

# Volatile Organic Carbon/Air Separation Test Using Gas Membranes

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## ABSTRACT

*An estimated 900 metric tons of carbon tetrachloride were discharged to soil columns during the Plutonium Finishing Plant Operations at the Hanford Site. The largest percentage of this volatile organic compound was found in the vadose region of the 200 West Area. Using a Vacuum Extraction System, the volatile organic compound was drawn from the soil in an air mixture at a concentration of about 1,000 parts per million. The volatile organic compounds were absorbed from the air stream using granulated activated carbon canisters. A gas membrane separation system, developed by Membrane Technology and Research, Inc., was tested at the Vacuum Extraction System site to determine if the volatile organic compound load on the granulated activated carbon could be reduced. The Vacuum Extraction System condensed most of the volatile organic compound into liquid carbon tetrachloride and vented the residual gas stream into the granulated activated carbon. This system reduced the cost of operation about \$5/kilogram of volatile organic compound removed. The U.S. Department of Energy Office of Technology Development Volatile Organic Compound-Arid Site Integrated Demonstration sponsored the test.*

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## INTRODUCTION

### Test Site Background

About 900 metric tons of carbon tetrachloride ( $\text{CCl}_4$ ) were discharged to three soil cribs between 1955 and 1973 in the 200 East Area at the Hanford Site, located near Richland, Washington. The majority of the volatile organic compound (VOC) was found in the vadose zone between the ground surface and water table. To prevent or minimize further migration of  $\text{CCl}_4$  contamination from unsaturated soils entering the ground water, an Expedited Response Action is being conducted. Figure 1 depicts the  $\text{CCl}_4$  migration from unsaturated soils into the ground water (G. V. Last).

A Vacuum Extraction System (VES) was installed at the test site to extract the VOC vapors from the vadose zone. The VOCs were removed from the gas stream using granulated activated carbon (GAC) canisters. The VES draws vapors from the ground at about 20 standard cubic meters per minute (scmm). The concentration of the  $\text{CCl}_4$  in the air stream fluctuates between 200 and 1,000 parts per million (ppm) by volume.

A pilot scaled test that uses gas membranes was developed to reduce the costs associated with removing the VOC from the extracted gas stream. Figure 2 illustrates the VES.

Figure 1. The Hanford Site in Washington. (The test was conducted in the 216-Z-1A Tile Field [R. G. Riley].)

