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WATER DIFFUSION MEMBRANES III
(Pervaporation and Heat Rejection through
Composite Membranes)

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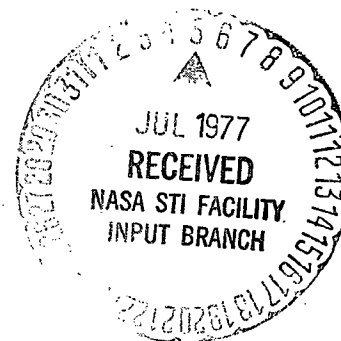
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PREFACE

This report covers the period from April 1976 to February 1977. In this period, water transport and heat rejection through composite membranes were studied employing a simulated urine (and wash) solution. Unlike the porous membranes that have been studied and reported previously, composite membrane semipermeability is based on a dense barrier in which the permeant has preferential solubility.

The participants in the present study were Dr. Israel Cabasso, Mr. Charles Eyer, and Mr. James K. Smith.

CONTENTS

	<u>Page</u>
I. INTRODUCTION.....	1
II. THEORETICAL.....	2
III. OBJECTIVES.....	5
IV. EXPERIMENTAL.....	8
A. Cell Design.....	8
B. Membranes.....	12
C. Measurements.....	12
V. METHOD OF APPROACH.....	14
A. Summary of Hollow Fibers Experiments.....	15
B. Experiments with Flat Sheet Composite Membranes.....	16
VI. DISCUSSION.....	39
A. Heat Removal.....	41
B. Precipitation of Solids.....	43
C. Waste Solution Product.....	45
D. Mode of Operation.....	46
E. Water Reuse (Collection).....	46
APPENDIX A - Properties of PA-300 and NS-100 Membranes.....	49
REFERENCES.....	60

FIGURES

<u>Number</u>	<u>Page</u>
1	Pervaporation, where microprecipitants are formed as a result of water removal..... 3
2	Shuttler orbiter wastewater storage and heat rejection..... 6
3	Proposed water discharge and heat dissipation system..... 7
4	Schematic diagram of test assembly..... 9
5	Pervaporation cell (effective membrane length 13 cm; total effective area 79.3 cm ²)..... 11
6	Volume decrease vs. time in continuous pervaporation ₂ run of standard waste solution (PA-300 membrane with 79 cm ² surface area). Initial permeation rate, calculated from the tangent, is 0.17 g/cm ² -hr..... 18
7	Permeation rate as a function of concentration increase in continuous pervaporation run (V _i = 8 liters; computer printout). Points were calculated from the volume collected..... 19
8	Permeation rate as a function of time in continuous pervaporation run (see Figure 7). The data points are calculated from the total mass accumulated in the condensation trap..... 20
9	Buildup of dissolved and suspended solids in a pervaporation concentration run (V _i = 8 liters)..... 21
10	Time vs. total organic carbon found in product effluent of continuous pervaporation run (V _i = 3 liters; data points represent 28 hr batch samples)..... 22
11	Concentration variation of ammonia, inorganic carbon and total organic carbon during a pervaporation run (V _i = 6 liters). (The ammonia and inorganic carbon are degradation products of urea and follow the same trend.)..... 24
12	Buildup of dissolved and suspended solids in the waste solution during a pervaporation concentration run (V _i = 6 liters)..... 25
13	Permeation rate as a function of time for continuous pervaporation run (V _i = 6 liters)..... 26

14	Heat dissipation in pervaporation vs. flow rate.....	29
15	Waste solution vs. time in a cyclic pervaporation run.....	30
16	Permeation rate of effluent in a cyclic pervaporation run.....	31
17	Waste solutuion volume vs. time in a cyclic pervaporation run.....	33
18	Permeation rate of effluent of cyclic pervaporation run.....	34
19	Solids wt% in concentrate vs. time.....	35
20	Inorganic carbon and total organic carbon (TOC) concentrations in effluent water as a function of time in a cyclic peervaporation run.....	36
21	Time vs. conductivity of permeant.....	37
22	Aging urine vs. time (1 mMole/liter = 17 ppm).....	40
23	Thermopervaporation unit designed by Aptel <u>et al.</u>	48

APPENDIX

1-A	Cross sectional drawing of PA-300 (ether/amide) thin-film composite membrane.....	49
2-A	Relationship between water flux and salt rejection, as a function of applied pressure, for PA-300 poly(ether/amide) thin-film composite membrane (from UOP publication).....	50
3-A	Relationship between water flux and salt rejection, as a function of feed pH, for PA-300 poly(ether/amide) thin-film composite membrane (for UOP publication).....	51

TABLES

<u>Number</u>		<u>Page</u>
1-A	Reverse Osmosis Performance of PA Thin-Film Composite Membrane for Various Solutes.....	52
2-A	Rejection Data for NS-100 Membranes.....	53

I. INTRODUCTION

While a manned space vehicle is isolated from Earth, liquid waste material is generated at a fairly regular rate¹, approximately two liters of urine (containing ~4% dissolved solids) plus about one liter of washwater (containing ~2% dissolved solids) per man day. Such a generation rate means, for example, that for a seven man vehicle operating in space for 30 days, a total of about 630 liters of waste fluids, containing approximately 3.3% dissolved solids, would be generated.

Such waste can be accounted for in one of four ways: (1) the waste may be dumped into space; (2) it may be accumulated for return to Earth; (3) the waste may be separated into two fractions, one fraction (water) to be dumped into space and the remaining portion to be returned to Earth; or (4) the waste components may be beneficially reused.

Of these choices, the first (currently considered for the space shuttles) is the simplest but has major drawbacks. Waste dumped into space near the spacecraft capsule would move in the orbit for a period of time, conceivably interfering with visual, electrical, or mechanical operations. Special precautions would have to be taken to prevent such interferences; for example, moving sensitive instruments into the capsule prior to jettisoning waste. Waste attracted back to the surface of the spacecraft would cling there until burnoff upon re-entry into the atmosphere.

The second choice, accumulating the waste for return to Earth (previously in effect), is wasteful of energy, space, and other resources. In the above example, a mass of ~630 kg must be shifted from a stable orbit and deposited carefully upon the Earth's surface. A volume somewhat greater than three 55 gallon drums (208 liters) would have to be allocated to the accumulation of liquid waste (~95% water) aboard the spacecraft.

Simultaneous separation of pure water from the residual waste components, requisite for the latter two alternatives, appears to be a desirable goal. If 90% of the water could be removed from the waste solution, approximately 560 liters of water would be rendered available for reuse or for cooling by evaporation into space (dissipation of accumulated heat); any excess water could be dumped into space before re-entry. This would leave only a small, concentrated waste to be returned to Earth.

II. THEORETICAL

The most common means of separation of water from simple solution is distillation. However, a distillation unit loads the spacecraft with heat and requires a procedure by which organic volatiles are kept behind or trapped (e.g., a sorbent column of activated charcoal). Low temperature vacuum distillation would be required to slow down the chemical and biological degradation of organic molecules into volatile species. Such a distillation could be carried out within the spacecraft either by employing a vacuum pump or by making use of the inexhaustible vacuum supply external to the spacecraft. Employing a vacuum pump would load the spacecraft with additional heat and energy requirements, and the utilization of space vacuum would require a set of specially designed valves. This is, of course, an oversimplification of the two alternatives; even so, the drawbacks of distillation justify a third and unconventional proposition of using a semipermeable membrane to separate water from the waste solution in spacecrafts.

Such a membrane should allow water transport only; the driving force behind the permeation mechanism is the difference in the chemical potentials of the water in the entities which are separated by the membranes. There are several membrane processes to effect separation. The technique suggested here is called "pervaporation," in which the membrane serves as a selective barrier between a gas and a liquid phase (Fig. 1). If the water fraction is to be discharged into space, liquid (waste) would be circulated facing one side of the membrane, allowing water molecules to preferentially diffuse through the membrane to the side exposed to the space vacuum. This process resembles selective evaporation.

When the water vapors are to be released directly to space, the system can serve as an auxiliary heat dissipation device in addition to beneficially decreasing the mass and volume load of the spacecraft. Alternatively, condensation of the permeant would provide water for reuse. (If water reuse is required, the thermopervaporation process described in the following pages can be employed.)

In previous reports^{1,2}, a distinction was made between two membrane transport mechanisms. In the first, permeation occurs through a dense (nonporous) membrane, where the transport rate is determined by the water-

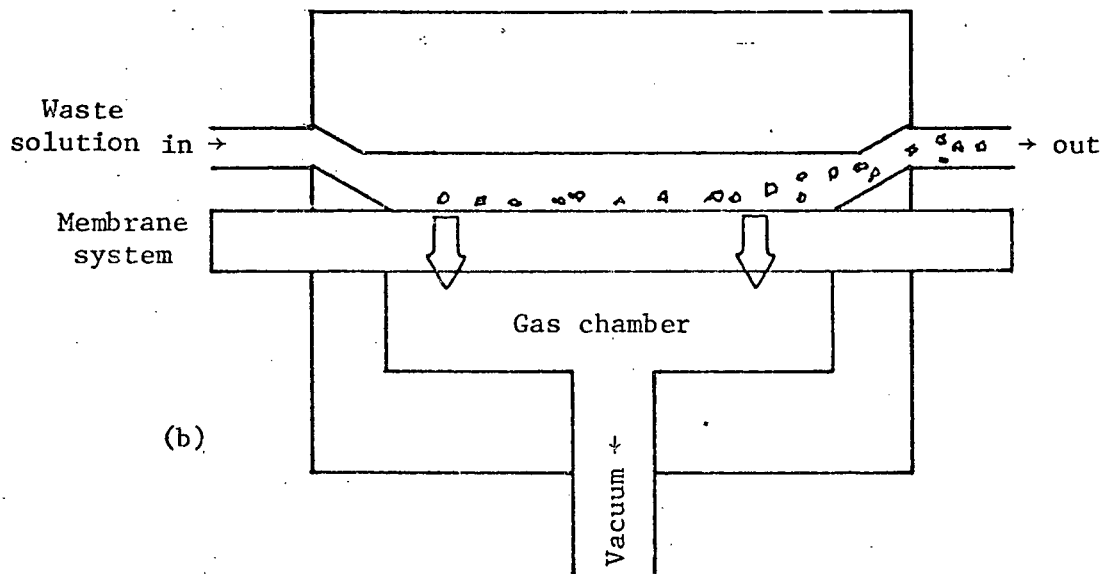
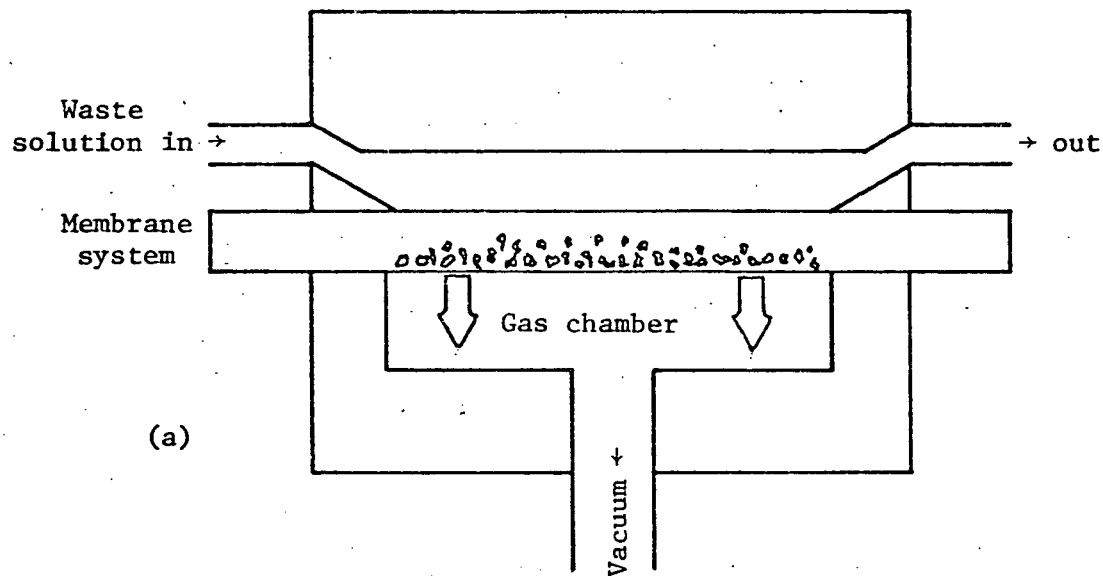


Figure 1. Pervaporation, where microprecipitants are formed as a result of water removal: (a) buildup of precipitants in the membrane system; (b) dense, smooth membrane where particles are carried away by the flow.

membrane interaction; that is, water molecules dissolve and diffuse within a dense polymeric matrix. If a hypothetical polymeric membrane of less than 25 μm thickness is to be used, the process is not feasible unless the diffusion coefficient of water in the membrane is in the range of 10^{-6} cm^2/sec . This is an extremely high value, not yet available for highly selective dense membranes.*

The other possibility, permeation through a porous membrane, provides a convective gas (vapor) transport through small diameter pores. This process is a straight evaporation, and hydrophobic, porous membranes are used to eliminate suction of liquid into the pores; thus, only vaporized permeant (gas phase) can be transferred. An extensive study of porous, nonwettable membranes proved them to be efficient when urine was employed^{1,2}. However, the introduction of wash (soap) water to the waste liquid reduces the contact angle between the fluid and the polymeric substrate, and water intrusion into the pores--under the pressure gradient--occurs instantaneously, causing contamination of the product water.

At this phase of the R&D, pervaporation through a nonisotropic membrane was studied. The membranes used had proven to be efficient in reverse-osmosis desalination processes. It consists of an ultrathin dense layer (0.01-0.1 μm) resting on a porous support (100-200 μm). Such membranes are known as "asymmetric membranes" when cast from the same polymeric material (e.g., cellulose acetate) or "composite membranes" where the dense and porous layers consist of two different materials (e.g., a dense polyamide layer resting on a polysulfone porous support, Appendix, Fig. 1-A). The actual removal of water from the waste solution is through the dense, selective barrier which faces the waste solution. The water molecules which diffuse through this layer are removed through the porous support backing. The backing is not susceptible to clogging, since solids which precipitate on the surface of the membrane cannot dissolve into the dense layer and do not affect the inside pores. Precipitation which occurs on the membrane surface can be reduced in a properly designed cell, which utilizes the hydrodynamic flow of the circulated waste solution to keep the membrane surface scrubbed clean.

* In such a mechanism $J = f(D/L)$, where J is the permeation rate ($\text{g}/\text{cm}^2\text{-sec}$), D is the diffusion coefficient, and L is the membrane thickness.

III. OBJECTIVES

The objective of this program was the development of membrane technology for water/waste separation to be employed in a spacecraft. The program included screening for the availability of membranes for one-step separation by pervaporation. The efficiencies of water separation and mass transfer rates were evaluated under different conditions, and the possible heat dissipation to be gained by pervaporating the permeant water to outer space was considered. Other program elements were the production of high-quality water effluent from mixed urine-wash water wastes and evaluation of controlled release of waste mass from a spacecraft.

Objectives to be met for the possible usage of such a system as a supplemental spacecraft cooling device were outlined by us in coordination with NASA³ and are presented as an example in Figures 2 and 3).

FIG. 2. SHUTTLE ORBITER WASTEWATER STORAGE AND HEAT REJECTION

PROBLEM

- o Water availability to meet all anticipated needs is limited
 - o Metabolic water
 - o Personal hygiene water
 - o Habitability/housekeeping
 - o Spacecraft cooling
 - o Requirement to not dump waste (solids) overboard
 - o Urine is stored onboard
 - o Limited volume for hand/body washing fluids
-

PROPOSAL

Evaporate waste fluids to space vacuum and obtain supplemental spacecraft cooling. Evaporation is accomplished so that all nonvolatile solids are retained.

ADVANTAGES

Significantly reduces on-board storage requirement for waste fluids (factor of 10:1 minimum) 30 day, 7-man mission - 570 liters or 1254 pounds.

Provides supplemental cooling which conserves fuel cell water previously required for cooling. This water is then available for other uses, i.e., personal hygiene and housekeeping.

Heat rejection ~1822 BTU/hr

SAMPLE CALCULATIONS -

Space Shuttle Waste Reduction.

Urine ~ 2 liters/man-day @ 4% solids
Wash Water ~ 1 liter/man-day @ 2% solids
Equivalent ~ 3 liters/man-day @ 3-1/3% solids
3 liters/man-day X 7 men X 30 days = 630 liters/30-day mission
Reduce volume by 10:1 increases solids to 33-1/3%
Volume available for evaporation 570 liters
or 19 liters/day
or 792 milliliters = 1.75 pounds/hr

Theoretical Heat Removal

Heat of vaporization ~580 cal/gr @ 25°C
or 580X792 = 459,360 cal/hr (1 BTU - 252 cal)
1,822 BTU/hr (12,000 BTU/ton of AC) or 0.15 Ton

If we assume ambient (72°F)

Membrane Flux = 0.2 lb/ft²

1.74/0.2 = 8.7 ft² of the membrane area required

If the area is doubled (17.5 ft²) to allow for flux decline, then the membrane package dimensions would be:

Tube Volume = 15 cm X 10 cm

Weight = 3 lb.

Pump Flow Rate = 500 ml/min

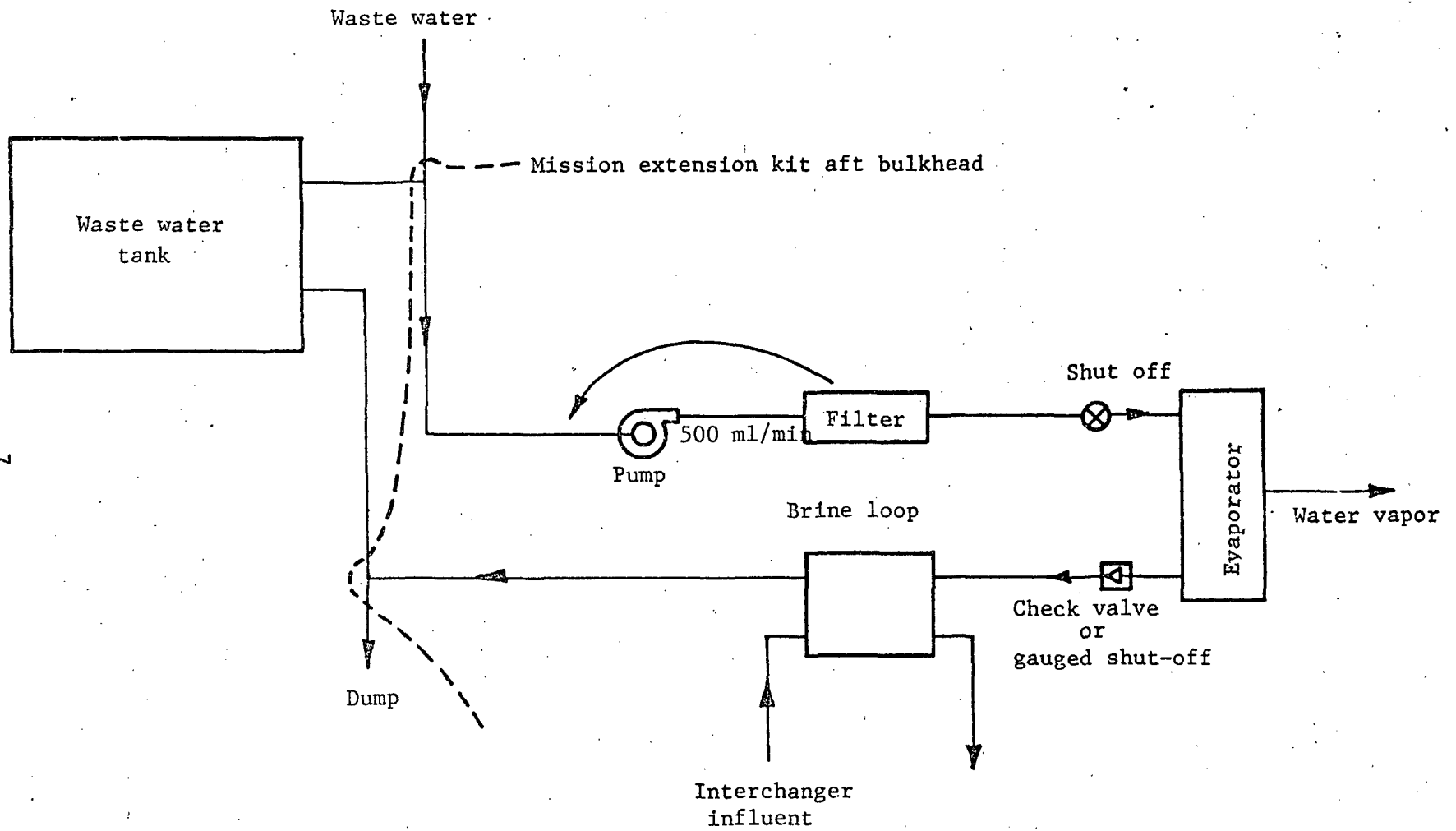


Figure 3. Proposed water discharge and heat dissipation system.

