

AVAILABLE TO THE PUBLIC

GULF SOUTH RESEARCH INSTITUTE

POST OFFICE BOX 26500 NEW ORLEANS, LOUISIANA 70186 TELEPHONE 504 283-4223

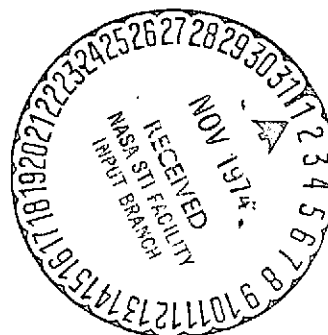
NASA CR-137545

(NASA-CR-137545)	WATER VAPOR DIFFUSION	N74-34569
MEMBRANES Final Report (Gulf South		
Research Inst.)	65 p HC \$6.25 CSCL 06K	
		Unclas
		G3/05 52144

WATER VAPOR DIFFUSION MEMBRANES

F.F. Holland, Jr. and J.K. Smith  
Gulf South Research Institute  
P. O. Box 26500  
New Orleans, Louisiana 70186

September 27, 1974  
Final Report  
NAS 2-7650



Prepared for:  
National Aeronautics and Space Administration  
Ames Research Center  
Moffett Field, California

## Table of Contents

I.	INTRODUCTION.....	1.
II.	OBJECTIVES.....	2.
III.	THEORETICAL BACKGROUND.....	3.
	A. Separation by Nonporous Diffusive Membranes.....	3.
	B. Convective Transport Through Porous Wetting Membranes.....	4.
	C. Convection Through Nonwetting Porous Membranes.....	5.
IV.	MEMBRANE SELECTION.....	7.
	A. Water Vapor Permeation Studies.....	9.
	1. Experimental Procedures.....	9.
	2. Membrane Permeability - Results.....	12.
	B. Mechanical and Chemical Stability.....	25.
	1. Experimental Method.....	25.
	2. Results of Mechanical and Chemical Stability Tests.....	26.
	C. Membrane Recommendation for 30-Day Trial.....	30.
V.	WATER VAPOR DIFFUSION RECOVERY DEMONSTRATION TRIAL.....	35.
	A. Experimental Procedure.....	35.
	B. Results.....	38.
	C. Additional VDR Trials Using Natural Urine.....	50.
VI.	CONCLUSIONS AND RECOMMENDATIONS.....	55.
VII.	APPENDIX I.....	57.
VIII.	APPENDIX II.....	59.
IX.	REFERENCES.....	63.

## INTRODUCTION

The water vapor diffusion process for recovery of potable water from urine has previously been investigated with emphasis on design, fabrication, and testing of experimental modules (1). Membranes used in these modules were selected from those commercially available. Programs directed specifically toward development of membranes for vapor diffusion application were limited (1). Studies were designed mainly to fabricate membranes from available polymers and to test these membranes for water flux and durability. Little effort was made to develop the basic membrane technology specifically directed at the vapor diffusion water recovery process.

This program was designed to define the membrane technology of the vapor diffusion water recovery process and to test this technology using commercially available or experimental membranes. One membrane was selected, on the basis of the defined technology, and was subjected to a 30-day demonstration trial.

## OBJECTIVES

The overall objective of this program was to develop the membrane technology specifically for the vapor diffusion water recovery process. This involved:

1. Defining the most appropriate membrane mechanism for vapor diffusion recovery (VDR) application, i.e., diffusive, convective, or a combination.
2. A relative evaluation of the components of mass transfer resistance for both the liquid boundary and gas boundary layers versus the membrane transport resistance.
3. An evaluation of available membranes which can be projected to have the requisite transport mode, and also the necessary chemical and physical stability.
4. A 30-day trial demonstration using a membrane chosen by the technology developed during this program.

## THEORETICAL BACKGROUND

In the water vapor diffusion process for recovery of potable water from urine, a semipermeable membrane is utilized to separate the product water from the urine feed solutions. In the process of this separation, three mechanisms of transport can be visualized based on the structure of the membranes presently available. The three types of transport modes include:

1. Transport through nonporous diffusive membranes;
2. Convective transport through the pores of membranes wetted by the urine solution where solutes are restricted by the pore size of the membrane;
3. Convective transport of water vapor through the nonwetted pores of a membrane.

### Separation By Nonporous Diffusive Membranes

Water vapor transport through a diffusive membrane will consist of three discrete steps:

1. Partitioning of the water into the urine side of the membrane;
2. Diffusion of the water through the membrane; and
3. Vaporization on the downstream side.

The driving force is the difference in partial pressure of water (more precisely, the difference in fugacity) on either side of the membrane. The permeation constant is typically of the order of  $10^{-7} \text{ cm}^2 \text{ sec}^{-1} \text{ cm Hg}^{-1}$ .

