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Characteristics of Gas Transport Through Inorganic Ceramic Membranes as Porous Media using Air and Nitrogen

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Abstract: Permeation experiments have been conducted using porous ceramic membranes having different pore sizes of 200nm and 6000nm respectively. Air and N_2 gases were used as the characterizing fluids and experiments were carried out at temperatures of 20ºC, 50ºC and 100ºC respectively. The data obtained show that pore size, pore size distribution and pressure affect the flow response of the individual gas used. Furthermore, the permeation of N_2 was relatively higher than that of air through the 6000nm membrane and this correlates with the molecular weights and density of the different gases employed. It was also observed that the flow dichotomy exists with the highest difference observed in the non-Darcy flow region. Contact angle measurements and scanning electron microscopy (SEM) analysis was also carried out and the result of this characterization indicate that the morphology is highly hydrophilic and will be a good candidate for the separation and purification of gases by incorporation of ionic liquids based on the fluid properties such as molecular weight, density, and viscosity. Meanwhile, contact angle measurement, SEM, and electron diffraction x-ray (EDAX) showed that the morphology of the membranes was compact and had roughness on the internal surface. Furthermore, a lower contact angle was observed for 200nm when compared to the 6000nm membrane and was found to be less hydrophilic based on the contact angle results obtained.

Keywords: *membrane, pore size, permeation, contact angle, SEM, EDAX*

INTRODUCTION

Membrane technology and its application date back to the last century for the separation of different fluids and gases (2,3). The importance of ceramic membranes cannot be overemphasized in the separation of not only gases but other types of fluids as well, such as oil/water emulsion and other liquid waste sources. Ceramic membranes are semi-permeable barriers that are structurally dense, porous and with layers of the same or different material that make up and enable the permeation of certain fluids or gases through their outer surface area (11,12,10). The membrane support usually is either classified as a mesoporous, intermediate or macroporous support while the Top layer usually is Microporous and consists of the following metal oxides (Al_2O_3),(TiO_2),(SiO_2) and (ZrO_2) etc. The pore size distribution of the Ceramic membrane support is usually, a graduated pore sizes and is arranged structurally in an Asymmetric order consisting of one particular material or different layers of other materials in its composition. Furthermore, a combination of different materials made up of metal oxides as previously outlined earlier could also be utilized(11).

This research was carried out with a 200nm and 6000nm ceramic membrane support, with membrane composition of the metallic oxides as stated above in the permeation run of Nitrogen N_2 and Air as the characterizing fluids at Pressure ranging from 0.2 to 3.0 bars and temperature from 20^0C, 50^0C and 1respectivelyively. Ceramic membrane supports in recent times have attracted a wide range of research interest and usage due to their exceptional advantages, when compared to others. For example, based on their unique properties they are preferred for industrial operations, they are Chemically and Thermally stable and have better Mechanical strength. They work effectively in high temperatures and pressure(9,3).

The experiment conducted, a 200nm and 6000nm inorganic ceramic membrane support was used to perform a permeation test on Air and Nitrogen (N_2) gases, being used as the characterizing fluids at temperatures ranging from 20ºC, 50ºC and 100ºC respectively. The data shows that pore size, pore size distribution, temperature and pressure affect the flow response of each gas respectively. Furthermore, the Nitrogen (N_2) flow rate was relatively higher than Air permeation through the 6000nm support membrane. This correlates with the molecular weights and densities of the different gases. It is also observed that the flow dichotomy is highest in the non-Darcy region. Contact angle and Scanning Electron microscopy (SEM) results of the membrane characterization indicate that the morphology is rough and highly hydrophilic for 6000nm support, while the 200nm membrane support with rough morphology was less hydrophilic compared to the 6000nm support. Hence, both support membranes will be good candidates for separation operations, which is the separation of water from spent drilling waste on the bases of fluid properties such as molecular weight, density, and viscosity. This approach will however achieve the advantages of E&P waste treatment on site due to the comparability of membrane usage for water recycling or reuse from spent drilling waste and reduce the cost implication required to transport drilling waste for further treatment onshore and reduce environmental footprints resulting from drilling operations.

