

Ozone and Oxygen Permeation Behavior of Silicone Capillary Membranes Employed in Membrane Ozonators

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ABSTRACT: The permeabilities and selectivities of O₃, O₂, and N₂ through silicone capillary membranes employed to degrade organic pollutants in water or air have been experimentally determined. These characteristics have been studied for silicone membranes used in membrane reactors having the following conditions: O₃ in O₂ on one side of the membrane, and either water containing pollutants or a perfluorocarbon (FC) phase containing pollutants on the other side. The permeability of O₃ (8.8 e-13 kgmol · m/m² · s · kPa) is four times that of O₂ through virgin silicone rubber. Exposure to O₃ modifies the polymer and alters the permeabilities of O₃ and O₂. The presence of water with O₃ leads to an increase in O₃ and O₂ permeability (~ 30%) and an increase in the selectivity, $\alpha_{O_2-N_2}$ (~ 10%). The increased permeabilities are likely to be due to the formation of peroxides on the surface and possibly in the polymer. When the silicone capillary membranes were exposed to a perfluorocarbon (FC), the permeabilities of O₃ and O₂ decreased (~ 9%) due to an increase in crosslinking in the polymer matrix; there was also a slight increase in $\alpha_{O_2-N_2}$ (~ 2%), which can be ascribed to the smaller molecular sieving radius of O₂ compared to N₂. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* 69: 1263–1273, 1998

Key words: silicone membrane; ozone; permeability; selectivity

INTRODUCTION

Nonporous polymeric membranes are being successfully used in the chemical process industry for large-scale separation of gas mixtures. These gaseous species for example, N₂, O₂, CO₂, CH₄, H₂O, He, etc., are generally inert to the polymeric membrane materials commonly employed. The possibility of large-scale separation of a number of other gaseous species, for example, Br₂, Cl₂, F₂, O₃, etc., is, however, limited by the membrane durability under the extreme oxidizing environment typical of these species. Membrane-based separation of gaseous mixtures containing such

species and processes utilizing such species in a reactive environment with the aid of membranes are of considerable interest. For example, ozone, a well known disinfecting agent, has been used to successfully destroy a large number of pollutants, for example, phenol, acrylonitrile, nitrobenzene, etc., in membrane reactors.^{1–3} The performances of these reactors were excellent. If, however, the membrane material is prone to oxidative attack, then the membranes and consequently the membrane ozonator is compromised.^{4,5} Therefore, the selection of the membrane material is critical to the function and the subsequent use of the membrane device. Scale up of the membrane reactors^{1–3} requires basic information about the permeation characteristics of candidate gases like O₃ through relevant polymeric membranes.

Ozone is a highly reactive gas with a limited

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half-life. Of the polymeric materials available, the only materials known to be resistant to oxidative degradation and available as tubular membranes are polytetrafluoroethylene (PTFE, Teflon), polyvinylidene fluoride (PVDF), and polydimethylsiloxane (PDMS, silicone rubber). Teflon and PVDF membranes are microporous in nature, while PDMS membranes are nonporous. We have already employed Teflon and PDMS membranes in our extensive work with aqueous and gaseous waste streams.¹⁻³

Silicone rubber (PDMS, polydimethylsiloxane) has been extensively used to separate O₂ and N₂. It possesses a large permeability for oxygen (933 barrers) compared with most membrane materials⁵ and a moderate permselectivity for O₂ over N₂. In this article we report the permeability behavior of O₃ through PDMS capillary membranes. We also present the permeabilities of O₂ and N₂ through PDMS capillary membranes exposed to O₃ over extended times in different oxidizing environments. In the ozonation of aqueous waste streams the membrane is exposed to O₃ on one side. On the other side, an aqueous stream containing organic pollutants exist in single phase ozonation processes;¹ in two-phase ozonation processes the liquid medium on the other side of the PDMS membrane is a perfluorocarbon (FC) liquid, wherein the ozonation of an organic pollutant extracted from the aqueous stream occurs.² In a three-phase ozonation process,³ ozone flows through a silicone capillary while volatile organic compounds (VOCs) flow through another silicone capillary; an aqueous stream flows through a set of microporous Teflon tubules. The shell side of this device has a fluorocarbon liquid. Each situation modifies the polymer in a unique manner. It is useful to study the properties, viz. gas permeability under such conditions because the performance of the membrane device is affected.

EXPERIMENTAL PROCEDURE

Membrane Materials and Modules

Membrane modules were constructed with nonporous silicone capillaries (Silastic, medical grade, Baxter Diagnostics, Edison, NJ), of the following dimensions: 1.6 mm i.d., 2.4 mm o.d. for the module labeled SILCAP #1 and 0.3 mm i.d., 0.63 mm o.d. for other modules (Table I). The logarithmic mean area available for permeation for each module is defined as follows:

Log Mean Permeation Area

$$= \pi \frac{d_o^{\text{sil}} - d_i^{\text{sil}}}{\ln(d_o^{\text{sil}}/d_i^{\text{sil}})} N_{\text{fibs}} L \quad (1)$$

The silicone capillaries (silastic medical grade) were counted, cut to length, and laid out in a mat. The ends of the capillaries were bunched and tied; then the capillaries were inserted in a transparent FEP shell of dimensions 0.61 cm i.d., 1.03 cm o.d., (Cole Parmer, Chicago, IL) fitted with barbed polypropylene Y-fittings at the two ends (Cole Parmer, Chicago, IL). The two fiber ends were potted using two sets of epoxies (Beacon Chemical Co., Mount Vernon, NY). The external tube sheet was formed using the A2 epoxy with activator "A"; the internal tube sheet was formed using the C4 epoxy with activator "D." The epoxies were allowed to cure for 7 days. Then each module was filled with water on the shell side at 10 psig to check for leaks. The module labeled NEWCON #1 had two sets of silicone capillaries, of which one set was used for membrane permeability measurements (Fig. 1).