IV. EXPERIMENTAL

A diagram of the membrane separation apparatus as it has been operated most recently is shown in Figure 4. Photographs of the setup are also included. Basically, the waste solution stored in the reservoir is picked up by the pump and is circulated through a heat exchanger, through one compartment of the pervaporation cell, and back to the reservoir. A vacuum is pulled on the other side of the membrane, and the permeation product is collected on the wall of an evacuated condensation chamber immersed in ethylene glycol at -8°C .

Other parts of the system include a needle valve for fine-tuning flow rate, pressure gauges, thermocouple probes, a flowmeter, a stirrer, thermometers, a vacuum gauge, and a drying column.

The thermocouple probes are inserted through septa into Swagelok tees at the entrance and exit ports of the pervaporation cell. The digital readout of the electronic thermometer may be set to display the waste solution inlet and outlet temperatures or the differential temperature between the two probes. The accuracy of the unit is within one-tenth degree Centigrade and is calibrated against a reference mercury thermometer.

A. Cell Design

The cell first used in these experiments was a square reverse osmosis PVC cell with a membrane surface area of 42.32 cm^2 . The cell was slightly modified to serve for pervaporation. After some runs which helped to characterize the system, a new cell, with a membrane area of 79.3 cm^2 , was fabricated from Plexiglas. This new cell, shown in Figure 5, was designed to accommodate a mesh turbulence promoter in the flow stream. In later runs, the turbulence promoter was removed because it contributed markedly to membrane fouling by holding up precipitated solids and allowing them to form dense barrier coatings on the face of the membrane. With the mesh turbulence promoter removed, those parts of the membrane subjected to the high velocity portion of the waste stream were kept scrubbed clean; deposits formed only along the edges of the cavity and in places where eddy currents were observed.

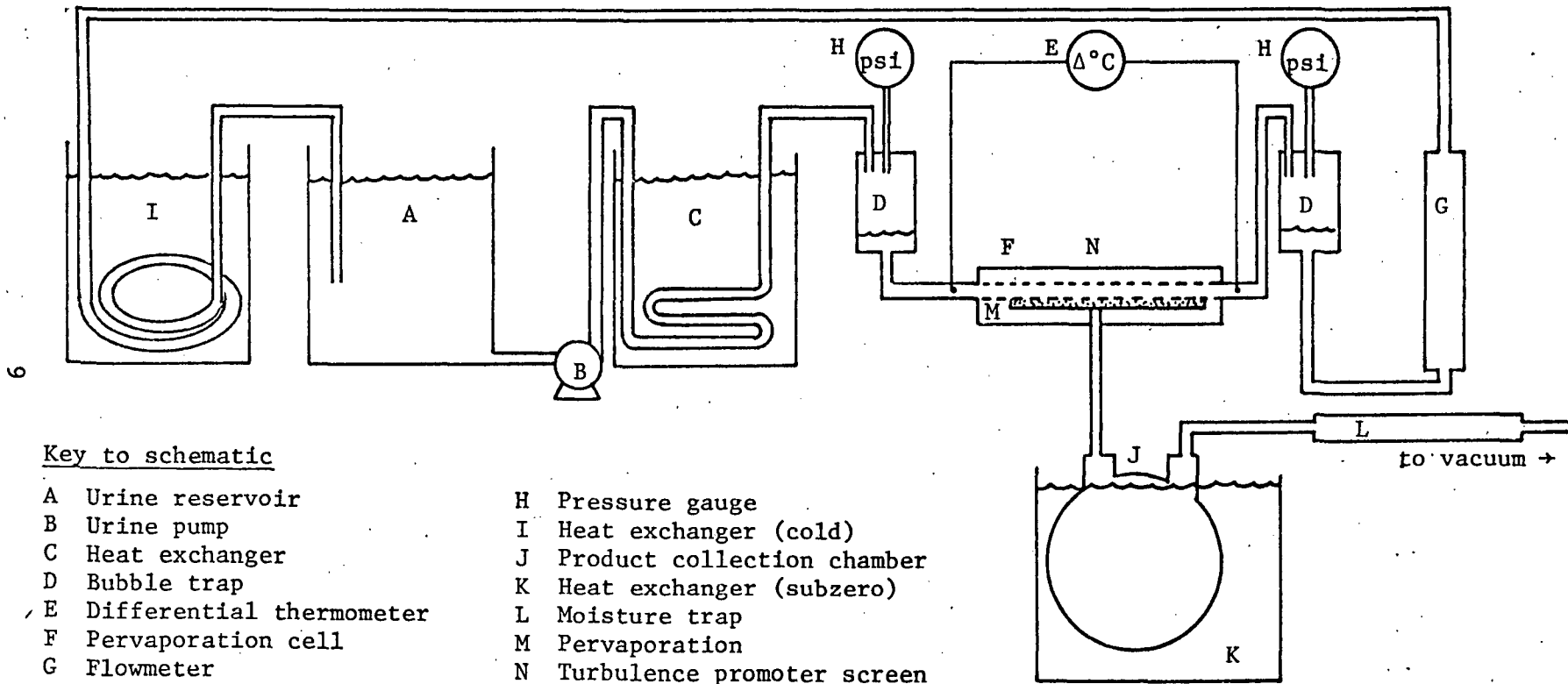
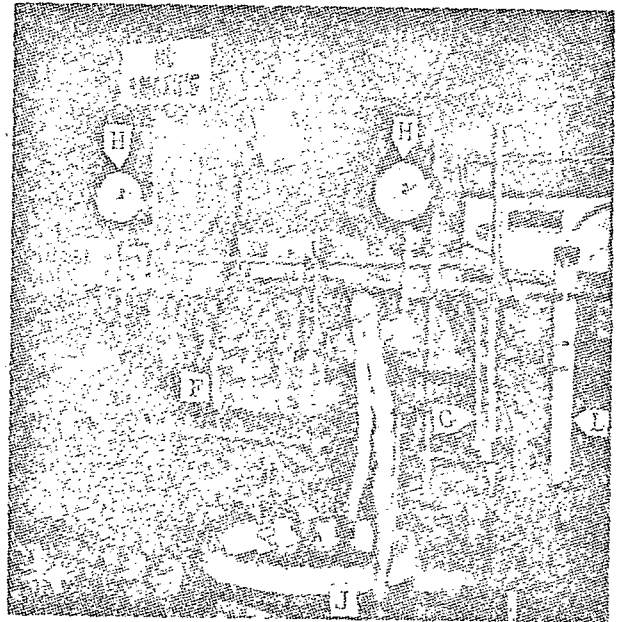
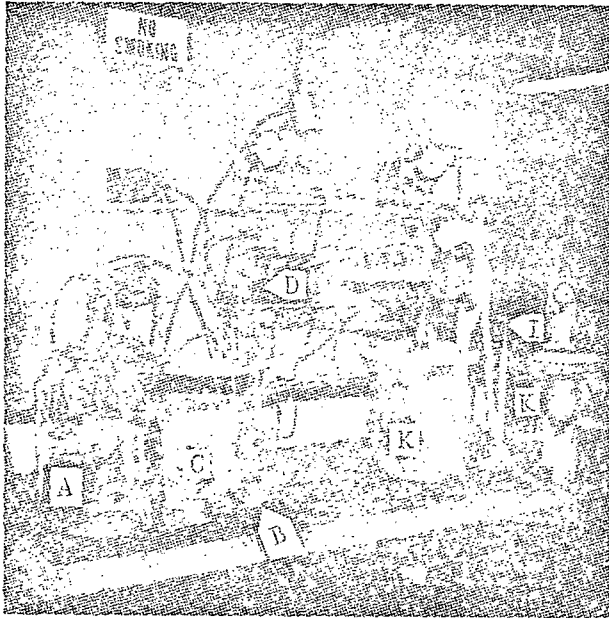


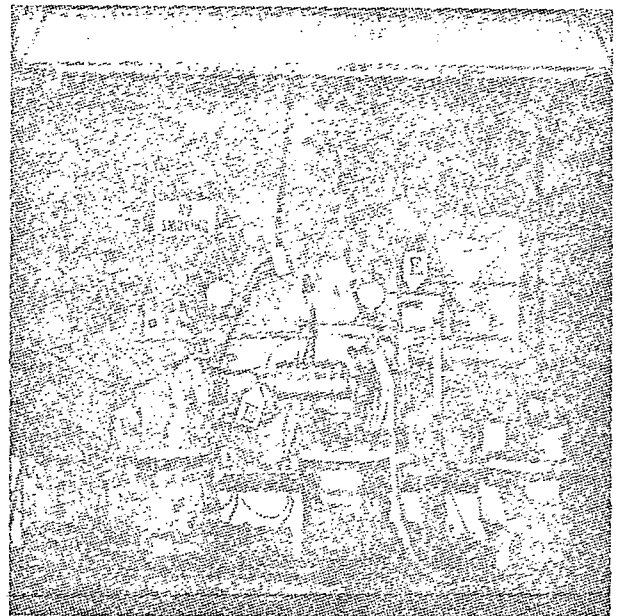
Figure 4. Schematic diagram of test assembly.



Key to Photographs

- A Urine reservoir
- B Urine pump
- C Heat exchanger
- D Bubble trap
- E Differential thermometer
- F Pervaporation cell
- G Flowmeter
- H Pressure gauge
- I Vacuum gauge
- J Product collection chamber
- K Heat exchanger (subzero)
- L Moisture trap

(Note: Upon removing the screen turbulence promoter from the pervaporation cell, N, Figure 4, heat exchanger I was eliminated, as shown in the photographs.)



Pervaporation Test Assembly

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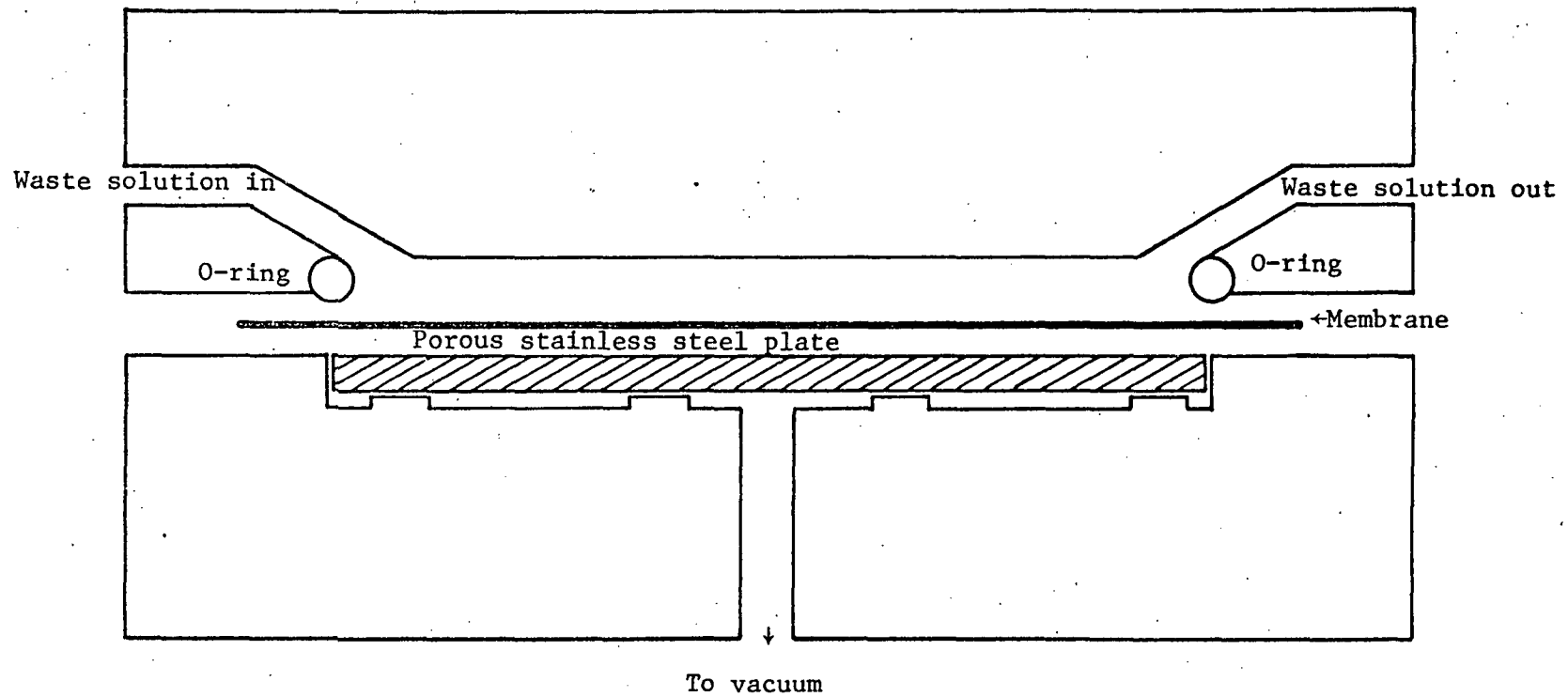


Figure 5. - Pervaporation cell (effective membrane length 13 cm; total effective area 79.3 cm²).

B. Membranes

Composite membranes made of polysulfone porous supports coated by dense, ultrathin, semipermeable membranes were employed. (The membranes had already proven effective for desalination.) The ultrathin membranes consisted of three different types of polymers; polyurea (designated NS-100); poly(ether/amide)(PA-300), and furan resin (NS-200). These membranes can perform under severe pH conditions, have excellent water transport, and display low permeabilities for most organic compounds (see Appendix).

The NS-100 and NS-200 were produced at GSRI. The NS-200 membrane was studied in its hollow fiber configuration. The PA-300 was supplied by Fluid Systems Division/UOP, Inc., and is commercially available. These membranes can be easily fabricated with tightly woven backing support (the PA-300 in effect is made this way), which eliminates the possibility of sudden collapse and rupture of the membrane under vacuum.

C. Measurements

1. Volume (liters) of waste solution in reservoir

The waste reservoir was calibrated in 100 ml increments prior to use. During use the volume was read directly from the attached scale.

2. Nonvolatile solids content (wt%) of waste solution

An aliquot of waste solution was weighed in a tared porcelain crucible, dried overnight at 110°C, cooled in a desiccator, and reweighed. (In such a procedure, all the organic compounds that are volatile or decompose to gas below 110°C are not included in the arbitrary definition "solids content.")

3. Flow rate (ml/min) of circulated waste solution

A ball-type flowmeter monitored the flow rate of the waste solution. This flowmeter was calibrated with waste solution at 25°C and at 49°C. Periodically, a timed output of the waste stream was weighed to confirm the flowmeter readings.

4. Operating pressure (psi) on the circulated waste

A pressure gauge was coupled through a bubble trap chamber to inlet and outlet ports of the pervaporation cell. The pressure was maintained within the range of 1-3 psi.

5. Temperature (°C)

The temperatures associated with the pervaporation cell were monitored with an electronic thermometer and thermocouple probes. These probes (0.050 inch diameter) were inserted through Neoprene septa into Swagelok tees at the inlet and outlet ports of the cell. The digital readout unit could be set to read either inlet temperature and outlet temperature or the differential temperature between the two probes.

Temperatures of the heating and cooling baths were monitored either by mercury thermometers or by stainless steel Weston dial thermometers.

6. Conductivity (µmhos) of waste solution product

Conductivity was read from a YSI conductivity bridge equipped with a standard rubber bulb operated aspiration probe equipped with black platinum electrodes.

7. Dissolved ammonia in permeant (NH₃)

Ammonia concentration (ppm) was read directly with a calibrated ammonia electrode.

8. Total organic carbon (ppm) in permeant

Total organic carbon was expressed as the difference between total carbon content and total inorganic carbon content as measured by a Beckman TOC apparatus.

9. Vacuum (mmHg) in permeant line

Vacuum was measured by a mercury vacuum gauge placed in the permeant line immediately prior to the vacuum pump.

10. Standard waste solution

The feed solution consisted of 50 parts of urine, 49 parts of deionized water, and 1 part soap solution (0.1% palmetto soap v/v). The urine was collected from the laboratory staff and does not represent the metabolic diet of a spacecraft crew.

V. METHOD OF APPROACH

Membrane separation by pervaporation was selected as the most suitable technique for continuous unloading of wastewater from the spacecraft in short space missions. The alternative membrane method, separation by reverse osmosis, was ruled out of the present study but should be reconsidered for long missions or for space colonies. In such an evaluation, reverse osmosis should be compared with pervaporation, especially for water reuse.

The membranes chosen for study are all commercially available. Since a relatively small membrane area (up to $1 \text{ m}^2 \sim 10 \text{ ft}^2$) would be used in any spacecraft application, the membranes were tested chiefly in a flat sheet form. Hollow fibers in general are unsuitable for processes where continuous precipitation occurs. However, one set of experiments was carried out to characterize major problems involved.

The membranes were of the "composite" type, produced with fabric-reinforced backing which protects the membrane from collapse under reduced pressure. Two types of experiments were carried out:

1. Characterization of membrane transport employing an initial volume of waste solution recirculated through a reservoir. Transport data were collected while the volume was progressively reduced and the waste concentration simultaneously increased.
2. Simulation of operational conditions in a spacecraft, where an initial volume of waste solution was introduced to the apparatus and additional volumes of the same solution grade were added periodically (whenever initial volume was reduced 2-3 times). In such experiments, the volume during the run never exceeded the initial volume. The mass transfer plot as a function of time for such a run is a series of hysteresis curves that are functions of the concentration buildup and membrane characteristics.

In the present study, the waste solution was not treated or pretreated before circulation over the membrane (unlike our previous study). The effect of the bacteria and enzymatic degradation on the waste solution, on the membrane, and on the product effluent were examined. The quality for reuse was evaluated simply by the quality of the product effluent from the pervaporation system.

A. Summary of Hollow Fibers Experiments

Hollow fibers are considered a preferred configuration for separation by pervaporation⁴. They are mechanically self-supporting, and for pervaporation, they display a high packing density (occupying rather small volumes while providing large surface areas). A large diameter hollow fiber can be employed by circulating the feed liquid either within the fiber bore or on the external surface. Small diameter fibers are susceptible to plugging when heterogeneous solutions (liquid plus solid) are employed.

Porous fluorocarbon and composite NS-200 (dense furan resin coated with porous polysulfone substrate) hollow fibers were studied. Both were potted into standard hollow fiber module configurations. The fluorocarbon fiber set had a bore diameter sufficiently large (790 μm)* to permit pumping of the urine-soap solution directly through the bore. However, in the presence of soap, the surface tension of the urine solution dropped so far that the membrane wetted and urine solution came through the membrane.

The NS-200 coated polysulfone hollow fiber set had such a small bore diameter (80 μm) that the waste solution had to be pumped past the outside of the fiber while vacuum was applied to the bore. Several trials were made with this hollow fiber. In one case, vacuum was applied to the bottom of the module and nitrogen gas was bled in through the top at 10 psig. In another trial, the top was opened to the atmosphere in an attempt to drive the water out of the bore. The maximum effective pervaporation rate attained was $1.16 \times 10^{-3} \text{ g/cm}^2\text{-hr}$. This yielded a total of 5.1 g of water from a 200 cm^2 area over a period of 22 hours. These results show that small diameter fibers exhibit poor transport properties which may be attributable to the following:

1. Water vapor passing through the membrane to the bore could accumulate faster than the vacuum pump could remove it, thus decreasing the water vapor pressure gradient to zero toward the lower end of the module.
2. The extreme form of this effect would result in condensation of a microdroplet of water within the bore near the bottom end of the fiber, effectively reducing the operational area of module from the inside area of the fiber to the area of the bead of water.

