Membrane Systems for Recovery of CFC-12 and Other Aerosol Propellants

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INTRODUCTION

The phaseout of ozone-depleting substances like CFC-12 has placed tremendous pressure on many industries to find workable replacements or to find effective ways of recovering and recycling existing supplies. In industries where use of these substances is expected to continue beyond the production phaseout date, short supplies and high prices of chlorofluorocarbons (CFCs) will demand careful conservation of these materials. The medical aerosol industry, which received a tentative exemption from the 1978 ban on aerosol use of CFCs until an acceptable alternative could be found, currently uses CFC-12 as a propellant in metered-dose inhalers. Because CFC-12 is so volatile, a significant amount of the vapor is lost to the atmosphere during container filling and testing. Conventional vapor recovery methods, such as carbon or zeolite adsorption or condensation, do not effectively recover CFC-12.

A new separation technology, called VaporSep™, is able to recover 90-99% of the CFC vapor from the aerosol filling process. The recovered material can be recycled directly or reclaimed at a fraction of the cost of new material. VaporSep™ recovery systems are based on polymeric membranes that are much more permeable to organic compounds than they are to air. These systems have been successfully demonstrated for the recovery of CFCs, hydrofluorocarbons (HFCs), and other volatile organic compounds, such as hydrocarbons, and chlorinated hydrocarbons.

The VaporSep™ process has recently been installed at Nu·Pharm, Inc. to recover CFC-12 emitted during filling of medical aerosol containers. With minor modification to the filling enclosure and installation of the VaporSep™ system, Nu·Pharm will recover more than

90% of the CFC-12 losses. The membrane process will also recover HFC-134a with equal efficiency.

MEMBRANE PROCESS PRINCIPLES

The key element of the membrane vapor recovery process is a high-flux composite polymeric membrane that is 10-100 times more permeable to organic compounds than to air. The membrane consists of a very thin, organic-selective top layer, and a porous support layer. The top layer performs the separation; the porous support provides mechanical properties necessary for manufacturing strong, defect-free membranes. A non-woven fabric serves as the backing material for the composite membrane structure.

The vapor separation membrane is incorporated into a two-step process that combines membrane separation with compression-condensation. The membrane separation step enhances the recovery possible with compression and condensation alone, allowing the process to operate at much higher recovery rates, or allowing the same recovery at higher temperature and/or lower pressure conditions.[1]

The basic VaporSep™ process is shown in Figure 1. A vapor/air mixture is first compressed to 45-200 psig. The compressed mixture is sent to a condenser, where a portion of the organic vapor condenses and is directed to a solvent storage tank for recycle or reuse. The non-condensed portion of the vapor/air mixture passes across the surface of MTR's high-performance organic-selective membrane. The membrane separates the gas into two streams: a permeate stream containing most of the remaining solvent vapor from the condenser, and a solvent-depleted stream essentially stripped of organic vapor. The permeate stream is drawn back into the inlet of the compressor. The solvent-depleted air is vented from the VaporSep™ system, or may be recycled to create an closed, emission-free loop.

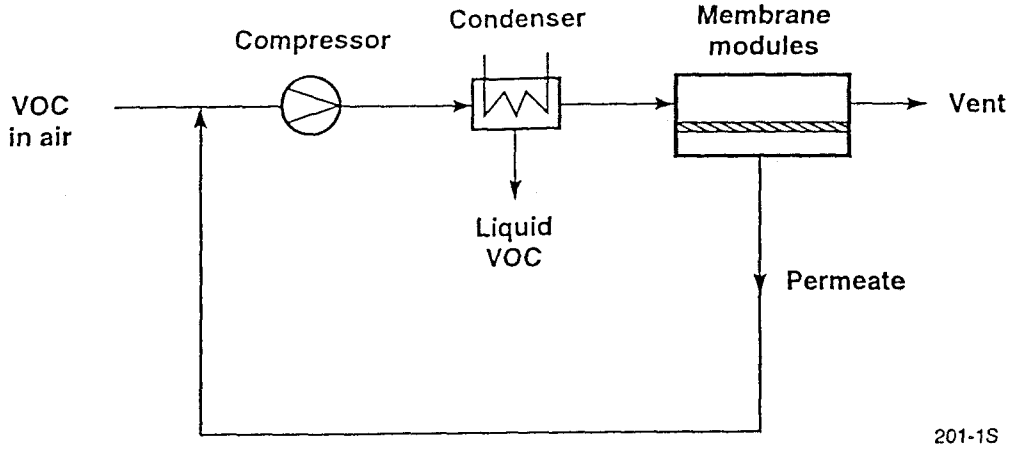

Figure 1. Flow diagram of a membrane vapor separation process.

