# MEMBRANE TECHNOLOGY: A SEARCH FOR MEMBRANES FOR SUBMARINE ATMOSPHERE CONTROL

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# Membrane Technology: A Search for Membranes for Submarine Atmosphere Control



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## Abstract

*This overview of membrane technology covers the development of devices which can separate carbon dioxide from air and many other feed gases, and the factors influencing selection and performance of such systems. Of the polymeric materials investigated for the separation of carbon dioxide from air, dimethyl silicone (25%) rubber membranes exhibit the highest permeability for carbon dioxide, while cellulose acetate exhibits the highest separation factor (10.9) of carbon dioxide to oxygen. However, an immobilized film membrane (IFM) device constructed of a cellulose acetate membrane impregnated with a cesium bicarbonate and sodium arsenite solution exhibits the highest recorded separation factor of 4100. Since a membrane must exhibit a separation factor of at least 100 in order to be effective in any life support system, the IFM method is at present the only approach worthy of further research and development in support of submarine atmosphere control.*

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# *Membrane Technology: A Search for Membranes for Submarine Atmosphere Control*

## 1. Introduction

The purification of atmospheres in sealed manned vessels such as submarines and spacecraft has been a concern since their inception. Traditionally on a diesel powered submarine the carbon dioxide has been removed from the atmosphere by either ventilation (snorkeling) or absorption into soda lime or lithium hydroxide canisters, while in nuclear powered submarines the removal of carbon dioxide is afforded by absorption into a monoethanolamine (MEA) scrubber unit.

The removal of carbon dioxide from the atmosphere in a submarine is obligatory, since excessive amounts of carbon dioxide in the atmosphere produce toxic effects, the severity of which depends on exposure time and the partial pressure of carbon dioxide. Under ordinary conditions on a submarine the average consumption rate of oxygen is 28.3 l/h per person and the average carbon dioxide production rate is 24.0 l/h per person. On the new Royal Australian Navy (RAN) Collins class submarines being constructed in Adelaide, South Australia, the removal rate of carbon dioxide from the atmosphere is expected to be approximately 2.2 kg carbon dioxide per hour. The maximum permissible concentration (MPC) limit over eight hours for carbon dioxide on this submarine will be set at 0.8%, or 0.5% over 12 days. Indeed, limits would be set even lower if the technology was available to achieve such levels.

Carbon dioxide will be removed from the atmosphere of the Collins class diesel powered submarines using a monoethanolamine (MEA) scrubber unit. In this system, carbon dioxide from the atmosphere reacts with the amine groups to form a carbamate-rich solution which is then pumped to a heater/desorption unit to liberate the carbon dioxide and regenerate the amine. A single MEA scrubber unit is claimed to achieve a MPC over 24 hours of 0.8% carbon dioxide, but not lower. Nuclear powered submarines of the US Navy operate two MEA units in series, to reliably maintain a carbon dioxide level of approximately 0.5%. MEA is a hazardous material which has a 24 hour MPC of 3.0 ppm in a submarine [1]. It is also highly corrosive to metals and leaks of MEA from the scrubber unit also pose significant health problems. Other methods of removing carbon dioxide from the atmosphere of submarines require investigation since this potential exposure to MEA is a significant concern to submariners.

Membranes which selectively separate carbon dioxide from air could conceivably be incorporated into systems for submarine atmosphere control. The application of semi-permeable membranes for the separation of carbon dioxide from atmospheres has received sporadic research attention, with very little development towards commercialization. Most work in this area has proceeded under defence or space exploration contracts. In this review the types of polymers which have been investigated for separation of gases are considered, with a view to identifying the best membrane devices for the separation of carbon dioxide from air. The commercial application of membranes for gas separation and the research and development towards new membranes reported in the open literature do not constitute a complete coverage of membrane technology because a considerable number of research and development reports are unaccessible industrial, defence and space agency research publications. This review is not therefore exhaustive and must be considered an overview of membrane systems worthy of consideration for the removal of carbon dioxide from the atmosphere of the Collins class submarine. Submarine atmospheres are distinguished by the need to remove a large quantity of carbon dioxide present in low concentration in a large floodable volume, over a long period with restrictions on power, size, mass, volume and "foot print". The existing MEA scrubber unit is expected to just meet the MPC specifications, but presents some potential toxic and corrosive hazards. Considering the significant developments in membrane technology in other applications, it is appropriate to examine its potential for this unique application.