* 1/32 inch

B.. Experiments with Flat Sheet Composite Membranes

1. Experiment 1. Continuous pervaporation run - reduction of a given volume of waste solution at ambient temperature (25°C)

a. Conditions

Membrane - PA-300 (fabric reinforced)

Membrane area - 79.30 cm²

Initial volume (V_i) - 8 liters

Volume addition - none (no additional waste solution was added through the entire run)

Total volume of run - 8 liters

Final volume (V_f) - 1.5 liters

Operational temperature - 25° ± 1°C (~77°F)

Solution composition - Standard waste solution

Duration of run - 637 hr - Continuous, except for periodic 10 min breaks to remove product (permeant)

Flow rate - 400 ml/min

b. Results summary (see Figures 6-10)

Initial permeation rate 0.17 g/cm²-hr

Final permeation rate 0.089 g/cm²-hr

Permeant: Initial TOC - 4 ± 1 ppm Initial NH₃ - 2 ± 1 ppm

Final TOC - 9 ± 1 ppm Final NH₃ - 33 ± 1 ppm

c. Description

PA-300 membrane is a poly(ether/amide), thin-film composite membrane which has been coated upon a tightly woven fabric support. Figures 2-A and 3-A and Table 1-A in the appendix contain data provided with the membrane³ for operation in a reverse osmosis mode. Figure 2-A indicates better than 99% sodium chloride rejection (at pH 5.4) above 650 psi and a water flux of 10-25 gal/ft²-day between 600 and 1,000 psi. Figure 3-A reveals rejections varying from 99.2% to 98% as the pH increases from 5.5 to 8.7 and a water flux ranging from 17.3 to 17.9 gal/ft²-day over the same pH range (all at 1000 psi). Table 1-A lists the rejections for a variety of solutes at specified pH levels and solute concentrations. These performance properties illustrate theselective transport properties of the membrane as they might apply to pervaporation.

Sealing difficulties were encountered during the first trial run of the PA-300 membrane (Figure 5). Air from outside the system was drawn through the fibers of the support fabric, making it impossible to achieve adequate vacuum and contributing atmospheric moisture to the product collection chamber. This problem was eliminated by sealing the edges of the membrane with RTV Silastic, assembling the cell, and then allowing the RTV to cure in situ. No further sealing difficulties were encountered.

Chiller No. 2 (Figure 4) was removed from the system to make a run with the waste solution at ambient temperatures. The heating bath was left in the system but was operated at 25°C (77°F). This value was expected to be the upper limit of the temperatures encountered within the laboratory and could, therefore, be expected to yield a reasonably constant value during the run.

A large reservoir was charged with 8 liters of the standard urine/water/soap mix and the system was operated continuously for 640 hours, reducing the waste solution volume from 8 to 1-1/2 liters (concentration factor = 5.33). Figure 6 shows a plot of the decrease in waste solution volume with time. The dashed line, which is a straight line overlay extending from the initial portion of the curve, illustrates that the water removal rate is constant until the volume reduction is 2X; the pervaporation rate falls off appreciably thereafter.

The pervaporation rate is shown in Figures 6,7, and 8. Figure 8 illustrates the decrease in permeation rate as a function of time. The slight increase early in the run was duplicated in other runs and appears to be an actual characteristic of the membrane and not an artifact. Figure 7 is a computer print-out of a least-squares best fit line to the same pervaporation rate plotted against the concentration factor of the waste solution.

The increase of solids in the waste solution as a function of time is shown in Figure 9. Note that although the volume concentration reached a factor of ~5.5X, the solids concentration increased only by a factor of ~3.4X. It should be re-emphasized that analysis of solids was done gravimetrically by weighing out a sample of waste solution, drying at 110°C, and reweighing the dried solids. This technique records only the suspended, dissolved solids which are being circulated in the waste solution stream. It does not measure those solids which have deposited out on the inner surfaces of the apparatus (tubing walls, flowmeter, membrane surface, etc.), or precipitated in the waste solution reservoir where the flow rate is at its minimum.

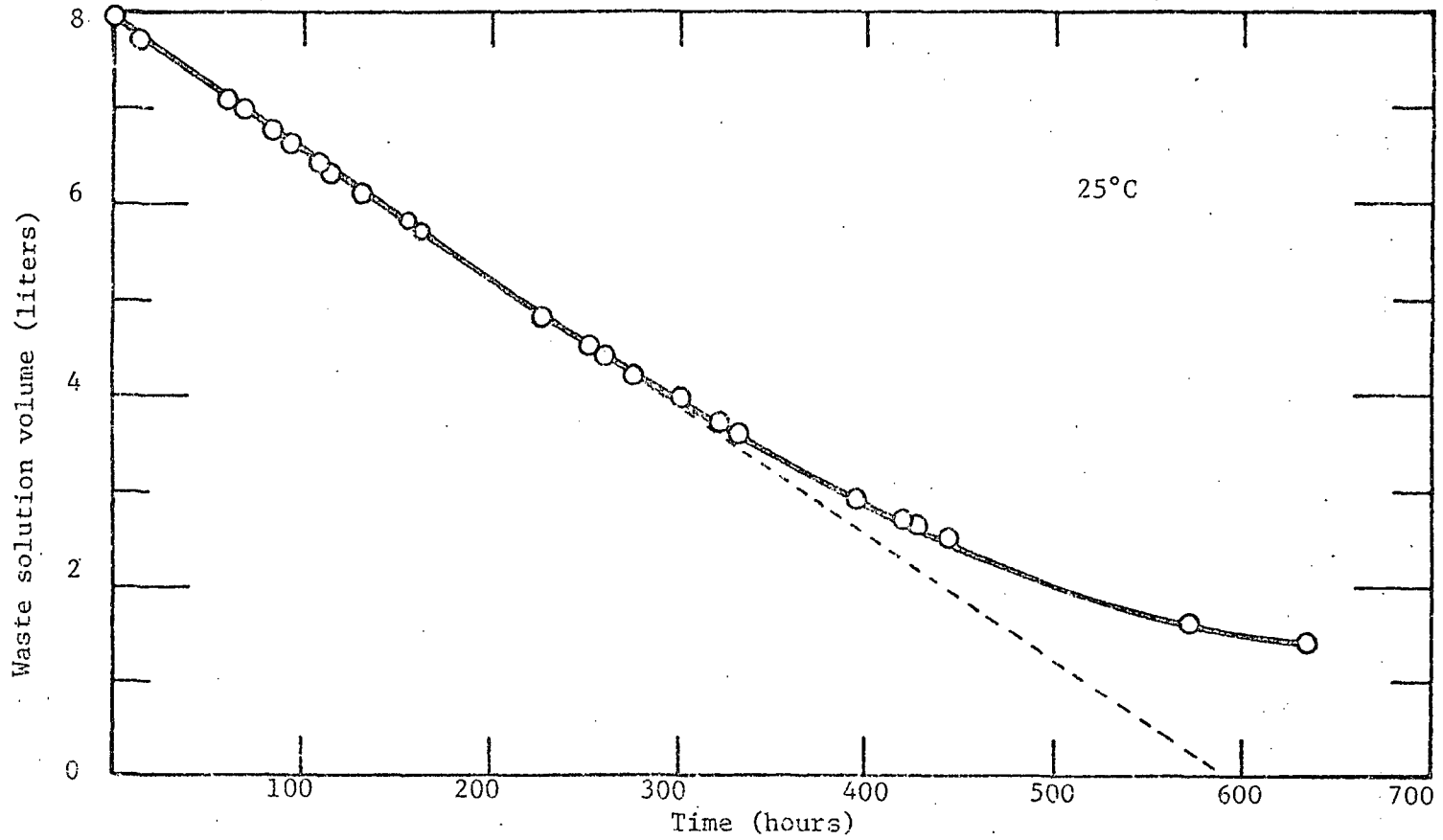


Figure 6. Volume decrease vs. time in continuous pervaporation run of standard waste solution (PA-300 membrane with 79 cm² surface area). Initial permeation rate, calculated from the tangent, is 0.17 g/cm²-hr.

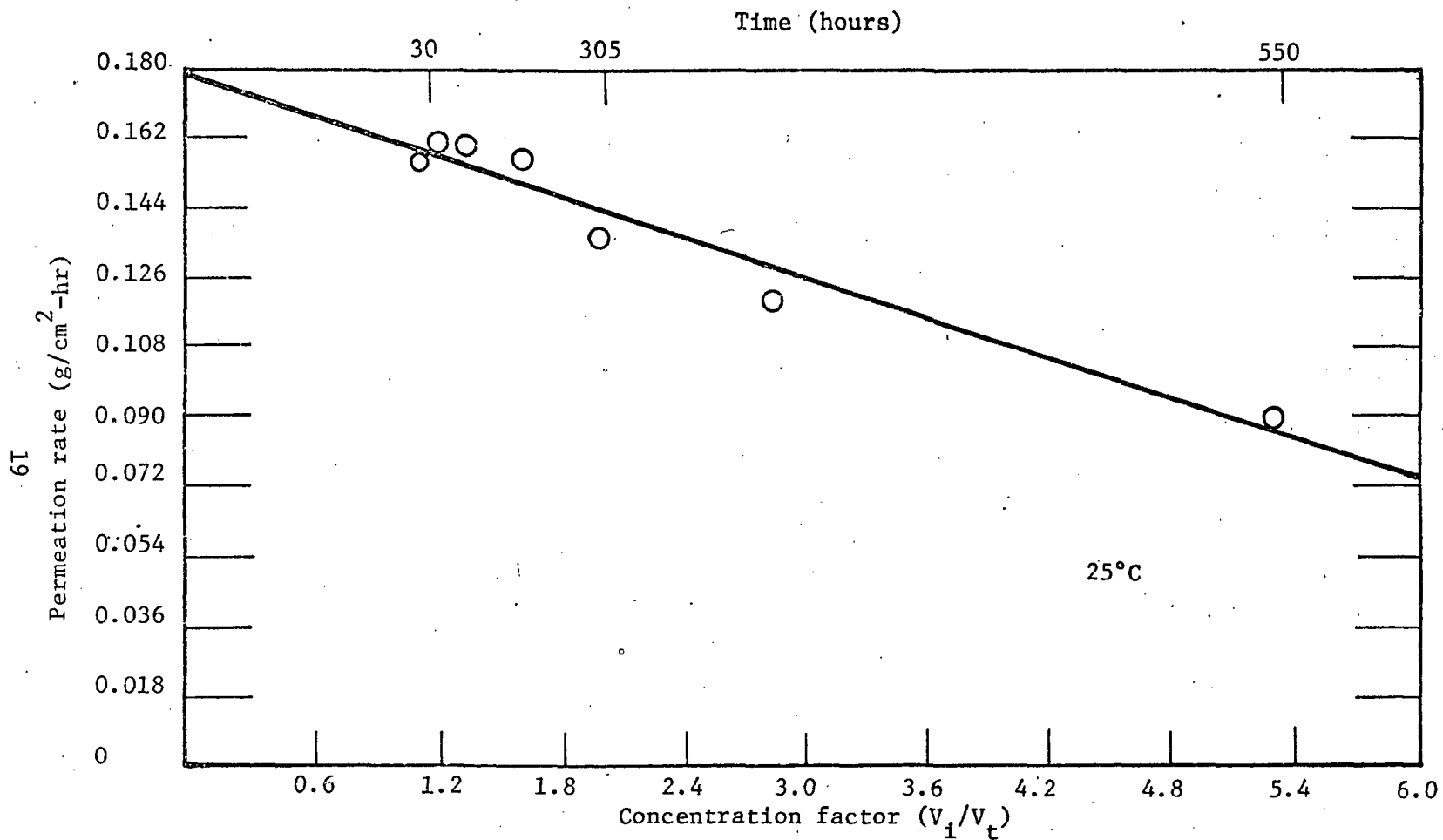


Figure 7. Permeation rate as a function of concentration increase in continuous pervaporation run ($V_i = 8$ liters; computer printout). Points were calculated from the volume collected.

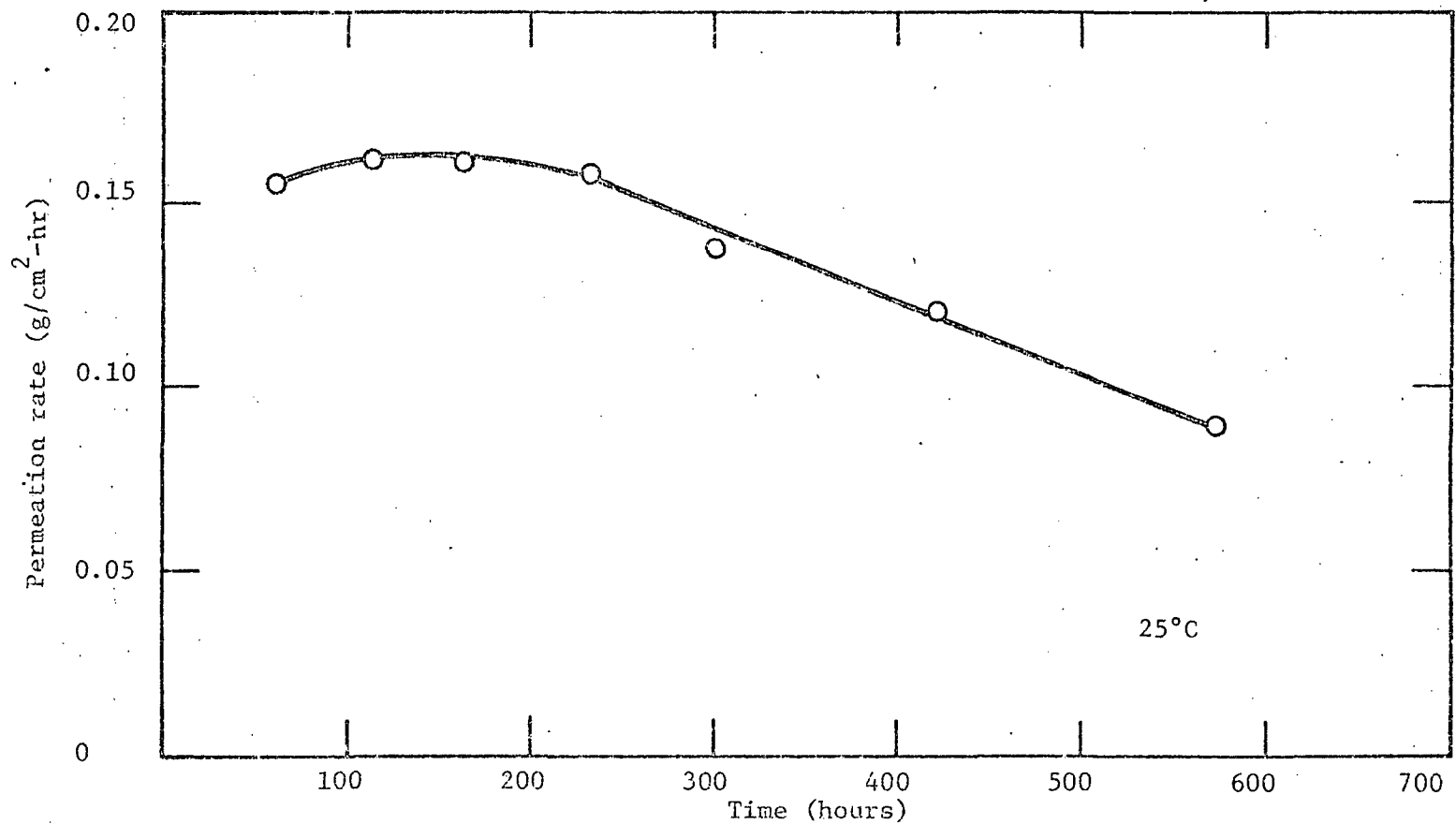


Figure 8. Permeation rate as a function of time in continuous pervaporation run (see Figure 7). The data points are calculated from the total mass accumulated in the condensation trap.

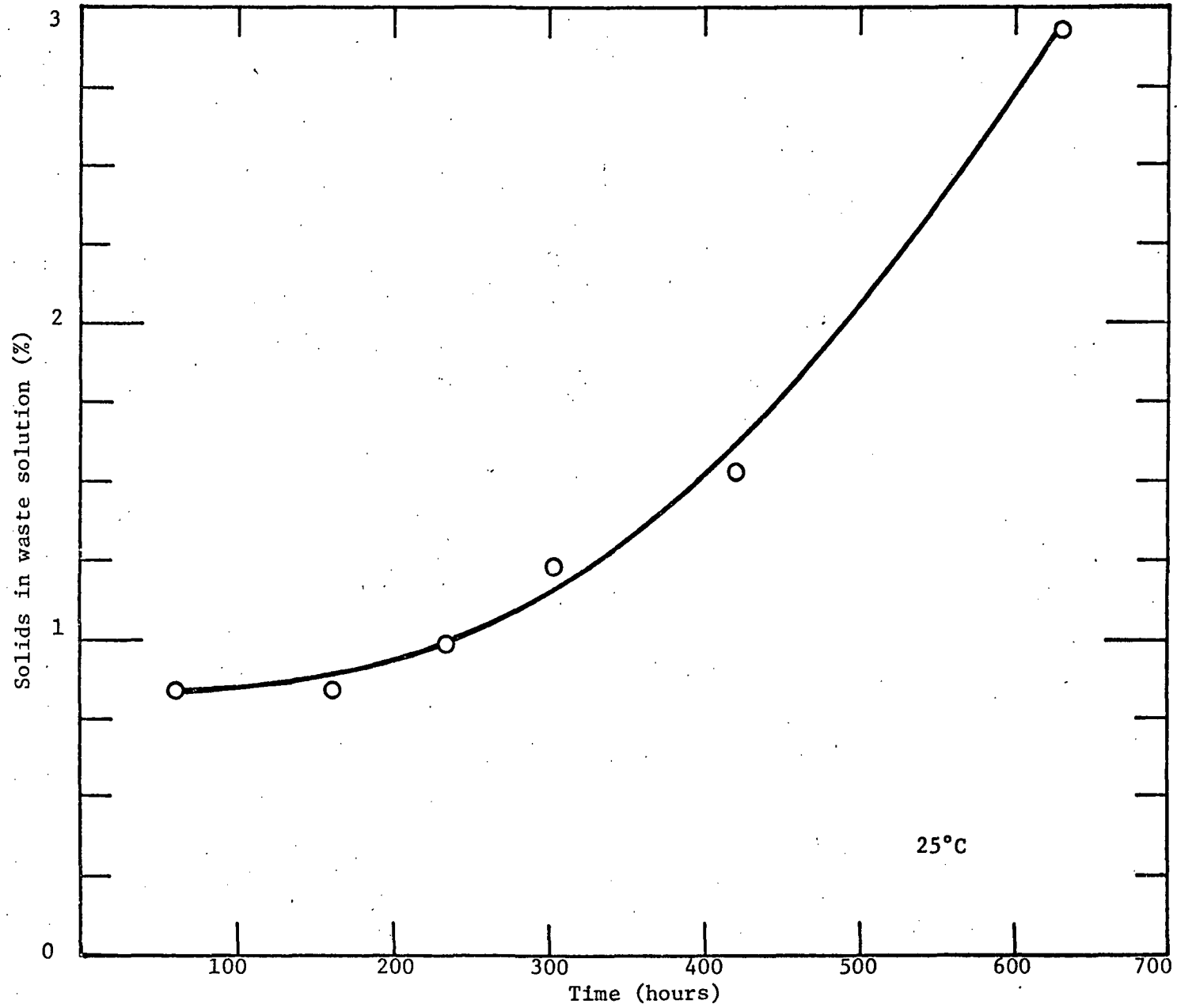


Figure 9. Buildup of dissolved and suspended solids in a pervaporation concentration run ($V_i = 8$ liters).

