Defence Science Journal, Vol. 54, No. 3, July 2004, pp. 335-343

Preparation of Gas Separation Membranes and their Evaluation

P. Pandey and R.S. Chauhan

Defence Research & Development Establishment, Gwalior–474 002

ABSTRACT

Asymmetric membranes have been prepared from the polysulfone using dry-wet phase-inversion technique. These membranes show a thin dense skin at one surface and porous substructure underneath. Test facility has been developed in-house to evaluate the permeability as well as the selectivity of membranes. In addition an online permeate composition analysis system has also been setup to quantify the concentration of the two major components of atmospheric air, namely oxygen and nitrogen using a gas chromatograph. Membranes have been tested at various feed pressures. The developed membranes are capable of enriching atmospheric air to a level of 30 per cent and more.

Keywords: Asymmetric membrane, phase-inversion technique, permeability, membrane selectivity, polysylfone

1. INTRODUCTION

Separation of gases by membranes is one of the most active areas and rapidly growing field among the separation technologies[1]. Membrane separation process offers a number of advantages in terms of low energy and capital investment. The process requires simple, easy to operate, and compact modules. As a result, the process has acquired a significant role in the field of chemical technology and is being used increasingly in a range of applications like ultrafiltration, pervaporation, and industrial separation of materials[2]. The separation of gases by membranes has favourable economic considerations, and therefore, has resulted in commercial implementation in a range of applications[3-5].

A membrane is a thin barrier between two phases through which differential transport can occur under a variety of driving forces of pressure, concentration, and electrical potential. Differential transport can occur when the membrane restricts the transport of different species in some specific way[6-8].

For effective separation of materials of smaller dimensions (Å) asymmetric membranes are utilised. An asymmetric membrane has a dense skin layer integrally bonded in series with a thick porous substrate. The membrane skin that acts as the effective separation layer is one of the key elements in determining the membrane permeability and selectivity[9,10].

Many defence applications can be linked to the enrichment of atmospheric oxygen, for example, increasing efficiency of heavy vehicles having diesel engines[6], provision of air having enriched oxygen levels at high altitude to avoid hypoxia and like. In western countries, onboard oxygen generation

Revised 24 June 2003

using membranes are being used in the military aircraft. Enriched nitrogen can be used for protective blanketing of fuel tank in an aircraft using membrane-based devices. Carbon dioxide selective membranes have potential applications in the removal of CO_2 from the confined spaces like submarines.

Loeb and Sourirajan" invented the first asymmetric integrally skinned cellulose acetate reverse osmosis membrane. Pinnau and Koros[12] made integrally skinned asymmetric gas separatiQn membranes from the polycarbonate and polyimide polymers for gas separation.

The field of gas separation in India, is in a nascent stage and requires concerted and focused efforts to utilise this technplogy to,4ts full-potential. National Chemical Laboratory (NCL), Pune, had studied permeation properties of polyarylate-based asymmetric membranes for various applications[13]-[14]. The paper describes the work done for the preparation of asymmetric membranes using phase-inversion process for oxygen enrichment as well as test facilities developed and established at the Defence Research & Development Establishment, Gwalior, to evaluate the polysulfone-based membranes and quantify the enrichment of atmospheric oxygen.

2. MATERIALS

The polysulfone was selected as the base material because of its good film forming properties as well as its thermal and biological resistance. The material is amorphous, having a Mw 35,000 and Tg of 185 °C. The polysulfone was purchased from the Aldrich and was used as such. 1,1,2-Trichloromethane, teritary amyl alcohol, hexane, methanol and poly (dimethylsiloxane) were purchased from the Across; dichloromethane was procured from the E. Merck. Room temperature-curable poly (dimethylsiloxane) was used as the coating material.

3. METHODS OF PREPARATION

3.1 Preparation of Asymmetric Membranes

Asymmetric membranes are generally formed by a phase-inversion process. It is a process whereby a homogeneous polymer solution is transformed in a controlled manner into two phases, a polymer-rich phase, and a polymer-lean phase. At a certain stage of membrane formation, under optimum conditions, the polymer-rich phase solidifies to form the dense matrix, while the polymer-lean phase constitutes the porous support. Both these substructures are coupled in series and are of the same material.

