption rates were calculated as described for the amine impregnated samples. The same procedure was used to test commercial zeolite 13X extrudes obtained from UOP.

3.6.3. CO_2 adsorption isotherms

Adsorption isotherms were obtained with the TGA at 25 °C for zeolite 13X powder and the PE-MCM-41 impregnated with DEA in ethanol with an amine content of 6.98 mmol DEA/g_{ads} (6.98-DEA-Et(PE-MCM-41)). The tests were carried out using the adsorption procedures previously described, but exposing the samples to dry CO_2/N_2 certified mixtures with the following nominal concentrations: 2%, 5%, 10%, 20%, and 100%.

3.6.4. The effect of moisture on CO_2 adsorption capacity

The effect of moisture on the CO_2 adsorption capacity was examined for sample 6.98-DEA-Et(PE-MCM-41) and zeolite 13X powder. The samples were activated as previously discussed and subsequently exposed to humidified gases with a relative humidity of 28% at 25 °C. This was achieved by passing the dry gases through a gas saturator filled with distilled, de-ionized water held at 5 °C, then passing these humidified gases over the samples. The tests were used to investigate the effects of moisture in the low humidity range, similar to the humidity of a gas stream that has been dehumidified through a condenser using cooling water at 4-6 °C. To decouple the adsorption of moisture from the adsorption of CO_2, samples were first exposed to moist nitrogen until the water uptake ceased. Moist CO_2 was then passed over the samples for one hour to determine the CO_2 adsorption capacity. The mass spectrometer response verified that the adsorption of water and CO_2 was non-competitive since the specific response for water showed minimal deflection upon introduction of humid CO_2.

3.6.5. CO_2 capacity in the presence of methane

Since one potential application of the DEA impregnated PE-MCM-41 is the purification or enrichment of gaseous fuels, a preliminary study was conducted to examine the effect of methane on the CO_2 adsorption capacity. This was achieved by performing the standard CO_2 adsorption test on sample 6.98-DEA-Et(PE-MCM-41) while using a gas mixture available in the lab that contained both CO_2 and CH_4. This certified mixture was composed of 2% CO_2, and 8% Ar in CH_4, which was used to represent a natural gas feed containing CO_2 and inert components. This gas mixture was convenient since it allowed for the comparison to the adsorption capacity already obtained with the mixture of 2% CO_2 in N_2. A separate test was also carried out with a certified mixture of 10% Ar in CH_4 to decouple the CO_2 and CH_4 adsorption capacities of the material.

3.6.6. Cyclic CO_2 adsorption capacity

Cyclic adsorption studies were also carried out to examine the stability of certain materials of interest. Following the initial adsorption cycle, the samples were regenerated by heating in dry nitrogen at 10 °C/min from 25 °C to 75 °C. The samples remained isothermal for 5 min, were cooled to 25 °C, and again exposed the CO_2/N_2 gas mixture. These adsorption-desorption cycles were repeated several times.

3.7. Bench-Scale Adsorption Column Studies

To evaluate the performance of the DEA impregnated PE-MCM-41 under conditions more closely resembling those used in industry, tests were conducted in a fixed-bed adsorption column. This allowed for the determination of breakthrough curves and temperature responses under various flow and concentration conditions. The performance of the agglomerated adsorbent was compared to the performance of UOP zeolite 13X agglomerates under identical experimental conditions.

3.7.1. Column adsorption system

The bench-scale adsorption system was designed and built in-house. Figure 7 shows a simplified schematic representation of the test apparatus, which consisted primarily of the following components: an adsorption column, gas cylinders, heating tape, an in-line gas heater, three-way valves, manual two-way valves, 1/4" and 1/8" outside diameter stainless steel tubing, a data acquisition system, customized control software, thermocouples, a multiposition valve, pressure transducers, mass flow controllers, a mass flow meter, and a CO_2 detector.

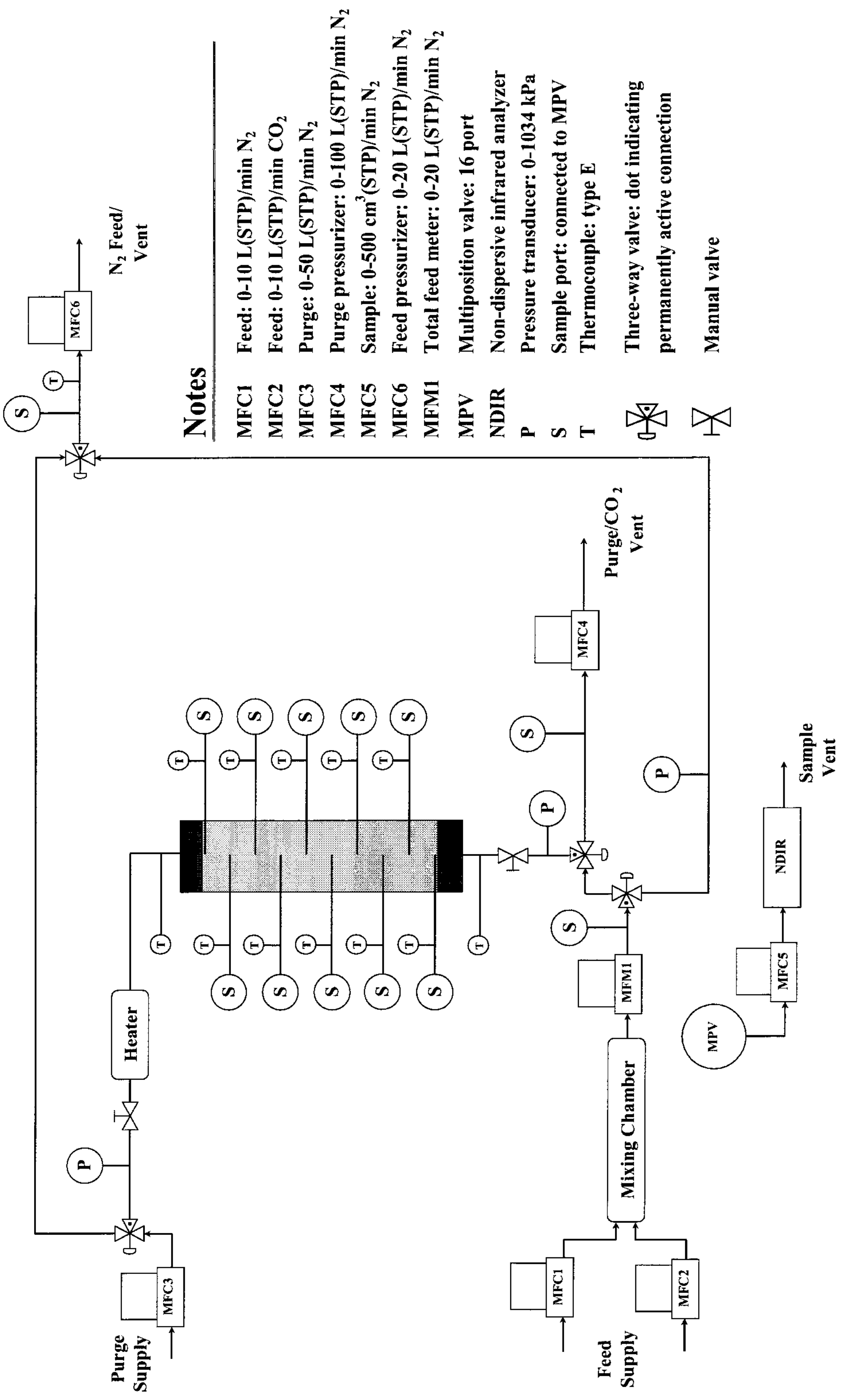

Figure 7: Schematic diagram of the bench-scale adsorption system.

The configuration of the adsorption system allowed for adsorption followed by in-situ regeneration of the saturated adsorbent. Regeneration was carried out by modification of the valve positions and a combination of purging with UHP N_2 and heating. The UHP N_2 was used as both the purge gas and as a component of the feed. The other component of the feed was pure CO_2 (99.99%). Heating to a specified temperature was achieved by adjusting the voltage of a heating tape wrapped around the column. For high temperature regeneration of the zeolite material, the in-line gas heater was also used, and the gas temperature was controlled in a similar manner.

The adsorption column was made from 316 stainless steel. The inside diameter was 3.49 cm, and the length available for the adsorption bed was 93.0 cm. The column was coupled to inlet and outlet flow distributors also made from 316 stainless steel. The interior of the distributors was conical with a cone angle of 20°, and it was filled with 3.2 mm stainless steel balls to create plug-flow conditions at the outlet of the flow distributor. Teflon O-rings formed the seals between the column and the flow distributors. The column had ten ports that were used for both gas sampling and temperature measurement. The first and last ports were positioned approximately 6 mm from the extremities of the bed, while the others were spaced 10.2 cm apart in the axial direction of the column. The column could be completely isolated from the rest of the system by closing two manual two-way valves located at the inlet and outlet of the column.

The various components of the adsorption system were connected by 1/4" outside diameter stainless steel tubing. Sample lines were made from 1/8" outside diameter stainless steel tubing.

The control computer was interfaced with the adsorption system by means of a National Instruments SCXI data acquisition system (DAQ). The DAQ was designed to have 32 thermocouple input channels, 32 analog input channels, 8 analog output channels, and 32 digital relay channels. In conjunction with the Labview software, the DAQ collected, recorded and displayed the following: temperature, pressure, CO_2 concentration, and flow rate data. The control parameters were the following: the valve configuration of the three-way valves, the mass flow rates, the system pressures, the sampling location, the functions of the CO_2 detector, and the output of the heating tape.

Temperatures were measured using Omega model TJC36-CXSS-062E-6 Type E exposed tip thermocouples. These had a reported accuracy of ± 1 °C. Ten thermocouples measured the temperature in the centre of the adsorption column at various axial positions. During regeneration of the saturated adsorbents, the average of all the column temperatures was used as the control temperature. This value was fairly representative of the true column temperature when low purge flow rates were used.

At the location of each temperature probe in the column was a sample port that could be used to sample the gas at that location. Three other sample ports were located throughout the system, as indicated in Figure 7. The sample location was selected using a Valco model SD 16-port micro-electric actuated multiposition valve. This valve was also used to select the span and zero gases for calibration of the CO_2 detector.

Pressure was measured using MKS Model 750B pressure transducers. These transducers were capable of measuring absolute pressures from 0-1034 kPa with an accuracy of 1% of the reading. The pressure in the column was taken as the average of the inlet and outlet pressures. This average pressure was used as the control pressure, and due to the low pressure drops (3-

14 kPa) in the range of flow rates studied, it accurately represented of the true pressure in the column.

The feed and sample flow rates were controlled by MKS type M100B mass flow controllers. The purge flow rate was controlled by a MKS type 1559A mass flow controller. These controllers had an accuracy of 1.5% of the full scale. The measurement resolution was 0.1% of the full scale.

The other controllers and the mass flow meter were MKS type 1179. The controllers and the mass flow meter had an accuracy of 1.0% of the reading. The measurement resolution was 0.1% of the full scale.

3.7.2. CO_2 detection

The concentration of CO_2 was determined using a Horiba model VIA-510 non-dispersive infrared (NDIR) analyzer. This device allowed for the continuous detection of CO_2 as opposed to performing periodic injections as required with commonly used gas chromatographs. Continuous detection was advantageous since it made it possible to accurately define the breakthrough curve even for process conditions that resulted in very sharp breakthrough profiles. A disadvantage of the NDIR was that it required a constant sample flow rate of 500 cm^3(STP)/min, which could affect results for systems operating at low feed flow rates, however, this was not the case for the current study.

The VIA-510 measured CO_2 concentrations between 0-100%, with the following four measurement ranges available: 0-5%, 0-10%, 0-50%, and 0-100%. The instrument resolution was up to four digits. The reproducibility of the measurement was stated as ± 0.5% of the range full scale. The zero and span drifts were stated as ± 1.0% of the range full scale. The instrument specifications reported that the signal response reached 90% of the true value within 30 s of the gas arriving at the instrument inlet.

The measurement range of primary interest for the column studies was the 0-5% range. Using this range resulted in the following measurement specifications: measurement resolution up to the third decimal place, measurement reproducibility of ± 0.025%, zero drift of ± 0.05%, and span drift of ± 0.05%.

Prior to each test, the 0-5% measurement range was selected and the NDIR was zeroed using UHP N_2. The span was then set using a mixture of 4.0% CO_2 in N_2 as specified by the manufacturer in the instrument documentation. The span mixture was created using the feed mass flow controllers.

3.7.3. CO_2 adsorption tests

The pellet density and the bed density were measured manually before filling the column with the adsorbent. These values were used to calculate the bed porosity, which was used to determine the interstitial velocity.

The adsorbents were first activated in an oven to remove any pre-adsorbed gases. The DEA impregnated adsorbent was heated to 75 °C under nitrogen flow, while zeolite 13X was heated to 230 °C under nitrogen flow. The column was filled by pouring the pellets into the column while tapping the sides of the column to encourage uniform distribution of the material. The mass of adsorbent contained in the column was recorded.

Prior to each test, the NDIR was zeroed and spanned as described previously. The column was then pressurized to the adsorption pressure by introducing UHP N_2 to the column through MFC3 and controlling the pressure using MFC4. While the column was being pressurized, the adsorption gas mixture was created using the two feed controllers (MFC1 and MFC2) and brought up to the adsorption pressure using MFC6. Adsorption runs were carried out at a slightly elevated pressure (1.156 atm) to ensure proper sample flow through the mass flow controller to the NDIR (MFC5).

The concentration of the mixture to be used for the adsorption run was then monitored using the NDIR to establish the average concentration and the variability in the concentration. These values were used to determine the concentration representing complete breakthrough of the gas mixture at the end of the adsorption run. The zero gas was also monitored to determine similar parameters, which were used to determine the first sign of breakthrough of the gas.

The following adsorption tests were conducted with zeolite 13X:

1) total flow rate of 10.0 L(STP)/min with a mixture of 4.32% CO_2 in N_2
2) total flow rate of 10.0 L(STP)/min with a mixture of 1.73% CO_2 in N_2
3) total flow rate of 5.0 L(STP)/min with a mixture of 4.32% CO_2 in N_2

These concentrations were chosen since they represented CO_2 partial pressures of 0.02 and 0.05 atm at the slightly elevated adsorption pressure. The results of tests under these partial pressure conditions could be compared to those obtained previously using the TGA. The flow rates were chosen to examine the performance of the materials under both high and medium interstitial velocity (49.7 cm/s and 24.9 cm/s). Due to the low concentrations used for the tests, the two flow rates represented values that were close to the upper and lower limits of accuracy achievable with the system.

Tests were conducted under identical conditions with the DEA impregnated PE-MCM-41, and test 1 was repeated at the end to determine if the performance of the material degraded significantly over the course of testing. The same flow rates were chosen even though the interstitial velocities were lower (36.5 cm/s and 18.2 cm/s) since the equipment limited the maximum total flow to approximately 10 L(STP)/min under the low concentrations examined. Also, it was desired to obtain the performance of the materials under the same system conditions.

During each run, the CO_2 concentration, temperatures, flow rates, and pressures were monitored continuously, and the data were written to a data file every second. The CO_2 concentration at the last sampling position in the column (P10) was monitored throughout the test. When the concentration at P10 reached the concentration of the feed gas as measured at the start of the run, the system was switched from the adsorption mode to the counter-current regeneration mode, and the feed flow was stopped. The sample location was switched to the sample probe located immediately before MFC4 in Figure 7, which allowed for sampling of the desorbed gas. The flow rate of UHP N_2 purge gas was set to 3 L(STP)/min, and the heating tape voltage was adjusted to raise the column temperature to 75 °C. The average column temperature typically reached the target desorption temperature in 15-25 min for zeolite 13X. For the DEA impregnated PE-MCM-41 a lower heating rate was used to prevent a large temperature overshoot, hence the target desorption temperature was reached in 30-40 min. The flow of purge gas was used to remove the desorbed CO_2 and maintain the pressure in the column slightly above atmospheric pressure for sampling purposes. A low flow rate was chosen since it was more representative of the conditions used in industry, where the purified product gas is typically used to purge the column, leading to the need for low flow rates.

The CO_2 concentration of the desorption gas was monitored until it returned to the baseline zero value determined for UHP N_2 at the beginning of the run. This condition represented complete regeneration of the adsorbent. When studying the DEA impregnated adsorbent, the temperature was kept at 75 °C for the entire regeneration phase since it was not known if higher temperatures would cause the material to degrade too quickly in the flow-through configuration of the adsorption column. This isothermal condition was usually maintained for 120 min.

To reach complete regeneration for zeolite 13X, the temperature of the column had to be raised to approximately 230°C, and the purge flow rate had to be increased to 10 L(STP)/min. This was necessary because it was found that the desorption conditions selected for the DEA impregnated adsorbent were insufficient to regenerate zeolite 13X in a reasonable amount of time.

Once regeneration was complete, the heating tape was turned off, and the column was allowed to cool to room temperature under flowing UHP N_2. When the column was cool, the purge flow was stopped, and the column was completely isolated from the rest of the system by closing the manual valves located at the inlet and outlet of the column (see Figure 7).

3.7.4. Calculation of performance parameters

To quantitatively compare the performance of the adsorbents, the CO_2 adsorption capacity at breakthrough was calculated. The breakthrough adsorption capacity represents a true indication of the useful capacity of the material since, when used in industry, the column would typically be regenerated at the first sign of breakthrough. Calculation of this parameter was achieved using the following integral:

$$\int_{t=0}^{t=t_b} F_{o_{CO_2}} (1-C/C_o)dt$$

Numerical integration was carried out using the average of the relative concentration (C/C_o) over each one second time interval (i.e. the Trapezoid rule) from the time of initial introduction of CO_2 into the column ($t = 0$), to the breakthrough time ($t = t_b$). A breakthrough concentration of $C/C_o = 0.02$ was selected since it was fairly representative of values used in industry, and it was sufficiently large to be easily distinguishable from the natural fluctuations of the detection device.