# 2. *Discussion*

## 2.1 *Requirements of a Membrane*

The role of a membrane in a separation process is to act as a selective barrier, permitting the preferred passage of a certain component (permeate gas) out of the mixture (feed gas). Gases permeate through thin polymer membranes at different rates, and by adopting the appropriate polymer material and physical parameters, gases may be selectively separated. When considering membrane separation of gases the process for a permanent gas is governed by Fick's First Law of Diffusion:

$$\mathrm{d}v/\mathrm{d}t = (PA.{}^{*}p)/T$$

where $\mathrm{d}v/\mathrm{d}t$ is the gas flux rate through the membrane; $P$ is the permeability constant of the membrane for the gas; $A$ is the membrane surface area; $T$ is the membrane thickness and ${}^{*}p$ is the partial pressure differential across the membrane. Although carbon dioxide is not a permanent gas this relationship identifies the main parameters that must be considered, especially when the membrane is also permeable to oxygen and nitrogen. A good membrane is one which has a large permeability yet minimized membrane surface area with an enhanced selectivity or separation factor (ratio of permeabilities for different gases).

As Fick's first law of diffusion defines the isothermal diffusion of a pure gas through a membrane subject to a pressure mixture of gases (feed gas) [2], the selectivity of the membranes could be controlled by changes in the temperature and pressure associated with the membrane and the feed gas. To obtain the partial pressure differential across the membrane the feed gas is normally compressed on one side while the other side is evacuated to maintain a lower pressure. The product streams are the low pressure extract, rich in one gas, and the high pressure raffinate, rich in the other component gas(es) [3]. In submarine atmosphere control the raffinate needs to be oxygen/nitrogen while the extract contains only carbon dioxide. That is, the membrane must selectively pass only carbon dioxide because a submarine cannot allow the loss of any other atmospheric gas, especially oxygen and nitrogen. Assuming that gas solubility is proportional to the gas partial pressure (Henry's Law), and the diffusion coefficient is independent of time, position and concentration [3], then the only process variables to be considered are those defined within Fick's first law of diffusion. Other factors to be considered in the development of the membranes are the durability, strength, geometry, chemical resistance, temperature resistance and response to humidity of the membrane. That is, the membrane must be robust and "void free", and ideally configured into a cartridge unit for ease of handling by the submariners. A working temperature range of 20 to 35°C must be tolerated without change to the selectivity of the membrane because this will be the working temperature range on a submarine. To function as a life support system on a submarine with a crew of 46 men, the membrane system must remove 2.2 kg of carbon dioxide per hour from the air, which represents approximately 0.6% of the total air vented through the scrubber unit at a flow rate of 200 $m^3$ per hour. With regard to separation efficiency of carbon dioxide from oxygen/nitrogen, this parameter is obviously dependent on the type of polymer used to form the membrane. However, it has been concluded that "no practical gas separation can be performed with conventional (solid state polymeric) membranes in a conventional (single stage) package" [3]. Staging the process to achieve higher separation requires increased energy and membrane area, which would have defined limitations on a diesel powered submarine. Table 1 lists selected polymers and their separation factors for the main constituents of air.

For a submarine life support system the membrane device requires a high separation factor (selectivity coefficient) of $CO_2/O_2$ and $CO_2/N_2$, since the closed environment must not lose nitrogen or oxygen. From the data cited it may be suggested that the dimethyl silicone (DMS) rubber is the best candidate solid polymer membrane for carbon dioxide removal from air, however its oxygen permeability is too high for a closed environment. For a life support system it is imperative that the separation factor of carbon dioxide to oxygen be at least 100 to be effective [6]. Consequently even DMS is not practical for a membrane device to serve as a component in a submarine life support system.