3.1.1 *Preparation of Polymer Dope*

Polysulfone (13.65 wt %) was dissolved in a binary mixture of dichloromethane (44.29 wt %) and 1,1,2-tricloromethane (23.04 wt %) by constant stirring without the loss of solvents. Tertiary amyl alcohol was added dropwise till the first sign of stable turbidity appeared. In the present study, tertiary amyl alcohol {19.02 wt %) was required to attain the cloud print.

The viscosity of the dope was measured using a Brookfield viscometer. The casting dope viscosity was 100 cps.

The following steps were used to incorporate the asymmetric structure in the membrane:

(a) *Casting:* The polymer dope was poured on a (24" x 24") specially designed glass plate having a raised boundary. The volume of the dope was so selected that it filled the area with uniform thickness.

(b) *Quenching:* The nascent pour-cast membrane was subsequently exposed to a non-solvent water vapour generated *in situ.* The time of forced convective evaporation varied from 1 min to 2 min till a turbid top layer appeared.

(c) *Coagulation:* The membrane having a turbid top layer and a viscous sublayer was then dipped into a coagulation bath having an external non-solvent (methanol).

In this step, the dope below the skin that was destabilised during quenching, separates slowly into a polymer-rich and a polymer-poor phases. The polymer-rich phase forms continuous membrane matrix, while the polymer-poor phase gets trapped in between this matrix in the form of droplets that form voids or cells. The coagulated films are left in the coagulation bath for 24 h for the complete exchange of solvent and non-solvent.

(d) *Drying:* The membrane was then removed from the coagulation bath and air dried for 24 h at room temperature. The membrane was subsequently dried at 100 °C for 24 h to ensure complete removal of the solvent.

(e) *Coating:* A thin coating of poly (dimethylsiloxane) was applied on the membrane surface to seal the possible surface defects. Membranes were coated with 5 per cent PDMS in hexane.

3.2 Characterisation of Membranes

Membrane morphology was studied using a JEOL JSM-840 scanning electron microscope. The samples were coated with a thin layer of gold in a JFC-1100 °C sputter-coating unit before observation. The top and the bottom surfaces as well as the cross section were studied. The membrane cross sections were obtained by cryo-fracturing.

3.2.1 *Calculation of Skin Thickness*

The resistance to permeation in asymmetric membranes is affected by the three layers-the dense skin constituting the upper layer, the microporous transition layer from the middle layer and the porous substrate forming the bottom layer. The resistance in these morphologically different layers is extremely nonhomogenous, being maximum for the dense skin. The permeance or the thickness-corrected permeability has been used and is defined by the following equation[15]:

$$P/L_{(gas)} = \frac{p}{760}\cdot\frac{V}{A}\cdot\frac{273}{T}\cdot\frac{1}{\Delta p}\cdot\frac{1}{60} \qquad (1)$$

where

$P/L_{(gas)}$ Permeance of gas

p Actual atmospheric pressure during the experiment

A Effective area of membrane

T Temperature in Kelvin

Δp Pressure difference between the feed and the permeate side

V Permeate flux of the gas.

Permeance is often reported in gas permeation units (GPU) and is defined as

$$1\,\mathrm{GPU} = 1\times10^{-6}\,\mathrm{cm^3(STP)/cm^2.s.cmHg} \qquad (2)$$

The skin thickness (L) for an asymmetric membrane was calculated from permeation data using the following equation[16]:

Skin thickness (for a gas)

$$= \frac{\text{Intrinsic permeability of the material}}{\text{Pressure nomalised flux (of the gas)}} \qquad (3)$$

$$L_{(gas)} = \frac{P_{(gas)}}{P/L_{(gas)}}$$

where

$L_{(gas)}$ Calculated skin thickness of the membrane for the gas

P Intrinsic permeability of the material,

$P/L_{(gas)}$ Permeance of the gas across the asymmetric membrane.