Equilibrium was indicated when the inlet and outlet adsorbate concentrations were equal ($C/C_o = 1$), and the column temperature returned to room temperature. The equilibrium adsorption capacity was calculated to determine the fraction of the equilibrium capacity that was achieved prior to breakthrough. To obtain the equilibrium adsorption capacity, numerical integration was continued until equilibrium was reached ($t = t_e$):

$$\int_{t=0}^{t=t_e} F_{o_{CO_2}} (1 - C/C_o) dt$$

To illustrate the effect of the difference in breakthrough adsorption capacities on the size of the equipment, the extra column length and adsorbent mass required to achieve the same capture performance were calculated for the adsorbent with the lower capacity. This was achieved by assuming that the bed density and adsorption capacity were uniform throughout the entire length of the column and multiplying the actual length of the column by the ratio of the breakthrough capacities. The additional adsorbent mass was determined using the calculated additional bed length and the experimentally determined bed density.

4. Results and Discussion

4.1. Support Characterization

The porous supports used in the study were characterized to determine their structural properties prior to carrying out the impregnation procedure. The supports were characterized by nitrogen adsorption at -196 °C, and some samples were also characterized by X-ray diffraction. The results were used to determine:

- the effects of the pore size expansion procedure for the MCM-41 silicas
- the relative quality of materials synthesized in the two vessels
- the reproducibility of the synthesis procedure with the large vessel
- the structural characteristics of the supports used for the preliminary study

4.1.1. Effect of the pore expansion procedure

The pore expansion procedure was used to increase the pore diameter and pore volume of the MCM-41. The data in Figure 8 were obtained from nitrogen adsorption experiments with calcined MCM-41 and PE-MCM-41 synthesized in the small vessel. As shown in the adsorption isotherms (Figure 8A), the total amount of nitrogen adsorbed increased from roughly 630 to 1550 cm^3(STP)/g upon pore expansion. Conversion of the gas volume into the equivalent liquid volume revealed a change in pore volume from 1.0 to 2.4 cm^3/g. The onset of the sharp increase in the amount adsorbed, resulting from multilayer condensation in the mesopores, shifted from a partial pressure of approximately 0.30 to 0.70, indicating a significant increase in the pore diameter.

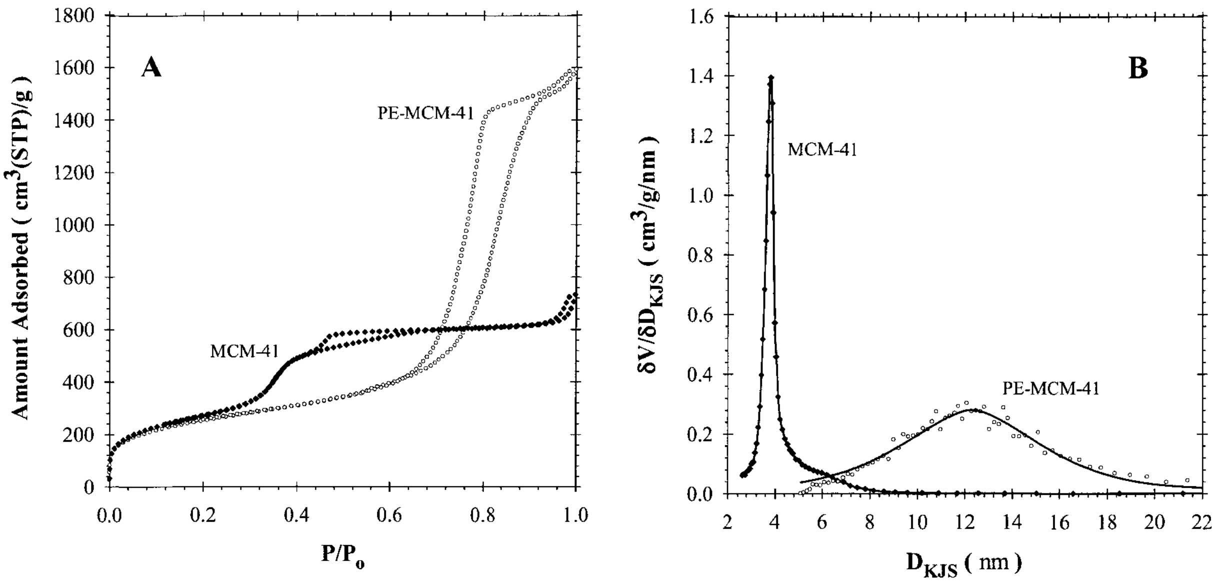

Figure 8: N_2 adsorption isotherms (A) and calculated KJS pore size distributions (B) for MCM-41 and PE-MCM-41 synthesized in the small vessel.

The locations of the peaks of the pore size distributions (Figure 8B) indicated that the average pore diameter of MCM-41 was 3.8 nm, while that of PE-MCM-41 was 12.3 nm. Further examination of Figure 8B revealed that the pore size distribution widened as the average pore diameter and pore volume increased, however, the distribution for PE-MCM-41 was still fairly narrow in comparison to other mesoporous supports. The nitrogen adsorption isotherms and pore size distributions shown in Figure 8 were consistent with results obtained by other groups using similar synthesis and expansion procedures (Sayari et al., 1998; Kruk et al., 2000; 2002).

4.1.2. Comparison of MCM-41 silicas synthesized in the small and large vessels

The properties of the material synthesized in the two vessels were compared to determine if the scale-up of the synthesis procedure had any effects on the quality of the silicas. Four random samples of MCM-41 and PE-MCM-41 obtained using the large vessel were characterized by nitrogen adsorption, and the results are summarized in Table 1.

Table 1: Structural characteristics of MCM-41 and PE-MCM-41 synthesized in the small and large vessels

Material		S_{BET} (m^2/g)		V (cm^3/g)		D_{KJS} (nm)	
		Avg.	σ	Avg.	σ	Avg.	σ
MCM-41	Small batch	990	-	1.0	-	3.8	-
	Large batch [a]	1155	28	1.0	0.07	3.6	0.10
PE-MCM-41	Small batch	899	-	2.4	-	12.3	-
	Large batch [a]	880	62	2.0	0.05	10.0	0.44

a) Average properties of four samples

Synthesis in the large vessel resulted in MCM-41 with higher surface area, similar pore volume, and smaller pores. The expansion procedure was somewhat less effective with the large vessel since both the pore diameter and the pore volume were smaller. These differences could possibly be due to a lower average synthesis temperature resulting from the larger mass of material, which required longer to reach the desired temperatures. As discussed by Kruk et al. (1999), a higher temperature during the initial synthesis step results in the partial decomposition of the cetyltrimethylammonium ion leading to the formation of N,N-dimethylhexadecylamine. The presence of this compound was shown to induce a moderate expansion of the pores. Likewise, to a certain extent, higher temperatures during expansion also result in larger pore diameters and pore volumes as described by Sayari et al. (1998).

Based on the information obtained from these sources, it is probable that the difference in structural properties of materials obtained from the two vessels could be minimized by ensuring that the same average temperature is achieved during the synthesis and expansion procedures. This could be accomplished for the large vessel by increasing the length of time for the heating step, or by increasing the oven temperature.

Increasing the ratio of DMDA to MCM-41 during expansion was also shown by Sayari (2000) and Kruk et al. (2000) to result in a larger pore diameter and pore volume of PE-MCM-41. Adjusting this ratio could minimize the differences in structural properties of the materials obtained from the two vessels. To definitively determine both the reason for the structural differences and an effective method to improve the structural properties, further studies using the large synthesis vessel would be required.

4.1.3. Large batch reproducibility

Two batches of MCM-41 were synthesized using the large vessel, and the resulting material underwent pore expansion in five separate batches. A preliminary evaluation of the repeatability of the synthesis procedure in the large vessel was carried out by examining the X-ray diffraction patterns for the two batches of MCM-41 and comparing nitrogen adsorption data obtained for several samples of MCM-41 and PE-MCM-41.

The MCM-41 structure and the XRD patterns for the two batches of MCM-41 are shown in Figure 9. XRD data were not obtained for the expanded product since it was shown by Sayari (2000) that PE-MCM-41 obtained by post-synthesis hydrothermal restructuring displayed no visible XRD pattern due to the loss structural order.

The resulting XRD patterns obtained during the current study were typical of high quality MCM-41. Three diffraction peaks were visible in the low diffraction angle range, indicating a highly ordered pore structure (Beck et al., 1992). Despite the fact that the pattern for the second synthesis batch was shifted vertically upwards for clarity, it was evident that the patterns obtained for the two batches were virtually identical. The only obvious difference in the patterns was the intensity of the first diffraction peak, which suggested a small difference in the degree of structural order between the two batches.

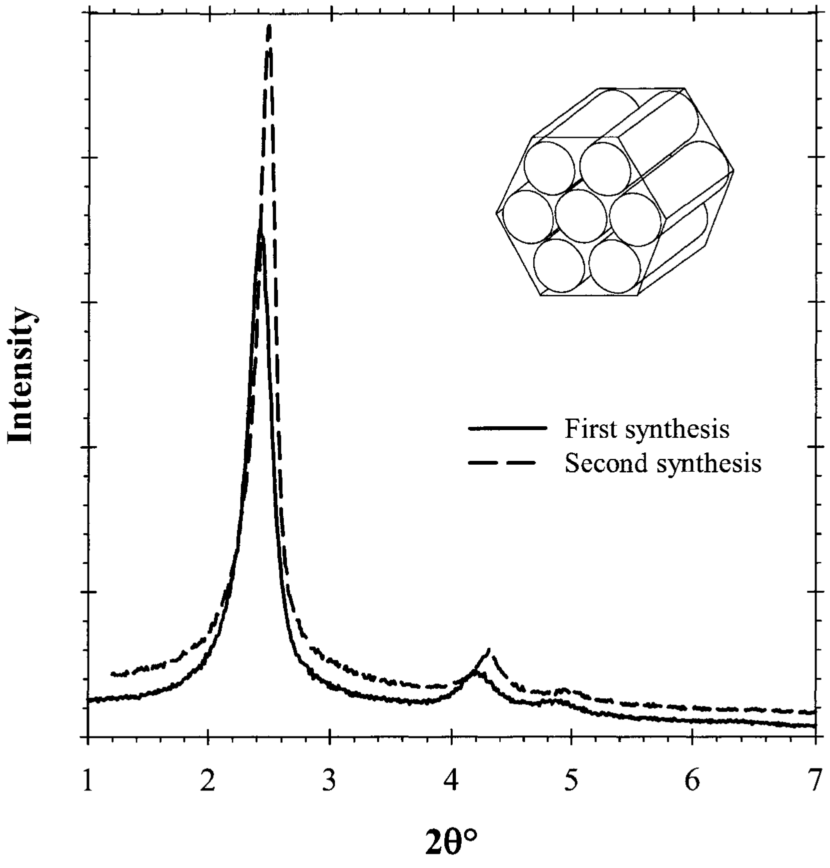

Figure 9: MCM-41 structure depiction and XRD patterns for two separate batches synthesized in the large vessel.

The results of nitrogen adsorption studies for several samples of both MCM-41 and PE-MCM-41 are shown in Figure 10. Since the nitrogen adsorption isotherms and pore size distributions overlapped closely, it was clear that only small differences in the structural characteristics existed between the different samples.

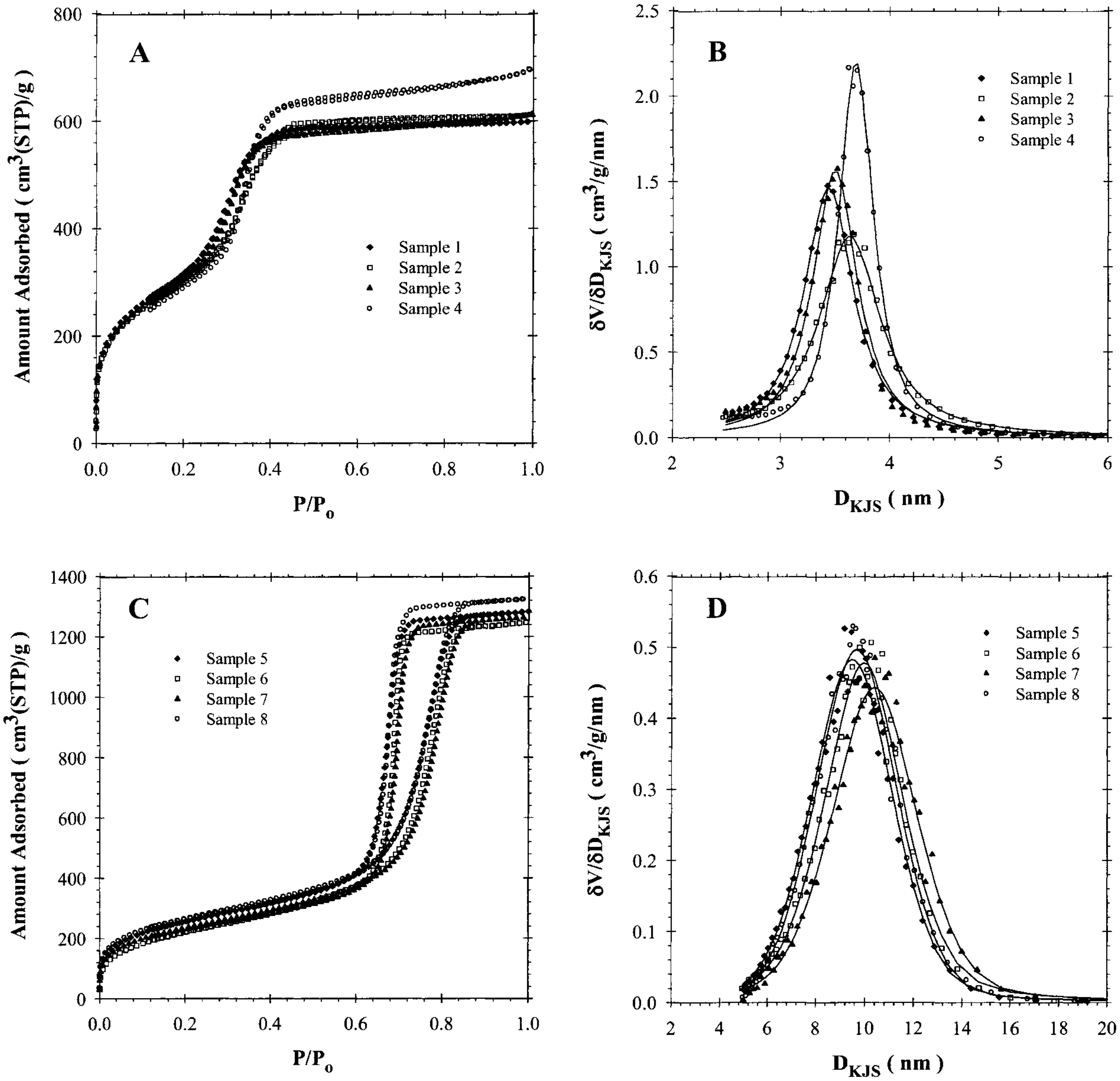

Figure 10: N_2 adsorption isotherms and calculated KJS pore size distributions for MCM-41 (A and B) and PE-MCM-41 (C and D) produced with the large vessel.

The XRD and nitrogen adsorption results comprised several sources of variability. The XRD patterns included the variability due to the synthesis and calcinations procedures, as well as the variability in the measurement procedure itself. The nitrogen adsorption results included the variability due to synthesis, expansion, calcination, and the nitrogen adsorption measurement. Considering the multiple sources of variability and the remarkable consistency of the data presented, it was concluded that synthesis with the large vessel showed good reproducibility. Based on this conclusion, it was decided that the use of the support synthesized in the large vessel was justified without requirements of further characterization.

4.1.4. Comparison to other supports

As discussed in section 3.3.2., in addition to MCM-41 and PE-MCM-41, activated carbon and silica gel were also examined as supports for amines. All the supports were characterized by nitrogen adsorption experiments. These results are summarized in Table 2.

Table 2: Structural characteristics of the materials examined as supports for amines

Support	S_{BET} (m^2/g)	V (cm^3/g)	D [a] (nm)
Activated carbon [b]	1640	1.5	< 2
Silica gel [c]	256	0.9	11-19
MCM-41	1175	1.0	3.6
PE-MCM-41	917	2.0	9.7

a) Reported by manufacturer for activated carbon
b) Norit Darco KB-B
c) Davisil Grade 643

The characterization results demonstrated that the supports covered a fairly wide range of structural properties. Activated carbon had a very high surface area, a fairly large pore volume, and pores in the micropore range. Silica gel had a pore volume similar to that of MCM-41, but a much lower surface area, and much larger pores. MCM-41 had a high surface area with a moderate pore volume and fairly small pores, while the PE-MCM-41 also had a fairly large surface area, but a much larger pore volume and average pore diameter compared to MCM-41.

The pore volumes of the various supports were of primary importance since these data were used to determine the quantity of amine required to achieve pore saturation during the impregnation procedure. By multiplying the density of the amine by the total pore volume of the support, the mass of amine that could be accommodated by the support was determined. The other structural properties, such as surface area and pore diameter, were used to gain insight into the adsorption performance of the resulting impregnated supports.

4.2. Preliminary Studies

Preliminary studies were carried out to determine a suitable alkanolamine for further investigation. The selection was based primarily on the physical characteristics of the amines, however, some samples were also prepared for brief adsorption studies. Once an appropriate amine was chosen, the four supports previously characterized were impregnated to pore saturation, and the adsorbents were tested for CO_2 adsorption capacity and uptake rate using the TGA.

4.2.1. Selection of an alkanolamine

When selecting an amine for impregnation of the solid support, several physical characteristics were considered. The important physical properties of the amines examined are found in Table 3. Four of the alkanolamines that were examined are commonly used in the absorption industry (MEA, DEA, MDEA, DGA), while AEAE was thought to be a promising compound due to the presence of two amine groups.