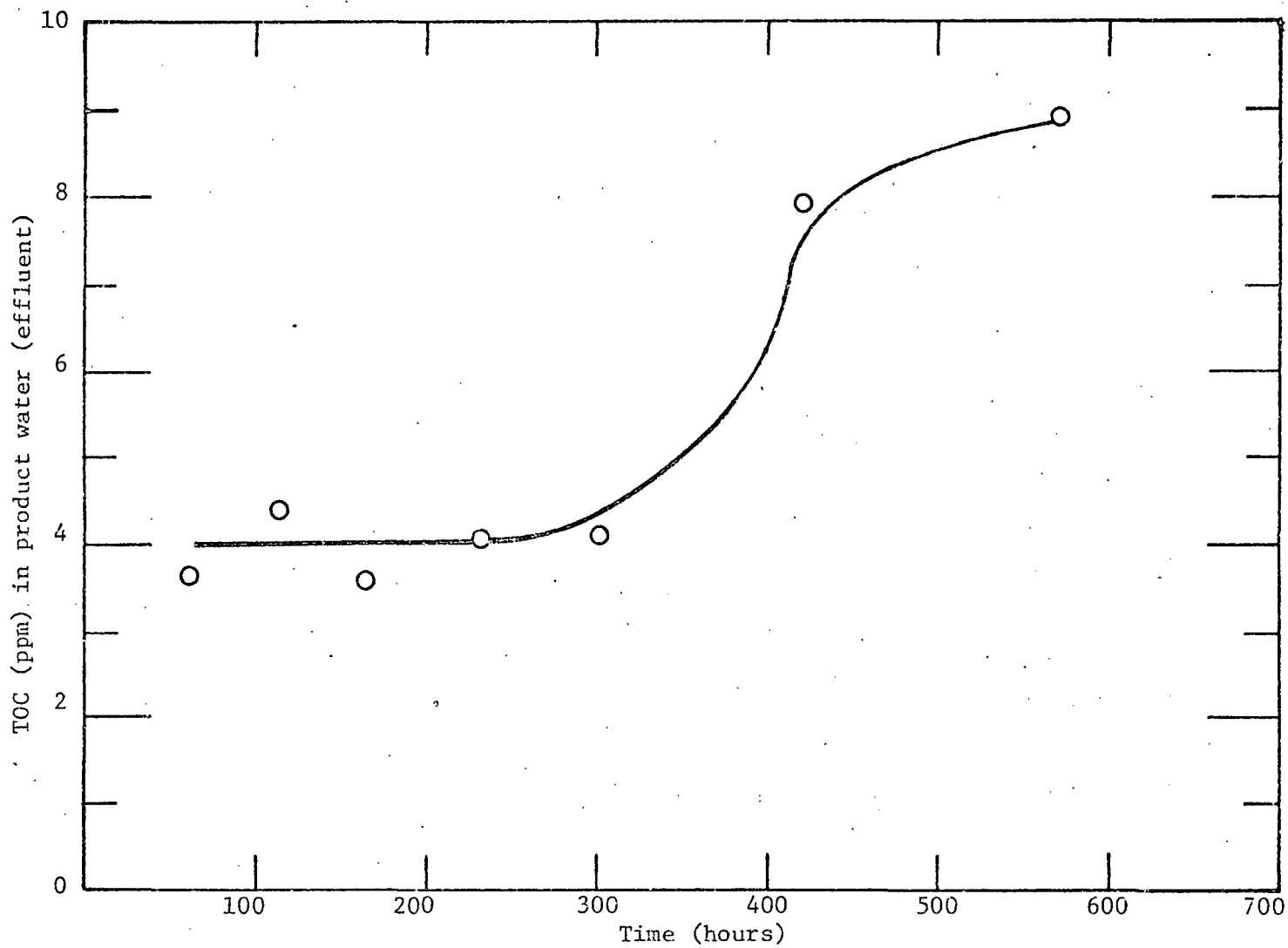


Figure 10. Time vs. total organic carbon found in product effluent of continuous pervaporation run ($V_i = 8$ liters; data points represent 24 hr batch samples).

2. Experiment 2. Continuous pervaporation run - rate of membrane fouling and membrane regeneration technique

a. Conditions

Membrane - PA-300 (fabric reinforced)

Membrane area - 79.30 cm^2

Initial volume (V_i) - 6 liters

Volume addition - none

Final volume (V_f) 1.8 liters

Operational temperature - $48^\circ\text{C} \pm 0.8^\circ\text{C}$ ($\sim 120^\circ\text{F}$)

Solution composition - Standard waste solution

Duration of run - 148 hr - continuous, except for 1-min breaks to remove product.

Flow rate - 400 ml/min.

b. Results summary (see Figures 11-13)

Initial permeation rate - $0.6 \text{ g/cm}^2\text{-hr}$

Final permeation rate - $0.25 \text{ g/cm}^2\text{-hr}$

Permeant: Initial TOC - $10 \pm 1 \text{ ppm}$ Initial NH_3 - $14 \pm 1 \text{ ppm}$

Final TOC - $6 \pm 1 \text{ ppm}$ Final NH_3 - $31 \pm 1 \text{ ppm}$

Heat dissipation ($\Delta^\circ\text{C} \times \text{flow rate}$): Initial - 520 cal/min

Final - 160 cal/min

After regeneration - 600 cal/min - Distilled water at 49°C

c. Description

A short run (150 hr) was made at 49°C (120°F), which was the temperature recommended by NASA for testing waste solution intended for use in the cooling system of a spacecraft. Total organic carbon and inorganic carbon in the product water are plotted vs time in Figure 11. The figure illustrates that the ammonia permeant follows the same transport characteristics as the inorganic carbon. A plot of the solids concentration in the waste solution vs time is shown in Figure 12.

At the conclusion of the run, as much waste solution as possible was removed from the cell, and then inlet and outlet ports were hermetically sealed. A vacuum was continuously applied to the product side of the membrane until all traces of liquid were removed from the liquid side of the cell (4 days). At that time, the solids deposited on the membrane were fully dried and had flaked to some extent. Distilled water was circulated across the face of

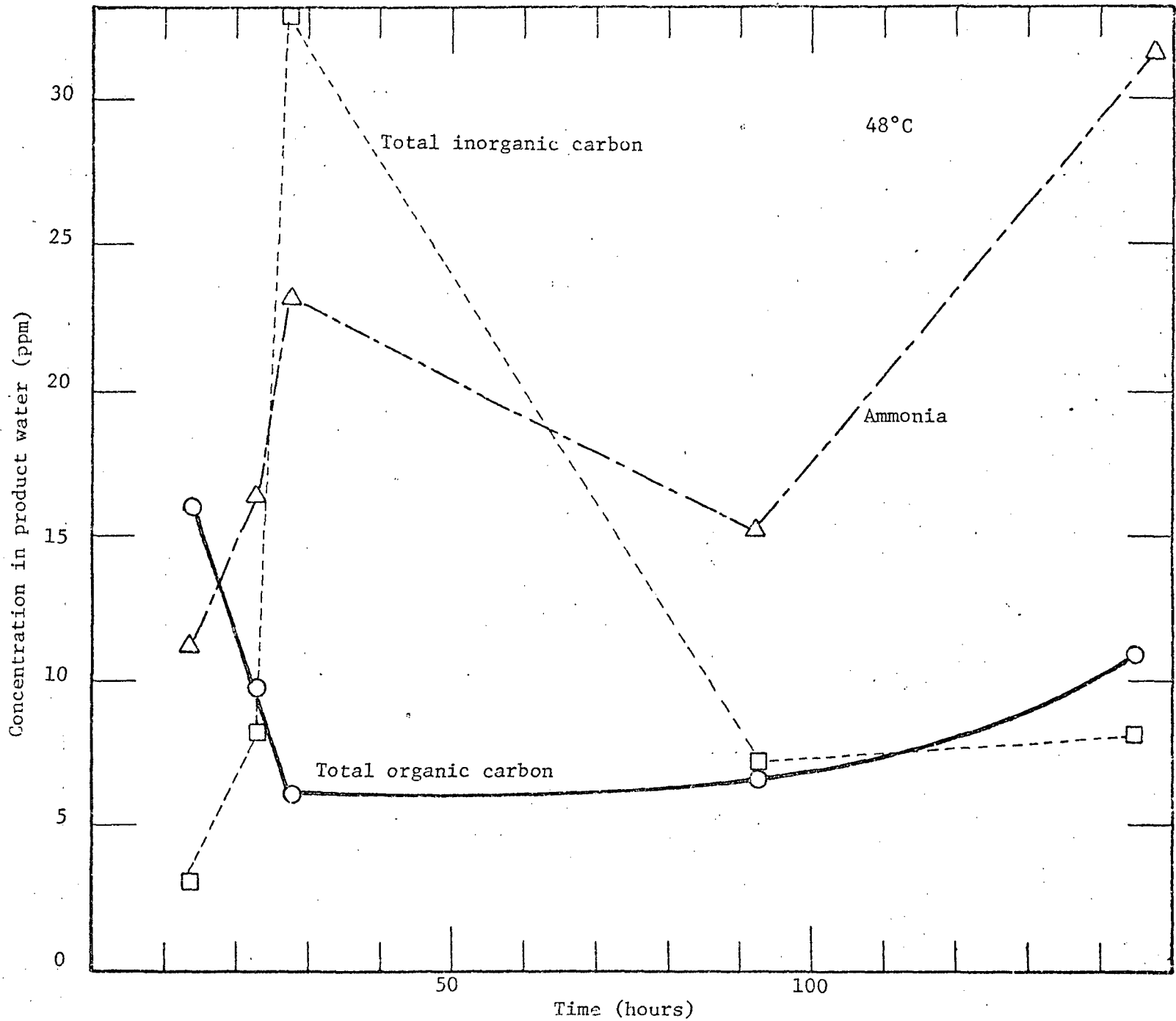


Figure 11. Concentration variation of ammonia, inorganic carbon and total organic carbon during a pervaporation run ($V_i = 6$ liters). (The ammonia and inorganic carbon are degradation products of urea and follow the same trend.)

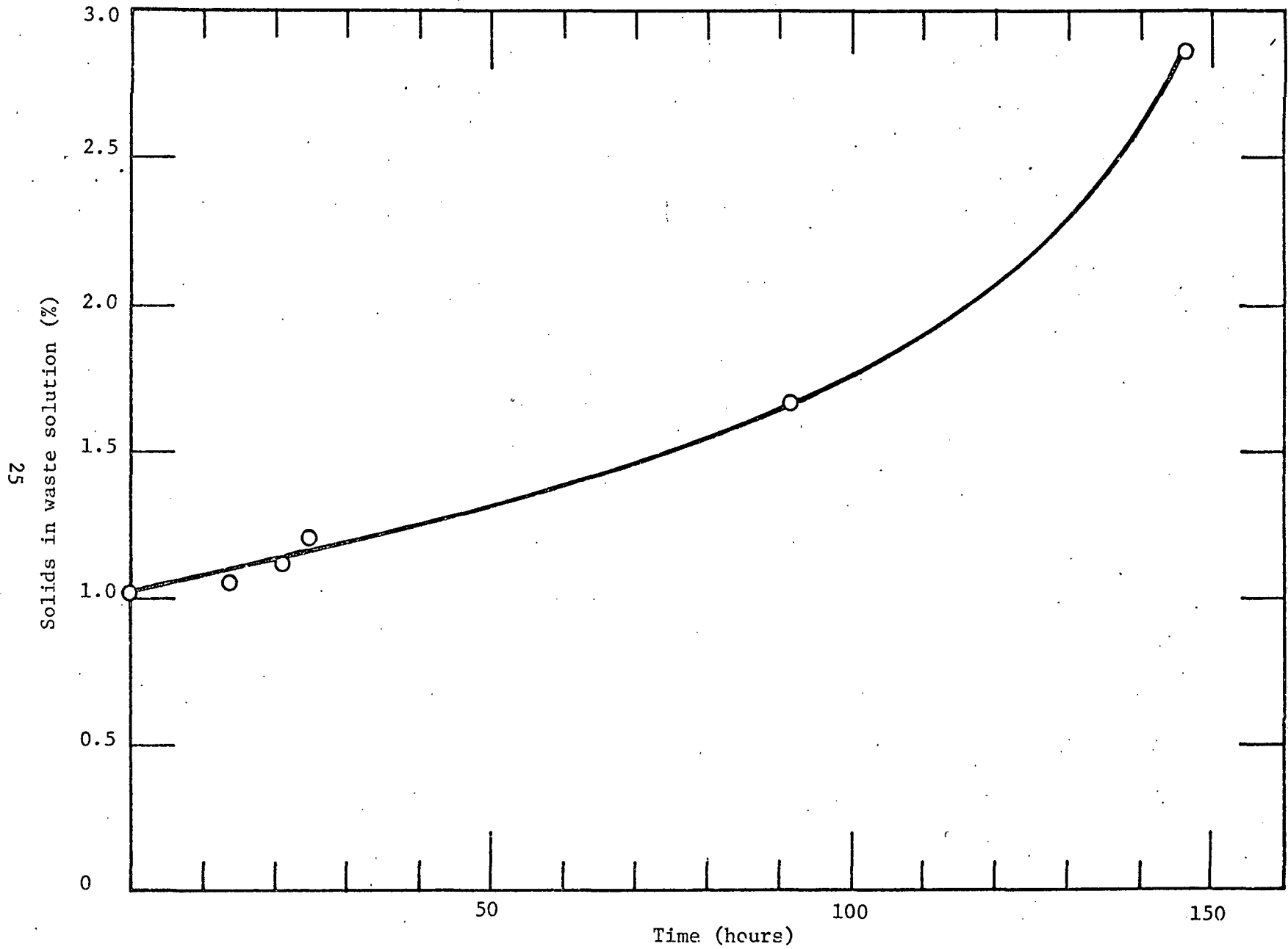


Figure 12. Buildup of dissolved and suspended solids in the waste solution during a pervaporation concentration run ($V_i = 6$ liters).

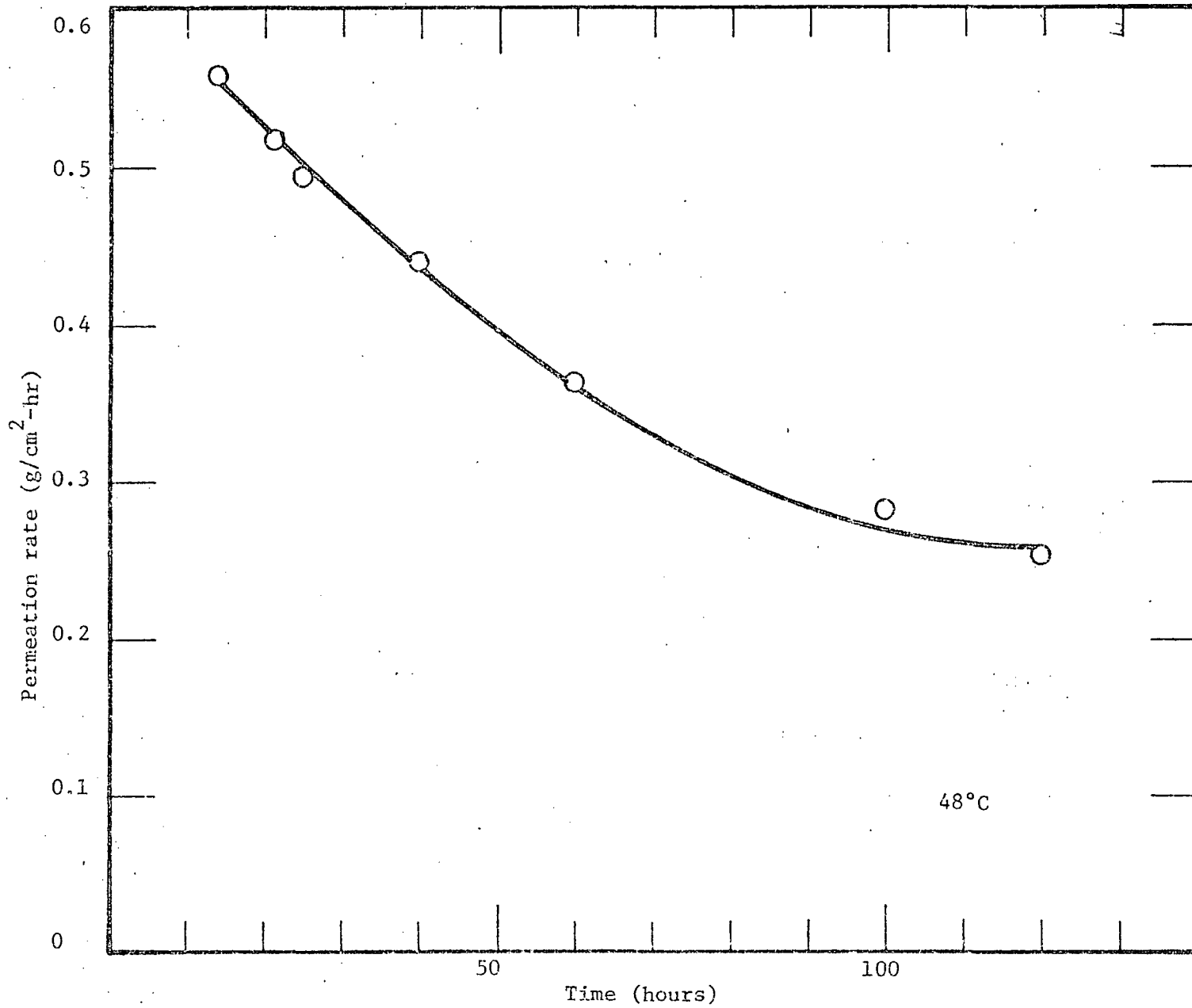


Figure 13. Permeation rate as a function of time for continuous pervaporation run ($V_i = 6$ liters).

the membrane in an attempt to flush the scale away and regenerate the pervaporation capabilities.

Approximately 50% of the original surface of the membrane was re-exposed by the flushing action. While no specific pervaporation data were recorded, the temperature differential across the cell rose to its original value at the beginning of the run, indicating full regeneration of the pervaporation capabilities.

3. Experiment 3. Permeation and heat dissipation rates at various waste solution flow rates

a. Conditions

Membrane - PA-300 (fabric reinforced)

Membrane area - 79.3 cm²

Initial volume (V_i) - 2 liters (volume kept constant at 2 liters by returning all permeant to reservoir)

Operational temperature - 48° ± 1°C (≈120°F)

Solution composition - Standard waste solution

Duration of run - 9 runs of 100 min each at different flow rates

b. Results summary

Day	Run No.	Flow Rate (kg/hr)	Temp. Gradient Δ°C	Product			Pervaporation Rate (g/cm ² -hr)	Heat Dissipation (Kcal/m ² -hr)	
				H ₂ O Rate (g/hr)	TOC (ppm)	NH ₃ (ppm)		by Δ°C*	by Heat of Vaporization**
1	1	2.61	7.35	36.87	16.5	8.6	0.465	2419	2643
1	2	5.76	5.17	48.42	11.2	11.2	0.611	3755	3472
2	3	7.56	3.65	42.42	17.3	42.8	0.535	3479	3042
2	4	13.86	2.45	47.34	27.2	66.5	0.597	4282	3393
2	5	19.80	1.80	56.46	10.1	76.0	0.593	4494	3373
2	6	24.24	1.40	50.16	12.2	80.5	0.632	4280	3596
2	7	31.02	1.10	49.80	12.0	118	0.628	4303	3570
5	8	33.00	1.10	61.05	14.7	187	0.770	4576	4377
5	9	41.88	0.90	60.39	15.9	190	0.761	4753	4323

*Δ°C method. Total mass of fluid through the cell times the average temperature drop.

**Heat of vaporization. Total mass of product water times heat of vaporization of water at 49°C.

c. Description

A small reservoir was charged with 2 liters of the standard waste solution. This reservoir was kept topped off to the 2 liter mark by adding the product effluent throughout the run to keep the solids concentration constant in the waste solution. Two methods were used to derive the heat dissipation values presented in Figure 14.

Lower transport rate and hence lower heat transfer rates are observed for the very low waste solution flow rates. This can be attributed to laminar flow occurring across the membrane at very low flow. There is little exchange of solution at the waste solution channels through the center of the cell and the membrane edges. Increased flow rates would provide improved turbulence, better mixing, and a more nearly homogeneous solution across the membrane.

These data are presented in tabular form in the results summary, above. The heat dissipated is presented as kilocalories per square meter per hour to facilitate comparison with other systems. The heat loss varies from 2400 to 4750 Kcal/m²hr as flow rates increase.