The selectivity of asymmetric membrane can be reported as the ratio of permeance of any two penetrating species for a given membrane.

$$\alpha = \frac{P_A/L}{P_B/L} \text{ or } \frac{P_A}{P_B} \qquad (4)$$

4. PERMEATION TEST SETUP & MEMBRANE PERFORMANCE EVALUATION

Figure 1 shows the general layout of the indigenously designed and fabricated test setup for the evaluation of permeate flux and selectivity of membranes. The system consists of gas cylinders, regulators, permeation cells, two-way valves, soap bubble flow meters and an online 5700 series Nucon gas chromatograph.

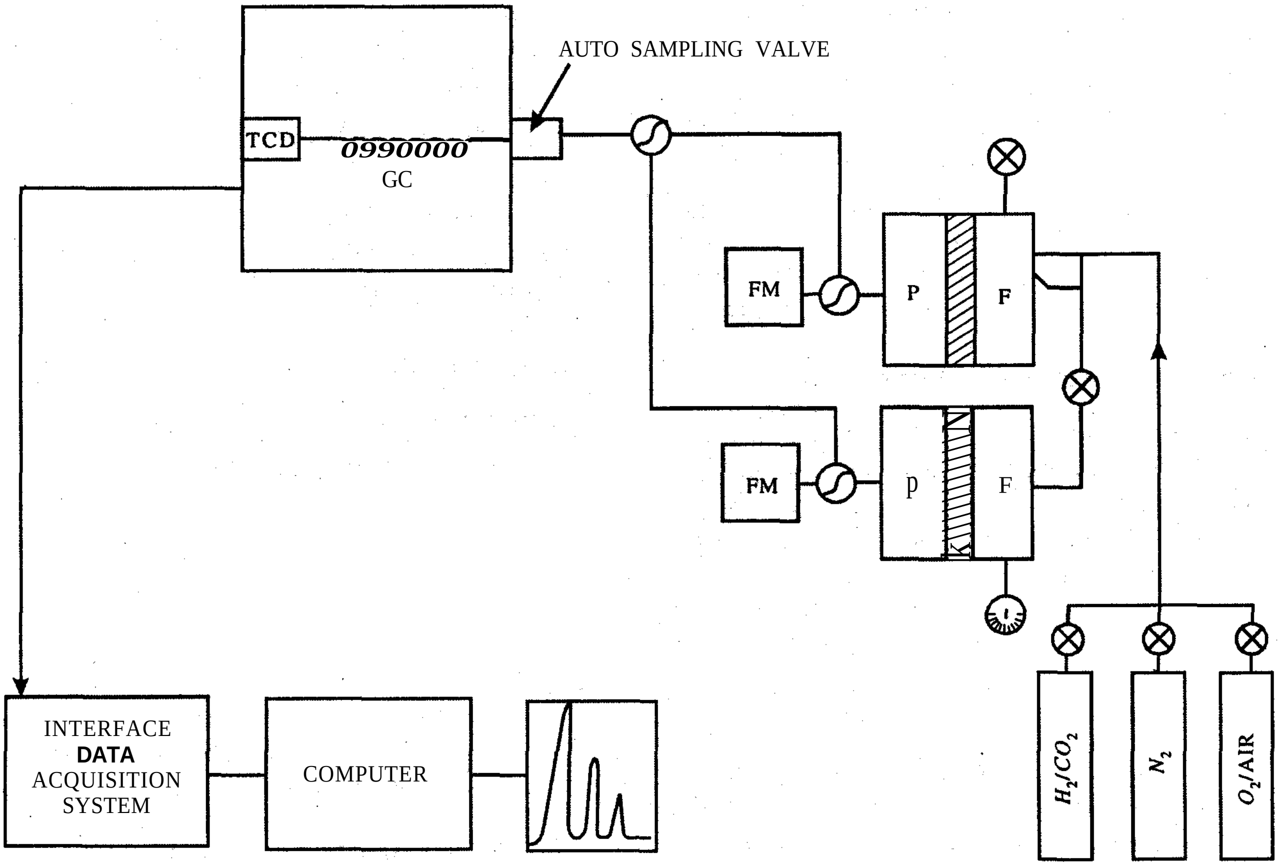


Figure 1. Setup for quantitation of membrane selectivity

The permeation cells are made up of two halves, the upper feed and the lower half. Both the halves can be fitted with the help of four pairs of nuts and bolts. The test membrane supported on a porous disc is placed in the lower half of the cell in a groove designed for it. The vacuum-tight sealing can be achieved by putting a rubber O-ring above the membrane.