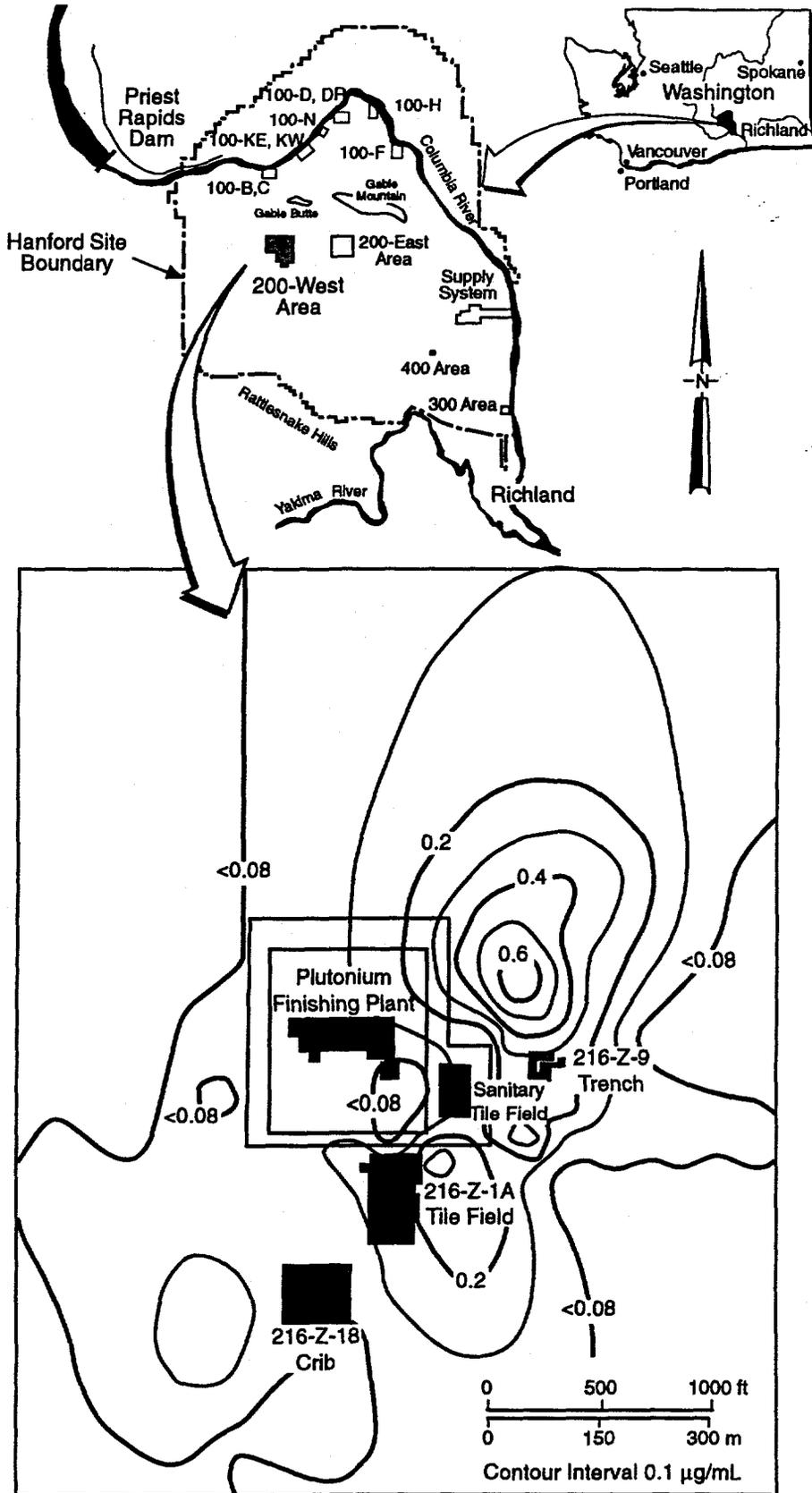
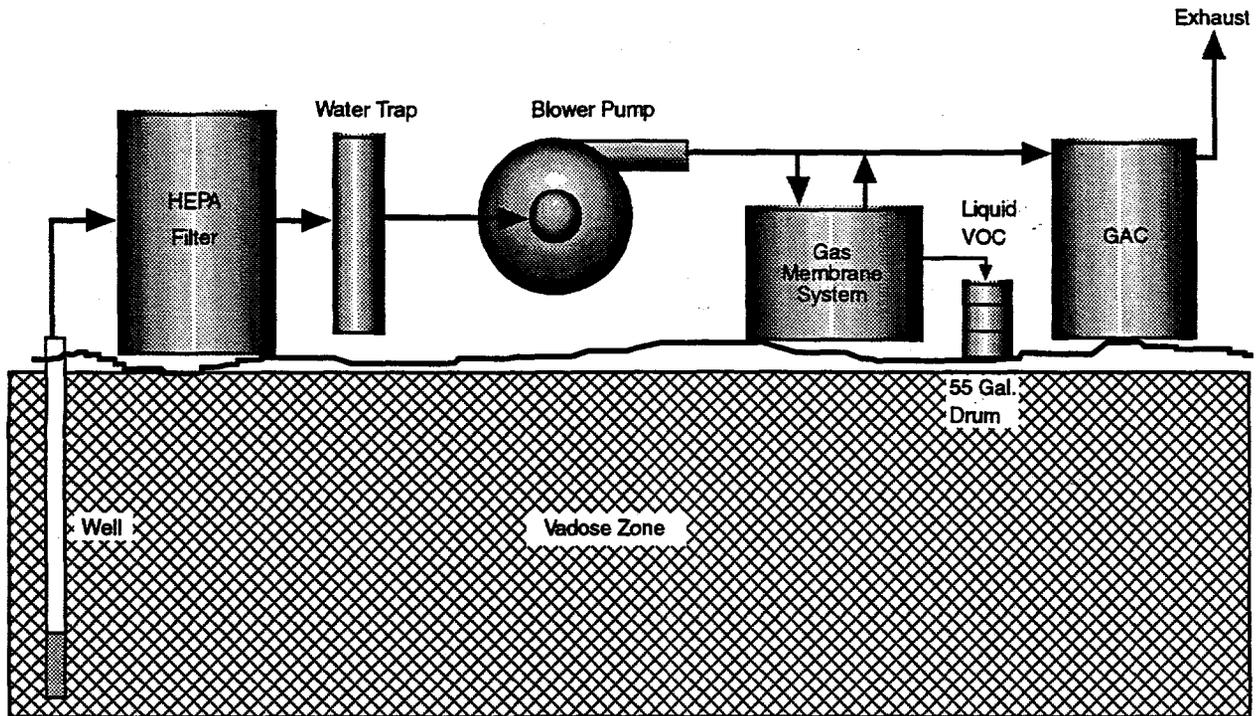


Figure 2. The Vacuum Extraction System with the Gas Membrane System Pilot Plant.