The waste solution was allowed to age in order to study the effect of aged urine on a fresh membrane which did not contain a deposited layer of precipitants. Runs 1 and 2 were carried out within 8 hrs; runs 3-7 within 20-30 hrs, and the last two runs within 96-104 hrs. The pronounced effect can be seen in ammonia product generation, which is 22 times larger in run 9 than in run 1; while the water permeation rates increased by a factor of only 1.64.

4. Experiment 4. Cycle runs of waste solution

a. Conditions

Membrane - NS-100

Membrane area - 79.30 cm²

Initial volume (V_i) - reservoir (2 liters) + system volume
(350 ml) = 2350 ml

Volume addition - Standard solution was added periodically
(see Figures 15 and 16)

Total volume of the run - 11 liters (total permeant collected,
10 liters)

Operational temperature - 40°-50°C (104°-122°F)

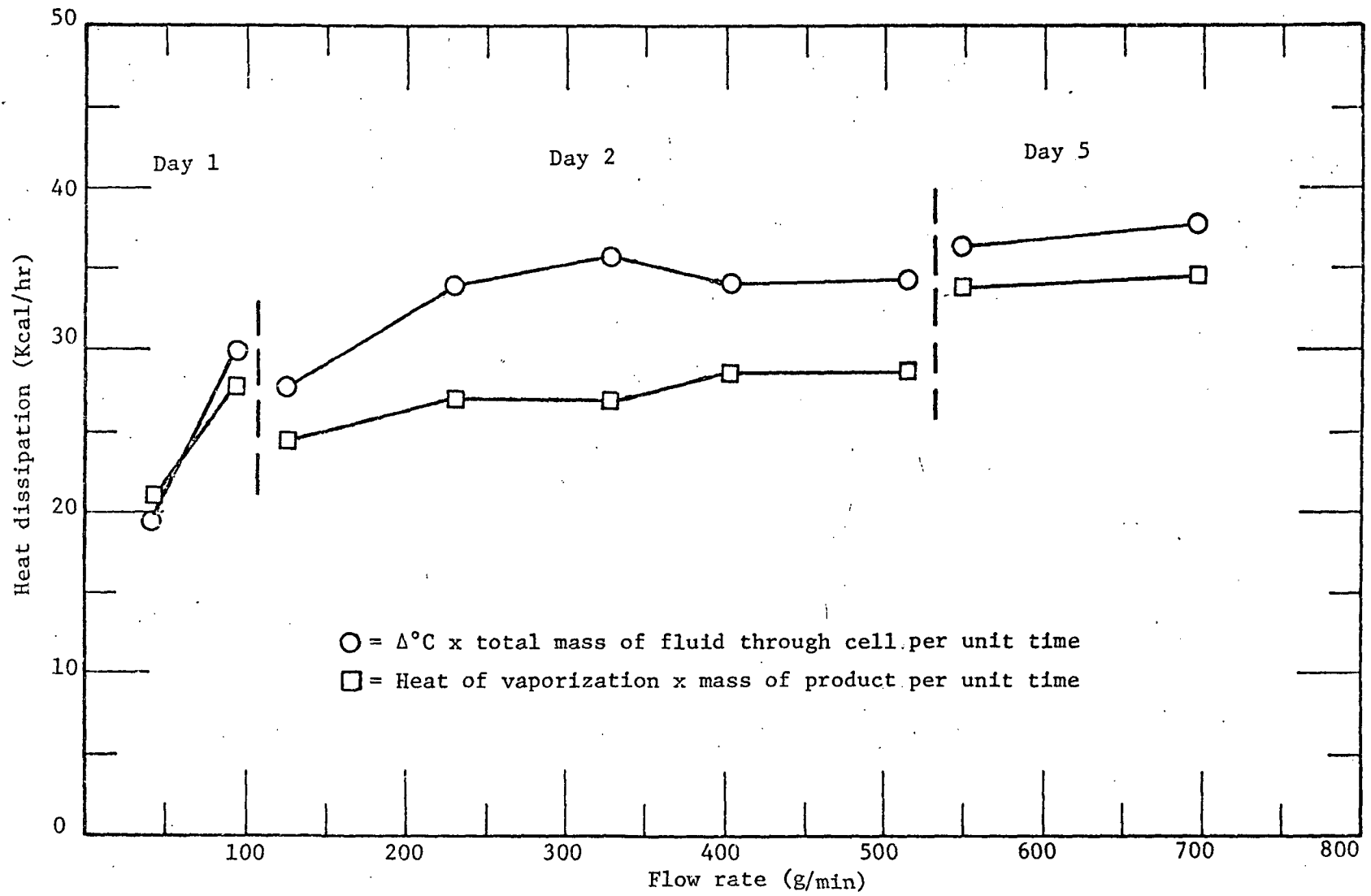


Figure 14. Heat dissipation in pervaporation vs flow rate.

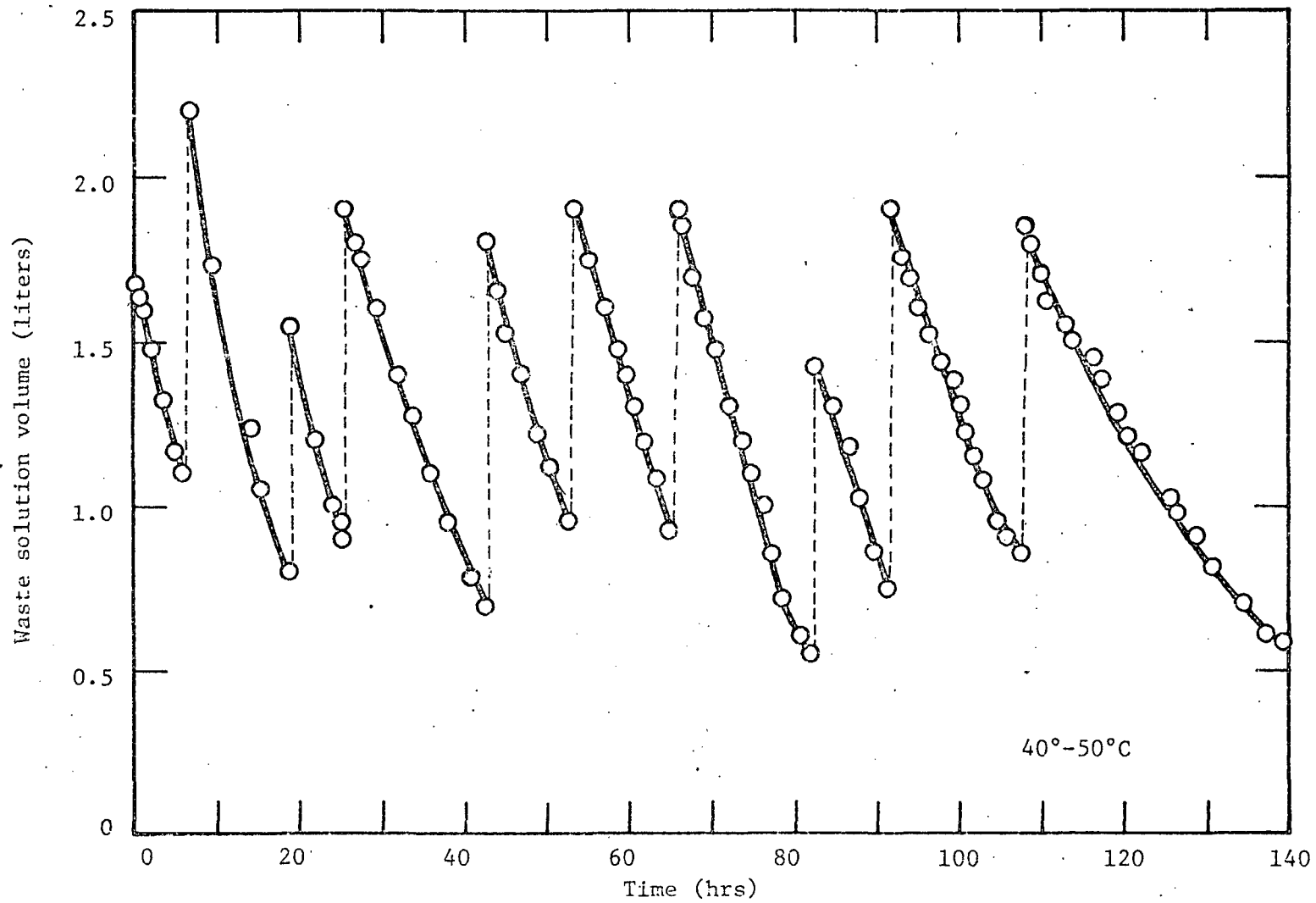


Figure 15. Waste solution volume vs time in a cyclic pervaporation run.

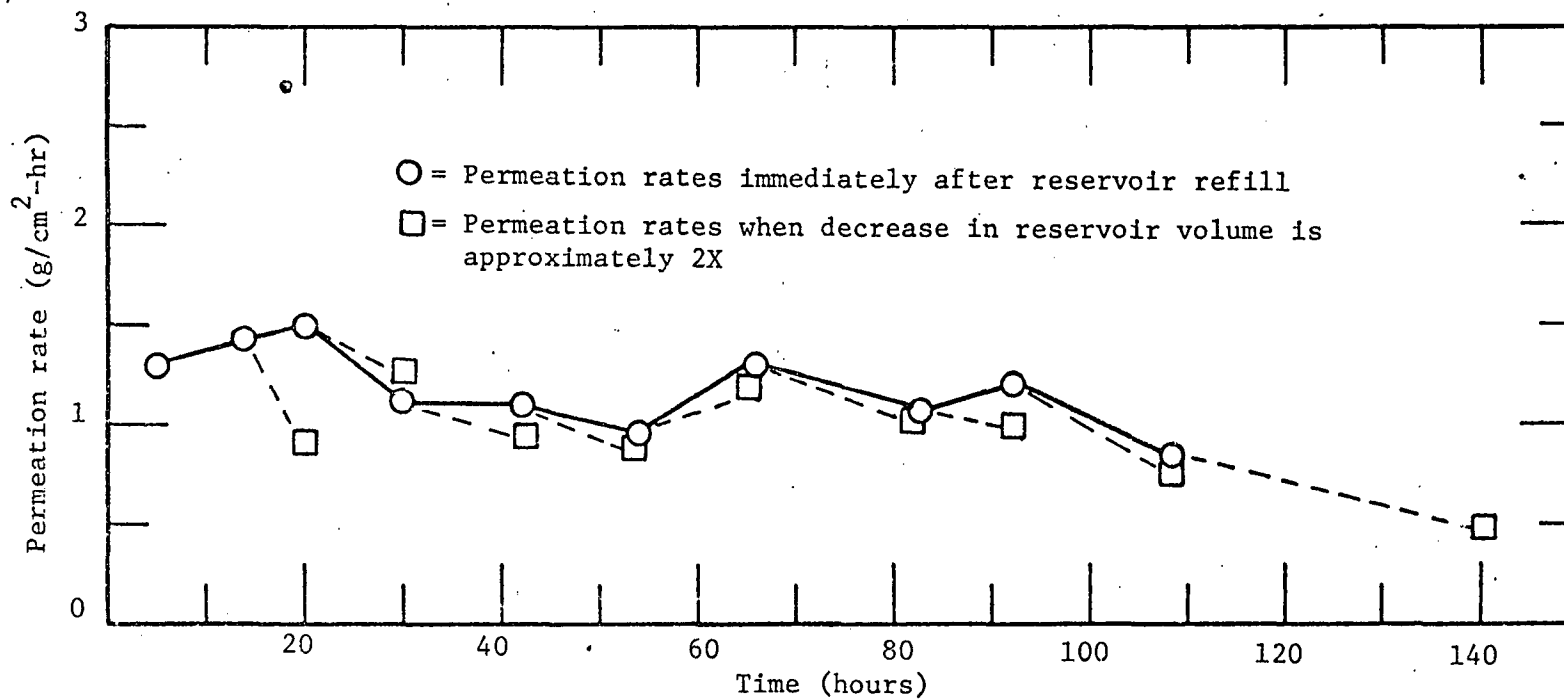


Figure 16. Permeation rate of effluent in a cyclic pervaporation run.

Solution composition - Standard waste solution

Duration of run - 140 hr (8 hr/day)

Solution flow rate - ~500 ml/min

b. Results summary

Initial permeation rate - $1.24 \text{ g/cm}^2\text{-hr}$

Final permeation rate (100 hr) - $0.83 \text{ g/cm}^2\text{-hr}$

c. Description

The reservoir initially held 2 liters of the standard waste solution. Another liter of the same formulation was added every time the level fell below the one liter mark. This cyclical change in reservoir volume (Figure 15) parallels actual operation expected within a spacecraft.

The waste solution was heated to $40\text{-}50^\circ\text{C}$ ($104\text{-}122^\circ\text{F}$) before transit through the cell and was chilled to $\sim 35^\circ\text{C}$ (95°F) as it returned to the reservoir. The temperature drop across the cell was in the range of $1\text{-}2^\circ\text{C}$. The cooler temperature prior to the reservoir was used to promote precipitation of any solids in the reservoir rather than in the cell. There was precipitation in the reservoir, but the flowing waste stream carried the solids through the entire system and allowed solids deposition to occur fairly uniformly on all surfaces; heavy depositions formed around the turbulence promoter. Upon removal of the turbulence promoter, there was no further need to use the cooling bath since the linear velocity in the cell did not allow precipitation due to gravity.

5. Experiment 5. Cycle runs of waste solution

a. Conditions

Membrane - NS-100

Membrane area - 43.32 cm^2

Initial volume (V_i) - reservoir (2 liters) + system volume
(350 ml) = 2350 ml

Volume addition - one liter of standard solution was added periodically (see Figures 17-21)

Total volume of the run - 11 liters (~10 liters of permeant was collected)

Operational temperature - Pervaporation cell inlet $50\text{-}60^\circ\text{C}$
($122\text{-}140^\circ\text{F}$)

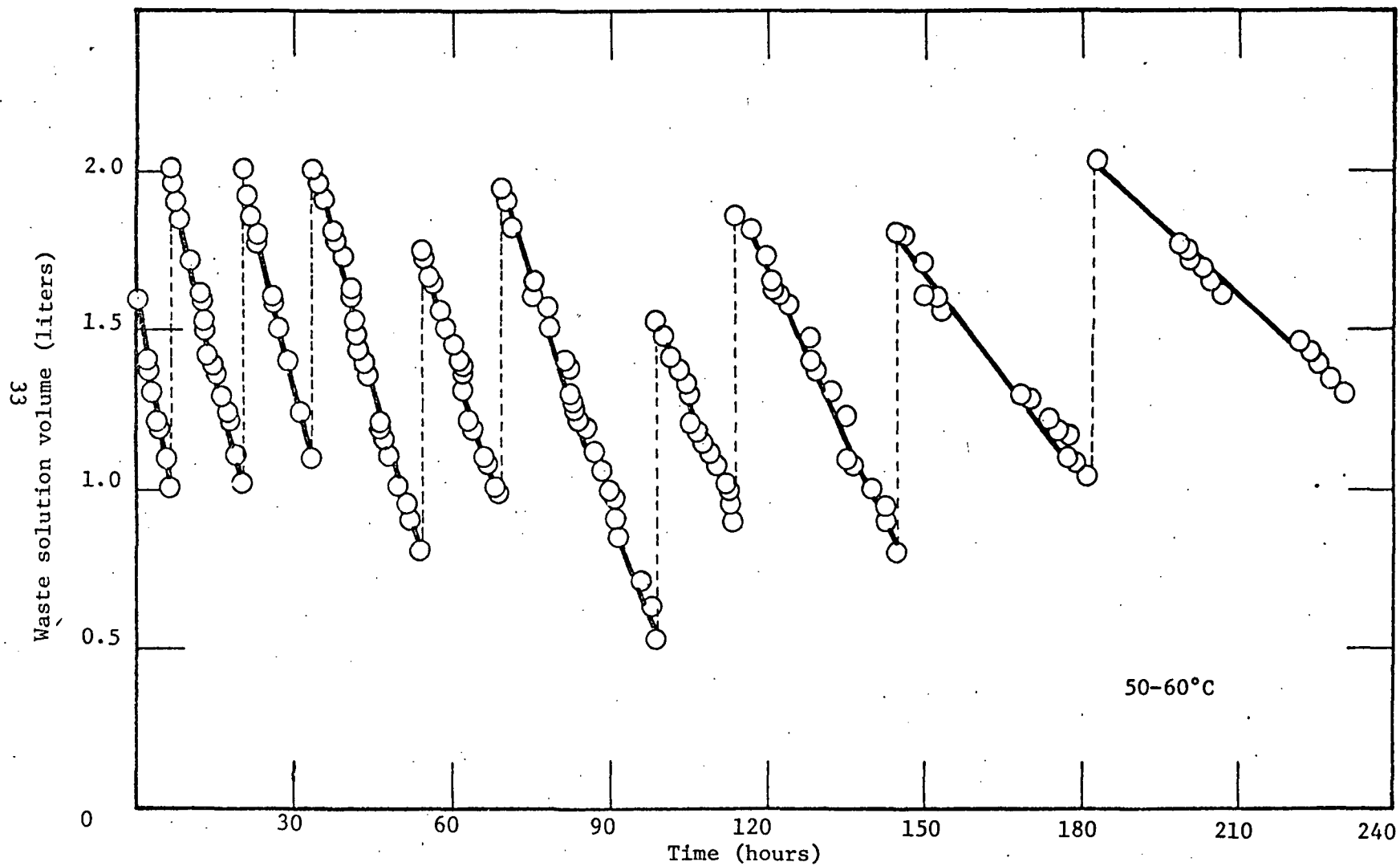


Figure 17. Waste solution volume vs time in a cyclic pervaporation run.

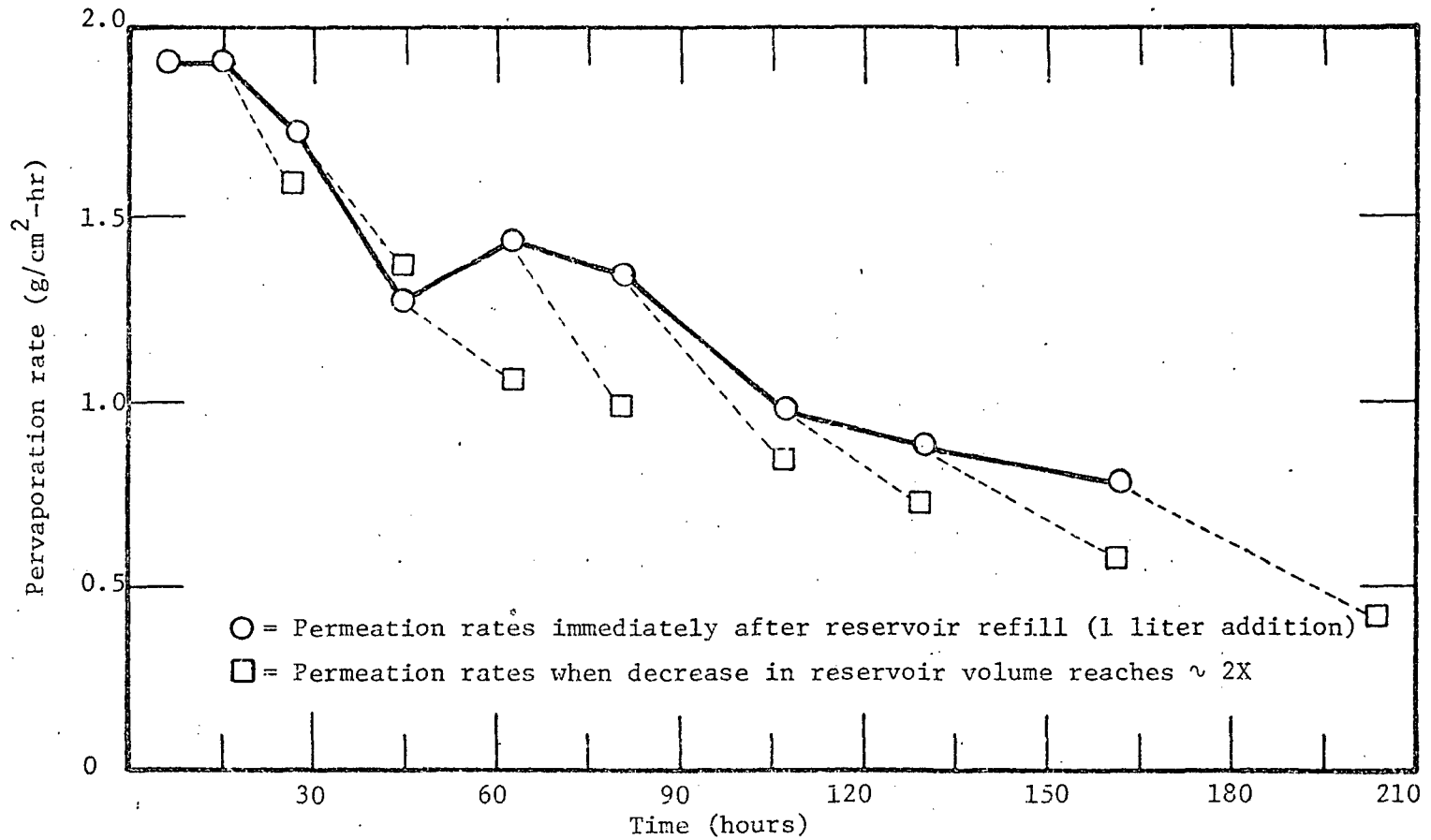


Figure 18. Permeation rate of effluent of cyclic pervaporation run.

