

Carbon Membrane Separator for Elimination of SF₆ Emissions from Gas-Insulated Electrical Utilities

Gil Dagan, Giora Agam, Vitaly Krakov, Len Kaplan.
Carbon Membranes Ltd, Rotem Industrial Park, D.N. Arava 86800, Israel.
☎ (972) 7 6555961 📠 (972) 7 6554888 e-mail c_m_l@netvision.net.il

Introduction

The electric power industry uses sulphur hexafluoride (SF₆) as a gaseous dielectric in circuit breakers, gas-insulated substations, and switchgear. This industry uses about 80% of the 6,500 to 7,500 metric tons of SF₆ produced worldwide each year.⁽¹⁾ The reason for this high consumption is not only the “natural growth” in the electric power industry but also significant SF₆ emissions from the above-mentioned systems.

Recently, two important issues are causing the industry to renew its concern about the use of SF₆ for this purpose.

The first issue is the increasing cost of SF₆ due to changes in the fluorine and fluorine derivatives market. Small consumers may pay up to \$25 per kg of SF₆, and the price is expected to rise.

Besides its price, SF₆ is a very potent greenhouse gas. The global warming potential of this gas is 23,900 times greater than that of CO₂, and its atmospheric lifetime is about 3,000 years. Estimates place 1997 U.S. emissions of SF₆ at 7 million metric tons of carbon equivalent (MMTCE); a significant proportion of these emissions is naturally attributable to the electric power industry.

International concern over the global warming phenomenon has already resulted in efforts to reduce SF₆ emissions, and may produce limiting regulations in the future.

Most SF₆ emissions occur during the process of venting air that accumulates within dielectric gas and reduces its efficiency. Hence, a possible way to reduce SF₆ emissions is to capture and reuse the SF₆ in the vented gas. A relatively simple recycling system can be designed using membranes which will permeate air faster than SF₆. Obviously, the performance of the recycling system is in tight correlation with the membrane permeance (the flux of the fast gases through a certain membrane area) and selectivity (the ratio between the permeances of the fast and slow components of the mixture).

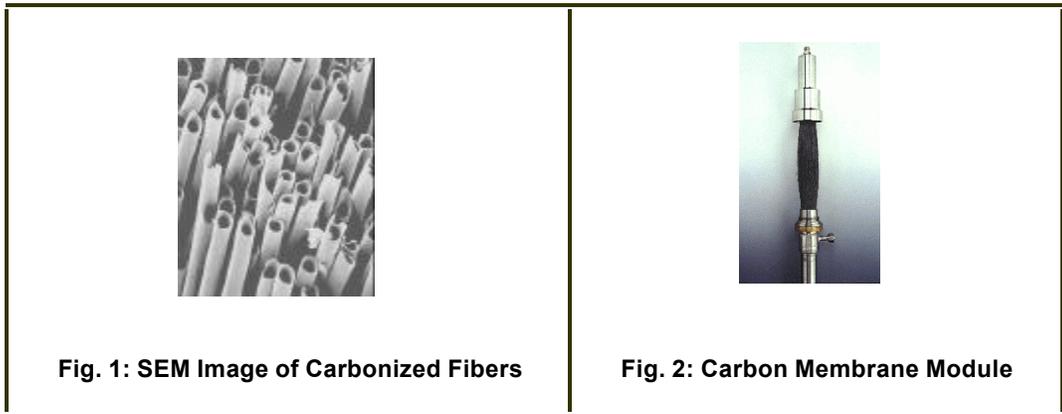
This paper describes a tailor-made carbon molecular sieve membrane (CMSM), optimized specifically for the separation of PFC gases (e.g., SF₆, C₂F₆, etc.) from various “fast” gases (e.g., air, CO₂, etc.). The tailored CMSM has both high air permeance (500 lit/m²*bar*hr) and excellent selectivity - the SF₆ is virtually completely retained by the membrane. The result is a superb separation whereby the SF₆ can be concentrated to more than 99% purity with 99.7% recovery.