EXPERIMENTS

This research is categorized into two main laboratory phases to achieve reasonable outcomes based on the outlined experimental processes to be carried out at the RGU engineering Center for Process Integration and Membrane Technology, School of Engineering laboratory. Figure 1, shows the experimental setup describing the process for the permeation run test done, using N_2 and Air at 20ºC, 50ºC and 100ºC with pressure ranging from 0.2 to 3.0 bars respectively and reading shown in table 1, on both the 200nm and 6000nm inorganic ceramic membrane used in the experiment and shown below, After a lick test was conducted on the membrane reactor using Snoop and confirmed no licks observed.

MATERIALS AND METHOD

The commercially available 200nm and 6000nm ceramic membranes used in the experiment were inserted inside a Tubular membrane reactor, one after the other at different times with seals corresponding to the outer diameter of the membrane tightly on both ends and mounted on a rig set up shown below. The reactor on the rig was connected with a heat jacket and wiring, a thermometer, transducer, Temperature control source, earth wiring and an electric source. Two gas cylinders with contents Nitrogen N_2 and Air and regulators for both gases were used and connected to the reactor and mounted on the rig. Two Flow meters are connected at the inlet point of the reactor and outlet for accurate reading and further to fume cupboard to enable the controlled expulsion of the used gases. The experiment was carried out by regulating the flow rate measured in litres per minute (LPM) of the gases using a control valve recorded on a pressure gauge with a flow of gas at 0.2 to 3.0 Bars, through the membrane reactor housing the inorganic ceramic membrane. The permeate flow rate was recorded using a flow meter (Cole Parmer model) and the reading were recorded for temperatures at 20ºC,50ºC and 100ºC using

a thermometer. Figure 1, shows a schematic diagram of the gas permeation run test process and experimental setup.

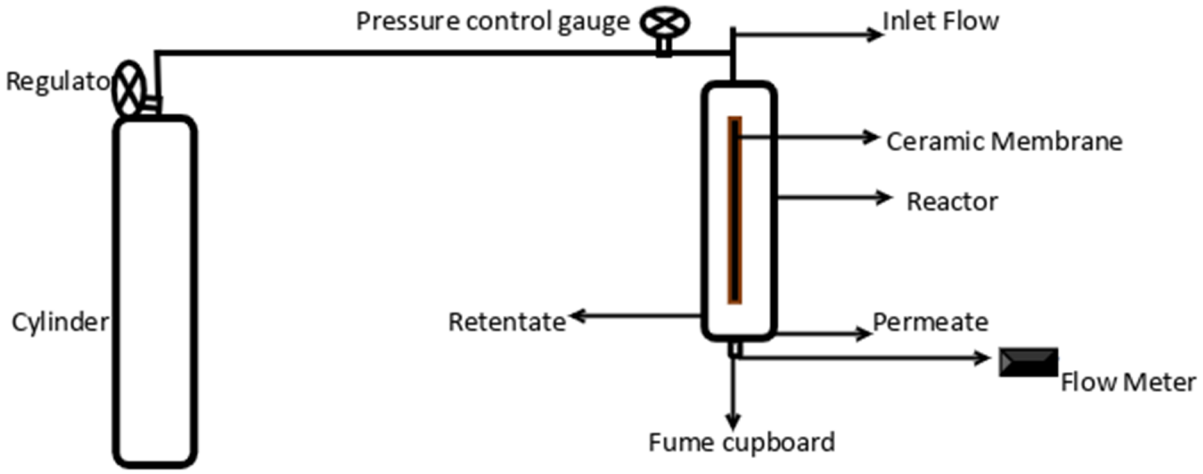


Figure 1. Schematic Diagram of laboratory experimental set-up

The gas permeation test was obtained from the mathematical expression from equation 1, given below.

$$Q_i = F_i / A\ \Delta P_i \quad (1)$$

Where
Q_i = Permeance (mol. $s^{-1}m^{-2}Pa^{-1}$) of gas $_i$
Fi = Flow rate (mol. s^{-1}) of gas $_i$
A = Surface Area of the membrane (m^{-2})
ΔP_i = Pressure difference of gas $_i$ across the membrane.