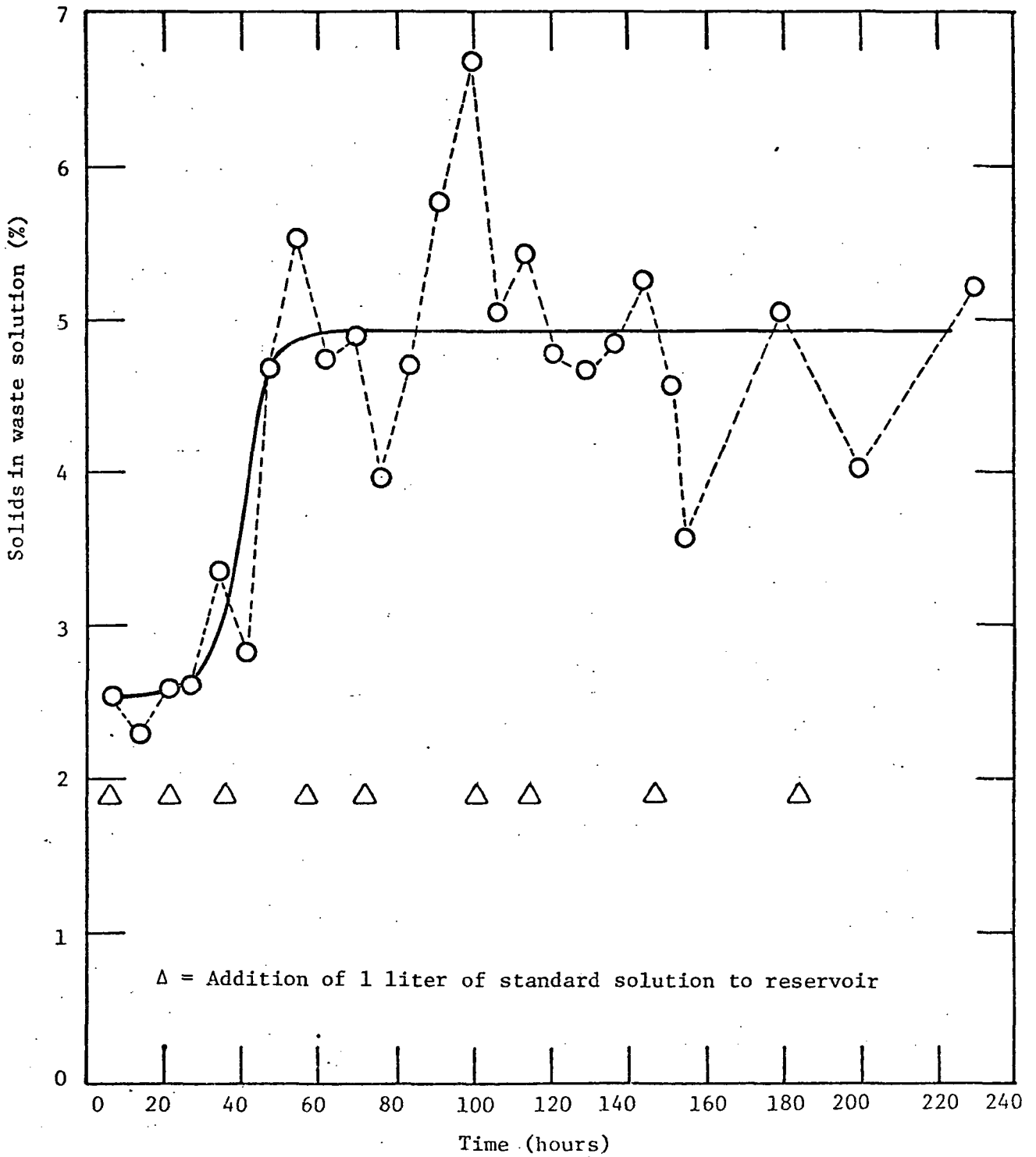


Figure 19. Solids wt% in concentrate vs time.

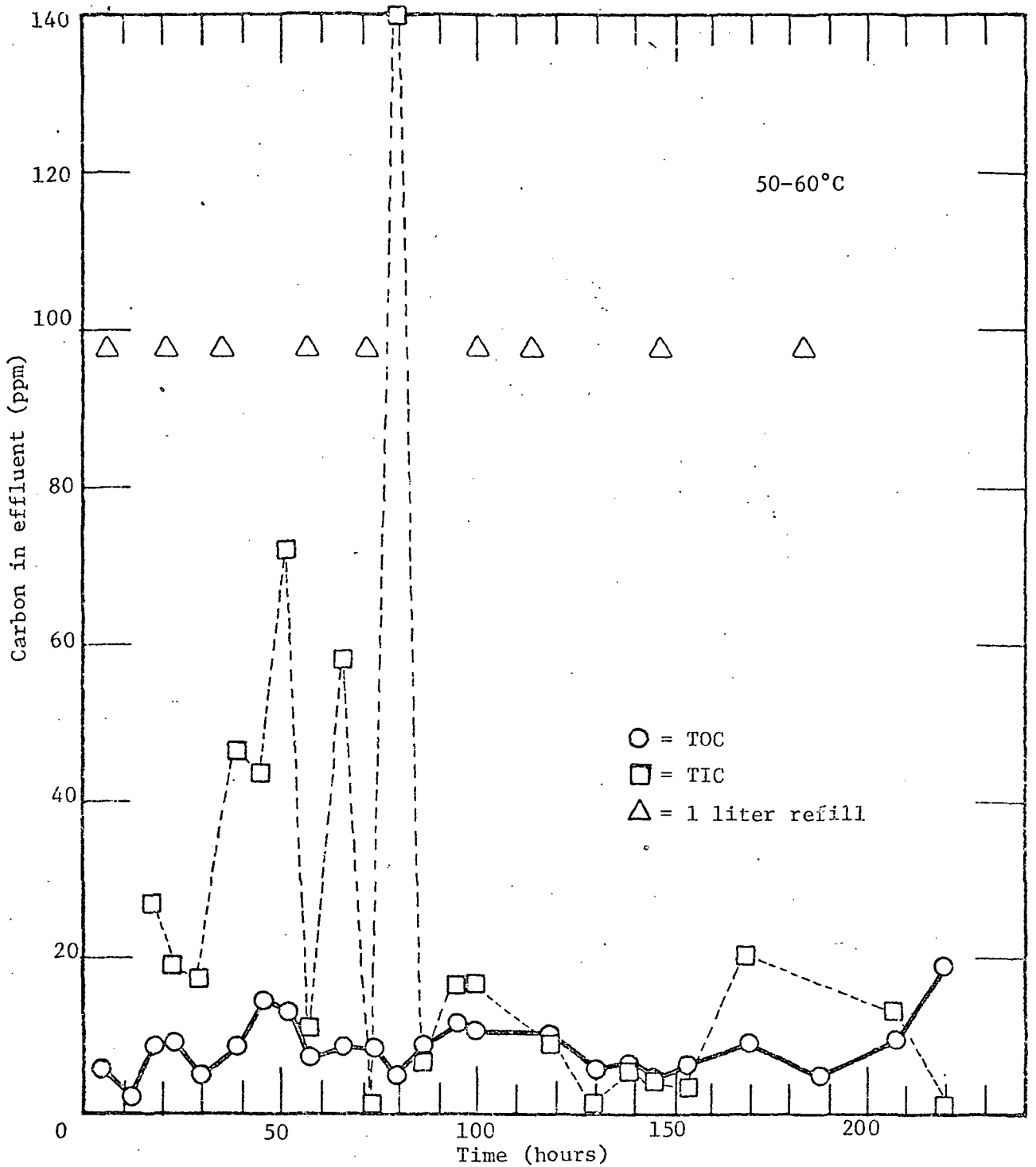


Figure 20. Inorganic carbon and total organic carbon (TOC) concentrations in effluent water as a function of time in a cyclic pervaporation run.

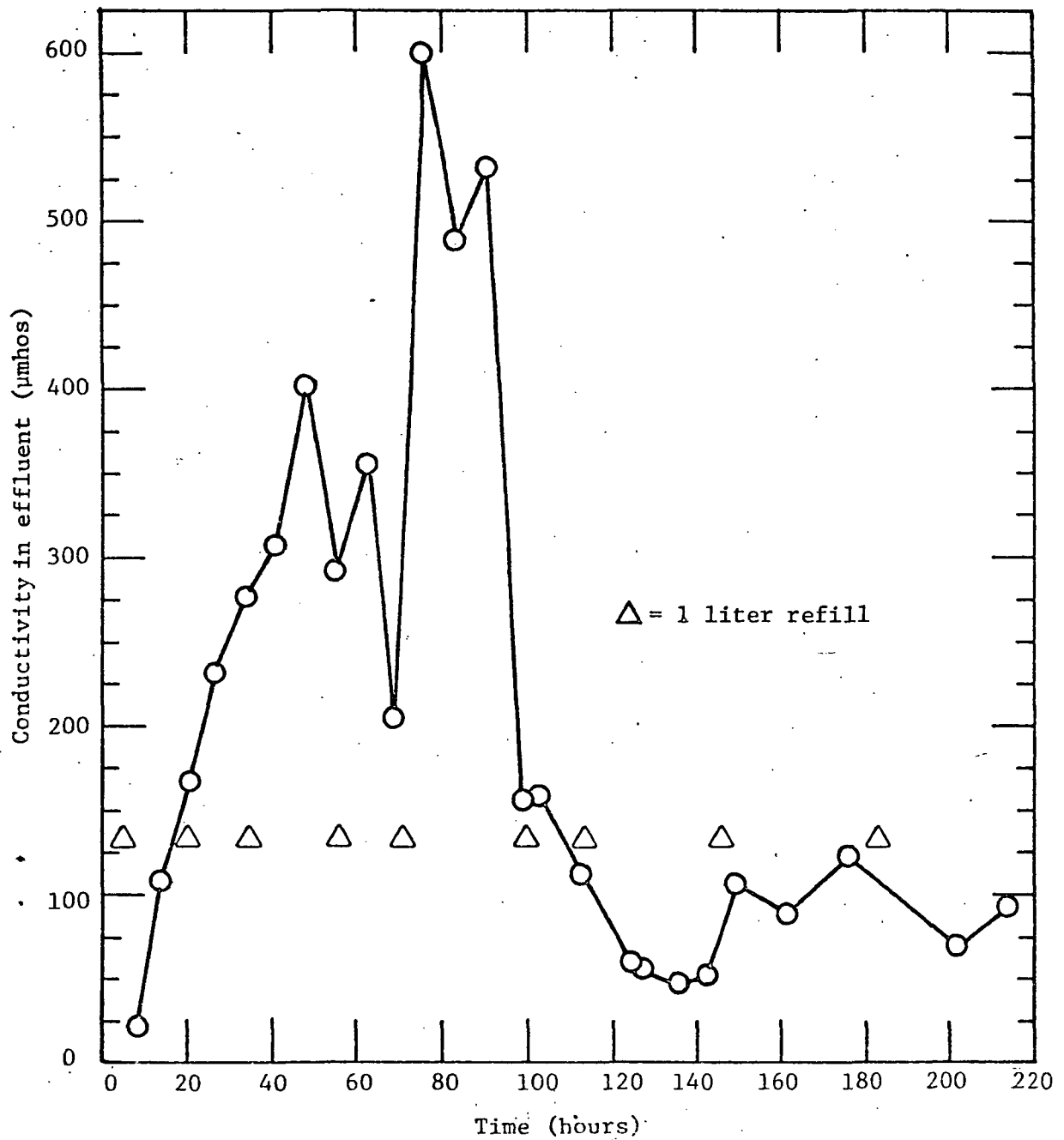


Figure 21. Time vs conductivity of permeant.

Solution composition - Standard waste solution

Duration - 225 operational hr (6 hr/day)

Flow rate - 500 ml/min

b. Results summary

Initial permeation rate - $1.9 \text{ g/cm}^2 \text{ hr}$

Final permeation rate - $0.75 \text{ g/cm}^2 \text{-hr}$ (190 hr)

Permeant: Initial TOC - 4 ± 1

Final TOC - 10 ± 1

Total organic carbon collected - 71 mg

Total inorganic carbon collected - 172 mg

c. Description

Permeation rates are shown in Figures 17 and 18. The values in Figure 18 were calculated from the initial and final slope of each cycle in the run; thus, permeation rate is recorded before and after refilling the reservoir. Effluent (product water) quality was high throughout the run, with solids content averaging $5 \pm 1\%$ (Fig. 19); conductivity after 100 hr stabilization averaged 100 μmhos (Fig. 21), and total organic carbon content averaged $8 \pm 1 \text{ ppm}$ (Fig. 20).

The solids content of the urine mixture never exceeded 7% (Fig. 19) because of solids precipitation during the run. The erratic solids content is an outcome of the refilling procedure during the run.

VI. DISCUSSION

The following points were considered in analyzing the experimental data against the goals of the project.

1. Membrane durability and performance.
2. The adaptability of the membrane to (a) controlled release of mass (water) to space and (b) generation of quality water for reuse.
3. Energy requirements and heat dissipation gain employing such a membrane.

These data are sufficient to characterize membrane separation capabilities; however, detailed specifications from NASA would be required in order to "tailor" a workable membrane system for a spacecraft.

In previous studies, a substantial effort was devoted to stabilizing the waste solution in order to eliminate precipitation of solids in the system. Natural urine, which contains $\sim 0.02-0.06\%$ Ca, $\sim 0.01-0.04\%$ mg, $\sim 0.3-0.5\%$ Na, and $\sim 0.15-0.3\%$ K, is pH sensitive (fresh urine pH ranges between 4.8-7.5). As urine pH and concentration increase, some of the divalent calcium and magnesium ions precipitate as bicarbonates. The increase in the pH of an aging urine is thought to be due to bacterial decomposition⁵ of urea to give ammonium bicarbonate buffer; the pH levels off at about pH 9 (Fig. 22).

Since in the pervaporation system water is removed while circulating waste solution, a build-up of total dissolved solids is expected along with the build-up of precipitants. In addition, bacteria and ammonia concentrations should increase far beyond initial concentrations. Thus, while the concentration of ammonia in fresh urine is in the range of 600-800 ppm⁶, the ammonia concentration in urine aged for 20 days was found to be 4000 to 7000 ppm, with a pH shift to ~ 9 ⁵.

The results from the current study illuminate some of the differences between the performance of porous membranes studied previously² and that of the composite membranes. The semipermeability of the latter (based on diffusion and solubility of permeants in the dense skin) is a safeguard (100% rejection) against permeation of high molecular weight species or bacteria. This is an important characteristic, especially with regard to possible water-reuse and pretreatment (sterilization) of the waste before exposure to pervaporation. While bacteria rejection can be achieved with porous membranes (employing hydrophobic, small diameter pores), fouling of

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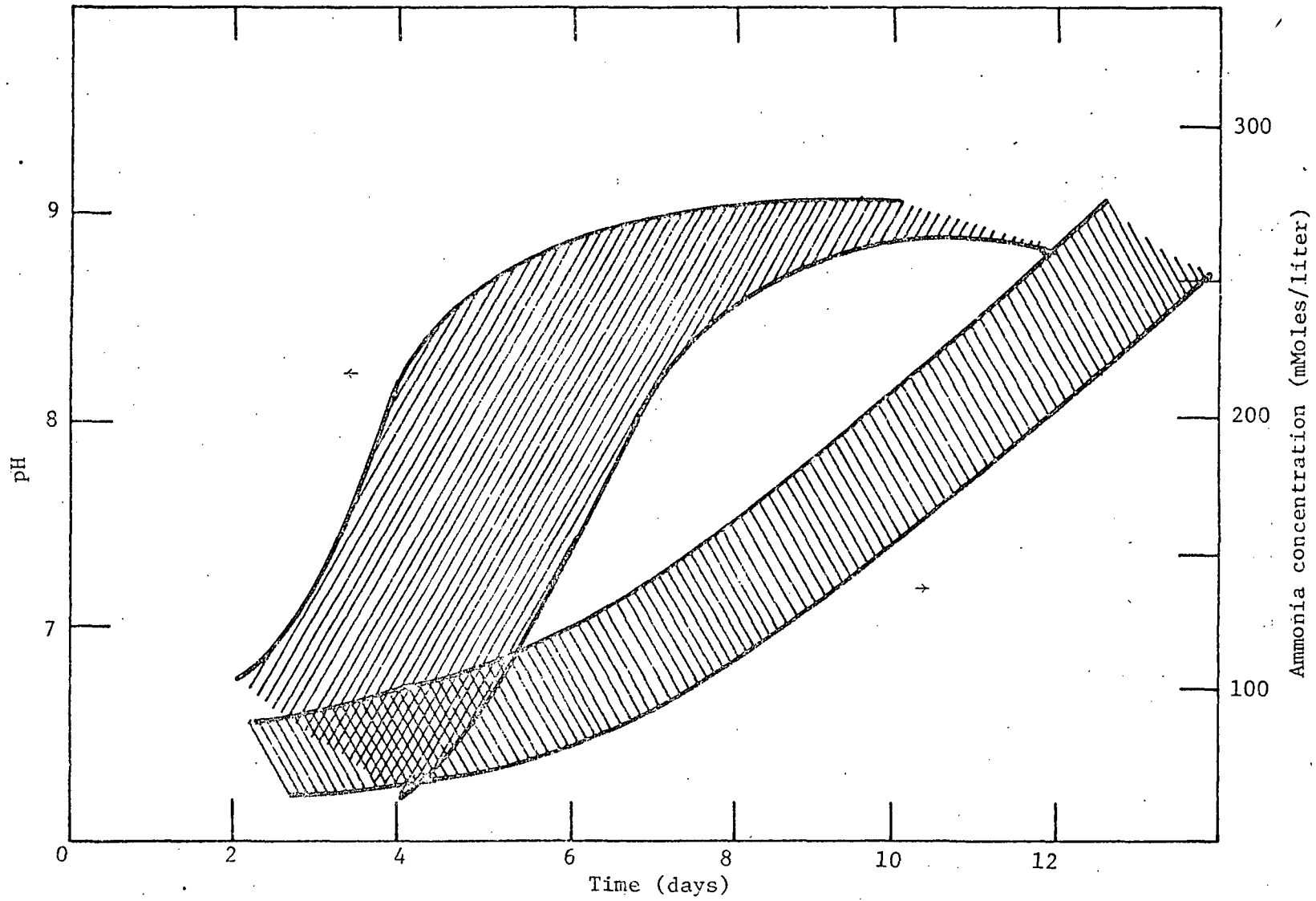


Figure 22. Aging urine vs time (1 mMole/liter = 17 ppm)⁵.

such membranes by precipitants and their susceptibility to the presence of detergents make them inferior to composite membranes. From the above experiments, it is shown that the pervaporation process can be carried out without any pretreatment of the waste solution. The only undesired effect is the presence of ammonia and inorganic carbon in the product water. Ammonia and inorganic carbon are metabolites of enzymatic and bacterial degradation of urine solutes. The rates at which other unspecified organic compounds are released into the product water are relatively constant, and have been found quite low, as evidenced by the TOC measurement.*

The experiments demonstrate that the release of waste mass from the spacecraft can be carried out by pervaporation at a rate comparable to its generation rate. Moreover, the quality of the membrane product is adequate to project that a small secondary purification cartridge would provide a source of potable water if recovery is preferred to disposal.