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### Condensation/Membrane Hybrid Systems

Numerous industrial and commercial processes produce gas streams containing VOCs. Because venting such gases into the atmosphere (atm) causes pollution problems and squanders resources, industries are under increasing pressure to clean up waste gas emissions. Condensation is widely used by industries, which involves gas cooled and/or compressed beyond the dew point of the condensable constituent. A portion of this component condenses and can be drawn off as a liquid for reuse or disposal. Two problems exist while using this method: (1) a low concentration of the condensable component in the stream, or a condensable component with a low boiling point, make it difficult to reach the dew point, and (2) there is a need for regular defrosting of the condenser when condensation is below the freezing point of

water. These two problems place limits on the practical operating range of a condensation system. Compressing the gas stream above 10 to 15 atm consumes large amounts of energy and costs increase rapidly in proportion to compressor capacity. If the gas must be cooled below 0 °C (celsius), ice formation in the condenser from water vapor entrained in the feed vapor may occur. Twenty percent (%) or more of the condensable component may remain in the non-condensed bleed gas from the condenser under favorable operating conditions.

Although condensation proves to be a valuable method of waste treatment and pollution control, condensation technology must be improved. Recent evidence regarding the adverse environmental effects of chlorinated hydrocarbons as VOC emissions intensifies the need to improve condensation technology.

The Membrane Technology and Research/Westinghouse Hanford Company pilot project involves a combined, or hybrid, process of condensation and membrane separation that reduces the concentration of a condensable component in a gas stream to 5% or less of its original level. Because of the inherent complementary features of the two methods, the hybrid process is efficient and economically feasible when applied to hydrocarbon condensation applications.

Condensation and membrane concentration are the two main steps in the process. The conventional condensation step compresses the feed gas stream and then chills it to condense a portion of the VOC. The membrane step uses high performance membranes that are selectively permeable to organic vapors over nitrogen, air, or other gases. The hybrid process is designed to yield

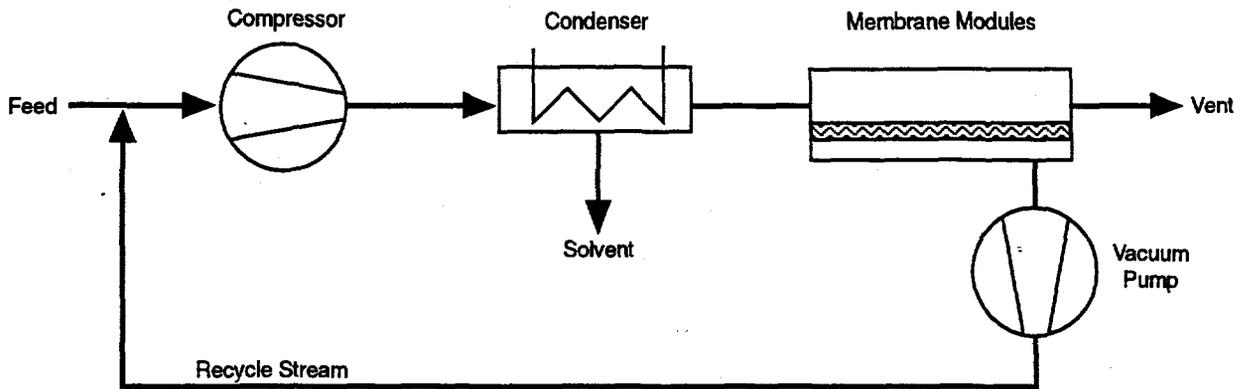
only two product streams: the condensed liquid which is ready for recovery and reuse, and a gas stream, which contains as little as 1% or less of the original condensable content. This result is achieved by recycling streams within the process.

If the VOC is present at higher concentrations as determined by the condenser temperature and pressure, the combined compression-condensation/membrane system is expected to remove VOCs more efficiently. The VOC concentration, which is fed to the membrane system, is independent of the actual VOC concentration in the overall system inlet stream. If the system's inlet VOC concentration is lower than the condenser equilibrium concentration, the membrane modules will increase the condenser inlet concentration with the VOC enriched permeate until the VOC concentration is high enough to start condensation.

Figure 3 schematically illustrates the process. The process compresses a VOC-contaminated air stream and then cools it in a condenser to remove a portion of the VOC content. The compressor condenser bleed air, which contains a substantial amount of VOC, is then passed to a membrane unit that removes the remaining VOC, producing a VOC-depleted air stream (R. W. Baker).