Table 3: Properties of some potential alkanolamines for impregnation of porous supports

Property [a]	MEA	DEA	AEAE	MDEA	DGA
Amine group [b] (number - type)	1 - 1°	1 - 2°	1 - 1° 1 - 2°	1 - 3°	1 - 1°
Molar mass (g/mol)	61.1	105.1	104.1	119.2	105.1
Vapour pressure @ 20 °C (Pa)	48.0	< 1.3	< 1.3	< 1.3	< 1.3
Boiling point @ 1.0 atm (°C)	171	268 [c]	243	247	221
Freezing point (°C)	11	28	-45	-21	-10
Absolute viscosity [d] @ 20 °C (Pa·s)	0.024	0.380	0.141	0.101	0.026

a) Data obtained from Kohl and Riesenfeld, 1985; Dow Product Information, 2001; 2003

b) 1° - primary = bonded to one carbon atom, 2° - secondary = bonded to two carbon atoms, etc.

c) Estimated - starts to decompose at approximately 200 °C (Dow Product Information, 2003)

d) 30 °C for DEA, 24 °C for DGA

The characteristics of MEA that were considered potentially valuable were the presence of a primary amine, a low molar mass, and a fairly high freezing point. Primary amines are often used in absorption systems due to the high heat of reaction, resulting in the formation of strong bonds with CO_2. The low molecular mass was viewed as advantageous because most alkanolamines have similar densities, hence those with a lower molar mass would allow for the impregnation of the porous supports with a larger number of amine groups.

A material with a high freezing point was considered advantageous since it could be expected to have a lower vapour pressure if operated close to the freezing point. In addition to preventing losses due to volatilization of the amine, a high freezing point would also prevent the compound from being displaced from the pores if the adsorbent was subjected to a large pressure gradient; as could be the case under conditions of high gas flow or during the agglomeration process.

A sample was prepared for adsorption testing by impregnating PE-MCM-41 with MEA. Upon testing with the TGA, it was found that although the adsorbent had a high adsorption capacity and rate, it was not thermally stable at the required regeneration conditions. This was attributed to the combination of a comparatively high amine vapour pressure and the presence of a primary amine group. Since primary amines have a high heat of reaction with CO_2, they require a higher temperature to break the bond between the two compounds. The higher temperature resulted in an increase in vaporization losses.

Aminoethylaminoethanol (AEAE) was considered for impregnation because it exhibited a lower vapour pressure than MEA, and it possessed two amine groups, which could potentially double the capacity of the resulting adsorbent. A sample was prepared using PE-MCM-41 as the support, and the adsorbent was tested for CO_2 adsorption capacity and rate using the TGA. Both the adsorption capacity and adsorption rate were very high, however, as with the MEA impregnated adsorbent, this material required regeneration at a temperature that resulted in high amine losses. Based on the findings for both MEA and AEAE, it was decided that DGA would also be unsuitable for impregnation due to the presence of a primary amine. Methyl-diethanolamine was also eliminated from the possible candidates for impregnation because of the presence of only a tertiary amine. As discovered from the literature and verified with some brief experiments, tertiary amines suffer from a low rate of reaction with CO_2, and are typically used with primary or secondary amines only to increase the selectivity for H_2S. Furthermore, MDEA exhibited both a high molar mass and a low freezing point; two undesirable properties that could result in a low amine content and an unstable adsorbent, respectively.

Examination of the properties of DEA revealed that the compound possessed several desirable characteristics that made it an excellent candidate for impregnation. The presence of a secondary amine group would reduce the temperature required for regeneration, yet still result in a strong bond with CO_2. The presence of two hydroxyl groups was expected to result in a low vapour pressure (Kohl and Riesenfeld, 1985), which is desirable since it would reduce vaporization losses. The high freezing point further supported the expectation that the material would not suffer from high volatilization losses. The high viscosity was also viewed as advantageous since it would limit the displacement of the compound from the pores under a large pressure gradient.

When a sample was prepared and tested, it was found that the adsorbent exhibited good adsorption capacity and adsorption rate and could be regenerated by heating to only 75 °C. When operated under these conditions, the material appeared to be very stable.

DEA was chosen for further impregnation studies based on its favourable physical characteristics and its performance during the preliminary adsorption studies. It addition, as DEA is a commonly used alkanolamine, it was readily available at a reasonably low cost, unlike some of the less-common polyamines examined by other researchers (Birbara and Nalette, 1994; 1996; 1997; Satyapal et al., 2001; Birbara et al., 2002; Contarini et al., 2003; Nalette et al., 2004).

4.2.2. Comparison of adsorption performance of different DEA impregnated supports at pore saturation

Based on the pore volumes determined from nitrogen adsorption experiments, the various supports under consideration were impregnated with the quantity of DEA that was required to fully saturate the pores. The samples were then tested with a dry mixture of 5% CO_2 in N_2 to determine the adsorption capacity and adsorption rate, and decomposed in dry N_2 to determine the amine content of the adsorbents. The results are presented in Table 4.

Table 4: Adsorption parameters for various supports impregnated with DEA to pore saturation

Support	Amine loading [a] (g_{DEA}/g_{sup})	Amine content ($mmol/g_{ads}$)	CO_2 capacity [b] ($mmol/g_{ads}$)	CO_2 uptake rate ($mmol/g_{ads}/min$)	CO_2/DEA ratio (mmol/mmol)
Activated carbon	1.62	5.41	1.51	0.95	0.28
Silica gel	1.03	4.61	1.88	0.69	0.41
MCM-41	1.13	4.49	1.26	0.57	0.28
PE-MCM-41	2.22	6.34	2.36	0.54	0.37

a) Based on amount of DEA added during the impregnation procedure
b) Obtained with dry 5% CO_2 in N_2

The results showed that the highest adsorption capacity was obtained with the impregnated PE-MCM-41, while the highest adsorption rate was obtained with the impregnated activated carbon. Examination of the CO_2/DEA ratios revealed that this quantity decreased with increasing support surface area. This was demonstrated by the low ratios obtained for activated carbon and MCM-41, the supports with the highest surface areas, while silica gel, which had the lowest surface area, obtained the highest ratio. These observations suggested that the DEA could have interacted with the surface of the support through a strong adsorptive bond, or possibly a chemical reaction with surface species. This interaction may have rendered a portion of the amine inactive for CO_2 adsorption, which also explained the failure of any sample to achieve the stoichiometric maximum CO_2/DEA ratio of 0.5.

While the impregnated activated carbon exhibited the highest adsorption rate, it did not result in efficient use of the amine, since it exhibited one of the lowest CO_2/DEA ratios. The high adsorption rate could be explained by the deposition of a larger quantity of the amine on the surface of the particles due to the small pores of the support. Although the quantity of amine that was added was only sufficient to saturate the pores, small pores are more likely to suffer from blockage. This would lead to the deposition of some amine on the outer surface of the particles before exceeding the amine content required for saturation. If a small quantity of amine was deposited on the surface of the particles, this amine would be highly dispersed over a large surface area and would be easily accessible to the gas molecules, resulting in a high rate of adsorption. Pore blockage, however, would eventually hinder the performance of the adsorbent, as it would limit the maximum quantity of amine that could be retained by the support before the adsorbent developed an unsuitable texture.

Silica gel outperformed MCM-41 despite the similarities in pore volume and amine content. This support was found to be promising, considering that it resulted in the most effective use of the amine, and suppliers report that the material can be obtained with a pore volume of up to 2.5 cm^3/g.

PE-MCM-41 was chosen for further studies since it attained the highest adsorption capacity, while still maintaining a reasonably high adsorption rate and achieving a high

CO_2/DEA ratio. It was viewed as the most promising support since it has been synthesized with a pore volume up to 3.6 cm^3/g (Kruk et al., 2002).

4.3. TGA Adsorption Studies with DEA Impregnated PE-MCM-41

DEA impregnated PE-MCM-41 was studied more closely to improve the performance of the adsorbent compared to the pore saturated material previously discussed. The effects of amine content, impregnation solvent, gas phase moisture, and the presence of methane were examined. The performance of the adsorbent was compared to that of zeolite 13X and other solid supported amines.

4.3.1. CO_2 Adsorption capacity and rate as a function of amine content for samples impregnated with water as the impregnation solvent

The CO_2 adsorption capacity and rate were evaluated as functions of the amine content using samples impregnated with water as the solvent. As shown in Figure 11A, the adsorption capacity of the bare support was actually slightly higher than that of the first impregnated sample. This was most likely due to an increase in weight of the material, with no accompanying increase in adsorption capacity. It was speculated that this was caused by deactivation of the small quantity of amine by interactions with the surface.

After the initial decrease, the capacity increased at a fairly constant rate with increasing amine content. This trend continued even as the amine content exceeded the amount required for pore saturation (approximately 6.5 mmol DEA/g_{ads}). A maximum adsorption capacity of approximately 2.7 mmol CO_2/g_{ads} was reached at an amine content of 7.3 mmol DEA/g_{ads}, and the adsorption capacity decreased after this point. This apparent decrease in capacity was found to be related to the adsorption rate, as will be discussed shortly.

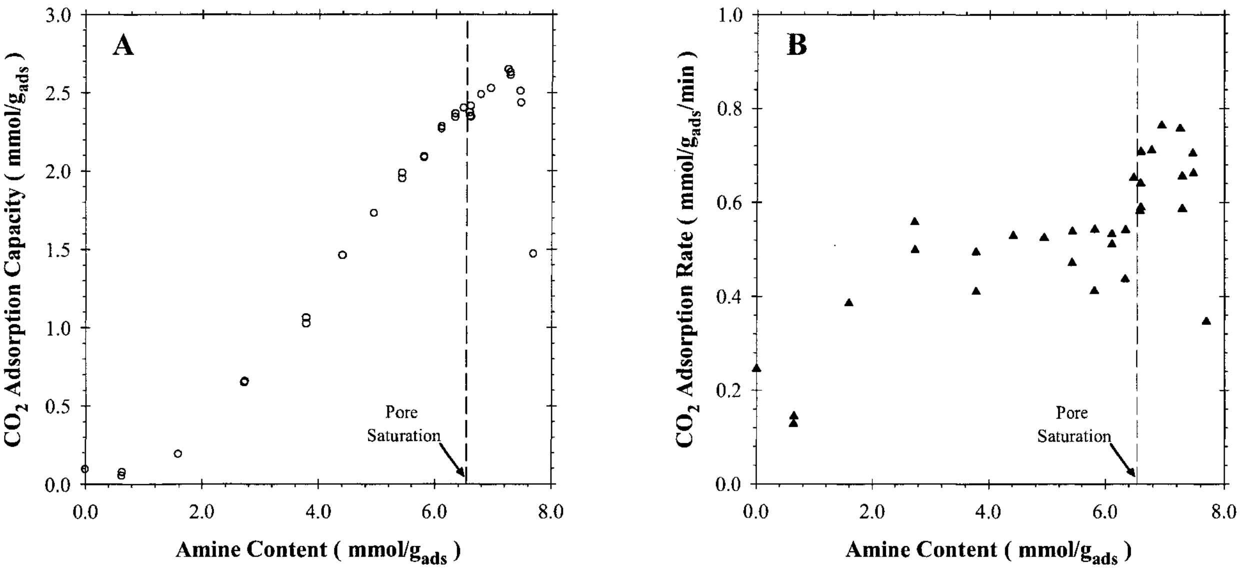

Figure 11: CO_2 adsorption capacity (A) and rate (B) as functions of DEA content on PE-MCM-41 obtained with dry 5% CO_2 in N_2.

The adsorption rate, shown in Figure 11B, also dropped initially for the same reason discussed for the adsorption capacity. It then increased to a value between 0.40 and 0.55 mmol CO_2/g_{ads}/min, which remained fairly constant until the amine content reached the vicinity of pore saturation. When pore saturation was exceeded, there was a sudden increase in the rate to a maximum of approximately 0.76 mmol CO_2/g_{ads}/min at an amine content between 6.9-7.3 mmol DEA/g_{ads}. The increase was attributed to the deposition of the small quantity of excess amine on the exterior surfaces of the particles, as discussed previously for the impregnated activated carbon. As the amine content was increased further, the adsorption rate decreased due to the accumulation of a large amount of excess amine on the exterior surface of the particles. This caused the particles to agglomerate, which likely hindered the diffusion of the gas molecules to the majority of the adsorption sites. This contention was supported by observations of the texture of the impregnated materials, which changed gradually from a free-flowing powder to an agglomerated powder as the amine content exceeded pore saturation.

The decrease in adsorption rate consequently resulted in the apparent drop in adsorption capacity at high amine loadings, since it caused the uptake of CO_2 to proceed slowly after initially reaching a reasonable maximum rate of adsorption. As described previously in section 3.6.1., to ensure consistency between samples, the adsorption capacity was calculated after one hour of exposure to the gas mixture. Adsorbents with very high amine contents were unable to reach equilibrium during this time, hence the reported adsorption capacity was lower than the actual equilibrium capacity.

Although it appeared from the figure that the decrease in capacity and rate occurred over a very narrow range of amine contents, it was noted that in this region, the adsorbents were asymptotically approaching the amine content of pure DEA (9.5 mmol DEA/g_{ads}). For this reason, a large increase in the ratio of the mass of DEA to the mass of the solid support was represented by a small increase in the amine content of the adsorbent.

Included in the data shown in Figure 11 are the results of several replicate tests that were conducted. The data indicated that both the adsorption capacity and amine content measurements showed good repeatability, but the adsorption rate measurements had a higher degree of variability. This was due to the influence of the method of loading the material into the TGA sample pan, and described previously in section 3.5.3..

4.3.2. Amine deactivation

According to stoichiometry under dry conditions, secondary amines should react with CO_2 at a molar ratio of 0.5 mol CO_2/mol amine. Figure 12 shows the calculated CO_2/DEA ratios for the samples prepared with water as the impregnation solvent.

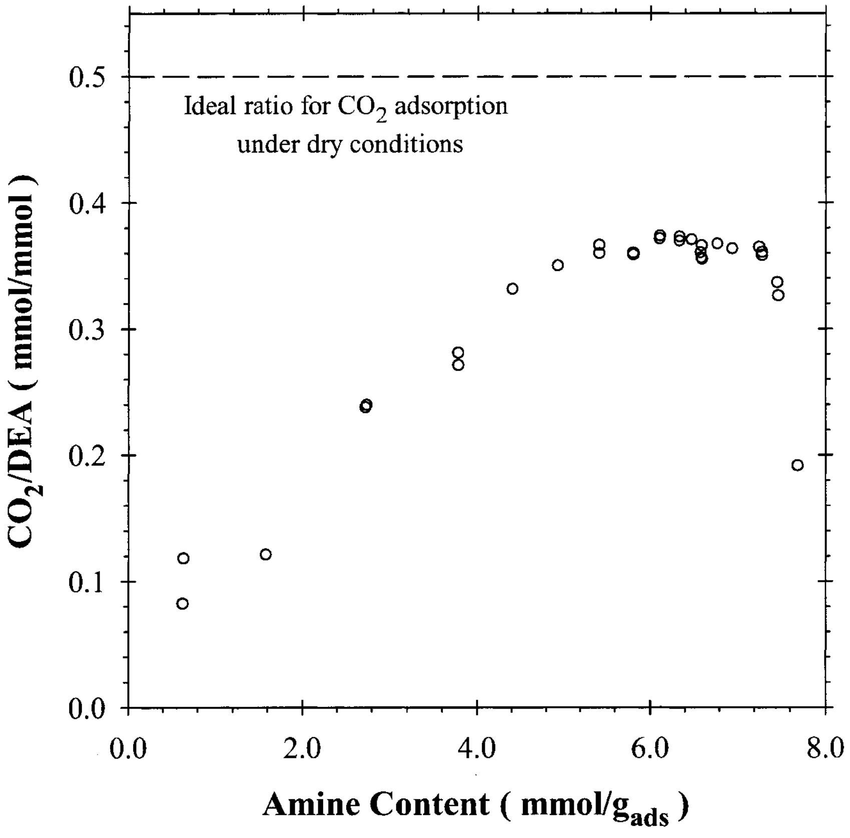

Figure 12: CO_2/DEA ratio obtained with dry 5% CO_2 in N_2 as a function of the DEA content of PE-MCM-41 impregnated with DEA.

The ratio was found to increase fairly steadily in the region of low amine content, and plateau at a value of approximately 0.37 in the region of amine contents between 5.4-7.3 mmol DEA/g_{ads}. The ratio then decreased since the CO_2 adsorption capacity decreased for reasons previously mentioned.

The reason for the lower than stoichiometric CO_2/DEA ratios was mentioned briefly in regards to the preliminary results. It was hypothesized that this was related to an interaction with the surface of the support that rendered a portion of the amine inactive. Examination of the thermal decomposition data, an example of which is shown in Figure 13, supported this contention. The data revealed that the loss of amine occurred in two separate stages; one at temperatures below 280°C, and a secondary loss that occurred at temperatures greater than 300 °C.

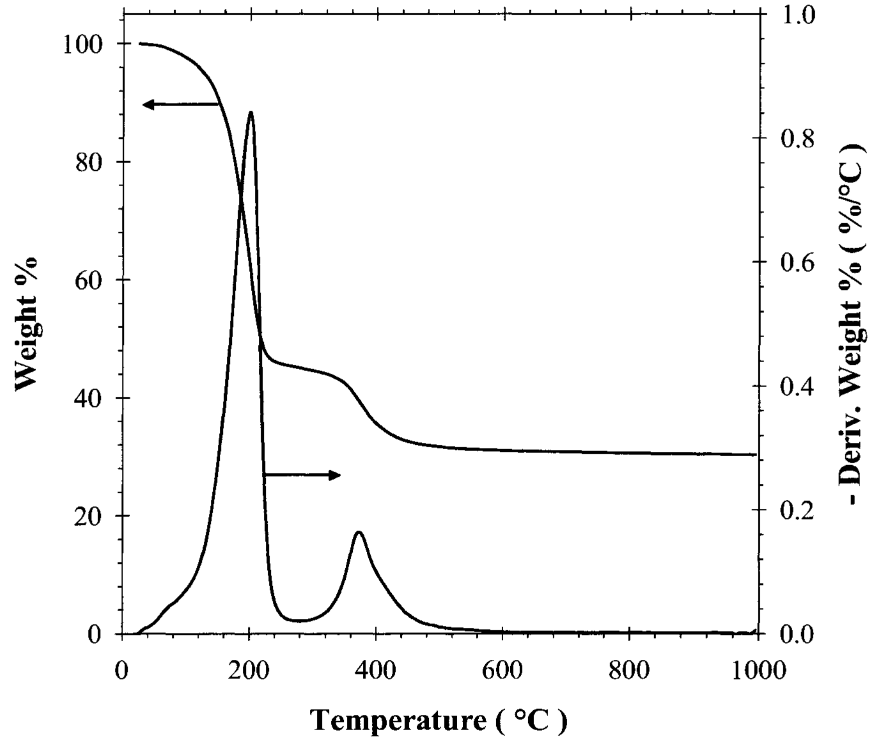

Figure 13: Thermal decomposition profile for sample 6.34-DEA-H_2O(PE-MCM-41) using a temperature ramp of 10 °C/min in dry N_2.