A. Heat Removal

If the composite membrane PA-300 is to be used at an operational temperature of 49°C (120°F) and at a permeation rate of about 0.5 g/cm²-hr (≈ 1 lb/ft²-hr), then a membrane area of ≈ 0.2 m² (≈ 2 ft²) would remove 24 liters per day in a continuous operation. This amount exceeds the original goal delineated in the objectives (Fig. 2).

The amount of heat dissipation gained by removing 24 liters of water at 49°C is a minimum value determined by the heat of vaporization of water. At 49°C (120.20°F), the heat of vaporization of water is 569 calories/kg (Kcal) or 1024.3 BTU/lb. Thus, the removal of 24 liters of water per day would yield a minimum of 13656 Kcal or 24583 BTU.

The actual heat removed is greater, since the enthalpy (ΔH*) of the above membrane separation process in its simple formulation would be:

$$\Delta H^* = \Delta H_{sw} + \Delta H_w + \Delta H_{wm} - \Delta H_{mw}$$

where ΔH_{sw} is the enthalpy involved in separating pure water from the waste

* The rejection of organics when calculated as $R \% = [1 - (TOC_p / TOC_c)] \times 100$ was found to be ≈ 99.9 (25°C) and > 99.75 (49°C), where
 TOC_p - organic carbon in the product
 TOC_c - organic carbon in the circulated waste.

solution; ΔH_w is the heat of vaporization of pure water; ΔH_{wm} is the enthalpy of dissolution of water in the membrane matrix; and ΔW_{mw} is the enthalpy involved in removing water from the membrane.

In a simple situation where the temperature across the membrane remains constant, $\Delta H_{wm} = \Delta H_{mw}$ and $\Delta H^* = \Delta H_{sw} + \Delta H_w$. This accounts for the results shown in Figure 14; ΔH^* , calculated from the temperature gradient across the cell, $\Delta^\circ\text{C}$, displays higher values than ΔH_w . (Where there is a temperature gradient across the membrane, $\Delta H_{wm} \neq \Delta H_{mw}$, and a typical case of thermodiffusion⁷ would exist; however, its values are too low to substantially affect the conclusions.)

Figure 14 and the results summary table of Experiment 3 express the heat dissipation as a function of the flow rate over the membrane, which correlates with the water permeation rate across the membrane. It is clear from the data that the flow rate of the waste solution over the membrane has a significant influence on the permeation rate. This is a predictable outcome because an increase in the flow rate contributes to a decrease in the unmixed, boundary layer on the membrane surface, and a decrease in the concentration and temperature gradients across the cell. For example, in the 13 cm long cell with a flow rate of 43 ml/min, a temperature gradient of $\sim 7^\circ\text{C}$ is developed. Since the permeation rate is temperature dependent, its respective low permeation value can be attributed to the temperature drop across the cell.

As expected, an increase in the flow rate results in a higher transport rate and respectively high heat dissipation values. However, in the pervaporation scheme (Fig. 3), the pumping energy requirement and pump efficiency have to be evaluated; that is, while the heat dissipation and the permeation increase with the pumping, the load on the pump itself is higher and their net enthalpy is calculated from $\Delta H = \Delta H_{\text{pump}} + \Delta H^*$. If used as an auxiliary to the cooling unit in a spacecraft $\Delta H^* \gg \Delta H_{\text{pump}}$.

In our laboratory experiments, a low efficiency (<1%) electric (AC) pump was used. When linked to a 115V outlet and regulated to pump at a flow rate of 450 ml/min, such a pump draws an electrical current of 0.6 amps. The power generated was 69 watts or ~ 235 BTU/hr. Even if we consider that all this electrical energy is transferred to heat in the fluid, then $\Delta H \sim 800$ BTU/hr. The same pump head can be operated according to the manufacturer's instructions with a 12V DC, 0.3 amp motor. This pump assembly (0.5 kg [~ 1 lb])

requires only 3.6 watts to do the same job, which amounts to ~ 12 BTU/hr. Even with an efficiency of 2%, heat dissipation of $\Delta H \sim 1020$ BTU/hr will be gained.

B. Precipitation of Solids

Precipitation of solids occurs all over the system during the pervaporation runs. The precipitants contain mainly calcium salts (5-10% Ca^{++}) and to a lesser content, magnesium (0.2-1% Mg). It was possible to obviate fouling of the porous membranes by maintaining a low pH (preventing precipitation of CaCO_3), by employing in-line ion exchange resins, or by filtration. None of these measures was taken in the present study. It was found that the system would tolerate the presence of precipitants and suspended solids in the circulated waste as long as capillary channels in the cell or low diameter tubes were eliminated from the system.

The removal of the turbulence promoting net from the pervaporation cell (which was found to attract the suspended solids through blocking the flow channels in the cell), obviated the need for filtration. The solids level increased as a function of the pervaporation time; however, in long runs (Experiment 5) the level was found to remain stable at ~ 5 wt % solids after 50 hrs (Fig. 19). This means that in a cycle run of waste solution, the level of saturation is achieved rather rapidly. In Experiment 5, the total volume of waste treated after 60 hr was 6350 ml, from which 4000 ml was removed. If we define the concentration factor F_c as V'_i/V_t , where V'_i is the total volume treated and V_t is the volume remaining, then for $F_c \sim 2.7$ (60 hr) and for $F_c \sim 8.4$ (240 hr), the total dissolved solids remains approximately the same, $5 \pm 1\%$ throughout the run. This is an extremely important observation since the permeation rate in a pervaporation process is highly dependent on the activity (concentration) of the permeant in the solution. The activity of water in the solution is decreased as salt concentration increases, resulting in a decrease of the water solubility in the membrane. The permeation rate equation⁸ of such a process shows an exponential dependency between the permeation rate, J ,* and C_1 , which in most cases leads to an exponential

*The empirical flux equation for pervaporation for a given dense membrane is $J = K_1 (e^{K_2 C_1} - 1)$ where J is the permeation rate and C_1 is the solubility of the permeate in the side of the membrane which faces the liquid.

decrease in the water permeation rates as water activity decreases. (This characteristic of solution can be calculated as an osmotic pressure increase of the waste solution which acts in the reverse direction to the pervaporation process.) The precipitation of solids out of the waste solution keeps the activity and the viscosity of the water at an adequate level for the pervaporation process even at high values of F_c .

The precipitation build-up on the membrane surface is the predominant factor in the permeation rate decrease for a long pervaporation run. On the other hand, the data indicate that the selectivity of the membrane increases as a result of this precipitant coating. When a flow rate of 500 ml/min is employed, the precipitation on the membrane surface results from the water removal at the solution boundary layer (between the membrane surface and the laminar flow) and not from gravitational precipitation. Such a layer builds up with the duration of the run, and is mainly composed of inorganic salts.

A turbulence promoter is commonly included in membrane permeation systems and serves to distribute the flow over the membrane and to diminish the boundary layer effect. However, as mentioned above, its effectiveness is nullified when concentrated waste solution which contains suspended solids is circulated. Its effect on the membrane permeability is especially noticeable when the product effluent composition in Experiment 3 is compared with that of all the other experiments. In Experiment 3, short runs of 100 min each were carried out within a period of 5 days. The initial volumes were kept constant and no waste solution was added. In these short runs, the membrane surface was not modified by the deposition of the precipitant. The product effluent TOC measurements and permeation rates correspond to the initial values of other pervaporation runs. However, it is shown that the ammonia concentration in the product effluent increases as a function of time and flow rate far beyond the corresponding values of the TOC and water permeation rates. When the ammonia and the TOC values of this run are compared with those of Experiment 2, where a membrane of the same type was used in continuous pervaporation, it seems that the initial TOC and ammonia readings are, in effect, the same. But as the process continues, the TOC drops and levels around 6 ppm, while the ammonia reaches a maximum of about 23 ppm in a period of 24 hours. The corresponding values in the results summary table of Experiment 3 show that the TOC values remain the same (within fluctuation

range) but the ammonia reading consistently increases to 88 ppm after 24 hrs.

The deposited layer of precipitants on the membrane can be removed upon drying the membrane in the cell. By stopping the waste solution circulation, the membrane which is exposed to vacuum dries out, the coating flakes off the membrane, and the water permeation rate is fully restored to its initial value. Such an experiment was carried out with a PA-300 membrane that was under a workload for 148 hr (see Experiment 2).

C. Waste Solution Product

The untreated waste solution undergoes continuous decomposition⁸ which affects the quality of the product effluent. The total organic carbon values in the collected permeants were found relatively low in all the experiments (less than 10 ppm at 25°C and up to 16 ppm at 50°C). The conductivity curves of the product water correspond to those of the ammonia and the total inorganic carbon (TIC). By comparing Figures 11, 20 and 21, it can be seen that ammonia and TIC follow the same permeation trend, while the conductivity and TIC curves almost overlap (Figures 20 and 21). This leads to the conclusion that the inorganic salts in the product water are ammonium carbonates, which result from ammonia and carbon dioxide permeation; both are degradation products of urea. The release of CO₂ in a cyclic pervaporation run follows the refilling pattern (Figs. 20 and 21); however, it can be assumed that the aging of the solution hastens the release of CO₂ (urea decomposition), but the increase in pH keeps it in the waste solution as carbonate ion. Thus, the CO₂ content levels down as can be seen in Figures 11 and 20.

Bacterial decomposition of urea can be eliminated by adding oxidizing agents to the waste solution; this, in effect, sterilizes the solution. In previous studies², chromic acid was added to the solution and was found to be an efficient treatment in some cases; however, the use of chromic acid is not recommended when composite membranes are employed because: (1) the chromic acid might degrade the membranes and (2) the use of chromic acid would possibly increase the TOC values substantially as a result of organic degradation by oxidation in the waste solution. The NS-100 and PA-300 membranes are also known to be chlorine sensitive; however, iodine in the form of KI₃ can be added to increase the reduction potential of the solution and thus eliminate bacteria growth. Such treatment would not harm the membrane and would not

contribute any low molecular weight degradation products that can permeate the membrane. Treatment of this kind has been found successful in reverse osmosis technology.

D. Mode of Operation

The cyclic pervaporation runs, where the reservoir is refilled periodically, simulate an actual operational case. In Figures 6 and 12 (Experiments 1 and 2), where the initial volume was reduced by pervaporation without refill, it is shown that the permeation rates of water do not change appreciably when the initial volume is decreased by a factor of 2. This is also shown in the cyclic pervaporation curves of Experiment 4, Figures 15 and 16. Between the ranges of 1 and 2 liters, the water permeation rates are almost the same; below the 2X range, the decrease in the permeation rate is indicated by the curvature of the plots. Comparison of Experiments 2 and 4 demonstrates the advantage of the cyclic pervaporation run.

By operating a rather small reservoir (2 liters plus the system volume), large volumes of waste can be disposed (Fig. 15). Such an operation would substantially decrease the volume required for waste storage in spacecraft. The ratio between the membrane surface area and the waste volume is an important factor determining the durability and efficiency of a membrane after a given period, as shown in comparing Figures 16 and 18. The membrane area ratio between the two experiments is 1.83 (in favor of Experiment 4). The higher initial permeation rate shown for Experiment 5 is attributed to the higher operational temperature; however, the larger membranes in Experiment 1 show better durability and permeation rates as time lapses. Nevertheless, the permeability of the membrane can be restored quite easily, as shown above.

E. Water Reuse (Collection)

Several pervaporation processes have been reported in the literature^{8,9}. Most of them employ the same principles used in the present experiments to collect the product water effluent; that is, a "cold trap" is used to condense the effluent product. In such an operation, the energy requirement of the system is the condensation enthalpy. If the system is well designed, the vacuum pump (Fig. 4) is employed only to reduce the initial vapor pressure of the gas chamber and then can be cut off from the system. The vapor pressure

in the gas chamber would be that of the condensate. If the product effluent is water condensed at -8°C , then the corresponding vapor pressure will determine the activity (or concentration) gradient of the permeant within the membrane, and hence, the permeation rate.

It was shown that such a pervaporation can be efficient when the permeant is condensed on a cold wall which parallels the membrane face in the gas chamber. From such a wall, the condensate drips into a cold reservoir (Fig. 23). It was shown by Aptel *et al.*⁹ that water transport across a membrane when a proper temperature gradient is maintained (50°C for the circulated liquid and 20°C for the cold wall) can be in the same order of magnitude as in a conventional pervaporation ($0.1 - 0.5 \text{ g/cm}^2\text{-hr}$), such as that shown in Figure 4. Thus, the membrane system can be installed to operate within the spacecraft employing the internal cooling system of the vehicle. The major drawback of the process (which utilizes vacuum) stems from the dissolved gases and gases that are generated in the wastewater system. Where porous membranes are used, such gases will contribute to the partial water vapor pressure in the gas chamber. Our experiments show that the generation of CO_2 and NH_3 can be reduced by adding an oxidizer to the system (KI_3 , for example). Also, these gases can be forced to react to form ammonium carbonate salt in the product effluent. Experimental runs with such a thermopervaporation system (Fig. 23) show that the dissolved oxygen and nitrogen (when the solution is equilibrated in a 760 mmHg atmosphere) in the liquid effluent did not cause any substantial increase in the partial pressure in the gas chamber. This is attributed to the fact that a dense, composite membrane was used, and the gaseous species can not be transferred through on a pressure gradient. Rather, they have to be dissolved in the membrane with the same mechanism that prevails for water permeation. Such a thermopervaporation unit proved to operate through a period of 4 days without a decrease in the permeation rate and without the need to restore low vapor pressure (by reoperating the vacuum pump) in the gas chamber. Elaboration on the water reuse product of such a mechanism would be the subject of our future work.

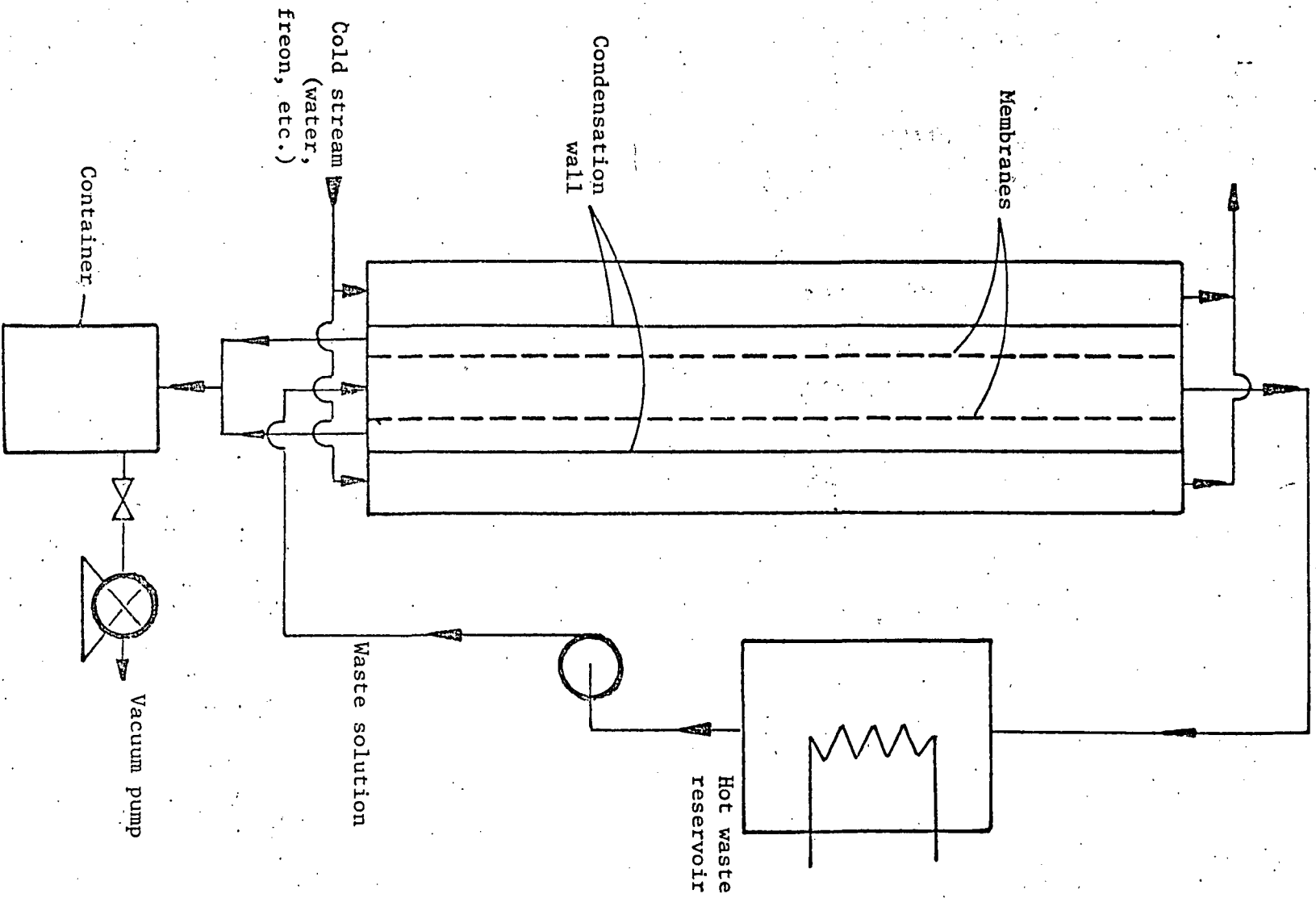


Figure 23. Thermopervaporation unit designed by Aptel et al.

Appendix A

PROPERTIES OF PA-300 AND NS-100 MEMBRANES

Poly(ether/amide) thin-film composite membrane, designated PA-300, is formed by an in situ interfacial polymerization technique conceived by Cadotte¹⁰ in 1972. Briefly stated, the membrane is prepared by depositing a thin layer of an aqueous solution of an epichlorohydrin-ethylene diamine condensate on the finely porous surface of a polysulfone support membrane and subsequently contacting the poly(ether/amine) layer with a water immiscible solution of isophthalaldichloride. A thin semipermeable film, crosslinked poly(ether/amide) copolymer, is formed at the interface. Subsequently, the membrane is dried at an elevated temperature. A cross-sectional drawing of the membrane is shown below. Some properties of the membrane are illustrated in the following tables and figures.

NS-100 membrane has the same structure but is made via in situ interfacial cross-linking of polyethyleneimine with diisocyanate. Some of its transport properties are given in the following tables¹¹.

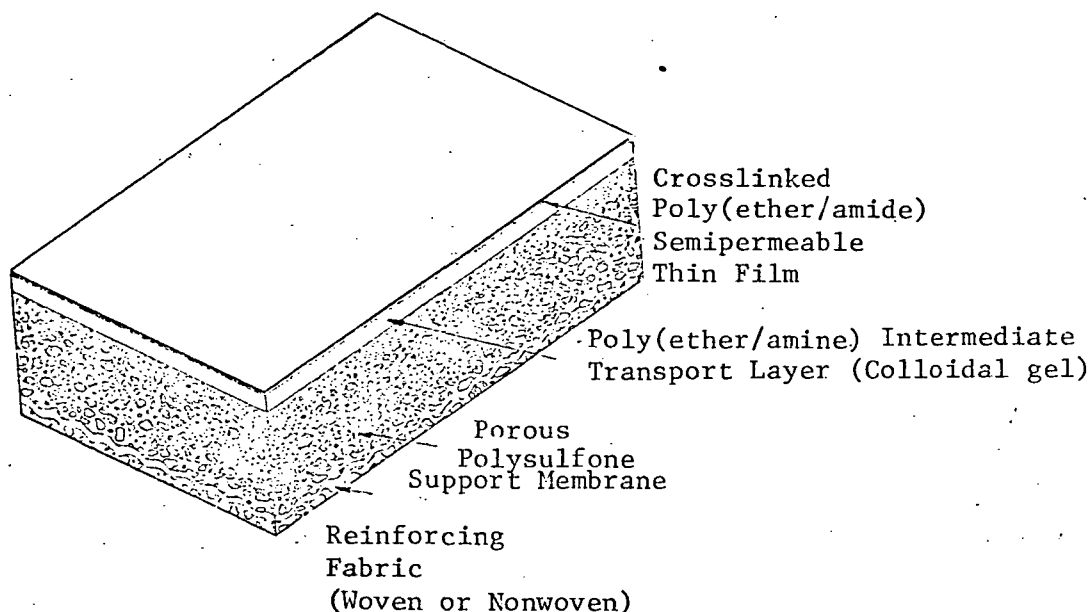


Figure 1-A. Cross sectional drawing of PA-300(ether/amide) thin-film composite membrane¹².

