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## EXPERIMENTAL STUDY OF GAS FLUX CHARACTERISTICS IN A CO<sub>2</sub> SELECTIVE SILICA BASED MODIFIED MEMBRANE

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### ABSTRACT

The purpose of membrane gas separation for CO<sub>2</sub> capture from flue gas process is to reduce greenhouse emissions as well as associated environmental challenges globally. This study looks at gas separation in a single gas permeation experiment using CO<sub>2</sub>, O<sub>2</sub>, CH<sub>4</sub> and N<sub>2</sub> gases by means of a highly selective and permeable inorganic ceramic membrane. A fresh ceramic membrane has been prepared by dip-coating technique through immersion in a silica-based precursor solution for pore size modification and used for gas purification purposes. Results obtained show excellent performance of the silica based membrane for CO<sub>2</sub> recovery applications through adsorptive transport mechanism. Effect of pressure drop on gas flux showed a linear proportionality. The gas flux has high CO<sub>2</sub> flux of 1.71mols<sup>-1</sup>m<sup>-2</sup> at room temperature in comparison to that of other gases. Further results show that CO<sub>2</sub> permselectivity to that of N<sub>2</sub> supported the theoretical Knudsen with a high selectivity factor of 3.83 confirming a reasonable capture of CO<sub>2</sub> to that of N<sub>2</sub> as a major component of a flue gas stream.

**Keywords:** Carbon Capture, Composite Membrane, Gas Permeation, Gas Flux & Perm Selectivity.

### 1. INTRODUCTION

Fossil fuel fired power plants used for production of electricity are the most disreputable emitters of green house gases of which carbon dioxide is a major green house gas. Accordingly fossil fuels accounts for about 69 percent of the total global electricity produced [1]). Combustion of fossil fuels such as oil, natural gas, coal and bio fuels results in large amount of CO<sub>2</sub> emissions in the atmosphere. Other causes of CO<sub>2</sub> gas emissions into the atmosphere are through chemical reactions in cement production facilities and land or bush burning. Studies show that CO<sub>2</sub> alone accounts for about 70 percent of global warming [2], and about 80 percent of atmospheric CO<sub>2</sub> upsurge are due to use of fossil fuels [3]. Additionally, incessant concentration of Carbon dioxide gas through

anthropogenic sources cause an increase in atmospheric temperature by the absorption of infrared radiation emitted by the earth surface trapping the intensity from the sun to form a blanket over the surface of the earth leading to threat to the environment and humans which is currently a global concern [1][2]. Going by the ever growing evidence, CO<sub>2</sub> atmospheric concentrations will increase to 700 parts per million by volume (ppmv) by 2100 even if emissions of CO<sub>2</sub> stay the same as they are at present [4]. Consequently, this is predictable to raise the mean global temperatures by about 1.9°C more in the next 100 years [1].

The need for a long-term and cost-effective technology for CO<sub>2</sub> capture from flue gas come into play as a result of reviews from different researchers by finding solution to the problem of climate change. Consequently, inorganic membrane applications have remained a substitute to conventional methods of gas separations and carbon capture generally. The difference in individual gas flux and permeation features makes the membrane a good contender for gas separation from one another, acting as a selective barrier [5]. This essential characteristic has been applied in gas processes, treatment of waste water, purification and ultra filtration industrial processes. Accordingly, inorganic membranes show gleaming evidence of chemical and substantial properties, high temperature stability as well as insensitivity to harsh environment and considerable tensile strength which will overcome the limitations of polymer membrane [6]. Thus, the utilization of inorganic membranes in the industry have been demonstrated in its application for the production of hydrogen gas, CO<sub>2</sub> capture and H<sub>2</sub>S recovery from related gas supply flow because of their ease and minimal energy requirement [7]. Dip-coating, chemical vapour deposition (CVD), and pulsed layer deposition are some techniques for porous membrane fabrication and modification [8, 9, 10]. Nonetheless dip-coating method in comparison to others has in built feature such as homogeneous surface and good organization of the membrane pore structure leading to its frequent broad range of application [8].