The Carbon Molecular Sieve Membrane

Carbon membranes are thin porous layers of carbonized polymers, with pore size distribution adapted to gas separations. There are flat as well as hollow fiber carbon membranes, either coating a very porous support or homogenous (only in material, not necessarily in the inner structure) such as CMLs. Such hollow fiber membranes were developed [2] and now are commercially produced by Israel's Carbon Membranes Ltd.

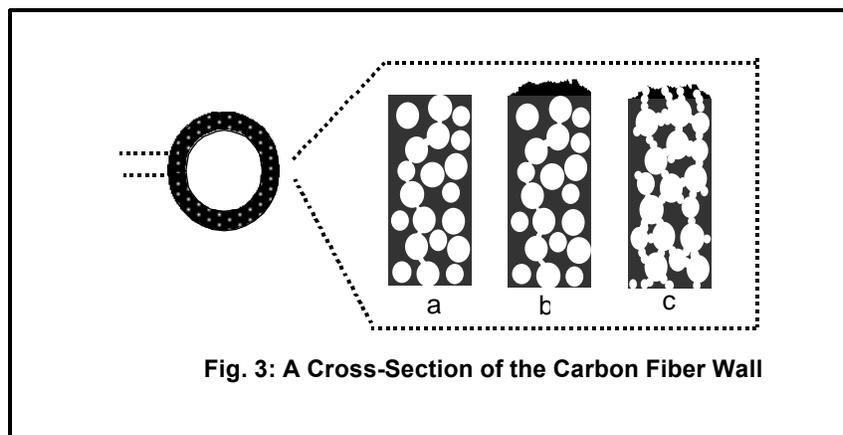
The production of this membrane is composed of three main stages. The first stage is to carbonize a bundle of polymeric precursor fibers. The carbonized fibers (Fig. 1) are potted together to form a module (Fig. 2), while any broken fiber is clogged and thus neutralized.

The third production stage is tailoring the pore size distribution within the membrane fiber walls to the specific separation task this module is meant to perform. The fact that the same membrane can be adapted for optimal performance in various separation applications is a major advantage of this type of membrane.



After carbonization, the wall of the carbonized fiber is already porous (Fig. 3a), but the pores are rather small and randomly interconnected. As a result, permeation rate is low for all of the gases, which means also a poor selectivity.

In order to plug these random passages through the membrane wall, the inner side of the fibers is coated in a CVD process with a thin dense layer of carbon (Fig. 3b).



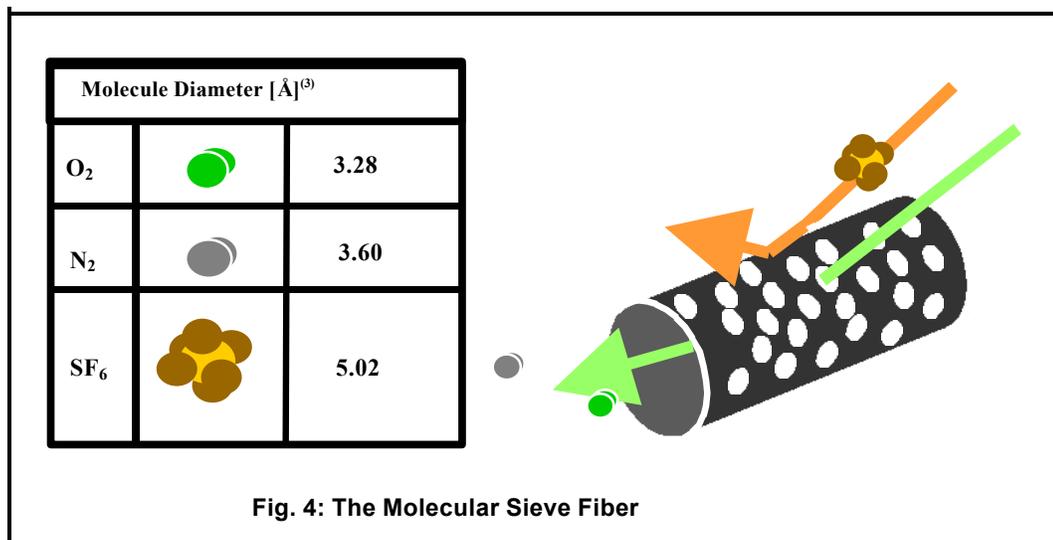
After the CVD coating, the membrane is actually not permeable for all gases. At this stage comes the process of gradually opening up the passages through the membrane wall (Fig. 3c). The pores are progressively opened by a very controlled method; the result is a narrow pore size distribution. The intensity and duration of this pore development process determines the pore diameter and the adaptation of the module to a certain application. The mechanism of the separation, or the selective transfer of molecules through the porous membrane, will be explained in the next chapter.