DEA decomposes at a temperature below its estimated boiling point of 268 °C (Dow Product Information, 2003), however, the decomposition profiles indicated that some amine was lost at temperatures well above this value. For this to occur, the amine must have been retained in the support by means of a strong interaction with the surface. It is likely that this interaction occurred between a surface species and the amine group of DEA, which could have resulted in the amine being incapable of further reaction with CO_2.

To probe the adsorption properties of the material lost at high temperatures, sample 6.60-DEA-H_2O(PE-MCM-41) was tested using the standard procedure, and a CO_2 capacity of 2.41 mmol CO_2/g_{ads} was obtained (CO_2/DEA = 0.37). The same sample was then rapidly heated in nitrogen to 250 °C and held at this temperature for 15 minutes, during which time the sample mass decreased by 54.1% (representing a loss of 5.05 mmol DEA/g_{ads}), and the mass appeared to stabilize. The sample was then cooled to 25 °C and exposed to the dry mixture of 5% CO_2 in N_2. The CO_2 capacity was found to be only 0.10 mmol CO_2/g_{ads} (CO_2/DEA = 0.07). Upon continuation of the decomposition, the sample lost an additional 16.6% of its mass (or 1.55 mmol DEA/g_{ads}). This suggested that the DEA decomposing at the higher temperature was almost completely deactivated, which accounted for the lower than stoichiometric CO_2/DEA ratios.

Further evidence of amine deactivation was found by noting that the CO_2/DEA ratios depicted in Figure 12 increased with increasing content in the region of low amine content. A possible reason for the lower CO_2/DEA ratios in this region was discovered by examining the ratio of the secondary, high temperature loss to the total mass loss upon decomposition. These results are presented in Figure 14.

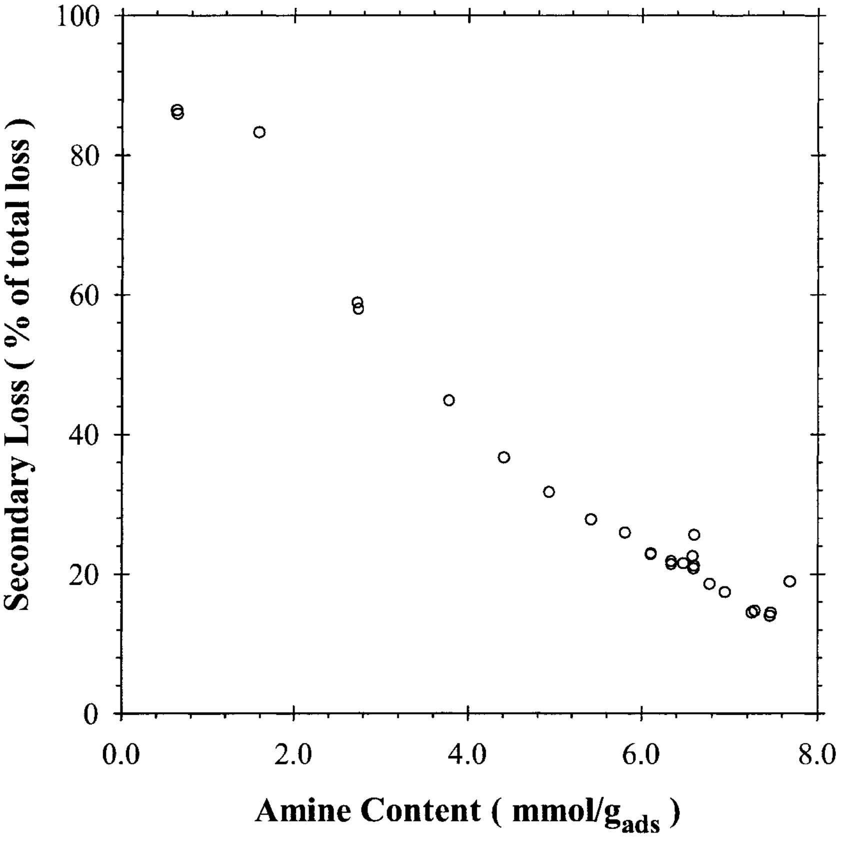

Figure 14: Secondary mass loss as a function of DEA content for samples prepared with water as the impregnation solvent.

The secondary loss decreased as the amine content increased. If the material lost at the higher temperature was indeed incapable of reacting with CO_2, the results from Figure 14 suggested that the lower CO_2/DEA ratios at low amine content were the result of a higher portion of inactive amine. For samples prepared at low amine contents, the ratio of available surface area to amine was large, increasing the likelihood of interaction. This explanation was found to be consistent with the results of earlier experiments with the other supports, where it was noted that the CO_2/DEA ratio decreased with increasing support surface area.

In order to confirm the existence of an interaction between the silica surface and DEA molecules, a study using Fourrier-Transform Infrared (FT-IR) spectroscopy was considered, however, adequate evidence confirming the interaction of amine groups with surface hydroxyl species was found in the literature. Iu and Thomas (1990; 1993) described the adsorption of several secondary and tertiary amines onto silica gel surfaces through hydrogen bonding with silanol groups and surface bonded water. Davydov (2000) discussed the formation of strong hydrogen bonds between the silanol groups and a primary amine, ethelenediamine, resulting in the formation of an adsorbed layer suitable for the separation of carbohydrates from aqueous solutions. Kim et al. (2005a; 2005b) conducted detailed studies of the adsorptive interaction between a tertiary amine, triethylenediamine, and the hydroxyl groups of high surface area γ-Al_2O_3. The authors showed through FT-IR and temperature programmed desorption studies that a significant amount of amine was adsorbed on the surface at a temperature of 27 °C, and the strong bonding resulted in desorption which continued to temperatures of over 400 °C.

4.3.3. The effect of the impregnation solvent

During the impregnation studies conducted with water as the solvent, it was noticed that samples with very high amine contents required a considerably longer time to dry. To decrease the time required for impregnation, the solvent was changed from water to ethanol. The samples were analyzed using the TGA with a dry mixture of 5% CO_2 in N_2, and the results were compared to results obtained for the samples impregnated with water as the solvent. The comparative data are presented in Table 5.

Table 5: Comparison of DEA impregnated PE-MCM-41 using water or ethanol as the impregnation solvent

Solvent	Amine loading [a] (g_{DEA}/g_{sup})	Amine content ($mmol/g_{ads}$)	CO_2 capacity [b] ($mmol/g_{ads}$)	CO_2/DEA ratio (mmol/mmol)	Secondary loss (% of total)
water	2.22	6.34	2.36	0.37	14.5
ethanol	2.25	6.42	2.54	0.40	13.5
water	2.50	6.60	2.41	0.37	14.9
ethanol	2.50	6.68	2.64	0.40	12.6
water	2.75	6.78	2.49	0.37	13.4
ethanol	2.72	6.84	2.74	0.40	11.9
water	2.99	6.95	2.53	0.36	12.9
ethanol	3.00	6.98	2.81	0.40	10.8
water	3.51	7.26	2.65	0.37	11.1
ethanol	3.48	7.31	2.93	0.40	9.7
water	4.13	7.47	2.51	0.34	11.0
ethanol	3.98	7.54	2.76	0.37	9.2

a) Based on amount of DEA added during impregnation procedure
b) Obtained with dry 5% CO_2 in N_2

By changing the solvent from water to the more volatile ethanol, the time required for impregnation was decreased by a factor of four. In addition, for the same sample preparation, the amount of DEA retained by the support increased slightly (ca. 1%), whereas the CO_2 adsorption capacity of the impregnated material increased significantly (ca. 10%). The adsorption rate of these samples also increased by approximately 10%, which was likely due to the increase in adsorption capacity.

The increase in adsorption capacity resulted in a noticeable increase in the CO_2/DEA ratio, suggesting that the use of ethanol as a solvent resulted in a larger fraction of amine being available for CO_2 adsorption. Examination of the ratio of the secondary loss to the total mass loss revealed that this quantity was lower for the samples impregnated with ethanol. This could explain the higher CO_2/DEA ratio, since it suggested that a lower portion of the amine was deactivated in theses samples.

Due to the lower impregnation time and improved performance obtained using ethanol during impregnation, this solvent was used for the preparation of samples for further studies. Based on the adsorption capacity, uptake rate, CO_2/DEA ratio, and physical texture of the samples impregnated with ethanol as the solvent, it was found that the optimum combination of these parameters was obtained with the sample impregnated at a ratio of 3.0 g_{DEA}/g_{sup}. When the amine loading ratio exceeded this value, the powder began to change texture dramatically from a fairly free flowing material to an agglomerated clumpy material, which made it difficult to work with and resulted in an increase in drying time. Samples impregnated at the chosen ratio resulted in an adsorbent with an amine content of approximately 7.0 mmol DEA/g_{ads}, which was used for a comparative study with a commonly employed CO_2 adsorbent, zeolite 13X.

4.3.4. Comparison of the performance of the impregnated adsorbent and zeolite 13X

CO_2 adsorption isotherms were obtained with the TGA for sample 6.98-DEA-Et(PE-MCM-41) and zeolite 13X at 25 °C. The standard adsorption test method described previously was used with various concentrations of CO_2 in nitrogen. The resulting isotherms are shown in Figure 15. The data indicated that under dry conditions, the amine impregnated material had a higher adsorption capacity than zeolite 13X below a partial pressure of approximately 0.15 atm. This behaviour was the result of the strong chemisorptive interaction between DEA and

CO_2 molecules which occurred even at very low partial pressures. This type of adsorption was absent with zeolite 13X since CO_2 molecules are known to be primarily physisorbed to its surface through electrostatic interactions. As the partial pressure of CO_2 increased, the adsorption capacity of the amine impregnated material was limited by stoichiometry as discussed earlier, hence only marginal increases in CO_2 adsorption occurred for large increases in CO_2 partial pressure.

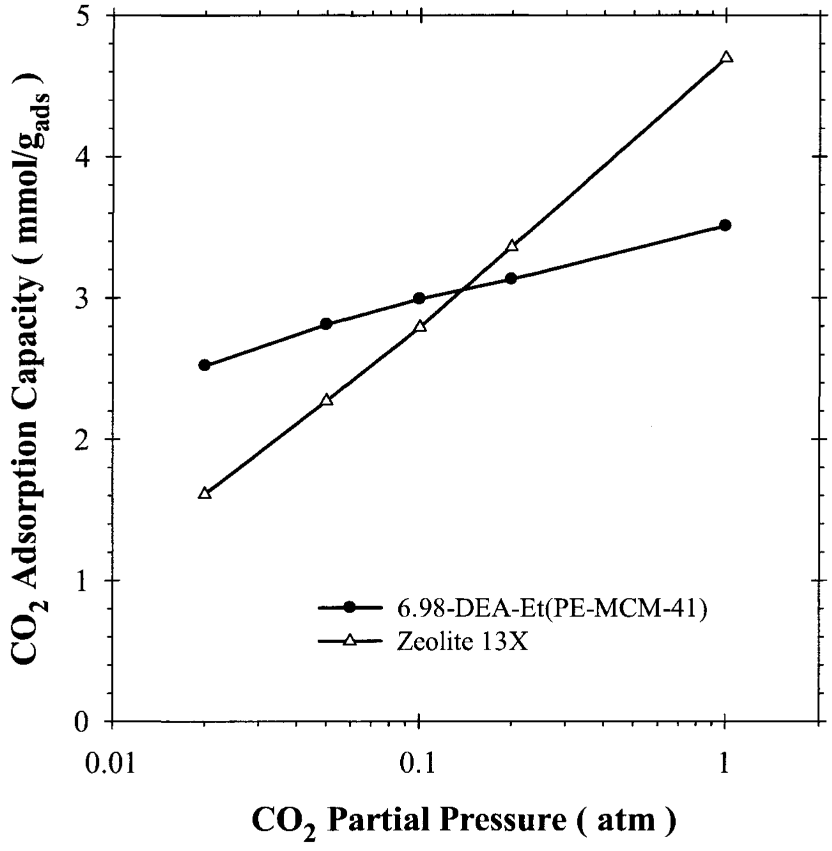

Figure 15: CO_2 adsorption isotherms (25 °C) for 6.98-DEA-Et(PE-MCM-41) and zeolite 13X.

The adsorption behaviour of the impregnated material suggested that it would be a promising adsorbent for applications that require the removal of CO_2 at low partial pressures. When zeolite 13X is used for such applications, it is necessary to compress the feed gas to elevated pressure in order to achieve a high adsorption capacity, as is commonly done for the pre-purification of air prior to cryogenic separation. A material with high adsorption capacity in the low partial pressure range would reduce the cost associated with the compression step.

The adsorption kinetics of the two materials was also compared by testing the adsorbents under identical conditions using the TGA. Figure 16 shows the adsorption profiles obtained with a dry mixture of 5% CO_2 in N_2 at 25 °C and the desorption profiles obtained with dry N_2 at 75 °C for both 6.98-DEA-Et(PE-MCM-41) and zeolite 13X. The two materials showed similar favourable adsorption kinetics since both reached a maximum adsorption rate of 1.0 mmol CO_2/g_{ads}. Due partly to the higher adsorption capacity of the impregnated material, it required 12 minutes to reach 95% of the equilibrium capacity, while zeolite 13X required only 6 minutes. This lag in the uptake by the impregnated material was also possibly the result of diffusional resistance through the amine filled pores.

Examination of the desorption portion of the cycle revealed one of the main advantages of the amine impregnated material. Upon heating to 75 °C in nitrogen, the amine impregnated material quickly desorbed all the CO_2, whereas zeolite 13X showed evidence of incomplete desorption since the mass did not return to the original pre-exposure mass. This was expected since zeolite 13X is typically regenerated at temperatures above 200 °C when used for the removal of CO_2 (Sircar and Kratz, 1981).

In an industrial setting, incomplete desorption would reduce the working capacity of the adsorption bed, since CO_2 would accumulate on the adsorbent from cycle to cycle. This would result in reduced process throughput, which is undesirable for any industrial process. According to these results, the DEA impregnated material should allow for more efficient use of the length of an adsorption bed when employed at the industrial scale since it can be regenerated more easily. Under these conditions, the desorption dynamics and energy requirements favour the amine impregnated material in comparison to zeolite 13X. These attributes could result in lower operational costs and increased amounts of processed gas for a given adsorption bed.

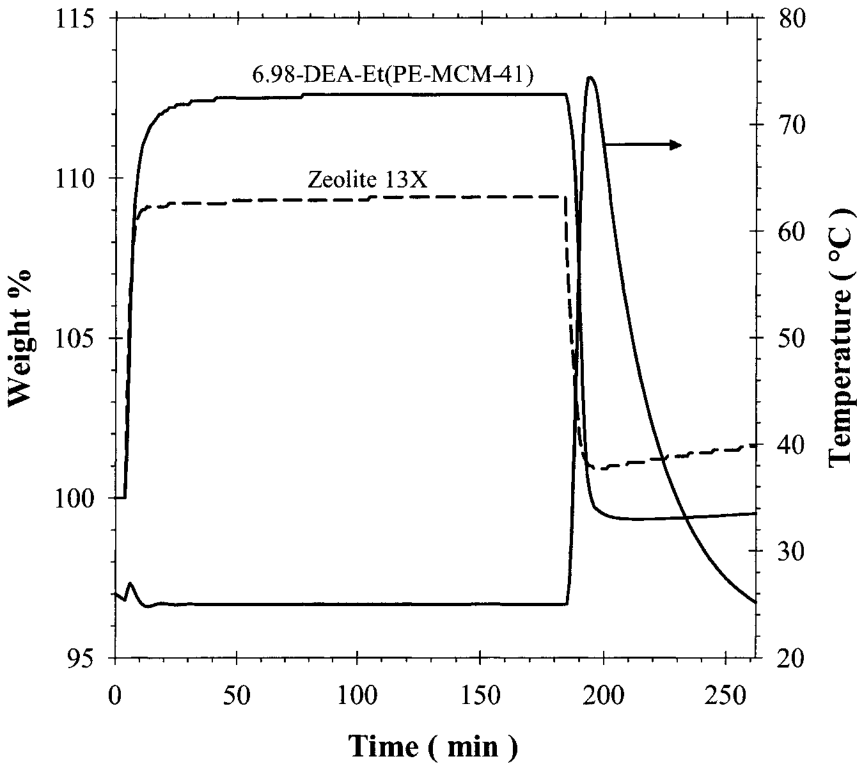

Figure 16: Adsorption – desorption profile obtained with dry 5% CO_2 in N_2 for 6.98-DEA-Et(PE-MCM-41) and zeolite 13X.

4.3.5. Comparison of the performance of DEA impregnated PE-MCM-41 with other solid supported amines

As discussed in the introduction, several other groups have examined the use of porous solids and amines to develop adsorbents for CO_2. A summary of the adsorption capacities obtained during the current study and other studies is found in Table 6. Examination of the table revealed that the CO_2 adsorption capacities of the solid supported amines developed by other groups were all significantly lower than that of the adsorbent developed in the current study for the same CO_2 partial pressure.

In the case of the impregnated materials, represented in the first five rows of the table, although the amine contents were fairly high, they were still far below the level achieved during the current study. This was likely due to the very high pore volume of the PE-MCM-41, which allowed for the occlusion of a larger quantity of DEA in the pores of the support.

The grafted materials (Leal et al., 1992; 1995; Huang et al., 2003; Gray et al., 2004) all had very low amine contents, which were limited by the quantity of reactive species on the surface of the supports.

