



MASTER THESIS 2011

Title: Mass transfer study for carbon dioxide capture in a gas-liquid membrane contactor.	Subject: Absorption of CO₂ in K₂CO₃ - NaOH solution by using PTFE and PVA Membrane contactor.
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ABSTRACT <p>In membrane based contacting equipment, a membrane not only acts as a definite interface between two phases but it also plays a vital role in determining the overall performance of the system. Keeping in view the significance of membrane, porous PTFE (GORE-TEX®) and dense PVA membranes were studied for removal of CO₂ from a mixture of N₂ and CO₂. Potassium carbonate solution (10% by weight) with NaOH (as promoter) was used at room temperature to absorb CO₂ at different operating pressures (1.3-2.7 bar) and liquid flowrates (2-4 ml/s). For all experiments overall mass transfer coefficient was calculated on the basis of liquid stream analysis.</p> <p>Goal of work :</p> <ul style="list-style-type: none"> To investigate the effect of CO₂ partial pressure on performance of system by using mix gas (30% CO₂/70% N₂) at three different operating pressure (1.36, 2.0 and 2.7 barg). 	

- To Study the effect of liquid composition and liquid flowrate on the flux of CO_2 at all operating pressures.
- To examine different membranes i.e. PTFE (porous) and PVA (dense) membrane for CO_2 absorption in membrane contactor and evaluate of their performance on the basis of overall mass transfer coefficient calculated on the basis of liquid stream analysis.
- Study solvent-membrane interaction by testing hydrophobicity of membrane after every experiment.
- Study the performance of system over time and consider the effect of partially wetted pores on flux of CO_2 .

Conclusions :

- In experiments conducted with PTFE membrane contactor, availability of CO_2 for absorption was found to be the limiting factor. It can be concluded that resistance to mass transfer offered by membrane ($1/k_m$) and gas film ($1/k_g$) plays an important role in determining the overall performance of absorption system.
- Flux of CO_2 calculated from experiments with PVA was higher than PTFE membrane contactor, under all operating conditions.

Recommendations for future work

Keeping in view the high flux of CO_2 observed in experiments with PVA membrane contactor, it is recommended that, a thin cross-linked film of PVA should be developed between two macro-porous and hydrophobic flat sheet membranes (say PTFE) and applied in membrane contactor. The hydrophobicity of PTFE will provide a high pore entry pressure while PVA will result in high flux. The resulting membrane will act as a facilitated membrane for transportation of CO_2 with a fine control over degree of swelling.

**I declare that this is an independent work according to the exam regulations
of the Norwegian University of Science and Technology**

Date and signature.....

Foreword and acknowledgments

This project started in January 2011, the coldest winter in last 135 years of Norwegian history and ended in bright and warm summer. In between, this report was assembled in Trondheim, on planes and airports between Europe and South Asia. Results were compiled and conclusions were drawn over cups of tea in Lahore. I started this work with lots of challenges, few suggestions and little knowledge of this field. As I went through the project, ideas started to take shape and valuable guidance came along to help. Almost one third of the experiments were repeated and over 400 titrations were performed to verify the data. This work reminds me that hard work and firm belief is the key to success.

I am thankful to Prof. May-Britt Hagg for her invaluable guidance and for giving me this opportunity to work on a fascinating project. I thank Prof. Hallvard Svendsen for his valuable suggestions through out the project. All member of our membrane group provided a supportive, friendly and wonderful working environment. I am thankful to all members of MEMFO group especially Lily, Marius, Taek-Joong, Inger Lise and above all Karen Nessler. My deepest gratitude goes to Dr Arne Lindbrathen; his innovative ideas have been a great support through out the project.

My Parents should know that I appreciate their love and support immensely; they have always been positive about my life decisions. I would also like to thank Mrs. Shala Gondal, who has been an inspiration and true guideline for me.

Trondheim, May 2011

Muhammad Saeed.

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List of symbols

Symbol	Description	units
Latin Characters		
A	Knudsen selectivity	-
$C_{A,i}$	Concentration of component A at interface	mol/m^3
$C_{A,b}$	Concentration of component A in bulk gas	mol/m^3
$C_{B,b}$	Bulk concentration of solvent	mol/m^3
$C_{l,i}$	Interfacial concentration of absorbed gas usually CO_2	mol/m^3
$C_{l,b}$	Bulk concentration of absorbed gas usually CO_2	mol/m^3
$C_{\text{CO}_2,i}, C_{\text{CO}_2,o}$	Gas inlet and outlet concentration of CO_2 for membrane cell	mol/m^3
$C_{sl,i}, C_{sl,o}$	Concentration of lean and rich solvent	mol/m^3
d	pore diameter	m
dC_A	Concentration difference of component A between 2 points	mol/m^3
dC_i	concentration difference of component I between 2 points	mol/m^3
dz	Distance between two points in gas/liquid film	m
dx	thickness of one layer/entire membrane	m
D_{AB}	Diffusion coefficient of gas A in a mixture of A&B	m^2/s
D_i, D_i	Diffusivity of component i	m^2/s
D_m	Mean diffusion coefficient	m^2/s
E	Enhancement factor	-
ΔF	Applied force to pull the ring through liquid surface	N
H	Henry's law constant	$\text{m}^3 \cdot \text{Pa}/\text{mol}$
$J_A, J_A, J_{\text{CO}_2}$	Flux of component A usually referred to flux of carbon dioxide	$\text{mol/m}^2 \cdot \text{s}$
k_{ov}	Overall mass transfer coefficient	m/s
k_g	Individual mass transfer coefficient for gas film	m/s
k_L	Individual mass transfer coefficient for liquid film	m/s
k_l°	Liquid film mass transfer coefficient for physical absorption	m/s
k, k_m	Individual mass transfer coefficient for membrane	m/s
K'	Equilibrium concentration in membrane divided by that of feed	-
K	K is partition coefficient for partially wetted hydrophobic porous	-

	membrane	
k_R	Reaction rate constant	$\text{m}^3/\text{mol}\cdot\text{s}$
k'	Boltz man constant	J/K
LMCD	Log mean concentration difference	mol/m^3
l	thickness	m
M_H	Hatta number	-
M_a, M_b	Molecular weight of component A and B	kg
M_a, M_b, M_w	Molecular weight of component a and b,w	kg, gm
N_k	Knudsen number	-
P_i	Permeability of component I through membrane	barrar
P	Pressure	bar, psi
$p, p_{Cg,b}$	Partial pressure of CO_2 in bulk	bar
$p_{Cg,i}$	Partial pressure of CO_2 at interface	bar
P_f	Feed pressure (for permeation of solvent)	bar
p_P	Partial pressure of solvent in gas stream in case of solvent permeation	bar
P	Perimeter	m
ΔP	Pressure difference	bar
r	Pore radius	m
R	General gas constant 8.314	J/mol-K
S_i	Solubility of component i	$\text{mol}/\text{m}^3\cdot\text{bar}$
T	Temperature	$^{\circ}\text{C}, \text{K}$
V_a, V_b	Diffusional volume of gas A and B	
$W_{\text{dry}}, W_{\text{wet}}$	Membrane weight dry and wet	mg

Greek characters

ε	Porosity	-
r	Radius, referred to pore radius	$\mu\text{m}, \text{m}$
η	Viscosity	$\text{Kg}/\text{m}\cdot\text{s}$
γ	Surface tension	N/m
τ	Tortuosity	-
λ	Mean free path	m

π	pi	-
		-
θ_c	Contact angle	

Abbreviations

CCS	Carbon dioxide capture and storage
GHG	Green house gas
GA	Glutaraldehyde solution
IGCC	Integrated gas combined cycle
LMCD	Log mean concentration difference
PVA	Poly vinyl alcohol
PV	Pervaporation
PTFE	Poly tetra fluoro-ethylene
PSf	Poly sulphone
R.O	Reverse osmosis
SLM	Suspended liquid membrane
SEM	Scanning electron microscope
S01	10% K_2CO_3 solution with 0.1M NaOH
S05	10% K_2CO_3 solution with 0.5M NaOH
UF	Ultra filtration
WGS	Water gas shift

Abstract

Emission of green house gases especially CO_2 has become a major environmental issue. In order to control and reduce the CO_2 emissions, carbon capture and storage (CCS) is an important tool. Removal of acidic gases by absorption in alkanolamines (MEA, DEA, etc), alkali salt (Na_2CO_3 , K_2CO_3 , etc) and alkali solutions (NaOH, KOH. etc) by using packed/ tray absorber column is a well known process.

Membrane technology is a relatively new but promising candidate in this field. Since its introduction, several goals have been achieved but still a lot more is needed to make this technique compatible with existing technology. Gas-liquid membrane contactor is a hybrid process that offer advantages such as high specific surface area and selectivity. Numerous studies have been carried out for better understanding of mass transfer mechanism and to address the difficulties in operation for one of the most attractive and challenging application of membrane contactor: the absorption of CO_2 .

Membrane contactors based on micro-porous hydrophobic materials offer remarkable performance; flux of CO_2 can be significantly enhanced by using highly permeable membrane. Nevertheless, undesirable effects, as gradual changes in membrane structure due to interaction with solvent and/or partial wetting of the pores can dramatically affect the performance of entire system.

This project intends to provide a basic mass transfer study in membrane contactor by focusing on the effect of membrane-solvent interaction and alkalinity of solvent on performance of system. Microporous PTFE (GORE®TEX) and dense composite poly vinyl alcohol (PVA) membranes were used in a contactor to absorb CO_2 by the help of K_2CO_3 solution (promoted by NaOH) at a pressure range of 1.36 to 2.7 bars. Based on liquid stream analysis, overall mass transfer coefficient was used to study the effect of pressure and solvent flowrate on performance of system. Mixture of N_2 and CO_2 containing 30% CO_2 was used as feed gas and all experiments were conducted at room temperature with a constant volumetric flowrate of gas, while liquid flowrate was varied in a range of 2 to 4ml/s at room temperature. Contact angle of distilled water on PTFE membrane was used to analyze the hydrophobicity of membrane after every experiment. A time based experiment was conducted to see the effect of membrane aging on the performance of system and hydrophobicity of membrane.

Results from experiments conducted with PTFE membrane shows that membrane and gas film resistance have a significant contribution in overall resistance to mass transfer.

Presence of NaOH in potassium carbonate solution increases its precipitation/fouling potential and a decline in hydrophobicity of PTFE membrane with increase in pH of solvent was observed.

A thin film composite membrane with a dense layer of highly cross-linked PVA (hydrophilic material) was used in membrane contactor to study absorption of CO₂. Performance of PVA membrane contactor was compared with PTFE, flux of CO₂ was observed to be appreciably high for PVA than PTFE membrane contactor. PVA membrane swells by absorbing water, and permeability of CO₂ increases, presence of excess OH⁻ ions makes PVA act like a facilitated membrane for transport of CO₂. On the other hand, PVA is a hydrophilic material and permeation of water through membrane can not be avoided.

Based on experimental results it can be said that PVA membrane is a potential candidates for low pressure applications such as post combustion CO₂ capture.

Thesis outline

The intention of this thesis is to present mass transfer study for absorption of CO₂ in a gas-liquid membrane contactor, based on lab scale experimentation.

In membrane based contacting equipment, a membrane not only operates as a definite interface between two phases but it also has a vital contribution in overall performance of the system. Keeping in view the significance of membrane, porous PTFE (GORE-TEX®) and dense PVA membranes were studied to remove CO₂ from a mixture of N₂ and CO₂. Potassium carbonate solution with NaOH (as promoter) was used at room temperature to absorb CO₂ at three different operating pressures (1.3, 2.0 & 2.7 bars) and liquid flowrates (2-4 ml/s). For all experiments overall mass transfer coefficient was calculated on the basis of liquid stream analysis.

This report consists of two sections. First section (part 1) presents a preface to CO₂ capture, introduction to membrane separation technology (focusing on its application in membrane contactor), and details of mass transfer phenomena in membrane contactor and reaction kinetics involved in chemical absorption of CO₂ in solvent.

Second section (part 2) elaborates the experimental procedure for mass transfer study (in membrane contactor), testing of PVA and PTFE membranes, results & discussion from experiments, conclusions from this project and recommendations for future work in this field.

The title of this thesis is mass transfer study for CO₂ capture in a membrane contactor. The main objective of investigations is to develop a basic understanding of mass transfer through different materials; therefore high pressure was not needed. The setup used for experimentation had a limitation of 100 psi (6.8bar) design pressure so; experiments were conducted at low pressure. Most important parameter for mass transfer through a membrane is the partial pressure difference of CO₂ which was achieved by operating at three different pressures (1.36, 2.0 and 2.7 bar).

Keeping in view the closed environment of lab and hazards involved with H₂S and other acidic gases present in a typical process stream, only a mixture of nitrogen and carbon dioxide was used for experimentation.

PART 1

Theoretical background

Introduction

1.1 Introduction

The global energy consumption increases as a result of economic growth. To meet this ever growing demand in energy, a number of processes are employed. At present, combustion of fossil fuel is a major source of energy production. In 2004, 78% of the primary energy demand was met by combustion of fossil fuels (Beretta, 2007). According to data provided by Mascon (2007), current growth in energy demand is 2% per year and at the moment over 80% of world's energy requirement is full filled by combustion of oil and gas.

BP (2011) provided a review of energy requirement in last forty years and also presented the contribution of different sources in fulfilling the requirement. Based on their work, the growth in energy demand for last forty years, contribution of different energy sources and provided a prediction of future trends (presented in figure 1.1).

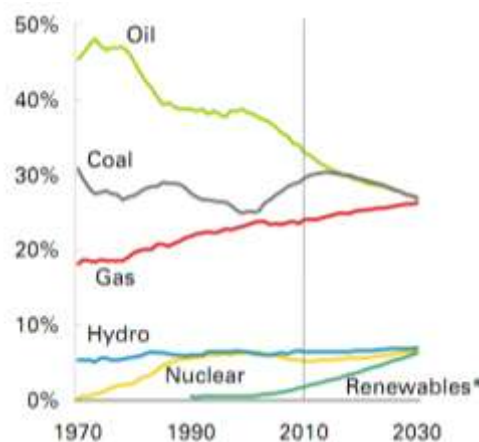


FIGURE 1.1: SHARE OF DIFFERENT ENERGY SOURCES IN MEETING ENERGY DEMANDS. (BP, 2011)

Due to combustion of fuel in high quantity emission of CO_2 has become an important environmental issue. A well to wheel analysis by Lopez et al. (2009) shows that approximately two thousand gram-

equivalent of CO₂ is emitted per kilometer by combustion of fuel for transportation purposes. Compared to the data from 1990, a report from United Nation Statistic Division (2010) shows an increase in CO₂ emission by 29% for Norway and 128% for Pakistan. In order to address the effect of CO₂ on our environment and limit the emissions, several protocols and conventions had been signed.

In addition to power generation and transportation, large quantity of CO₂ is produced as byproduct in some industrial processes. Steam reforming of natural gas is an example of industrial process which uses methane from natural gas to produce hydrogen and carbon dioxide. In USA about ten million ton hydrogen is produced every year, 95% of it from natural gas reforming (Wise, 2006); CO₂ is a major byproduct of this process.

Natural gas itself is a mixture of several gases; its composition varies from field to field and well to well. Generally it contains methane over 80% and rest is CO₂, H₂S, N₂, primary alkenes & alkenes (working group 3, 2005). Carbon dioxide present in natural gas not only reduces its calorific value but also causes corrosion in pipes & process equipments (due to its acidic nature). Natural gas pipeline specifications usually limits the CO₂ content in a range of 2 to 5% and in case of liquefied natural gas (LNG) the CO₂ concentration should be in a range of 50 to 100 ppm (Ma'mun et al., 2007). To meet the set standard, natural gas is treated prior to distribution; this process of CO₂ removal is called natural gas sweetening and it involves different techniques, primarily based on absorption of CO₂ in a solvent.

12 Carbon capture and storage

Introduction of green technology is one promising way to reduce CO₂ emissions. Besides switching over to new fuel, development of carbon dioxide capture and storage (CCS) is also necessary. Carbon capture from point source of emissions has been widely recognized as one of the several approaches to mitigate the effect of unregulated release of CO₂. IEA analysis report (2008) suggests that by 2050 CCS will have to contribute over 19% in green house gas (GHG) emission control.

Carbon dioxide capture is a vast field which cover the removal of CO_2 from high pressure process streams and low pressure flue gas treatment plants, however, due to process economy, application of this technique is limited to facilities where large quantity of CO_2 is produced. Carbon dioxide capture, a major part of CCS process is further divided into three basic types (Working group 3, 2005; Olajire, 2010).

- Pre-combustion CO_2 capture process.
- Post-combustion CO_2 capture process.
- Oxy-fuel CO_2 capture process.

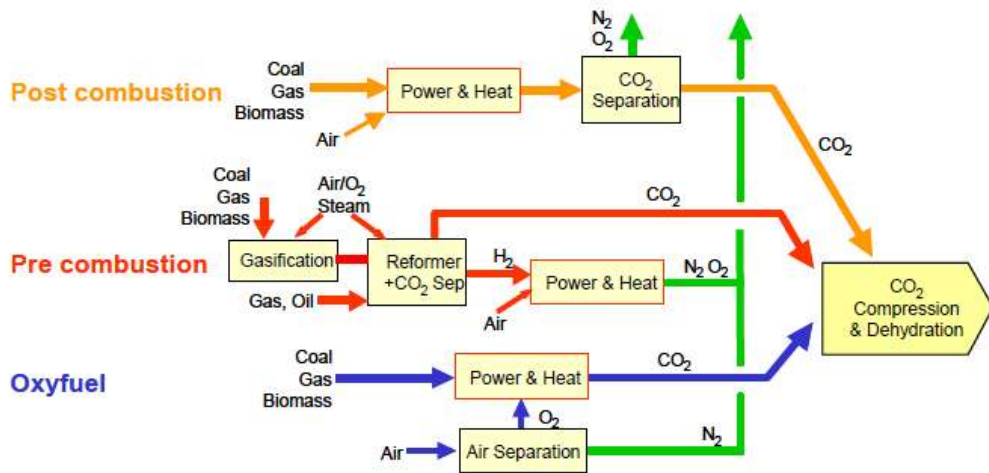


FIGURE 1.2 PATHWAYS TO CO_2 CAPTURE (adapted from Svendsen, 2007).

12.1 Pre-combustion CO_2 capture process

Pre-combustion CO_2 capture deals with removal of carbon dioxide prior to complete oxidation. It is generally related to integrated gas combined cycle (IGCC) power plants or steam reforming unit. CO_2 is removed from a mixture of H_2 and CO_2 after water gas shift (WGS) reaction (working group 3, 2005). Pre-combustion capture offers a more moderate energy penalty compared to post combustion. The high partial pressure of CO_2 encourages the use of highly efficient technology

(physical absorption), which further reduces the energy penalty. The primary disadvantage of pre-combustion capture is high power generating cost (Olajire, 2010).

12.2 Post-combustion CO₂ capture process

Post combustion treatment deals with removal of CO₂ from flue gas. Like desulfurization it is also a down stream process. A large volume of process stream and low concentration of CO₂ results in huge process equipments and high capital cost. Apart from low CO₂ partial pressure some challenges faced during designing phase of post-combustion CO₂ capture plant are high temperature, high energy consumption in solvent regeneration and solvent loss (Olajire, 2010).

12.3 Oxy-fuel CO₂ capture process

Oxy-fuel combustion is a modified post-combustion process. In this process pure oxygen is used instead of air in combustion process, this gives high concentration of CO₂ in flue gas. “Due to absence of nitrogen in combustion mixture production of No_x is limited, while a large quantity of pure oxygen is required, which is expensive, both in terms of capital cost and energy consumption”. (Olajire, 2010).

12.4 CO₂ capturing techniques

Capturing CO₂ contributes up to seventy five percent in the overall CCS cost and adds fifty percent to electricity production cost (Feron et al., 2005). These numbers may vary with different CCS schemes but reduction in capture cost is the most important issue for the CCS process to be acceptable to the industry. CO₂ removal processes can involve several physical & chemical separation methods. Some popular techniques used for CO₂ removal are as:

- Membranes, using selective barriers to separate gases
- Solvents, using absorption liquids to separate gases
- Sorbents, using selective particles to separate gases
- Cryogenic, using difference in points of condensation to separate gases.

Since more than one method can be used for a set of conditions, process economy is the deciding factor for selection of a method or group of methods. Tables 1.1 summarize the existing and emerging CCS techniques for all process conditions.

TABLE 1.1 CAPTURING PROCESSES (working group 3, 2005).

Capturing technology	Process stream CO ₂ /CH ₄		Post-combustion CO ₂ /N ₂	
	Current	Emerging	Current	Emerging
Solvent (absorption)	Physical solvents Chemical Solvents	Improved solvents, Novel contacting equipments.	Chemical solvents	Improved solvents, Novel contacting equipments.
Membrane	Polymeric	Ceramic Facilitated transport CMS Contactor	Polymeric	Ceramic Facilitated transport CMS Contactor
Solid sorption	Ziolite Activated carbon		Ziolite Activated carbon	Carbonates/carbon based process
Cryogenic	Ryan-Holmens process		Liquefaction	Hybrid process

12.5 CO₂ storage

CO₂ is used to increase oil recovery in depleting oil fields; Horn and Steinberg (1982) were among the first ones to suggest CSS for mitigation of climate changes and its use in oil production. After removal of CO₂ from process stream, next energy demanding step is its compression and transportation of CO₂ to under ground geological formations. Carbon dioxide is compressed to 0.2% of its volume at STP and transported through pipe, ships and road tankers (Skovholt, 1993).

An over view of complete CSS process is schematically described in figure 1.3.

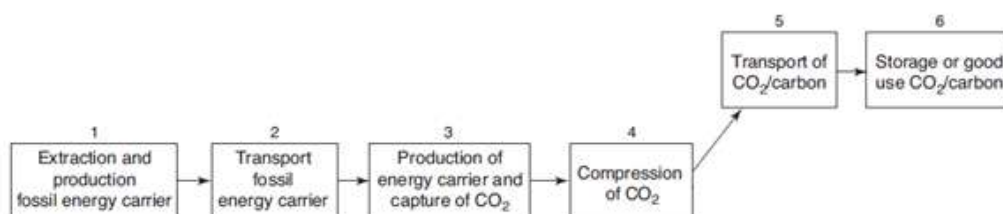


FIGURE 1.3 SCHEMATIC DIAGRAM OF CSS PROCESS (FERON, 2005)

13 Sweetening of natural gas

As discussed earlier, concentration of CO₂ in natural gas is usually higher than maximum permissible level for transportation (in pipes) and industrial processes, acidic gas is treated to reduce CO₂ content before distribution; this process is known as sweetening of natural gas. Depending on operating conditions and level of sweetening, single process or combination of different processes (mentioned in table 1.1) can be applied (Khol and Nielsen, 1997).

Sweetening of natural gas is analogous to flue gas treatment, except for different operating conditions. The most common method for carbon dioxide capture is the use of alkanolamines.

In 1980, membrane was introduced for gas separation with many unknown parameters (Noble and stern, 1995). Membrane technology is now more established technique with some advantages over alkanoamines (Tabe-Mohammadi, 1999).

14 Carbon dioxide capturing techniques

As listed in table 1.1, there are several techniques available for removal of CO₂ from a gas stream, but due to its wide scale use, importance of solvent process can not be denied. Membrane technology is an emerging technique with promising prospects. Keeping in view the theme of this project these two methods for CO₂ capturing are briefly discussed in this section.

14.1 Solvent absorption process

Solvent absorption process is based on sorption of CO₂ in a regenerable physical or chemical solvent. It is widely used and the most developed CO₂ capture process (Khol and Nielsen, 1997)

Chemical absorption involves a fast and reversible reaction between solvent and CO₂; it can perform well even at low CO₂ partial pressure. Carbon dioxide is acidic in nature and chemical absorption takes place through neutralization reaction. Carbon dioxide reacts with chemical solvents to form a weakly bonded intermediate compound (Kohl and Nielsen, 1997). Since chemical absorption has the ability to perform well at low CO₂ concentrations, it is preferred for post combustion treatment. Another application of solvent absorption process sweetening of natural gas and is regarded as the most mature technology. Natural gas industry usually employs alkanoamines or Benfield solution to absorb CO₂ from natural gas. (Olajire, 2010)

In physical absorption, CO₂ is absorbed in a solvent without reacting with solvent, absorption is temperature and pressure dependent. Physical solvent process contains organic solvents which attach themselves with acid gas components rather than reacting with them and forming new compounds. High partial pressure of CO₂ in feed stream favors absorption of CO₂ (Olajire, 2010). Regeneration of solvent takes place by multistage flashing of solvent down to atmospheric pressure (Khol and Nielsen, 1997). Physical absorption takes place at high pressure and equipment sizes are smaller than post combustion units. Due to regeneration by simple flashing, energy requirement in case of physical absorption is less compared to chemical absorption. The drawback of this process is interaction of solvent with hydrocarbons in process stream and its high price.

