MEMBRANE VAPOR SEPARATION SYSTEMS FOR THE RECOVERY OF HALONS AND CFCS

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Since the drafting of the Montreal Protocol, intensive research has been directed at identifying replacement compounds for halons, chlorofluorocarbons (CFCs), and other substances that deplete the ozone layer. It has become apparent that drop-in replacements for these compounds may not be available prior to the mandated phase-out by the year 2000. This is a particular problem for halon 1301, for which no adequate substitute is available.[1,2] Thus, the importance of an aggressive recovery and recycling program is clear. Recovery and recycling of halons now in service can stretch existing supplies into the next century and provide a means of bridging the gap between production phase-out and availability of alternatives.

The recovery of halons and CFCs by conventional technologies is difficult. Efficient recovery of halon 1301 is especially challenging because of its low boiling point and high vapor pressure. Membrane Technology and Research, Inc. (MTR) has developed a halon and CFC recovery process based on membranes that are very permeable to volatile organic compounds. This process has been demonstrated at industrial sites; a number of pilot plants and five commercial systems are in operation. This paper will describe the principles of the membrane process and characterize the most favorable applications for this technology. Specific examples and data from installed systems will be used to illustrate how these membrane systems can be applied to the recovery of halons and other volatile organic compounds.

BACKGROUND

The vapor separation process is shown in its simplest form in Figure 1. A VOC-laden air stream is introduced into an array of membrane modules. The membrane material is permeable to organic vapors, and relatively impermeable to air. After permeation, the organic vapor is condensed and removed as a liquid. The purified airstream is removed as the residue. Transport through the membranes is induced by maintaining the vapor pressure on the permeate side of the membrane lower than the vapor pressure on the feed side of the membrane. This pressure difference can be achieved by means of a vacuum pump on the permeate side of the membrane or by compressing the feed stream. **Air** and organic vapor permeate the membrane at rates determined by their relative permeabilities and the pressure difference across the membrane. Because the

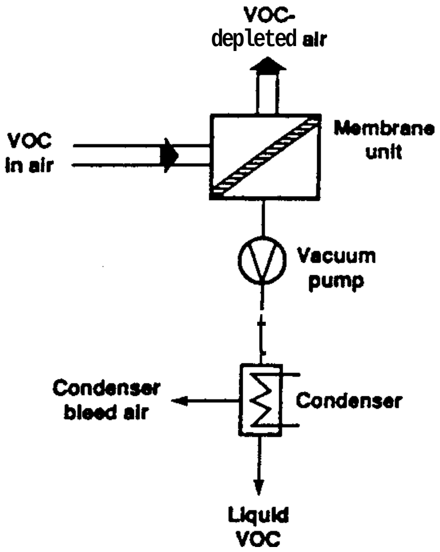

Figure 1. Flow diagram of a membrane vapor separation process.

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 90-99% of the organic vapor is removed from the feed air stream, and a permeate stream, enriched 5- to 50-fold in organic vapor, is produced.[3-7]

To achieve an effective and economical separation, the membrane system shown in Figure 1 must meet three requirements. First, the membrane materials must have adequate selectivity for organic vapors from air. Second, these materials must be formed into high-flux, defect-free membranes. Third, these membranes must be formed into space-efficient, low-cost membrane modules. MTR has developed composite membranes and spiral-wound modules that meet these requirements.

MTR vapor separation systems can be used to treat a wide range of organic vapor streams. Ideal streams are those in which recovery can be applied up-stream, at a point where the VOC concentration is maximized and the total air flow minimized. One of the most promising application areas is the recovery of chlorinated hydrocarbons, chlorofluorocarbons (CFCs), hydrochlorofluorocarbons (HCFCs), and halons.[8] Most of these solvents are expensive (typically \$1-10/lb) and difficult to recover using conventional processes, such as carbon adsorption and compression/condensation. MTR's membrane systems for the recovery of halons, CFCs, and HCFCs represent a major advance in separation technology for these streams.

To illustrate how the membrane vapor recovery process is applied, three representative installations are described below. A total of seventeen VaporSep systems are in operation; five of those are full-scale commercial installations.

Vinyl Chloride Recovery from PVC Manufacturing

An example of an application where membrane vapor separation has dramatic advantages over alternative technologies is the retrofitting of an existing vent condenser with a membrane unit.[9] A VaporSep system has been installed in this way to recover vinyl chloride monomer from the polyvinyl chloride (PVC) manufacturing process. PVC manufacture, and many other polymerization reactions, produce an off-gas stream that contains a significant amount of unreacted monomer. Most PVC processes compress and cool this off-gas to recover a portion of the unreacted vinyl chloride monomer. However, vinyl chloride is extremely volatile (boiling point, -13 "C) and the condenser vent still contains up to 50% vinyl chloride. Because of the toxicity of vinyl chloride, most **U.S.** PVC manufacturers incinerate this condenser vent stream.