*Table 1: Selected selectivity coefficients for some polymers**

| Polymer | $O_2/N_2$ selectivity | $CO_2/O_2$ selectivity | $CO_2/N_2$ selectivity |
|---|---|---|---|
| Saran | 5.0 | 5.7 | 30.0 |
| Mylar | 6.0 | | |
| Nylon-6 | 3.8 | 4.2 | 8.0 |
| Polyvinyl chloride | 3.0 | | |
| Methyl cellulose | 2.5 | 10.9 | 31.1 |
| Polystyrene | 7.6 | | |
| Butyl rubber | 4.1 | | |
| BPA polycarbonate | 6.7 | | |
| Polyethylene | 2.8 | | |
| Natural rubber | 2.7 | | |
| Dimethyl silicone rubber (25%) | 2.2 | 5.4 | 11.6 |
| Teflon | | 0.29 | 0.81 |
| Polyvinyl chloride - vinyl acetate | | 6.7 | 26.7 |

* The oxygen permeabilities of Saran, Mylar, nylon-6, PVC, MC, PS, BR, BPA-PC, PE, natural rubber and DMS (25%) are 0.0005, 0.0019, 0.004, 0.014, 0.08, 0.12, 0.14, 0.16, 0.8, 2.4 and 60.0 [cc (STP), cm/s, $cm^2$, cmHg] $\times 10^9$ respectively [3]. The $CO_2$ permeabilities for Saran, nylon-6, CA, DMS and PVC-VA are 0.003, 0.016, 0.87, 325.0 and 1.6 [cc (STP), cm/s, $cm^2$, cmHg] $\times 10^9$ respectively [5].

## 2.2 *Membranes for Carbon Dioxide Removal*

### 2.2.1 *Gas/Gas Separation Using Solid Polymers*

The most relevant investigations to submarine atmosphere control using membranes for gas/gas separation have been reported by Sarich [5], describing the development of permeable membranes for carbon dioxide scrubbing in naval citadel systems, submarines, saturation diving systems, underwater habitats and self-contained breathing systems (Table 1). Staging or a "cascade" of membrane units would be required to increase the separation performance at the expense of increased power consumption. The latter is not readily available on a diesel powered submarine, whereas Sarich's suggestion [5] was based on the power facility of the US nuclear powered submarines. Consequently a staging of DMS devices would not be viable for the Collins class submarine. Nylon-6 hollow fibres have also been considered for submarine atmosphere control but were shown to be unsuitable since they impose excessive volume and power requirements on a submarine [5, 7]. Notwithstanding the fact that DMS membranes possess more potential for carbon dioxide separation than any other pure polymer or composite investigated to date, there has been no commercial application of these membranes, possibly because even this polymer cannot separate enough carbon dioxide from air to be of any commercial advantage over other carbon dioxide scrubbing methods available.

### 2.2.2 *Membrane Contactors*

As the closed environment of a space vehicle is similar to that of a submarine, it is relevant to consider the membrane technology investigated for spacecraft life support systems. NASA has investigated the use of membranes in a gas/liquid process for the life support system of long-duration space missions with the aim of developing a carbon dioxide scrubber component of a regenerable closed environment [8]. The device is based on a membrane-contactor/liquid-sorbent design, where the membrane is not a solid polymer but a gas permeable microporous hollow fibre polymer of a proprietary nature. The principle of carbon dioxide separation in this system is based on circulating the carbon dioxide-rich cabin air through one side of a hollow fibre absorption membrane-contactor. Only carbon dioxide is absorbed into the liquid sorbent which is circulated on the other side of the membrane-contactor. The carbon dioxide-rich liquid sorbent is then heated and circulated by pump to a second hollow fibre regeneration membrane-contactor. At the regeneration membrane-contactor the carbon dioxide is removed by establishing a low pressure on the other side of this membrane. The regenerated sorbent is then cooled and returned to the absorption membrane-contactor. A process using only the liquid sorbent of this membrane contactor process may possibly be applied to submarine atmospheres without using the membrane contactors, especially if the liquid sorbent is less toxic and less corrosive than MEA.