Table 6: Comparison of the CO_2 adsorption capacities of selected solid supported amines

Source	Support / amine	Amine content (mmol/g_{ads})	CO_2 pressure (atm)	CO_2 capacity (mmol/g_{ads})	Conditions [a]
Zinnen et al., 1989	Carbon molecular sieve / DEA	4.8	0.05	1.4	Dry, CO_2 CV isotherm, 23 °C
Chang, 2003 [b]	Carbon molecular sieve / DEA	5.2	0.05	2.2	Dry, CO_2 CV isotherm, 23 °C
Satyapal et al., 2001	Polymethyl methacrylate / PEI, PEG	N/A [c]	0.02	0.9	Humid, CO_2 in N_2, 21 °C
Xu et al., 2002; 2003	MCM-41 / PEI	N/A [c]	1.00	3.0	Dry, pure CO_2, 75 °C
Contarini et al., 2003	Alumina / DEA	4.5	1.00	2.0	Dry, pure CO_2, 25 °C
Leal et al., 1992; 1995	Silica gel / APTES	0.6	0.10	0.3	Dry, CO_2 CV isotherm, 23 °C
		0.6	1.00	0.6	
Huang et al., 2003	MCM-48 / APTES	2.3	0.05	1.1	Dry, CO_2 in He, 25 °C
		2.3	1.00	2.2	Dry, CO_2 CV isotherm, 25 °C
Gray et al., 2004	SBA-15 / APTES	1.2	0.10	2.0	Humid, CO_2 in He, 25 °C
Current study	PE-MCM-41 / DEA	7.0	0.02	2.5	Dry, CO_2 in N_2, 25 °C
			0.05	2.8	
			0.10	3.0	
			1.00	3.5	

a) CV isotherm = constant volume isotherm, pure CO_2 at reduced pressure

b) Amine content, CO_2 partial pressure, and CO_2 capacity were estimated from the data in the text

c) N/A = data not available

4.3.6. Capacity for CO_2 in the presence of moisture

Since CO_2 is frequently found in gas streams containing water vapour, a highly desirable characteristic of a CO_2 adsorbent is tolerance to moisture. Although the adsorption isotherm obtained under dry conditions demonstrated that zeolite 13X exhibited a high capacity for CO_2 especially at elevated partial pressure, it is known that the adsorbent cannot tolerate moisture. Upon exposure to moisture, high temperature regeneration is required to recover the initial CO_2 adsorption capacity. As discussed in section 2.2.1.2., moisture should actually increase the CO_2 adsorption capacity of the amine impregnated material by allowing the formation of bicarbonate ions instead of carbamate ions, resulting in a doubling of the CO_2/DEA stoichiometric ratio.

The effect of moisture on both adsorbents was examined, as described earlier, by exposing the activated samples to a moist stream of N_2 (28% relative humidity at 25 °C). Once the uptake of moisture ceased, the samples were exposed to a stream of 5% CO_2 in N_2 under the same humidity conditions. Sample 6.98-DEA-Et(PE-MCM-41) adsorbed 5.38 mmol H_2O/g_{ads} and was still capable of adsorbing 2.85 mmol CO_2/g_{ads}. Zeolite 13X adsorbed 15.11 mmol H_2O/g_{ads} but could subsequently only adsorb 0.09 mmol CO_2/g_{ads}.

The results demonstrated that the impregnated material was capable of independently adsorbing H_2O and CO_2. This suggested that while the CO_2 molecules reacted with the amine group, the adsorption of H_2O either occurred through the interaction with other functional groups, or that the interaction of H_2O with the amine group did not prevent the adsorption of CO_2 at the chosen experimental conditions. With zeolite 13X, the same sites that interacted with CO_2 also interacted with H_2O, thereby preventing the adsorption of both compounds simultaneously.

Some researchers (Leal et al., 1992; Birbara et al., 1994; Huang et al., 2003) found that moisture greatly enhanced the performance of amine-containing adsorbents suggesting that H_2O interacted with the amine and CO_2 by the mechanism discussed in section 2.2.1.2.. Since no enhancement in CO_2 adsorption capacity was found under the experimental conditions used for the current study, it is possible that an alternate mechanism was responsible for the adsorption of H_2O. This mechanism could have occurred through the formation of hydrogen bonds between the water molecules and the hydroxyl groups of DEA. If hydrogen bonding was more thermodynamically favourable than the interaction with the amine group, it would prevent, or delay the onset of the former interaction, explaining the lack of enhancement of the CO_2 adsorption capacity. This explanation is likely since the hydrolysis of the carbamate is known to be a relatively slow process, whereas interactions relying on the hydrogen bonding between the hydroxyl group and water (i.e. dissolution of DEA in water) occur quickly.

Although the presence of moisture did not enhance the performance of the amine impregnated material as suggested in the literature, the results showed that this material drastically outperformed zeolite 13X under the humidity conditions of the current study. This suggests that gas streams to be treated with DEA impregnated PE-MCM-41 would not require stringent moisture control, whereas extensive drying is necessary in the case of zeolite 13X.

An adsorbent that is capable of adsorbing CO_2 in the presence of H_2O, or is capable of adsorbing both compounds, could be employed for several applications. Some of these applications include: the pre-purification of air prior to cryogenic distillation, emergency SCBAs and enclosed habitable environments, removal of CO_2 from flue gas, the purification of natural gas, and purification of air for fuel cells.

4.3.7. Capacity for CO_2 in the presence of methane

To simulate the removal of CO_2 from natural gas, CO_2 adsorption tests were conducted with the TGA in the presence of methane, as described in section 3.6.5.. A baseline adsorption test was conducted during which sample 6.98-DEA-Et(PE-MCM-41) was exposed to a dry gas mixture composed of 10% Ar in CH_4. The small increase in mass was attributed to the adsorption of methane, and a methane adsorption capacity of 0.16 mmol CH_4/g_{ads} was calculated. The sample was then exposed to a dry mixture composed of 2% CO_2 and 8% Ar in CH_4. After subtracting the mass gain due to the adsorption of methane as determined from the baseline test, the CO_2 adsorption capacity was found to be 2.43 mmol CO_2/g_{ads}. The capacity was compared to the capacity obtained with a dry mixture of 2% CO_2 in N_2 as shown in Figure 15, which was slightly higher (2.52 mmol CO_2/g_{ads}). Based on these preliminary results, it appeared that the presence of methane had a small effect on the CO_2 adsorption capacity of the impregnated material, however, further replicate tests would be required to verify the significance of this small effect.

Assuming that the measured difference in the adsorption capacity accurately represented the effect of methane, this indicated that the selectivity of the separation, although high, would not be perfect. Under these circumstances, some methane would be lost during the processing of natural gas in an industrial setting. Also, the CO_2 adsorption capacity of the adsorbent would be slightly lower than in a nitrogen atmosphere. These results demonstrated the importance of further studies pertaining to specific applications if the material were to be used for industrial separations.

4.4. Stability Studies

In order for an adsorbent to be employed industrially, it must provide long term, stable performance. To evaluate the stability of the adsorption capacity for both the impregnated material and zeolite 13X, several adsorption-desorption cycles were carried out in succession using the TGA and a dry mixture of 5% CO_2 in N_2 as described in section 3.6.6.. Based on the results of this study, it was decided to also examine the stability of the support to determine if it was feasible to re-impregnate the support. This was achieved by calcining the impregnated adsorbents to remove the DEA, then characterizing the remaining support by nitrogen adsorption experiments.

4.4.1. CO_2 adsorption capacity stability

The cyclic adsorption performance of 6.98-DEA-Et(PE-MCM-41) is shown in Figure 17 along with results obtained for zeolite 13X. The results of Xu et al. (2002) for MCM-41 impregnated with PEI at 50 wt% (MCM-41-PEI-50) are also shown for comparison purposes. The performance of the DEA impregnated adsorbent was fairly stable, with only a minor decrease in adsorption capacity of approximately 0.08 mmol CO_2/g_{ads} (i.e. 2.8% of the initial capacity) over the course of six adsorption-desorption cycles. The sample showed a steady rate of decrease in capacity, and after twenty-one cycles, the adsorption capacity decreased by 0.28 mmol CO_2/g_{ads} (i.e. 9.9% of the initial capacity). The loss in capacity was believed to be due to a slow loss of DEA, which appeared in the TGA data as a loss in adsorbent mass over time. The presence of DEA, however, could not be detected by the mass spectrometer. According to Satyapal et al. (2001), the addition of PEG to their polymethyl methacrylate supported PEI adsorbent resulted in improved thermal stability. Further research could reveal that PEG may also increase the stability of the current DEA impregnated adsorbent.

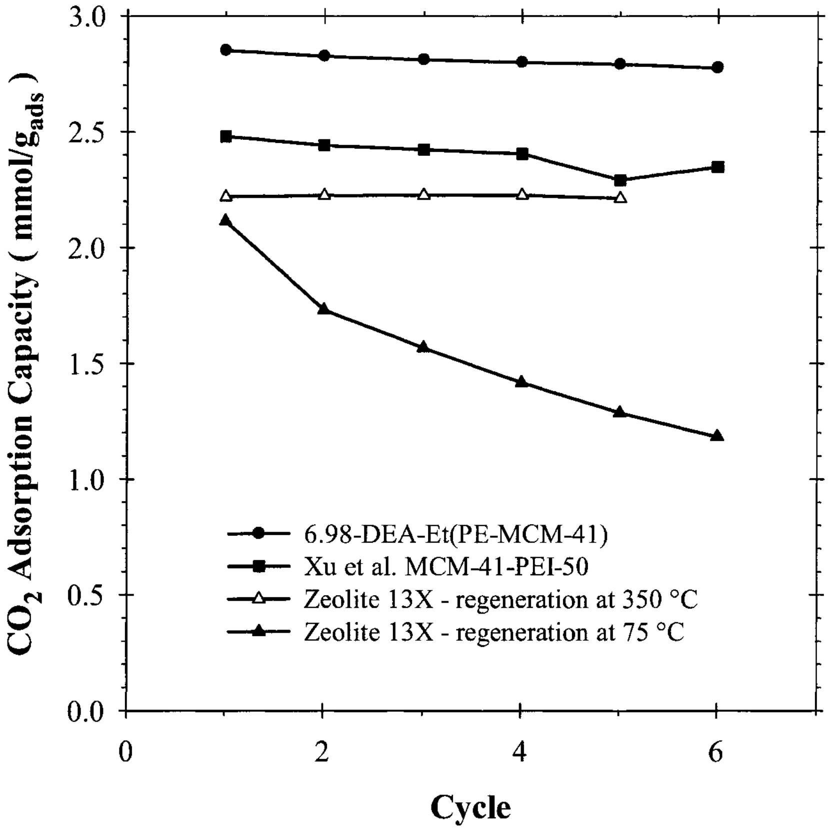

Figure 17: CO_2 adsorption capacity as a function of adsorption cycle for 6.98-DEA-Et(PE-MCM-41) and other CO_2 adsorbents.

The results shown for the material developed by Xu et al. (2002) were obtained by the authors using CO_2 at a partial pressure of 1.0 atm, while operating at 75 °C. Although the data showed a similar decrease of 0.13 mmol CO_2/g_{ads} (i.e. 5.3% of the initial capacity) over the course of six cycles, the authors concluded that the performance of the material was stable.

The tests conducted with zeolite 13X indicated that under high temperature regeneration conditions (350 °C), the cyclic performance of zeolite 13X was stable with virtually no decrease in adsorption capacity. When the milder regeneration temperature of 75 °C was used, the adsorption capacity decreased by 0.93 mmol CO_2/g_{ads} (i.e. 44.1% of the initial value) over the course of six cycles. TGA-MS data obtained upon heating this material to 350 °C suggested that the loss in capacity was due to the incomplete regeneration of the zeolite. This led to the accumulation of CO_2 and a small amount of H_2O, the latter due to trace moisture in the gas streams. Another possible reason for the decrease in capacity, which was not visible from the TGA-MS data, was the accumulation of adsorbed nitrogen. Literature confirmed that zeolite 13X is capable of adsorbing nitrogen under the experimental conditions used in the current study (Chue et al., 1995; Harlick and Tezel, 2004), however, during the current study the MS signal of desorbed nitrogen was masked since regeneration was carried out in nitrogen.

These results illustrate both the need for higher temperature regeneration conditions and the importance of moisture control when employing zeolite 13X, two major disadvantages that do not occur with the adsorbent developed during the current study.

Although the cyclic stability of the impregnated adsorbent was acceptable for the purpose of laboratory studies, it was clear that the stability required improvement if the adsorbent was to be used at the commercial level. Most industrial applications would not employ an adsorbent unless the capacity was stable for hundreds to thousands of cycles under the ideal test conditions used for the current study (Abanades et al., 2004). As discussed in section 2.2.2.4., degradation of the adsorption capacity can occur for many reasons, and none of these alternate causes of degradation has been examined in the current study. It remains to be determined how the presence of O_2 and SO_2, two compounds that are known to degrade alkanolamines, would affect the stability of the adsorbent (Kohl and Riesenfeld, 1985).

4.4.2. Support stability

Based on the results of the cyclic capacity studies, it was decided to examine if the support could be re-impregnated with DEA by first removing the DEA through a calcination procedure. Samples prepared under different conditions were calcined and analyzed by nitrogen adsorption experiments. The amine content, the impregnation solvent, and the impregnation drying temperature (as indicated in the brackets at the end of the sample name) were examined to determine the influence on the support stability. The calculated pore size distributions are shown in Figure 18 along with the pore size distribution of a typical PE-MCM-41 sample prior to impregnation.

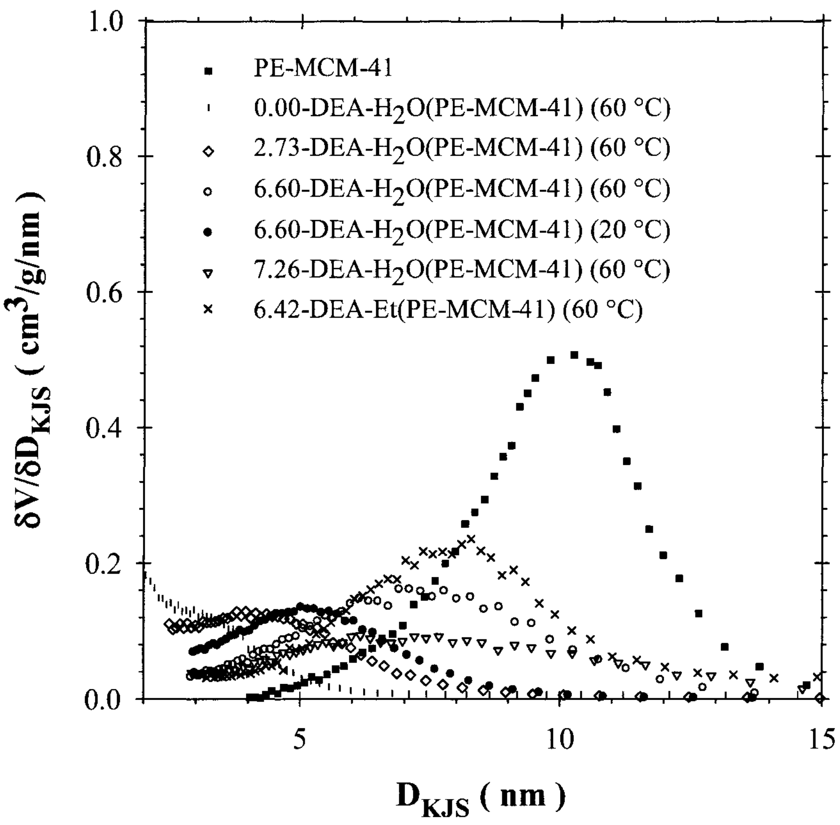

Figure 18: Pore size distributions of PE-MCM-41 supports after calcination of impregnated materials.

Examination of the pore size distributions revealed that all samples that were subjected to the impregnation procedure showed signs of support degradation. In each case, the pore size distribution shifted to a lower average pore size, and the height of the distribution was reduced, indicating a loss in pore volume as compared to the original PE-MCM-41. Interestingly, sample 0.00-DEA-H_2O(PE-MCM-41) (60 °C), which was subjected to the impregnation procedure in water with no DEA added, showed the highest degree of support degradation. Since the effects of moisture on MCM-41 are well known (Koyano et al., 2001; Broyer et al., 2002) it was not surprising that this sample degraded, although it was interesting to find that the presence of DEA appeared to result in lower degradation of the support. This was unexpected due to the basic nature of aqueous DEA solutions. A possible explanation for these results could be that the interaction of the support with the DEA resulted in a lower reactivity of the surface siloxane bridges towards water molecules. This would have prevented the hydrolysis of the PE-MCM-41 supports, resulting in a lower degree of degradation. Further studies would be needed, however, to confirm this contention.

The structural properties of the calcined adsorbents are summarized in Table 7. The surface area and average pore diameter results offered little insight besides the fact that all materials suffered some degree of support degradation. Of primary concern when considering the possibility of re-impregnation of the support was the degradation of the pore volume. As shown from the pore volume results, in every case, the pore volume of the calcined materials was significantly lower than that of the support prior to impregnation.

The pore volume results suggested a relationship between the degree of support degradation and the amine content of the sample. For samples 0.00-DEA-H_2O(PE-MCM-41) (60 °C), 2.73-DEA-H_2O(PE-MCM-41) (60 °C), and 6.60-DEA-H_2O(PE-MCM-41) (60 °C), the degree of degradation decreased with increasing amine content. This further supported the contention that the presence of DEA resulted in a lowering of the reactivity of the surface towards water molecules.

Table 7: Structural properties of supports after calcination of impregnated materials

Sample	S_{BET} (m^2/g)	V (cm^3/g)	D_{KJS} (nm)
PE-MCM-41	917	2.00	9.7
0.00-DEA-H_2O(PE-MCM-41) (60 °C)	573	0.36	-
2.73-DEA-H_2O(PE-MCM-41) (60 °C)	647	0.55	4.3
6.60-DEA-H_2O(PE-MCM-41) (60 °C)	626	0.94	7.4
6.60-DEA-H_2O(PE-MCM-41) (20 °C)	734	0.65	5.2
7.26-DEA-H_2O(PE-MCM-41) (60 °C)	632	0.82	7.9 [a]
6.42-DEA-Et(PE-MCM-41) (60 °C)	809	1.42	8.1

a) Very broad distribution

Another possible relationship was suggested by examining the pore volumes of samples 6.60-DEA-H_2O(PE-MCM-41) (60 °C), 7.26-DEA-H_2O(PE-MCM-41) (60 °C), and 6.60-DEA-H_2O(PE-MCM-41) (20 °C). These materials respectively required increasing lengths of time for drying. The pore volume of these samples suggested that the degree of degradation increased as the length of time required for drying increased. This trend was found to be logical since hydrolysis of the material is a slow process that should benefit from longer exposure to the humid environment.