The enriched permeate stream from the membrane step is returned to the condensation process. The technical feasibility of membrane systems for treatment of streams containing organic vapors has been demonstrated during pilot plant testing, using developmental membranes, modules, and systems. Some of this technology is now commercially available.

Figure 3. The Hybrid Gas Membrane System as Developed by Membrane Technology and Research (US Patent).

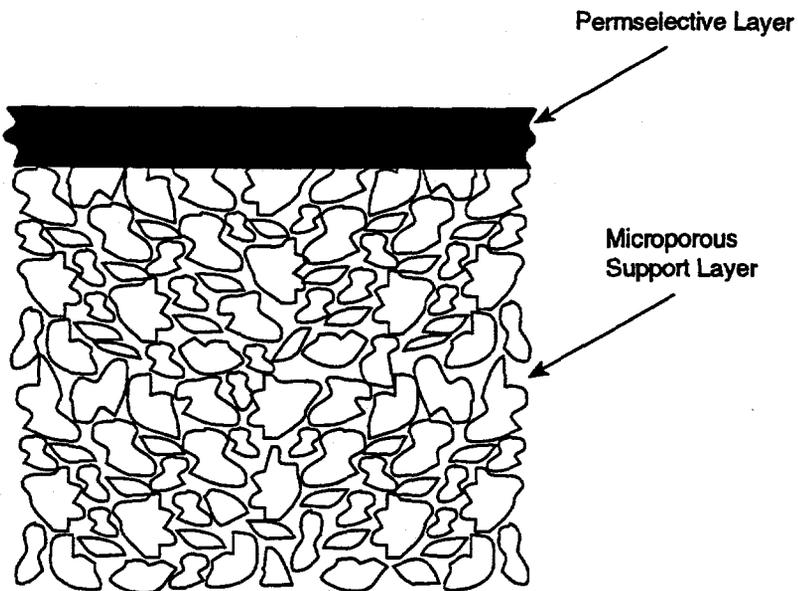


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**Membranes and Modules**

Figure 4 shows the composite membranes multilayer structure. A tough, open microporous polymer layer provides mechanical strength, and an ultrathin, dense polymer coating produces the separation properties. These membranes have high fluxes and are very selective for organic vapors over air.

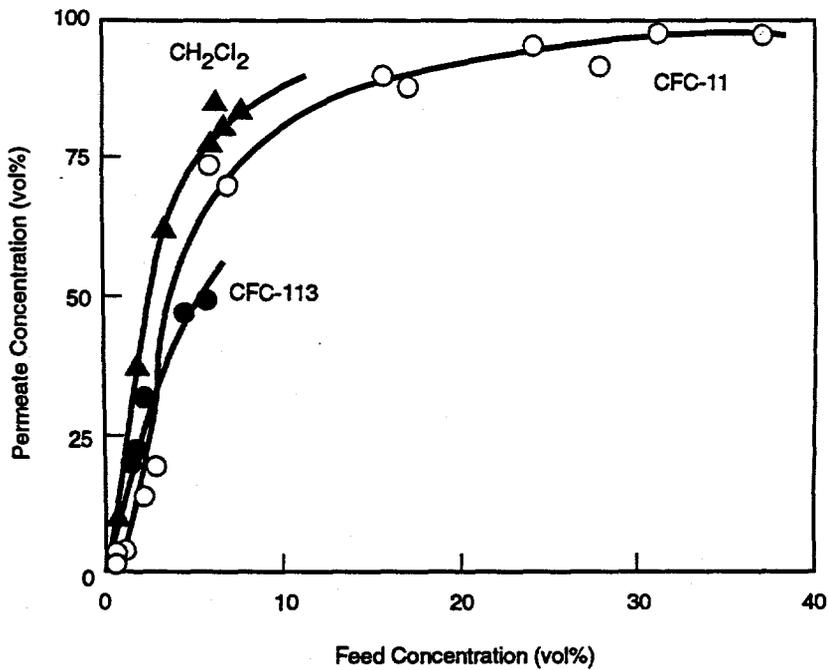
Figure 4. The Gas Membrane Construction.



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Figure 5 represents data obtained when the membranes are used to treat airstreams containing various halocarbons. Similar data have been generated for a wide variety of organic vapors, including hydrocarbons, chlorinated hydrocarbons, and chlorofluorocarbons.

Figure 5. Typical Separation Achieved by the Gas Membrane System.



