

A Tailor-Made Membrane for SF₆ Recycling – An Environmentally Friendly Method to Reduce Costs

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Introduction

For the past 25 years, mixtures of SF₆/air or SF₆/air/CO₂ have served the magnesium industry as the main melt protection gas. Recently, two important issues are causing the industry to renew its concern about melt protection and 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 customers may pay up to \$25 per kg of SF₆, and the price is expected to rise. For a melt surface of 1 square meter, with an enclosure volume of 100 liters, the 0.2% SF₆ mixture feed rate should be about 10 lit/min [1]. This results in an SF₆ cost of 25 cents per hour for the aforementioned small unit. Worldwide, the SF₆-related expenses of the magnesium industry total millions of dollars each year.

Besides its price, SF₆ is also a very potent greenhouse gas. The global warming potential of this gas is 24,900 times greater than that of CO₂, and its atmospheric lifetime is about 3,000 years. International concern about the global warming phenomena has already resulted in efforts to reduce SF₆ emissions and will likely cause limiting regulations in the future.

One way of dealing with these two issues is moving back to SO₂ as a melt protection gas. SO₂ is about 10 times cheaper than SF₆ and is not considered a greenhouse gas. But, this gas is extremely toxic with a TLV of 2 ppm (for comparison, cyanide has a TLV of 1,000 ppm). Further, SO₂ is also corrosive and using it will inherently cause severe safety and maintenance problems.

Another possible way to reduce SF₆ emissions is to capture and reuse the vented gas. A relatively simple recycling system can be designed using membranes that will permeate air and CO₂ 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 of 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.

SF₆ Membrane Recovery System

The basic design of the recovery system is quite simple, as can be seen in Figure 1. The description is simplified and does not show the remixing and control components. Nevertheless, it is easy to notice that there is no need for solvents or any other chemicals within this system. Nor are any high-energy consumers, such as distillation or liquefaction units, part of this system.

One of the challenges in the design of such a system is to collect the gas mixture coming out of the magnesium melting vessel with as little as possible dilution by the surrounding air. Even more important is that, for obvious reasons, the collecting system must not cause sub-atmospheric pressure above the molten magnesium.

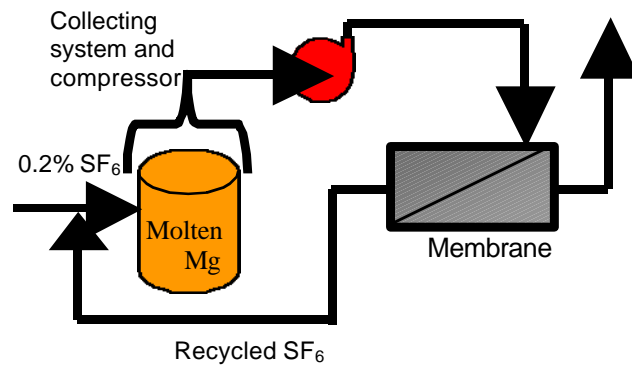


Figure 1: Membrane SF₆ Recycling System

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 a homogenous (only in material, not necessarily in the inner structure). Such hollow-fiber membranes were developed and are now commercially produced by Carbon Membranes Ltd from Israel [2].

The production of this membrane consists of three main stages. The first stage is to carbonize a bundle of polymeric precursor fibers. The carbonized fibers (Figure 2) are potted together to form a module (Figure 3), while any broken fiber is clogged and thus neutralized.

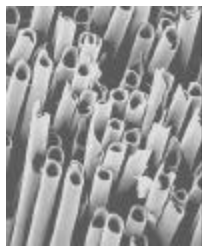


Figure 2: SEM Image of Carbonized Fibers



Figure 3: Carbon Membranes Module

The third production stage is tailoring the pore size distribution within the membrane fiber walls to the certain separation task that this module performs. The ability to adapt the same membrane to optimal performances for various separation applications is one of the advantages of this type of membrane.

After carbonization, the wall of the carbonized fiber is already porous (Figure 4a), but the pores are rather small and randomly interconnected. As a result, permeation rate is low for all of the gases, which also means a poor selectivity.

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 (Figure 4b).

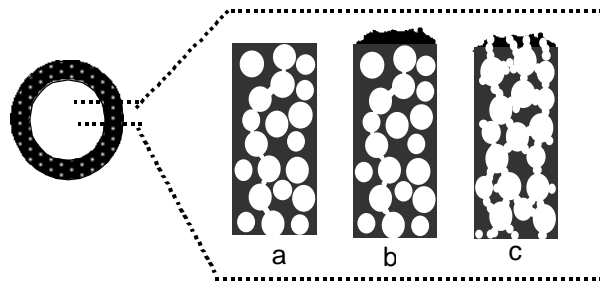


Figure 4: A Cross-Section of the Carbon Fiber Wall




After the CVD coating, the membrane is actually not permeable for all gases. At this stage, the process that gradually opens up the passages through the membrane wall (Figure 4c) is initiated. The pores are gradually opened by a very controlled method, and the result is a narrow pore size distribution. The intensity and duration of this pore development process determines the pores' 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 section.

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 membrane fibers 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' diameter will fall between the size of the big and small molecules of the gas mixture to be separated. When the gas mixture is blown 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 bigger molecules, on the other hand, can hardly pass through the pores and hence will be concentrated on the outside of the fiber (Figure 5). 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 always be higher than that on the inner side).