The installation of **an MTR** membrane vapor recovery system allows **90-99%** recovery and **direct** recycle of the vinyl chloride from the condenser vent, eliminating the need for an HCI scrubber on the incinerator. The process is illustrated in Figure **2.** The vent gas from the process is compressed to 65 psig and liquid vinyl chloride is condensed from this stream at -10 "C. The vent from this existing condenser, containing up to 50% vinyl chloride monomer, is sent to the membrane unit. The membrane unit recovers the vinyl chloride monomer contained in the stream as a concentrated permeate which is recycled to the process. The vent from the membrane unit may be discharged directly or sent to an incinerator without the need for a scrubber.

A VaporSep unit installed at the Goodyear Tire and Rubber Company in Niagara Falls, NY is recovering **100-200** pounds of vinyl chloride per hour and has reduced the emissions from their incinerator sufficiently to meet stringent New York State requirements. Based **on** the value of the recovered vinyl chloride, this unit will have a payback time of **6-12** months.

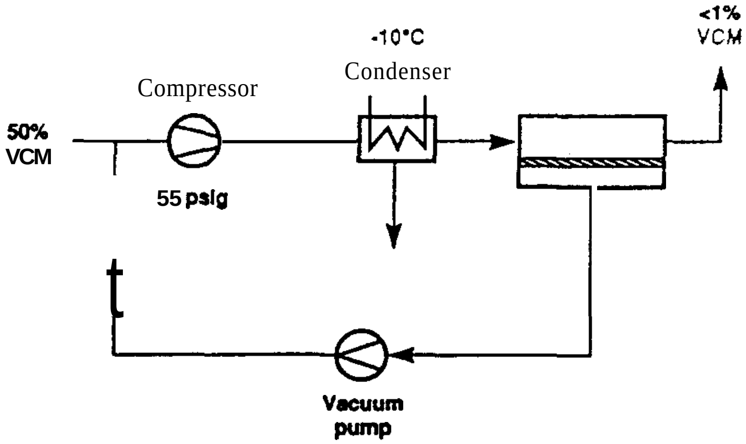

Figure 2. Flow diagram of a membrane system for the recovery of vinyl chloride monomer from the PVC manufacturing process.

Vapor Recovery During Tank and Drum Filling

In this example, we consider a vent stream produced during CFC-11 and CFC-113 tank filling options. The air vented from the container as it fills is saturated with CFC vapor. This stream is sent to a dryer and then to a -15 °C condenser. The condenser reduces the CFC concentration to approximately 21%, for CFC-11. In the past, this 21% stream would have been vented without further treatment Now, however, recovery of the CFC from the vent stream is both economically and environmentally desirable. Adding a membrane system reduces the vented CFC concentration by a further 90%, producing a CFC-enriched permeate that is recycled to the front of the condenser. The final CFC11 concentration in the vent gas is reduced from 27% to 0.3%. A flow diagram for this system is shown in Figure 3. The cost of operating this unit is a tiny fraction of the value of the recovered CFC. The system will pay for itself after only a few hundred hours of operation.

An alternative to the membrane process would be lowering the temperature of the condenser. However, to achieve 1.2% CFC-11 in the final vent gas would require a condenser operating at -50 °C, at a cost substantially more expensive than the membrane unit

MTR has installed two membrane units at CFC drum filling locations. Each unit recovers approximately 2 lb of CFC for every 55-gallon drum filled. Similar systems have been demonstrated for the recovery of breathing losses from gasoline tanks.