Transport through the membranes is induced by maintaining a lower vapor pressure on the permeate side of the membrane than on the feed side. This pressure difference can be achieved by compressing the feed stream, as shown in Figure 1, or by using a vacuum pump on the permeate side of the membrane. In some cases, a combination of vacuum on the permeate stream and compression on the feed stream is used.

Air and organic vapor go through the membrane at rates determined by their relative permeabilities and the pressure difference across the membrane. Because the membrane is 10-100 times more permeable to organic vapor than air, a significant enrichment of organic vapor on the permeate side of the membrane is achieved. Depending on the system design, between 90% and 99.99% of the organic vapor is removed from the feed air stream.

The membrane vapor separation process shown in Figure 1 has several features that distinguish it from conventional volatile organic compound (VOC) recovery methods. First, the process can accommodate variations in inlet conditions. This feature makes it well-suited for the intermittent, variable emission streams produced by the batch operations common to the chemical and pharmaceutical industries. Because the feed streams are compressed and condensed before entering the membrane modules, the VOC concentration introduced to the membrane is regulated by the delivery pressure of the compressor and the condenser temperature. Second, the membrane vapor separation process serves as its own internal "preconcentrating" device. Even if the original feed stream concentration is below the saturation concentration set by the compressor and condenser, recycle of the enriched permeate stream through the system produces a steady-state concentration high enough for condensation to occur. Thus, unlike recovery by low-temperature condensation, the membrane process achieves high recovery rates even if the initial feed stream VOC concentration is less than 1%.

APPLICATIONS

MTR's membrane VaporSep™ process can be used to treat a wide range of important industrial vapor streams. A list of some organic compounds that can be recovered by this process is shown in Table 1. Ideal applications are those in which recovery can be accomplished upstream, at a point where the vapor concentration is maximized and the total air flow minimized. Some of the most attractive applications involve the recovery of CFCs, and their likely replacement materials, such as hydrochlorofluorocarbons (HCFCs), hydrofluorocarbons (HFCs), and perfluorocarbons (PFCs). These volatile materials are expensive ($1-15/lb) and difficult to recover using conventional processes, such as carbon adsorption and compression-condensation. VaporSep™ systems for the recovery of these and similar compounds are a major advance in separation technology.

Table 1. CFCs and Other Volatile Organic Compounds Recoverable by the VaporSep™ Membrane Process

Acetone	Hexane
Benzene	Methanol
Carbon tetrachloride	Methyl bromide
CFC-11	Methyl chloroform
CFC-12	Methyl isobutyl ketone
CFC-113	Methylene chloride
Chlorine	Perfluorohexane
Chloroform	Toluene
Ethylene dichloride	Trichloroethylene
Ethylene oxide	Vinyl chloride
HCFC-123	Xylenes
HFC-134a	

To date, twenty-six VaporSep™ systems have been installed in full-scale commercial operations. Over half of these systems are recovering CFCs, HCFCs, HFCs, or PFCs. The application of this technology to recover CFC-12 from a medical aerosol filling operation is described in detail below. Related applications, including recovery of CFC-12/ethylene oxide from sterilizer vents, and PFCs from manufacturing processes, are also described.

CFC-12 Recovery from Aerosol Filling

Metered-dose inhalers are used worldwide by approximately 70 million people who suffer from asthma and other respiratory ailments.[2] Approximately 330 million inhalers were produced in 1991. The inhalers rely primarily on CFC-12 as the propellant that delivers metered doses of drugs to the lungs. In 1991, an estimated 14 million pounds of CFCs were used in medical aerosol products, 8.5 million pounds of which were CFC-12.[3] The phase-out of CFC-12 and other ozone-depleting compounds has put pressure on the manufacturers of metered-dose inhalers to develop alternative propellants. While substitute compounds undergo evaluation, the EPA has asked the United Nations Environment Program to grant an exemption that will allow manufacturers of inhalers to continue using CFC-12. The most promising replacement compound, HFC-134a, like CFC-12, is very volatile and expensive. Thus, manufacturers of metered-dose inhalers are driven both by environmental stewardship and by economic incentives to recover the propellants emitted from their operations.