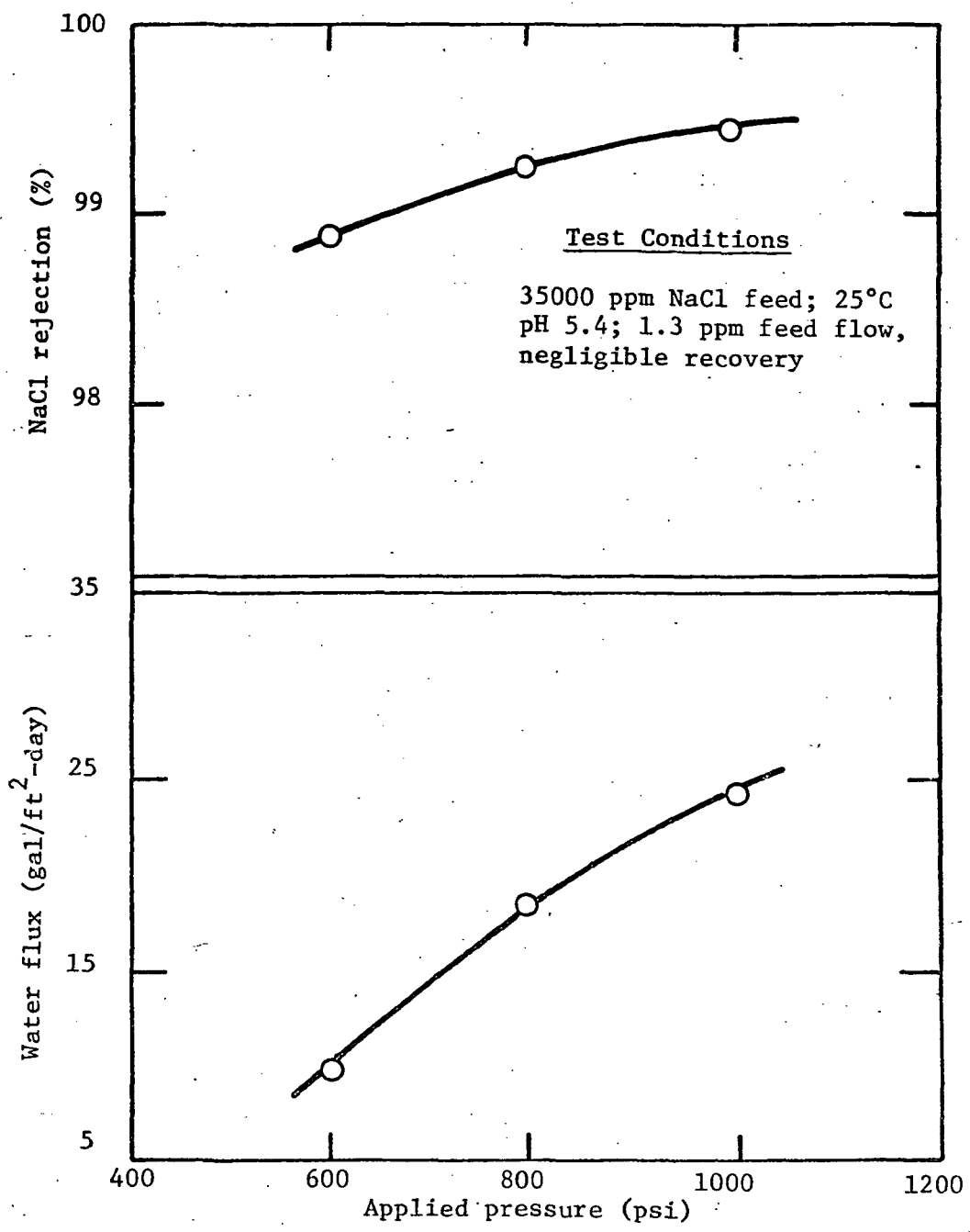


Figure 2-A. Relationship between water flux and salt rejection, as a function of applied pressure, for PA-300 poly(ether/amide) thin-film composite membrane (from UOP publication)¹².

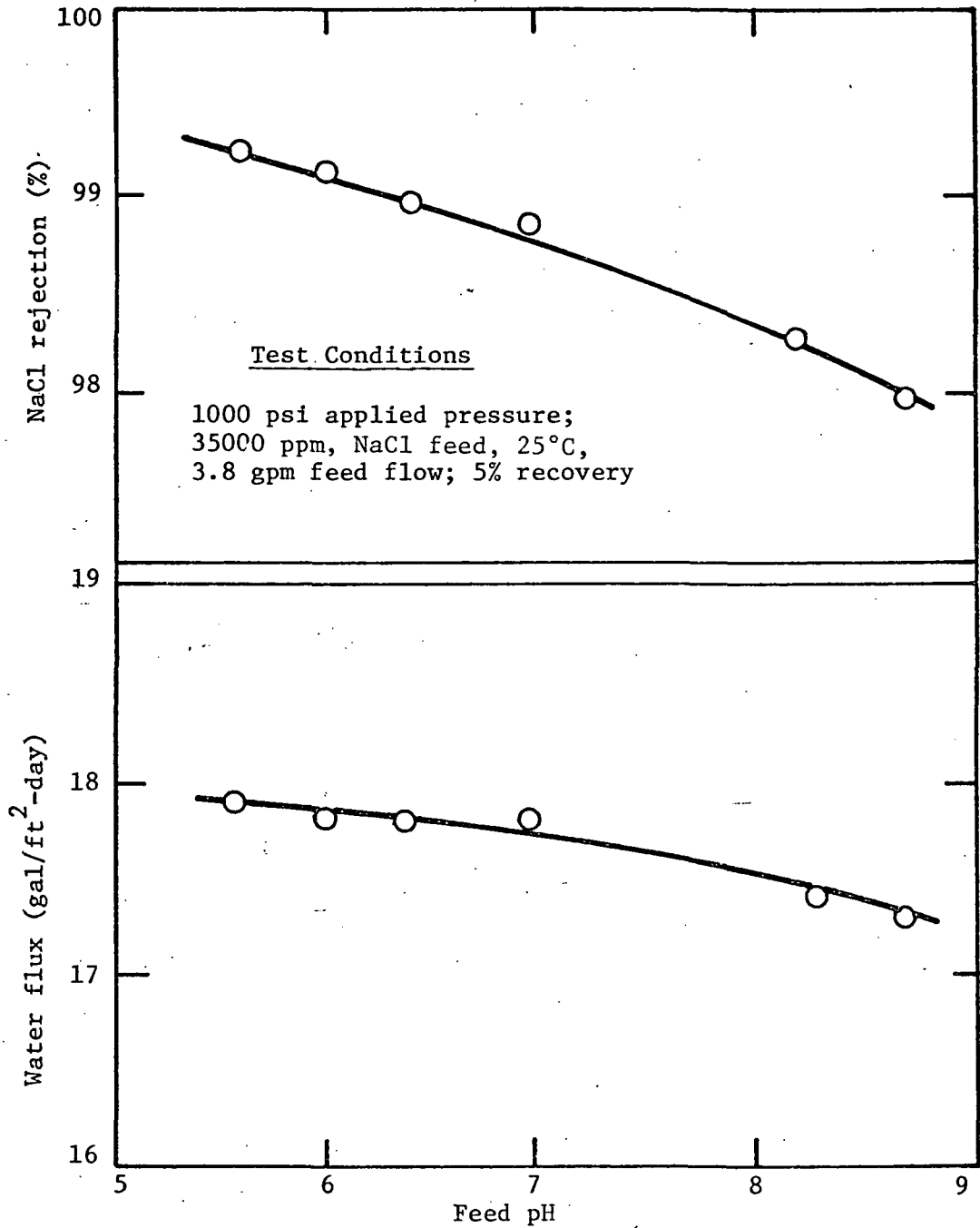


Figure 3-A Relationship between water flux and salt rejection, as a function of feed pH, for PA-300 poly(ether/ amide) thin-film composite membrane (from UOP publication)¹².

TABLE 1-A

REVERSE OSMOSIS PERFORMANCE OF PA THIN-FILM
COMPOSITE MEMBRANE FOR VARIOUS SOLUTES

Conditions: 1000 psi applied pressure, 25°C

Solute	Solute Concentration (ppm)	pH	Solute Rejection (%)
Sodium nitrate	10,000	6.0	99.0
Ammonium nitrate	9,600	5.7	98.1
Boric acid	280	4.8	65-70
Urea	1,250	4.9	80-85
Phenol	100	4.9	93
Phenol	100	12.0	>99
Ethyl alcohol	700	4.7	90
Glycine	1,400	5.6	99.7
DL-aspartic acid	1,500	3.2	98.3
Ethyl acetate	366	6.0	95.3
Methyl ethyl ketone	465	5.2	94
Acetic acid	190	3.8	65-70
Acetonitrile	425	6.3	>25
Acetaldehyde	660	5.8	70-75
Dimethyl phthalate	37	6.2	>95
2,4-dichlorophenoxy acetic acid	130	3.3	>98.5
Citric acid	10,000	2.6	99.9
Alcozyme (soap)	2,000	9.3	99.3
O-phenyl phenol	110	6.5	>99
Tetrachloroethylene	104	5.9	>93
Sodium silicate	42	8.6	>96
Sodium chromate	1,200	7.8	>99
Chromic acid	870	3.9	90-95
Cupric chloride	1,000	5.0	99.2
Zinc chloride	1,000	5.2	99.3
Trichlorobenzene	100	6.2	>99
Butyl benzoate	220	5.8	99.3

TABLE 2-A

REJECTION DATA FOR NS-100 MEMBRANES

<u>No.</u>	<u>Solute</u>	<u>Membrane Designation</u>	<u>Conc. ppm</u>	<u>Lp₅ x10</u>	<u>Press. atm</u>	<u>Rej. %</u>	<u>pH</u>
1.	Methanol	Standard	1000	1.0			
		Modified	"	"	54.4	33.2	-
		52C	"	0.5	"	41.0	-
		53J	"	1.1	40.8	-5.98	5.77
		52C	"	1.3	"	18.06	"
		53J	"	1.1	102	1.41	"
		Standard	"	1.3	102	9.87	"
2.	Ethanol	Modified	"	1.0	54.4	79.8	-
		52C	"	0.5	"	86.7	-
		53J	"	1.1	40.8	64.78	5.42
		52C	"	1.3	"	65.66	"
		53J	"	1.1	102	70.01	"
		Standard	"	1.3	"	73.57	"
		Modified	"	1.0	54.4	92.7	-
			0.5	"	93.6	-	
3.	n-Propanol	Standard	"	1.3	"	73.57	"
		Modified	"	1.0	54.4	92.7	-
			0.5	"	93.6	-	

(continued)

TABLE 2-A (continued)

<u>No.</u>	<u>Solute</u>	<u>Membrane Designation</u>	<u>Conc. ppm</u>	<u>Lp₅ x10⁵</u>	<u>Press. atm</u>	<u>Rej. %</u>	<u>pH</u>
4.	Isopropanol	Standard	1000	1.0	54.4	91.4	-
		Modified	"	0.5	"	92.3	-
		52C	"	1.1	40.8	82.01	5.91
		53J	"	1.3	"	85.10	"
		52C	"	1.1	102.0	56.06	"
		53J	"	1.3	"	40.16	"
5.	n-Butanol	Standard	"	1.0	54.4	94.2	-
		Modified	"	0.5	"	96.3	-
6.	n-Pentanol	Standard	"	1.0	54.4	95.2	-
		Modified	"	0.5	"	97.7	-
7.	3-Pentanol	Standard	"	1.0	54.4	97.9	-
		Modified	"	0.5	"	99.4	-
8.	Phenol	52C	"	1.1	40.8	68.57	6.25
		53J	"	1.3	"	55.68	"
		Standard	"	1.0	54.4	84.1	-
		Modified	"	0.5	"	87.1	-
		52C	"	1.1	102.0	70.21	6.25

(continued)

TABLE 2-A (continued)

<u>No.</u>	<u>Solute</u>	<u>Membrane Designation</u>	<u>Conc. ppm</u>	<u>Lp₅ x10⁵</u>	<u>Press. atm</u>	<u>Rej. %</u>	<u>pH</u>
8.	Phenol (cont.)	53J	1000	1.3	102.0	65.72	6.25
9.	p-Chlorophenol	Standard	"	1.0	54.4	81.0	-
			"	"	17.0	66	-
			"	"	40.8	79	-
			"	"	68.0	80	-
			"	"	102.0	80	-
		Modified	"	0.5	54.4	83.2	-
10.	Formaldehyde	52C	"	1.1	40.8	37.05	4.64
		53J	"	1.3	"	38.62	"
		Standard	"	1.0	54.4	54.7	"
		Modified	"	0.5	"	70.0	-
		52C	"	1.1	102.0	49.96	4.64
		53J	"	1.3	"	50.65	"
11.	Acetaldehyde	Standard	"	1.0	54.0	75.0	
		Modified	"	0.5	"	80.6	
12.	Benzaldehyde	Standard	"	1.0	"	37.6	
		Modified	"	0.5	"	95.0	

(continued)

TABLE 2-A (continued)

<u>No.</u>	<u>Solute</u>	<u>Membrane Designation</u>	<u>Conc. ppm</u>	<u>Lp₅ x10⁵</u>	<u>Press. atm</u>	<u>Rej. %</u>	<u>pH</u>
13.	Acetone	52C	1000	1.1	40.8	80.44	5.48
		53J	"	1.3	"	76.03	"
		Standard	"	1.0	54.0	93.4	
		Modified	"	0.5	"	96.1	
		52C	"	1.1	102.0	78.26	5.48
		53J	"	1.3	"	77.32	"
14.	Acetophenone	Standard	500	1.0	54.0	96.7	
		Modified	"	0.5	"	98.2	
15.	Cyclohexanone	Standard	"	1.0	"	97.3	
		Modified	"	0.5	"	98.7	
16.	Methyl ethyl ketone	Standard	1000	1.0	"	90.8	
		Modified	"	0.5	"	95.5	
17.	Acetic acid	52C	"	1.1	40.8	68.70	3.77
		53J	"	1.3	"	48.02	"
		Standard	"	1.0	54.0	71.0	
		Modified	"	0.5	"	80.3	

(continued)

TABLE 2-A (continued)

<u>No.</u>	<u>Solute</u>	<u>Membrane Designation</u>	<u>Conc. ppm</u>	<u>Lp₅ x10⁵</u>	<u>Press. atm</u>	<u>Rej. %</u>	<u>pH</u>
17.	Acetic acid (cont.)	52C	1000	1.1	102.0	9.00	3.77
		53J	"	1.3	"	69.86	"
18.	Lactic acid	Standard	"	1.0	54.0	87.6	
		Modified	"	0.5	"	89.3	
19.	Benzoic acid	Standard	500	1.0	"	66.3	
		Modified	"	0.5	"	82.0	
20.	Ethylamine	Standard	1000	1.0	"	86.2	
		Modified	"	0.5	"	92.8	
21.	Triethylamine	Standard	"	1.0	"	99.7	
		Modified	"	0.5	"	98.5	
22.	Aniline	52C	"	1.1	40.8	31.36	6.62
		53J	"	1.3	"	51.80	"
		Standard	"	1.0	54.0	91.8	
		Modified	"	0.5	"	95.9	
		52C	"	1.1	102.0	14.99	6.62
		53J	"	1.3	"	31.31	"

(continued)

TABLE 2-A (continued)

<u>No.</u>	<u>Solute</u>	<u>Membrane Designation</u>	<u>Conc. ppm</u>	<u>Lp₅ x10⁵</u>	<u>Press. atm</u>	<u>Rej. %</u>	<u>pH</u>
23.	Methyl acetate	52C	1000	1.1	40.8	36.37	5.38
		53J	"	1.3	"	28.32	"
		Standard	"	1.0	54.0	89.2	
		Modified	"	0.5	"	91.7	
		52C	"	1.1	102.0	23.02	5.38
		53J	"	1.3	"	44.62	"
24.	Ethyl acetate	Standard	"	1.0	54.0	95.8	
		Modified	"	0.5	"	96.9	
25.	Ethyl ether	52C	"	1.1	40.8	90.93	5.59
		53J	"	1.3	"	82.18	"
		52C	"	1.1	102.0	65.62	"
		53J	"	1.3	"	77.09	"
26.	Glycerol	52C	"	1.1	40.8	96.87	5.97
		53J	"	1.3	"	89.15	"
		52C	"	1.1	102.0	96.18	"
		53J	"	1.3	"	91.69	"
27.	Hydroquinone	52C	"	1.1	40.8	82.23	5.20

(continued)

TABLE 2-A (continued)

<u>No.</u>	<u>Solute</u>	<u>Membrane Designation</u>	<u>Conc. ppm</u>	<u>Lp₅ x10⁵</u>	<u>Press. atm</u>	<u>Rej. %</u>	<u>pH</u>
27.	Hydroquinone (cont.)	53J	1000	1.3	40.8	71.93	5.20
		52C	"	1.1	102.0	86.29	"
		53J	"	1.3	"	77.98	"
28.	Urea	52C	"	1.1	40.8	64.15	7.72
		53J	"	1.3	"	55.37	"
		52C	"	1.1	102.0	74.32	"
		53J	"	1.3	"	63.38	"

REFERENCES

1. Holland, F.F. and J.K. Smith, "Water Vapor Diffusion Membrane Development," NASA Contractor's Report CR-137546 (1974).
2. Holland, F.F., E. Klein, J.K. Smith and C. Eyer, "Water Vapor Diffusion Membranes II" Annual Report, NASA, CR-137814 (1976).
3. Communication with R. Saucer (NASA Johnson Space Center, Houston) and C. Malich, NASA (Amex Research Center, California).
4. Cabasso, I. and E. Lion, AIChE 80th National Meeting, "Liquid Mixture Separations by Flat Sheet and Hollow Fiber Membranes," (Fisch 32, 1975).
5. Montalvo, J.G., "Stablizing Urine for Abusable-Drug Screening," Report for the National Institute of Drug Abuse, Grant No. 1-R01 DA00642-01 (1974).
6. Documenta Geigy Scientific Tables, 7th Ed. Published by Geigy Pharmaceuticals, Ardsley, N.Y. (1974). p. 661-678.
7. M.S. Dariel, "Thermosmosis in Synthetic Membranes," XXIVth IUPAC, International Symposium on Macromolecules, Jerusalem (1975).
8. Cabasso, I., J. Jagur-Grodzinsky, and D. Vofsi, "Separation of Azeotropic Mixtures by Pervaporation," J. Appl. Polymer Sci. 18 2117 (1974), and Ibid. 18 2137 (1974).
9. Aptel, P., N. Challard, J. Cunny and J. Neel, "Separation of Azeotropic Mixtures by Pervaporation," XXIVth IUPAC, International Symposium on Macromolecules, Jerusalem (1975).
10. Cadotte, J.E. and R.T. Rozelle, Report to the U.S. Department of the Interior, Office of Saline Water Research and Development, Contract 14-30-2883 (1972).
11. Cabasso, I., C.S. Eyer, E. Klein, J.K. Smith, "Evaluation of Semi-permeable Membranes for Concentration of Organic Contaminants in Drinking Water," U.S. NTIS, PB 243245 (1975).
12. Riley, R.L., R.L. Fox, C.R. Lyons, C.E. Milstead, M.W. Seroy and M. Tagami, Desalination 19 13 (1976).