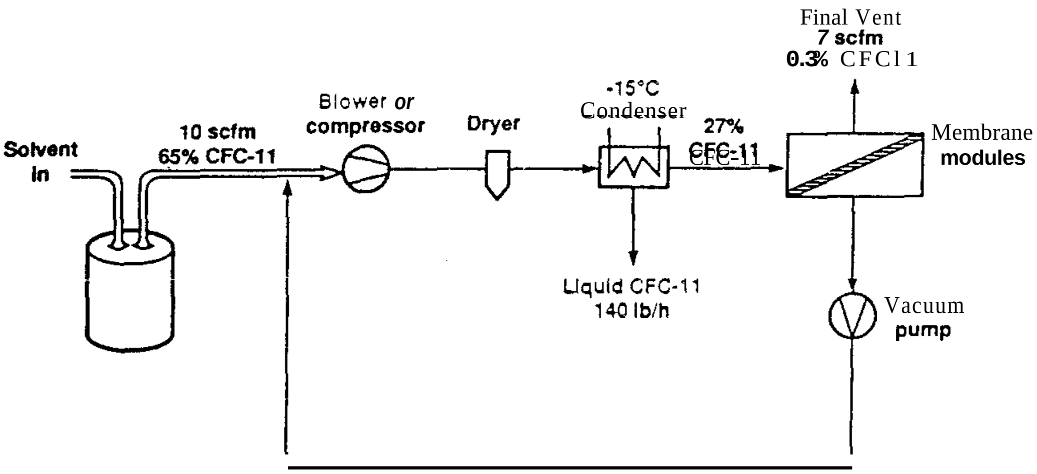

Figure 3. A membrane system for solvent recovery from tank filling options. The system recovers **98%** of the CFC-11 contained in the original feed stream.

HCFC-123 Recovery from a Film-Drying Process

The third example of how VaporSep technology has been applied is in the recovery of HCFC-123 from a **film-drying** process. Industrial coating and cleaning operations rely heavily on the use of volatile organic solvents, such as CFCs and 1,1,1-trichloroethane. The available replacement solvents, such as HCFC-123, are very expensive and subject to stringent environmental emission limits. Therefore, viable conversion of an existing process to the new materials also requires the availability of efficient recovery technology. The MTR membrane vapor recovery process has been demonstrated to be effective for recovery of HCFCs, hydrofluorocarbons (HFCs) and perfluorinated compounds (FCs).

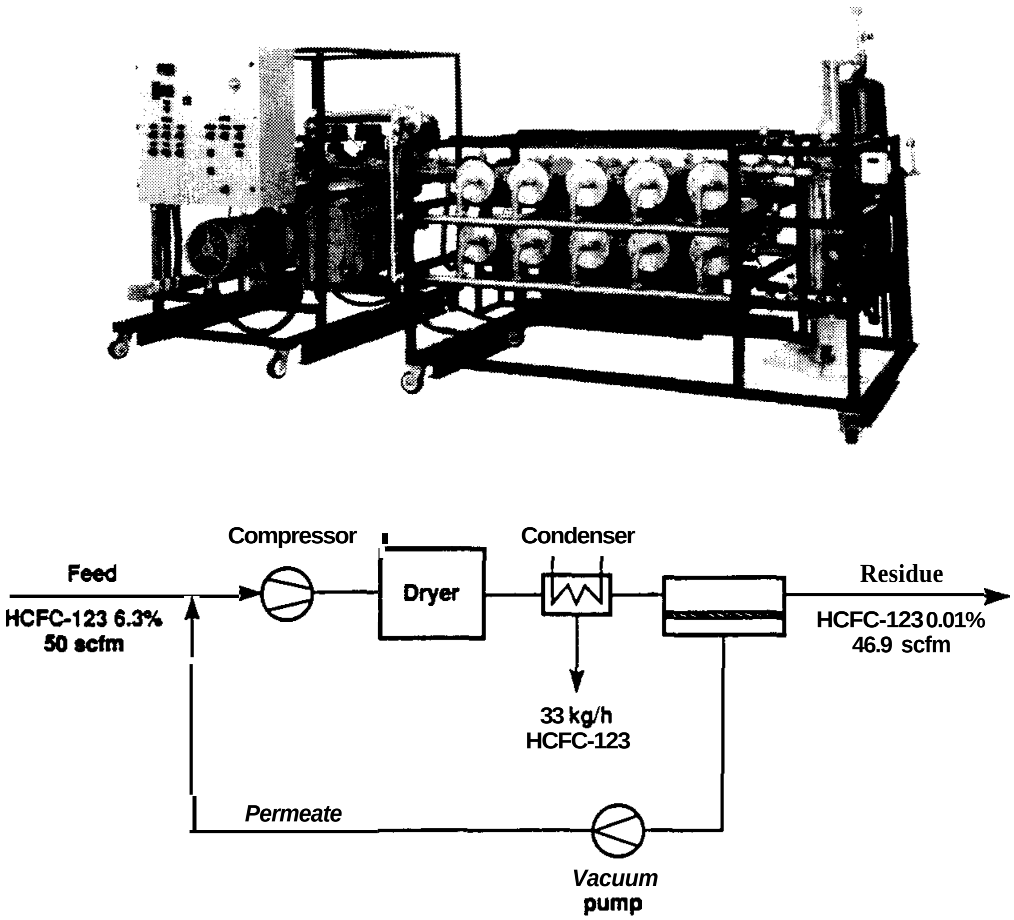

Figure 4. Flow diagram and photograph of a VaporSep membrane system to recover 99.99% of the HCFC-123 lost in a film drying operation.