Permeability Coefficient and Separation Factors of Oxygen and Nitrogen across the Silicone Membrane

Permeability coefficients of nitrogen (N₂) and oxygen (O₂) across the silicone capillary membranes were measured before and after exposure to ozone. Gas phase mixtures of different compositions were generated by mixing air (extra dry) and helium (extra dry) cylinders (Matheson, E. Rutherford, NJ) connected to mass flow controller transducers (Matheson, E. Rutherford, NJ). The mass flow controllers allowed precise flow control of each gas phase. The gas chromatograph (GC) (HP 5890, Hewlett Packard, Paramus, NJ) was equipped with a thermal conductivity detector (TCD) and a gas sampling valve. The GC was calibrated for O₂ and N₂ by sampling gas phase mixtures of known proportions of air and helium and noting the peak areas obtained from the GC on an integrator (HP 3393A, Hewlett Packard, Paramus, NJ). The GC employed a Molecular Sieve column (13×, Mesh 80/100, 0.085" i.d., 0.125" o.d., 10 feet long, Alltech Associates, Waukegan, IN). The gas was sampled at a rate of 10–30 mL/min. The GC column was maintained at 50°C, while the injector and detector were maintained at 100 and 300°C, respectively.

The schematic to measure the permeability co-

Table I Details of Modules Used to Measure Permeabilities of O₃, O₂, and N₂

Module	Silicone Capillaries		Module Length (m)	Membrane Wall Thickness (m)	LMP Area ^a (m ²)
	ID/OD (cm)	Number			
SILCAP #5	0.03/0.06	98	0.22	1.65 e-4	2.99 e-2
SILCAP #1	0.16/0.24	4	0.28	4.19 e-4	6.90 e-3
NEWCON #1	0.03/0.06	25	0.38	1.65 e-4	1.32 e-2

^a Log Mean Permeation Area [Eq. (1)].

efficients of O₂ and N₂ is shown in Figure 2. Experiments were conducted by passing the air stream through the tube side and the helium stream co-

currently through the shell side of the module, and then changing the streams so that air was fed into the shell and helium fed into the tube

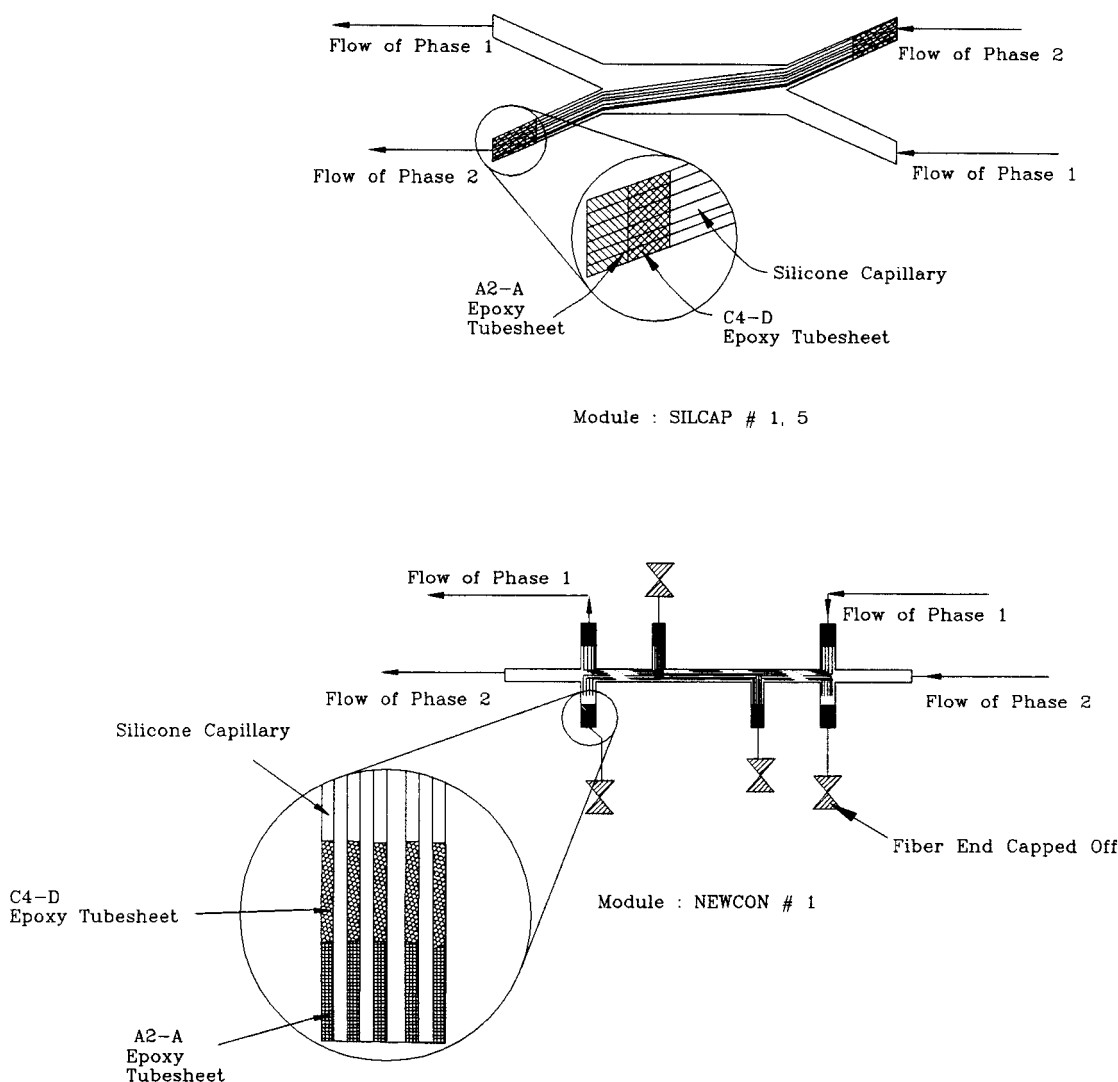


Figure 1 Schematic of the membrane ozonator modules showing the fiber ends embedded in an epoxy layer.