The sample impregnated with ethanol as the solvent showed the lowest degree of degradation in terms of surface area, pore volume, and average pore diameter. From this sample alone, it was not possible to definitively conclude if the decreased degradation was due to the nature of the solvent or the short time required for drying during the impregnation procedure. Further studies were not pursued, however, since it seemed obvious that the support could not be re-impregnated based on the results obtained thus far.

4.5. Agglomeration

To perform the adsorption column studies, it was first necessary to determine a suitable means of producing agglomerates. The criteria for evaluating the agglomeration process were the overall complexity of the agglomeration process, and the strength, size, uniformity, and adsorption capacity of the resulting agglomerates.

4.5.1. Preliminary Trials

During the preliminary agglomeration trials, several methods of agglomerate formation were examined. The majority of the trials were carried out in small batches using the granulation technique, since this was the easiest to implement for small sample sizes. As most of the methods failed to produce adequate agglomerates, only a general description of the results will be given. The specific details are summarized in tabular format in Appendix I.

4.5.1.1. Kaolin

One of the first binders examined was kaolin, which is commonly used as a binder for zeolites. It was mixed with the support (PE-MCM-41) and water, dried at 60 °C for several hours and then heated at 500 °C, as is commonly done for zeolites. The resulting material crumbled to a dust and was completely unsuitable.

Several problems were discovered during this trial. Due to the high pore volume of PE-MCM-41, it was necessary to add a large quantity of water to produce a uniform mixture. The high moisture content made it difficult for the green agglomerates to retain their shape, and it is known in industry that high moisture agglomerates are prone to cracking if the drying rate is not carefully controlled. Another problem was the difference in density of the materials. Due to the high density of the binder compared to PE-MCM-41, a high binder content would be required to achieve an adequate volumetric ratio of binder to support. With the low binder contents used during the trials (and hence low volumetric ratios of binder to support), an insufficient number of inter-particle bonds were formed to produce a strong agglomerate.

4.5.1.2. Silicas

Granulation was attempted with several formulations of DuPont Ludox colloidal silica solutions. These formulations contained different compounds in solution, which resulted in slightly different binder properties. It was found that Ludox HS-30 resulted in the strongest pellets, however, excessive binder contents were needed to obtain suitable agglomerates, which resulted in low CO_2 adsorption capacities. The Agglo-miser was employed in an attempt to obtain regular spheroid agglomerates. This method was very difficult to implement without a constant feed of material and poor particle size distributions resulted.

Extrusion was attempted, however, the results were similar to those obtained using the granulation technique. In addition, the use of the pre-formulated solutions made it impossible to independently control the binder content and the green extrude moisture. This resulted in pastes with excessive moisture contents, which were unsuitable for extrusion.

The problems encountered with the Ludox solutions led to the examination of Cab-O-Sil / DEA / H_2O solutions as binders, which made it possible to independently control the binder content and green agglomerate moisture content. The DEA was added in an attempt to counteract the high binder content, but the resulting agglomerates were not sufficiently strong.

This indicated that the additives used in the Ludox solutions must have contributed to the strength of the agglomerates.

4.5.1.3. Cement

Granulation with Portland cement was also attempted with both the support and the impregnated adsorbent. It was expected that the support or adsorbent could be substituted for the aggregate (as in concrete formation), resulting in the formation of a rigid agglomerate. However, similar problems to those discussed for kaolin were encountered, resulting in very poor agglomerate strength.

4.5.1.4. MCC and Bentonite

Microcrystalline cellulose and bentonite are two materials commonly used for pressure agglomeration. These binders were used for compression agglomeration trials using a hydraulic press and an IR disk die, as described in section 3.4.2.. Several binder contents and agglomeration pressures were examined, but none of the resulting agglomerates were suitable. The lack of strength of the agglomerates could have been due to the presence of DEA on the surface of the adsorbent particles, which prevented the formation of strong inter-particle bonds. This contention was supported by the observation that the strength of the agglomerates seemed to decrease with increasing adsorbent amine content. The method was abandoned due to the poor results and the fact that it was not practical with the available equipment and the large quantity of material to be agglomerated.

4.5.1.5. PVOH

As shown in Figure 19, the molecular weight and the degree of hydrolysis have important effects on the characteristics of polyvinyl alcohol. For the preliminary trials with polyvinyl alcohol, polymers with a high degree of hydrolysis were examined as binders for both the support and the amine impregnated adsorbent. Two molecular weights were examined; medium and high molecular weight (PVOH2 and PVOH3 respectively). A high degree of hydrolysis was selected to ensure a high tensile strength, while the different molecular weights were selected to ensure that at least one of the binders could be easily dissolved in water.

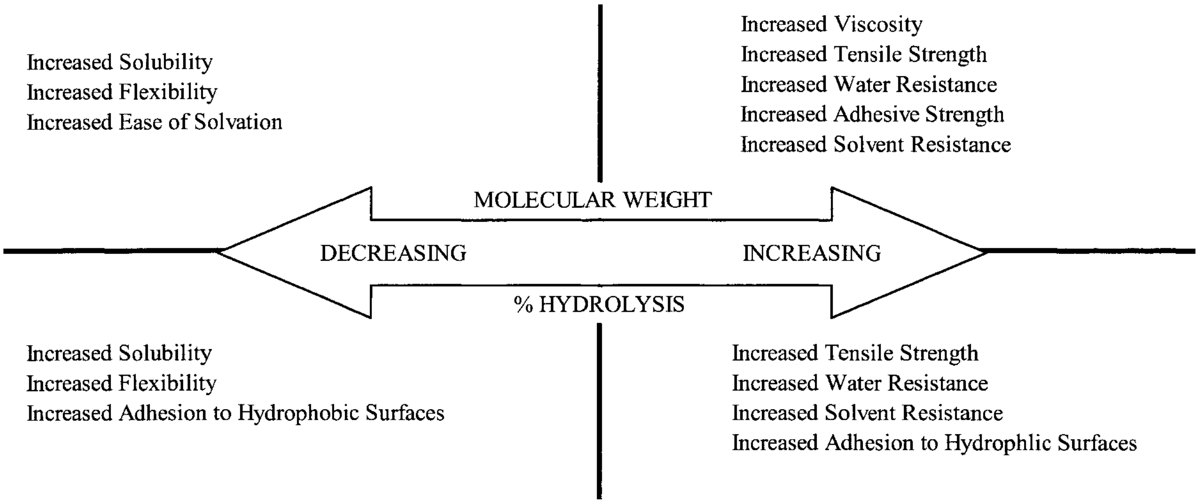

Figure 19: The effects of molecular weight and degree of hydrolysis on PVOH physical properties (adapted from Marten, 2002).

Several samples were prepared with different binder contents. Granulation usually resulted in agglomerates with a soft interior and a hard outer "skin" composed mostly of PVOH, which produced weak agglomerates. The results were also found to be very sensitive to the moisture content of the green agglomerates. When the moisture content was too high, the agglomerates did not retain their shape, and the binder solution separated from the active component, resulting in the skin formation.

To minimize the effects of the skin formation, extrusion was attempted followed by spheronization with the Agglo-miser. It was hoped that this procedure would increase the strength of the agglomerates by increasing the surface area to volume ratio, resulting in more of the hard skin and less of the soft interior. Unfortunately, the method failed because the agglomerates coalesced to formed large clumps.

While most of the granulation trials failed, it was clear from the results that PVOH3 resulted in stronger agglomerates, but due to the high molecular weight, the material was more difficult to dissolve. Extrusion without subsequent spheronization was attempted with a 50/50 mixture of PVOH2 and PVOH3. This mixture was used to facilitate the dissolution and lower the viscosity of the PVOH solution compared to that of solutions of PVOH3 alone. The resulting samples were found to be of sufficient strength for use in the adsorption column.

4.5.2. Detailed agglomeration trials using PVOH and the extrusion method

Since PVOH was the only binder found to produce adequate agglomerates with the means available in the laboratory, it was decided to carry out more detailed studies using this binder. Extrusion was chosen as the agglomeration method since it was the only acceptable means to control the shape of the agglomerates, and the method could be scaled-up with minimum difficulties.

A number of parameters were examined in order to develop a suitable agglomeration method. These parameters included: the degree of hydrolysis and molecular weight of the PVOH, the amine content of the powdered adsorbent, and the binder content of the agglomerate. The results of the previously conducted preliminary studies revealed that suitable agglomerates should be attainable with binder contents below approximately 10 wt%, which should result in minimal decreases in adsorption capacity. As a result, it was decided to examine a range of binder contents between approximately 3-15 wt%. The moisture content of the green agglomerates was also recorded, since the preliminary trials revealed that this parameter had a large effect on the quality of the agglomerates. Agglomerates deemed suitable for use in the adsorption column were tested for CO_2 adsorption capacity using the TGA with a dry mixture of 5% CO_2 in N_2. Table 8 summarizes results obtained from these studies.

The three grades of PVOH were used with adsorbents of varying amine content at approximately the same binder content (6-7 wt%). The polyvinyl alcohol with a low degree of hydrolysis and a low molecular weight (PVOH1) resulted in aqueous solutions with comparatively low viscosity. Although the moisture content of the resulting pastes was similar among all the grades of PVOH, the pastes formed using PVOH1 as the binder had lower viscosity, which made the extruded material incapable of retaining its shape. The use of PVOH2 resulted in a similar problem, hence further testing with these grades was abandoned due to the poor results.

The above mentioned study also revealed that increasing the amine content of the powdered adsorbent had a similar effect on the viscosity of the paste. For a given grade of PVOH, as the amine content was increased from 6.84 to 7.31 mmol DEA/g_{ads}, the paste became less viscous, and the resulting extrudes were too weak to be employed in the column even though they had higher adsorption capacities. The lower strength of the agglomerates prepared with the higher amine content adsorbent was likely the result of two factors; the poor agglomerate shape and the low mass fraction of support. The poor agglomerate shape was the result of the lower viscosity of the green agglomerates, and the lower mass fraction of support prevented the formation a sufficient number of bonds between adsorbent particles and the binder.

Table 8: Results of the detailed agglomeration studies with polyvinyl alcohol binders and the extrusion method - drying at 80 °C

Active component	Binder	Binder content [a] (wt%)	Pellet moisture (wt%)	Strength [b]	CO_2 capacity [c] (mmol/g_{ads})
6.84-DEA-Et (PE-MCM-41)	PVOH1	6.9	73.4	weak	-
	PVOH2	6.8	70.9	inadequate	-
	PVOH3	5.6	72.4	good	2.3
6.98-DEA-Et (PE-MCM-41)	PVOH1	6.8	72.4	weak	-
	PVOH2	6.8	71.1	inadequate	-
	PVOH3	5.9	75.4	good	2.4
7.31-DEA-Et (PE-MCM-41)	PVOH1	6.7	70.8	weak	-
	PVOH2	7.0	73.2	inadequate	-
	PVOH3	5.6	72.3	good	2.5
6.68-DEA-Et (PE-MCM-41)	PVOH2 + PVOH3	13.3	67.9	good	1.7
		11.2	67.4	good	-
		9.5	72.2	good	1.8
		6.6	64.9	good	2.1
		3.9	82.6	weak	-
6.98-DEA-Et (PE-MCM-41)	PVOH3	11.6	68.7	good	2.1
		9.8	68.5	good	-
		7.5	64.4	good	2.4
		5.9	65.0	good	2.4
		4.3	73.3	weak	-

a) Calculated binder content of dried agglomerate based on the amount of binder added during preparation

b) Qualitative evaluation of strength – weak = agglomerate formed but very weak; inadequate = agglomerate formed with some resistance to pressure, good = agglomerate suitable for use in bench-scale column

c) First pass capacity using dry 5% CO_2 in N_2 mixture

The effect of increasing the binder content was first examined with a 50/50 mixture of PVOH2 and PVOH3 and a comparatively low amine content adsorbent (6.68-DEA-Et(PE-MCM-41)). As discussed earlier, the use of both polymers facilitated the initial dissolution and lowered the viscosity, which made it easier to control the concentration of the binder solution. As the binder content of the agglomerates was increased, the strength of the agglomerates improved, however, there was a noticeable decrease in the adsorption capacity. This was the result of a higher proportion of binder, which was inert with respect to the adsorption of CO_2.

Since a higher molecular weight results in higher tensile strength (Marten, 2002), and the results thus far showed that suitable agglomerates could be formed with a mixture of PVOH2 and PVOH3, it was believed that the strength of the agglomerates could be improved by using PVOH3 alone. With a higher tensile strength, the binder content could be lowered while maintaining the same agglomerate strength, resulting in a higher adsorption capacity. Samples were prepared with increasing contents of PVOH3 to determine the minimum binder content that resulted in suitable agglomerates. Based on the previous study using adsorbents with different amine contents, it was decided to use sample 6.98-DEA-Et(PE-MCM-41) since agglomeration with the higher content adsorbent resulted in a weaker agglomerate.

The study revealed that although PVOH3 was difficult to dissolve, a binder content of only 7.5% resulted in fairly strong agglomerates, with an acceptable penalty on the adsorption capacity. Also, when using PVOH3, a paste with a suitable texture for extrusion could be produced if the moisture content of the paste was between 65-68 wt%.

4.5.3. Evaluation of agglomerates for column studies

The results of the detailed agglomeration trials with PVOH resulted in the decision to use PVOH3 as the binder at a content of 7-8 wt%. A target moisture content of 65-67 wt% was chosen for the resulting paste. This produced a paste with a viscosity that was sufficiently low to allow for extrusion to be carried out with plastic laboratory syringes and sufficiently high to ensure that the extrudes retained their shape upon extrusion. The final procedure that was adopted is described in section 3.4.4.. The resulting agglomerates were evaluated for their physical characteristics, CO_2 adsorption capacity, and cyclic stability.

4.5.3.1. Physical characteristics of impregnated adsorbent extrudes and commercial zeolite 13X extrudes

The extrudes formed from the amine impregnated adsorbent and the commercial zeolite 13X extrudes were measured manually to determine the length (L_a), diameter (D_a), agglomerate density (ρ_a), and bed density (ρ_b). Several extrudes were measured after undergoing the typical activation procedure to determine the approximate values of these parameters. The external void fraction of the bed (ε_b) was calculated using the following formula (Levan et al., 1997):

$$\varepsilon_b = 1 - \frac{\rho_b}{\rho_a}$$

The physical characteristics of the extrudes are summarized in Table 9. The densities and void fraction measured for the impregnated agglomerates were consistent with results reported by Zinnen et al (1989) for another impregnated material. Chue et al. (1995) reported similar values of bed density and void fraction for zeolite 13X agglomerates as those obtained in the current study.

Table 9: Approximate properties of agglomerates used for column studies

Agglomerate	L_a x D_a (mm)	ρ_a (g/cm^3)	ρ_b (g/cm^3)	ε_b
Impregnated	8 x 2.1	0.76	0.40	0.47
Zeolite 13X	5 x 1.7	1.00	0.65	0.35

The measured parameters showed that the commercial zeolite 13X agglomerates exhibited some advantages over the agglomerates formed in the lab. The smaller diameter of the extrudes would reduce diffusional limitations on the adsorption rate, since the gas molecules would not have to diffuse as far to reach the adsorption sites. The higher agglomerate density could permit the column to process a higher gas flow rate since fluidization occurs at higher gas flows for agglomerates with a higher density, while the higher bed density would result in a larger mass of material in the column. The higher adsorption capacity of the amine impregnated material, however, could potentially counteract the more favourable physical properties of the zeolite 13X agglomerates. In addition, improvements in agglomeration methods could reduce the agglomerate size and increase the agglomerate and bed densities of the impregnated material.

4.5.3.2. CO_2 adsorption capacity

The adsorption capacity and rate of the agglomerates were determined using the TGA and a dry mixture of 5% CO_2 in N_2. As several batches were required to produce a sufficient quantity of extrudes for the column studies from the impregnated material, the adsorption capacity and rate varied slightly from batch to batch. A composite sample of all the batches had an adsorption capacity of 2.5 mmol CO_2/g_{ads}, while the rate was 0.49 mmol CO_2/g_{ads}/min.

These values represented a decrease in capacity of approximately 11% and a decrease in adsorption rate of approximately 51% in relation to the powdered form of the adsorbent. The loss in capacity was greater than would be expected from the PVOH content of 7-8%. This was probably due to the large drop in rate, which prevented the adsorption capacity from attaining its equilibrium value in the allotted time period of one hour. The drop in rate was likely due to a combination of the increase in "particle" diameter experienced upon agglomeration and the decreased adsorption capacity due to the presence of the inert binder. Increasing the diameter by agglomeration forced the CO_2 to diffuse through the pore network of the agglomerate to reach a large portion of the adsorption sites, resulting in a slower rate of adsorption.

The zeolite 13X extrudes had first pass adsorption capacity of 1.8 mmol CO_2/g_{ads} and an adsorption rate of 0.51 mmol CO_2/g_{ads}/min. These values represented a decrease in capacity of approximately 15% and a decrease in adsorption rate of approximately 49% in relation to the powdered form of the adsorbent. As the composition of the commercial extrudes was unknown, it was not possible to predict the expected decreases.

The results of the testing showed that the decrease in performance upon agglomeration was similar for the two materials. While the extrudes formed from the impregnated adsorbent exhibited a higher adsorption capacity, the commercial zeolite 13X extrudes were more dense. The higher density would result in a larger mass of adsorbent contained in the adsorption column, which could potentially offset the reduced adsorption capacity. Calculations were carried out to predict the expected equilibrium CO_2 capacity of the adsorption column based on the measured bed densities and adsorption capacities of the agglomerated adsorbents. The calculations showed that when the column was filled with the extrudes of the impregnated adsorbent, it could be expected to retain approximately 0.89 mol CO_2 (19.8 L(STP)) when allowed to reach equilibrium under dry conditions with a CO_2 partial pressure of 0.05 atm. The column filled with the commercial zeolite 13X extrudes on the other hand, could be expected to retain approximately 1.04 mol CO_2 (23.3 L(STP)) under the same conditions. These results emphasized the importance of the agglomerate characteristics in relation to the performance of industrial fixed-bed adsorption columns.