The selection of a technology for a given application depends on many factors; partial pressure of CO₂ in the gas stream, required level of sweetening, regeneration of the solvent, sensitivity to impurities, particulates, purity of the desired CO₂ product, capital and operating costs of the process, the cost of additives necessary to overcome fouling and corrosion and the environmental impacts plays an important role in designing a process. A list of popular physical and chemical solvents is given in table 1.2.

Table 1.2 Commercial solvents and their chemical names. (Working group 3, 2005)

Solvent Name	Type	Chemical Name
Rectisol	Physical	Methanol
Selexol	Physical	Diethyl ether of polyethylene glycol(DMPEG)
Benfield	Chemical	Potassium carbonate
MEA	Chemical	Mono ethanol amine
MDEA	Chemical	Methyldiethylamine

142Membrane Technology

A novel concept in gas separation is the use of selective membranes to remove certain components from a gas stream; CO₂ from natural gas (natural gas sweetening) or CO₂ from hydrogen (pre-combustion systems) or CO₂ from flue gas (post-combustion). Membranes are semi-permeable barriers, able to separate substances by various mechanisms (solution/diffusion, adsorption/diffusion, molecular sieve and ionic transport). They are available in different materials, either organic (polymeric) or inorganic (carbon, zeolite, ceramic or metallic) and can be porous or dense (Mulder, 1997; Luebke, 2006). Membranes act as a perm-selective barrier which separates one or more gases from a feed mixture and generate a specific gas rich permeate as shown in Figure 1.4.

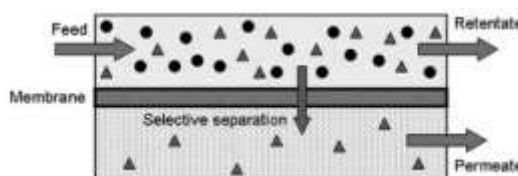


FIGURE 1.4: SCHEMATIC OF MEMBRANE GAS SEPARATION (adapted from Olajire, 2010.)

Since the introduction of membrane in this field a lot has been done to understand and develop an economical membrane based process for CO₂ separation. But limitations such as high energy consumption for compression of gas and maintenance cost have made the use of membrane less economical compared to MEA or any other alkanoamine process (Feron et al. 1992; Morimoto et al. 2002). None the less several advantages such as high specific surface area and ease of operation offered by a membrane can not be denied.

143 Membrane Contactor

A new approach towards separation of CO₂ from process stream or flue gas is the use of gas-liquid membrane contactor. It is a hybrid process derived from conventional gas-liquid absorption and membrane separation. A membrane act as a permeable barrier between liquid and gas phase, it provides high surface area for two fluids to get in contact and keep them separate at the same time. Mass transfer takes place at the interface (membrane). High surface area to volume ratio of membrane results in a compact system while, affinity of solvent towards absorption of CO₂ results in high selectivity. By using hollow fibers membrane module, specific surface area up to 30 times higher than conventional absorber columns can be achieved (Qi and Cussler, 1985(a, b)). A comparison between specific surface area for different contacting equipments is presented in table 1.3.

Table 1.3 specific surface area of different contacting equipments (adapted from Noble and stern, 1995)

Contactor	Surface area per volume (ft ⁻¹)
Free dispersion columns	1-10
Packed tray columns	10-100
Mechanically agitated columns	50-150
Membrane contactor	500-2000

Note 3.28 ft = 1 meter

In gas-liquid membrane contactor liquid and gas streams do not mix, problems such as loading or flooding are avoided and an independent control over individual flow rates of liquid and gas stream

is possible. Selectivity of the system depends on liquid stream only but the permeability of membrane plays a vital role in determining the over all performance of the system (Working group 3, 2005).

Selection of membranes and solvent are closely related to each other. Solvent selection is determined by partial pressure of acid gas in feed and retentate stream where as for membrane, high permeability and its inert nature towards gases and solvent are important parameter. In order to provide a better control over the system and maintain a uniform layer of liquid at membrane-liquid interface, pressure of liquid stream is kept at slightly higher pressure than gas. For porous membranes, maximum pressure difference depends on pore entry pressure (Mulder, 1997). Since the liquid and gas streams are independent of each other high concentrations of solvents can be used at low liquid flowrate but, with increasing the alkanolamine concentration surfaces tension of solvent decreases and pore entry pressure is reduced (Alvarez et al., 1998). Attributes of gas-liquid contactor are summarized in table 1.4.

Table 1.4 Attributes of membrane contactor (adapted from Drioli and Giorno, 2009)

Advantages	Disadvantages
No flooding	Channeling and bypassing of fluids
No loading	Operative pressure depend upon breakthrough ones
No foaming	Membrane fouling
No need of phase separation down stream	Membrane lifetime is limited
No dispersion between phases	Additional resistance is offered by membrane
Reduces size and weight	Low stability of solvent and carrier in supported liquid membrane.
Well defined constant interface	
High interfacial area in small volume	
Flexibility and modularity	
No nee to work with fluids of different densities	

15 Problem formulation

Membrane gas absorption may still be considered in its developing stages, the major objective of this project is to develop a fundamental understanding of mass transfer mechanism involved in membrane based absorption. This study has been limited to application of gas-liquid membrane contactor for absorption of CO_2 in alkali salt solution. Two set of solvents were used for experimentation (10% K_2CO_3 in water, promoted by 0.1 and 0.5 M NaOH).

In a gas-liquid membrane contactor, membrane acts as a semi permeable interface between the gas and liquid stream. To understand the role of membrane in determining the performance of process and ease of operation, two different membranes (PTFE and PVA) were tested. Being a fundamental study this work has been limited to flat sheet membrane only. Following points are the focus of attention in this report:

- To investigate the effect of CO_2 partial pressure on overall performance of system by using mix gas (30% CO_2 /70% N_2) at three different operating pressure (1.36, 2.0 and 2.7 barg).
- To study the effect of liquid composition and liquid flowrate on the flux of CO_2 at all operating pressures.
- To examine different membranes i.e. PTFE (porous) and PVA (dense) membranes for CO_2 absorption in membrane contactor and evaluating their performance on the basis of overall mass transfer coefficient calculated from liquid stream analysis.
- To study the interaction of solvent with membrane by testing hydrophobicity of membrane after every experiment.
- To monitor the performance of system over time and investigate the effect of partially wetted pores on flux of CO_2 .

PTFE has been studied by several researchers for application in gas-liquid membrane contactor but PVA based pervaporation membrane has been used for first time in this field. The theme of the project is to present an experimental based mass transfer study in membrane contactor. This required an innovative lab-scale setup, which is a major part of this work.

Membrane Contactor

Membrane contactor, although an emerging technology, yet is a potential replacement for conventional absorbers. Conventional scrubbers for flue gas cleaning are distinguished by huge space requirement and high capital cost. In addition, a scrubber suffers from several operational limitations such as entrainment and loading. The membrane contactor can simply overcome these operational challenges by physically separating liquid and gas streams. A number of advantages including high specific surface area, separate gas and liquid flow channels, small foot print of plant, ease of scale up and definite gas- liquid interfacial area makes a membrane contactor promising candidate for industrial scale application (Drioli and Giono, 2009).

The first known application of membrane for gas-liquid contact was oxygenation of blood using hydrophobic Gore-Tex membrane (Esato and Eiseman, 1975). Qi and Cusler (1985) were the first ones to study micro porous membrane contactors on industrial scale. They studied micro-porous PP hollow fibers and found that mass transfer area for membrane remains unchanged even for very low flowrate of liquid or gas stream. Qi and Cusler also concluded that for absorption in strong acid and alkali, membrane offers the maximum resistance to mass transfer, which is not surprising as absorption in such system is gas film controlled. Comparing the results of membrane contactor and packed towers, they found the overall mass transfer coefficient to be 30 times higher for membrane contactor.

TNO group in Netherland has studied the application of PP membrane contactor for CO₂ removal from flue gas, they estimated the cost to process to be 30% less compared to the cost of process using packed towers (Feron and Jansen, 2002).

2.1 Mass Transfer in membrane contactor

For absorption of CO₂ in a solvent by using membrane contactor mass transfer takes place in three steps.

- Transfer of CO₂ from gas bulk to membrane interface (through gas film).
- Transfer of CO₂ through membrane.
- Transfer of CO₂ from membrane-liquid interface to liquid bulk (through liquid film).

2.1.1 Diffusion through gas film

Molecular diffusion is the principal phenomenon responsible for transportation of CO₂ from bulk gas to gas-membrane interface. Motion of a gas molecule is described as random walk (Brownian motion), as illustrated in figure 2.1. These molecules move in random direction with an average velocity, collision of molecules with one and other or walls of container results in change of their direction. Average distance traveled by a molecule is called mean free path (λ), usually the magnitude of λ has in an order of 10^{-7} meters and it is a direct measurement of diffusivity for a substance (Basmadjian, 2007).

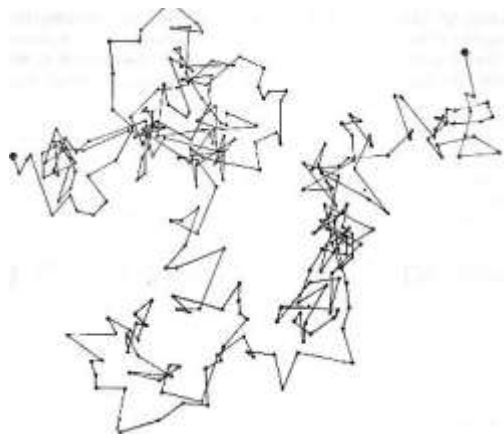


FIGURE 2.1 BROWNIAN MOTION OF GAS MOLECULES (ADDAPTED FROM LEE AND HOON, 2001)

Transport of molecules from a point of high concentration to a point of lower concentration by diffusion is described by Fick's law (equation 2.1).

$$J_A = -D_{AB} \frac{dC_A}{dz} \quad (2.1)$$

Equation 2.1 describes the flux of gas "A" between two points, having a concentration difference of " dC_A " and distance dz apart from each other. At any time molecules diffuse in both directions (high to low and low to high concentration) but the number of molecules diffusing from high concentration is greater and based on concentration difference of two points a net positive flux is observed. Bulk gas contains higher number of CO_2 molecules than gas-membrane interface. The number of molecules moving towards the membrane is higher than the number of molecules moving back, a net driving force is observed which results in a positive flux of CO_2 from bulk gas to gas-membrane interface (Geankoplis, 2003).

The lower concentration of CO_2 at membrane interface is due to following reasons (Mulder, 1997; Geankoplis, 2003):

- Diffusion of molecules from gas-membrane interface towards bulk gas.
- Transportation of gas through membrane.

In a mixture of gases, bulk concentration of a particular gas remains constant but within gas film concentration profile shows a decreasing trend up to gas-membrane interface. Gas film resistance ($1/k_g$) is a function of diffusion coefficient and thickness of film. Diffusion coefficient in gas phase is usually of an order $10^{-4} \text{ m}^2/\text{s}$ which is appreciably high compared to $10^{-9} \text{ m}^2/\text{s}$ for liquids (Basmadjian, 2007; Mulder 1997). If the permeation of CO_2 through membrane is low, then interfacial concentration approaches bulk concentration. Gas film resistance can become negligible if single gas is used (Sobieszuk and Pohorecki, 2010).

Based on Fick's law the resistance to mass transfer offered by gas film can be calculated by a simple flux equation (2.2).

$$J = k_g (p_{\text{Cg,b}} - p_{\text{Cg,i}}) \quad (2.2)$$

In equation (2.2) J is flux of CO_2 through gas film, p_{Cgb} , P_{Cgi} are bulk and interfacial partial pressures of diffusing gas, k_g is mass transfer coefficient for gas film, which depends on diffusivity & film thickness. Gases with low diffusivity shows high gas film resistance ($1/k_g$) and a concentration profile shown in figure 2.2 (a) is observed. For gases with high diffusivity concentration profile in figure 2.2(b) is observed.

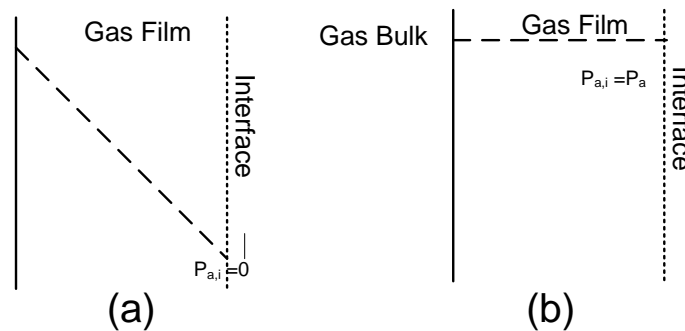


FIGURE 2.2 CONCENTRATION PROFILES OF CO_2 IN GAS FILM SHOWING HIGH RESISTANCE (A) AND NO SIGNIFICANT RESISTANCE IN FILM (B).

Resistance to mass transfer offered by gas film can become the most dominating factor in expression for overall mass transfer coefficient if highly reactive solvent is employed (Qi and Cusler, 1985).

2.1.2 Liquid Side Mass Transfer

Absorption of gas in any solvent also depends on two parameters.

- Diffusion through liquid film
- Rate of reaction between gas and solvent

In case of physical absorption the amount of gas taken up by solvent is estimated by Henry's law. Flux of a gas based on liquid film resistance can be estimated by equation 2.3 (Olav Erga, 1993).

$$J = k_l (C_{l,i} - C_{l,b}) \quad (2.3)$$

Here (in equation 2.3) C_{li} and C_{lb} are interfacial and bulk concentrations of absorbed gas. k_l^o is liquid side mass transfer coefficient, when no reaction takes place. For chemical absorption, where reaction between CO_2 and solvent takes place, mass transfer is increased by a factor called enhancement factor (E). Equation 2.4 shows the expression for mass transfer coefficient through liquid film (k_l) when reaction between gas and solvent takes place.

$$k_l = E \cdot k_l^o \quad (2.4)$$

In absorption process where chemical reaction occurs, diffusion through liquid film and reaction between solvent & gas molecules takes place as two parallel steps and concentration of gas and solvent both changes within the liquid film. Enhancement factor is a “ratio of amount of gas absorbed with reaction and the amount of gas that is physically absorbed”. Simply it is ratio of liquid side mass transfer coefficients with (k_l) and without reaction (Olav Erga, 1993).

$$E = \frac{k_l}{k_l^o} \quad (2.5)$$

Furthermore, enhancement factor for absorption of a gas can theoretically be calculated by the help of, Hatta number and infinite enhancement factor.

Hatta number (M_H) related the maximum conversion (reaction) with in film and maximum transport (diffusion) through the film.

$$M_H^2 = \left(\frac{\text{maximum conversion in film}}{\text{maximum transport through film}} \right)$$

For a reaction between two reactants “A” and “B” equation (2.6) represents the expression for hatta number.

$$MH = \frac{\sqrt{D_A k_l C_{B,b}}}{k_l^o} \quad (2.6)$$

Here D_A is diffusion coefficient of “A” through gas film, k_1 is kinetic rate constant of r the reaction, $C_{B,b}$ bulk concentration of solvent and k_1^0 is mass transfer coefficient without reaction. On the base of rate of reaction, absorption is further divided into three types.

- Slow reactions.
- Fast reaction.
- Instantaneous reactions.

In slow regime, rate of reaction is slightly faster than diffusion of gas in liquid. Reaction occurs uniformly through out liquid (bulk) and rate of absorption is diffusion controlled. On the other hand in fast regime the reaction takes place within liquid film and a concentration gradient of diffusing gas is observed in liquid film. For instantaneous regime the reaction is so fast that the gas and the solvent cannot coexist, a reaction plane is formed within the liquid film and mass transfer is governed by the diffusion of both gas and solvent within the film. Concentration profile for slow, fast and instantaneous reactions is given in figure 2.3 (Olav Erga, 1993).

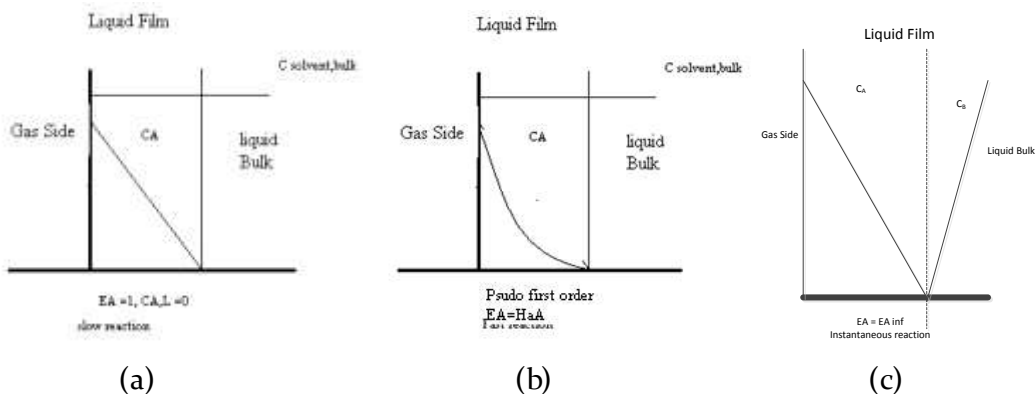


FIGURE 2.3 CONCENTRATION PROFILES OF CO_2 IN LIQUID FILM SLOW, FAST, INSTANTANEOUS REACTION WITH SOLVENT.

213 Mass transfer through membrane

In a gas-liquid membrane contactor membrane acts as a permeable interface; permeability of membrane plays a vital role in determining the amount of gas available for absorption, solvent flowrate and overall performance of the system (Mulder, 1997).

As mentioned earlier, a membrane contactor promises high interfacial area at all flowrates (Qi and Cusler, 1985), phase separation helps in overcoming the problems like entrainment or flooding (Mulder, 1997) but it also has some disadvantages. With respect to mass transfer one disadvantage of membrane based gas-liquid absorption is the addition of a new phase (membrane). Contribution of membrane in overall mass transfer coefficient depends on operating conditions and transport mechanism of gas through membrane (Mulder, 1997). Generally porous membranes are used in membrane contactor but dense membranes can also be used for high pressure application (Mansourizadeh and Ismail, 2009).

Porous membranes

For porous membranes two scenarios can exist.

- Pores are filled with gas
- Pores are filled with liquid

If membrane pores are filled with liquid the concentration profile of permeating gas within membrane is presented in figure 2.4 (a), for gas filled pores, the concentration profile for gas within membrane is illustrated in figure 2.4(b). From this figure it is clear that gas filled pores offered less resistance to mass transfer and a high concentration of gas at membrane-liquid interface is available for absorption. Wang et al. (2005) suggested that if number of wetted pores increases by 5% then overall resistance to mass transfer is increased by 20%. Hydrophobic materials such as PTFE, PP or PE are preferred for use as porous membranes to ensure gas filled pores.

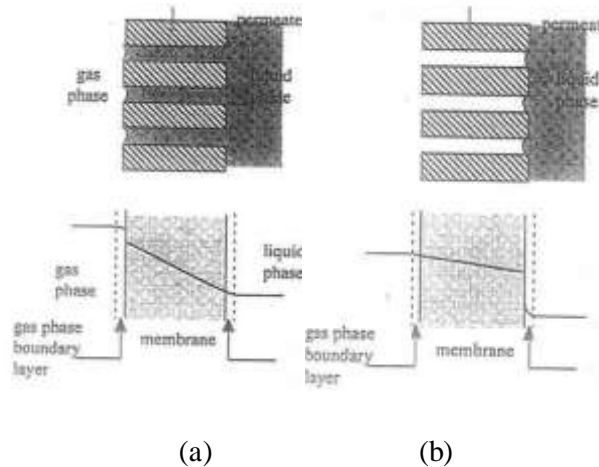


FIGURE 2.4 CONCENTRATION PROFILE OF A IN MEMBRANE (A) PORES ARE FILLED WITH LIQUID; (B) PORES ARE FILLED WITH GAS (ADAPTED FROM MULDER, 1997)

Dense membranes

Self supporting dense membranes or composite membranes can be used in membrane contactors. Use of dense silicon rubber for oxygenation of blood is an example. As the penetration of liquid in dense membrane is difficult, a good phase separation results in high stability of operating system. On the other hand nonporous layer acts as an additional resistance to mass transfer. This resistance can be reduced by applying a thin layer of dense polymer over a macro porous support and operating at a temperature higher than glass transition temperature. In this thesis PVA composite membrane is used which shows swelling and high CO_2 permeation. Figure 2.5 shows concentration profiles of a permeating gas in composite membrane and self supporting dense membrane. It is clear that resistance to mass transfer offered by the dense layer is highest among all layers in a composite membrane and this resistance depends on thickness of dense layer (Mulder, 1997).

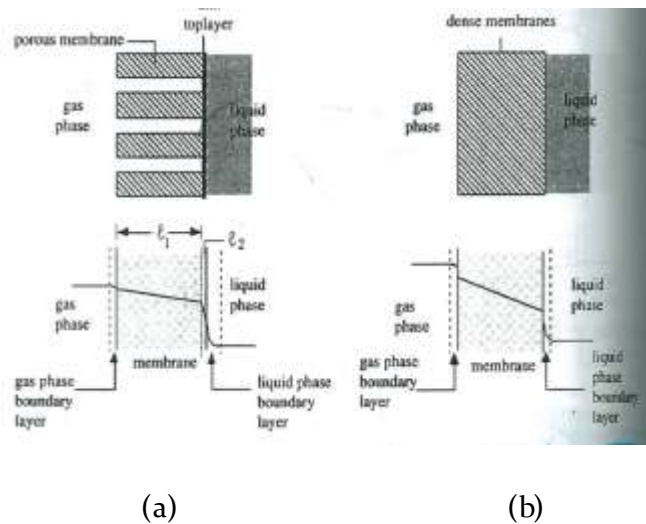


FIGURE 2.5 CONCENTRATION PROFILE OF GAS IN COMPOSITE (A) AND SELF SUPPORTING (B) DENSE MEMBRANE (ADAPTED FROM MULDER, 1997).

Summarizing all the aspects discussed regarding mass transfer through gas film, membrane and liquid film, a generalized concentration profile for absorption of gas by using gas-liquid membrane contactor is shown in figure 2.6.

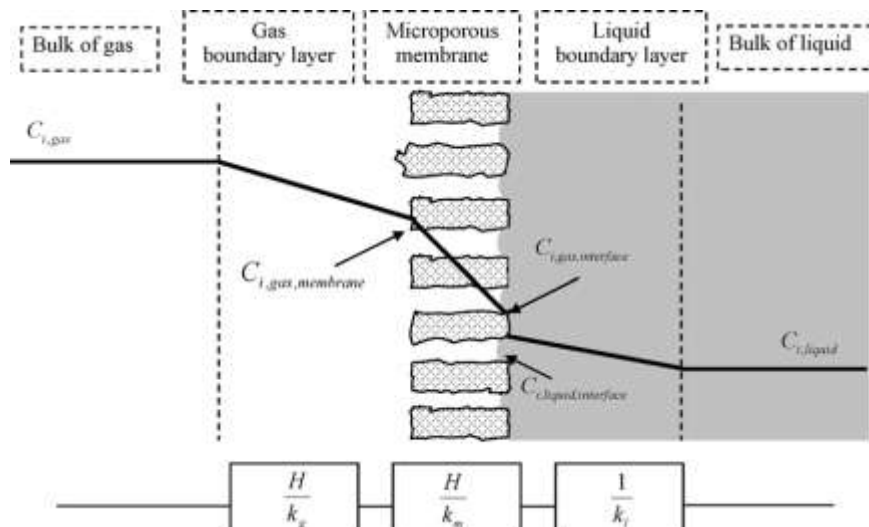


FIGURE 2.6 CONTRIBUTION OF LIQUID/GAS FILM AND MEMBRANE TO OVERALL RESISTANCE TO MASS TRANSFER. (IVERSEN ET AL., 1997)

2.2 Mass Transfer coefficient

This work aims to characterize the main resistance in mass transfer for absorption of CO₂ in chemical solvent (potassium carbonate solution promoted by sodium hydroxide) using gas-liquid membrane contactor, PVA (poly vinyl alcohol) and PTFE (GORE-TEX) membranes were subjected to study in membrane contactor.