The feed-halves of the cells can be connected to one of the gases like nitrogen, oxygen, hydrogen, air, or any other pure or mixed gas of known composition as an input or feed gas. Applied pressure can be varied in a range 10 psi to 150 psi or even more. A pressure gauge directly connected to the feed-half of the cells gives accurate reading of the applied pressure on the membranes. At the feed side of the cell, a leak valve is provided to flush the feed compartment while changing from one gas to the other gas as well as to generate a cross flow during mixed gas permeation to keep the feed composition constant.

Permeate flux across the membrane for various gases was monitored with a flow meter. The separation factor (a) was calculated from the permeance of individual pure gases using Eqn (4). The gas chromatograph has been used for the detection of a real separation factor or enrichment of a particular component in the gas mixture by analysing permeate composition in terms of their concentrations. Two permeation cells parallel to each other have been selected to facilitate simultaneous evaluation of two membranes. The system is suitable for the rapid evaluation of membranes as well as for the comparison of performance of different membranes under essentially similar conditions.

To determine the enrichment of atmospheric oxygen, a zero-air cylinder was used. The air was fed as the input feed and the level of oxygen in the permeate was recorded with an online gas chromatograph. The identification of individual gases was done based on their retention times.

5. RESULTS & DISCUSSION

Figure 2(a) shows the scanning electron micrograph of top surface of the membrane, and smooth and unstructured texture having occasional holes of sub-micron size. Figure 2(b) shows the lower surface of the membrane that was in contact with the casting surface. The membrane surface revealed macropores of various sizes distributed on the surface. Flakes seen on the surface is the excluded polymer material during the formation of the membrane. Figure 2(c) shows the cross section of the above membrane showing asymmetric structure developed during its formation. It consists of a thin dense layer and a porous structure coupled in series. The bulk of the membrane thickness has an open, porous, granular or cellular texture.

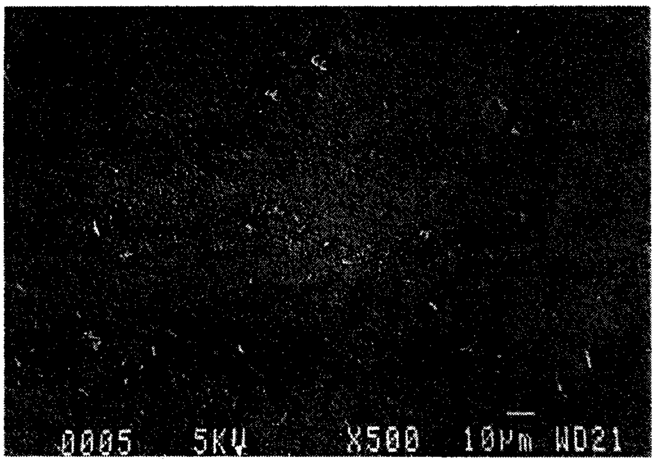


Figure 2(a). Top surface of the membrane at 500X showing smooth surface.