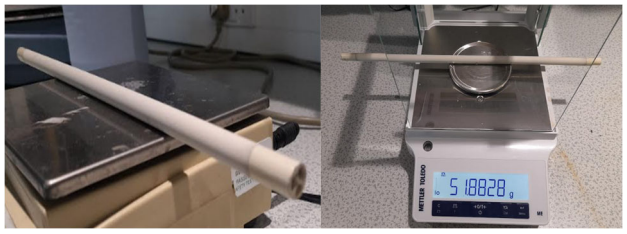
The unmodified ceramic membranes shown in Figure 4, have an internal diameter of 2.07cm and outer diameter of 2.59cm respectively with a permeable length of 32.8cm and a total height of 37.7cm for The 6000nm membrane while the 200nm. Figure 5. With internal and outer diameters of 0.78 & 1.50cm, a total height of 37.7cm and a permeable length of 33.8cm. The membrane porosity was determined using the Archimedes principle, Where the dry (W1) weight of the Membranes was taken after oven drying both the 200nm and 6000nm inorganic ceramic membrane for twelve hours to remove moisture from the membrane at a temperature of 110ºC. The wet weight of the membrane was gotten after immersion of the membrane in a beaker with pure water for twelve hours, then removed and tip wiped with tissue paper and wet weight (W2) measured. Furthermore, the displacement of the water inside the beaker was determined by the calibration on the beaker, the volume of water based on the amount of water displaced inside the beaker was obtained and porosity was determined using the relationship below.

$$\mathscr{E} = (W2-W1)/W1 \quad (2)$$

Where $\mathscr{E}$ is porosity, W1 is dry weight and W2 is wet of the membrane

(a) (b)

Figure 2. 6000nm Commercial unmodified inorganic ceramic Membrane (a) Internal diameter inlet and (b) Membrane outer surface area



(c) (d)

Figure 3. 200nm Commercial unmodified inorganic ceramic Membrane (c) Internal Diameter inlet and (c) Membrane outer surface area

RESULTS AND DISCUSSION

The results of the permeation test, Contact Angle, SEM analysis and EDAX from the experiments conducted are shown below begging with the permeation results in Table 2. For Air and Nitrogen on 200nm and 6000nm unmodified Inorganic Ceramic Membrane for flow-rate and pressure from 0.2 to 3.0 (Bar) at Temperatures 20ºC, 50ºC and 100ºC respectively.

Table 1. Shows Results from Permeation run test For Air and Nitrogen on 200nm unmodified Inorganic Ceramic Membrane at 20ºC, 50ºC and 100ºC respectively.

Pressure Atm (Bars)	Flow rate LPM (200nm Air)20^{0}C	Flow rate LPM (200nm N_2)20^{0}C	Flow rate LPM (200nm Air)50^{0}C	Flow rate LPM (200nm N_2)50^{0}C	Flow rate LPM (200nm Air) 100^{0}C	Flow rate LPM (200nm N_2)100^{0}C
0.20	0.98	1.00	0.98	0.98	0.93	0.96
0.60	1.88	1.88	1.86	1.91	1.87	1.9
1.00	2.23	2.26	2.25	2.27	2.24	2.29
1.40	2.44	2.46	2.44	2.49	2.44	2.5
1.80	2.59	2.61	2.6	2.62	2.61	2.67
2.20	2.71	2.73	2.72	2.77	2.74	2.8
2.60	2.8	2.84	2.82	2.87	2.85	2.92
3.00	2.88	2.92	2.91	2.97	2.96	3.01