For gas liquid absorption process overall resistance to mass transfer is expressed as resistance in series (Basmadjian, 2007). Mavroudi et al. (2003), Gabelman and Hwang (1999) used resistance in series model to study mass transfer in membrane contactor. By changing the operating conditions and solvent, contribution of gas film, membrane and liquid film in mass transfer can be increased or decreased and the rate limiting step can be shifted from gas film to liquid film or membrane. Equation 2.7 provides an expression for flux of gas as a function of concentration difference between two phases.

$$J = k_{ov} \left(\frac{p}{H} - C_l \right) \quad (2.7)$$

J is the flux of a gas “A” (say CO₂), k_{ov} is the overall mass transfer coefficient, p is partial pressure of “A”, H is Henry’s law constant and C_l is concentration of “An” in liquid phase.

The driving forces for transportation through gas film, membrane and liquid film are incorporated in concentration difference between bulk gas (p/H) and bulk liquid (C_l), an overall driving force for mass transfer. Similarly the overall mass transfer coefficient is a sum of individual mass transfer coefficients, as presented in equation 2.8.

$$\frac{1}{k_{ov}} = \frac{H}{k_m} + \frac{1}{k_L} + \frac{H}{k_g} \quad (2.8)$$

In this equation k_{ov} is overall mass transfer coefficient, k_m , k_l and k_g are membrane, liquid film and gas film resistance. Correlations of mass transfer coefficient for membrane contactor having porous and dense membrane operated with physical and chemical absorbents are given in table 2.1.

Table 2.1 Mass-transfer correlation for membrane contactor (adapted from Noble and Stern, 1995).

Basic situation	Correlation	Definitions	Remarks
Without reaction			
Nonporous membrane	$k = \frac{DK'}{l}$	D= diffusion coefficient K'= equilibrium concentration in membrane divided by that of feed l = thickness of membrane	D is the diffusivity coefficient of gas in membrane
Porous non wetted membrane	$k = \frac{D\varepsilon}{l\tau}$	ε/τ is void fraction to tortuosity ratio	
Porous membrane with pores wetted by solvent	$k = \frac{KD\varepsilon}{l\tau}$	K is partition coefficient	The value of K is dependent upon hydrophobic nature of membrane
With chemical reaction			
Fast reaction	$k = \sqrt{k_R D}$	k_R is reaction rate coefficient	Can often be applied to non first order reactions
Instantaneous reactions	$k = k_o \left(1 + \frac{reag_i}{n(solv)}\right)$	k^o is coefficient without reaction k is coefficient with reaction	Reaction is so fast that reactants can not co-exist.

22.1 Driving force in membrane contactor

For absorption of CO₂ in liquid, the driving force is the concentration difference of CO₂ between gas and liquid phase. In gas phase partial pressure of CO₂ represents its concentration; higher partial pressure ensures more CO₂ at the interface. Since the area of membrane used for experiments is very small, it is valid to assume that partial pressure of CO₂ is constant throughout the entire length of membrane. In liquid stream, the concentration of solvent leaving the module is lesser than that of fresh solvent. A concentration profile of solvent with respect to membrane length is presented in figure 2.7 (Wang R, et al., 2005).

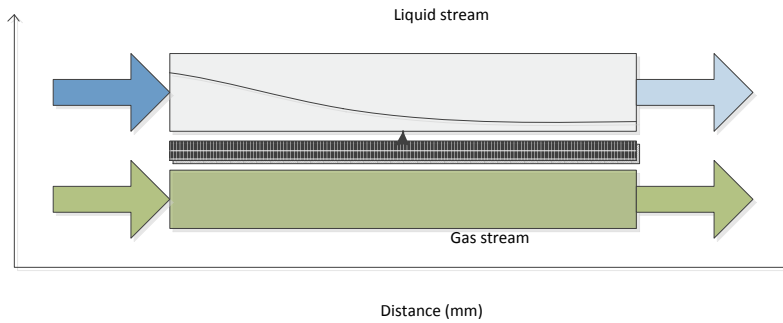


FIGURE 2.7 CONCENTRATION PROFILE OF SOLVENT WITH RESPECT TO DISTANCE TRAVELED IN MEMBRANE CONTACTOR

Due to absorption of gas in liquid, a decrease in concentration of solvent is observed; driving force through out the membrane length is not constant. A log means value of concentration difference between gas and liquid stream is used for calculation of overall mass transfer coefficient (Kohl and Nielsen, 1997; Wang R et al., 2005) and equation 2.7b is now written as (2.9)

$$k_{ov} = \frac{J}{LMCD} \quad (2.9)$$

$$LMCD = \frac{(C_{CO_2,i} - C_{sl,i}) - (C_{CO_2,o} - C_{sl,o})}{\ln \frac{C_{CO_2,i} - C_{sl,i}}{C_{CO_2,o} - C_{sl,o}}} \quad (2.10)$$

CO_2 is considered to be an ideal gas and general gas law is used to convert the partial pressure of CO_2 to concentration. $C_{\text{CO}_2,i}$ and $C_{\text{CO}_2,o}$ are inlet & outlet concentration of CO_2 in gas stream, and it is constant. $C_{\text{sl},i}$ and $C_{\text{sl},o}$ is inlet and outlet concentrations of CO_2 in liquid stream.

Membrane

In a gas-liquid membrane contactor, the membrane not only defines the interface between two fluids but also plays a fundamental role in overall performance of system. In order to understand the mass transfer process in membrane contactor, it is essential to know transportation mechanism of gas molecules through membrane.

3.1 Membranes separation

Membranes are used for separation of solids from liquids (filtration), liquid from saline solution (reverse osmosis), liquid from a mixture of liquids (pervaporation) and gas from gases (Mulder, 1997). Gas-liquid membrane contactor is a hybrid process similar to conventional alkali-carbonate process used for absorption of CO_2 but, the use of membrane introduces a new dimension with respect to contacting mechanism and influence the overall performance.

3.1.1 Principal of membrane separation

Membranes are perm-selective barrier between two streams (Mulder, 1997). A simple representation of membrane separation is presented in figure 1.4. The driving force needed for transportation of any single specie through a membrane is its potential difference across the membrane. Net driving force may be achieved in the form of pressure difference, concentration difference, temperature difference or electrical field. The difference in partial pressure can be maintained either by keeping feed stream at higher pressure than permeate or using a sweep gas to maintain a necessary pressure difference.

Equation (3.1) to (3.3) describes the flux of component i based on concentration difference or partial pressure difference as driving force for transportation. Equation (3.1) describing steady state diffusion, presented by Fick in 1855, it is the base for flux equation for gases passing through membranes.

$$J_i = -D_i \frac{dC_i}{dx} \quad (3.1)$$

In equation (3.2) dp_i is partial pressure difference of component i . This equation is used to define permeability of a gas through membrane.

$$J_i = -D_i \frac{dC_i}{dp_i} \cdot \frac{dp_i}{dx} \quad (3.2)$$

$$P_i = -D_i \frac{dC_i}{dp_i} \quad (3.3)$$

If Henry's law applies then equation (3.3) is modified to equation (3.4).

$$P_i = D_i \cdot S_i \quad (3.4)$$

Transport through a membrane can take place through one of the following processes:

- Knudsen diffusion.
- Viscous/Bulk diffusion.
- Solution diffusion.
- Surface diffusion.
- Molecular sieving.

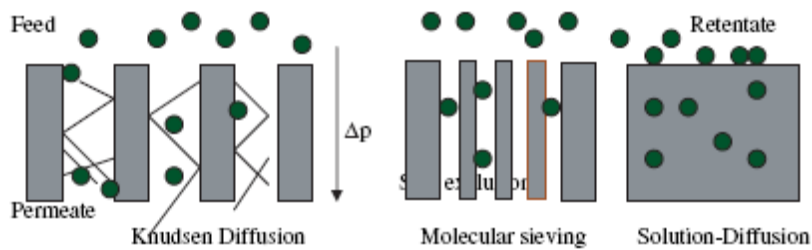


FIGURE 3.1 SCHEMATIC DIAGRAMS OF KNUDSEN DIFFUSION, MOLECULAR SIEVE AND SOLUTION DIFFUSION.

(Adapted from Olajire, 2010)

Knudsen diffusion is usually observed in membranes with a pore size of 2-100nm (Burggaaf and Cot, 1996); It occurs when collision between molecules and pore walls is significant. One simple way of predicting the type of diffusion is by calculating Knudsen number (N_{Ku}) (Geankoplis, 2003).

Diffusion is strongly dependent on molecular mass, shape of molecules and operating temperature. At high temperature more collision takes place between molecules and N_{ku} decreases. Equation (3.5) shows that Knudsen selectivity depends on square root of molecular mass ratio for permeating gases.

$$A = \frac{D_a}{D_b} = \sqrt{\frac{M_b}{M_a}} \quad (3.5)$$

Solution diffusion is the governing transport mechanism in dense membranes. On feed side of membrane, molecule of gas at gas-membrane interface absorbs into the membrane and desorbs on permeate side due to concentration difference. Usually polymeric membranes demonstrate higher solubility for organic gases/vapors; hence a membrane shows high permeability towards organic compounds. A polymer consists of amorphous and crystalline domains and transportation takes place through amorphous domain only. Solubility of non interacting gases in an elastomer is usually low and can be described by Henry's law, as illustrated in figure 3.1(a). Equation 3.4 shows that permeability also depends on diffusion; smaller molecules show high diffusivity in membranes. According to figure 3.1 (a and b) rubbery polymers show higher concentration of absorbed gas

compared to glassy polymers; this is due to high chain flexibility and free volume shown by a polymer in rubbery state. Organic molecules show high flux due to high solubility but they also tend to dissolve the membrane, so cross-linking of polymer is done to avoid loss of membrane if interacting solvents are present in process stream. (Mulder, 1997).

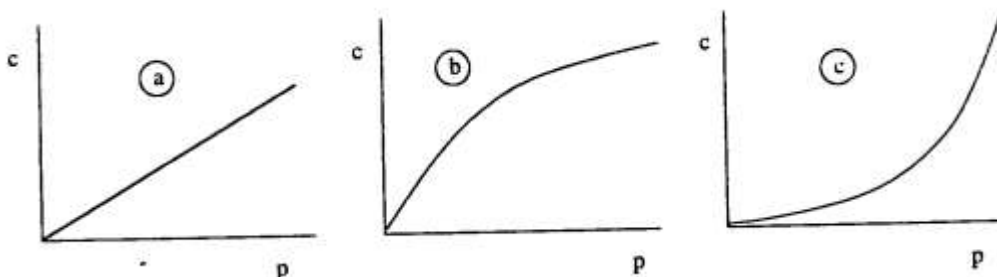


FIGURE 3.2 SORPTION ISOTHERMS FOR IDEAL AND NON IDEAL SYSTEM (ADAPTED FROM MULDER, 1997)

Surface diffusion is dominated in membranes with an effective pore diameter is in a range of 5-6 Å (Rao and Sircar, 1993, 1996), where the competitive adsorption of gases in porous become significant. Absorbed molecules diffuse over the surface, in these membranes smaller molecules can be retained compared to larger molecules based on interaction with membrane pore walls.

Molecular sieving takes place in pores of diameter 3-4 Å. Separation takes place on the basis of molecular size so these membranes are used for separation of small molecules from mixture of gases. Molecules diffuse through pores like Knudsen diffusion temperature has great effect on the selectivity.

In a membrane more than one phenomenon can be responsible for transportation. For example in composite membranes, Solution diffusion governs the transport in dense layer, where as in substrate and support layers Knudsen and/or Bulk diffusion is observed. (Mulder, 1997). In this chapter transport through PVA (dense) and GorTex (porous) membrane has been discussed.

3.1.2 Membrane preparation

The technique used to prepare a membrane not only influences its morphology but it also plays an important role in determining the transport mechanism and separation performance. The commonly used techniques for synthesis of polymeric membrane are as:

- Phase inversion: As suggested by the name, this process involves solidification initiated by transition from liquid state to liquid-liquid demixing. In this process, high concentration phase of polymer solidifies to form a solid matrix (Mulder, 1997).
- Stretching: Stretching is a technique used only to prepare porous membranes. A film or foil of partially crystalline polymer is stretched perpendicular to the direction of extrusion to form small ruptures and a porous structure is obtained with a pore size of 0.1-0.3 μm (Mulder, 1997). PTFE (GORE-TEX) membrane used in this project is an example of membrane prepared by stretching.
- Track-etching: Track-etching can be used to obtain the simplest pore geometry by applying high energy particle radiation to the film and then immerse the film in an acid/alkaline bath. The particle damage the polymer to create tracks, acid or alkali then etches the polymer along the track and uniform cylindrical pore with a narrow pore size distribution is formed (Mulder, 1997).
- Coating: coating is a technique used to prepare a thin, homogenous film of membrane on support. It is used to prepare composite membranes.

Composite membrane

The successful development of composite polymeric membrane is a milestone in the history of membrane technology. Defect free composite membrane can easily be developed in labs; an ultra thin selective layer of polymer with desired properties can be developed over porous support layer. In a composite membrane permeability and selectivity depends on thin dense layer where as porous

support layer is responsible for mechanical strength of membrane. Following techniques can be used to prepare composite membranes (Mulder, 1997).

- Dip-coating
- Sprat coating
- Spin coating
- Interfacial polymerization
- In-situ polymerization
- Plasma polymerization
- Grafting

Cross-linking

Cross-linking deals with connecting the chains of polymer by physical or chemical means. In physical cross-linking rearrangement or entanglement of crystalline groups take place by heating/freezing, pressurizing or radiation, whereas in chemical cross-linking reaction takes place between cross-linking agent and polymeric chains (Bolto et al., 2009). Cross-linking is an effective method to control undesired plasticization or swelling of polymeric membrane.

Procedure for development of a composite membrane is schematically illustrated in figure 3.3(a) and picture of PVA composite membrane is shown in figure 3.3(b).

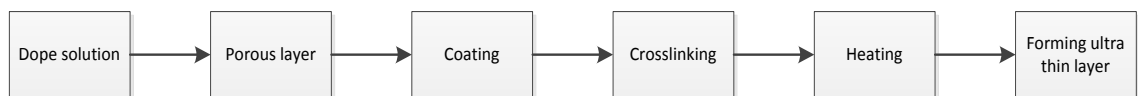


FIGURE 3.3(A) PROCESS DIAGRAM FOR SYNTHESIS OF COMPOSITE MEMBRANE (ADDAPTED FROM MULDER M., 1997)

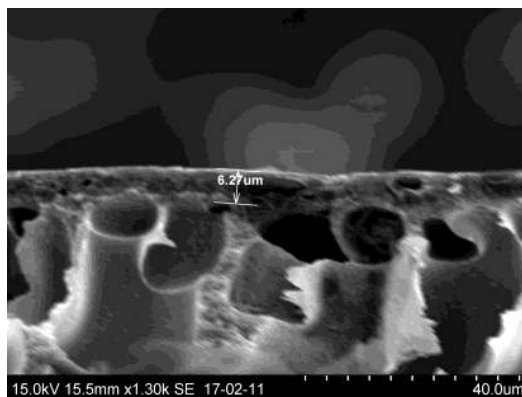


FIGURE 3.3(B) SEM PICTURE OF PVA COMPOSITE MEMBRANE.

3.2 PVA membrane

Poly vinyl alcohol is a well recognized polymer for water treatment in membrane separation technology. A cross-linked poly vinyl alcohol membrane (PVA) shows good chemical, thermal and mechanical stability. Highly polar nature of PVA makes it resistant towards fouling and it can be used for pressure driven water treatment application. Due to their oleophobic properties, PVA membranes are used for separation of organic compounds from one and other or from water by pervaporation (PV).

Permeation properties of a PVA membrane greatly depend on degree of cross-linking. Higher degree of cross-linking leads to more selective, less permeable and non porous membranes but due to its hydrophilic nature, PVA must be modified (cross-linked) to minimize swelling when applied to water based applications (Bolto et al., 2009; Immelman et al., 1993).

Peter et al. (1976) demonstrated that PVA membranes are highly resistant to acidic and alkaline environments. Due to its ability to form stable blends with many other polymers, a fine control over performance (by cross-linking) and inert behavior, PVA can be used for a wide range of applications. PVA shows good mechanical stability but a thick self supporting membrane results in low flux. To overcome this problem, composite membrane containing thin film of PVA cross-linked

with dialdehyde was developed by Cadotte (1990). The resulting membrane was used at pH as high as 13.

Low pressure R.O membranes made by cross-linking thin layer of PVA with polysulphone (PSf) and other ultra filtration (UF) substrate shows high salt rejection and they are commercially used in desalination plants (Kawada et al., 1987).

During 1980s Membrane based pervaporation proves gained acceptance as a tool for separation of liquid mixtures (Tusel and Brüschke, 1985). Keeping in view this strongly growing interest in use of membrane for pervaporation, Hoang and Yeom (1990) studies cross-linked PVA membranes and found that flux and selectivity of a membrane depends on cross-linking agent and reaction time for cross-linking. In 2009 Bolto et al. provided a detailed review of cross-linking agents for PVA membranes and industrial use of PVA membranes. Besides above mentioned application PVA is commercially used in a few more applications but low flux is the major hurdle for using PVA membranes in large-scale commercial operations. Some important features of PVA are listed in table 3.1.

Table 3.1 Attributes of PVA membranes (Bolto et al., 2009)

Positive	Negative
Excellent hydrophilicity	High degree of swelling
Permeability to water	Permeability to ions
Good mechanical properties	Compaction under pressure
Thermal resistance	Low flux when highly cross-linked
Resistance to chemicals	
Anti-fouling potential	
Film forming ability	
Low operating pressure	

As described above, PVA can be cross-linked with different material and used in a large number of liquid based applications, recently it has been investigated for gas treatment by blending PVA with other polymeric materials to induce facilitated transport. Deng et al. (2009) investigated PVAm /PVA blend membrane for CO₂/CH₄ separation. In this membrane permeability of 0.3 m³ (STP)/ (m²

bar h) for CO₂ and selectivity of 35 was observed. They also reported an increase in permeability with increase in humidity in gas stream. An increase in selectivity with increase in humidity up to 70% was also reported. Results obtained by Deng et al. (2009) for PVAm/PVA blend and PVA membranes are elaborated in table 3.2 and figure 3.4.

Table 3.2 Results of CO₂ permeation tests for PVA and PVAm membranes (Deng et al., 2009)

Membrane	CO ₂ permeance[m ³ (STP)/ (m ² bar h)]	Selectivity
PSf	0.14	12
PVA on PSf	0.10	16
PVAm/PVA on PSf	0.30	35

* PSf support (MWCO 50,000)

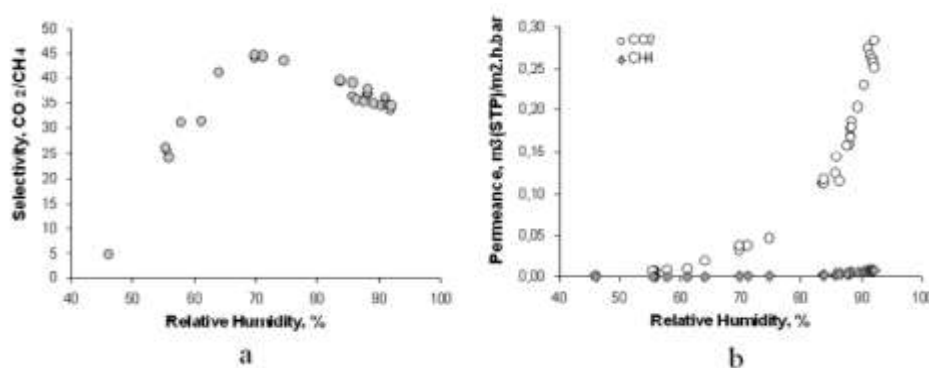


FIGURE 3.4 EFFECT OF RELATIVE HUMIDITY OF FEED GAS ON (A) CO₂/CH₄ SELECTIVITY AND (B) CO₂ PRESENCE (adapted from Deng et al., 2009)

Deng and Hagg (2010) studied the effect of swelling on permeation and selectivity for PVAm/PVA membrane and reported higher CO₂ permeance for a membrane operated in swollen state compared to the results from a membranes operating in dry state. Moreover, interactions between gases present in feed stream strongly effected the separation performance, as for separation of CO₂ from 10% CO₂-N₂ mixture, permeance up to 0.83 m³ (STP)/ (m² h bar) and selectivity up to 160 were observed at relative humidity 95%, while in separation of CO₂ from 35% CO₂-CH₄ mixture, CO₂ permeance up to 0.55 m³ (STP)/ (m² h bar) and selectivity up to 45 were obtained at relative humidity 92%.

In short good chemical, thermal and mechanical stability, film forming ability, antifouling potential, and high flexibility in performance (by cross-linking) makes PVA membranes a strong candidate for application in membrane processes containing liquid. Furthermore, high permeation of CO₂ in humid conditions makes PVA membrane a good candidate for CO₂ absorption by gas-liquid membrane contactor.

32.1 Transport mechanism of CO₂

Dense membranes are used when difference in molecular size is not significant enough to cause any separation. The PVA membrane had three layers; a thin and dense layer of PVA was supported by a micro porous substrate and support layer. In a composite membrane, resistance to mass transfer offered by dense layer is much higher than support layers so, transportation through dense PVA layer is considered to be as rate determining step.

The mechanism responsible for transport through dense layer is solution diffusion. Solubility is a thermodynamic parameter and predicts the amount of fluid sorbed at equilibrium conditions. Poly vinyl alcohol is a water soluble polymer and it shows high degree of swelling in presence of water. Existence of water in membrane increases chain mobility. This results in high flux and low selectivity. Moreover, if membrane is not properly cross-linked water may completely dissolve the membrane. CO₂ on the other hand does not interact with PVA so, diffusion through amorphous polymeric domains is the only transport mechanism for CO₂ under dry conditions. Trend for absorption of CO₂ in PVA (rubbery state) is similar to sorption isotherm shown in figure 3.1(a). Figure 3.1(c) shows interaction of water with membrane, consequently dissolving the PVA layer.

Poly vinyl alcohol is a water soluble compound which has a melting point higher than degradation temperature. Molecular weight of single repeating unit is 44 and it has a glass transition temperature of 85°C (Polymer processing, 2001). All the membranes used for experimental work were operated at room temperature.

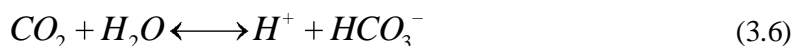
Deng and Hagg (2010) demonstrated that PVA membrane shows higher permeation in presence of moisture, in membrane contactor liquid stream consisted upon 10% K₂CO₃ aqueous solution so,

excess water was available for membrane to swell. Permeation of CO₂ through membrane takes place by two parallel mechanisms.

- CO₂ reacts with water to produce HCO₃⁻ and membrane behaves like suspended liquid membrane (SLM).
- CO₂ diffuses through free volume in membrane.

At membrane-gas interface CO₂ come in contact with moist membrane, it converts into HCO₃⁻ ions and permeates through membrane. Equation (3.6) represents the reaction which takes place in membrane. The dense PVA layer swells with water and acts more like a supported liquid membrane.

An appreciable increase in rate of absorption is observed at a pH of 9-10 compared to pH 7 (Bungay et al., 1983). The liquid stream used for absorption of CO₂ contain appreciable amount of NaOH and pH is in a range of 13.0 to 13.2 for different solvents thus PVA membrane acts like a supported gel layer of sodium hydroxide and its affinity to take up CO₂ is far higher than membrane swelled by water. The presence of NaOH in solution makes mass transfer mechanism through PVA membrane much more complicated, reactions involved in absorption of CO₂ are discussed in chapter 4(Absorption) of this report.



Due to presence of water, polymer chains become flexible and diffusion of CO₂ and N₂ also takes place at higher rate. Since both these phenomena (diffusion through membrane and solubilization) take place at the same time, the membrane acts as facilitated membrane. Although permeation of nitrogen should also increase with increase in swelling but the solvent on permeate side have very little affinity towards nitrogen. The PVA in membrane not only acts as an interface but also promotes the CO₂ transport.

3.2.2 Permeation of solvent

The PVA membrane used in membrane contactor was originally produced for application in pervaporation so, it is important to consider the chances of permeation of solvent through the membrane. Cross-linked PVA has been studied by several researchers for dehydration of organic compounds, appreciable flux of water, selectivity due to its chemical stability and hydrophilic nature of membrane has been observed (Bolto et al., 2009).