## 2. EXPERIMENTAL

### 2.1. Membrane design

In this study, the experiment was performed using a support having an average pore size of 6000nm with an inner and outer diameter of 19.8mm and 25mm respectively. In addition the support has a permeable length of 318mm with an impermeable length of 5mm deposited on a macro porous tubular filter. Design and fabrication of support can be made of several layers of different materials namely: Aluminum oxide (Al<sub>2</sub>O<sub>3</sub>), Titanium Oxide (TiO<sub>2</sub>), Zirconium Oxide (ZrO<sub>2</sub>), Silicon dioxide (SiO<sub>2</sub>), Silicon carbide, Zeolite or a mixture of two materials deposited on an underlying porous support,  $\alpha$ -alumina, zirconium supports [11]. Membrane separation of gases is a highly intricate procedure and therefore the material used for its research should demonstrate a long-lasting feature, stability and modified in a highly technological manner to be adapted to separate specific gases [12].

### 2.2. Sol-gel dip coating Technique

Fig 1 is the support immersion in the silica based solution while Fig 2 shows the initial mechanical drying before further heating in an oven. The ceramic support was immersed repeatedly in a silica based solution. The support is then removed to dry. Thereafter further drying is done by application of heat at a temperature of 65°C in an oven and left for 2hrs. These steps were done to obtain the desired thickness, gas purification purposes and reduction in pore size for permeability and selectivity optimization.

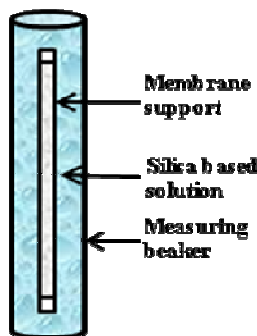


Figure 1: Support Immersion



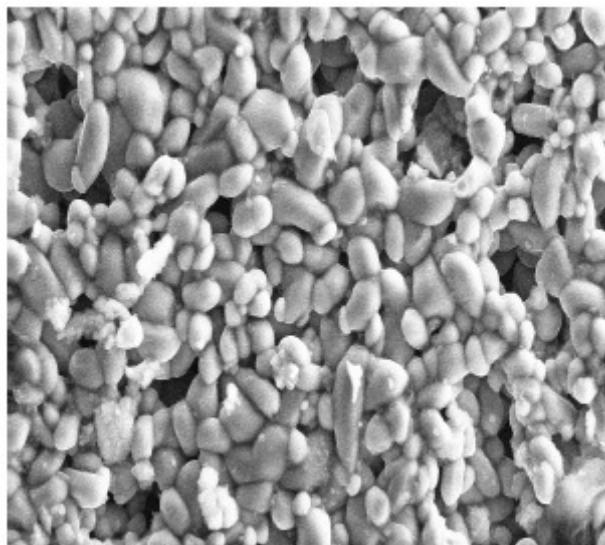
Figure 2: Deposited support on a spinning atmospheric drying device