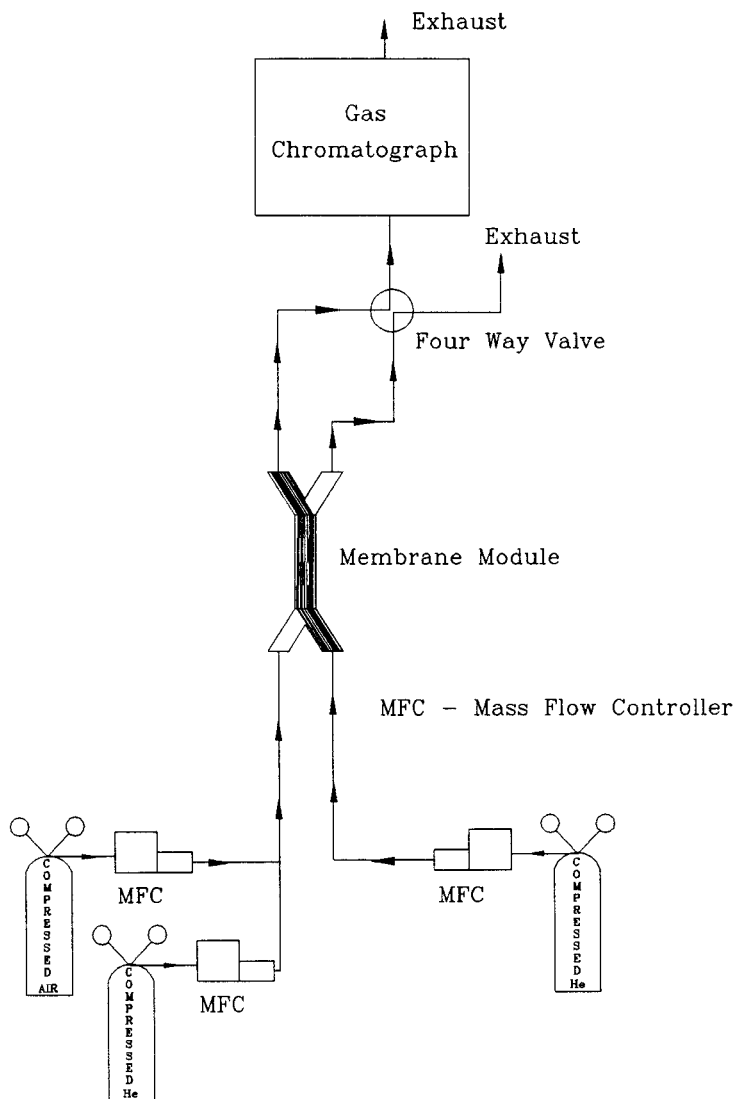


Figure 2 Schematic of the setup to measure the permeability of O_2 and N_2 through silicone capillaries.

side. The conditions of pressure and flow rates were kept as identical as possible when air was in the tube and vice versa. This precluded any possible variations of permeability coefficient due to the geometry and elasticity of the silicone capillaries. The pressures of both streams were kept as close to atmospheric as possible to preclude any pressure drop effects across the length of the capillaries. The sweep gas, He, was sampled via the gas sampling valve of the GC periodically. Steady state was rapidly reached, as ascertained by the constant peak areas obtained for N_2 and O_2 . At this point the feed outlet was also sampled to measure the change in the feed concentration. Because the feed flow rate and concentrations

were fairly high, the variation between inlet and outlet feed concentrations were found to be negligible. This was established by checking the feed outlet concentration after steady state had been reached.

Permeability Coefficient of Ozone across the Silicone Membrane

Ozone was generated by feeding a pure oxygen gas stream from a gas cylinder (Matheson, E. Rutherford, NJ) to the ozone generator (Model T-408, Polymetrics, Colorado Springs, CO). A small portion of the ozone/oxygen mixture (O_3/O_2) was diverted for experimental purposes. The major