Early in 1994, Nu-Pharm, Inc. of Richmond Hills, Ontario, asked MTR to design a VaporSep™ membrane recovery system to eliminate emissions of CFC-12 from their metered-dose inhaler filling operation. Nu-Pharm uses filling equipment common to this industry. The filling takes place within a 100-ft^3 enclosure. With minor modification to the enclosure to allow efficient capture of the CFC-12 vapor, the VaporSep™ system achieves greater than 90% recovery of the CFC-12 vapors.

The design of the VaporSep™ aerosol recovery system is shown in Figure 2. The vapor/air mixture is pumped from the filling chamber into the VaporSep™ system. The mixture is compressed to a pressure of 190 psig and then sent to a condenser. The condenser is fed with chilled water, which cools the mixture to approximately 5°C. A portion of the CFC-12 condenses inside the condenser and flows into a solvent collection tank. The non-condensed vapor flows into the membrane modules, where it passes across the surface of the MTR composite membrane. This membrane is much more permeable to CFC-12 than to oxygen or nitrogen, so the stream is separated into a CFC-depleted residue and a CFC-enriched permeate stream. The permeate stream is drawn into the permeate pipe located in the center of each module and is then recycled to the inlet of the compressor. A portion of the residue stream is returned to the inhaler filling chamber, and the remaining portion is vented to maintain a negative pressure in the filling chamber.

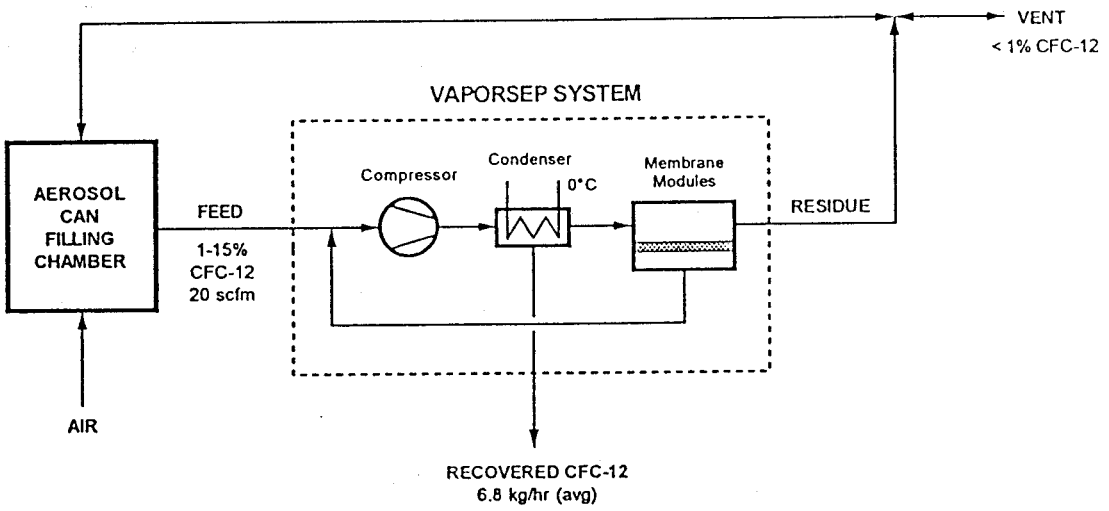

Figure 2. The VaporSep™ system constructed for use in Nu·Pharm's medical aerosol device manufacturing facility will recover 90-95% of all CFC-12 lost during the filling process.

The design basis and guaranteed recovery performance for the Nu·Pharm installation are summarized in Table 2.