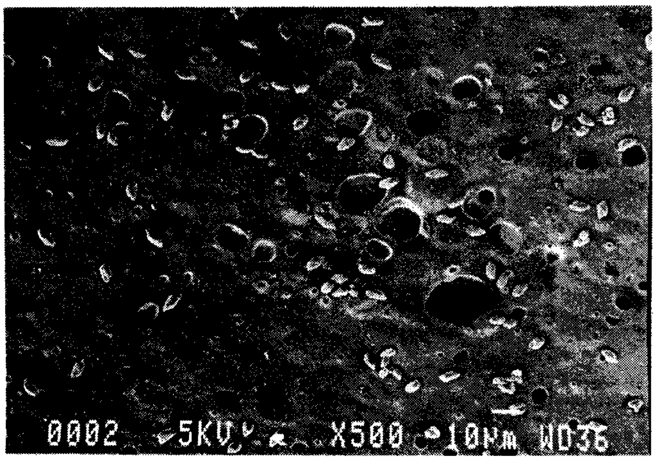


Figure 2(b). Lower surface of the membrane at 500X showing a range of macropores.

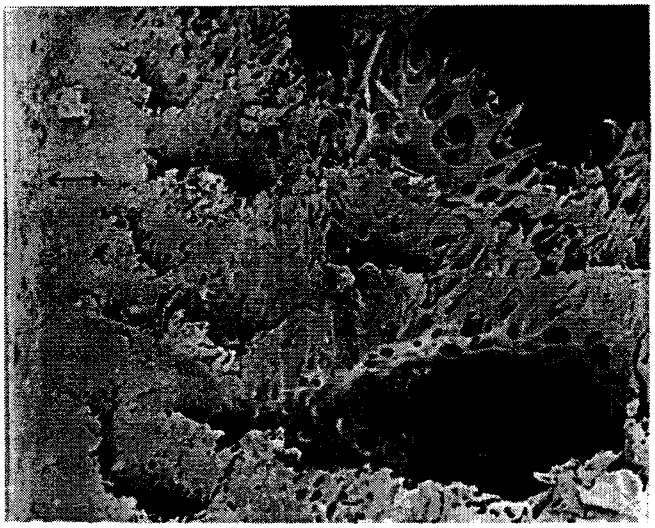


Figure 2(c). Cross section of the membrane showing a thin dense layer (arrow) and porous substructure.

It is known that for a given pair of gases *A* and *B*, there are two fundamental parameters characterising membrane separation performance. These are permeability (P) and permselectivity ($cc_{A/fl}$ = P_A/P_B, where gas *A* is more permeable compared to gas *B*). Permeability denotes the rate of permeation across the membrane, whereas permselectivity is the ratio of permeability of a pair of gases. Table 1 presents data on permeation of gases, namely nitrogen, oxygen and CO_2 across the membrane in milliliters per minute at different feed pressures. The table also shows the selectivity factor for the pair of gases, derived from the permeation of individual gases. The data shows that with increasing feed pressure of the gases,

Table 1. Permeation performance of polysulfone asymmetric membrane at different feed pressures

Pressure (kg/cm^2)	Flux (ml / min)			Selectivity	
	N_2	o2	CO_2	aO_2/N_2	aCO_2/N_2
2	0.075	0.220	1.000	2.93	13.33
4	0.120	0.450	0.925	3.75	7.71
6	0.225	0.700	2.500	3.11	11.11

there is an increase in the flux of the individual gases across the membrane. The selectivity factor, however, does not depend upon the input pressure and no particular trend was observed. This observation is in accordance with the published data[17].

It is known that the selectivity of the asymmetric membrane is influenced by the top two or three molecular layers constituting the dense layer of the membrane. Whereas, remaining substructure affects the overall permeation behaviour. It is reported that the structure and thickness of the top layer is dependent upon the kinetics of membrane formation as well as on the dope composition[15]. The effective thickness of the cast membrane can be computed using intrinsic permeation data of, the material and the pressure-normalised flux for the prepared asymmetric membrane. Table 2 shows the calculated values for the skin thickness for various gases. As can be seen from the data, the calculated skin thickness is different for different gases and ranged between 0.5 u, to nearly 1 ^. It is known that the thicker dense layer will pose greater resistance to the feed gas. Therefore, the casting parameters can be optimised to get thinnest possible, yet defect-free layer. These values can be used as guidelines for controlling the thickness of separating layer of the asymmetric membrane during the membrane casting.