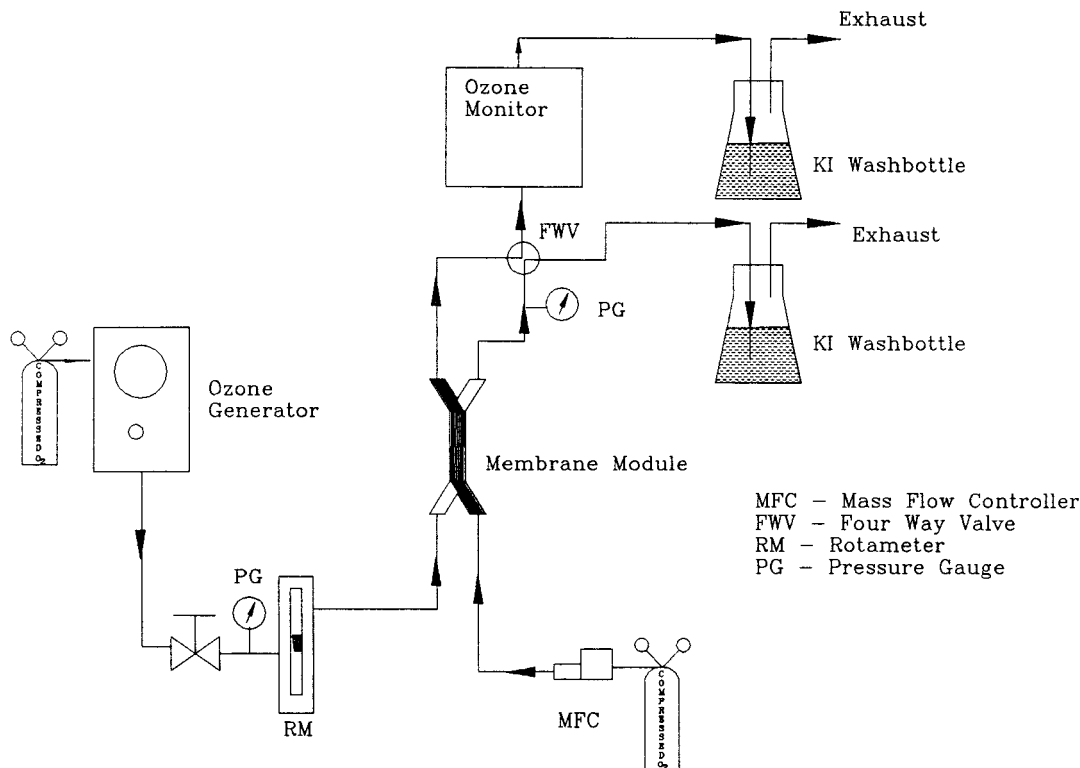


Figure 3 Schematic of the setup to measure the permeability of O₃ through silicone capillaries.

portion was vented after passing through two KI (2% concentration by weight) wash bottles linked in series to break down any ozone and a sodium thiosulfate bottle to trap any entrained iodine. The concentration of O₃ generated was typically 2–3 vol % in O₂. Ozone attacks most materials. Therefore, a gas flow controller in line with the O₃/O₂ gas stream was not used; instead a rotameter, calibrated prior to the experiment with O₂, was used to determine the flow rate of ozone through the module. The experimental setup used is shown in Figure 3.

The ozone monitor used in this study (model HC 400, PCI Technologies, West Caldwell, NJ) had a range of 0–15 wt % (0–99,000 ppm by volume). It was equipped with inlet needle valves for the sample and zero gas, a flow meter (of rotameter type), a solenoid valve, and a sample chamber. The unit measured ozone by comparing the UV absorption of the sample with that of the zero gas, which for this study, was oxygen. The switching of the flow between the zero and the sample gas was initiated by a solenoid valve built into the ozone monitor with a cycle time of 20 s. During the period when the zero gas was being sampled

via the solenoid valve, the sample gas flow was stopped.

For the measurement of the permeability coefficient of ozone in the silicone rubber capillaries in the set up (Fig. 3), each of the modules, SIL-CAP #1 and #5 and NEWCON #1, was taken in turn and connected to the setup. The measurement of permeability coefficient of ozone through the silicone capillaries for the module NEWCON #1 was carried with only one set of silicone capillaries. The four other ports comprising of the other silicone capillary set and the Teflon tubule set were capped during the experiment. Oxygen was used as a sweep gas because it was also used as a blank in the ozone monitor and was the diluent phase of the ozone stream. The four way valve ($\frac{1}{8}$ " NPT, Swagelock, R. S. Crum, Mountainside, NJ) allowed crossover of the two streams, so that the ozone concentration in each of the streams could be monitored. For a majority of the experiments, the sweep stream comprised of oxygen and any ozone that has permeated across the silicone membrane phase was sampled. After steady state was achieved, the outlet of the feed gas stream was sampled. Experiments were carried out by

Table II O₂ and N₂ Permeability Coefficients through Silicone Rubber for SILCAP #5^a

Feed Flow Configuration	Permeate O ₂ (vol %)	Permeate N ₂ (vol %)	$p_{O_2}^p$ (kPa)	LMPD ^b (kPa)	J_{O_2} (kgmol/m ² ·s)	$Q_{O_2}^m$ ^c	α_{O_2/N_2}
Feed in tube	1.05	1.89	1.06	20.54	2.78 e-08	2.23 e-13	2.11
	1.05	1.90	1.07	20.54	2.79 e-08	2.24 e-13	2.11
	1.05	1.90	1.07	20.54	2.78 e-08	2.24 e-13	2.11
Feed in shell	1.05	1.90	1.07	20.54	2.79 e-08	2.24 e-13	2.11
	1.05	1.90	1.07	20.54	2.79 e-08	2.25 e-13	2.11
	1.05	1.90	1.07	20.54	2.79 e-08	2.24 e-13	2.11

^a Freshly prepared module.

^b Log Mean Partial Pressure Difference between the feed and permeate channels [Eq. (3)].

^c Units of Permeability Coefficient (kgmol·m)/(m²·s·kPa). O₂ feed partial pressure: 21.8 kPa. Feed flow rate: 90.9 mL/min. Helium flow rate on permeate side: 112.2 mL/min.

admitting the feed of O₃/O₂ in the shell side of the module as well in the tube side of the module.

RESULTS AND DISCUSSION

The physical characteristics of the membrane reactors studied are summarized in Table I. Results of the experimental determination of the permeabilities and separation factor of O₂-N₂ are presented first followed by those of the permeability of O₃ in a silicone capillary membrane.