Diffusive barrier membranes, such as silicone films, polyethylene, dense cellulose acetate, etc., characteristically exhibit a low permeability to urinary solutes such as electrolytes, amines, purines, and urinary pigments. They have a relatively high permeability to low molecular weight vapors, fixed gases, and molecular species which have high solubility coefficients in the membrane. Thus the nonporous diffusive type of membrane would operate in the proposed application without the formation of urinary insolubles in the membrane. The only species which would permeate to the vapor gap side would be those which are soluble in the membrane. An associated benefit from this phenomenon is that all of the boundary layer resistances to mass transport would be outside of the membrane, where increased fluid flow could mitigate their effects.

The disadvantages of this mode of permeation are primarily those asso-

ciated with a low permeation rate. The net permeation is generally a function of the product of the solubility of the permeant, and the specific diffusion coefficient of the permeant in the membrane. That is,

$$P = \bar{D} \cdot S$$

where  $S$  is the solubility constant of water in the membrane and  $\bar{D}$  is the average diffusion coefficient (over the concentration range of interest, since  $\bar{D}$  is often a function of the concentration). Because diffusivities in polymers are typically of the order of  $10^{-9}$   $\text{cm}^2/\text{sec}$ , the net transport of water can be increased only by working either with ultrathin membranes, or by increasing the membrane areas to the extent necessary to accommodate the water recovery needed.

#### Convective Transport Through Porous Wetting Membranes

In the convective transport of the porous wetting type of membrane, such as cellophane films, it is readily conceivable that evaporation of the water occurs at the vapor gap side of the membrane; i.e., at the nitrogen gas-membrane interface. The membrane acts as a conduit for the urine, and residual solutes increase in concentration inside the membrane. The equilibrium level of solute in the membrane will be determined by the material balance between water loss via evaporation and the diffusion of the solutes back into the urine feed stream. Pore size, pore volume, and thickness of the membrane will determine the resistance to flow within the membrane. The vapor pressure of water above such a membrane will be lower than the vapor pressure above the urine itself due to a reduction in partial pressure of the water as a result of increased solute concentration in the stagnant layer within the membrane.

Nitrogen permeation in the opposite direction will be governed principally by the diffusion of nitrogen through a stagnant layer. This stagnant layer is equivalent to the membrane in thickness. The nitrogen permeation into the urine is, in essence, a diffusive process, as outlined earlier. The aqueous phase in the membrane serves as the conduit for the gas, and calculations of the nitrogen transport can be based on permeation through an aqueous layer.

Previous work on the water vapor diffusion recovery process (VDR) substantiates the expected behavior of porous wetting membranes (2). The cellophane membranes used in that study are permeable not only to the water

component of the urine, but also to all solutes of molecular weight below approximately 4,000. Thus, as the membrane imbibes the urinary fluid and water is lost to the vapor gap, the concentration of solutes increases in the remaining fluid in the membrane pore structure. If the water evaporation rate is higher than the rate of diffusion of the solutes back into the urine, the solubility product of the solutes will be exceeded and precipitation will occur in the membrane. This was, in fact, observed.

The permeability of the cellophane membranes to low molecular weight solutes also poses another problem: if physical contact is established between the vapor gap side of the film and the porous screen of the condenser, mass transfer of contaminants can take place by convection. However, an integral cellophane membrane is not permeated by either viruses or bacteria and, in fact, is not even permeable to the albumin component of urine. Thus bacterial contamination of the product water would not be a problem with this type of membrane.

#### Convection Through Nonwetting Porous Membranes

Permeation of nonwetted porous membranes by water vapor proceeds by a different mechanism. If the interfacial tension and pore size of the membrane are such that liquid penetration of the pores does not occur, the water vapor-nitrogen interface will be at the feed side of the membrane. Water vapor permeation through the membrane will then follow the mechanism associated with Knudsen effusion. The true membrane barrier resistance will be quite low in comparison to the other modes of transport outlined. The concentration polarization resulting from water evaporation will occur at the feed side of the membrane, and, as in the nonporous membranes, it can be dealt with hydrodynamically.

Similarly, the transport of nitrogen in the opposite direction will be facilitated. With the membrane acting as a porous divider permeable only to gases (because of surface tension constraints), the transport of nitrogen will be governed by the Knudsen coefficient and the net partial pressure of nitrogen on each side of the membrane. Steps to reduce the boundary layer to increase water vapor transport will also lead to increased nitrogen transport in the opposite direction.