### 2.3. Membrane Structural and Compositional Analysis

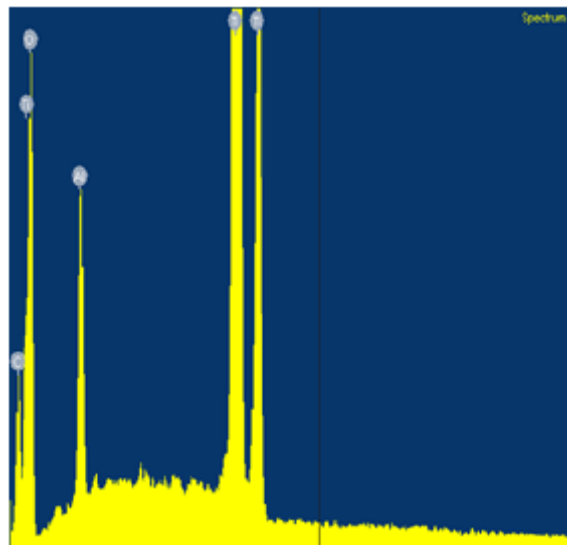
Membrane structure and its composition were obtained by using an inner section of the support to determine the materials characteristics. In this paper two ways used are scanning electron microscope (SEM) and Energy Dispersive x-ray analysis. The SEM was used in analysis and production of images of a sample material by scanning with a focused beam of high-energy electron and this creates a signal which produces information on the inside, outside and cross sectional morphology of the sample. The orientation of the material mark-up, chemical composition and the pore size distribution are equally obtained using the instrument. The elemental composition of the sample is identified using an x-ray technique (EDXA). The EDXA system is attached to the SEM. Data generated by EDXA analyses the true composition of the elements within the sample [16]. Subsequently a nano-structural material prepared from ceramics membrane has been fabricated by means of Nanotechnology, an environmentally-friendly, economical and highly efficient technology. It can be applied in all forms of CO<sub>2</sub> recovery from other gases and its efficiency increases relatively to the CO<sub>2</sub> concentration in the flue gas stream feed. Nanotechnology is amongst the various technologies of interest globally to explore carbon-capturing technology [12, 13, 14].

In this paper therefore a silica-based modified ceramic inorganic membrane is developed and tested for CO<sub>2</sub> capture applications. A combination of gas flux and permselectivity as important factors are explored with respect to individual gas permeations as well as comparative analysis of results obtained. Fig 3 shows the inner section of the membrane material sample scanning electron microscope (SEM) with 2.00K X magnification. A further result as presented in Fig 4 depicts the energy dispersive x-ray analysis of the membrane elemental composition.

Table 1, shows the list of elements present in the membrane sample. Namely: C – Calcium carbonate (CaCO<sub>3</sub>), O – Silicon dioxide (SiO<sub>2</sub>), Al – Aluminum Oxide (Al<sub>2</sub>O<sub>3</sub>), Ti – Titanium Oxide (TiO<sub>3</sub>). As shown, their individual concentrations, intensity correlations, weight percentage as well as atomic weight was also analyzed through these methods.



**Figure 3:** Membrane Sample SEM Image inner section with 2.00K X magnification



**Figure 4:** EDXA Analysis of Membrane Sample Elemental Composition

**Table 1:** EDXA Elemental composition of membrane sample

Element	App Conc.	Intensity Corr.	Weight %	Weight % Sigma	Atomic %
C K	17.24	0.6167	9.46	0.35	17.39
O K	33.62	0.2672	42.62	0.57	58.79
Al K	8.90	0.6184	4.88	0.09	3.99
Ti K	113.72	0.8946	43.04	0.45	19.83
Totals			100.00		

### 3. RESULTS AND DISCUSSIONS

The results for the membrane deposition are calculated as summarized in Table 2. Thus; the permeability for a single gas is given as:

$$Q = \frac{F\ell}{\Delta P \cdot A_s} \tag{1}$$

Where, F is the flux in mol/sec,  $\ell$ , the membrane layer thickness,  $\Delta P$ , Pressure Drop and  $A_s$ , the membrane surface area. To obtain the layer thickness, first the gain of silica after each dip is calculated. Density of silica is given as  $2.1\text{gcm}^{-3}$ .

The volume of silica,  $V_s$  can be calculated using the formula below:

$$\rho = \frac{m}{V_s} \tag{2}$$

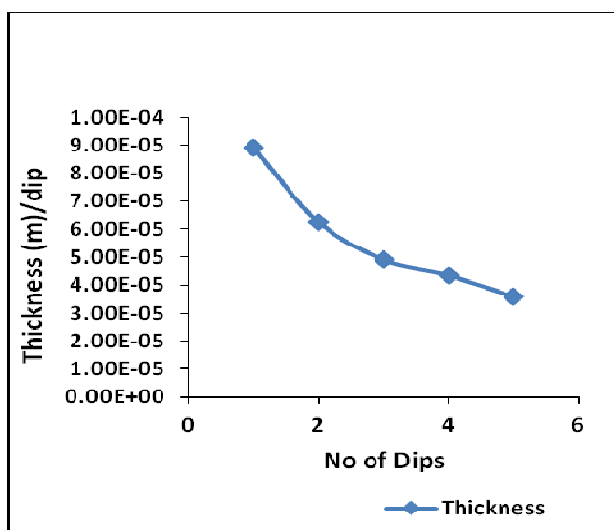
Where,  $m$  is the mass gained by support,  $\rho$ , density of silica and  $V_s$  the volume of silica dispersed on the surface of the support which determines its thickness and can be expressed as:

$$\ell = \frac{V_s}{A_s} \tag{3}$$

Figure 5 is the graph showing the relationship between the number of immersion of the support and the layer thickness per each dip. As shown the thickness of the membrane decreases for each dip. The mass of silica gained is also calculated, however, as the layer thickness reduces, its cumulative thickness increases. Overall result demonstrates a modification process on the membrane.

**Table 2:** Dip Coating Experimental calculations

	1 <sup>st</sup> Dip	2 <sup>nd</sup> Dip	3 <sup>rd</sup> Dip	4 <sup>th</sup> Dip	5 <sup>th</sup> Dip
<b>Mass of membrane (g)</b>	<b>277.4</b>	<b>280.7</b>	<b>283.3</b>	<b>285.6</b>	<b>287.5</b>
<b>Mass of Silica (g)</b>	<b>4.7</b>	<b>3.3</b>	<b>2.6</b>	<b>2.3</b>	<b>1.9</b>
<b>Volume of silica (m<sup>3</sup>)</b>	<b>2.24E-6</b>	<b>1.57E-6</b>	<b>1.24E-6</b>	<b>1.10E-6</b>	<b>9.05E-7</b>
<b>Layer thickness</b>	<b>8.92E-5</b>	<b>6.26E-5</b>	<b>4.93E-5</b>	<b>4.36E-5</b>	<b>3.60E-5</b>



**Figure 5:** Effect of Number of Dips on Membrane Layer Thickness

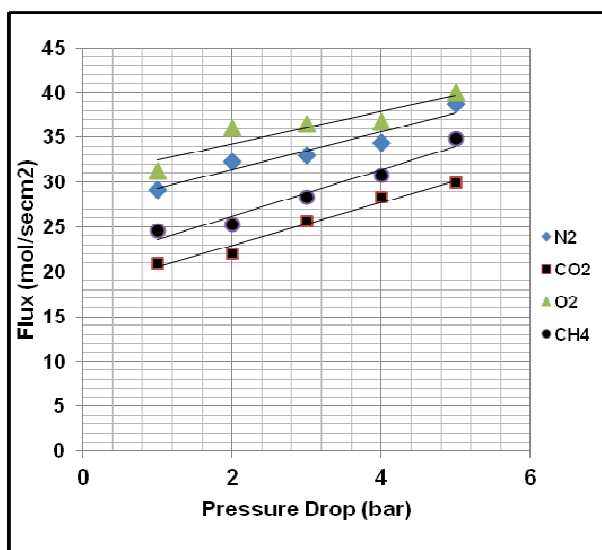
A characteristic feature is in the area of gas flux through the unmodified and modified membrane. This was done by determining the flux (flow)  $J$  ( $\text{mol m}^{-2} \text{s}^{-1}$ ) through the membrane, mathematically represented thus:

$$\text{Flux, } J = \frac{\text{Flowrate (mol/sec)}}{\text{Area (m}^2\text{)}} \quad (4)$$