The measurement of the permeabilities of oxygen and nitrogen across silicone rubber was carried out in three modules, SILCAP #5 and #1 and NEWCON #1. (1) SILCAP #5 was a freshly prepared module that had not been exposed to ozone prior to the measurement of O₂ and N₂ permeabilities; (2) SILCAP #1 had been exposed to ozone for a period of about 50 h prior to these measurements as part of the ongoing study with a single-phase membrane ozonator to degrade organic pollutants in wastewater;¹ and (3) the silicone membranes in the module NEWCON #1 had been exposed to both ozone and the fluorocarbon phase (FC) as part of the study to remove VOCs from air for a period of 80 h.³ The three modules represent the gamut of situations that were possible during membrane-based ozonation of organic compounds in waste streams.¹⁻³ It allowed consideration of any possible change in permeability or O₂/N₂ separation factor of silicone rubber due to the exposure to ozone in the absence or presence of the fluorocarbon phase.

For modules SILCAP #1 and #5 and NEWCON #1, the experimental values of the permeability coefficient of oxygen through silicone rubber and the separation factor for O₂/N₂, are listed in Tables II-IV, respectively. It is assumed that the

feed and permeate gas phases obey ideal gas law, and Fick's Law is applicable to the permeation of O₂ and N₂ through the polymer. Therefore,

$$J_{O_2} = \frac{Q_{O_2}^m}{l} (p_{O_2}^f - p_{O_2}^p)_{LM} \quad (2)$$

where J_{O_2} is the molar flux of O₂ across the silicone capillary membrane, $Q_{O_2}^m$ is the permeability coefficient of oxygen through silicone rubber, l is the wall thickness of the silicone capillary membrane given in Table I. The log mean partial pressure driving force is defined as follows:

$$(p_{O_2}^f - p_{O_2}^p)_{LM} = \frac{(p_{O_2}^f - p_{O_2}^p)|_{inlet} - (p_{O_2}^f - p_{O_2}^p)|_{outlet}}{\ln\left(\frac{(p_{O_2}^f - p_{O_2}^p)|_{inlet}}{(p_{O_2}^f - p_{O_2}^p)|_{outlet}}\right)} \quad (3)$$

For all experiments, the permeate side partial pressure of oxygen (and nitrogen) was negligible compared to the feed side partial pressure; this observation suggests that the separation factor for O₂-N₂ is given by the ratio of the two permeability coefficients:

$$\alpha_{O_2-N_2} = \frac{p_{O_2}^p/p_{O_2}^f}{p_{N_2}^p/p_{N_2}^f} \cong \frac{Q_{O_2}^m}{Q_{N_2}^m} \quad (4)$$

Based upon the above definitions, the separation factor for O₂-N₂ can be calculated knowing the feed and permeate concentrations for nitrogen and oxygen. It is seen from Tables II to IV that regardless of whether the feed is in the shell or

Table III O₂ and N₂ Permeability Coefficients through Silicone Rubber for SILCAP #1^a

Permeate O ₂ (vol %)	Permeate N ₂ (vol %)	$p_{O_2}^o$ (kPa)	LMPD ^b (kPa)	J_{O_2} (kgmol/m ² ·s)	$Q_{O_2}^m$ ^c	α O ₂ /N ₂
0.13	0.22	1.32 e-1	21.01	1.45 e-08	2.9 e-13	2.25
0.13	0.21	1.26 e-1	21.01	1.39 e-08	2.79 e-13	2.31
0.12	0.21	1.26 e-1	21.01	1.39 e-08	2.77 e-13	2.31
0.12	0.20	1.25 e-1	21.01	1.39 e-08	2.76 e-13	2.31

^a Module exposed to aqueous phase ozonation. Feed on tube side of module.

^b Log Mean Partial Pressure Difference between the feed and permeate channels [Eq. (3)].

^c Units of Permeability Coefficient (kgmol·m)/(m²·s·kPa). O₂ feed partial pressure: 21.8 kPa. Feed flow rate: 90.9 mL/min. Helium flow rate on permeate side: 112.2 mL/min.

in the fiber lumen, the measured permeability coefficient of O₂ is almost unchanged. The capillaries used in SILCAP #1 had a wall thickness about four times that in modules SILCAP #5 and NEWCON #1. This is the reason why the observed O₂ flux through the capillaries of SILCAP #1 is lower; the permeability coefficient calculated for oxygen is however higher. The permeability coefficient of O₂ and the separation factor, α between O₂ and N₂ increase with an exposure to ozone (Tables II and III). The permeability coefficient is seen to decrease by about 10% of the value for the virgin polymer, when the polymer is exposed to ozone in the presence of the FC phase (Table IV).

The permeability coefficient for a species through a polymer is generally described by the following equation:

$$Q_i^m = D_i S_i \quad (5)$$

where Q_i^m is the permeability coefficient of a species i , while D_i and S_i are the diffusivity and the solubility of species i in the polymer respectively.⁶

The solubility S_i of species i in a polymer matrix is thermodynamic in nature and is related to the condensability of the species and any interaction between the polymer matrix and the permeating species. A species that is easily condensable (a high T_C and a high T_b) will have a high solubility in the polymer. In literature, it is seen that for O₂ and N₂, the diffusivities, D_{N_2} and D_{O_2} , in silicone rubber are essentially identical, 21 e-10 m²/s but the solubility, S_{N_2} in silicone rubber is less than S_{O_2} , 4.35 e-5 kgmol/(m³-membrane·kPa) for N₂ vs. 8.37 e-5 kgmol/(m³-membrane·kPa) for O₂.⁷ This is attributed to the lower T_C of N₂ (decreased condensability), leading to a higher value of permeability coefficient of O₂.