A VaporSep system was recently installed to recover HCFC-123 vapors from the drying chamber of a film-coating operation. A flow diagram and photograph of the system are shown in Figure 4. HCFC-123 vapors exit the drying chamber at a concentration of 6.3% in air. The vapor stream is compressed to 125 psig and cooled to -15 °C. A dryer removes water vapor from the stream to prevent ice formation in the condenser. The condenser vent is routed to the membrane modules. The concentration of HCFC-123 in the resulting vent stream never exceeds 100 ppm. The unit recovers 15 pounds of HCFC-123 per hour. Based on a price of $5/lb for this material, the membrane system will pay for itself after 3,000 hours of operation.

HALON RECOVERY APPLICATIONS

MTR has also applied the membrane vapor recovery process to the recovery of halon vapors. Ongoing research and development work in this area is being funded in part by the Department of Defense through the Air Force Engineering and Services Center at Tyndall Air Force Base, and the Indusmal Waste Reduction Program of the Department of Energy. A small system is being evaluated at Great Lakes Chemicals production facility. Two systems are in the design phase.

Two opportunities for halon vapor recovery are described below. The first application uses a membrane system to recover halon 1301 vapor losses from fixed total-flooding systems, such as those used in oil production facilities and ground protection of aircraft. A second area where membrane vapor recovery systems could be applied is during servicing and testing of portable fire extinguishers.

Halon 1301 Vapor Recovery from Fixed Total Flooding Systems

Halon 1301 extinguisher systems contain liquid halon 1301 pressurized to approximately 360 psig with nitrogen. The systems typically consist of a large central storage tank which feeds many remote tanks. Tank volumes range from 50 to over 500 ft^3. During inspection and maintenance operations, storage tanks must be drained and opened. Liquid halon is removed from the storage tank, leaving the tank filled with nitrogen saturated with halon 1301 vapor. At 360 psig and ambient temperature, the halon 1301 concentration in the tank is approximately 70%, and this vapor would normally be vented without recovery. For a 300-ft^3 tank, this would release 2,100 pounds of halon vapor into the atmosphere.

Figure 5 shows the design of a membrane system to recover more than 98% of the 2,100 pounds of halon 1301 vapor from a 300-ft^3 tank under these conditions. The pressure in the storage tank is released down to 0 psig, at a rate of 40 scfm for 3 hours. This stream is compressed to 150 psig and condensed at -20° C. The vent stream from the condenser, containing 39% halon 1301, is sent to the membrane modules where the halon 1301 is separated from the nitrogen. The concentrated vapor stream contains 53% halon 1301, and is recycled to the compressor and condensed as liquid halon 1301. The vent stream will contain less than 1% halon 1301. To completely evacuate the storage tank, it will be necessary to repressurize the storage tank to 60 psig with nitrogen, and run a second recovery cycle. The total recovery process will take 4 hours. Of the total 2,100 pounds of halon 1301 originally in the tank, 2,065 pounds, or

98.3%. will be recovered by the membrane system. The system shown in Figure 5 will have a payback time of approximately 100 hours of operation.

Recovery of Halon 1301 During Extinguisher Maintenance

Membrane systems could also be used to recover halon vapors during portable extinguisher maintenance. Halon 1301 extinguishers contain a large amount of nitrogen, used to pressurize the contents of the cylinder. Therefore, an effective recovery system must capture the halon 1301 vapor purged with the nitrogen, as well as the liquid halon 1301. A simplified flow diagram for a membrane system to accomplish this is shown in Figure 6. The halon is pumped from the extinguisher and compressed into an intermediate storage vessel. The purged nitrogen containing 60% halon 1301 vapor is routed to a membrane module that reduces the vented halon by 95%.

MTR is investigating two different membrane materials for this application. In the first case, our standard VOC-permeable membrane would be used. Alternatively, a nitrogen-permeable membrane could be used. More membrane area is required if a nitrogen-permeable material is used, but this is easily offset by not having to recompress the recycled concentrated halon stream. This type of membrane system design would have distinct advantages for small purge streams, on the order of 1-5 scfm.