In summary, it is possible to achieve vapor diffusion recovery of water from urine using three modes of transport: diffusive transport through nonporous membranes; convective transport through solutions held in the pores

of wetted porous membranes; and convective transport of water vapor through nonwetted porous membranes. Each mode of transport has mass transfer resistance elements which must be evaluated for the problem under study. For convenience the mass transfer resistances can be categorized as solution resistance, "membrane" resistance, and gas phase resistance.

By thoroughly characterizing representative membranes for each mode of transport, it is possible to determine which mechanism of transport can best be applied to the water vapor diffusion recovery process (VDR). A thorough characterization of the chemical and physical stability of the commercially available membranes, and of those experimental membranes selected for the program, was also necessary for selection of one membrane material for a demonstration trial recovery.



## MEMBRANE SELECTION

As specified in the program, membrane selection was based on investigations of three mechanisms of membrane transport:

1. Transport through nonwetted pores of a membrane;
2. Transport through a wettable porous membrane;
3. Transport through a polymer matrix by diffusion.

In addition membrane selection was based on several other criteria specified in the contract. These criteria are:

1. The membrane should be capable of withstanding 0-1G loadings at a constant pressure differential.
2. The vapor diffusion rate should be at least 0.5 lbs/ft<sup>2</sup>-hr.
3. The membrane should retain its properties over a temperature range of 40 to 185°F.
4. It should be nonbiodegradable.
5. It should maintain its mechanical and permeability properties for at least 90 days upon exposure to stabilized urine (acidic oxidizing environment) at the required operating temperatures.
6. It should be capable of operating in a pressure range of 7-14.7 PSIA with a 1 PSIG pressure differential across the membrane.

Membranes representative of the three modes of transport were selected. They also were chosen to meet as many of the other specifications as possible. Some membranes were included in the evaluation scheme even though it was recognized that they could not meet all the criteria outlined above. All three modes of transport were represented in the program so that a complete analysis of all the variables for each transport mechanism could be made.

The membranes initially selected are listed in Table I according to mode of transport classification. The polymer type and the supplier also are listed. In addition to those membranes listed in Table I a sample of the polyvinyl chloride membrane previously tested by Kolnsberg (1) was obtained from Amicon Corp. for evaluation. However, permeability testing of this membrane showed no flux and this membrane was dropped from the program. (Apparently some irreversible morphological changes occurred during storage or shipment.)

Those membranes selected for the program were tested for the following properties:

TABLE I  
MEMBRANES SELECTED FOR TESTING

<u>Membrane Material</u>	<u>Supplier</u>	<u>Sample ID</u>	<u>Class of Membrane</u>
1. Polypropylene	Celanese Plastics Co.	Celgard 2400	Porous Nonwetting
2. Fluorocarbon	W.L. Gore and Associates	Gore-Tex 3SC6.5 S-1-109	Porous Nonwetting
3. Fluorocarbon	W.L. Gore and Associates	Gore-Tex L-10272	Porous Nonwetting
4. Polypropylene	Celanese Plastics Co.	Celgard 2400W	Porous Wetting
5. Polypeptide	GSRI	----	Porous Wetting
6. Cellophane	Enka Glanzstoff A.G.	Cuprophan PT-150	Porous Wetting
7. Dimethyl Silicone	General Electric Co.	----	Diffusive Nonporous
8. Polycarbonate / Silicone	General Electric Co.	MEM 213	Diffusive Nonporous
9. Polypeptide	GSRI	MDG	Diffusive Nonporous
10. Ethyl Cellulose	GSRI	----	Diffusive Nonporous

1. Water vapor permeation rate;
2. Mechanical stability and failure properties as functions of exposure time to stabilized urine\* at 160°F.

From the results of these tests, a suitable membrane candidate was chosen for the third phase of the program - an extensive 30-day water recovery run. During this trial, the permeation rates, brine properties, and effluent water quality were monitored closely to determine the feasibility of the membrane for the VDR process.

#### Water Vapor Permeation Studies

Experimental Procedures. Initially, water vapor permeation rates were determined by a method based on the ASTM E96-66 standard method for moisture permeation through plastic films. This method makes use of a shallow flanged cup# in which the membrane sample is held in place by a matching flat ring. The permeation rate is determined by following the weight loss of water from the cup as a function of time.

This method, however, can lead to erroneous results depending on the permeability of the membrane sample. For highly permeable membranes, severe mass transfer and/or heat transfer restriction greatly reduce the observed water permeability. In fact, a limiting value of 0.02 lbs/ft<sup>2</sup>-hr was measured for a cellophane membrane by this method. But when tested in a dynamic cell, this same membrane achieved permeation rates in excess of 1.0 lbs/ft<sup>2</sup>-hr. Obviously, any type of procedure based on the ASTM E96-66 method should not be used for VDR permeation studies.