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From this data of this type, the membrane selectivity  $\alpha_{(VOC/air)}$  can be obtained. This parameter is defined as the ratio of the VOC permeability through the membrane ( $P_{VOC}$ ) to the air permeability through the membrane ( $P_{air}$ ):

$$\alpha_{(VOC/air)} = \frac{P_{VOC}}{P_{(air)}}$$

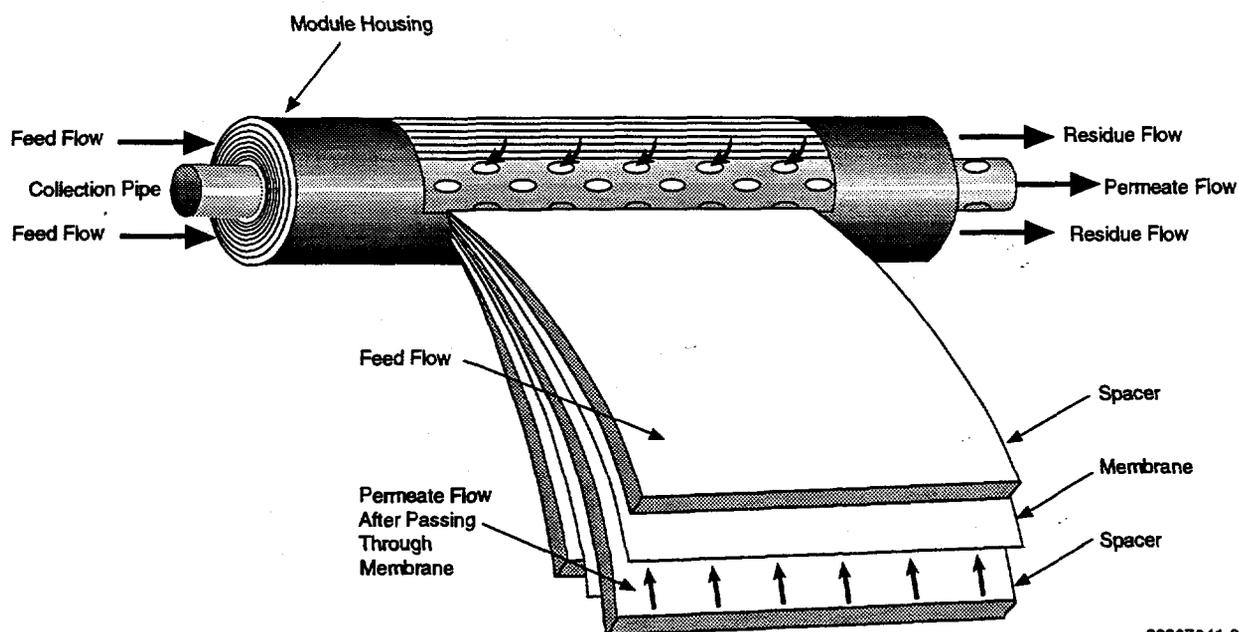
The membrane selectivity is a measure of membrane efficiency during separation of a particular VOC from an air stream. A membrane selectivity of 10 and preferably greater than 20 is required if a membrane process is to be economically viable. Under certain conditions, such as the gas stream being available at high pressure or at reduced temperature, a membrane selectivity of 5 to 10 is sufficient. Table 1 lists typical selectivity data obtained with a variety of organic compounds.

Table 1. Selectivities of Membrane Technology and Research Membranes to a Representative Series of Common Industrial Solvent Vapors.

Vapor	Membrane selectivity
Octane	90 - 100
1,1,2-Trichloroethane	60
Isopentane	30 - 60
Methylene chloride	50
CFC-11 ( $\text{CCl}_3\text{F}$ )	45
1,1,1-Trichloroethane	30 - 40
Isobutane	20 - 40
Tetrahydrofuran	20 - 30
CFC-113 ( $\text{C}_2\text{Cl}_3\text{F}_3$ )	25
Acetone	15 - 25
CFC-114 ( $\text{C}_2\text{Cl}_2\text{F}_4$ )	10
Halon-1301 ( $\text{CF}_3\text{Br}$ )	3 @ 20 °C 10 @ -20 °C

Figure 6 shows the type of composite membranes that are fabricated into spiral-wound modules. In these modules, the membrane is supported on the feed and permeate sides by plastic mesh spacers. The membrane and spacers are wound spirally around a central collection pipe. During operation, feed gas enters the module and flows between the membrane leaves. The permeate fraction spirals inward to a central collection pipe. The remainder of the

Figure 6. Spiral Wound Gas Membrane Construction.



feed flows across the membrane surface and exits as the residue. By compressing the feed gas with a compressor on the feed side and by drawing a partial vacuum with a vacuum pump on the permeate side a pressure difference across the membrane is induced.