Table 2. Shows Results from Permeation run test For Air and Nitrogen on 6000nm unmodified Inorganic Ceramic Membrane at 20ºC, 50ºC and 100ºC respectively

Press-Atm (Bar)	Flowrate Air LPM (Out) 20ºC 6000nm	Flow rate N2 LPM (Out) 20ºC 6000nm	Flow rate LPM Air(Out) 50ºC 6000nm	Flow rate N2 LPM (Out) 50ºC 6000nm	Flow rate LMP (Out) Air 100ºC 6000nm	Flow rate LPM (Out) N2 100º C 6000nm
0.2	0.62	0.60	0.61	0.60	0.63	0.62
0.6	0.99	1.21	1.08	1.29	1.01	1.27
1.0	1.19	1.49	1.41	1.82	1.28	1.77
1.4	1.39	1.64	1.56	1.99	1.46	2.00
1.8	1.50	1.78	1.64	2.09	1.55	2.19
2.2	1.61	1.85	1.72	2.23	1.63	2.32
2.4	1.69	1.91	1.77	2.29	1.69	2.45
3.0	1.78	1.95	1.82	2.32	1.75	2.53

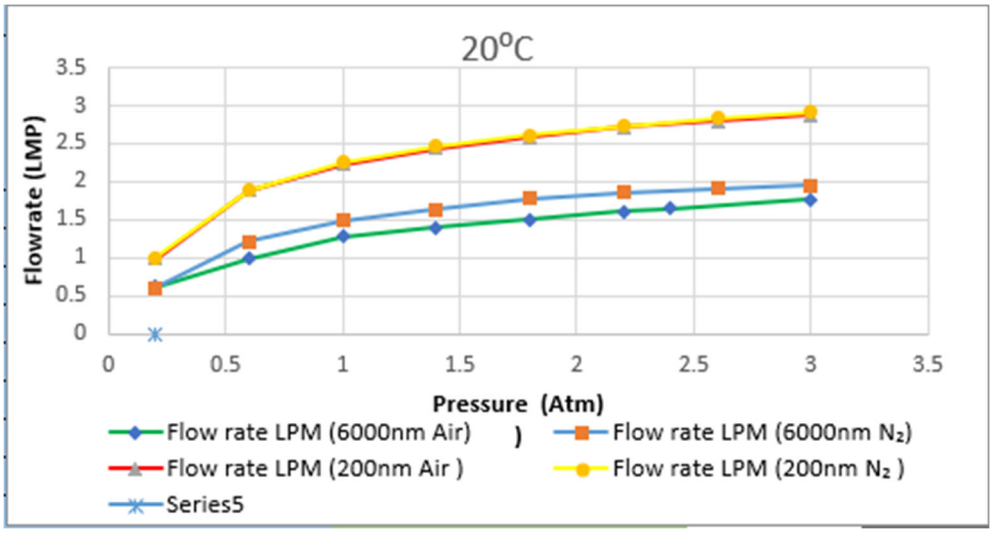


Figure 4. A Graph plot Showing Pressure against flow rate for Air and Nitrogen on 200nm and 6000nm membrane at 20ºC