In membrane contactor solvent contains 90wt% water and due to presence of water PVA layer shows appreciable swelling. To ensure a smooth/continuous film of liquid at membrane-liquid interface liquid stream is kept at slightly higher pressure than gas stream. The gas stream in membrane contactor contains dry CO₂/N₂ gases. The driving force for transportation of liquid through membrane is partial vapor pressure across the membrane. For absorption of CO₂ gas stream is considered as feed stream where as for pervaporation liquid stream of membrane contactor becomes the feed and flux of water through membrane can be calculated by equation (3.7) (Mulder, 1997; Huang, 1991).

$$J_{water} = \frac{P_i(p_f - p_p)}{l} \quad (3.7)$$

3.3 PTFE GORE-TEX® membrane

Unlike PVA, Poly tetra fluoro-ethylene (PTFE) porous membrane has been subjected to study in membrane contactors for various applications. Iversen et al. (1997) studied mass transfer mechanism for removal of SO₂ from flue gas using GORE-TEX flat sheet membrane. Hoff (2003) developed a model of CO₂ absorption in membrane contactor using PTFE (GORE) Hollow fibers. Wetting of polymer is an important parameter for selecting a membrane in membrane contactor. Polymers with

higher surface energy are more wettable. In table 3.3 surface energies of some polymers that can be used to produce micro porous membrane is given.

Table 3.3 Surface energy of polymers (Mulder, 1997)

Polymer	Surface energy (10^{-3} N/m)
Polytetrafluoroethylene(PTFE)	19.1
Polypropylene(PP)	30
Polyvinylchloride(PVC)	36.7
Polyethylene(PE)	33.2

PTFE has the lowest surface energy and it is the most hydrophobic polymer among the four listed in table 3.3. For PE and PP membranes Kreulen et al. (1993) and Nishikawa et al. (1995) tested absorption of CO_2 in alkanolamine and concluded that after long term application resistance to liquid penetration breaks down, probably due to surface wetting and swelling of polymers. This work intends to present a wettability study of PTFE membrane with respect to operating conditions.

3.3.1 Membrane wetting

The effect of membrane wetting on the PP hollow fiber membrane by DEA solutions was theoretically studied by Wang et al. (2005). They found that if number of wetted pores is increased by 5% overall mass transfer decreases by 20%. More recent studies include Keshavarz et al. (2008), and Bottino et al. (2008). The mathematical model developed by Keshavarz et al. (2008) has analyzed the effect of partially wetted membrane on the absorption performance. The small fraction of membrane wetting can significantly decrease the flux. In addition, the effect of chemical reaction inside the wetted membrane pores on predicting membrane wetting fraction was also considered. Bottino et al. (2008) developed the mathematical model for predicting the gas removal efficiency of CO_2 separation from N_2 in gas-liquid membrane contactor.

332 Breakthrough pressure (pore entry pressure)

Since most of the systems used for CO₂ absorption are controlled by liquid film resistance, a smooth, homogeneous layer of liquid is required in contact with membrane on the other hand penetration of liquid in pores must be avoided for minimum overall resistance to mass transfer. The penetration of liquid in membrane depends on a trans-membrane pressure and wettability of membrane. Young-Laplace equation (3.8 a) is used to determine the breakthrough pressure for a hydrophobic, micro-porous membrane (Mulder, 1997).

$$\Delta P = \frac{-2\gamma \cos \theta}{r} \quad (3.8a)$$

ΔP is the pressure difference between liquid and gas streams as described in equation (3.8b)

$$\Delta P = P_{liquid} - P_{gas} \quad (3.8b)$$

The condition of hydrophobicity is fulfilled if $\theta > 90^\circ$, the breakthrough pressure increases with increase in surface tension of solvent, contact angle of liquid on membrane and decrease in pore size.

333 Transportation mechanism

The membrane used for experimentation was a PTFE porous membrane with average pore size of 0.2 μm . For a porous membrane a large variety of pore geometry is possible, some simple structures are schematically presented in figure 3.5 (a) and SEM picture of PTFE membrane is also shown in figure 3.5(b)



FIGURE 3.5(A) SCHEMATIC DIAGRAMS OF SIMPLE POROUS STRUCTURES (ADAPTED FROM MULDER, 1997)

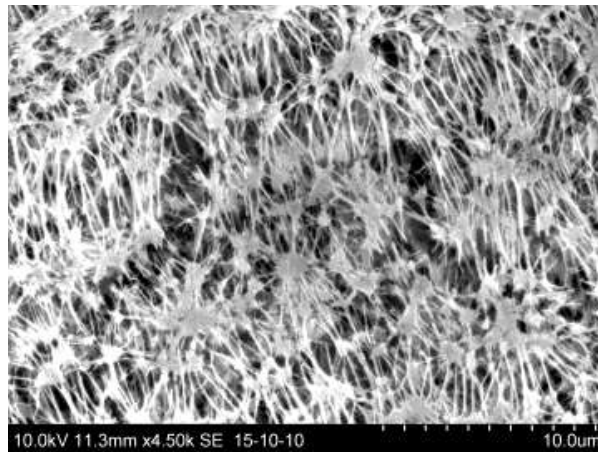


FIGURE 3.5(B) SEM PICTURE OF PTFE MEMBRANE.

The type of flow through a membrane depends on several parameters such as pressure, temperature and pore size. Above all, pore size plays an important role in determining the nature of flow through the membrane. Transport through a porous membrane takes place by diffusional and/or convective flow. For simplicity cylindrical pores are assumed and expression of flux for convective flow is described by Hagen Poiseulles equation (3.9) (Mulder, 1997).

$$J = \frac{\varepsilon r^2}{8\eta\tau} \cdot \frac{\Delta P}{l} \quad (3.9)$$

In poiseulle flow interaction between gas molecules is higher than interaction between molecule and pore wall, this leads to very poor separation properties. As the pore radius is reduced diffusional flow becomes the governing mechanism for transportation through membrane. Poiseulle flow can be converted to Knudsen flow by reduction in operating pressure in addition to reduction in pore size. Figure 3.6 illustrates poiseulle flow and Knudsen diffusion regimes for gas molecules passing through a cylindrical pore. Based on pore size diffusional flow through membrane can be described as bulk/viscous flow (based on Fick's law) or Knudsen flow.

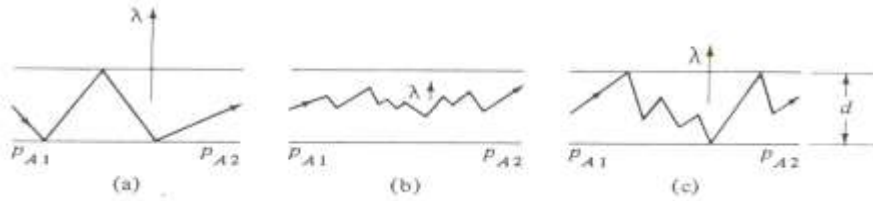


FIGURE 3.6 TYPE OF DIFFUSION IN CAPILLARY TUBES: (A) KNUDSEN DIFFUSION, (B) MOLECULAR DIFFUSION, (C) TRANSITION GAS DIFFUSION (ADAPTED FROM GEANKOPLIS C.J, 2003).

If transport through membrane is the main resistance to mass transfer then equation 3.2 and 3.3 can be simplified as equation 3.10.

$$J = \frac{P_i}{l} (\Delta p) = k_m \Delta p \quad (3.10)$$

If diffusion is dominating parameter for transportation through the pores then k_m can be calculated based on Fick's (molecular) or Knudsen diffusion. Pore size and mean free path for diffusing molecule play a fundamental role in determining the dominant type of flow. Mean free path is the average distance traveled by a gas molecule before collision; it is strongly dependent on temperature and pressure. Equation (3.11) gives an expression for mean free path as a function of temperature, pressure and pore diameter (Mulder, 1997).

$$\lambda = \frac{kT}{\pi d^2 P \sqrt{2}} \quad (3.11)$$

In order to determine the dominating transportation mechanism, Knudsen number (N_k) must be calculated (see equation 3.12).

$$N_k = \frac{\lambda}{2r} \quad (3.12)$$

If the value of Knudsen number is greater than 10 then Knudsen diffusion will be the domination mechanism and if its value is less than 1/10 then molecular/ Fick's gas diffusion is governing mechanism, between these two a transition region contribution by both mechanisms should be taken into account (Geankoplis, 2003). If Knudsen diffusion is governing mechanism then flux through membrane can be calculated with the help of equation (2.13) (Mulder, 1997, Geankoplis, 2003).

$$J = \frac{\pi n D_k r^2 \Delta p}{RT \tau l} \quad (3.13a)$$

Here D_k , the Knudsen diffusion coefficient is given by equation (3.13b).

$$D_k = 0.66r \sqrt{\frac{8RT}{\pi M_w}} = 97r \sqrt{\frac{T}{M_w}} \quad (3.13b)$$

If molecular gas diffusion is dominating then diffusivity coefficient can be calculated by the help of Fuller method (Fuller et al., 1966). Expression for calculation of diffusion coefficient for a binary gas mixture diffusing through a pore by molecular diffusion proposed by Fuller et al. (1966) is given in equation 3.14.

$$D_{AB} = \left(\frac{1.00 \times 10^{-3}}{P \left[(\sum v_A)^{1/3} + (\sum v_B)^{1/3} \right]^2} \right) \cdot \left(T^{1.75} \sqrt{\left(\frac{1}{M_A} + \frac{1}{M_B} \right)} \right) \quad (3.14)$$

Values of v_A and v_B are given in appendix D

For transition region diffusivity can be calculated by using equation (3.15) (Geankoplis, 2003).

$$D_m = \left(\frac{1}{D_{AB}} + \frac{1}{D_k} \right)^{-1} \quad (3.15)$$

Since the membrane does not have straight cylindrical pores so it is necessary to account for porosity and tortuosity, effective diffusivity is calculated by multiplying D_m with a factor of (ϵ/τ) when both Knudsen diffusion and molecular diffusion play a significant role.

Absorption

As briefly discussed in section 2.1.2 and 2.2 absorption of permeate gas has a significant contribution in performance of CO₂ capture system, a solvent with higher affinity for CO₂ results in a lower resistance to mass transfer. In this project 10% by weight K₂CO₃ solution with two different concentrations of NaOH is used to study the effect of solvent on overall mass transfer coefficient.

4.1 Background for selection of solvent

Sodium and potassium carbonate solutions were once widely used for CO₂ absorption from flue gases in dry ice production. In this process, the alkali carbonate is converted to bicarbonate in the absorber and back to the carbonate in the regenerator. Two packed absorbers in series are often used because of the low rate of CO₂ absorption. A major drawback of the process is low CO₂ recovery and the high regeneration cost. On the other hand sodium/ potassium carbonate (with free hydroxyl due to excess caustic) have also been used to remove the last traces of carbon dioxide from hydrogen (or other process streams). In this process carbonate ions are produced by reaction of CO₂ with free hydroxyl ions, and the alkalinity is maintained at a high level by the periodic addition of fresh caustic. No attempt is made to regenerate the solution, when its alkalinity is reduced to the point where it is no longer effective for CO₂ removal solvent solution is simply discarded (Kohl and Nielsen, 1997).

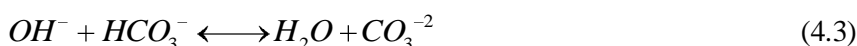
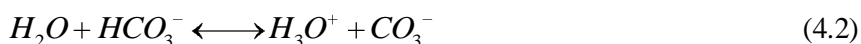
In the carbonate-hydroxide solution, the rate of absorption for CO₂ is found to be much higher than in the carbonate-bicarbonate solution. Theoretically this is because the molecular carbon dioxide can react directly with hydroxyl ions to form the carbonate ion and this reaction proceeds rapidly in strong basic solutions. Sherwood and Pigford (1952) provided a comprehensive review of early work for absorption of CO₂ in carbonate- hydroxyl systems.

42 Reaction Kinetics

Absorption of CO₂ in aqueous solutions of alkali hydroxides and alkali carbonates has been studied by many investigators, because of theoretical interest as well as industrial importance (Pohorecki and Moniuk, 1987; Knuutila et al., 2009).

42.1 Reaction of CO₂ with K₂CO₃ and 0.1, 0.5 M NaOH

When potassium carbonate is dissolved into water it dissociated into potassium ions and carbonate ions. For each carbonate ions there are two potassium ions. Equation 4.1 to 4.3 shows the reaction between K₂CO₃ and water (Kohl and Nielsen, 1997). These are equilibrium limited reactions and CO₃ ions are in equilibrium with HCO₃.



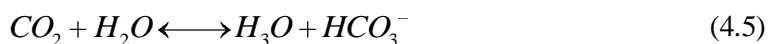
At room temperature 10% wt solution of K₂CO₃ shows 100% solubility as predicted by solubility chart of CO₃²⁻/HCO₃⁻ (Kohl and Nielsen, 1997). Sodium hydroxide is a strong alkali and shows high solubility in water. Equation 4.4 shows dissociation of NaOH in water.



Each mole of NaOH produces 1 mole of OH⁻ ions, for all solutions used in this project a fixed concentration of potassium carbonate was used so, the strength of OH⁻ ions help determining the pH of system.

Absorption of CO₂ in potassium carbonate solution

Absorption of CO₂ takes place in two steps, if the solution contain K₂CO₃ alone as absorbent then the reaction between CO₂ and potassium carbonate are as (Dindore et al., 2005; Shalygin, 2008).



Shalygina (2008) described reaction (4.5) and (4.6) to be rate determining reactions for absorption of CO₂ and an overall reaction for absorption of CO₂ in aqueous carbonate solution (equation 4.7). Since it is an equilibrium reaction the amount of CO₂ can not be higher than equilibrium concentration at any set of operating conditions. Cents et al. (2005) studied absorption of CO₂ in carbonate/bicarbonate system and described a similar overall rate expression.

Absorption of CO₂ in carbonate/bicarbonate-hydroxyl system

Hikita et al., (1976) studied the absorption of carbon dioxide in aqueous solution of sodium hydroxide and sodium carbonate/bicarbonate. They studied a general mechanism for absorption by using experimental data and compared the results with theory based on two step model by Hikita and Asai. (1976), for absorption of CO₂ in alkali solution two reactions (4.6 and 4.3) were found to be important.

Harned and Owen (1958) suggested both theses reactions to be fast due to a high equilibrium constant. Among these two reactions, reaction 4.3 has higher rate constant and it is practically irreversible. Concentration of HCO₃ ions is negligible and reaction 4.6 governs the overall rate of absorption (Pohorecki and Moniuk, 1987).

The concentration profiles formed in liquid film for sodium hydroxide and carbonate/bicarbonate system observed by Hikita et al., (1976) are illustrated in figure 4.1 and 4.2.

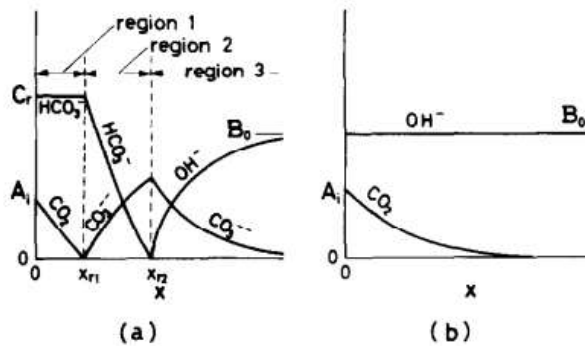


FIGURE 4.1 CONCENTRATION PROFILES FOR CO₂-NAOH SYSTEM: (A) INSTANTANEOUS REGIME AND (B) PESUDO FIRST ORDER REACTION REGIME (ADAPTED FROM HIKITA ET AL., (1976))

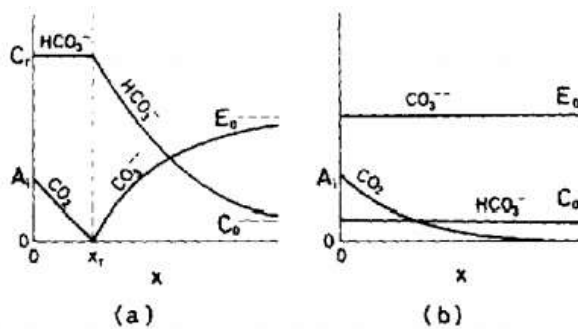


FIGURE 4.2 CONCENTRATION PROFILES FOR CO₂-CO₃/HCO₃ SYSTEM: (A) INSTANTANEOUS REGIME AND (B) PESUDO FIRST ORDER REACTION REGIME (ADAPTED FROM HIKITA ET AL., (1976))

From the above discussion it is clear that rate of absorption of CO₂ increases by a direct reaction of CO₂ with OH⁻ ions and reaction of absorbed CO₂ (HCO₃⁻) with OH⁻ ions in an alkaline environment. Since the rate of absorption of CO₂ in potassium carbonate solution is very low at room temperature, Sodium hydroxide is used as promoter for absorption in this work. It is intended to study the effect of concentration of promoter (OH⁻ ions) on rate of absorption by using 10% K₂CO₃ solution with 0.1 and 0.5 M NaOH.

PART 2

EXPERIMENTAL RESULTS AND DISCUSSION

Materials and experimental study

The modular configuration of gas-liquid membrane contactor has a major advantage of linear scale-up. This adds great value to the lab scale experimental study in developing an understanding for individual effect of gas/liquid flowrate, composition of streams and participation of membrane to overall mass transfer process. A lab scale experimental setup that can manipulate one parameter at a time is needed to understand the individual effect of said parameters for mass transfer study.

5.1 Experimental setup

The setup used for analysis was fabricated at the department to fulfill the needs of project. A schematic diagram of process is shown in figure 5.1.

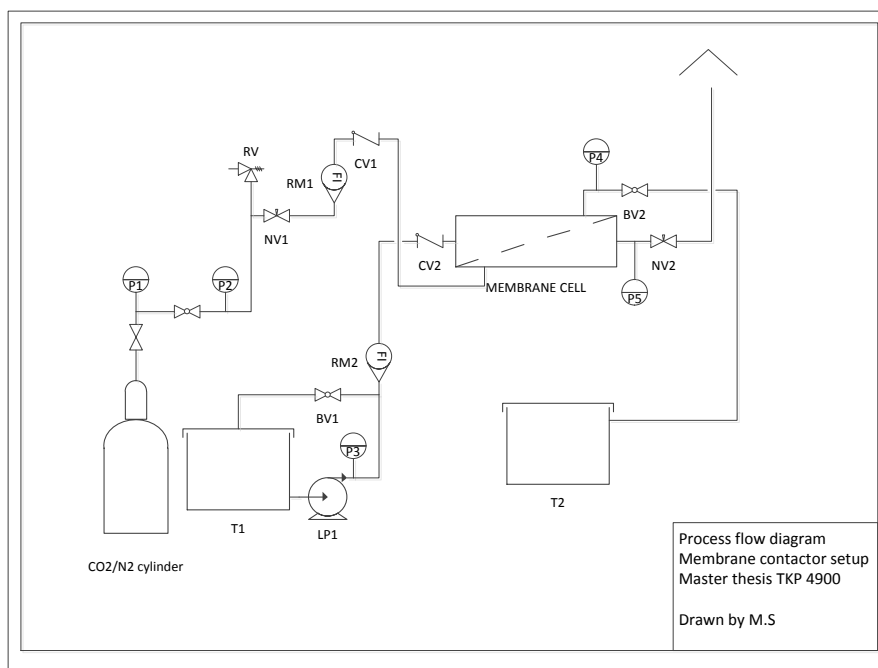


FIGURE 5.1 SCHEMATIC DIAGRAM OF MEMBRANE CONTACTOR SET UP

Description of legends and specification of equipments used in figure 5.1 are given in table 5.1.

Table 5.1 Description of process flow diagram

Abbreviation	Details
P1	Pressure gauge at gas cylinder outlet
P2	Pressure gauge at gas regulator
P3	Pressure gauge at solvent pump outlet
P4	Pressure gauge at liquid stream leaving module
P5	Pressure gauge at gas stream leaving module
RM1 & RM2	Rotameter at gas and liquid streams entering module
CV1 & CV2	NRV at gas and liquid streams entering module
NV1 & NV2	Needle at gas stream entering and leaving module
BV1 & BV2	Ball valve at liquid recycle stream and rich solvent leaving module
T1 & T2	Solvent feed tank and effluent collection tank
LP1	Liquid feed pump

5.1.1 Membrane cell

The membrane cell used in this project was supplied by Osmonics Europa in 1994, this cell was originally designed for microfiltration and ultra filtration. Some modifications were made to use it for membrane contactor experiments. The cell has two chambers one for liquid and one for gas. Any one of them can be used for gas or liquid. Membrane cell used for experimentation is shown in figure 5.2.



(a)

(b)

FIGURE 5.2 (A) MODIFIED MEMBRANE CELL USED FOR CONTACTOR EXPERIMENTS, (B) SEPA MEMBRANE CELL SUPPLIED BY OSMONICS

For experimentation lower chamber of cell was used for gas stream and upper chamber was used for liquid. Two main reasons for using this configuration are as:

- Contact of liquid and membrane at all operating conditions is ensured.
- If liquid permeates through membrane, it must not develop a film of liquid on gas side of membrane.

The presence of an extra layer of liquid on the membrane can result in an additional resistance to mass transfer, in this configuration if liquid permeate through the membrane it will fall down from membrane surface and ensures constant and smooth contact between gas and membrane. Mass transfer in membrane contactor is schematically described in figure 5.3.

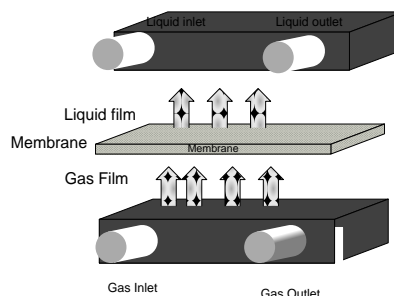


FIGURE 5.3 SCHEMATIC DIAGRAM OF CO₂ FLOW IN MEMBRANE CONTACTOR.

The cell was originally supplied with a hydraulic press system to but the modified cell has nuts and bolts instead of hydraulic press. Due to this reason it is difficult to operate the system at designed pressure of 100 psi (6.8 bars), keeping in view this limitation all experiments were conducted at pressure up to 40 psi (2.7 bar). Figure 5.2 shows pictures of original and modified cell.

As mentioned above, the cell was designed for filtration and had three channels for feed, permeate and retentate streams. In order to be used for gas-liquid membrane contactor study, the liquid permeate stream was closed and two new channels were introduced, resulting in total four channels capable of handling feed and retentate streams of liquid and gas separately. The new channels were not properly drilled; this resulted in uneven distribution of fluids near the openings. In order to avoid the effect of complex flow regime produced at ends of the cell, membrane was masked to smaller dimensions.

For better understanding of membrane cell, its dimensional drawings are presented in figure 5.4 and 5.5.

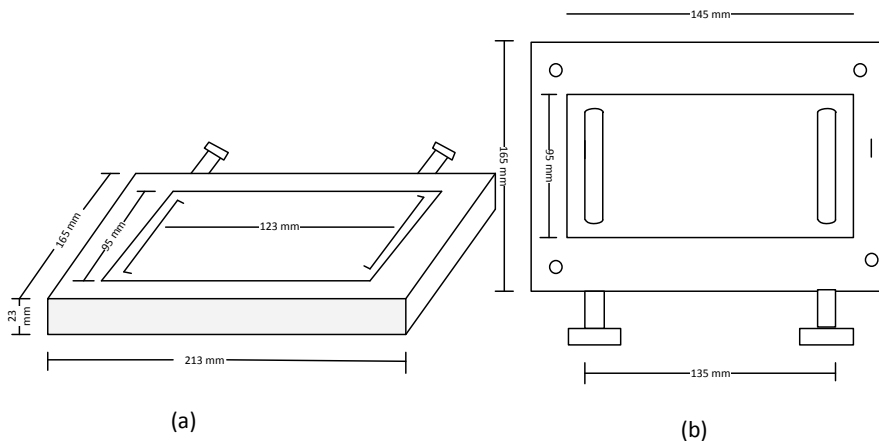


FIGURE 5.4 (A) FRONT VIEW OF LIQUID CHAMBER OF MEMBRANE CELL. (B) TOP VIEW OF LIQUID CHAMBER OF MEMBRANE CELL. (DRAWING MADE NOT TO SCALE)

The length, width and depth of liquid chamber are 145mm, 95 mm and 0.1 mm. The chamber is more like a rectangular duct. The chamber of membrane cell assigned for gas stream also has similar layout except for sealing rings. Detailed dimensions of gas chamber are shown in figure 5.5.