Table 2. Calculated skin thickness of asymmetric polysulfone membrane from permeation data

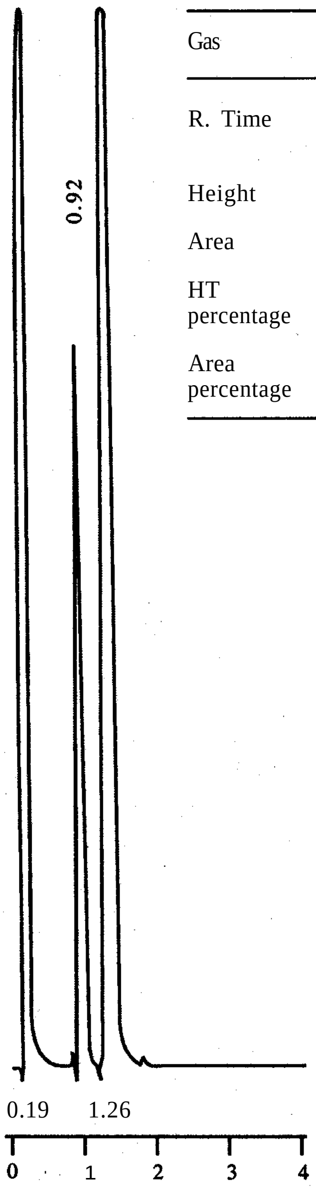
Intrinsic permeability of psf material (COS units)[1]	Permeance of polysulfone asymmetric membrane (CGS* units)	Calculated skin thickness
$P_{O_2} = 25 \times 10^{-10}$	**$P/L_{(02>}$ = 0.482 X $10^{'6}$	5180 A
$P_{N_2} = 1.4 \times 10^{-10}$	**$PIL_{Wl})$ = 1.619 x $ID^{'6}$	8647 A
$P_{CO_2} = 25 \times 10^{-10}$	**$P/L_{(CO_2)}$ = 5.784 x KT^6	9682 A

* cm^3 [STP] / cm^2.S.cm(//g)

** The pressure normalised flux were calculated for different gases from permeation data of Table 1 at 6 kg/cm^2

[1] Reference 1

Figure 3 shows the gas chromatograph for the zero-grade air obtained from the commercial air cylinder. This cylinder has been used to simulate atmospheric air. The gas chromatograph shows the percentage of two major components of the atmoshpheric air, namely oxygen (21.1391) and nitrogen (78.8609) in terms of peak area. The peak area is directly related to the percentage composition of the components. Area percentage is used routinely for quantitative analysis. The



Gas	O_2	N_2
R. Time	0.92	1.26
Height	990	2296
Area	99526	371288
HT percentage	30.1278	69.8722
Area percentage	21.1391	78.8609

Figure 3. Gas chromatograph output of zero-grade air giving two major components of nitrogen and oxygen.

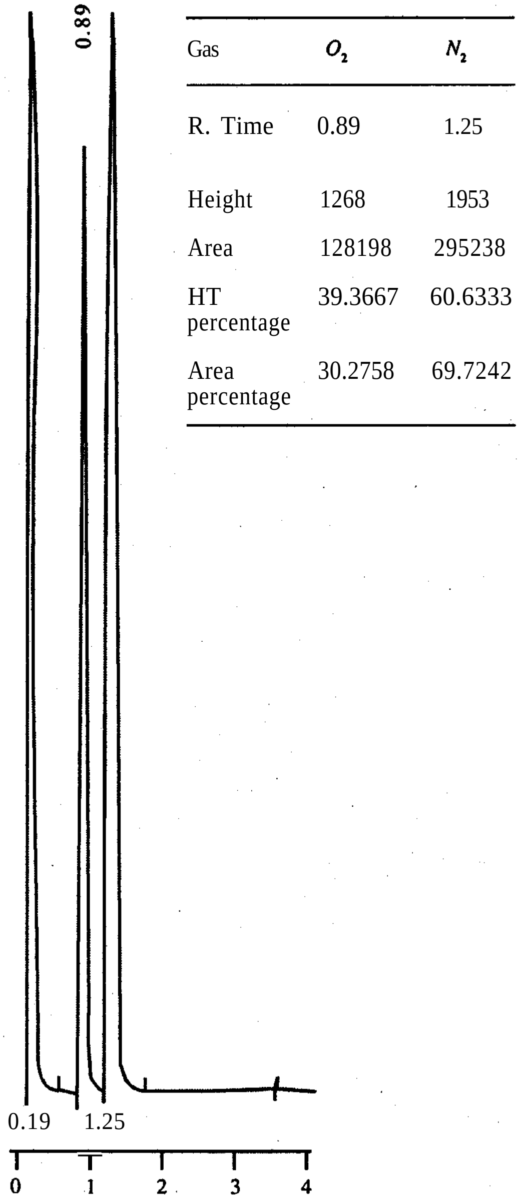
Table 3. Permeation and separation factors of gases for membranes