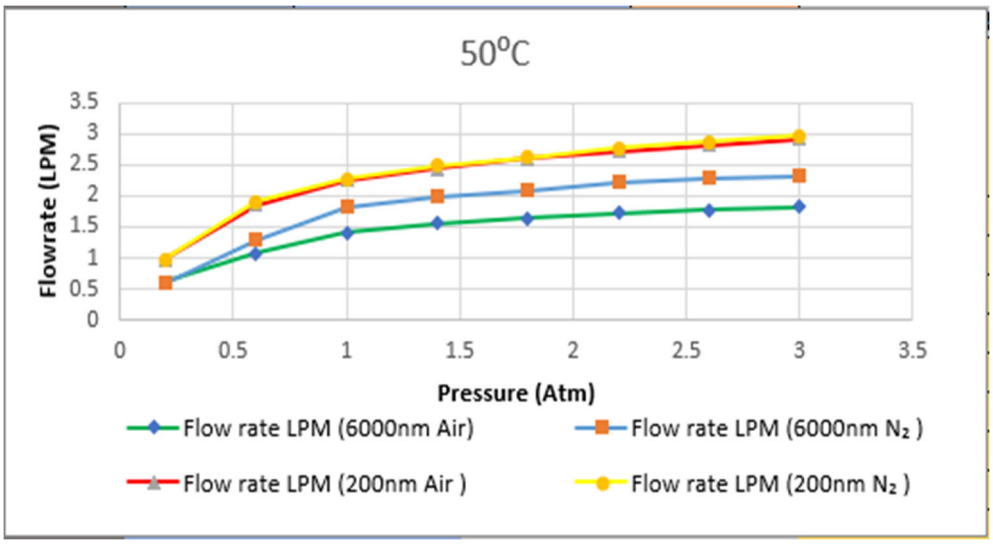


Figure 5. A Graph Plot Showing Pressure against flow rate for Air and Nitrogen on 200nm and 6000nm membrane at 50ºC

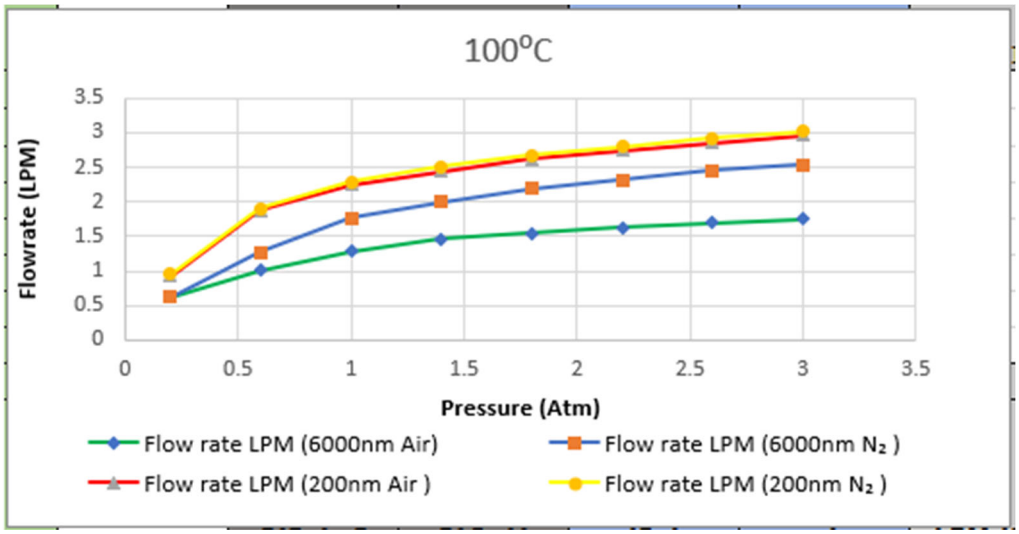


Figure 6. A Graph Plot Showing Pressure against flow rate for Air and Nitrogen on 200nm and 6000nm membrane at 100ºC