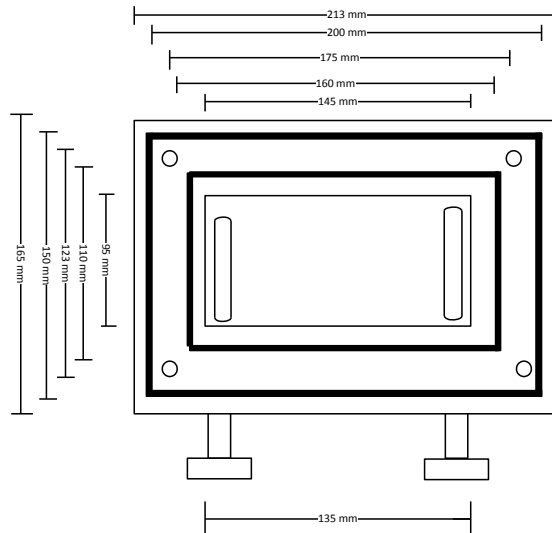


FIGURE 5.5 DIMENSIONAL DRAWING OF GAS CHAMBER OF MEMBRANE CELL.

The length and width of gas chamber is exactly the same as that of liquid chamber but its depth is 2mm. This lower part of cell also has two openings and either one of them can be used for gas inlet or outlet. Pictures of both chambers of membrane cell is shown in figure 5.6



FIGURE 5.6 LIQUID AND GAS CHAMBERS OF MEMBRANE CELL

5.1.2 Membrane masking and sealing

The cell has available membrane area of 162 cm^2 . As discussed earlier, the modified cell shows uneven distribution near the openings, a small area of membrane was used for experimentation. For each experiment 16 cm^2 of membrane was used. This area was kept constant for every experiment and masking of membrane took place in 3 steps.

- Sandwiching the membrane between two rectangular layers of aluminum tape with a square slit of required dimensions.
- Masking the membrane onto upper chamber of cell by using aluminum tape with a slit of same size as membrane.
- Sealing the membrane edges by applying glue on gas side of the membrane.

Aluminum tape (3M 7940) was used for masking and Araldite (strength bonding 2012) glue was applied on gas side of membrane to ensure complete sealing. Figure 5.7 illustrates a PVA membrane masked for experimentation. In section 2.1.3 it has already been established that for composite membranes dense layer should be in contact with liquid film so the picture of PVA membrane in figure 5.8 shows the support layer of membrane, sealed with glue, facing towards the gas film and masked on liquid chamber of cell.



FIGURE 5.7 MASKED PVA MEMBRANE

In the membrane cell there are two O-rings to isolate the fluid streams from environment. The inner O-ring prevents the process fluid from going out under pressurized conditions and the outer O-ring

prevents the atmosphere from getting in due to partial pressure difference. To ensure complete sealing Vacuum grease was also applied.

52 Operating parameters

In gas-liquid membrane absorption effect of several parameters can be studied by slight change in gas/liquid stream or membrane. Keeping in view the objectives defined in section 1.5 of this report, the operating range of fixed and manipulated parameters are as:

Fixed parameters

- Gas composition (30% CO₂/70% N₂).
- Gas volumetric flowrate (1E10⁻⁵ m³/s).
- Operating temperature at 25⁰C.

Manipulated variables

- Operating pressure (1.3-2.7 bar).
- Liquid stream flowrate (2-4ml/s).
- Liquid stream composition (10% K₂CO₃ with 0.1 and 0.5 M NaOH).
- Membrane (PTFE porous and PVA dense membrane).

Studied parameters

- CO₂ absorption based on liquid stream analysis (liquid loading).
- Overall mass transfer coefficient (calculations based on liquid stream analysis).

53 Gas stream

The gas used for experimental work contained 30% CO₂ and 70% N₂. Both CO₂ and N₂ were ultra pure (99.999%). Water, oxygen and light hydrocarbons were also present but concentration of all these compounds was less than 4 ppm and hence their presence was neglected. The gas was supplied by YARA in 50L cylinder.

As mentioned above, the gas volumetric flowrate and composition were kept constant, molar flowrate however increased with raise in operating pressure. Molar flowrate of mixed gas and partial pressure of CO₂ in feed stream at different operating pressures are given in table 5.2.

Table 5.2 Specifications of gas stream

Operating Pressure		Mix gas flowrate	Molar flowrate	Partial pressure of CO ₂	Partial pressure of N ₂
psi	bar	m ³ /s	Mol/s	bar	bar
20	1.36	1E-05	1.647E-04	0.4	0.95
30	2.04	1E-05	2.471E-04	0.612	1.428
40	2.71	1E-05	3.295E-04	0.813	1.897

The gas inlet and outlet pressures were monitored by Omega Bourdon tube pressure gauges where as gas flowrate and pressure were regulated by needle valves installed at inlet and outlet of membrane cell.

5.4 Liquid stream

For experimentation 10% potassium carbonate solution in 0.1M and 0.5 M sodium hydroxide aqueous solutions were used. These solutions were freshly prepared in lab before every experiment. Every batch of solvent weighted 5 kg prepared by dissolving 500 grams of potassium carbonate, 99+% purity (supplied by SIGMA-ALDRICH) in 4500 grams of 0.1M or 0.5M solution of sodium hydroxide. For our convenience the solution with 0.1M NaOH was named S01 and solution with 0.5M NaOH as S05. Details of these solvents are given in table 5.3.

Table 5.3 Specifications of solvent S01 and S05

Name of solvent	Weight of solution/batch	Weight of K_2CO_3	Weight of NaOH added	Concentration of NaOH	pH	Sp.gravity
	kg	gms	gms	M		
S01	5	500	18	0.1	13.05	1.084
S05	5	500	90	0.5	13.2	1.099

The solvent was pumped by the help of KnF Liquiport pump at three different flowrates. Liquid flowrate into the cell was measured by rotameter, solvent flowrate was regulated by needle valve at liquid outlet of membrane cell and a recycle stream placed just after the solvent pump. Since the two solutions (S01 and S05) had different densities, liquid flowrate was verified by frequent sampling of solvent leaving the cell.

5.5 Analysis

To determine the amount of CO_2 absorbed, rich solvent was titrated against standard solution of HCl. As discussed in section 4.1 and 4.2, solvent contained K_2CO_3 and different concentrations of sodium hydroxide, therefore titrations were conducted with 0.1M/0.05M and 0.25 M HCl solutions. This section deals with chemistry involved in titrations and detail of sampling procedure for analysis.

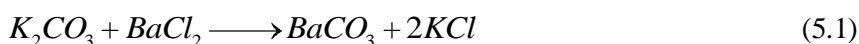
5.5.1 Sampling

For each experiment two samples were taken to verify the results. Each sample was taken after ensuring a smooth operation for 5 minutes at a constant pressure and flowrate. All experiments were conducted at pressure higher than atmosphere achieved by a throttling valve installed at solvent and gas outlet stream. Due to sudden pressure drop across this valve, solvent loses some CO_2 . This

process is widely used for partial regeneration of solvent in industrial CCS process. In order to ensure minimum CO_2 loss due to pressure swing all samples were taken in freshly prepared NaOH solutions of known concentration. For solvent S01, 0.1 M NaOH solutions was used for sampling and for S05 0.5M solution was used to simplify the calculations. 20 ml of sample was taken in 20 ml of NaOH solution. Potassium carbonate converts to bicarbonate on reaction with CO_2 , equation 4.7 shows the equation for this reaction. The addition of NaOH results in conversion of HCO_3^- ions back to CO_3^{2-} ions. This reaction (equation 4.3) is also reversible but addition of OH in excess makes it pseudo first order reaction in forward direction. Every sample then contains OH ions and CO_3^{2-} ions only.

5.5.2 Titration

The solvent samples were analyzed by neutralization titration. Every collected sample contained NaOH and K_2CO_3 . 20 ml of samples were added in equal volume of BaCl_2 solution. Barium chloride reacts with K_2CO_3 to produce insoluble BaCO_3 . Equation 5.1 shows the reaction between these two compounds.



The solution was left for 3 hours to allow complete precipitation of BaCO_3 , clear solution obtained after precipitation contains only OH ions. Since BaCl_2 solution is neutral and by addition equal volume of BaCl_2 solution samples were diluted by a factor of 2.

Samples from experiments conducted with S01 were titrated against 0.05 M HCl and samples from S05 were titrated against 0.25M HCl solution. Concentration of OH ions in each sample was calculated by relating moles of acid consumed to neutralize each sample. For every titrated 10 ml of sample solution was used. Concentration of OH ions in every sample was calculated by equation 5.2.

$$C_{\text{OH}} = \frac{C_{\text{HCl}} \cdot V_{\text{HCl}}}{V_{\text{sample}}} \quad (5.2)$$

Before every experiment OH^- concentration for fresh solvent (S01 and S05) was determined by same procedure. Difference in concentration of OH^- ions in sample solution and fresh solution was used to determine the amount of CO_2 absorbed.

5.5.3 Calculations

CO_2 absorbed by solvent by two parallel processes.

- Reaction with OH^- ions to produce HCO_3^- ions which further reacts to form CO_3^{2-} ions.
- Reaction of CO_2 with carbonate ions from K_2CO_3 to produce HCO_3^- ions which also reacts to produce CO_3^{2-} ions.

Equations (4.6), (4.7) and (4.3) present the Stoichiometry of the absorption reactions. From these reactions it is clear that to absorb 1 mole of CO_2 , 2 moles of OH^- ions are needed. So the concentration of CO_2 absorbed in an experiment can be calculated by equation 5.3.

$$C_{\text{CO}_2} = \frac{C_{\text{OH (fresh sample)}} - C_{\text{OH (sample)}}}{2} \quad (5.3)$$

The concentration determined by equation 5.3 is further used in equation 3.10 and equation 2.9 to calculate overall mass transfer coefficient.

5.6 Pore entry pressure for PTFE membrane

PTFE is a hydrophobic material, a porous PTFE (GORE) membrane with average pore size of 0.2 μm was used in experiments. As discussed earlier that liquid should be kept at slightly higher pressure but pore wetting must be avoided. In order to estimate breakthrough pressure Laplace equation (3.8) is used. According to this equation breakthrough pressure is a function of pore size, surface tension of liquid and contact angle of liquid on membrane.

To calculate the breakthrough pressure surface tension of solvent and wettability of membrane was determined experimentally.

5.6.1 Contact angle

Contact angle provides direct information on interaction energy between surface and the liquid. The contact angle can be measured by producing a drop of liquid on membrane surface. The angle formed between solid/liquid and liquid/gas interface at the point where all three interfaces meet is referred to as a contact angle as shown in figure 5.9. (Butt et al., 2003)

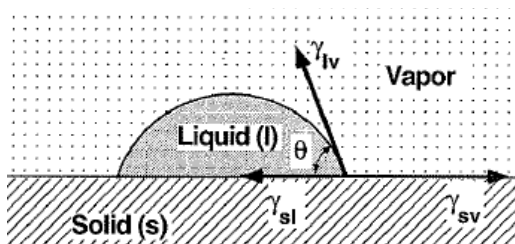


FIGURE 5.9 CONTACT ANGLE OF LIQUID SAMPLE ON SOLID SURFACE (ADDAPTED FROM BUTT ET AL., 2003)

In figure 5.9 θ is the contact angle, γ_{sl} is solid/liquid interfacial tension, γ_{sv} is surface tension of solid and γ_{lv} is surface tension of liquid. If the contact angle is less than 90° the surface is hydrophilic and if contact angle is greater than 90° then the surface is hydrophobic which can be exemplified as poor adhesiveness or poor wetting.

Since the solutions S01 and S05 are aqueous solutions so, water was used to determine contact angle for PTFE membrane. To study the effect of operating pressure and nature of solvent on hydrophobic nature of membrane, contact angle was taken for membrane used in every experiment. Contact angle measurements were made by using sessile drop method using KSV CAM 200 instrument. A drop of pure water was place don membrane surface by using a syringe. The contact angle was determined from digital silhouette drop images. These images were analyzed by using an optical contact angle (CAM 200, KSV) and pendant drop surface tension software (Ver 3.99 W2k XP). Picture of CAM 200 is shown in figure 5.10.

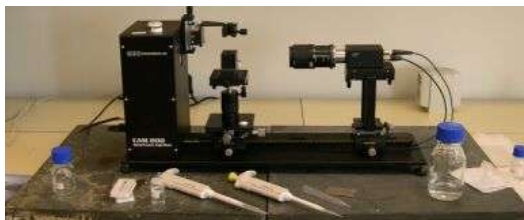


FIGURE 5.10 CAM 200 USED FOR CONTACT ANGLE EXPERIMENTS

5.6.2 Surface tension

Surface tension is a physical property of a liquid that depends upon cohesive forces between liquid molecules present at gas/liquid interface. It can be defined as the work needed to stretch a surface of liquid (Butt et al., 2003). Surface tension plays an important role in determining the capacity of a liquid to spread over a surface. From figure 5.9 it is clear that contact angle is a function of surface tension of liquid. Surface tension is an essential parameter in determining the break through pressure.

Du Nouy ring method was used to determine surface tension of solvent S01, S02 and distilled water at room temperature by the help of Sigma 70 tensiometer. In this method a ring of known parameter is slowly pulled out through liquid. Force needed to pass the ring through surface is determined and surface tension is calculated by equation 5.4.

$$\gamma = \frac{\Delta F}{P \cos \theta} \quad (5.4)$$

Figure 5.11 shows the diagram for Du Nouy ring method and picture of sigma 70 tensiometer is shown in figure 5.12

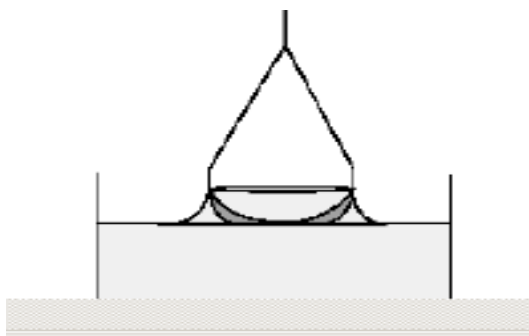


FIGURE 5.11 DU NOUY RING METHOD FOR CALCULATION OF SURFACE TENSION



FIGURE 5.12 SIGMA 70 TENSIO METER FOR CALCULATION OF SURFACE TENSION

5.7 Time based experiments

A time based experiment was performed to study the effect of time on overall performance of membrane contactor containing PTFE membrane operated at 1.36 bar. Both liquid and gas chambers of membrane contactor were filled with respective fluids and membrane cell was sealed at constant pressure of 1.36 bar for 1 days (24 hrs). After 24 hours experiment was conducted at constant liquid flowrate of 2ml/s for 2 hours and samples were collected with an interval of 5 minutes. After completion of experiment, contact angle for tested PTFE membrane was measured to observe the effect of operating time on membrane wettability.

Unlike PTFE, PVA membrane was not kept under operating conditions before experimentation. PVA is a hydrophilic material and swells in presence of water, hydrated PVA membrane have a higher potential for permeation of liquid. To minimize the risk of liquid permeation at the start of experiment dry membrane was used and liquid stream was kept at a pressure 0.1bar higher than gas stream.

5.8 Swell test for PVA membrane

PVA is a hydrophilic polymer and in presence of water, polymeric chains move apart to accommodate water molecules. Swell test can be conducted based on gravimetric analysis or dimensional analysis to estimate maximum concentration of water that can accumulate in membrane. Praptowidodo V.S (2005) conducted swelling tests for PVA membranes based on difference in weight for dry and wet states. Yeom and Lee (1996) cross-linked PVA composite membranes with G.A solution and conducted swell tests based on dimensional analysis.

In this work Swell tests for PVA were conducted by using gravimetric analysis. The dense layer of PVA was peeled off from composite membrane and was dried at 45°C for 24 hrs. Dried sample layer was weighted by using Mettler Toledo AB204-S/FACT balance and immersed in water at room temperature for 24 hours to establish equilibrium. Wet sample was wiped to remove excess water by the help of tissue paper and weighted. Percentage swelling based on wet and dry weight of PVA layer was calculated using equation 5.5. Results of swell test for PVA membrane are presented in appendix A.

$$\% \text{ Swell} = 100 * \left(\frac{W_{wet} - W_{dry}}{W_{dry}} \right) \quad (5.5)$$

5.9 SEM (Scanning electron microscopy)

The scanning electron microscope creates an image of surface by scanning it with the help of high energy electron beam. The electrons interact with atoms and create a signal that contain information about topology, composition and other properties like electrical conductivity (Egerton R.F, 2005).

To observe the pore structure of PTFE membrane and estimate the thickness of PVA layer in dry state LVSEM SEM (Hitachi S3400N) was used. Small sample were prepared by freezing the membrane with liquid nitrogen, breaking it in desired size and shape and then coating it with gold. For composite PVA membrane thickness of layer was measured by observing cross-section of membrane where as for PTFE membrane pore geometry was studied. SEM picture of both membranes are given in appendix E.

Results and discussions

6.1 Results and discussion for PTFE (GORE-TEX®) membrane

Results of all experiments conducted with PTFE membrane are categorized based on mass transfer study and wettability study membrane.

6.1.1 Experiments with membrane contactor

Flat sheet PTFE membrane with pore size of $0.2\mu\text{m}$ was used in membrane contactor to study the effect of operating pressure, flowrate of liquid and nature of solvent on mass transfer for absorption of CO_2 in solvent S01 and S02. All experiments were conducted at room temperature and mixed gas containing 30% CO_2 and 70% N_2 at constant volumetric flowrate. For simplicity results are further divided on the basis of solvents.

Experiments with S01

The solvent S01 is 10% K_2CO_3 solution promoted by 0.1M NaOH. Flux of CO_2 as a function of operating pressure at constant flowrate is graphically presented in figure 6.1.

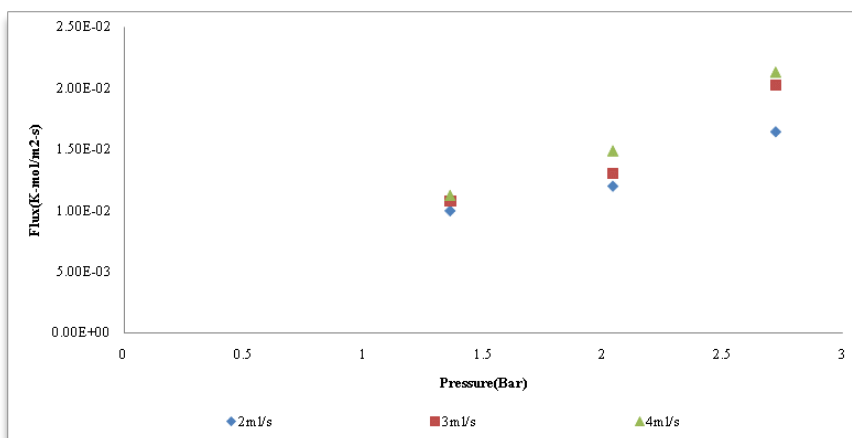


FIGURE 6.1 MOLAR FLUX OF CO_2 AS A FUNCTION OF PRESSURE FOR PTFE MEMBRANE OPERATING AT CONSTANT FLOWRATES

The results presented in figure 6.1 shows a trend of increasing flux with respect to pressure. The flux of CO_2 is directly related to its partial pressure in gas stream and concentration of CO_2 in liquid stream. With a raise in operating pressure, partial pressure of CO_2 increases where as the concentration of CO_2 in liquid stream entering membrane cell is constant and negligible (fresh solvent used every time). Equation 2.7(a & b) presents a relation between flux and partial pressure of CO_2 and experimental results are in close agreement with the theory. The flux of CO_2 was calculated from liquid stream analysis and results from all experiment conducted with S01 and sample calculations are presented in appendix C.

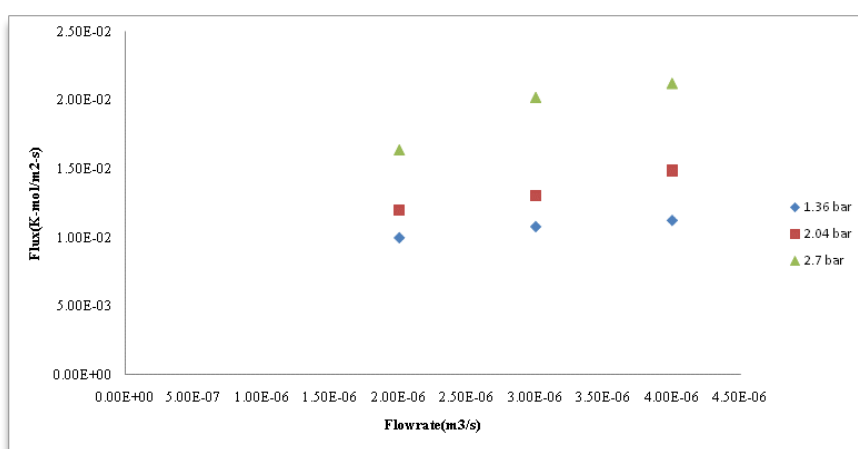


FIGURE 6.2 EFFECT OF LIQUID FLOWRATE ON FLUX OF CO_2 AT CONSTANT PRESSURE.

Experimental results presented in figure 6.1 also show an effect of liquid flowrate on CO_2 flux. For better understanding, CO_2 flux as a function of solvent flowrate at constant pressure is plotted in figure 6.2. It can be seen that at constant pressure flux increases with increasing solvent flowrate. To understand effect of liquid flowrate on flux of CO_2 penetration theory of mass transfer is a helpful tool, if liquid is considered to flow in small batches and each batch has same capacity to absorb CO_2 then the amount of gas absorbed by liquid will depend on number of batches that came in contact with gas/membrane. At low operating pressure concentration of CO_2 in contact with liquid is less compared to that of high pressure; the effect of flowrate is more visible at high pressure. Simioni et al. (2011) studied the stripping of CO_2 from 30% K_2CO_3 solution by using PTFE membrane of same pore size and these results are in close agreement to their findings.

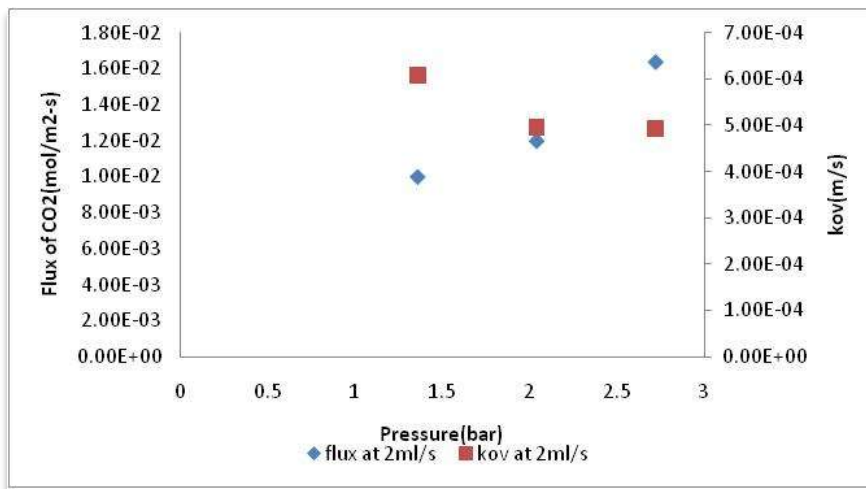


FIGURE 6.3 EFFECT OF OPERATING PRESSURE ON FLUX OF CO₂ AND OVERALL MASS TRANSFER COEFFICIENT

Experimental results presented in figure 6.3 show that at constant liquid flowrate, overall mass transfer coefficient decreases with increase in pressure. Overall mass transfer coefficient is an empirical factor that can be determined experimentally, liquid stream analysis and equation 2.9, 2.10 were used to calculate the value of k_{ov} . For each experiment results along with sample calculation of k_{ov} are presented in appendix C. Since the value of k_{ov} depends on operating conditions it is difficult to predict the trend for overall mass transfer coefficient.

In figure 6.4 effect of solvent flowrate on CO₂ flux and k_{ov} at constant pressure is presented. From these results it is clear that overall mass transfer coefficient increases with increase in liquid flowrate, hence resistance to mass transfer decreases.