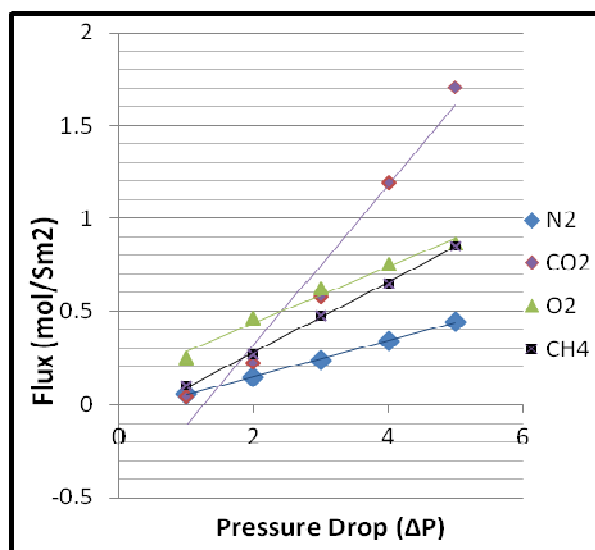
where  $J$  is the gas flux across the membrane,  $\text{mols}^{-1}\text{m}^{-2}$  given as the ratio of gas flow rate to the membrane surface area measured as  $0.025\text{m}^2$ .

Figure 6 presents the effect of pressure drop on  $\text{CO}_2$ ,  $\text{N}_2$ ,  $\text{CH}_4$  and  $\text{O}_2$  gas fluxes through an unmodified support. The relationship between the two parameters shows a linear proportion. Expectedly,  $\text{CO}_2$  gas flux supported Knudsen flow mechanism due its high molecular weight of 44 and having the lowest gas flux.

However in Fig 7 the relationship between the pressure drop and gas flux as the operating parameters for the silica modified support gave an entirely different trend line. At relatively low pressure  $\text{CO}_2$  gas flux was higher than other gases even though when it has a higher molecular weight. This however confirms that the mechanism in the flow is not molecular weight dependent and so unresponsive of Knudsen diffusion flow mechanism.



**Figure 6:** Effect of pressure drop on  $\text{CO}_2$ ,  $\text{N}_2$ ,  $\text{CH}_4$  and  $\text{O}_2$  gas fluxes for an unmodified membrane support



**Figure 7:** Effect of pressure drop on  $\text{CO}_2$ ,  $\text{N}_2$ ,  $\text{CH}_4$  and  $\text{O}_2$  gas fluxes for a modified membrane

The preference of a membrane to permit one gas and not another known as selectivity  $\alpha$  is also considered in this paper. This was determined through the membrane perm selectivity.

Perm selectivity of two single gases A & B is the ratio of the permeance gases A and B, calculated with the formula shown below:

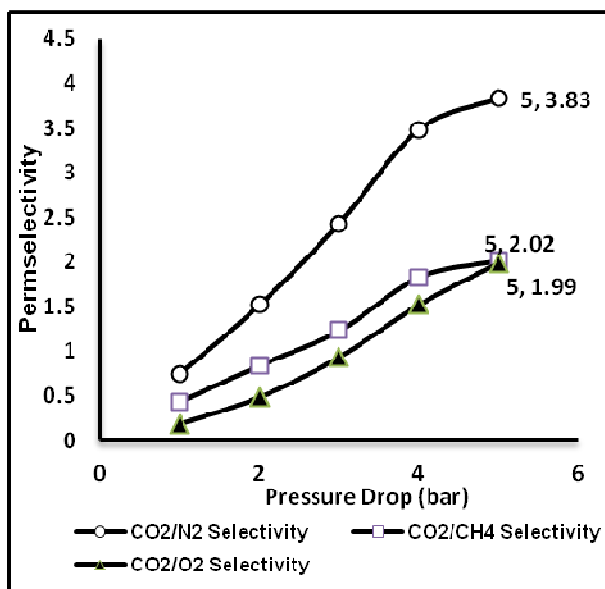
$$\alpha_{AB} = \frac{Q_A}{Q_B} \quad (5)$$

$Q_A$  is the permeability ( $\text{molmm}^{-2}\text{s}^{-1}\text{Pa}^{-1}$ ) of gas A and  $Q_B$ , the permeability for gas B