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

Molecules Diameter [Å] ⁽³⁾		
O ₂		3.28
N ₂		3.60
SF ₆		5.02

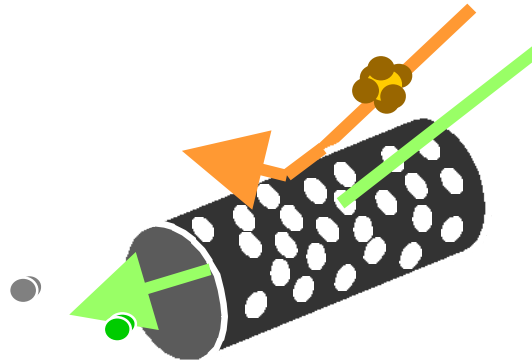


Figure 5 : The Molecular Sieve Fiber

Results and Discussion

The actual separation of SF₆ from air gases with the carbon membrane was tested using mixtures with a wide range of SF₆ concentration. The selectivity, or the separation factor, of the membrane was compared with that of polymeric membranes (Figure 6). The better selectivity of the carbon membrane results in higher SF₆ recovery rates for a certain extent of N₂ removal. (Being the “slowest” gas of the three, and hence most difficult to separate from SF₆, the N₂ represents also O₂ and CO₂). High removal rate of N₂ means that it becomes very diluted on the high-pressure side of the membrane. The effort to further remove N₂ will cause larger and larger quantities of the now concentrated SF₆ to pass through the membrane as well. For this reason, the real test of a membrane selectivity - or the quality of the separation this membrane could perform - is the “slow” gas recovery rate at high rejection, or removal rate, of the “fast” gases.

Besides the selectivity of a membrane, another important parameter is its permeance, or the flux through a unit area of the membrane at a unit time and at a unit partial pressure difference across it.

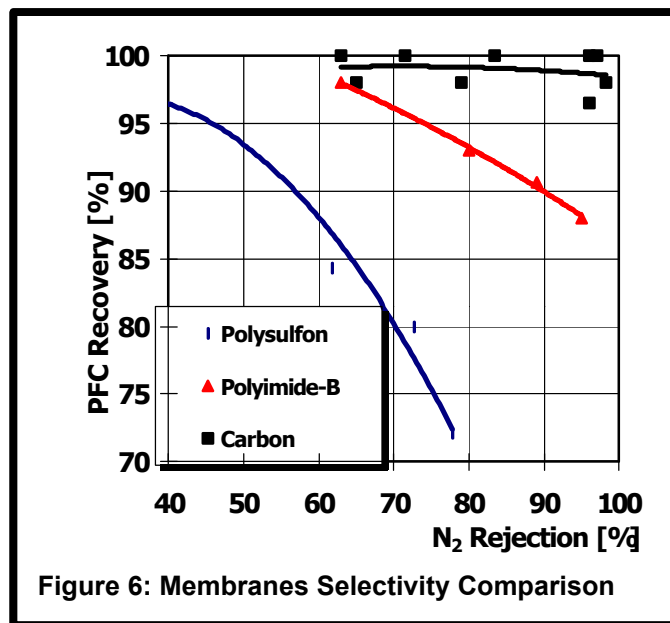


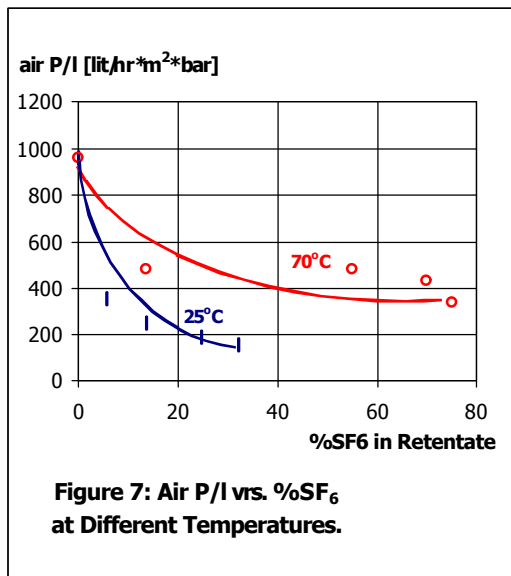
Figure 6: Membranes Selectivity Comparison

The productivity of a membrane, or the amount of gas mixture it will separate under certain conditions and in a given time, is proportional to the permeance figure of this membrane.

As was explained above, the mechanism by which gas permeates the carbon membrane is molecular sieving. The advantages of this mechanism over the diffusion mechanism of polymeric membranes are the aforementioned superb selectivity (Figure 5) and also a much higher permeance.

When separating a real gas mixture to its “fast” and “slow” components, there are interactions between the mixture’s gaseous components. The result of these interactions is an interference of each gas with the other’s permeation rates.

In the case of SF₆ separation, the heavy molecules of this gas, when concentrated, tend to



partially clog the membrane’s pores and thus reduce the flux of air or CO₂ (Figure 7). Elevating the operation temperature of the membrane module to 70°C significantly improves the air flux, probably because of the lower adsorption rate of SF₆ molecules upon the carbon face of the fibers.

It is important to note that despite the reduction in air flux at high SF₆ concentrations, the membrane permeance, even at room temperature, is not low at all. The level of permeance shown in Figure 7 is in any case several times higher than that of polymeric membranes.

In conclusion, the separation performances of the specially tailored carbon molecular sieving membrane are superior both in selectivity and productivity. SF₆ recovery units equipped with a low surface area of this membrane can recover more than 99.5% of the SF₆ while concentrating it to any desired value between 1% and 99%.

Conclusions

The high cost of SF₆, together with its environmental impact, drive the search for methods to reduce the emission of this gas.

Membranes can efficiently separate SF₆, making possible the design of cost-effective recycling systems.

Carbon molecular sieve membranes have extremely high selectivity. With these membranes, more than 99.5% of the SF₆ can be recovered.

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.