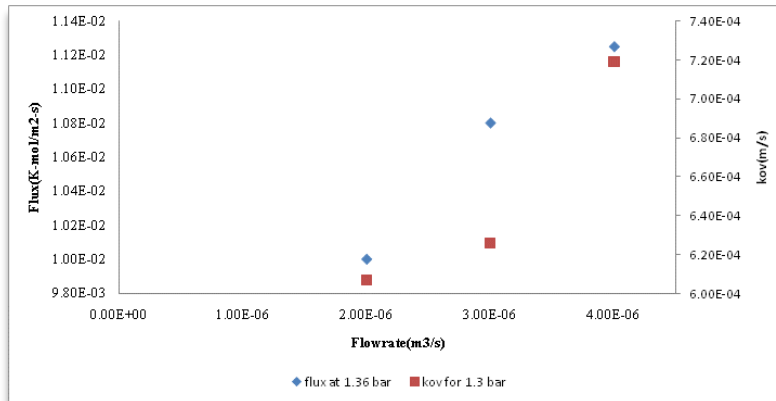


FIGURE 6.4 EFFECT OF FLOWRATE ON FLUX AND RESISTANCE TO MASS TRANSFER AT CONSTANT PRESSURE

As the liquid flowrate is increased more fresh solvent becomes available at membrane-liquid interface. This trend of k_{ov} with respect to solvent flowrate shows that resistance to mass transfer offered by liquid film has a significant contribution in overall resistance to mass transfer ($1/k_{ov}$). Khaisri et al. (2009) studied absorption of CO_2 in MEA using PTFE, PVDF and PP hollow fiber membrane contactor at much lower partial pressure of CO_2 and higher velocity of liquid. They observed an increase in mass transfer coefficient with increase in liquid velocity. Overall mass transfer coefficient discussed in figure 6.4 shows a trend similar to the one observed by Khaisri et al. (2009).

Experiments with S05 and comparison of results with S01

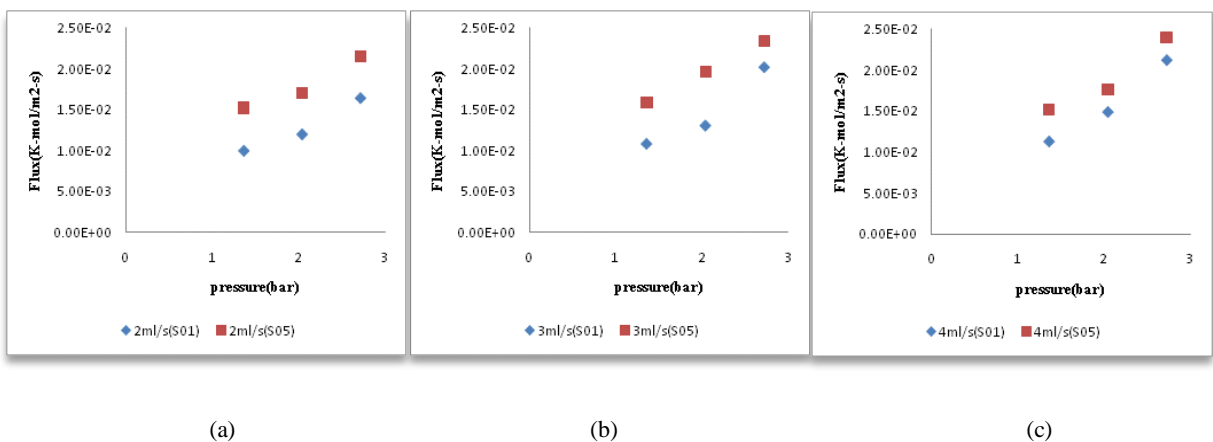


FIGURE 6.5 (A) EFFECT OF PRESSURE ON GAS FLUX AT LIQUID FLOWRATE OF 2ML/S, (B) EFFECT OF PRESSURE ON GAS FLUX AT LIQUID FLOWRATE OF 3ML/S, (C) EFFECT OF PRESSURE ON GAS FLUX AT LIQUID FLOWRATE OF 4ML/S. FOR SOLVENT S01 AND S02

Flux calculated from experiments with solvent S01 and S05 are compared in figure 6.5 (a, b and c). Solvent S05 contain NaOH 5 times higher than S01, this means that S05 has a higher affinity towards CO_2 . Experiments conducted with solvent S05 shows higher flux than solvent S01.

Reaction between CO_2 and NaOH is fast, pseudo first order reaction and absorption of CO_2 depends on concentration of CO_2 and NaOH at interface (Hikita et al., 1976). Concentration profile of CO_2 in liquid film is illustrated in figure 4.1. From results plotted in figure 6.5 it can be seen that flux for both solvent increases with increases in pressure as concentration of CO_2 available for reaction increases.

At all operating conditions flux of CO_2 for solvent “S05” is higher than “S01” due to higher concentration of OH^- ions in S05 but the difference in flux for both solvents tends to decrease with respect to flowrate. This effect is more noticeable in figure 6.5(c). High pressure should result in high concentration of CO_2 available at liquid interface for absorption, since solvent S05 contain NaOH 5 times more than S01, the trend of increasing flux for S05 should show a much steeper slope. The experimental results show that trend of flux for solvent S01 has a steeper slope than S05. If it is assumed that this trend of flux remains same at higher operating pressure and data in figure 6.5(c) is extrapolated then it can be predicted that at 6 bar operating pressure and 4ml/s liquid flowrate solvent S01 will show same flux of CO_2 as S05. For better understanding this argument is graphically presented in figure 6.6. Based on this hypothesis it can be said that the rate of absorption is limited by availability of CO_2 at liquid-membrane interface.

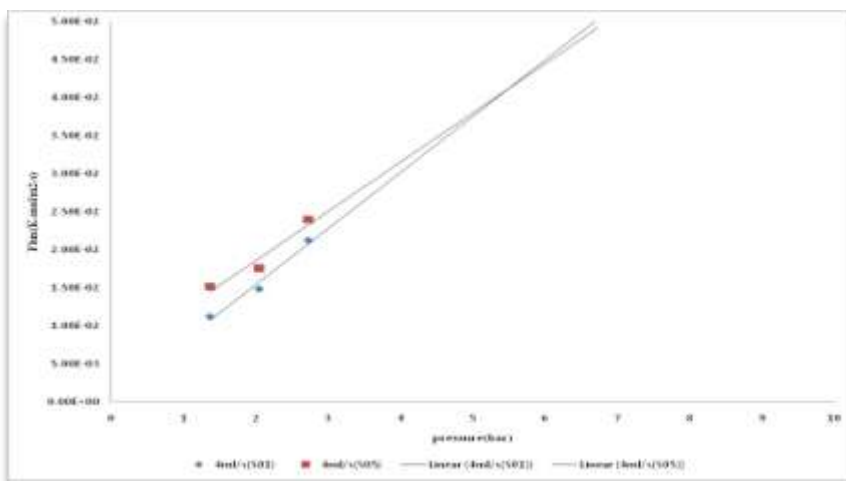


FIGURE 6.6 PREDICTION OF CO_2 FLUX FROM EXTRAPOLATION OF EXPERIMENTAL DATA

The feed gas used for experimentation consists of 30% CO₂ and 70% N₂, the operating pressure of 6 bar mean 1.8 bar CO₂ partial pressure. The concentration of CO₂ available for absorption is lesser than bulk concentration (due to gas film and membrane resistance). At low partial pressure of CO₂, vapor liquid equilibrium shows a straight line (Khol and Nielsen, 1997). This assumption is only valid at low partial pressure of CO₂. At high partial pressure, the contribution of physical absorption becomes significant and equilibrium curve is not a straight line.

Overall resistance to mass transfer in membrane contactor is a function of resistances to mass transfer offered by gas, liquid film and membrane (equation 2.8). Overall mass transfer coefficient as a function of liquid flowrate at constant pressure (2.7bar) is presented in figure 6.7.

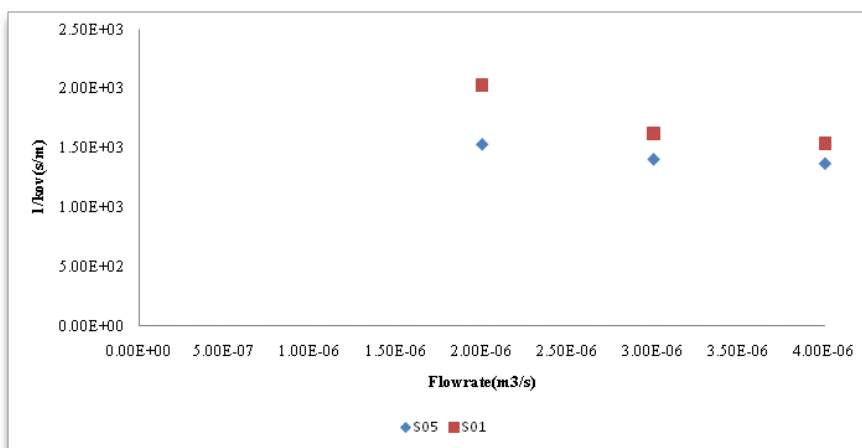


FIGURE 6.7 OVERALL RESISTANCE TO MASS TRANSFER AS A FUNCTION OF FLOWRATE FOR ABSORPTION OF CO₂ IN SOLVENT S01 AND S05 AT 2.7 BAR OPERATING PRESSURE

It can be seen that resistance to mass transfer calculated from experimental results of solvent S05 is less than the resistance calculated for S01 (due to higher alkalinity of S05) but, from the trend it can also be seen that with increase in flowrate the decrease in overall resistance to mass transfer is small and in case of S05 it is negligible. This result shows that the contribution of liquid film resistance in mass transfer is insignificant. These results support the hypothesis presented in figure 6.6.

In order to get absorbed every molecule of CO₂ must diffuse from bulk to gas-membrane interface and then diffuse from membrane to liquid-membrane interface. Sobieszuk and Pohorecki (2010) studied the effect of gas composition on gas film resistance by absorption of CO₂ (12-97% CO₂/N₂)

in 1M NaOH and they found that resistance offered by gas film decreases significantly by increasing the absorbing gas concentration but for only feed gas containing over 97% CO₂ gas film resistance can be neglected. In this project mix gas containing 30% CO₂ and 70% N₂ was used, so the resistance to mass transfer offered by gas film can not be neglected and experimental results show a significance contribution of $1/k_g$ in overall resistance to mass transfer.

k_m (resistance to mass transfer offered by membrane) was calculated for flux of CO₂ at operating pressures with and without reaction with solvent, calculations are presented in appendix D. Keeping in view these calculations and results obtained from membrane contactor experiments it is clear that membrane and gas film resistances have a significant contribution in overall mass transfer coefficient.

6.12 Hydrophobic nature of PTFE membrane

Based on hydrophobisity, a study by Falk-Pederson and Dannstorm (1997) suggested that PTFE is the only suitable membrane for use with alkanolamines. Even though the membrane used in gas absorption is intensively hydrophobic but aqueous solutions of solvents can penetrate into pores of the hydrophobic membrane and cause partial-wetting (Bottino et al., 2008, Zhang et al., 2008). Dindore et al. (2004) studied the effect of solvent on hydrophobicity of membrane materials and suggested PTFE and PVDF for consideration for further work.

To determine the effect of solvent and operating conditions on hydrophobicity of PTFE membrane, contact angle was measured for membrane before and after every experiment. These readings were further used in calculations break through pressure (see Appendix B). Contact angle of distilled water on PTFE membrane was found to be $127.6 \pm 1^\circ$ at room temperature, Experimental results published by Dindore et al. (2004) verifies our observation.

In this project aqueous solution of potassium carbonate promoted by NaOH was used. Potassium carbonate/bicarbonate solution shows high tendency of precipitation at room temperature. To avoid this problem just 10% wt solution of K₂CO₃ was used. Both solutions (S01 and S05) contain same

concentration of K_2CO_3 , at room temperature almost all CO_3 ions in 10% K_2CO_3 can be converted to HCO_3^- without precipitation (Khol and Nielsen 1997). This solution also contains NaOH in two different concentrations. NaOH dissociates into Na^+ and OH^- ions in water and it has a high solubility. The presence of excess Na^+ and OH^- ions suppress the solubility of K^+ and CO_3^{2-}/HCO_3^- ions. This phenomenon is known as common ion effect. Thus the solvents used for experimentation had higher potential of precipitation/fouling the membrane. One effect of salt precipitation over membrane surface is a drastic decline in hydrophobicity of membrane. The effect of precipitation potential of solvent on hydrophobicity of membrane is well reflected in results obtained by contact angle experiments.

Hydrophobicity of membrane was observed to decline with increase in operating pressure. Although PTFE shows very little or no interaction with solvent and CO_2 but still swelling of membrane takes place by sorption of solvent/gas (see figure 3.2a). The degree of swelling is very little and it follows Henry's law. Increase in wettability of membrane at higher operating pressure can be justified on the basis of swelling. Kreulen et al. (1993) and Nishikawa et al. (1995) tested absorption of CO_2 in alkanolamine using PE and PP membranes; they concluded that after long term application resistance to liquid penetration breaks down, probably due to surface wetting and swelling of polymers. Our experimental results also suggest that hydrophobicity of membrane decreases, probably due to swelling and precipitation of carbonates on membrane surface.

6.13 Time based experiments for PTFE with S01

From the experimental results discussed in section 6.1.1 and 6.1.2 it has been established that at these operating conditions flux increases with increase in pressure & flowrate, Concentration of NaOH does not have significant effect on flux (as illustrated in figure 6.5-6.7) and hydrophobicity of membrane depends on operating conditions.

From the experimental results of contact angle presented in appendix "A" it is clear that membrane operated at 20 psi (1.36 bars) remains more hydrophobic than other pressures. So, a time based experiment with PTFE membrane was conducted and contact angle at the end of experiment was determined. The contact angle was found to be $105 \pm 1^\circ$. This shows a clear decline in

hydrophobicity of PTFE membrane with respect to operating time. Results from this experiment are graphically represented in figure 6.8.

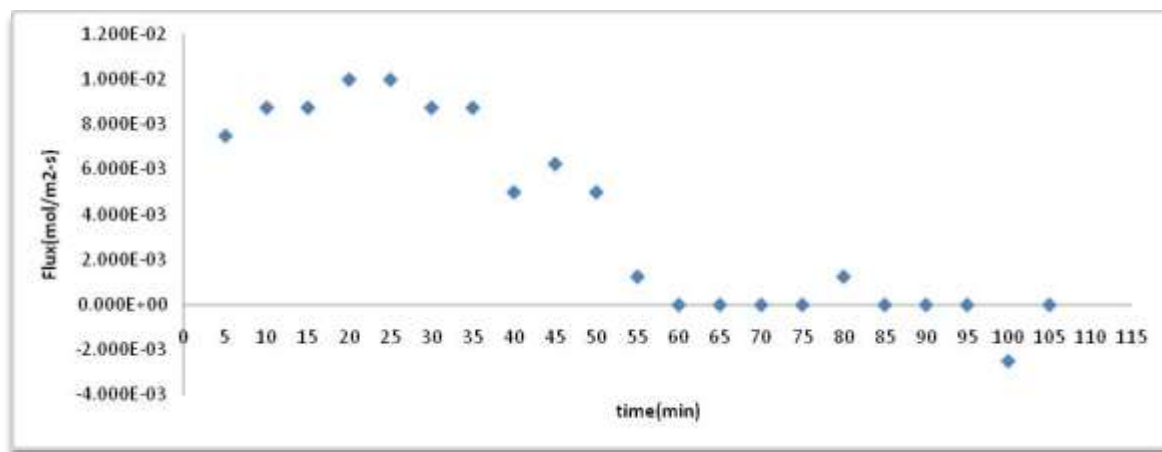


FIGURE 6.8 FLUX OF CO₂ AS A FUNCTION OF TIME FOR PTFE MEMBRANE OPERATING AT 1.36 BAR, SOLVENT S01 AND LIQUID FLOWRATE OF 2ML/S

In figure 6.8 the effect of operating time on flux of CO₂ is presented, from the figure it is difficult to draw a trend line due to the following reasons.

- After a smooth operation of 55 minutes permeation of liquid through membrane was observed.
- Titration was used to analyze all samples.

At the start of experiment flux varies from 8 E-03 to 1E-02 (mol/m²-s) and an average value of 9E-03 (mol/m²-s) can be considered as average flux. This value of flux is lesser than the value calculated at same operating conditions but with fresh membrane (see figure 6.1 and 6.5A). After 55 minutes of operation liquid was observed in gas (outlet) stream of membrane contactor. Samples taken during 40-55 minutes of operation shows the effect of pore wetting on performance of system. During this period flux dropped from 9E-03 to 1E-03 mol/m²-s. After 55 minutes of operation permeation of liquid started but still the experiment was continued to understand the impact of liquid permeation on performance of system, Samples taken during this time period shows no or negligible loading.

The purpose of membrane is to keep the two fluid phases separate and provide a definite interface for mass transfer. The gas molecules diffuse through gas film and membrane to get absorbed by liquid solvent. When the membrane pores are filled with gas high concentration of CO_2 is available at liquid-membrane interface which results in an appreciable concentration difference across the liquid film (driving force for absorption), Concentration profile of CO_2 under these conditions is similar to the one illustrated in figure 2.4(b). When liquid penetrates the membrane pores, the interface between gas and liquid is pushed towards gas side of membrane. Within the membrane gas molecules have to diffuse through liquid filled pores, diffusion coefficient of a molecule is ten thousand times lower in liquids compared to gases and membrane acts like an extension of liquid film. Hence lower absorption rate of gas is observed, concentration profile illustrated in figure 2.4(a) is applicable in this case.. Atchariyawu et al. (2008) characterized the main mass transfer resistance for CO_2 capture in the gas-liquid membrane contacting process by both physical and chemical absorption and concluded that overall resistance to mass transfer increases by 20% if 5% pores are wetted by liquid.

From these observations some strong conclusions challenging large scale application of membrane contactor can be drawn.

- Under these circumstances the high specific surface area of membrane contactor mentioned by Noble and stern (1995) is compromised.
- In table 1.4 Drioli and Giorno (2009) suggested that there is no need for down stream phase separation with a membrane contactor, but if a membrane contactor operate under condition similar to the one observed during experimentation, then absence of a down stream separation unit will badly effect the performance of system and result in loss of solvent.

6.2 Results and discussion for PVA membrane

Composite membrane with thin dense layer of PVA was used in membrane contactor to study the absorption of CO_2 in 10% K_2CO_3 solution promoted by NaOH. PVA is a water soluble material and even highly cross-linked PVA membranes show some swelling. Swelling of PVA promotes the permeation of gas through membrane but high swelling also results in dissolving

of membrane. The membrane used in experiments was not prepared in lab, to ensure its stability in water based applications swell test was conducted. The composite membrane consisted upon three layers, SEM image showing cross sectional view of substrate and dense PVA layer is given in figure 3.3(b) of this report.

6.2.1 Swell test

Percentage swelling for PVA membrane was determined according to the procedure explained in section 5.8 and results are presented in Appendix “A”. The results from test conducted with peeled PVA layer shows a swelling of 37%, PVA and substrate layer shows 34% swelling and test conducted on all three layers shows a percentage swelling of 20%. The test results show that PVA layer has the highest affinity towards water.

Membrane contactor was operated at a pressure range of 1.36-2.7 bar and swell test was conducted at atmospheric pressure. From figure 3.2 it can be seen that concentration of a compound in membrane is a function of pressure so, higher degree of swelling should be expected during operation.

6.2.2 Experiments with membrane contactor

Composite PVA membrane developed for pervaporation has never been tested for CO₂ absorption in a gas-liquid membrane contactor so, experimental results obtained from PTFE membrane were used to compare the performance of a membrane contactor containing PVA membrane and operating at same conditions.

Experiments with solvent S01 and S05

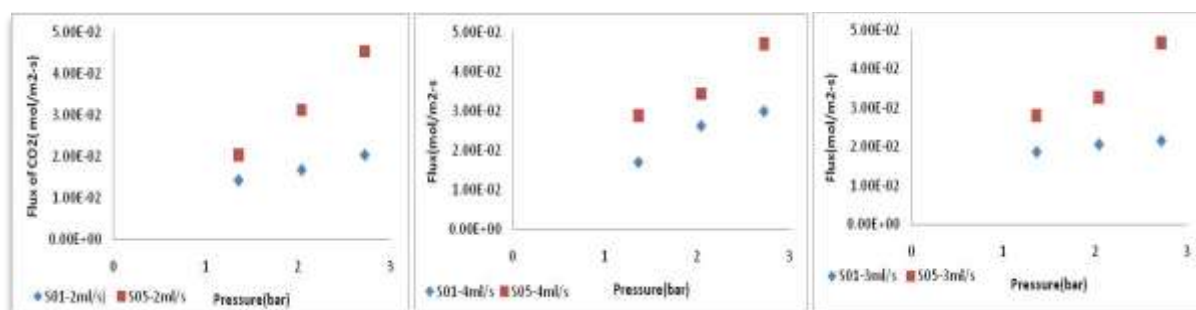


FIGURE 6.9 FLUX AS A FUNCTION OF OPERATING PRESSURE FOR S01 AND S05 AT CONSTANT LIQUID FLOWRATES OF 2ML/S, 3ML/S AND 4 ML/S

The results presented in figure 6.9 show that for both solvents flux of CO_2 increases with respect to pressure. The solvent S05 has NaOH 5 times higher than S01; this is why at all conditions flux calculated for S05 is higher than for S01. For PVA membrane permeability of CO_2 depends on swelling of membrane and partial pressure of CO_2 . Role of CO_2 partial pressure and swelling of membrane is as.

Partial pressure of CO_2 in feed stream

The driving force for mass transfer is concentration (partial pressure) difference of CO_2 across the membrane. Compared to the gas stream, concentration of CO_2 in liquid stream is negligible. The effect of CO_2 partial pressure on flux for PVA membrane is similar to the one discussed for PTFE membrane in figure 6.1.

Degree swelling of membrane

PVA is a hydrophilic material and composite PVA membrane used for experimentation shows swelling in presence of water. Deng and Hagg (2010) studied the effect of swelling on performance of PVAm/ PVA membrane for separation of CO_2 from CO_2/CH_4 mixed gas and observed an appreciable increase in flux of CO_2 for humid gas. The PVA membrane used for experimentation in this project showed 34% swelling (dense PVA layer) and in all experiments PVA layer was in contact with solvent stream rich with water.

Sorption of water in membrane depends on operating pressure, the membrane used for experimentation is cross-linked and in its glassy state. The sorption isotherm shown in figure 3.2(b) represents the sorption isotherm for PVA membrane.

Presence of solvent (water) makes the polymer chains more flexible and produces gaps between them, this result in high diffusivity of gas molecules. Increased chain flexibility also promotes the transportation of larger sized molecules through membrane (Mulder, 1997).

The solvents used in experimentation had a pH higher than 12, the free OH^- , CO_3^{2-} ions penetrated the membrane (Bolto et al., 2009) and promoted the absorption of CO_2 . PVA dense layer acts as an extension of liquid film and reactions given in equation 4.5-4.7 takes place within membrane (PVA dense layer).

Unlike PTFE ,absorption of CO_2 in PVA membrane contactor is a complex process and in short following are the parameters responsible for absorption of CO_2 .

- Partial pressure of CO_2 in feed stream.
- Operating pressure (as degree of swelling depends on it).
- pH of solvent (it describes the strength of free OH^- ions that can penetrate the membrane).
- Concentration CO_3^{2-} ions.
- Thickness of PVA layer (important of those molecules which diffuse through membrane).
- Operating temperature (glassy or rubbery state of polymer).
- Cross-linking of membrane.

The trends shown in figure 6.9 shows that trend of flux with respect to pressure has a steep slope for S05 than S01. Unlike PTFE membrane contactor, PVA membrane shows a significant effect of alkalinity on the flux of CO_2 .

The reason behind this noticeable effect of alkalinity on flux CO_2 in PVA membrane contactor is the penetration of solvent in membrane. As discussed above that PVA membrane shows high flux under moist condition, excess OH^- ions from NaOH penetrate the membrane and enhance absorption process. Theses results also support the idea that PVA dense layer acts as a liquid supported membrane (facilitated membrane) which not only provides an interface but also promotes the absorption process.