Membrane	Pressure (kg/cm2)	Flux(ml/min)			Selectivity	
		N_2	O_2	CO_2	$\alpha O_2/N_2$	$\alpha CO_2/N_2$
I	6	0.27	0.88	3.8	3.24	14.07
	7	0.32	1.08	4.5	3.38	14.06
	8	0.44	1.26	5.3	2.86	12.04
II	6	0.32	1.12	3.0	3.50	9.38
	7	0.45	1.48	-	3.28	-
	8	0.46	-	3.6	-	7.82
III	5	0.50	1.25	-	2.50	-
	7	0.64	1.62	-	2.53	-

identification of individual gases is done on the basis of their retention time.

Table 3 shows permeation and separation factors for individual gases for different membranes. By studying the transport properties of pure gases across the membranes, information on material as well as fabrication properties can be derived. The pure gas transport measurement, however, do not reveal any interaction effects between the gas molecules of different gases that may occur during mixed gas experiments[16], and therefore, may affect the separation performance of a membrane. Thus, examining the mixed gas system would provide a significant demonstration of the useful separation properties of the membranes. Table 4 shows the flux and calculated (ideal) as well as observed separation factors for the mixed gases obtained through the zero-air cylinder. The data have been derived on the same membranes for which the selectivity values have been given in the Table 3. Figure 4 shows the output from the gas chromatograph as a result of enrichment affected by the membranes (Table 1). The figure also shows the percentage of oxygen in the permeate gas after its passage through the membrane. There is an enhancement of oxygen content to a level of 30 per cent from the initial value of 21.13 per cent. Likewise, the nitrogen content is reduced to a level of 69.96 per cent from the initial value of 78.86 per cent.

It can be seen from the Table 4 that the enrichment of oxygen from atmospheric air (oxygen and nitrogen mixture) is lower than the expected values derived on the basis of ideal selectivity factor (mentioned in Table 3). It is known that gases behave differently in mixture than as an



Gas	O_2	N_2
R. Time	0.89	1.25
Height	1268	1953
Area	128198	295238
HT percentage	39.3667	60.6333
Area percentage	30.2758	69.7242

Figure 4. Gas chromatograph output of the enriched air affected by the membrane.

Table 4. Permeation and separation factors for oxygen and nitrogen from atmoshpheric air

Membrane	Pressure (kg/cm^2)	Air flux (ml/min)	Oxygen enrichment (%)	
			Expected	Obtained
I	7	0.55*	45.8	31.90
II	7	1.08**	39.92	32.55

* 400 $ml/min/m^2$
** 750 $ml/min/m^2$

individual gas in terms of permeability and separation factor. Transport of a component in a gas mixture is often affected by the presence of other penetrants due to plasticisation, hydrostatic compression or competitive sorption effejtt in a •fhulticomponent mixture. It is also known that the presence of faster permeating species enhance the permeation rates of slower species and *vice versa*[1*].

6. CONCLUSIONS

An in-house test facility for pure gases as well as quantification of separation factor for mixed gas system has been established at the Defence Research & Development Establishment, Gwalior. Asymmetric membranes have been developed for the enrichment of atmospheric oxygen to the level of 30 per cent.