APPLICABILITY TO HALON ALTERNATIVES

MTR vapor separation systems can be used to recover many organic vapors, including chlorinated hydrocarbons, CFCs, HCFCs, and halons. The process is also applicable to many of the chemical compounds being considered as replacements for halons 1301 and 1211. Seven specific candidates have been announced by industry[2] and many others are under investigation.[10] MTR has evaluated the effectiveness of the membrane recovery process for a number of these candidates. All of the halon replacement candidates we have tested could be recovered by the membrane process, i.e., FC-14 (CF_4), HCFC-22 ($CHClF_2$), HFC-23 (CHF_3), HCFC-123 (CF_3CHCl_2), HFC-134a (CH_2FCF_3), and HCFC-142b ($CClF_2CH_3$).

CONCLUSIONS

MTR has developed a halon and CFC recovery process. This process is a significant advance for recovery of this extremely volatile compound. The use of membrane recovery systems in recovering and recycling halon 1301 will conserve the dwindling supply of this material

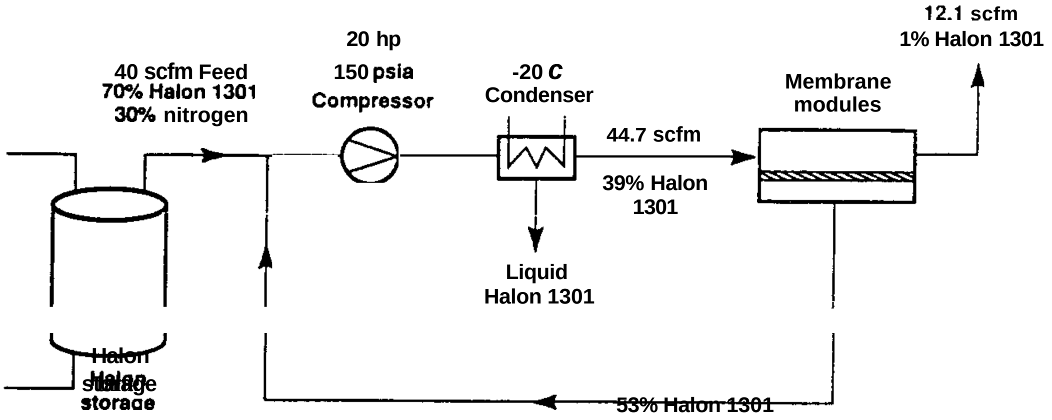

Figure 5. Flow diagram of a VaporSep membrane system to recover 98% of halon 1301 vapors from large storage facilities.

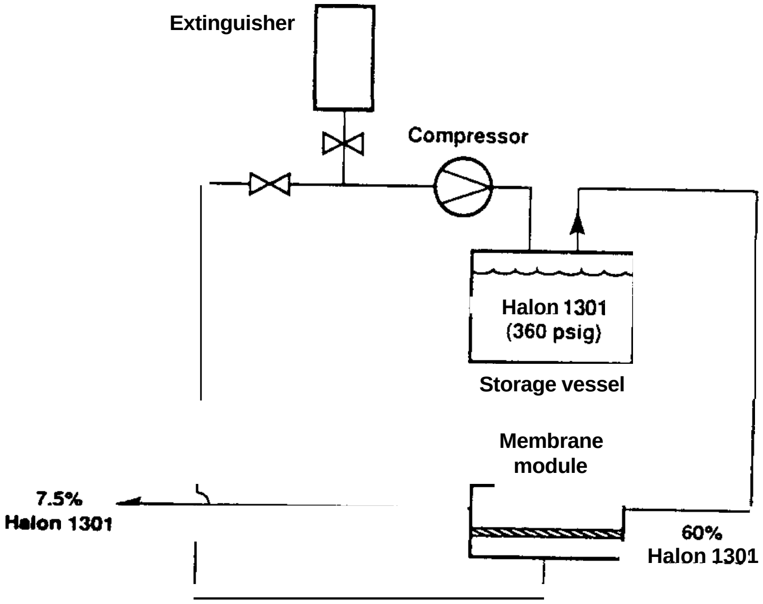

Figure 6. Flow diagram of a VaporSep membrane system to recover halon 1301 vapors during extinguisher servicing.

for essential uses and minimize the environmental impact caused by current vapor losses. In addition, the equipment can be justified on an economic basis. The positive payback from the recovered materials will become even more attractive when the halons are replaced by more expensive alternatives.

Five membrane vapor recovery systems are presently installed in industrial facilities. Data from the installations indicate that the process is technically solid and economically justified. In each case, recovery of volatile organic compounds by membranes has compelling advantages over alternative recovery methods such as carbon adsorption or low-temperature condensation alone.

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