In order to actually ascertain how much a membrane allows one gas more than the other, a selectivity factor of 1 is an evidence of no separation, the benchmark therefore in gas mixture selection should be geared towards achieving a selectivity higher than 1 because the more selective a membrane is to a particular gas, the higher the selectivity factor [7]. For the purpose of this experiment, the separation factor of CO<sub>2</sub> to N<sub>2</sub>, CH<sub>4</sub> and O<sub>2</sub> was determined through the membrane permselectivity of CO<sub>2</sub> over CH<sub>4</sub>, O<sub>2</sub> and N<sub>2</sub> and given as the ratio of CO<sub>2</sub> permeability to the other gases. For instance an estimation of CO<sub>2</sub> selectivity to N<sub>2</sub> can be calculated from the ratio of CO<sub>2</sub> permeability to that of N<sub>2</sub> given as,

$$\text{Selectivity, } \alpha = \frac{\text{Permeability of CO}_2}{\text{Permeability of N}_2}$$

Figure 8 is a graphical representation of CO<sub>2</sub> Gas Selectivity to CH<sub>4</sub>, O<sub>2</sub> and N<sub>2</sub> obtained in relation to pressure drop.



**Figure 8:** CO<sub>2</sub> gas Selectivity to CH<sub>4</sub>, O<sub>2</sub> and N<sub>2</sub> gases

The permselectivity indicated that the membrane showed the highest selectivity characteristic for CO<sub>2</sub> over N<sub>2</sub>, resulting in the high CO<sub>2</sub>/N<sub>2</sub> experimental separation factor value of 3.83 compared to other gases with 2.02 and 1.99 obtained from the gas separation between CO<sub>2</sub> over N<sub>2</sub> and O<sub>2</sub> respectively. This clearly shows that for a N<sub>2</sub>- rich flue gas stream, the membrane can actually be applied for CO<sub>2</sub> capture at a relatively low temperature and pressure due to the high CO<sub>2</sub> flux and selectivity features. This is because the membrane has a great affinity for CO<sub>2</sub> than other gases.

#### 4. CONCLUSION

The immersion of a support in a silica based solution via a repeated dip-coating technique with intervals of hydrothermal treatment procedure has led to the manufacture of hybrid ceramic membrane for CO<sub>2</sub> capture applications in flue gas stream. A single gas permeation test carried out confirmed that the membrane exhibited high CO<sub>2</sub> gas flux of 1.71mols-1m<sup>-2</sup> at low pressure and room temperature compared to other gases. The results also show that the flow is not molecular weight dependent and a possibility of the membrane affinity to CO<sub>2</sub> gas. The permselectivity calculations confirm that the membrane gave the highest selectivity characteristic of CO<sub>2</sub> over N<sub>2</sub>,

resulting in the high CO<sub>2</sub>/N<sub>2</sub> experimental separation factor of 3.83. In comparison the bare support showed theoretical Knudsen of the inverse of the molecular weight of the two gases. Further work on this study will be carried out at higher temperature and pressure.

## 5. LIST OF SYMBOLS

F	Flow rate of the permeating gas (l/min)
J	Gas flux (mol m <sup>-2</sup> s <sup>-1</sup> )
m	Mass of silica gained by fresh membrane support (g)
A <sub>S</sub>	Membrane surface area (m <sup>2</sup> )
Q <sub>A</sub>	Permeability of gas A (molm <sup>-2</sup> s-1pa <sup>-1</sup> )
Q <sub>B</sub>	Permeability of gas B (molm <sup>-2</sup> s-1pa <sup>-1</sup> )
Q	Permeability for a single gas (l/min .bar .m)
ΔP	Pressure difference (bar)
V <sub>S</sub>	Volume of silica dispersed on the surface of the support (m <sup>3</sup> )

### Greek symbols

ρ	Density of silicon elastomer (g cm <sup>-3</sup> )
ℓ	Membrane layer thickness (m)
α	Perselectivity/separation factor
α <sub>AB</sub>	Selectivity of two component gas molecules A and B

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