### 2.2.3 *Facilitated Transport Membranes*

It is apparent that in order for a system to have great potential to meet the scrubbing requirements of a submarine atmosphere control system it must be based on a hybrid membrane/liquid sorbent device using "facilitated transport". The development of such a device in the 1960s, known as an immobilized film membrane (IFM), offers much promise to meet this requirement. The IFM device was researched under a US Air Force contract to separate carbon dioxide from air [6, 9, 10] but has not been developed for commercial use. The best IFM device constructed to date was made using a porous cellulose acetate (CA) membrane 0.007 cm thick, similar to that made for a reverse osmosis process for desalination. The CA membranes were impregnated with a saturated cesium bicarbonate solution containing 0.5 M sodium arsenite catalyst, and this solution trapped within the porous membrane forms the immobilized liquid film. The transport of carbon dioxide across the film is facilitated by the diffusion of bicarbonate from one side of the membrane to the other. The principle reactions occurring in the film are:

1. $CO_2 + H_2O \rightarrow H^+ + HCO_3^-$

2. $2HCO_3^- \rightarrow CO_2 + CO_3^{2-} + H_2O$

The mechanism of carbon dioxide transport across a bicarbonate/carbonate film may be described as follows. On the side of the membrane exposed to a high partial pressure of carbon dioxide, reaction (1) tends to proceed to the right, thus carbon dioxide is absorbed at the surface of the film. This reaction is reversed on the other side of the membrane (reaction 2) where there is a low carbon dioxide partial pressure. This IFM device achieved a remarkable carbon dioxide/oxygen separation factor of 4100. Variations in this IFM construction have been reported [11, 12], however, the construction indicated above was developed further by Neulander and Martin [13] for a NASA life support system in 1971. This life support system served as a one-man life support system on a spacecraft and for an astronaut extravehicular back-pack. Further development and scale-up of this IFM system has not been recorded in the open literature, which suggests that it is either subject to NASA intellectual property restrictions or that the project has been terminated. The termination of many defence funded projects around 1971 to 1975 followed the decision to specialize in electrolysis of water (Bosch and Sabatier processes) for oxygen production, and monoethanolamine-based scrubber units for the removal of carbon dioxide. Notwithstanding these speculations, this IFM is the only membrane system worthy of consideration for scale-up development as a component of the Collins class submarine life support system. Factors to be considered in such a scale-up would be (1) whether the composition of the IFM could be maintained in a high gas flow of moderate humidity and (2) the effect of composition changes on the performance after scale up. An investigation to find alternative catalysts that meet the RAN specifications for carbon dioxide removal efficiency would also be required, even though the carbon dioxide/oxygen separation factor (selectivity coefficient) may not be optimal. With respect to systems incorporating arsenites as catalysts, it would be necessary to develop a filtering system to prevent the release of any arsenite into the atmosphere. Based on the volatility of these compounds, it is not envisaged that such problems would be a major concern, rather, a precautionary step.

# 3. *Conclusions*

It is evident that of the large range of pure polymers and composites investigated over the past three decades, siloxanes exhibit the highest permeability for carbon dioxide. Of these compounds a membrane of dimethyl silicone (25%) (DMS) exhibits a high separation factor of 5.4, while cellulose acetate exhibits an even larger separation factor of 10.9. Therefore it may be conceivable that a system incorporating both DMS and CA devices could be investigated for other defence applications. To be of practical use in a submarine life support system the membrane device must exhibit a separation factor of at least 100, and the only device known to meet this requirement is a facilitated transport membrane based on immobilized liquid films. The IFM device achieves a separation factor of 4100, and consequently is considered to be the only membrane system worthy of further research and development for RAN purposes. Another system worthy of consideration for the Collins class submarine atmosphere control or alternative life support system applications would be a liquid-sorbent recirculating system based on a bicarbonate/arsenite liquor. A project involving the IFM device has commenced at this laboratory, while the capacity of the liquid-sorbent recirculating system is to be evaluated later. Other current approaches to the removal of carbon dioxide from submarine atmospheres are (1) the photosynthetic conversion of carbon dioxide to oxygen using a euryhaline marine alga in a photobioreactor and (2) the high energy UV photolysis of carbon dioxide to oxygen and carbon monoxide. The application of an IFM device as a component of these photolysis based systems could also improve their overall efficiency.

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ABSTRACT

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