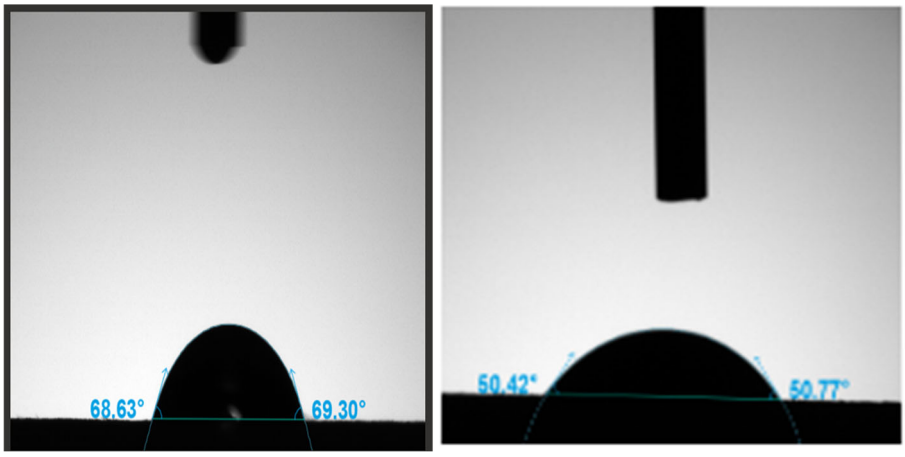
From the graphical plot above, Figure 5, the Permeation flow rate of air and Nitrogen (N_2) at 20ºC is relatively Normal. However, From the graphs above Figures, 6 and 7 did not record any significant change even with a corresponding increase in the temperature of the membrane at 50ºC and 100ºC respectively for both 200nm and 6000nm support, this is due to the high thermal resistance of the ceramic membrane support. Furthermore, inorganic ceramic membranes are known to have a high affinity for thermal resistance and stability in harsh environments. From the graphs plotted above, it is observed that the permeation flow rate of Nitrogen is higher than air, this is because the Permeation flow rate is a function of molecular weight and atomic radius of the gas molecule. The pressure at which a steady state permeation occurs could be assumed the optimum operating pressure. However, from figures 5,6 and 7 above the steady state permeation flowrate for 200nm and 6000nm support at the respective temperature of 20ºC, 50ºC, and 100ºC are taken at 1.80bars at 2.59,2.61,2.60,2.62,2.61,2.67 while, 6000nm the pressure was 0.2bars at 0.62, 0.61 and 0.63 for Air and Nitrogen (N_2) 0.60,

0.60 and 0.62 as the steady state flowrate of the gases at the pressure of 0.2 Bars and the given temperatures respectively and this satisfies Darcy's flow equation. Furthermore, from the graph plotted above, there are two distinct regions observed, and the results obtained to satisfy thse conditions required to divide the flow regimes into Darcy and Non-Darcy flow. Below the steady state permeation, the result obeyed the Darcy flow equation for both Air and (N_2) Permeability with pressure. While the second flow region was above the steady state flow permeation and non-Darcy flow was observed.

CONTACT ANGLE

Contact angle, in accordance with (6), is a macroscopic expression of the intricate interaction between a liquid and a solid surface that can reveal details about the surface chemistry, topography, and capillary forces at the micro- and nano-scale interaction of the liquid droplet and the solid surface properties of the material. It's crucial to remember that a reduced contact angle denotes wettability in a solid. Therefore, a greater contact angle denotes a sample that has absorbed less of the model liquid (water), which results in less interaction between the sample's substance and the water droplet (1,8).

The contact angles were evaluated at room temperature using the model liquids (Water) for the sample 6000nm and 200nm unmodified inorganic ceramic membrane and a contact angles (θ) measurement was recorded at 68.63º and 50.42º degrees respectively.



(a) **(b)**

Figure 7. Contact angle (θ) image taken after dropping on 6000nm sample (a) and 200nm sample (b).

Figure 7(a & b), shows images of contact angles with a water droplet for the membrane sample and imaging obtained immediately after dropping (at time t = 0 and t=0.20 sec), immediately after dropping with significant change on the droplet.