When the silicone elastomer is exposed to ozone, in the absence of any solvents, it is likely that ozone will participate in reactions that will lead to higher crosslinking densities; such behavior has been observed for structural silicone materials.⁸ Using ozone as a crosslinking agent in such a polymeric material can lead to several possibilities. The polymer becomes increasingly rigid, re-

Table IV O₂ and N₂ Permeability Coefficients through Silicone Rubber for NEWCON #1^a

Feed Flow Configuration	Permeate O ₂ (vol %)	Permeate N ₂ (vol %)	$p_{O_2}^o$ (kPa)	LMPD ^b (kPa)	J_{O_2} (kgmol/m ² ·s)	$Q_{O_2}^m$ ^c	α O ₂ /N ₂
Feed in tube	0.44	0.78	0.45	20.85	2.60 e-08	2.05 e-13	2.15
	0.44	0.78	0.45	20.85	2.60 e-08	2.05 e-13	2.15
	0.44	0.79	0.45	20.85	2.60 e-08	2.06 e-13	2.15
Feed in shell	0.43	0.78	0.44	20.86	2.55 e-08	2.01 e-13	2.13
	0.43	0.77	0.44	20.86	2.54 e-08	2.01 e-13	2.13
	0.43	0.77	0.44	20.86	2.54 e-08	2.01 e-13	2.13

^a Module exposed to O₃ and FC phase prior to measurement of permeability coefficient.

^b Log Mean Partial Pressure Difference between the feed and permeate channels [Eq. (3)].

^c Units of Permeability Coefficient (kgmol·m)/(m²·s·kPa). O₂ feed partial pressure: 21.8 kPa. Feed flow rate: 90.9 mL/min. Helium flow rate on permeate side: 112.2 mL/min.

ducing the dimensions of the openings between the polymer chains in the polymeric matrix, through which O_2 and N_2 can permeate. O_2 has a slightly smaller kinetic sieving diameter than N_2 (3.46 Å for O_2 vs. 3.64 Å for N_2); this would provide greater selectivity for O_2 than for N_2 , although the individual species diffusivity would be somewhat reduced.⁶ Because ozone works as a crosslinking agent, it can also be postulated that the increased concentration of oxygen atoms within the polymer matrix causes an increase in solubility of O_2 in the polymer matrix, leading to an overall higher permeability coefficient. This explains both the increase in permeability of O_2 and the increase in $\alpha_{O_2-N_2}$ between the modules SILCAP #5 and #1 shown in Tables II and III, respectively. Which of these mechanisms plays a more critical role in the increase in $\alpha_{O_2-N_2}$ and the permeability of O_2 is presently unknown.

The reduction in the permeability for silicone capillaries, on exposure to ozone in the presence of the FC medium in Table IV, could be explained by the higher ozone concentrations seen by the silicone capillaries, because ozone is highly soluble in the FC phase. This can lead to the polymer chains becoming extremely rigid in their lateral motions due to crosslinking (lateral to the axis of permeation of the solute species) resulting in "glass-like" behavior, and the observed drop in the permeability coefficients due to a drop in the species diffusivities. The diffusion coefficients of permanent gases through glassy polymers are roughly two orders of magnitude smaller than those through rubbery polymers. Also, the attack of free radicals present during the reaction of ozone with organic species dissolved in the FC medium could contribute to further modification of the polymer resulting in the concomitant reduction in O_2 permeability coefficient and the corresponding N_2 permeability coefficient. Other studies have observed increases in the Young's Modulus for silicone rubber due to exposure to ozone.⁸

Table V compares the experimental data for $Q_{O_2}^m$ and $\alpha_{O_2-N_2}$ in Tables II–IV with those found in the literature. The silicone capillaries used here are of the "Silastic Grade," with about 31 wt % fumed silica particles (0.011 μm).⁷ The experiments were conducted at an ambient temperature of $27 \pm 2^\circ\text{C}$. Considering the results found in the literature,^{9,10} the results for the virgin polymer in module SILCAP #5 appear to be in fair agreement. Majumdar et al.⁹ conducted their experiments at 22°C , while Robb¹⁰ conducted his experi-

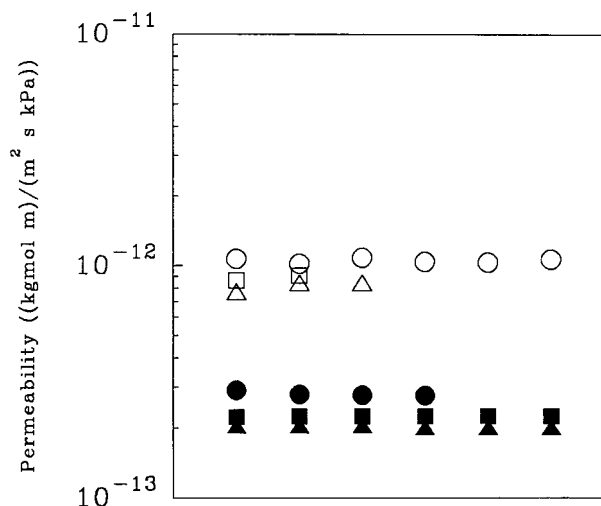


Figure 4 Comparison between the experimentally observed permeability values for O_2 and O_3 . ■, O_2 , SILCAP #5; ▲, O_2 , SILCAP #1; ●, O_2 , NEWCON #1; □, O_3 , SILCAP #5; △, O_3 , SILCAP #1; ○, O_3 , NEWCON #1.

ments at 25°C . The value of 933 barrers,⁶ appears to be for the PDMS polymer in the absence of any inert fillers and, therefore, represents the intrinsic value of the permeability. The separation factors for N_2 and O_2 observed experimentally seem to correspond well with those found in literature.