The ASTM E96-66 method was intended solely as a screening technique to eliminate those membranes not capable of achieving the required flux necessary for the process. The final membrane selection procedure made use of a dynamic cell that minimized the boundary restrictions observed with the static cell. The diagram of the cell and the schematic of the system used are shown in Figures 1 and 2. In this system, it is possible to vary both the liquid and gas flow rates independently. Temperature is monitored at the liquid return line and at both the input and outlet gas lines. Pressures are monitored at both liquid and gas inlet and outlet ports. Flow rates are measured by inline

---

\*Urine stabilized with 4gm/l chromic acid solution as devised by Putnam (3).

#Fisher-Payne Moisture Permeability Cups, Fisher Scientific Co. Pittsburgh, Pennsylvania.

- 1.) High pressure regulator from nitrogen supply tank.
- 2.) Molecular sieve pre-dryer.
- 3.) Low pressure regulator.
- 4.) Nitrogen pre-heater.
- 5.) Control valve.
- 6.) Pressure gauge.
- 7.) Thermistor probe.
- 8.) Membrane test cell.
- 9.) Desiccant column.
- 10.) Flow meter.
- 11.) Water reservoir.
- 12.) Variable speed pump.
- 13.) Bubble trap.
- 14.) Constant temperature bath.

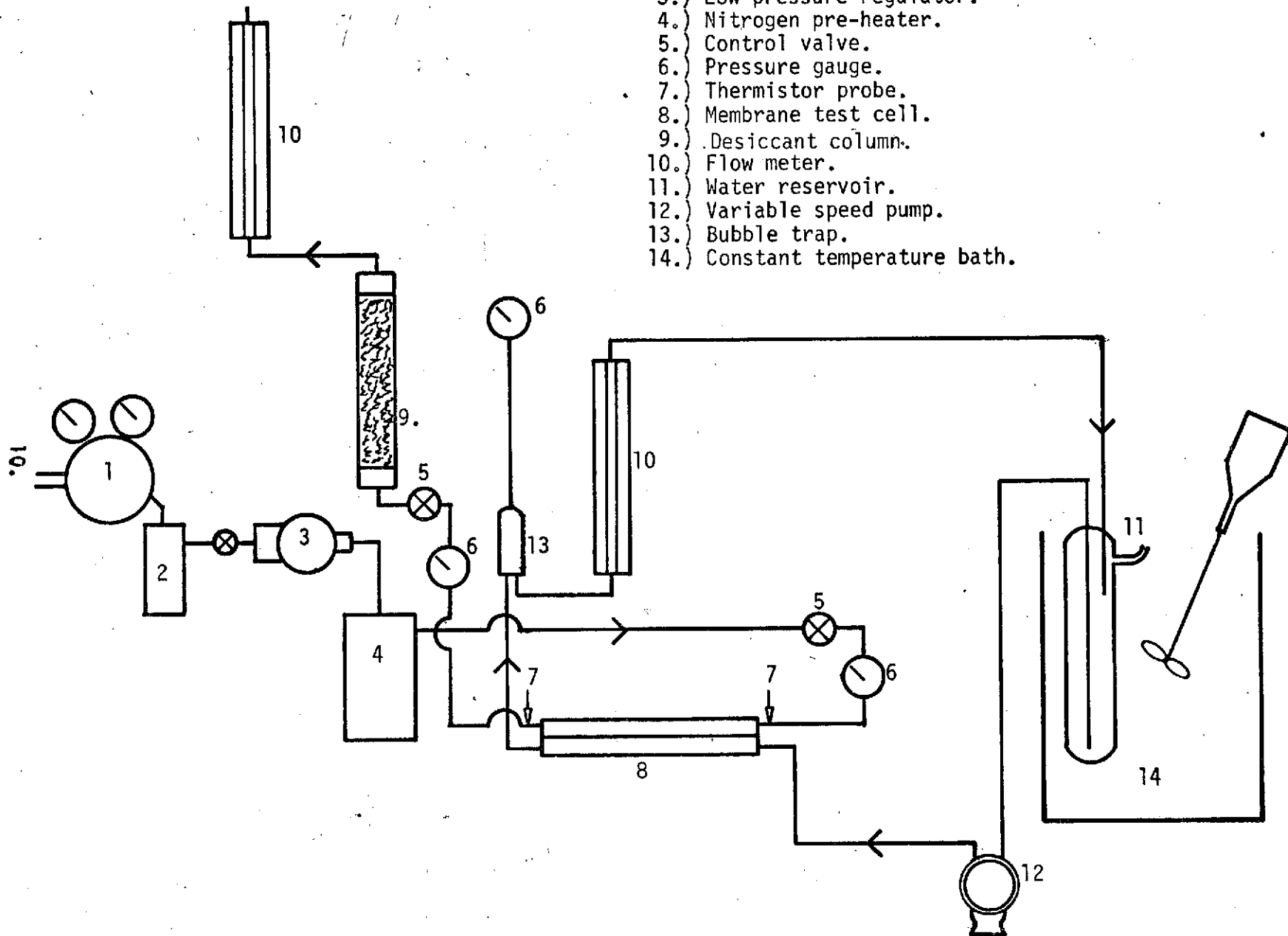


Figure 1.