### Description of the Field Demonstration System

Figure 7 represents a flow diagram of the field demonstration system. The system contains an oil-lubricated screw compressor, a condenser and pre-cooler connected with an air-cooled chiller, three modules that can each contain one membrane module insert, and oil lubricated, rotary-vane vacuum pump, and a level controlled solvent tank. The system handles a feed flowrate of 1 scmm and a feed concentration of 0.1 volume percent.



pump pumps the permeate vapor through an oil mist filter into the inlet of the compressor. The solvent-depleted air (residue) is drawn out of the system through the back-pressure valve.

The start-up, shut down, normal operation, and alarm sequences of the system are controlled by a programmable logic controller.

### **Test Objectives**

The primary test objective was to demonstrate the hybrid gas membrane system to determine its cost effectiveness, functionality, and safety in field applications. If the system could not maintain a steady state operation with concentration feed variation, the system could not be deployed in a production mode. Other secondary test objectives included: determine if the membranes would foul during system operation, determine the membrane selectivity, system mechanical durability, and quantity of water collected.

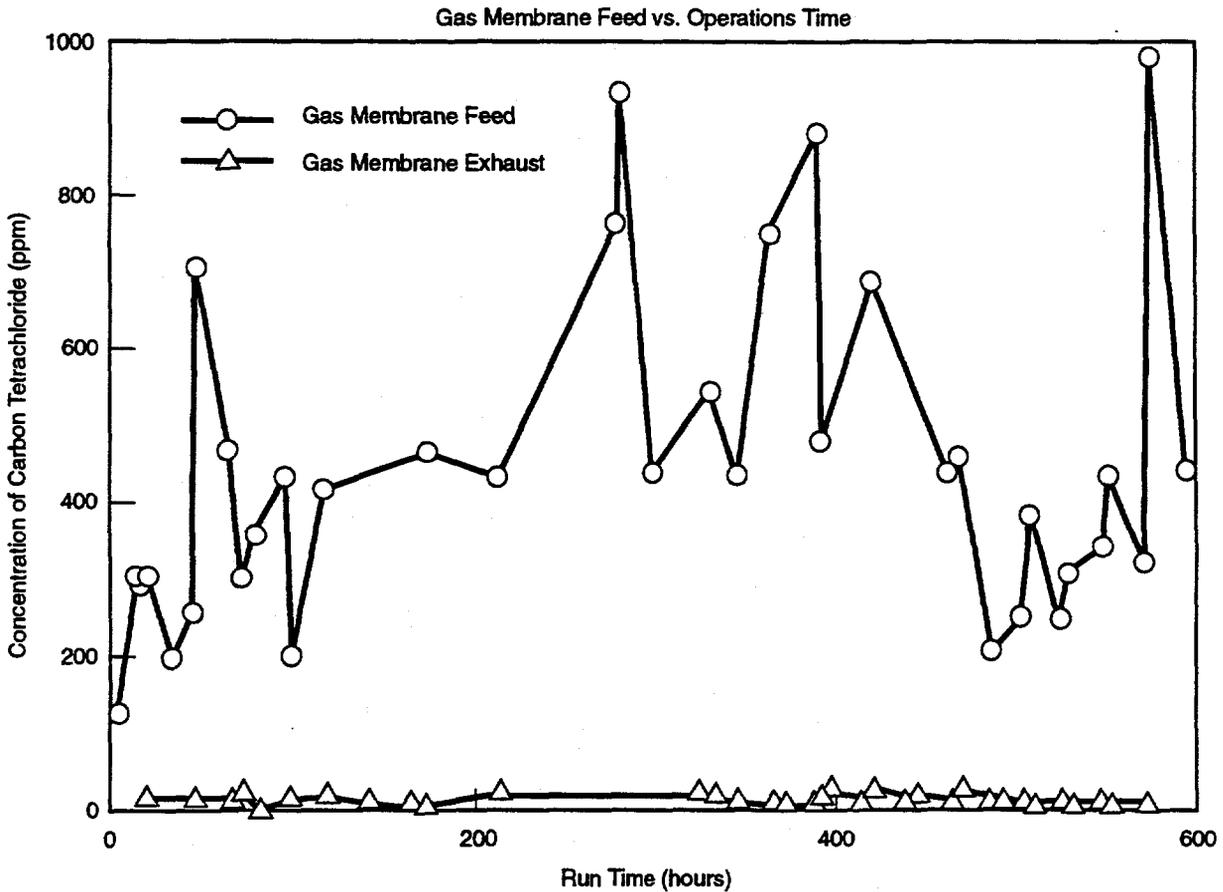
## **TEST RESULTS**

### **Membrane and System Performance**

Over a period of several months, the field demonstration system was operated at the Hanford Site in south central Washington. The membrane system did not run in continuous mode because of VES malfunctions. More than 600 operating hours were accumulated by the end of April, 1993.