Measurement of the Permeability Coefficient of Ozone across the Silicone Membrane

The physical details of the modules necessary to calculate the permeability coefficient of O_3 through silicone capillaries are shown in Table I. The results are provided in the following order: (1) SILCAP #5, which was not exposed to any ozone prior to the measurement of its permeability through silicone rubber; (2) SILCAP #1, which was exposed to O_3 and water prior to the permeability experiments; and (3) NEWCON #1, which was exposed to O_3 and the FC phase.

The SILCAP #5 module had the highest permeation area of the three modules and the observed change in the feed side O_3 composition between inlet and outlet was less than 2% of the inlet O_3 composition. Therefore, for the subsequent calculation of the permeability coefficient of O_3 for modules SILCAP #1 and NEWCON #1, the inlet O_3 was assumed to be essentially the feed O_3 composition.

From the results shown in Tables VI–VIII, it is clear that O_3 has a much higher permeability than O_2 through the silicone capillary mem-

Table V Comparison between Experimental Values and Literature Values for the Permeability Coefficient of O₂ and α of O₂-N₂

Reference	$Q_{O_2}^m$ ^a	α O ₂ -N ₂	Remarks
SILCAP #5	2.24 e-13	2.11	Fresh silicone capillaries
SILCAP #1	2.81 e-13	2.30	Exposed to O ₃ and H ₂ O
NEWCON #1	2.03 e-13	2.14	Exposed to O ₃ and FC
Ref. 6	3.12 e-13	2.12	No inert fillers
Ref. 7	1.77 e-13	1.89	—
Ref. 9	1.69 e-13	2.06	—
Ref. 10	2.00 e-13	2.14	—

^a Units of Permeability Coefficient (kgmol·m)/(m²·s·kPa).

branes. This can be explained by the higher solubility that O₃ has in silicone rubber because it has a much higher T_C and T_B than O₂ (T_B of O₂ is -183°C and T_C is -118.6°C, while for O₃, T_B is -112°C and T_C is -12.15°C) and, therefore, is more easily condensable than O₂. It is also immediately apparent that when the three modules are considered in turn, the permeability coefficient of O₃ follows the same trend shown by that of O₂ in Tables II–IV. The silicone capillary membranes show a slight increase in O₃ permeability coefficient when exposed to O₃ and water and a decrease in permeability when exposed to O₃ and the FC phase. The increase can be attributed to an increase in solubility of O₃ in the membrane that had been previously exposed to O₃. The subsequent decrease in permeability shown in Table VIII for the module NEWCON #1 can be attributed to the rigidity of the silicone polymer matrix as a result of extensive crosslinking in the presence of higher concentrations of O₃ and results in a decreased permeability of ozone across the silicone polymer matrix. Figure IV compares the values of the permeability of O₃ and O₂ for each

of the three modules studied and summarizes the results of this study.

Exposure of silicone films to O₃ gas has been shown to form considerable amounts of peroxides on the surface of the silicone films,¹¹ while the exposure of silicone sealants to ozone and moisture at low pH results in the formation of microscopic cracks (and a concomitant drop in the surface crosslink density) on the surface of the sealant.⁸ The presence of peroxides and surface cracking indicates that some of the surface bonds are being cleaved by ozone to form the peroxidic groups at least on the surface of the film. Aqueous phase ozonation of organic pollutants in silicone capillary membrane ozonator results in the formation of acidic reaction products close to the silicone–aqueous interface. This probably causes some surface cracking due to chain scission and the formation of small crannies close to the surface of the tubular membranes. The observed increase in the permeabilities of the diffusing species can be attributed to the slight decrease in diffusional resistance to the permeating species. The formation of peroxides on the surface of the

Table VI Permeability Coefficient of O₃ through Silicone Rubber for SILCAP #5^a

Permeate O ₂ Flow (mL/min)	$p_{O_3}^f$ (kPa)		$p_{O_3}^b$ (kPa)	LMPD ^b (kPa)	J_{O_3} (kgmol/m ² ·s)	$Q_{O_3}^m$ ^c
	In	Out				
60.7	3.62	3.55	1.15	2.97	1.55 e-8	8.61 e-13
112.1	3.62	3.51	0.705	3.19	1.75 e-8	9.05 e-13

^a Freshly prepared module.

^b Log Mean Partial Pressure Difference between the feed and permeate channels [Eq. (3)].

^c Units of Permeability Coefficient (kgmol·m)/(m²·s·kPa). Feed in fiber lumen of silicone capillaries. O₃/O₂ flow rate = 463 mL/min at 0 psig (atmospheric pressure).

Table VII Permeability Coefficient of O₃ through Silicone Rubber for SILCAP #1^a

Flow Configuration	Permeate Flow O ₂ (mL/min)	$p_{O_3}^f$ (kPa)	$p_{O_3}^p$ (kPa)	LMPD ^b (kPa)	J_{O_3} (kgmol/m ² ·s)	$Q_{O_3}^m$ ^c
Feed in shell	93.2	3.61	1.02 e-1	3.56	9.09 e-9	1.07 e-12
	134.5	3.61	6.77 e-2	3.57	8.73 e-9	1.02 e-12
	59.8	3.61	1.59 e-1	3.53	9.12 e-9	1.08 e-12
Feed in tube	98.6	3.74	9.53 e-2	3.69	9.00 e-9	1.04 e-12
	134.5	3.74	7.12 e-2	3.70	9.16 e-9	1.03 e-12
	59.8	3.74	1.61 e-1	3.66	9.25 e-9	1.06 e-12

^a Module exposed to aqueous phase ozonation.

^b Log Mean Partial Pressure Difference between the feed and permeate channels [Eq. (3)].