The Molecular Sieving Mechanism

Molecular sieving is a mechanism whereby different molecules are separated because of their different size. For the porous carbon membrane, this is the main (but not always the only) separation mechanism.

As was described above, the size of the pores along the carbon fiber membrane walls can be controlled during the production process. Hence, it is possible to “tailor” the pore size distribution so that virtually all of the pores’ diameters will fall between the size of the large and small molecules of the gas mixture to be separated. When the gas mixture is circulated around the molecular sieve fiber, the molecules smaller than the pores will readily penetrate through the fiber wall and will be concentrated in the fiber’s lumen. The larger molecules, on the other hand, can hardly pass through the pores, and hence will be concentrated on the outside of the fiber (Fig. 4). Obviously, this process can happen only with sufficient driving force, i.e., the partial pressure of the “faster” gas on the outer side of the membrane should at all times be higher than that on the inner side.

The big difference in molecular size between SF₆ on one hand and air components (as well as CO₂) on the other hand makes the separation of these gases very efficient. Single gases’ permeance measurements show that N₂ permeance is more than 500 lit/m²*hr*bar, while SF₆ is completely retained by an appropriately tailored membrane.



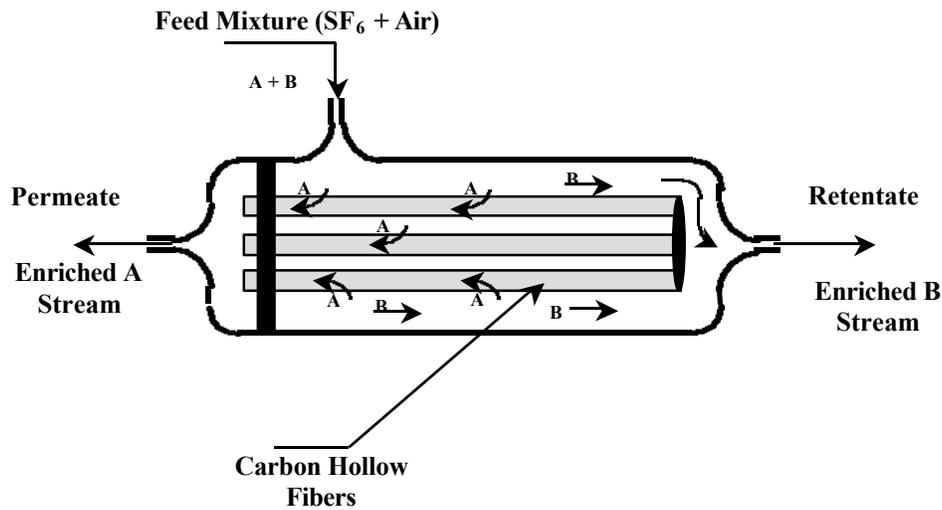


Fig. 5: Gas Separation Module

The SF₆ Recovery/Air Removal System

The schematic drawing in Fig. 6 demonstrates the simple design of the air removal system. The air containing SF₆ from the gas source (reservoir, GIS, conventional gas cart, etc.) is recycled through the one-stage carbon membrane separator. The clean air is constantly removed, while the SF₆ is recycled back to the gas vessel.