Table 2. Design Basis for Nu·Pharm's VaporSep™ Installation

Inlet Flow Rate	20 scfm
Inlet Composition (average)	8 vol% CFC-12
Inlet Pressure	15 psia
Cooling Water Temperature	0° C
Vent Composition	<1 vol% CFC-12
Recovered CFC-12 (average)	6.8 kg/h

Performance data for the system are given in Figure 3 which charts the CFC-12 compositions of the inlet and vent streams during the pre-installation testing of the unit. As the data show, the VaporSep™ system's performance is relatively unchanged by fluctuations in the feed CFC-12 concentration. In this test, the feed CFC-12 concentration was varied from 3.5 to 8 vol%. The final vent concentration never exceeded 0.6 vol%, well below the guaranteed level of 1 vol%.

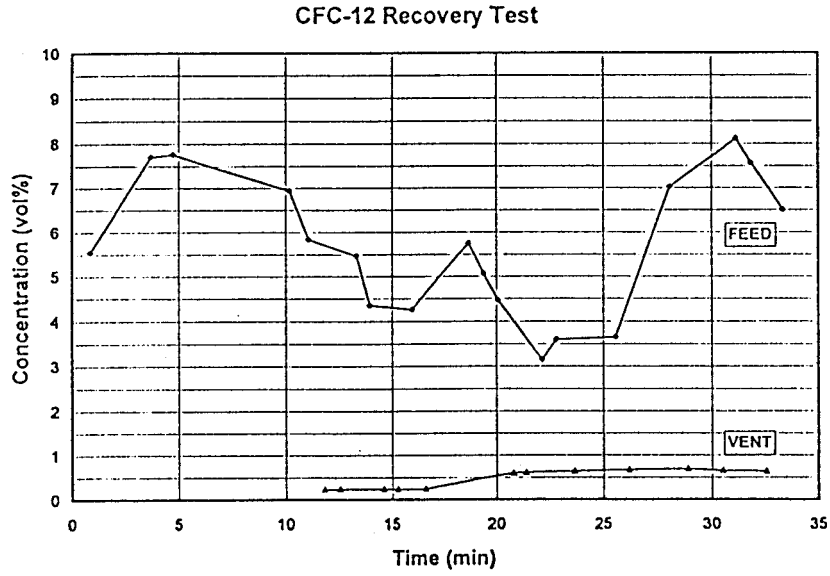

Figure 3. Pre-installation performance of the VaporSep™ system constructed for Nu·Pharm. The amount of CFC-12 vented from Nu·Pharm's process will not exceed 1 vol%, regardless of variation in the inlet concentration.

Nu·Pharm's initial motivation to install CFC-12 recovery equipment was the desire to proactively address the environmental issues associated with CFC usage. The favorable economics of the VaporSep™ installation, however, offer an equally compelling driving force.

The VaporSep™ system will recover an average of $424,000 worth of CFC-12 annually. The annual operating cost of the membrane system, including a charge for capital, is detailed in Table 3. When the appropriate credit is applied for the recovered CFC-12, the VaporSep™ installation results in a net annual savings of $392,000. Compared to low-temperature condensation, the only other viable recovery option for this application, VaporSep™ is much more cost-effective. To achieve equivalent recovery, a condenser temperature of -116°C would be required. The annual cost of the liquid nitrogen coolant alone would be more than double the total operating costs of the VaporSep™ system.

Table 3. Annual Operating Costs of a VaporSep™ System to Recover CFC-12 from Aerosol Inhaler Filling Operations[1]

	Operating Case I (4,200 h/yr)	Operating Case II (6,200 h/yr)
Annual Operating Costs ($):		
Capital charge	17,031	17,031
Maintenance	4,250	4,250
Module replacement	7,000	7,000
Electrical power	3,879	5,819
Chilled cooling water	125	187
Total Annual Operating Costs ($)	**32,285**	**34,287**
Annual Credit for Recovered CFC-12 ($)	424,150	636,225
Total Annual Operating Credit ($)	**391,865**	**601,938**

[1] Assumptions: 20% capital charge, 3-yr module lifetime, $0.05/kWh electricity cost, $0.50/1,000 gal chilled water cost, $6.80/lb CFC-12 value.