4.5.3.3. Cyclic stability

The cyclic stability of the CO_2 adsorption capacity was evaluated to verify that the agglomerates behaved similarly to the powdered form of the adsorbents. The results of the study are shown in Figure 20.

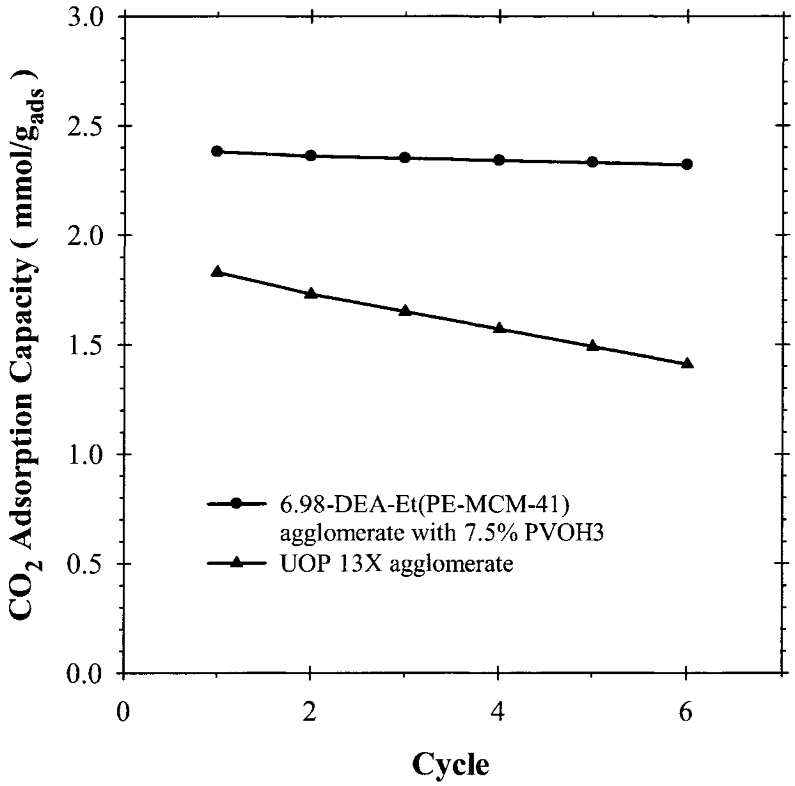

Figure 20: CO_2 adsorption capacity as a function of adsorption cycle for the agglomerated adsorbents.

The stability of the agglomerated impregnated adsorbent was similar to that of the powdered form. The extrudes showed a decrease in adsorption capacity of approximately 0.06 mmol CO_2/g_{ads} (i.e. 2.5% of the initial capacity) over the course of six adsorption-desorption cycles. The results suggested that the agglomerated impregnated adsorbent could be studied in the packed-bed configuration of the adsorption column with minimal degradation over the course of the planned testing.

As with the powdered form of zeolite 13X, the adsorption capacity of the commercial zeolite 13X extrudes decreased quickly when the material was regenerated at the relatively low temperature of 75 °C. Over the course of six adsorption-desorption cycles, the capacity was reduced by approximately 0.42 mmol CO_2/g_{ads} (i.e. 23% of the initial capacity). The decrease in capacity was not as severe as that experienced by the powdered form, which could be the result of an elevated content of inert binder.

4.6. Column Studies

As described in section 3.7.3., the column was filled with the adsorbent while tapping the sides of the column to ensure uniform distribution of the adsorbent. The column was capable of holding 373.3 g of the DEA impregnated adsorbent activated at 75 °C. This was 5.4% more material than estimated based on the experimentally measured bed density, and was likely due to a slightly higher bed density obtained when filling the column.

Zeolite 13X was first heated to 230 °C in an oven to remove pre-adsorbed compounds. This temperature was chosen since it was more representative of the regeneration conditions used in industry (Sircar and Kratz, 1981), and it was also the maximum temperature achievable during in-situ regeneration of the column using the heating tape. Further, the elevated temperature was necessary since it was already shown that the capacity decreased quickly when the zeolite was regenerated under the same conditions as the impregnated material. Using the lower regeneration temperature would make it difficult to evaluate the performance of the material at the different experimental conditions, since the adsorption capacity would decrease significantly from one test to another. The column was capable of holding 604.6 g of the zeolite when activated at 230 °C, which was approximately 4.6% greater than estimated based on the experimentally measured bed density. This could have been due to the presence of some pre-adsorbed compounds remaining on the adsorbent, or a slightly higher bed density obtained when filling the column.

Once the column was filled with the agglomerates, the tests were conducted as described in section 3.7.3.. Test 1 was conducted first and then repeated at the end of testing for the impregnated material.

4.6.1. Column temperatures

The column temperatures at various positions were recorded as adsorption progressed, and the average column temperature was calculated based on these numbers. Examination of the temperatures provided insight into the relative performance of the two materials. The temperature trends were similar for all adsorption conditions. Representative data are shown in Figure 21 for the test conducted with a CO_2 partial pressure of 0.05 atm and a total feed flow rate of 5 L(STP)/min.

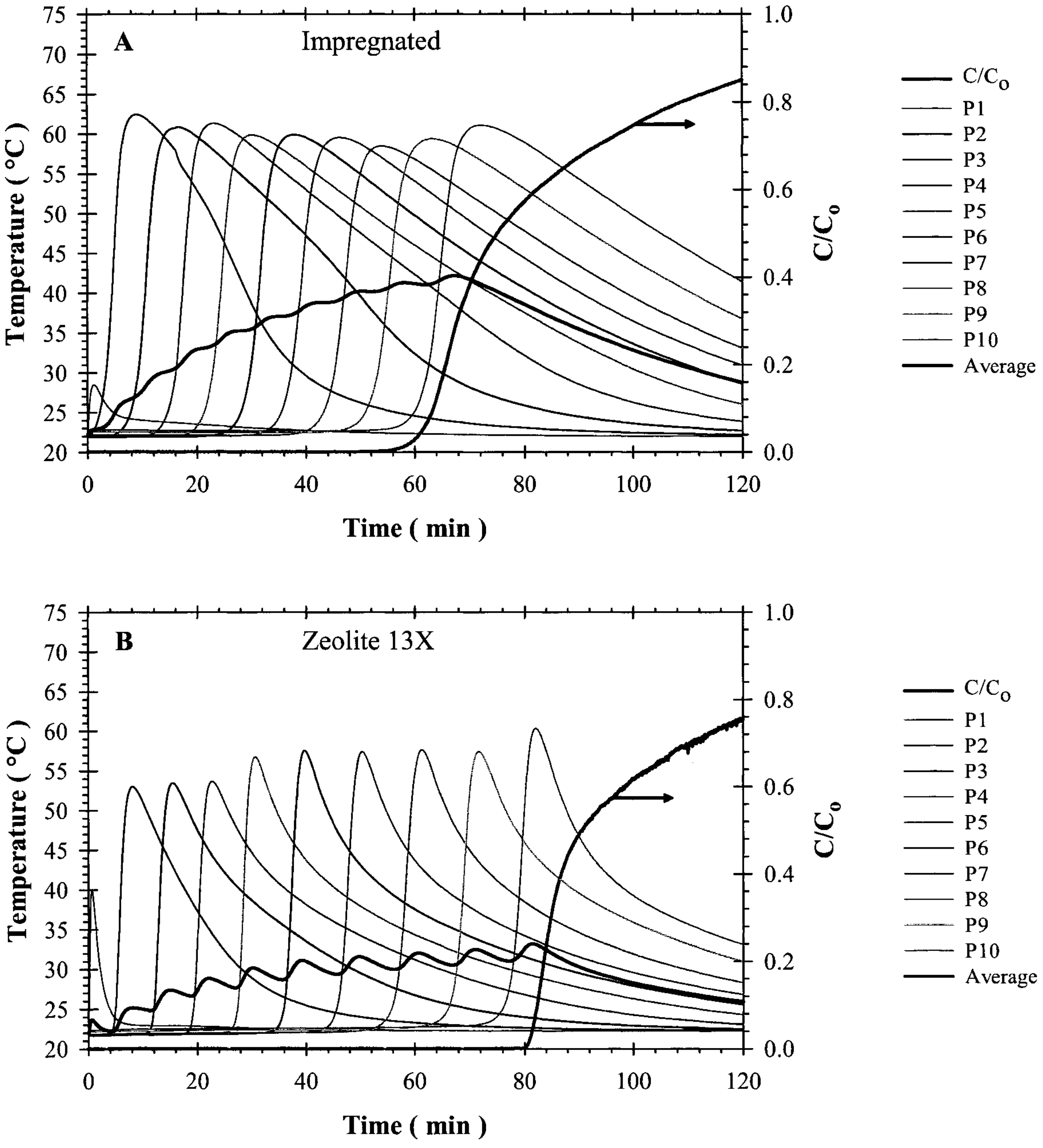

Figure 21: In-column temperature profiles during adsorption – CO_2 partial pressure of 0.05 atm, total feed flow rate of 5 L(STP)/min.

4.6.1.1. Maximum temperatures as a function of column position

Figure 21 revealed that for both materials, the thermocouple at P1 did not reach a maximum temperature comparable to the other column positions. Since this thermocouple was located close to the inlet, very little material preceded the thermocouple, resulting in the release of only a small amount of heat due to the adsorption of CO_2. Movement of the agglomerates caused by loose packing could have further decreased the amount of material preceding P1, which would have further reduced the amount of heat released.

Comparison of the maximum temperatures as a function of bed location for the two materials indicated that while the impregnated material showed no noticeable trend in these maxima, the maxima increased with position along the bed for zeolite 13X. This occurred because the various zones of the bed exhibited different CO_2 adsorption capacities. The observation indicated that the zeolite was not adequately regenerated prior to the adsorption test. Since regeneration was carried out in counter-current mode, the portions of the bed closer to the adsorption inlet were exposed to CO_2 for the longest period. Despite the fact that the zeolite was regenerated at a higher temperature with a larger flow of purge gas, incomplete regeneration still occurred, demonstrating that the impregnated material required much milder regeneration conditions.

4.6.1.2. Breakthrough of CO_2 in relation to temperature changes

In order for heat to be produced during adsorption, CO_2 must first be adsorbed onto the active sites of the adsorbent, therefore, it could be expected that the thermal and mass transfer fronts would travel through the bed at similar velocities. Further examination of Figure 21A showed that during the test with the impregnated material, the presence of CO_2 was detected at the column outlet in advance of temperature changes, while the same was not true for the test with the zeolite. For example, when the average column temperature reached the maximum value of 42.2 °C for the impregnated material, C/C_0 had reached a value of 0.28. When P10 reached the maximum temperature of 61.1 °C, C/C_0 was approximately 0.42. This rise in concentration prior to the rise in temperatures was indicative of premature breakthrough. As discussed in section 2.2.2.4., this could have been due to diffusional limitations caused by the larger pellet size, or the high void fraction of the column resulting in lower tortuosity (Levan et al., 1997) compared to the zeolite. Higher tortuosity results in a higher likelihood of the adsorbate molecules colliding with the agglomerates and a lower likelihood of bypassing occurring.

During the test with zeolite 13X, the change in the temperature at P10 coincided with the appearance of CO_2 at the column outlet. When the average column temperature reached the maximum value of 33.2 °C, C/C_0 was approximately 0.03-0.04. When P10 reached the maximum temperature of 60.3 °C, C/C_0 was only 0.08. This indicated sharp thermal and mass transfer fronts, which traveled through the column at approximately the same rate. A sharp mass transfer front is favourable since it allows a greater portion of the adsorbent bed to be used before the column requires regeneration.

4.6.1.3. Average bed temperatures

As shown in Figure 21, the average bed temperatures for the two materials appeared to periodically increase and decrease. This apparent trend was the result of the fact that the thermocouples were located 10.2 cm apart, which allowed the zones preceding the thermal front to cool before the front reached the next thermocouple location. The phenomenon was more pronounced for the zeolite material possibly due to a higher rate of cooling. Since the zeolite had a higher bed density and lower porosity, it could be expected to have a higher effective thermal conductivity due to the lower proportion of gas in the bed (Wang et al., 1999). In addition, as alumina has a thermal conductivity that is roughly twenty-eight times larger than silica (Liley et al., 1997), the elevated alumina content of zeolite 13X could also be expected to increase the thermal conductivity of the adsorbent compared to the impregnated material.

Examination of the maximum average column temperatures obtained under the various test conditions, as summarized in Table 10, revealed further insight into the relative performance of the two materials.

Table 10: Maximum average temperatures during the column tests

CO_2 partial pressure (atm)	Inlet gas flow rate (L(STP)/min)	Adsorbent	Maximum average column temperature (°C)
0.02	10	13X	29.9
		Impregnated	36.6
0.05	5	13X	33.2
		Impregnated	42.2
0.05	10	13X	37.9
		Impregnated	46.8
		Impregnated (rep)	48.4

Under all test conditions, the average column temperature reached a higher value for the tests conducted with the impregnated material. This occurred even though the breakthrough curves suggested that a lower quantity of CO_2 was adsorbed at the breakthrough point with the impregnated material. As discussed in the literature, the heat of reaction for secondary amine-CO_2 interactions has been reported as 72 kJ/mol (Satyapal et al., 2001), while the heat of adsorption for CO_2 on zeolite 13X has been reported to be between 36 and 50 kJ/mol (Chue et al., 1995; Harlick and Tezel, 2004). The combination of a higher heat of adsorption and a lower cooling rate would have caused higher peak temperatures and average column temperatures for the impregnated material, consistent with the data reported in Figure 21 and Table 10. The elevated average bed temperature exhibited by the impregnated material would have further contributed to a lower breakthrough adsorption capacity since the capacity of adsorbents decreases with increasing temperature.

4.6.2. Effect of system parameters on the breakthrough profiles

The column performance was examined under two different CO_2 partial pressures and flow conditions. The goal of this study was to determine if the relative performance of the two materials was a function of the system parameters.

4.6.2.1. CO_2 partial pressure

The effect of the CO_2 partial pressure on the shape of the breakthrough profiles is demonstrated in Figure 22. The data revealed that during the test conducted at a partial pressure of 0.05 atm, the presence of CO_2 was detected much earlier for the impregnated adsorbent compared to the zeolite, indicating that a lower quantity of CO_2 was adsorbed prior to breakthrough. As the partial pressure was lowered to 0.02 atm, the breakthrough time for the impregnated material approached that of the zeolite.

According to the adsorption isotherm previously discussed (see Figure 15), the adsorption capacity of the zeolite decreased significantly as the partial pressure of CO_2 decreased, while the capacity of the impregnated material was not affected as drastically. This relationship is consistent with results shown in Figure 22, which resulted in improved performance for the impregnated material relative to the zeolite. It is therefore reasonable to assume that if the partial pressure of CO_2 was further decreased, the impregnated material could be expected to outperform the zeolite in terms of the amount of CO_2 retained by the column prior to breakthrough. This suggested that despite the disadvantages of lower agglomerate and bed densities, the use of the impregnated material would be preferable for gas streams with low CO_2 partial pressures.

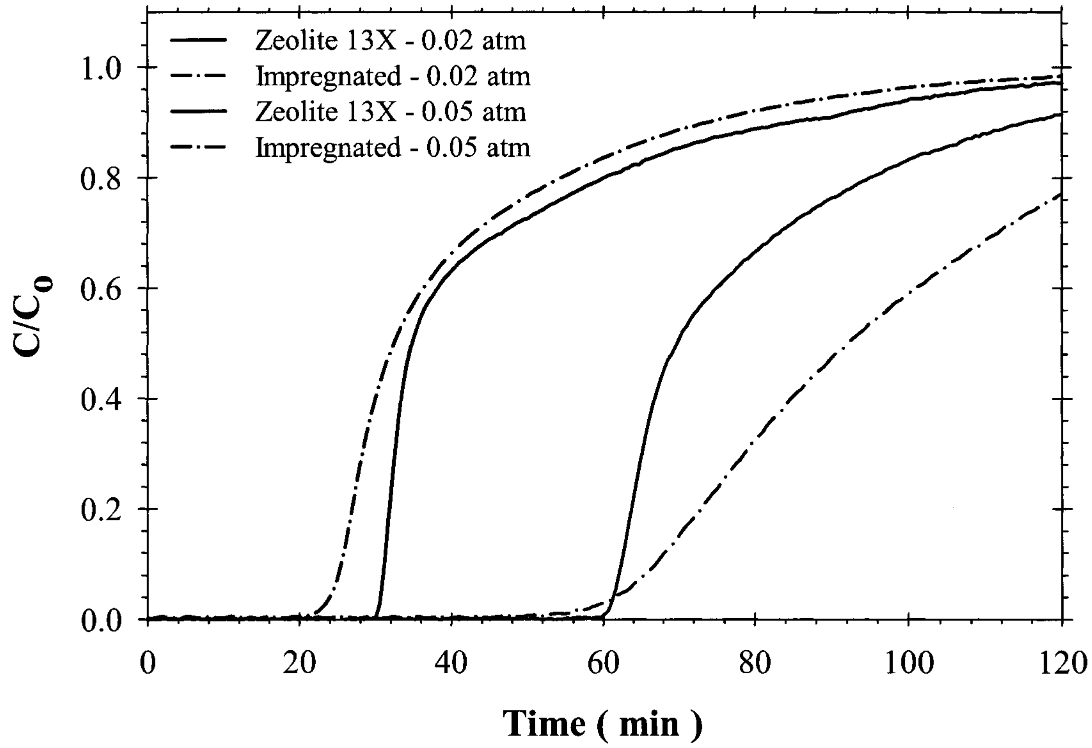

Figure 22: Breakthrough profiles obtained at two different CO_2 partial pressures – total feed flow rate of 10 L(STP)/min.

Both materials showed an elongation of the breakthrough curve as the partial pressure was lowered, however, the effect was much more drastic for the impregnated material. Also, when the partial pressure was lowered, the impregnated material exhibited a noticeable initial period where the concentration of CO_2 at the column outlet increased very slowly. These two observations suggested a significant decrease in the adsorption rate with the impregnated material at the lower partial pressure, causing premature breakthrough of CO_2.