Flux of CO_2 also depends on solvent flowrate. The effect of solvent flowrate on flux of CO_2 for solvent S01 and S05 operating at 2.04 bar are graphically compared in figure 6.10

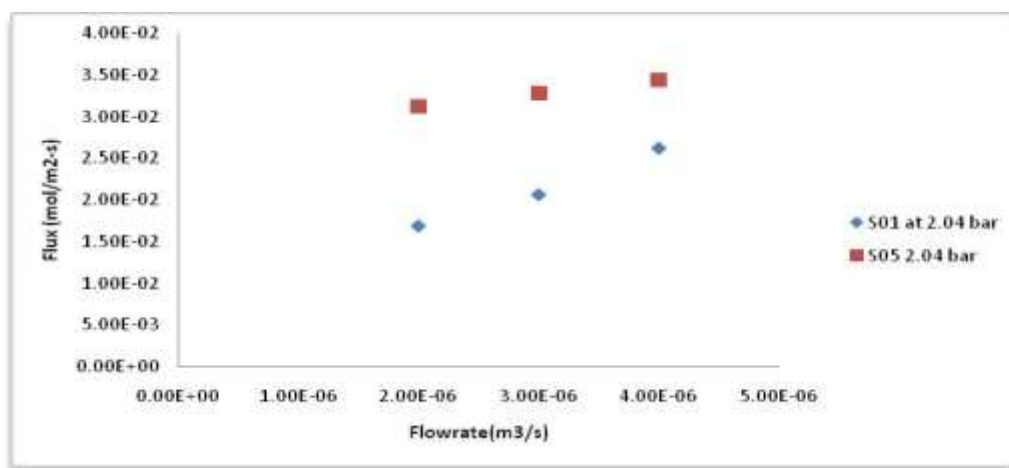


FIGURE 6.10 EFFECT OF FLOWRATE ON FLUX OF CO_2 FOR SOLVENT S01 AND S05 OPERATING AT CONSTANT PRESSURE OF 2.04 BAR

Flux observed for solvent S05 is higher than S01 due to its high alkalinity. Absorption of CO_2 in an alkali is a fast, irreversible; it depends on concentration of CO_2 and OH^- ions available for reaction. In both experiments concentration of CO_2 was kept constant by fixing operating gas pressure and gas flowrate. From this figure it can also be observed that trend of flux with respect to flowrate for S01 has a steeper slope compared to S05. The effect of flowrate on flux of CO_2 is more prominent for S01 as it has a lower pH. For better understanding penetration theory of mass transfer should be considered. Each batch of solvent that come in contact with membrane has a constant capacity for absorption, Concentration of OH^- ions in S05 is five times higher than S01. The loss in concentration of OH^- ions in liquid is used to estimate CO_2 loading. Since S01 has lower initial OH^- ion concentration, it shows a handsome change in loading with respect to flowrate.

From this experiment it can be concluded that for highly alkaline solvent liquid flowrate does not have a significant effect on CO_2 flux, for a PVA membrane contactor, solvent with highest possible alkalinity should be used at low flowrate.

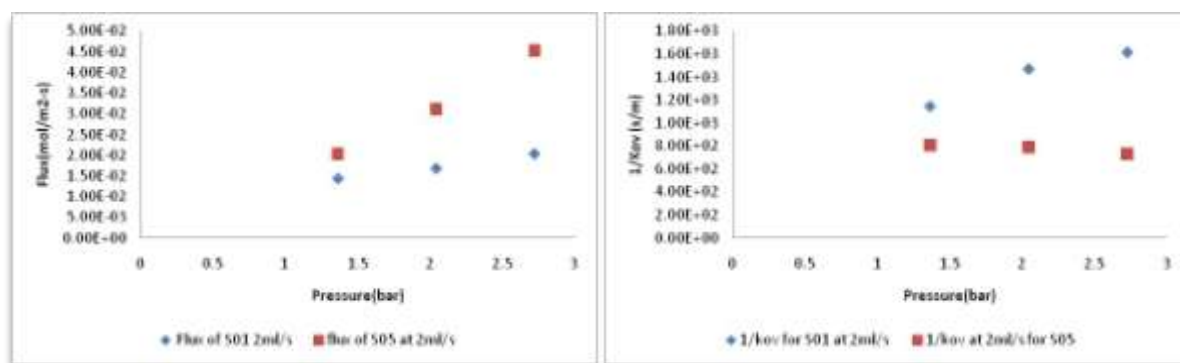


FIGURE 6.11 FLUXES AND OVERALL RESISTANCE TO MASS TRANSFER AS A FUNCTION OF OPERATING PRESSURE FOR SOLVENT S01 AND S05 AT A CONSTANT FLOWRATE OF 2ML/S

Figure 6.11 graphically compares the effect of solvent alkalinity on performance of the system with respect to operating pressure. Due to its higher pH Solvent S05 shows greater flux than S01. Overall resistance to mass transfer depends on resistance offered by gas film, membrane and liquid film; these results demonstrate the effect of liquid film (including dense PVA layer) resistance on mass transfer process. Overall resistance to mass transfer decreases 10 times by increasing the pH of solvent from 13.05 to 13.2. It can be concluded that liquid film has a significant contribution in overall mass transfer coefficient.

6.23 Time based experiment of PVA membrane contactor with S01

From the experimental results so far it has been established that PVA membrane shows appreciable flux of CO_2 due to the influence of swelling and solvent alkalinity. Based on these experimental results PVA membrane is a strong candidate for large scale membrane contactor application.

The membrane used for experimentation was originally developed for dehydration by pervaporation and it is hydrophilic in nature, permeation of solvent through membrane is expected in long term operations. To avoid permeation of liquid, in all experiments liquid stream pressure was kept just 2-4psi (0.13-0.26 bar) higher than gas stream. In order to study the effect of operating time on performance of system, time based experiment was performed. Solvent S01 was used at a flowrate

of 2ml/s to compare the results with experiment conducted with PTFE membrane. The results from this experiment are graphically presented in figure 6.12.

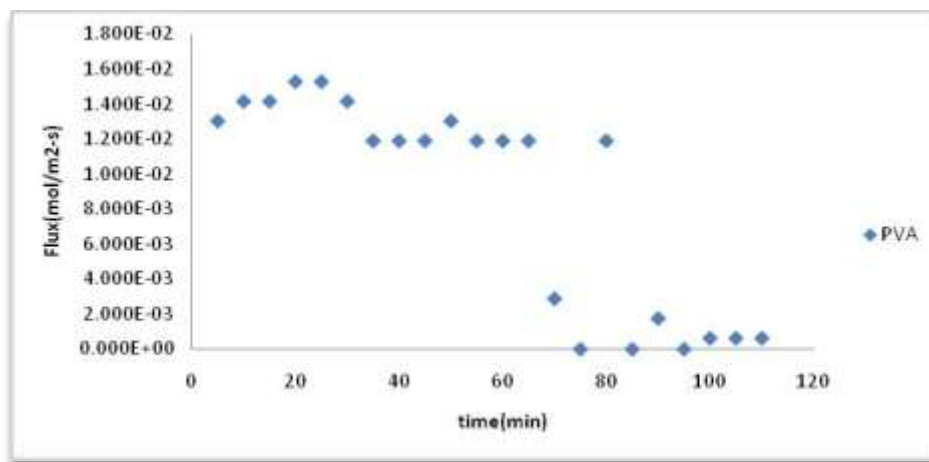


FIGURE 6.12 TIME BASED EXPERIMENT WITH PVA MEMBRANE CONTACTOR WITH S01

The time based experiment shows that flux of CO₂ first increases and then become constant. For first 60 minutes of smooth operation flux was observed to maintain an average value of 1.20E-2 mol/m²·s but, after 60 minutes it suddenly decrease to 4E-03 mol/m²·s and after 70 minute of operation flux of CO₂ becomes zero, at same time permeation of liquid was observed. After the start of liquid permeation, experiment was continued to observe study CO₂ flux but, after the start of liquid permeation negligible CO₂ loading was reported.

From this experiment it was observed that permeation of liquid starts after a certain period of time when membrane is saturated with water.

In membrane contactor experiments dry gas was used as feed gas. Partial pressure of water in gas stream was negligible so, it acts more like a sweep gas and generates a partial pressure difference for permeation of water through membrane. The membrane contactor runs well until the membrane is saturated with solvent, the concentration of liquid in membrane depends on operating pressure. From operational point of view permeation of solvent through PVA membrane can not be avoided but it can be delayed by reducing operating pressure.

6.3 Comparison of PTFE (Gore) and PVA membrane

Flux of CO_2 has been considered with respect to operating pressure, liquid flowrate and alkalinity of solvent to develop an understanding of membrane behavior.

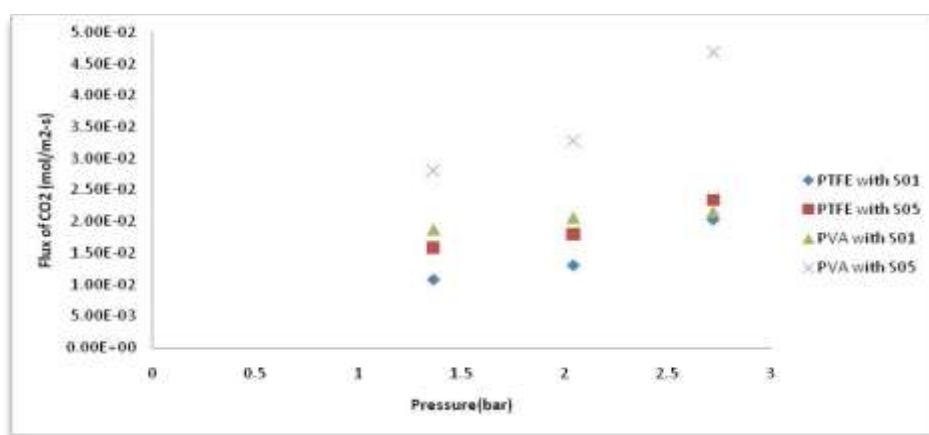


FIGURE 6.13 EFFECT OF OPERATING PRESSURE ON FLUX OF CO_2 FOR PVA AND PTFE MEMBRANES OPERATING WITH SOLVENT S01 AND S05 AT A CONSTANT FLOWRATE OF 3ML/S

Results from experiments conducted with Solvent S01 and S05 on PTFE and PVA membrane at constant flowrate of 3ml/s are graphically compared in figure 6.13. These results show that the flux of CO_2 for PVA membrane is higher than PTFE membrane at all operating pressures. The difference in flux at any pressure depends on permeability of membrane and alkalinity of solvent. These results show that PVA membrane performs better than PTFE in a gas-liquid membrane contactor for absorption of CO_2 under these operating conditions.

With solvent S05 PVA clearly shows better result at all pressures. From these findings it can be concluded that alkalinity of solvent (i.e. capacity to absorb CO_2) has an appreciable impact over performance of PVA membrane contactor. On the other hand PTFE membrane contactor does not show a noticeable effect of alkalinity on flux of CO_2 . Flux of CO_2 at 2ml/s and 4ml/s liquid flowrate was also calculated for both membranes but for the sake of discussion only results of 3ml/s is presented, all results are presented in appendix C.

Effect of solvent flowrate on CO_2 flux is also compared for both membrane contactors. Figure 6.14 gives flux of CO_2 as a function of solvent flowrate at a constant operating pressure of 2.04 bar.

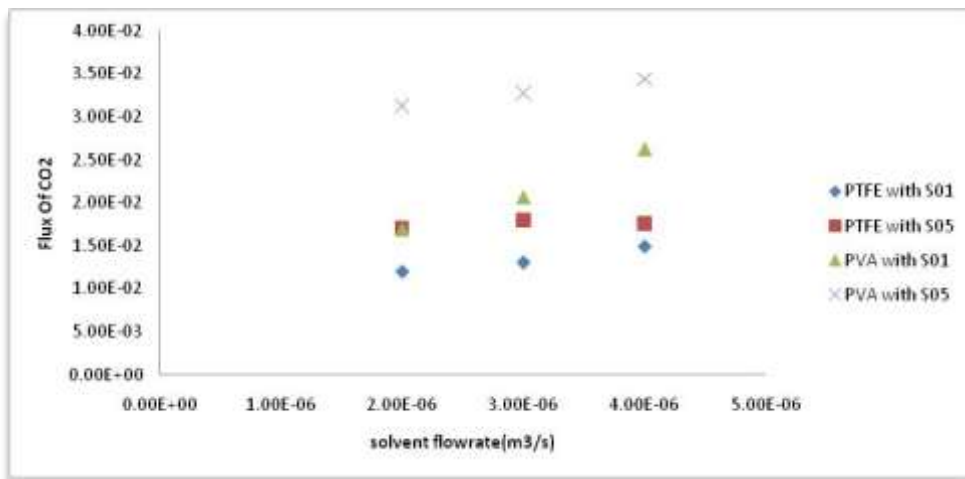


FIGURE 6.14 FLUX OF CO_2 AS A FUNCTION OF SOLVENT FLOWRATE AT CONSTANT OPERATING PRESSURE FOR PTFE AND PVA MEMBRANE WITH SOLVENT S01 AND S05.

Observations from figure 6.14 are as:

- Flux of CO_2 increases as a function of solvent flowrate (liquid film resistance decreases).
- Flux of CO_2 increases as alkalinity of solvent is increased (liquid film resistance decreases).
- For PTFE membrane contactor Flux of CO_2 is almost constant for both solvent i.e. liquid film resistances do not have a significant effect on mass transfer.
- In PVA membrane contactor flux increases as a function of flowrate and alkalinity.
- Alkalinity has an appreciable effect on flux even at high flowrate

Challenges related to operation

In a membrane contactor liquid stream is kept at slightly higher pressure to ensure smooth film of liquid in contact with membrane, to avoid penetration of solvent in membrane hydrophobic material is used. PTFE is hydrophobic and shows high break through pressure (over 3 bar) at operating

conditions. These properties of PTFE help in smooth operation of process even if some disturbance (sudden increase or decrease in pressure) occur. PTFE membrane seems to lose its hydrophobicity with time, in this project role of precipitation/fouling potential of solvent in increasing hydrophilicity of membrane can not be neglected. To prolong the life of membrane contactor solvent with low precipitation/ fouling potential and high surface tension should be used.

During experimentation with PVA membrane contactor some challenges faced from operational point of view are as:

PVA is a hydrophilic material and swells in presence of water, the degree of swelling depends on operating pressure. Although PVA membrane shows higher flux compared to PTFE but during experimentation pressure difference between liquid and gas stream was kept just 0.1 bar. In large scale operation it will be quite difficult to maintain a smooth operation with this little margin to counter any disturbance (sudden change in pressure). PVA membrane absorbs water from solvent stream, when membrane is saturated with water permeation of liquid starts. The saturation of membrane depends on following factors.

- Operating pressure.
- Solvent composition.

From the results discussed above PVA membrane contactor performed better than PTFE in terms of CO_2 flux but it is difficult to operate at high pressure and permeation of solvent can not be avoided.

Advantages and disadvantages of PVA membrane contactor are listed in table 6.1.

Table 6.1 Attributes of PVA and PTFE membranes in a membrane contactor

Membrane	Positive	Negative
PTFE	Virtually compatible with almost any solvent (Dindore Y.V et al. 2004)	Irregular geometry of pores (from SEM images)
	Excellent phase separation due to highly hydrophobic nature (Nishikawa N. et al.,1995)	Performance is compromised under wetted state (this work)
PVA	High mechanical strength	Compaction under pressure(Bolto et al., 2009)
	High flux of gas under swelled conditions (this work; Deng and Hagg,2010)	High degree of swelling can result in loss of membrane (Bolto et al., 2009)
	Resistant to high pH (Peter et al. 1976)	Permeation of liquid can be delayed but not be avoided. (this work)
	Good film forming ability(Bolto et al., 2009)	Low pressure difference between liquid and gas stream has to be maintained to delay permeation of liquid
	Enhance the flux of CO ₂ in presence of OH ions, hence acts as a facilitated membrane for transportation of CO ₂ (this work; Deng et. al,2009)	As flux increases with swelling, selectivity of membrane decreases. (Deng and Hagg, 2010)
		Difficult to operate (this work)

6.4 Sampling and analysis

In this project liquid stream was analyzed to determine CO₂ loading, flux and overall mass transfer coefficients were calculated based on this liquid stream analysis. For every reading two samples of Solvent were analyzed to estimate concentration of CO₂ in liquid stream leaving the membrane cell. Following are the challenges faced to analyze every sample.

Membrane contactor was operated at a pressure higher than atmospheric; in order to maintain this pressure a throttling valve was placed at liquid outlet of membrane cell. When pressurized liquid passed through this valve some of the absorbed CO_2 was released due to pressure swing. This is a highly practiced procedure used in CSS industry to partially regenerate solvent before sending it to stripper column for complete regeneration. To avoid the loss of CO_2 by throttling NaOH was added in solvent, the reaction between NaOH and CO_2 is irreversible so, the loss of absorbed gas was minimized this way. Furthermore in order to account for flashed gas (CO_2) samples were taken in NaOH solution. Sampling procedure has already been discussed in section 5.5.1.

Besides sampling several challenges were faced in analysis of these samples. To determine the concentration of CO_2 each sample was titrated against stander solution of HCl. This was a simple acid base titration but before titration, equal volume of BaCl_2 solution was added to each sample, 3 hours precipitation time was given to ensure complete removal of CO_3^{2-} ions, but still in some samples complete removal of CO_3^{2-} ions did not take place and presence of these ions resulted in lower apparent loading of CO_2 , in figure 6.8 at $t = 100$ minute negative concentration of CO_2 is observed.

The solvent S01 contains 0.1 molar NaOH in it, samples of S01 were taken in 0.1M NaOH solution so, for a sample with zero CO_2 loading and added with equal volume of BaCl_2 , concentration of NaOH was 0.05M. If 0.1 M HCl solution is used titrate such sample than only 5 ml of acid solution are enough to neutralize 10 ml of sample, on burette the smallest division of volume is 1 ml so, it is very difficult to determine a slight change in CO_2 loading by using this method. On the other hand if dilute solution of HCl is used to provide a wider range for observation then, the presence of impurities becomes more pronounced and chances of error due to contamination of solution from environment increases. In order to counter check the results two samples were taken for every reading and several experiments were repeated to verify the results.

Conclusions and recommendations

From the experiments conducted with PVA and PTFE membranes following conclusions are drawn.

- Flux of CO_2 increase with respect to operating pressure, partial pressure of CO_2 is a function of operating pressure.
- Flux of CO_2 depends upon solvent alkalinity, it can be seen that under all studied conditions flux of CO_2 was higher for solvent S05 than S01, this effect of alkalinity is not prominent for PTFE, where as for PVA flux of CO_2 is observed to increase up to 10 times with slight increase in pH of solvent (from 13.05 to 13.2).
- In experiments conducted with PTFE membrane contactor, availability of CO_2 for absorption was found to be the limiting factor so, it can be concluded that resistance offered by gas film ($1/k_g$) and membrane ($1/k_m$) plays an important role in determining the overall performance of absorption system.
- From the experimental work it is concluded that PVA membrane contactor shows higher flux of CO_2 than PTFE membrane.
- Compared to PTFE, PVA membrane contactor shows a considerable effect of solvent alkalinity on flux of CO_2 .
- From the experiments conducted with PVA membrane contactor, an appreciable increase in flux with respect to liquid flowrate is observed for solvent S01, where as experiments with S05 show negligible change in flux with flowrate. It is concluded that PVA membrane contactor should be operated with highest possible level of alkalinity and lowest possible liquid flowrate.

- PVA is a hydrophilic polymer that swells in presence of water and along with water it also allows ions to pass through it. Due to the presence of excess OH^- ions in membrane, absorption of CO_2 increases, from these experiments it can be concluded that in presence of OH^- ions PVA membrane acted like a facilitated membrane for transportation of CO_2 .
- PTFE membrane is hydrophobic in nature but its hydrophobicity decreases with time of operation, time based experiments showed the decline in hydrophobic nature of PTFE. One reason for this rapid decrease in hydrophobicity is precipitation/ fouling potential of solvent.
- From time based experiment with PTFE membrane contactor, it has been confirmed that Performance of a porous membrane decline dramatically with pore wetting.
- From the experimental work with PVA membrane, it is concluded that permeation of liquid through membrane can be delayed by operating it at low pressure and keeping liquid stream at a pressure equal to gas stream but permeation of liquid through membrane can not be avoided.
- Due to its hydrophilic nature PVA should be used at lowest possible operating pressure.
- For PVA membrane contactor maintaining a smooth operation in case of slight variation is difficult so, despite of high flux PVA membrane can not be recommended for industrial scale operation.
- In this project titration was used to analyze liquid stream, from this work it is concluded that titration can not detect small change in flux and chances of error in analysis is high so, gas stream analysis should be used to determine CO_2 flux and liquid stream analysis should only be used to verify the readings.

Recommendations for further work

Based on findings from this project following are the recommendations for further work in this field.

The overall mass transfer coefficient is a combination of resistance in series so, resistance offered by gas film should also be studied by using different composition of gases, in order to neglect gas film resistance, experiments should be conducted with over 97% CO_2 (as recommended by Sobieszuk and Pohorecki, 2010)

Instead of relying on liquid stream analysis, gas stream should also be monitored to verify the flux of CO_2 . Digital flow controller must be used to monitor and regulate the gas flow rate and pressure.

K_2CO_3 solution is usually operated at 70°C in industrial scale processes; effect of temperature on performance of membrane contactor should also be studied. In this project a rough idea about the impact of hydrodynamics on liquid film resistance is given by changing solvent flowrate, detailed hydrodynamic study of liquid and gas stream should be done to develop better understanding of the process.

Keeping in view the high flux of CO_2 for PVA membrane, it is recommended that thin cross-linked layer of PVA should be developed between two macro-porous, hydrophobic flat sheet membranes (say PTFE). The hydrophobicity of PTFE will provide a high break through pressure where as hydrophilicity of PVA will result in high flux. One advantage of this membrane can be low in resistance to mass transfer and swelling of PVA layer would also be controlled by gap between hydrophobic layers.

Since this was a basic study, flat sheet membranes were used. It is recommended to use hollow fiber macro porous PTFE membranes with a thin layer of PVA inside the fiber for further work.

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Appendix

List of Appendix

- A. Swell test for PVA membrane
- B. Wet ability and entry pressure for PTFE membrane
- C. Flux and kov calculations for PVA and PTFE membrane contactor
- D. Calculation of k_m for PTFE membrane
- E. SEM images of PVA and PTFE membranes.

A. Swell Test for PVA membrane

Swelling of PVA membrane was calculated based on gravimetric analysis. Procedure of this test is elaborated in section 5.6 of this report. Results of this test are presented in table A1 and A2.

Table A1 Swell test of composite PVA membrane

Water at Room temperature				Water at Room temperature		
	Dry	wet	% swell	dry	wet	% swell
membrane	0.02	0.024	20	0.023	0.027	17.3913
weight	0.021	0.026	23.80952	0.025	0.03	20
S01 at R.T				S01 at R.T		
	Dry	wet	% swell	dry	wet	% swell
membrane	0.023	0.028	21.73913	0.024	0.029	20.83333
weight	0.02	0.024	20	0.023	0.027	17.3913
S05 at Room temperature				S05 at R.T		
	Dry	wet	% swell	dry	wet	% swell
membrane	0.02	0.024	20	0.023	0.028	21.73913
weight	0.02	0.025	25	0.02	0.024	20

Table A2 Swell test of PVA layer.

Membrane wt	PVA		PVA+substrate	
	Sample 1	sample2	Sample 1	Sample 2
Dry	0.0041	0.003	0.0151	0.023
Wet	0.0055	0.0042	0.021	0.03
Difference	0.0014	0.0012	0.0059	0.007
Swell %	34.14634146	40	39.07285	30.43478
Avg swell	37.07317073		34.75381515	

Units of weight are gram and Swelling is a percentage and it has no units

B. Wetability experiment for PTFE membrane.

To calculate entry pressure of solvent following data was needed.

- Surface tension of solvents
- Contact angle of water on membrane.

Surface tension was calculated by tensiometer, a graph of surface tension plotted against time is presented in figure AF1.