Recovery of Sterilizer Vent Gas

MTR has also applied the membrane separation process to the recovery of sterilizer vent gas. Ethylene oxide is a widely used sterilant in both hospitals and industrial applications. Ethylene oxide is flammable and toxic, and it is commonly diluted with a carrier gas such as CFC-12 or HCFC-124 to reduce the flammability hazard. The most common sterilant gas mixture consists of 12 wt% ethylene oxide and 88 wt% CFC-12. The ethylene oxide vented from the sterilization chamber is currently controlled using catalytic oxidation or a scrubbing technique. Due to their ozone depleting properties, CFC-12 and HCFC-124 also require control technology in some states. California and Wisconsin already have regulations in place, and other states are expected to follow their lead.

MTR VaporSep™ technology can be used to recover the ethylene oxide/CFC-12 mixture, as shown in Figure 4. The membrane system is able to recover more than 95% of the sterilant gas mixture, which can then be purified and re-blended. Residual ethylene oxide not recovered by the membrane system is catalytically converted to carbon dioxide and water. The ethylene oxide abator (EtO-Abator™) is an existing product of the Donaldson Company, the market leader in hospital ethylene oxide emission control. MTR and Donaldson collaborated to bring the CFC-12/HCFC-124 recovery system to the market. Eight systems are currently operating.

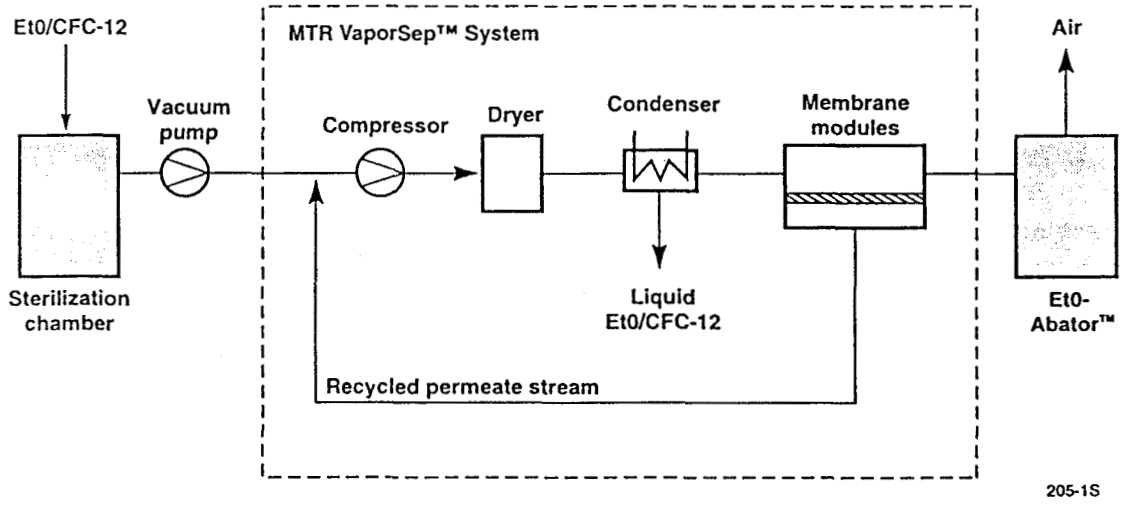

Figure 4. The combination of MTR's membrane process and the Donaldson ethylene oxide abator addresses the recovery requirements for hospital and industrial sterilization applications.

Recovery of Perfluorocarbons

The VaporSep™ membrane process has also been demonstrated for the recovery of perfluorocarbons (PFCs). Liquid PFCs can be used as alternatives to ozone-depleting solvents, such as CFC-113 and CFC-12, in many demanding applications. PFCs have many of the desirable properties of CFCs, but do not contribute to destruction of the ozone layer. Currently, these compounds are used successfully in the electronics and other industries for precision cleaning, spot-free drying, and heat transfer applications; they are also proposed as

alternative propellants for medical aerosol devices. Because PFCs are expensive, their use has been somewhat limited. The availability of high-efficiency recovery technology for PFCs would make them a viable alternative in many processes.

In a recent three-month pilot demonstration, a VaporSep™ membrane system recovered C_6F_{14} (PFC-5060 by 3M) from a manufacturing process. The full-scale system, scheduled for installation in late 1994, will save the customer more than $100,000 each year in recovered PFC.

REFERENCES

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3. J.J. Daly, Jr., "Replacements for CFC Propellants: A Technical/Environmental Overview," Spray Technology & Marketing, February 1993.