Schematic of flow through moisture vapor permeability cell.

Figure 2

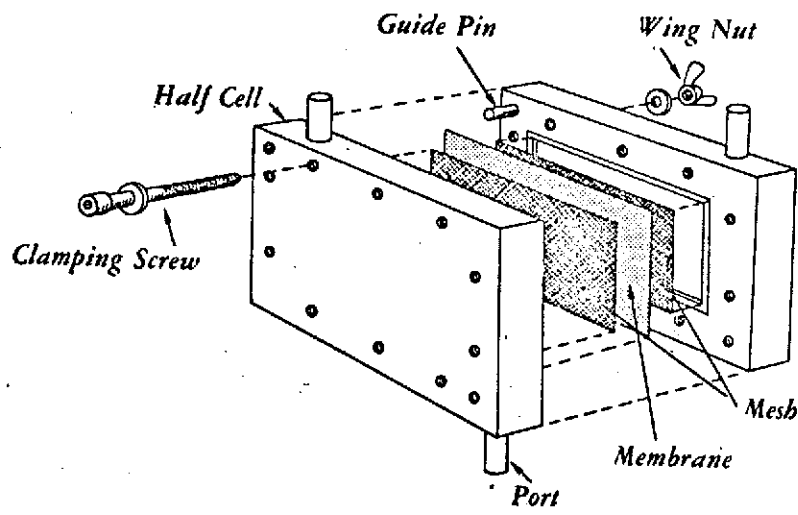


Diagram of Flow-through Cell

rotometers. The nitrogen gas supply can be either filtered and dried compressed tank gas or liquid nitrogen vaporized just prior to use. In all cases the nitrogen is preheated to operating temperature just before input to the cell. The cell was always operated using concurrent liquid and gas flows to minimize pressure gradients across the membrane. The permeation rate is measured by the weight gain of a tared desiccant column. Usually indicating Dryrite (anhydrous calcium sulfate) was the desiccant. The basic cell design is shown in Figure 2. Two cells with surface areas of  $55.5 \text{ cm}^2$  and  $28.6 \text{ cm}^2$  were constructed according to this design. Both cells had the same channel height (approximately 80 mils) and width, and therefore the same cross sectional area. This would provide the same linear velocity for a given gas or liquid flow rate in each cell. However, the purge gas in the smaller area cell would not reach saturation as quickly as in the larger cell; thus the smaller cell could be used for higher flux membranes.

Both cells were constructed from plexiglass. They relied on perfect surface mating with the membrane clamped between for sealing. No sealing problems were encountered except for supported membranes, that is, membranes backed with a rigid porous paper or plastic. In these cases, wicking invariably occurred, causing leaks at the edges of the cell. This was remedied by use of teflon tape as a gasket material.

To reduce mass transfer resistances as much as possible, turbulence promoters were installed in both the gas and liquid channels. These turbulence promoters consisted of polypropylene mesh\* 76 mils thick, cut to fill the entire channel. The turbulence promoters also acted as a membrane support and aided in maintaining constant channel dimensions at all operating pressures.