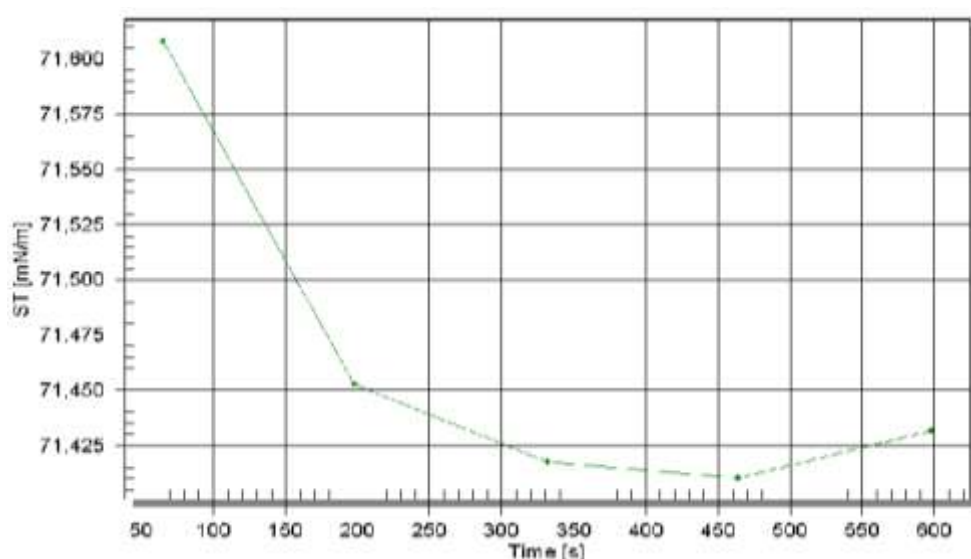


FIGURE AF1 SURFACE TENSION VERSUS CURVE FOR WATER BASED ON CALCULATIONS FORM TENSIOMETER AT ROOM TEMPERATURE.

Contact angle of distilled water on membrane surface after every experiment was determined by procedure elaborated in section 5.5.1 and results of these experiments along with calculation of liquid entry pressure are presented in table A3.

Table A 3 Surface tension of solvent, contact angle of membrane and break through pressure

Membrane	solvent	surface tension		operating pressure				Contact angle		pore size		pressure difference	
		mN/m	N/m	psi	bar	Kpa	N/m ²	θ	cosθ	micro meter	m	N/m ²	bar
PTFE-GORE	10%K ₂ CO ₃ -0.1M NaOH	74.156	7.42E-02	20	1.36E+00	1.36E+02	1.36E+05	127.83	-0.613	2.00E-01	2.00E-07	4.55E+05	4.55E+00
PTFE-GORE	10%K ₂ CO ₃ -0.1M NaOH	74.156	7.42E-02	20	1.36E+00	1.36E+02	1.36E+05	128.12	-0.617	2.00E-01	2.00E-07	4.58E+05	4.58E+00
PTFE-GORE	10%K ₂ CO ₃ -0.1M NaOH	74.156	7.42E-02	20	1.36E+00	1.36E+02	1.36E+05	89.89	0.017	2.00E-01	2.00E-07	-1.26E+04	-1.26E-01
PTFE-GORE	10%K ₂ CO ₃ -0.1M NaOH	74.156	7.42E-02	30	2.04E+00	2.04E+02	2.04E+05	117	-0.45	2.00E-01	2.00E-07	3.34E+05	3.34E+00
PTFE-GORE	10%K ₂ CO ₃ -0.1M NaOH	74.156	7.42E-02	30	2.04E+00	2.04E+02	2.04E+05	122.1	-0.53	2.00E-01	2.00E-07	3.93E+05	3.93E+00
PTFE-GORE	10%K ₂ CO ₃ -0.1M NaOH	74.156	7.42E-02	30	2.04E+00	2.04E+02	2.04E+05	119.5	-0.49	2.00E-01	2.00E-07	3.63E+05	3.63E+00
PTFE-GORE	10%K ₂ CO ₃ -0.1M NaOH	74.156	7.42E-02	40	2.72E+00	2.72E+02	2.72E+05	112.53	-0.383	2.00E-01	2.00E-07	2.84E+05	2.84E+00
PTFE-GORE	10%K ₂ CO ₃ -0.1M NaOH	74.156	7.42E-02	40	2.72E+00	2.72E+02	2.72E+05	116.4	-0.446	2.00E-01	2.00E-07	3.31E+05	3.31E+00
PTFE-GORE	10%K ₂ CO ₃ -0.1M NaOH	74.156	7.42E-02	40	2.72E+00	2.72E+02	2.72E+05	113.74	-0.402	2.00E-01	2.00E-07	2.98E+05	2.98E+00
PTFE-GORE	water	71.5	7.15E-02					128.2	-0.642	2.00E-01	2.00E-07	4.59E+05	4.59E+00
PTFE-GORE	10%K ₂ CO ₃ -0.5M NaOH	74.12	7.41E-02	20	1.36E+00	1.36E+02	1.36E+05	112.78	-0.387	2.00E-01	2.00E-07	2.87E+05	2.87E+00
PTFE-GORE	10%K ₂ CO ₃ -0.5M NaOH	74.12	7.41E-02	20	1.36E+00	1.36E+02	1.36E+05	115.9	-0.436	2.00E-01	2.00E-07	3.23E+05	3.23E+00
PTFE-GORE	10%K ₂ CO ₃ -0.5M NaOH	74.12	7.41E-02	20	1.36E+00	1.36E+02	1.36E+05	91.4	-0.024	2.00E-01	2.00E-07	1.78E+04	1.78E-01
PTFE-GORE	10%K ₂ CO ₃ -0.5M NaOH	74.12	7.41E-02	30	2.04E+00	2.04E+02	2.04E+05	113.22	-0.4	2.00E-01	2.00E-07	2.96E+05	2.96E+00
PTFE-GORE	10%K ₂ CO ₃ -0.5M NaOH	74.12	7.41E-02	30	2.04E+00	2.04E+02	2.04E+05	116.84	-0.45	2.00E-01	2.00E-07	3.34E+05	3.34E+00
PTFE-GORE	10%K ₂ CO ₃ -0.5M NaOH	74.12	7.41E-02	30	2.04E+00	2.04E+02	2.04E+05	110.1	-0.343	2.00E-01	2.00E-07	2.54E+05	2.54E+00
PTFE-GORE	10%K ₂ CO ₃ -0.5M NaOH	74.12	7.41E-02	40	2.72E+00	2.72E+02	2.72E+05	111.5	-0.36	2.00E-01	2.00E-07	2.67E+05	2.67E+00
PTFE-GORE	10%K ₂ CO ₃ -0.5M NaOH	74.12	7.41E-02	40	2.72E+00	2.72E+02	2.72E+05	115.2	-0.425	2.00E-01	2.00E-07	3.15E+05	3.15E+00
PTFE-GORE	10%K ₂ CO ₃ -0.5M NaOH	74.12	7.41E-02	40	2.72E+00	2.72E+02	2.72E+05	113.4	-0.397	2.00E-01	2.00E-07	2.94E+05	2.94E+00
PTFE-GORE	water	71.5	7.15E-02					127.6	-0.64	2.00E-01	2.00E-07	4.58E+05	4.58E+00

Dindore V.Y., et al (2004) calculated entry pressure for 0.45μm PTFE membrane to be 310 Kpa. Compared to his data membrane used in this project has smaller pore size and hence higher breakthrough pressure is expected.

C. Calculations of flux of CO₂ and k_{ov}

Liquid stream was analyzed to determine the flux of CO₂. Sampling and calculation procedure is presented in section 5.4 of this report. Based on equation 5.3 CO₂ concentration was calculated in liquid stream. The flux of CO₂ and k_{ov} calculated for all experiments is presented in table A4 and A5, sample calculations for an experiment conducted with solvent S05 are as:

Volume of sample = 20 ml

Volume of 0.5 M NaOH solution = 20 ml

Added volume of BaCl₂ solution = 40 ml, Dilution factor =2

Volume of sample for titration = 10ml

Concentration of HCl used for titration = 0.25M

Volume of HCl consumed = 9.2 ml (say).

Concentration of NaOH in titrated sample = $(0.25 \times 9.2) / 10 = 0.23 \text{ M}$

Concentration of NaOH in sample before addition of BaCl₂ = 0.46M

Concentration of CO₂ present in sample = $(0.5 - 0.46) / 2 = 0.02 \text{ M} = 2.0 \text{E-}5 \text{ mol/m}^3$

Molar flowrate of CO₂ = $0.02 \times 2 / 1000 = 4 \text{E-}5 \text{ mol/s}$ (say volume flowrate is 2ml/s)

Membrane area = $1.6 \text{E-}3 \text{ m}^2$

Flux of CO₂ = $(4 / 1.6) \text{E-}2 \text{ mol/m}^2\text{-s}$

Operating pressure = 1.36 bar

Volumetric flowrate of gas = $1.0 \text{E-}5 \text{ m}^3/\text{s}$

Percentage of CO₂ in gas = 30%

Molar concentration = 16.47 Mol/m^3

LMCD (log mean concentration difference) = see equation 2.10

k_{ov} = see equation 2.9

Table A4 Flux, mass transfer coefficient and resistance to mass transfer for membrane contactor operating with PVA membrane

PVA Data									
Pressure		Solvent	flowrate		Membrane area	Flux	Mass transfer coefficient		
Psi	bar		ml/s	m3/s					
20	1.360544	0.1 M NaOH + 10%	2	2.00E-06	1.60E-03	1.44E-02	8.74E-04	1.14E+03	
20	1.360544	0.1 M NaOH + 10%	3	3.00E-06	1.60E-03	1.87E-02	1.14E-03	8.77E+02	
20	1.360544	0.1 M NaOH + 10%	4	4.00E-06	1.60E-03	1.70E-02	1.03E-03	9.71E+02	
30	2.040816	0.1 M NaOH + 10%	2	2.00E-06	1.60E-03	1.68E-02	6.80E-04	1.47E+03	
30	2.040816	0.1 M NaOH + 10%	3	3.00E-06	1.60E-03	2.06E-02	8.34E-04	1.20E+03	
30	2.040816	0.1 M NaOH + 10%	4	4.00E-06	1.60E-03	2.63E-02	1.60E-03	6.25E+02	
40	2.721088	0.1 M NaOH + 10%	2	2.00E-06	1.60E-03	2.04E-02	6.19E-04	1.62E+03	
40	2.721088	0.1 M NaOH + 10%	3	3.00E-06	1.60E-03	2.16E-02	6.56E-04	1.52E+03	
40	2.721088	0.1 M NaOH + 10%	4	4.00E-06	1.60E-03	3.00E-02	9.11E-04	1.10E+03	
20	1.360544	0.5 M NaOH + 10%	2	2.00E-06	1.60E-03	2.03E-02	1.24E-03	8.06E+02	
20	1.360544	0.5 M NaOH + 10%	3	3.00E-06	1.60E-03	2.81E-02	1.71E-03	5.85E+02	
20	1.360544	0.5 M NaOH + 10%	4	4.00E-06	1.60E-03	2.88E-02	1.75E-03	5.71E+02	
30	2.040816	0.5 M NaOH + 10%	2	2.00E-06	1.60E-03	3.12E-02	1.26E-03	7.94E+02	
30	2.040816	0.5 M NaOH + 10%	3	3.00E-06	1.60E-03	3.28E-02	1.33E-03	7.52E+02	
30	2.040816	0.5 M NaOH + 10%	4	4.00E-06	1.60E-03	3.44E-02	1.39E-03	7.19E+02	
40	2.721088	0.5 M NaOH + 10%	2	2.00E-06	1.60E-03	4.53E-02	1.37E-03	7.30E+02	
40	2.721088	0.5 M NaOH + 10%	3	3.00E-06	1.60E-03	4.69E-02	1.42E-03	7.04E+02	
40	2.721088	0.5 M NaOH + 10%	4	4.00E-06	1.60E-03	4.70E-02	1.43E-03	6.99E+02	

Table A5 Flux, mass transfer coefficient and resistance to mass transfer for PTFE membrane

PTFE (Gore) Data									
Pressure		Solvent	flowrate		Membrane area	Flux	Mass Transfer coefficient	Resistance to Mass transfer	
Psi	bar		ml/s	m3/s					
20	1.360544	0.1 M NaOH + 10% k2CO3	2	2.00E-06	1.60E-03	1.00E-02	6.07E-04	1.65E+03	
20	1.360544	0.1 M NaOH + 10% k2CO3	3	3.00E-06	1.60E-03	1.08E-02	6.26E-04	1.60E+03	
20	1.360544	0.1 M NaOH + 10% k2CO3	4	4.00E-06	1.60E-03	1.12E-02	7.19E-04	1.39E+03	
30	2.040816	0.1 M NaOH + 10% k2CO3	2	2.00E-06	1.60E-03	1.20E-02	4.96E-04	2.02E+03	
30	2.040816	0.1 M NaOH + 10% k2CO3	3	3.00E-06	1.60E-03	1.31E-02	5.30E-04	1.89E+03	
30	2.040816	0.1 M NaOH + 10% k2CO3	4	4.00E-06	1.60E-03	1.49E-02	5.59E-04	1.79E+03	
40	2.721088	0.1 M NaOH + 10% k2CO3	2	2.00E-06	1.60E-03	1.64E-02	4.92E-04	2.03E+03	
40	2.721088	0.1 M NaOH + 10% k2CO3	3	3.00E-06	1.60E-03	2.03E-02	6.16E-04	1.62E+03	
40	2.721088	0.1 M NaOH + 10% k2CO3	4	4.00E-06	1.60E-03	2.13E-02	6.49E-04	1.54E+03	
20	1.360544	0.5 M NaOH + 10% k2CO3	2	2.00E-06	1.60E-03	1.52E-02	9.47E-04	1.06E+03	
20	1.360544	0.5 M NaOH + 10% k2CO3	3	3.00E-06	1.60E-03	1.58E-02	1.14E-03	8.77E+02	
20	1.360544	0.5 M NaOH + 10% k2CO3	4	4.00E-06	1.60E-03	1.52E-02	8.32E-04	1.20E+03	
30	2.040816	0.5 M NaOH + 10% k2CO6	2	2.00E-06	1.60E-03	1.70E-02	6.88E-04	1.45E+03	
30	2.040816	0.5 M NaOH + 10% k2CO3	3	3.00E-06	1.60E-03	1.80E-02	7.93E-04	1.26E+03	
30	2.040816	0.5 M NaOH + 10% k2CO3	4	4.00E-06	1.60E-03	1.76E-02	6.31E-04	1.58E+03	
40	2.721088	0.5 M NaOH + 10% k2CO3	2	2.00E-06	1.60E-03	2.15E-02	6.53E-04	1.53E+03	
40	2.721088	0.5 M NaOH + 10% k2CO3	3	3.00E-06	1.60E-03	2.34E-02	7.10E-04	1.41E+03	
40	2.721088	0.5 M NaOH + 10% k2CO3	4	4.00E-06	1.60E-03	2.40E-02	7.28E-04	1.37E+03	

D. Calculation of k_m for PTFE membrane

As discussed in section 3.3.3 that molecules can show Knudsen and/or molecular diffusion through membrane pores so, it is important to know the governing mechanism for transport of CO_2 through membrane. Figure AF4 shows a relation between pressure and flux by diffusion flow. From this figure it can be seen that our system is operated in transition region.

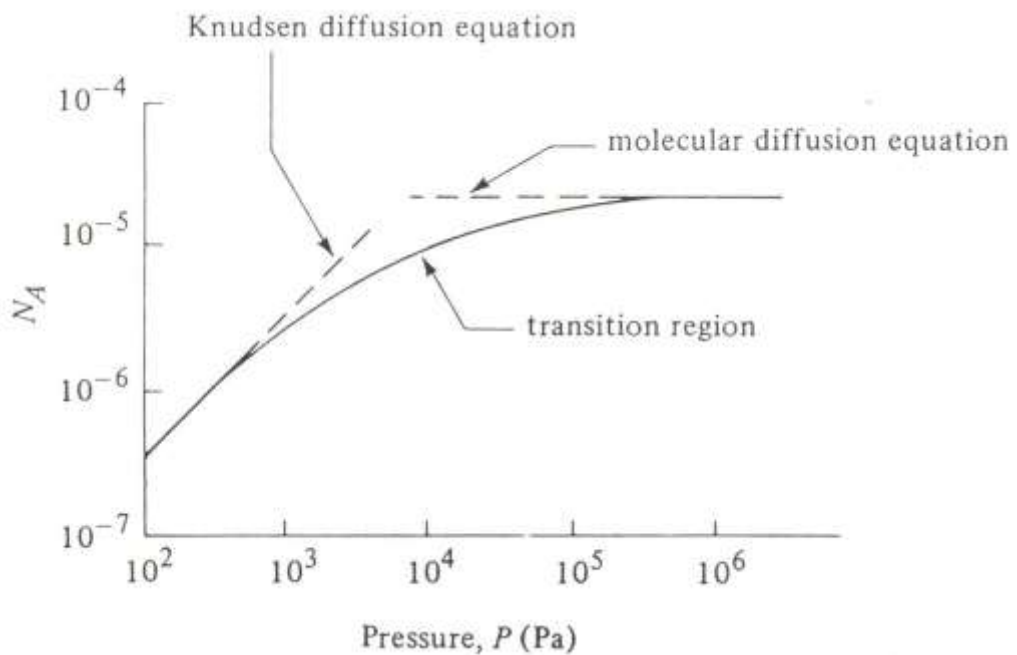


FIGURE AF 4 EFFECT OF PRESSURE ON DIFFUSIONAL FLUX OF CO_2 IN TRANSITION REGION
ADAPTED FROM (GEANKOPLIS C J, 2003)

This means that both Knudsen and molecular diffusion contributes to transportation mechanism.

Since the membranes show high polydispersity in terms of pore size so, it is also to consider convective flow. Hagen Poiseulles equation (3.9) represents the flux by convective flow. It can be seen that flux is a function of r^2 , in this case pore

radius has a magnitude of order $10E-7$ m so, this small value of radius results in a negligible value of flux by convective flow.

Now it is clear that diffusion is the only mechanism responsible for transportation of CO_2 through membrane so, only equation 3.13(b)-3.15 shall be considered for further calculations.

For calculation of D_{AB} Fuller's method is used. Calculations of D_m and K_m without reaction are presented as.

		Given Data			
Constants		value	units	value	units
T	Temperature	25	°C	298	K
r	pore radius	0.2	mm	$2.00E-07$	m
t	membrane thickness	0.5	mm	0.0005	m
M_{CO_2}	Molecular weight of CO_2	44			
M_{N_2}	Molecular weight of N_2	28			
ϵ	Porosity	0.7			
τ	tortuosity	1.3			
V_{CO_2}	Diffusion volume of CO_2	26.9	See table	A6	
V_{N_2}	Diffusional volume of N_2	17.9	See table	A6	
Variable					
P	Pressure	1.36	bar	$1.36E+05$	N/m^2
		2.04	bar	$2.04E+05$	N/m^2
		2.7	bar	$2.70E+05$	N/m^2

Calculation of D_k from equation 3.13b

$$D_k = 97 * r * (t / M_{CO_2})^{0.5} \quad 5.05E-05 \quad m^2/s$$

Calculation of D_{AB} by equation 3.14

$$\text{Constant part} \quad (T^{1.75} * ((1/M_{CO_2}) + (1/M_{N_2}))^{0.5} / ((V_{CO_2}^{0.33}) + (V_{N_2}^{0.33}))^2) \\ 167.4786$$

D_{AB}	constant/Pressure			
		at 1.36 bar	1.23E-03	m ² /s
	value of	at 2.04 bar	8.21E-04	m ² /s
	DAB	at 2.7 bar	6.20E-04	m ² /s

Calculation of Dm by equation 3.15

D_m	$1/((1/D_k)+(1/D_{AB}))$			
	at 1.36 bar	4.85E-05	m ² /s	
	at 2.04 bar	4.76E-05	m ² /s	
	at 2.7 bar	4.67E-05	m ² /s	

Calculation of km by equation table

k_m	$Dm*\varepsilon/\tau t$			
	at 1.36 bar	0.05223	m/s	
	at 2.04 bar	0.051221	m/s	
	at 2.7 bar	0.050279	m/s	

Table A6 Diffusion volume of simple molecules (adapted from Fuller et al., 1966)

Molecule	Diff vol	Molecule	Diff vol	Molecule	Diff vol
H₂	7.07	Ar	16.1	H₂O	12.7
D₂	6.7	Kr	22.8	CCl₂F₂	114
He	2.88	Xe	37.9	Cl₂	69.7
N₂	17.9	CO	18.9	Br₂	67.2
O₂	16.9	CO₂	26.9	SO₂	41.1
Air	20.1	N₂O	13.9		
Ne	5.59	NH₃	14.9		

E. SEM (Scanning electron microscope)

Gore-Tex membrane

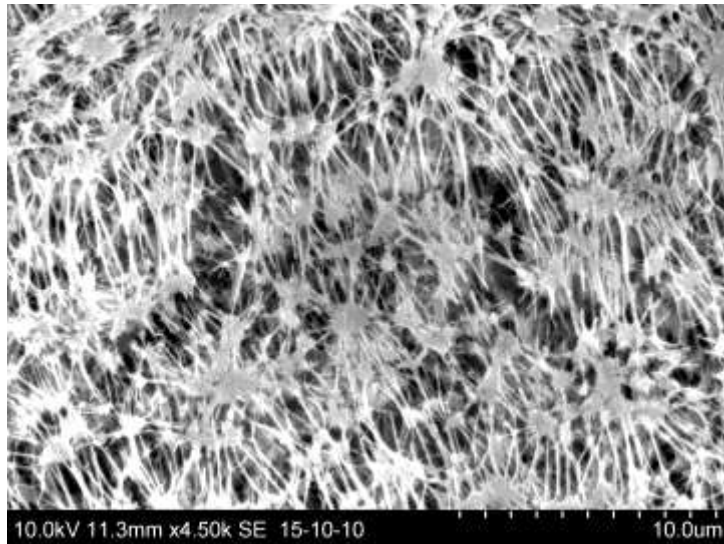


FIGURE AF 5 : SEM IMAGE OF PTFE (GORE-TEX) MEMBRANE, SELECTIVE LAYER.

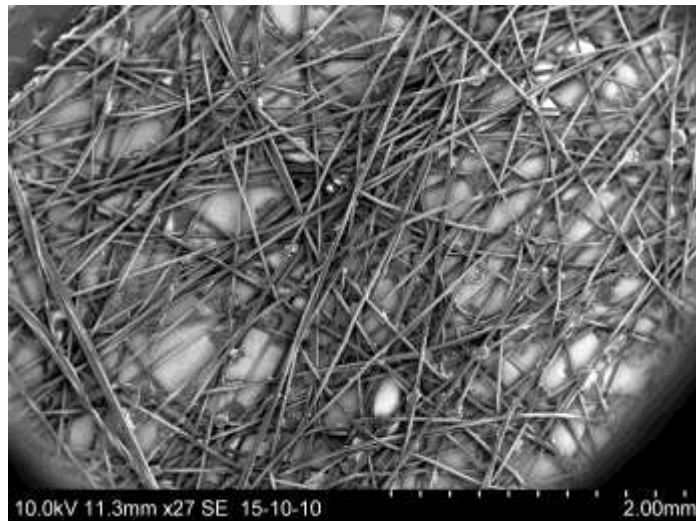


FIGURE AF 6: SEM IMAGE OF PTFE (GORE-TEX) MEMBRANE, SUPPORT LAYER.

PVA membrane

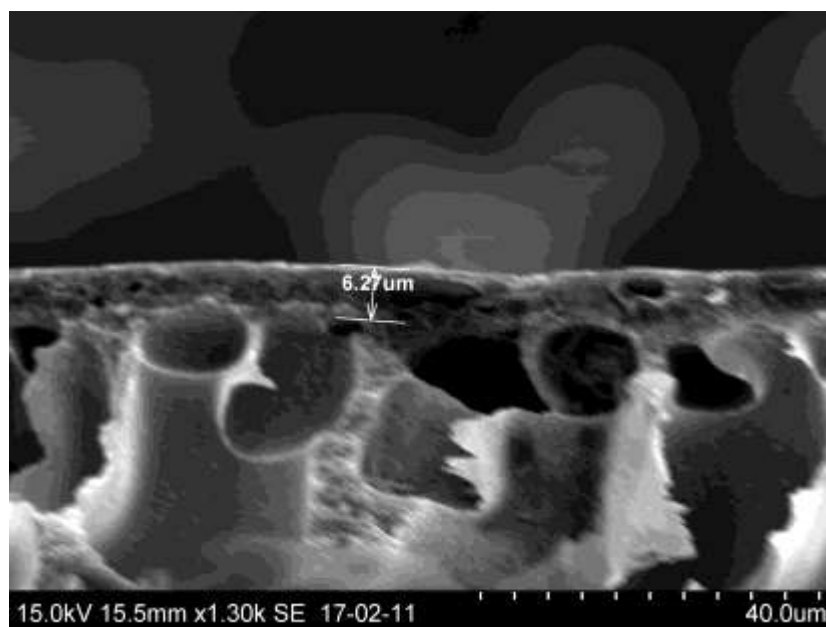


FIGURE AF 8: SEM IMAGE OF PVA MEMBRANE, CROSS SECTION.