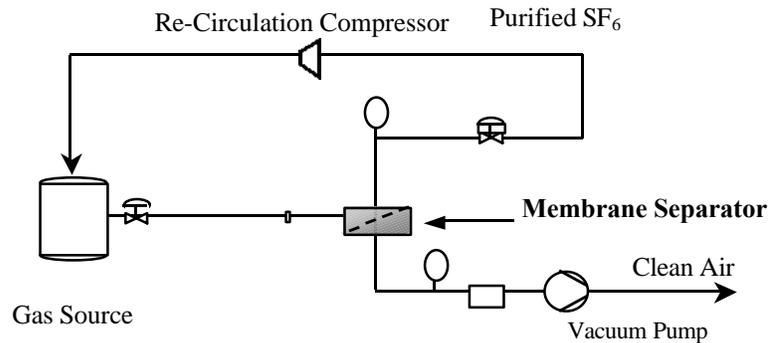
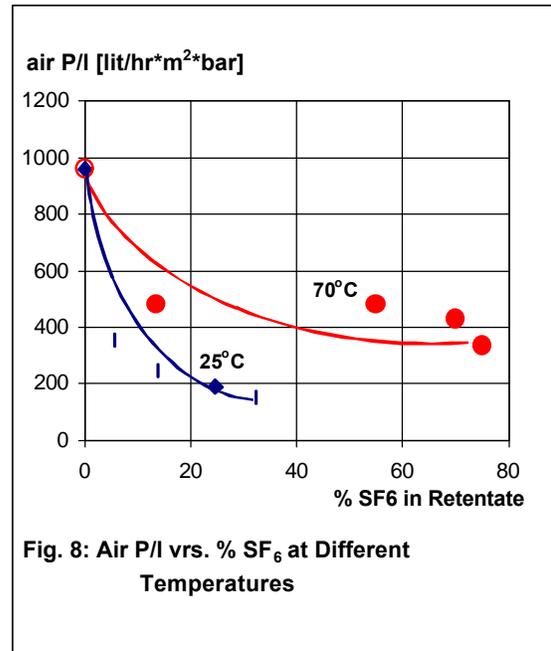
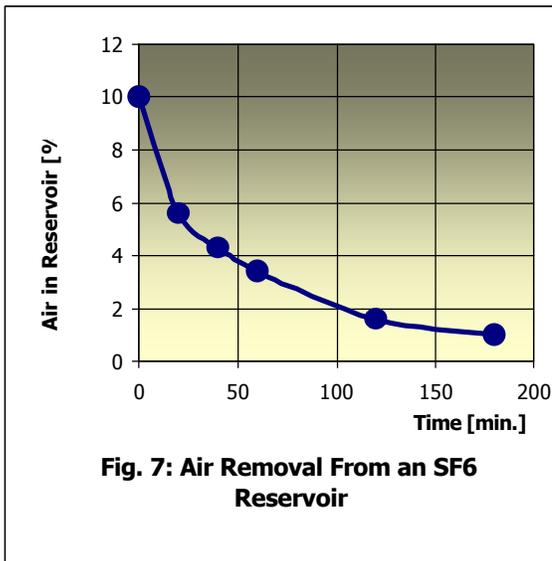


Fig. 6: SF₆ Recovery System

Results and Discussion

Fig. 7 shows the air removal rate. These measurements were made at 50 psig and with a reservoir capacity of 5 normal liters per 1 m² membrane area. It must be noted that the nonlinear shape of the curve is not only a result of the reduced driving force at lower air concentration, as can be seen in Fig. 8.



Intrapore condensation of concentrated SF₆ partially clogs the membrane's pores and thus reduces air flux. Fig. 8 shows that operating the membrane at elevated temperature eliminates the pore condensation and improves the performances of the membrane at high SF₆ levels, possibly thanks to the carbon thermal stability.

Conclusions

The high flux and selectivity of the carbon membrane separator enables the design of a single-stage SF₆/air separation system.

Such a system purifies the insulation gas of high voltage electric devices to a level >99%, with 99.7% SF₆ recovery, meaning practically no loss of this valuable and environmentally harmful gas.

Operating at a moderately elevated temperature can further improve the productivity of the separation system.

References

1. Technical Committee Report, International Magnesium Association, 1998
2. Soffer, A., et al., Process for the Production of Hollow Carbon Fiber Membranes, EP 5,925,591, 1995
3. Koresh, J., and Soffer, A., *Journal of Colloid and Interface Science*, Vol. 92 No. 2 p. 517, 1983