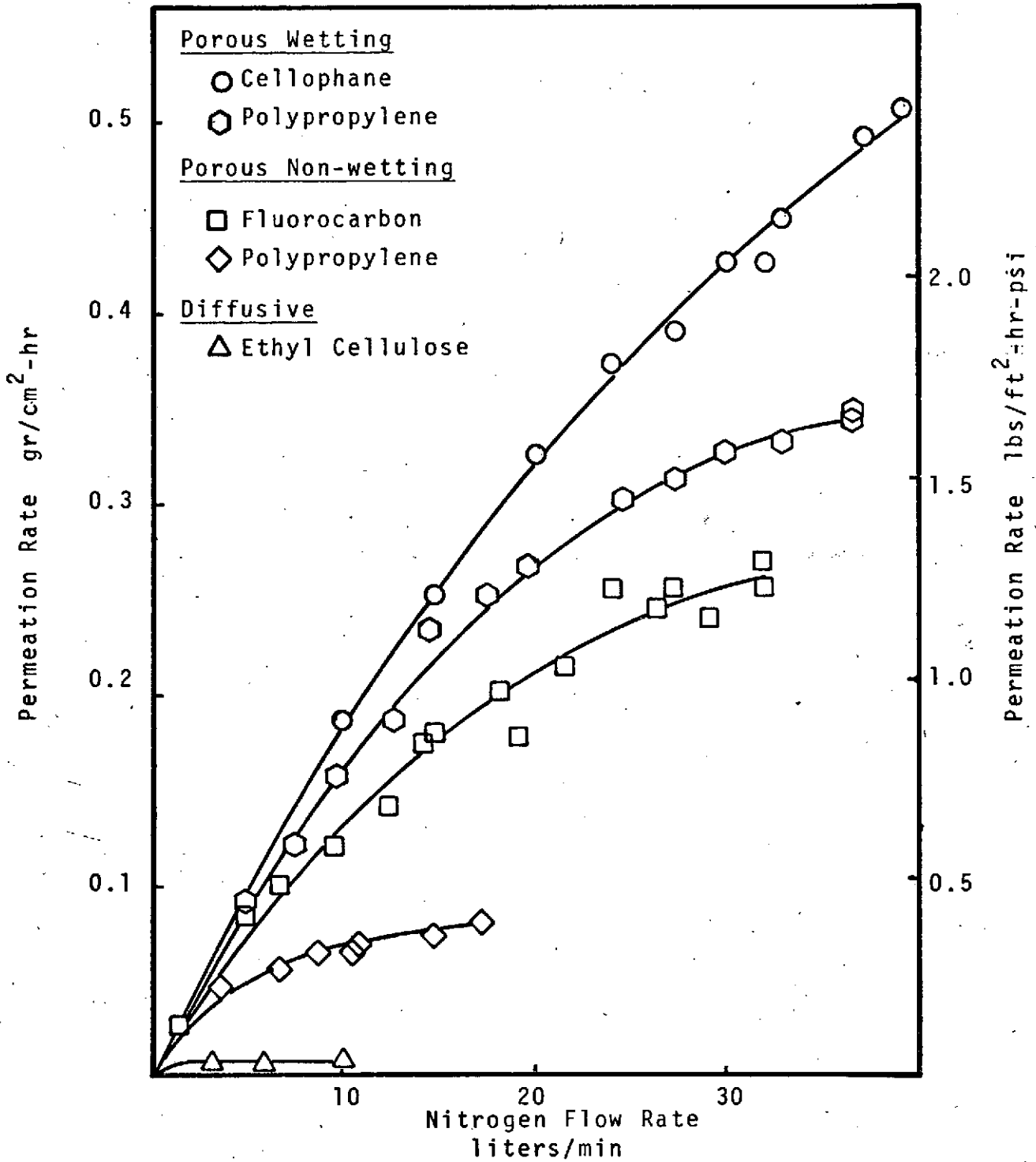
Membrane Permeability - Results. The selected membranes were tested for water vapor permeation rate using distilled water at room temperature. These water vapor permeability data, as a function of nitrogen purge gas flow rate in the  $56 \text{ cm}^2$  cell, are shown in Figure 3. The polypropylene porous nonwetting and the diffusive nonporous membranes did not have the required flux of  $0.5 \text{ lbs/ft}^2\text{-hr.}$  (Only ethyl cellulose is reported; however, the other nonporous diffusive membranes have permeabilities of the same order of magnitude.) Membranes which exhibited high permeation rates show increasing flux through the

---

\*Vexar Plastic Netting #40PDS-89, E.I. DuPont De Nemours & Co., Buffalo, New York.

Figure 3

Moisture Permeation Rate as a  
Function of Nitrogen Sweep Gas  
Flow Rate



entire gas flow range of 0 to 40 liters per minute. The fluorocarbon and polypropylene porous wetting membranes and the cellulose (porous wetting) all show transport rates in excess of the  $0.5 \text{ lbs/ft}^2\text{-hr}$  at the maximum purge gas flow rates. Definitive intrinsic membrane permeabilities were not demonstrated for these three membranes at the maximum flow conditions achievable for the larger cell in which they were tested. For this reason, additional testing was carried out in the smaller cell, where restriction on permeation rate due to device effects are less likely to occur. These data are shown in Figure 4. A recently acquired supported Gore-Tex membrane was also tested in this cell and is shown in Figure 4.

In the smaller cell, the maximum permeation rate for all the membranes except Cuprophane (cellophane) has been reached, as evidenced by a definitive plateau exhibited in the data at the higher purge gas flow rates. Apparently some loss of vapor pressure differential driving force due to buildup of water vapor in the purge gas still exists even in the smaller cell for the cellophane membrane. This indicates that the ultimate water vapor permeability is not achievable in this system.