CHARACTERIZATION OF MEMBRANE SUPPORT

Using a scanning electron microscope, the micro-structure of an inorganic ceramic membrane with no modifications was examined (SEM) for 200nm and 6000nm support. The unaltered samples of the inorganic ceramic membranes were gathered, placed safely on a stub, and transported to the SEM's sample carousel to begin the examination. At 500X, 1000X, and 3000X magnifications, the SEM yielded images of the sample's exterior and inner regions. Additionally, energy dispersive X-ray analysis was used to determine the inorganic ceramic membrane's elemental composition (EDAX).

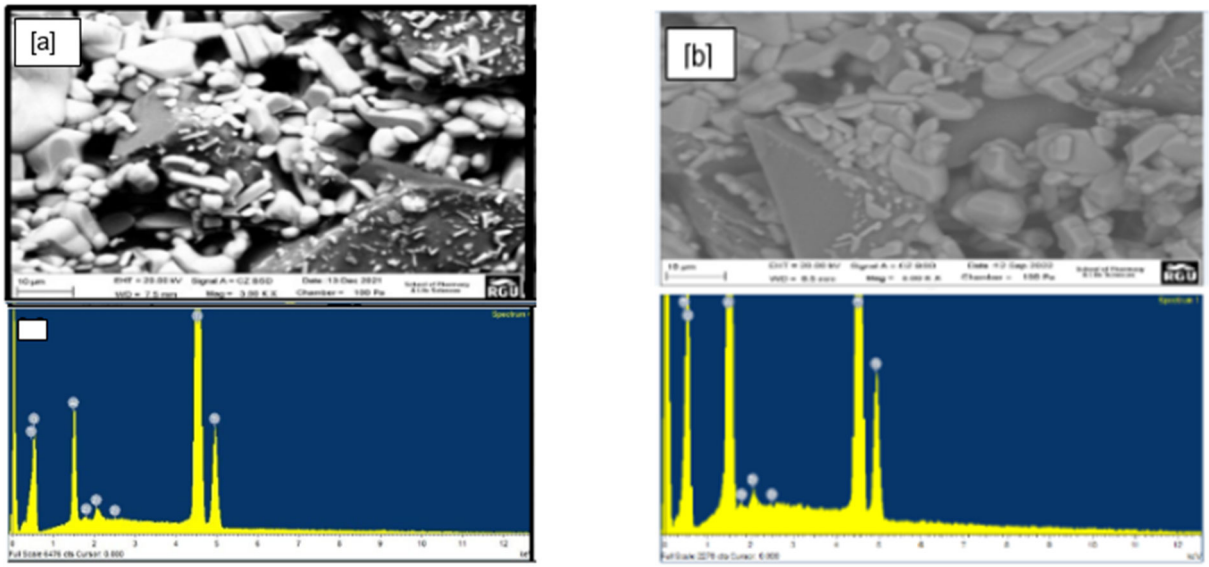


Figure 8(a & b): Micrographs of 200 nm and 6000nm support the inner surface and EDAX showing the chemical compositions of the outer surface.

Figure 8 a & b illustrates a porous membrane, rough, densely packed and irregular particle size as a result of scanning electron microscopy (SEM). This suggests a range in membrane pore sizes that can improve flow and be fault-free. Surface roughness in membranes has been shown to enhance contact angles, which may increase permeation flux (5,7). In Figure 8, the Energy Dispersive X-Ray Analysis (EDAX) performed to determine the 200nm and 600nm support membrane's elemental composition reveals the presence of titanium, aluminium, bromine, and zirconia oxides, all inorganic substances employed in the production of ceramic membranes respectively.

CONCLUSION

The chemical composition of the different types of ceramic membrane and morphological structures for the 200nm and 6000nm support as expressed in the SEM, EDAX and contact angle results shown above, influence the gases being transported through the membrane support and its flow characteristics. Furthermore, the respective densities and molecular weight of the gases are also key facts in determining the flow response and behavior of different membrane support pore diameters which is a critical factor for flow. However, this can clearly be seen in the graphical representation of the flow pattern as observed.

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