^c Units of Permeability (kgmol·m)/(m²·s·kPa). O₃/O₂ flow rate = 463 mL/min at 0 psig (atmospheric pressure).

silicone elastomer leads to making the silicone surface more hydrophilic compared to the virgin polymer. The selectivity for O₂/N₂ separation, from Table V, is found to increase relative to the virgin polymer; this may also be attributed to the increased solubility of O₂ in the polymer exposed to ozone and water, because O₂ has a higher solubility in water than N₂ (4.89 mL in 100 mL of water at 0°C for O₂, and 2.35 mL in 100 mL of water at 0°C for N₂).¹²

Extensive ozonation of silicone sealants in the presence moisture at low pH is also seen to cause considerable increase in crosslinking within the sample.⁸ The use of the silicone membrane in conjunction with a fluorocarbon is seen to cause a drop in the permeability for O₂ and O₃. From the literature⁷ it is seen that solutes like toluene and TCE have a substantial solubility in a silicone elastomer membrane. A fluorocarbon compound will also have high solubilities into the membrane. A fluorocarbon fluid saturated with ozone should, therefore, allow ozone to penetrate extensively into the silicone matrix and cause crosslinking of the polymer. This is seen from Tables IV and VIII, where the values for O₂ and O₃ perme-

abilities drop below those for the virgin polymer. The slight improvement in the selectivity is indicative of increased crosslinking because O₂ has a smaller sieving diameter than N₂.

CONCLUSIONS

The use of silicone capillary membranes in membrane reactors utilizing O₃ as an oxidant requires the membrane permeability of O₃. Experimental results show that O₃ permeability is about four times higher than that of O₂ through silicone membranes. The values of the O₃ and O₂ permeability and $\alpha_{O_2-N_2}$ increase relative to a virgin membrane when the membrane is exposed to O₃ and water containing organic pollutants.¹ The reasons for this increase are not altogether clear; it is speculated that ozonation in the presence of water introduces peroxidic groups and results in a higher solubility and permeability of O₃ and O₂ in the membrane phase. When the membrane is exposed to O₃ and a perfluorocarbon fluid during the ozonation of organic pollutants,^{2,3} the values of O₃ and O₂ permeability decrease. This is proba-

Table VIII Permeability Coefficient of O₃ through Silicone Rubber for NEWCON #1^a

Flow Configuration	Permeate Flow O ₂ (mL/min)	$p_{O_3}^f$ (kPa)	$p_{O_3}^p$ (kPa)	LMPD ^b (kPa)	J_{O_3} (kgmol/m ² ·s)	$Q_{O_3}^m$ ^c
Feed in shell	59.8	3.53	5.10 e-1	3.27	1.53 3-8	7.70 e-13
	112.1	3.53	3.07 e-1	3.37	1.73 3-8	8.42 e-13
	149.1	3.53	2.33 e-1	3.41	1.74 3-8	8.41 e-13

^a Module exposed to O₃ and FC phase prior to measurement of permeability coefficient.

^b Log Mean Partial Pressure Difference between the feed and permeate channels [Eq. (3)].

^c Units of Permeability Coefficient (kgmol·m)/(m²·s·kPa). O₃/O₂ flow rate = 463 mL/min at 0 psig (atmospheric pressure).

bly due to an increased crosslinking in the silicone polymer, which results in "glass-like" behavior of the polymer, resulting in lower O₃ and O₂ permeability through the membrane. Because the molecular sieving radius of O₂ is less than that of N₂, the increased crosslinking reduces the openings between the PDMS chains, which results in a slight increase in $\alpha_{O_2-N_2}$. The permeability of the silicone capillary membrane is strongly influenced by the environment in which it is exposed to ozone. Exposure to ozone in the presence of water enhances the permeability of O₃ and O₂; however, the presence of an inert, organic solvent like a perfluorocarbon fluid in combination with a high concentration of dissolved ozone reduces values of O₃ and O₂ permeability.

REFERENCES

1. P. V. Shanbhag, A. K. Guha, and K. K. Sirkar, *J. Hazardous Mater.*, **41**, 95 (1995).
2. A. K. Guha, P. V. Shanbhag, K. K. Sirkar, D. A. Vaccari, and D. Trivedi, *AIChE J.*, **41**, 1998 (1995).
3. P. V. Shanbhag, A. K. Guha, and K. K. Sirkar, *Environ. Sci. Technol.*, **30**, 3435 (1996).
4. D. H. Trivedi, M.E. Thesis, Stevens Institute of Technology, Hoboken, NJ (1992).
5. K. Castro and A. K. Zander, *J. AWWA*, **3**, 50 (1995).
6. R. R. Zolandz and G. K. Fleming, in *Membrane Handbook*, W. S. W. Ho and K. K. Sirkar Eds., Chapman and Hall, New York, 1992.
7. M. A. LaPack, J. C. Tou, V. L. McGuffin, and C. G. Enke, *J. Membr. Sci.*, **86**, 263 (1994).
8. R. Keshavaraj and R. W. Tock, *Polym. Plast. Technol. Eng.*, **33**, 397 (1994).
9. S. Majumdar, L. B. Heit, A. Sengupta, and K. K. Sirkar, *Ind. Eng. Chem. Res.*, **26**, 1434 (1987).
10. W. L. Robb, Report No. 65-C-031; R&D Center, General Electric Co., New York, Vol. 10, 1965.
11. K. Fujimoto, T. Takebayashi, H. Inoue, and Y. Ikada, *J. Polym. Sci., Part A: Polym. Chem.*, **31**, 1035 (1993).
12. R. H. Perry and D. W. Green, Eds., *Perry's Chemical Engineers' Handbook*, McGraw-Hill Book Co., New York, 1984.