Figure 8 depicts the feed and residue concentrations versus the operating hours. The feed concentration, between 200 and 1,000 ppm, was lower than expected. The membrane modules enriched the feed stream to a calculated value of about 3,000 ppm to get condensate of VOCs at the given feed pressure and condenser temperature. The permeate concentration varied between 4,000 and 10,000 ppm.

Figure 8. Feed and System Exhaust Concentrations During the Test Period.



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The feed and permeate pressures were stable at 10 atm and 103 mmHg throughout operation, indicating excellent compressor and vacuum pump performance. The air-cooled chiller showed poor cooling capacity at high ambient temperatures near the end of the test run period and had to be replaced with a larger chiller to maintain the condenser temperature between 5 °C and 10 °C.

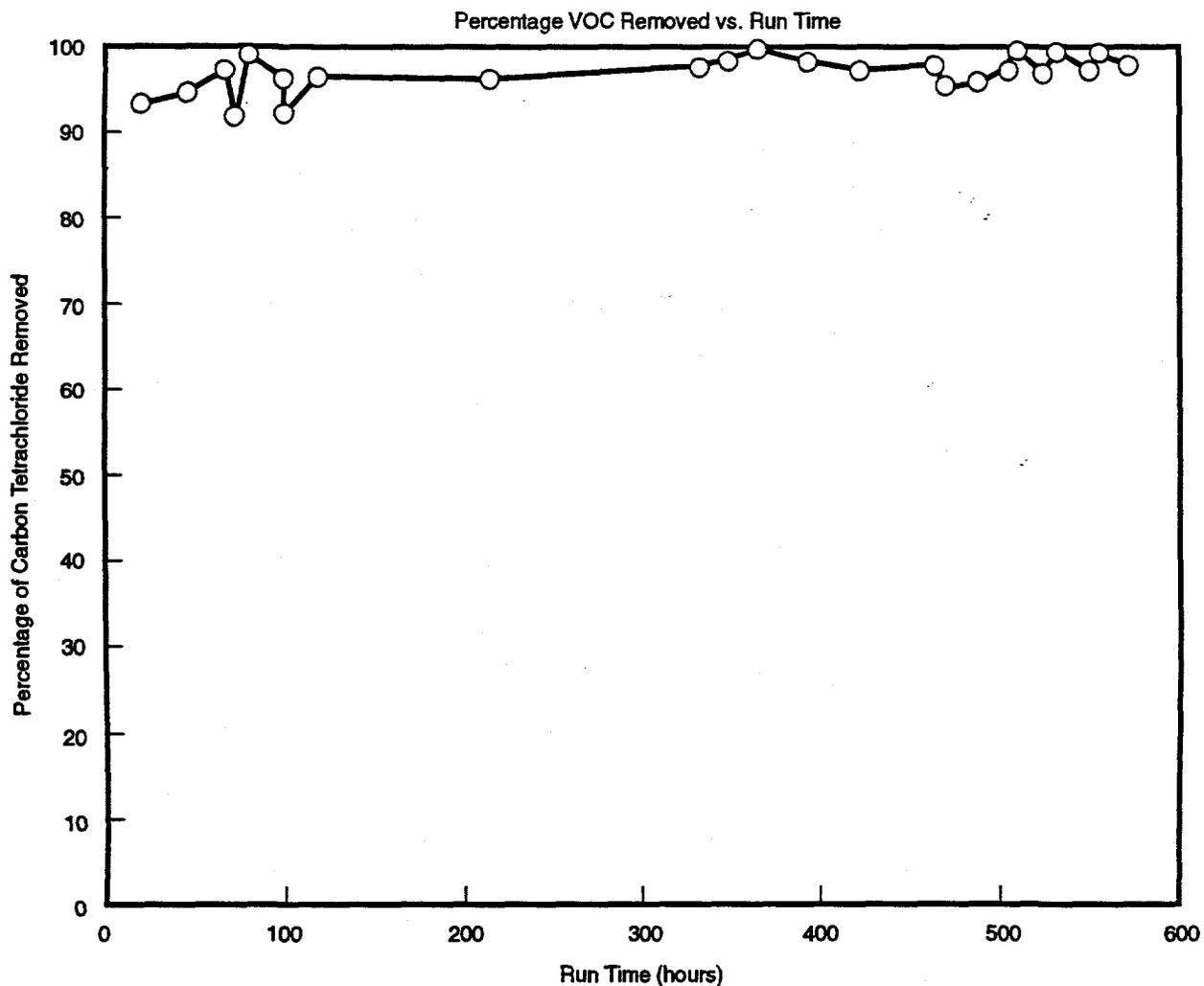
As the ambient temperature fluctuated, the pressure control valve was manually adjusted to maintain 10 atm. An automated control valve would resolve the need for manual adjustments. During subfreezing ambient temperatures, the tanks and tubing associated with the collected liquid was heat traced to prevent freezing of these lines.