ACKNOWLEDGEMENT

The authors thank Shri K. Sekhar, Director, Director Research & Development Establishment, Gwalior, for permission to publish the work and encouragement during the course of this study.

REFERENCES

1. Resting, R.E. & Fritzcsche, A.K. Polymeric gas separation membranes. John Wiley & Sons Inc., New York, 1993. 65p.

2. Cherien, Munir. Ultrafiltration and microfiltration handbook. Technomic, Lancaster, 1998.

3. Hagin, A. New generation of membranes developed for industrial separations. *Chem. Eng. News, 6,7* June 1999.

4. Rigby, G.R. Membrane gas separation and generation system for the process, horticultural, and agricultural industries. *In* Proceedings of the 18lh Australian Chemical Engineering Conference, Auckland, 27-30 August 1990. pp. 746-53.

5. Jain, R. Method for economic evaluation of membrane-based air separations. *Gas Sep. Purif.,* 1989, 3, 123-27.

6. Rigby, G.R. & Watson, Harry C. Application of membrane gas separation to oxygen enrichment of diesel engines. *J. Membn. Sci.,* 1994, 87, 159-69.

7. Pandey, P. & Chauhan, R.S. Membranes for gas separation. *Prog. Polym. Sci.,* 2001, 26, 853-93.

8. Mulder, M. Basic principles of membrane tech. Kluwer Academic Publication, Dordrecht, 1991.

9. Koros, W. J, & Pinnau, I. Membrane formation for gas separation process. CRC Press, Boca Raton, 1994.

10. Chung, T.S. A review of microporous composite polymeric membrane technology for air separation. *Polym. Polym. Composit.,* 1996, 4, 269-78.

11. Loeb, S. & Sourirajan, S. Sea water demineralisation by means of an osmotic membrane. *Adv. chem. Ser.,* 1962, 38, 117.

12. Pinnau, I. & Koros, W. J. Relationship between substructure resistance and gas separation properties of defect-free integrally skinned asymmetric membrane. *Ind. Eng. Chem. Res.,* 1991, 30, 1837-840.

13. Kulkarni, S.S. Polymer structure effect on gas permeation characteristics in polyarylates. *Bull. Mater. Sci.,* 1997, 17, 1307-310.

14. Kharul, U.K.; Joshi, S.G. & Kulkarni, S.S. Development of polymeric membranes for gas separation applications. *In* CSIR-DAAD Conference on Advances in Membrane Separation, 27-28 February 1996, Bhavnagar, Gujarat.

15. Pandey, P. Synthesis and characterisation of gas separation membranes. Jiwaji University, Gwalior, 2002. PhD Thesis.

16. Kurdi, J. & Tremblay, A.Y.J. Preparation of defect-free asymmetric membrane for gas separation. *Appl. Polym. Sci.,* 1997, 73, 1471-482.

17. Ettouney, H. & Majeed, U. Permeability functions for pure and mixed gases for silicone rubber and polysulfone membrane: Dependence upon pressure and composition. *J. Membn. Sci.,* 1997, 135, 251-61.

18. Chang, D.; Min, J.; Oh, S. & Moon, K. Perturbation solution of hollow fibre membrane module for pure gas permeation. J. *Membn. Sci.,* 1998, 143, 53-64.

Contributors

Dr P. Pandey obtained her MSc (Organic Chemistry) and PhD (Polymer Chemistry). She is working in Electron Microscopy Division at the Defence Research & Development Establishment(DRDE), Gwalior. Currently, she is engaged on the development of membranes for material separation. Her areas of work include: Synthesis, characterisation, and performance evaluation of membranes as well as establishment of membrane test systems.

Dr R.S. Chauhan obtained his MSc (Physical Chemistry) and PhD (Polymer Physics). He is heading the Electron Microscopy Division at the DRDE, Gwalior. He has worked extensively in the areas of electron microscopy of textile materials as well as textile material development; interaction of toxicants with bological tissues; and structure, and function correlation in polymeric materials. His area of research includes the development of oxygen-selective membranes. He has more than 80 papers published in the international journals.