4.6.2.2. Flow rate

Increasing the flow rate had only a minor effect on the shape of the breakthrough profiles for the two adsorbents. The sharpness of the breakthrough profiles showed a slight decrease when the flow rate was halved. The effect of flow rate on the breakthrough time, and hence the adsorption capacity, was more obvious. For the impregnated adsorbent, the first detectable increase in the concentration of CO_2 in the effluent was delayed from 18-19 minutes under the high flow condition to 53-54 minutes under the low flow condition. This represented an increase in breakthrough time by a factor of 2.9 as a result of decreasing the flow rate by a factor of 2.0. For zeolite 13X, the appearance of CO_2 in the effluent was delayed from 30 minutes under the high flow condition to 80 minutes under the low flow condition. This represented an increase in breakthrough time by a factor of 2.7 for the same decrease in flow rate.

Since the breakthrough time was more than doubled while the flow rate was halved, this suggested that both materials suffered from limitations due to the diffusion of CO_2 into the agglomerates at the higher flow rate. As the inlet flow rate was decreased, the gas residence time increased, allowing more time for the CO_2 molecules to diffuse into the agglomerate. This resulted in the disproportionate increase in the breakthrough time, which would manifest itself in an elevated adsorption capacity at the lower feed flow rate.

4.6.3. Summary of quantitative results from the column studies

As described in section 3.7.4., numerical integration of the breakthrough curves was carried out to quantitatively compare the performance of the adsorbents in the column configuration. The adsorption capacity and other performance parameters are summarized in Table 11.

Table 11: Summary of results obtained from column studies

CO_2 partial pressure	Inlet gas flow rate	Adsorbent	Eq'm. capacity	Parameters at breakthrough ($C/C_o = 0.02$)			
				Break. capacity	% of eq'm. capacity	Extra length req.	Extra mass req.
(atm)	(L(STP)/min)		(L(STP))	(L(STP))		(cm)	(g)
0.02	10	13X	14.0	10.5	75	-	-
		Impreg.	17.3	9.9	57	6.0	24.0
0.05	5	13X	23.1	17.3	75	-	-
		Impreg.	18.9	12.6	67	35.2	141.0
0.05	10	13X	20.3	13.0	64	-	-
		Impreg.	18.0	9.7	54	31.2	125.2
		Impreg. rep.	18.0	9.4	52	36.3	145.5

4.6.3.1. Adsorption capacities

The adsorption capacity data presented in Table 11 confirmed the effects of the CO_2 partial pressure and feed flow rate that were deduced by qualitative examination of the breakthrough profiles. As shown in the table, the breakthrough adsorption capacity of the zeolite filled column was higher than that of the column filled with the impregnated material. As the partial pressure was reduced from 0.05 to 0.02 atm, the breakthrough adsorption capacity of the impregnated material approached that of the zeolite. Based on these results, it was clear that further decreases in the CO_2 partial pressure would result in better performance from a column filled with the impregnated material, despite the lower bed density and adsorbent mass. As previously discussed, this was attributed to the significant decrease in the equilibrium adsorption capacity of zeolite 13X at the lower CO_2 partial pressure. While the equilibrium capacity of the zeolite filled column decreased by 31%, that of the column filled with the impregnated material decreased by only 4%. As indicated in the table, at a CO_2 partial pressure of 0.02 atm, the equilibrium capacity of the column filled with the impregnated material was higher than that of the column filled with zeolite 13X. This was true despite the fact that the zeolite filled column contained 62% more mass.

The adsorption capacities calculated for the tests conducted at the two different flow rates showed that both the equilibrium and breakthrough capacities increased when the flow rate was decreased. The effect on the equilibrium capacity was more pronounced with the zeolite material, which showed an increase of 14% compared to the 5% increase for the impregnated material. The effect on the breakthrough capacity was similar for the two materials, with an increase of 33% and 30% for the zeolite and impregnated material, respectively. These results confirmed that both materials suffered similarly from diffusional limitations resulting in a decreased CO_2 capture performance at the higher flow rate.

Comparison of the breakthrough capacities with the equilibrium capacities revealed that zeolite 13X reached a higher fraction of the equilibrium capacity prior to breakthrough of CO_2 under all test conditions. This suggested that the zeolite made more effective use of the adsorption bed, which is advantageous because it reduces the amount of unused adsorbent in the column. The higher fraction of the equilibrium capacity reached by the zeolite material was the result of the lower average bed temperature and more favourable bed characteristics, as previously discussed.

The repeat test conducted with the impregnated material served two purposes; it gave a preliminary indication of the repeatability of the column tests, and it made it possible to determine if the performance of the material degraded over the course of testing.

Despite the fact that the TGA studies revealed that the capacity of the impregnated material steadily degraded when exposed to several adsorption-regeneration cycles, the results obtained from the repeat test were fairly close to the results obtained at the start of testing. This preliminary evaluation of the variability suggested a high degree of repeatability for testing carried out with the adsorption column. However, since only one repeat was conducted, further testing would be required to adequately characterize the variability of the test procedure and obtain statistically significant comparisons between the two materials.

Assuming that the variability of the test procedure was very small, the results of the repeat test showed that the capacity of the impregnated adsorbent at breakthrough decreased slightly, while the equilibrium capacity remained constant. As the breakthrough capacity is highly dependent on the adsorption rate, the discrepancy in the breakthrough capacity between two tests suggested that the adsorption rate of the impregnated material decreased over the course of testing. The contention was verified by performing TGA tests on the used agglomerates and comparing the adsorption properties to those of the fresh agglomerates. These tests demonstrated that the adsorption rate of the used agglomerates had decreased by 22%, while the adsorption capacity was found to be approximately the same as that of the fresh agglomerates. No adequate explanation for the decrease in adsorption rate over the course of testing could be devised.

4.6.3.2. The effect of the breakthrough capacity on the size of the column

As shown in Table 11, under all test conditions, a larger adsorption bed would be required for an equivalent breakthrough adsorption capacity using the impregnated material. For an equivalent column diameter, the extra length of adsorption bed required varied from 6.0 to 36.3 cm, which represented 6.5 to 39.0% of the actual column length. In industry, a 39% increase in the length of an adsorption column can not always be achieved due to space and material strength limitations, hence these values were also expressed in terms of the extra mass required.

Due to the higher specific adsorption capacity of the impregnated material (i.e., L(STP)/g_{ads}), the extra mass required was significantly less than the difference in mass of the column filled with the two adsorbents (231.3 g). These results demonstrated that if the bed density of the impregnated agglomerates could be increased to approximately 0.58 g/cm^3 without hindering the adsorption characteristics of the bed, the CO_2 capture performance of the column filled with the impregnated material would exceed that of the zeolite filled column under all test conditions. Such an increase in bed density could possibly be achieved by improved agglomeration methods, which would reduce the amount of void spaces in the individual agglomerates as well as decrease the size and improve the uniformity of the agglomerates.

4.6.3.3. Comparison of the equilibrium capacities determined by column and TGA studies

As determined from the column studies, the equilibrium adsorption capacity of the impregnated agglomerates at a CO_2 partial pressure of 0.05 atm was 2.15 mmol CO_2/g_{ads} for the test conducted at the high flow rate. As the flow rate was decreased, the equilibrium capacity increased to 2.25 mmol CO_2/g_{ads}. Both of these values were significantly lower than the capacity of 2.50 mmol CO_2/g_{ads} determined by the TGA studies. The difference in performance was attributed to kinetic limitations resulting from a high convective flow of CO_2 through the column combined with the increased particle size due to agglomeration. The elevated convective flow may have resulted in insufficient time for the diffusion of the CO_2 molecules into all areas of the agglomerates. In addition, as the adsorbent approached saturation, the adsorption rate slowed due to a lower concentration driving force, while the convective transport remained constant. This could have prevented further adsorption of CO_2, resulting in an apparently lower equilibrium adsorption capacity. Since column studies indicated that the equilibrium adsorption capacity increased when the flow rate was lowered, it is possible that the capacity measured using the two experimental techniques would coincide for very low column inlet flow rates.

4.6.4. Stability of the DEA impregnated agglomerates

The mass of the impregnated agglomerates was recorded after testing, and it was found that the mass decreased by 3.6% over the course of testing (from 373.3 g to 360.0 g). This decrease in mass was attributed to loss of DEA due to volatilization, as demonstrated previously from the results of the TGA studies. It was expected that the loss in mass of the agglomerates would have been more severe since the agglomerates were exposed to elevated temperatures for extended periods. The lower mass loss was attributed to the fixed-bed configuration, which likely caused the DEA volatilized during regeneration from material close to the outlet of the column to be re-deposited on material closer to the inlet of the column. This phenomenon would result in an undesirable change in the composition of the adsorbent at different locations of the bed as a function of time, which would alter the performance of the column. While the loss in agglomerate mass was fairly low, further studies would be required to improve the stability prior to industrial use of the adsorbent. Additives may exist which could both reduce the volatility of the amine and increase the resistance to degradation due to the presence of other gas components (Satyapal et al., 2001).

5. Conclusions and Recommendations

5.1. Conclusions

Several conclusions were reached by considering the results of the studies involved in the development of the amine impregnated adsorbent. The most important of these conclusions are summarized as follows:

- Synthesis and pore-expansion with the large synthesis vessel resulted in high quality MCM-41 and PE-MCM-41. Comparison of the characteristics of materials obtained from replicate batches suggested that the procedures carried out in the large vessel were reproducible, however, further studies would be required to obtain a statistically significant conclusion.
- Compared to the small vessel, the use of the large vessel resulted in MCM-41 with higher surface area, similar pore volume, and smaller pores. The expansion procedure was somewhat less effective with the large vessel since both the pore diameter and the pore volume were smaller. These differences could possibly be due to a lower average temperature resulting from the larger mass of material.
- Based on both physical properties of the amines examined as well as the results of preliminary tests, DEA was found to be the most promising amine for the impregnation of porous solid supports.
- Of the four porous supports examined, PE-MCM-41 resulted in the adsorbent with the highest amine content and CO_2 adsorption capacity. The high amine content was attributed to the large pore volume of the support, enabling it to accommodate

a larger quantity of the amine while still maintaining the free-flowing nature of the powder. Compared to other similar adsorbents reported in the literature, the DEA impregnated PE-MCM-41 exhibited a significantly higher amine content and adsorption capacity, which could also be attributed to the large pore volume of the support.

- The adsorption capacity and adsorption rate of DEA impregnated PE-MCM-41 both reached maxima at an amine content exceeding that required for pore saturation.
- Due in part to a strong interaction between DEA molecules and the surface of the PE-MCM-41 support, the ratio of adsorbed CO_2 to impregnated DEA did not reach the stoichiometric maximum of 0.5.
- The use of ethanol as the impregnation solvent resulted in improved adsorption performance compared to the use of water.
- Based on comparative data obtained from adsorption isotherms as well as testing in the bench-scale adsorption system, it was found that under dry conditions the impregnated material is best suited for applications requiring the removal of CO_2 from gases with low CO_2 partial pressures. This was especially evident considering that the adsorption capacity of the impregnated material was higher than that of the most common industrially employed CO_2 adsorbent, zeolite 13X, for partial pressures below 0.15 atm.
- Compared to zeolite 13X, the impregnated material can be regenerated under much milder temperature conditions and can be used in humid streams with little humidity control.

- The adsorption capacity of the impregnated material for methane was very low, making it potentially suitable for the removal of CO_2 from natural gas streams.
- Under the conditions used for the current study, the cyclic stability of the impregnated adsorbent was comparable to that of another amine impregnated material reported in the literature, however, the stability requires improvement prior to use in an industrial setting.
- The agglomerate characteristics and the elevated heat of adsorption were found to hinder the performance of the amine impregnated adsorbent in the fixed-bed configuration.
- In the powdered form, the adsorption kinetics of the impregnated material were similar to those of zeolite 13X, however, when agglomerated and tested in a fixed-bed configuration, the zeolite outperformed the impregnated material. Improvements in the agglomeration method may result in performance improvements for the impregnated material by reducing the size of the agglomerates and reducing the void fraction of the bed. These improvements should limit premature breakthrough of the adsorbate. Increasing the bed density of the column filled with the amine impregnated adsorbent to approximately 0.58 g/cm^3 would be sufficient to increase the performance to a level which would exceed that of the zeolite filled column, assuming no decrease in the performance was associated with the increased bed density.

In general, the amine impregnated adsorbent exhibited several promising characteristics, and with further studies, the performance of the material could potentially reach a level suitable for testing under actual industrial conditions. Applications that should be considered when conducting future developmental studies include the pre-purification of air prior to cryogenic distillation, emergency SCBAs and enclosed habitable environments, natural gas purification, and purification of air for fuel cells.

5.2. Recommendations

Based on the conclusions presented, the following recommendations should be considered for future developmental work:

- Studies should be carried out to determine if modifications to the experimental conditions could be made to achieve similar support characteristics using the large synthesis vessel as those obtained using the small synthesis vessel. Also, repeat tests are required to verify if the differences in characteristics are statistically significant.
- The cyclic stability of the amine impregnated PE-MCM-41 should be studied in more detail. Stabilizing compounds such as PEG should be examined, as should alternate methods of imparting amine functionality to porous supports (i.e. grafting). Also, the effects of other possible feed compounds on the performance of the adsorbent must be ascertained prior to suggesting the material for use in an industrial setting.
- FT-IR studies could be used to verify the existence of the hypothesized chemical interaction between DEA and the surface hydroxyl groups of the support. Following verification of this interaction, chemical modification of the support

surface could be employed prior to impregnation to prevent deactivation of the DEA and improve the CO_2/DEA ratio.

- Alternate agglomeration methods and binders should be explored to obtain more favourable agglomerate characteristics and improve the performance of the impregnated material in a fixed-bed configuration.
- Testing with the fixed-bed adsorption system should be pursued to obtain statistically significant test results. Also, testing should be carried out to verify the hypothesis that the performance of the column filled with the impregnated material would exceed that of the column filled with zeolite 13X when exposed to lower CO_2 partial pressures (< 0.02 atm).
- Researchers working on solid supported amines should remember that the density of the final form of the adsorbent (powder, agglomerate, etc.) will be very important in most applications and especially in those employing a fixed-bed configuration. While high specific adsorption capacities may be achievable (i.e. high wt%), this may be counteracted by low adsorbent density, which will limit the quantity of adsorbent contained in the bed.

By implementing these recommendations, it will be possible to obtain a more complete evaluation of the amine impregnated adsorbent and determine the true potential of the material for the removal of CO_2 from gas streams.

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Appendix I: Summary table of preliminary agglomeration trial results

Active component	Binder	Method	Binder content [a] (wt%)	Drying temp. (°C)	Strength [b]
6.34-DEA-H_2O (PE-MCM-41)	Starch	granulation, aqueous binder sol'n	50	65	good [c]
PE-MCM-41	Kaolin	granulation, dry mix + water	30	500	none
6.78-DEA-H_2O (PE-MCM-41)	Ludox HS-30	granulation, aqueous binder sol'n	32	35	inadequate
PE-MCM-41	Ludox HS-30, diluted	granulation, aqueous binder sol'n	63	200	none
6.78-DEA-H_2O (PE-MCM-41)	Ludox HS-30	extrusion	18	60	good [c]
6.34-DEA-H_2O (PE-MCM-41)	Ludox HS-30	granulation with Agglo-miser, sprayed aqueous binder sol'n	28	60	good [d]
6.78-DEA-H_2O (PE-MCM-41)	Cab-O-Sil + DEA	granulation, aqueous binder sol'n	50	60	weak
6.78-DEA-H_2O (PE-MCM-41)	MCC	compression, 105 atm	50	25	weak
5.5-DEA-H_2O (PE-MCM-41)	none	compression, 210 atm	-	25	inadequate
5.5-DEA-H_2O (PE-MCM-41)	MCC	compression, 105 atm	50	25	inadequate

Active component	Binder	Method	Binder content [a] (wt%)	Drying temp. (°C)	Strength [b]
5.5-DEA-H_2O (PE-MCM-41)	MCC	compression, 210 atm	50	25	inadequate
6.6-DEA-H_2O (PE-MCM-41)	Bentonite	compression, 148 atm	28	25	weak
6.6-DEA-H_2O (PE-MCM-41)	Bentonite	compression, 295 atm	28	25	weak
PE-MCM-41	Cement	granulation, dry mix + water	27	25	none
6.6-DEA-H_2O (PE-MCM-41)	Cement	granulation, dry mix + water	27	25	none
PE-MCM-41	PVOH2	granulation, aqueous binder sol'n	27	75	inadequate
PE-MCM-41	PVOH3	granulation, aqueous binder sol'n	20	75	inadequate
6.78-DEA-H_2O (PE-MCM-41)	PVOH2	granulation, aqueous binder sol'n	4.5	75	inadequate
6.78-DEA-H_2O (PE-MCM-41)	PVOH2	granulation, aqueous binder sol'n	5.8	75	inadequate
6.78-DEA-H_2O (PE-MCM-41)	PVOH2	granulation, aqueous binder sol'n	7	77	inadequate
6.78-DEA-H_2O (PE-MCM-41)	PVOH2	granulation, aqueous binder sol'n	11	75	inadequate
6.78-DEA-H_2O (PE-MCM-41)	PVOH2	extrusion, shaping with Agglo-miser	8.8	60	good [d]

Active component	Binder	Method	Binder content [a] (wt%)	Drying temp. (°C)	Strength [b]
6.6-DEA-H_2O (PE-MCM-41)	PVOH3	granulation, aqueous binder sol'n	6.6	75	inadequate
6.78-DEA-H_2O (PE-MCM-41)	PVOH3	granulation, aqueous binder sol'n	7	65	good
6.78-DEA-H_2O (PE-MCM-41)	PVOH3	granulation, aqueous binder sol'n	8	65	good
6.6-DEA-Et (PE-MCM-41)	PVOH2 + PVOH3	extrusion	8.7	80	good

a) Binder content of dried agglomerate

b) Qualitative evaluation of strength – none = no agglomerate formed; weak = agglomerate formed but very weak; inadequate = agglomerate formed with some resistance to pressure, good = agglomerate suitable for use in bench-scale column

c) CO_2 adsorption capacity was low

d) Poor agglomerate size distribution, method was difficult to carry out