Figure 9 shows the VOC removal in percent of the incoming feed stream as a function of time. The removal nearly always remained above 95% and showed no decrease at the end of the test period. Good performances were sustained even at feed concentrations below 500 ppm. The membrane selectivity and the membrane permeate flow rate remained constant and the membrane showed no indication of fouling or membrane integrity failure. The designed selectivity was 20 and remained fairly steady over the range of the test.

#### **Granulated Activated Carbon Performance**

The 8-foot (ft) by 4-ft diameter GAC canisters were regularly changed out during testing. The GAC canisters required about two hours of labor during each change out. Operation of the GAC required careful observation to ensure

Figure 9. Percentage of Carbon Tetrachloride Removed from the Vacuum Extracted Air Stream.



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that the exhaust concentration threshold limits were not exceeded. If the feed concentrations for the GAC increased too high, the heat of adsorption caused the GAC canister to overheat thus ending its ability to scavenge the  $CCl_4$  from the gas stream. The saturated GACs were shipped off site for regeneration and returned for reuse at the VES Site.

About 27.8 grams of  $\text{CCl}_4$  per liter (L) of water and  $\text{CCl}_4$  mixture for a total of 605 L were collected during the 600 operating hours. The  $\text{CCl}_4$  concentration in the water was between 400 and 800 ppm and the remaining VOC formed a separate layer at the bottom of the drum.

The VOC contaminated water was treated using an existing ultraviolet light oxidation (UV/OX) organic destruction system to destroy the VOCs. The  $\text{CCl}_4$  was shipped off site for disposal.

### **Full Size Vapor Recovery System**

A full size membrane system treats a feed stream of about 28 scmm. Based on the field site demonstration test data, the full size system would be 28 times larger than the pilot system. Table 2 estimates the price and the operating costs for a full size vapor recovery system that is designed to treat a 28-scmm feed stream. The utility consumption requirements are also listed in Table 2.

### **CONCLUSIONS**

There are several advantages to using the vapor separation system over the traditional GAC when removing  $\text{CCl}_4$  from a vadose zone vacuum extracted waste stream. The vapor separation system does not require as much maintenance as the GAC. The vapor separation system costs less to operate and minimizes safety risks when feed concentrations vary significantly. The

Table 2. Estimated Price and Operating Costs.

System budgetary estimate	\$850,000 ( $\pm 20\%$ )
Annual depreciation and interest <sup>1</sup> (system excluding modules inserts)	\$116,000
Annual operating costs <sup>2</sup>	
Maintenance (5% of capital cost)	\$ 42,000
Module (6") inserts replacement <sup>3</sup>	\$ 47,000
Energy (\$0.05/kWh)	
Compressor (350 kW)	\$138,000
Vacuum pump (150 kW)	\$ 59,000
Chiller (15 kW)	\$ 6,000
Water/CCl <sub>4</sub> UV/OX destruction (\$0.04/L)	\$ 10,000
Cost of CCl <sub>4</sub> liquid offsite disposal	\$ 75,000
Operating costs	\$494,000
Cost per unit recovered solvent	\$ 6.06/kg
GAC Operating costs per unit solvent	\$ 11/kg
Savings using hybrid gas system per year	\$402,610

<sup>1</sup>Interest rate: 10%, lifetime system: 10 years.

<sup>2</sup>Based on 24 h/day, 330 day/year.

<sup>3</sup>Spare modules: \$3,500/module (6") insert, 3-year lifetime.

<sup>4</sup>Based on 1,000 ppm VOC in feed stream  
(81,500 kilograms/year).

membranes showed no signs of fouling during the 600 hours of field operation. The system was mechanically sound and required no repairs during the test. The separation of the CCl<sub>4</sub> and water mixture would be required for a full-scale system to be economically feasible. The water would need to be free of the VOC so it could be returned to the soil. This is not a major problem because a variety of methods exist to make the separation. For the above reasons, we recommend that this system be used as a viable alternative to GAC treatment of a VES offgas stream.

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