The water vapor permeation rate of a membrane is dependent on the water vapor pressure differential across the membrane. This vapor pressure differential is controlled by the temperature at which the cell operates (the vapor pressure of water on the liquid side of the membrane) and the water vapor pressure on the purge gas side of the membrane. It has already been demonstrated (See Figures 3 and 4) that the more rapid the purge gas flow rate and the more turbulence introduced, the higher the observed water vapor permeability. This increased flow rate (and turbulence) reduces the resistance to mass transfer caused by a water vapor buildup immediately adjacent to the membrane surface on the purge gas side of the membrane. Also, the increased flow rate reduces the average water vapor pressure in the purge gas. Thus, both turbulence and increased gas flow rate increase the effective differential pressure across the membrane or reduce the resistance to mass transfer and increase the observed membrane permeability.

Increased liquid temperature also can enhance the observed permeation rate if the water vapor pressure in the purge gas is maintained at a low level. Figures 5 and 6 demonstrate the effect of purge gas flow rate at several temperatures for the Gore-Tex S-10109 and L-10272 membranes. Figure



Figure 4

MEMBRANE PERMEATION RATE AS  
A FUNCTION OF PURGE GAS FLOW RATE

TEMPERATURE 25°C  
CELL AREA 28.6 cm<sup>2</sup>

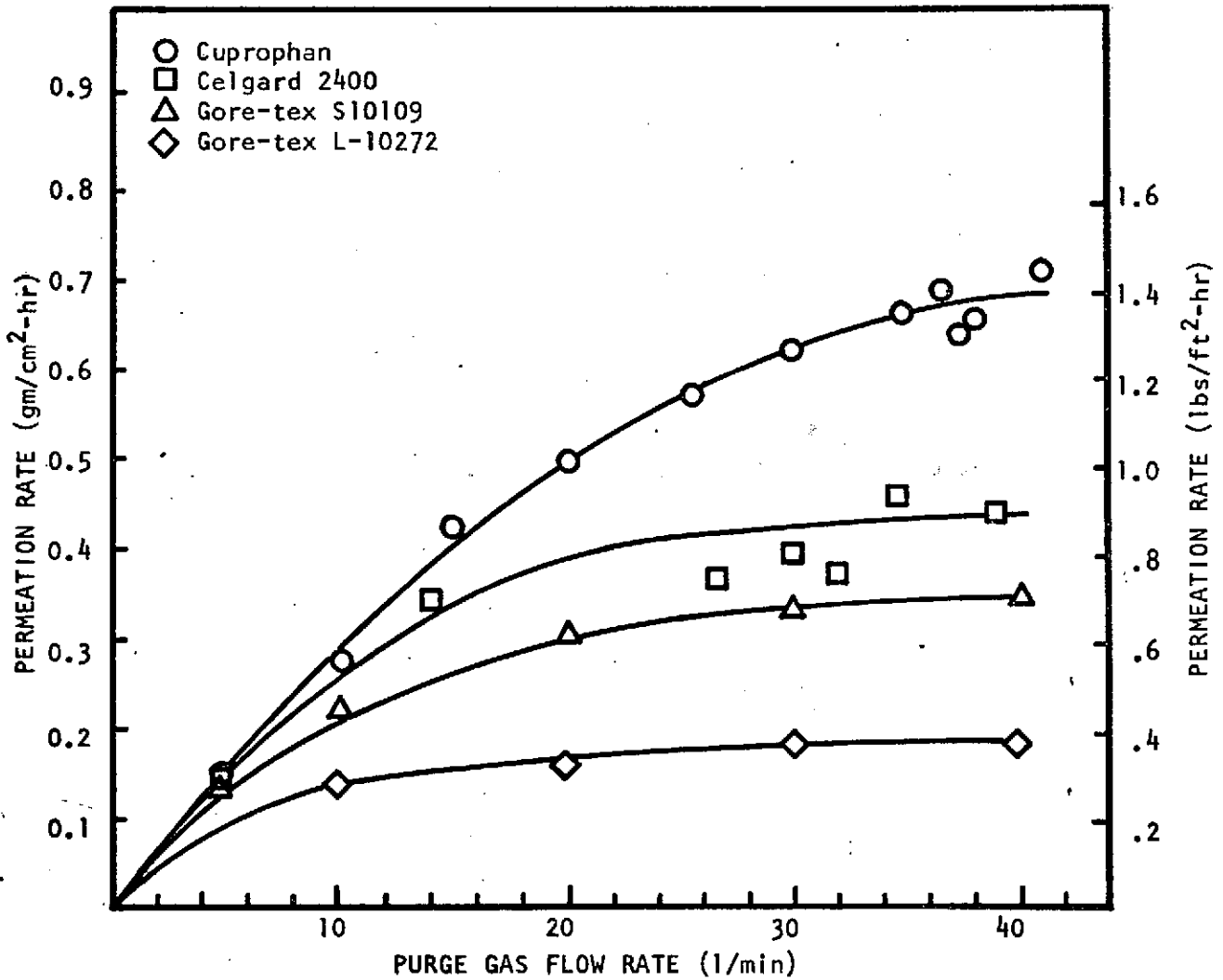


Figure 5

WATER VAPOR PERMEATION RATE AS A  
FUNCTION OF PURGE GAS FLOW RATE AND  
TEMPERATURE GORE-TEX S-10109

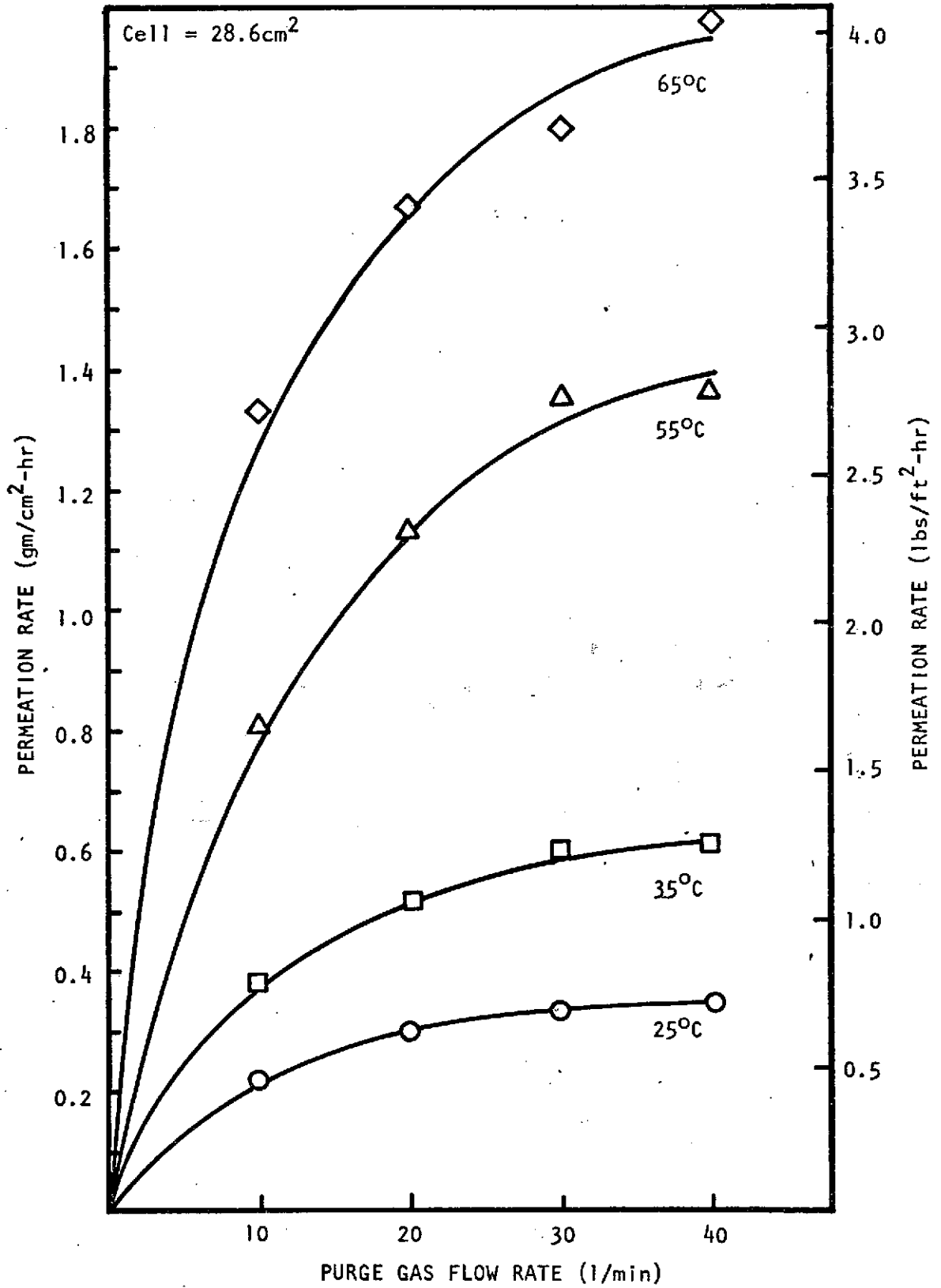
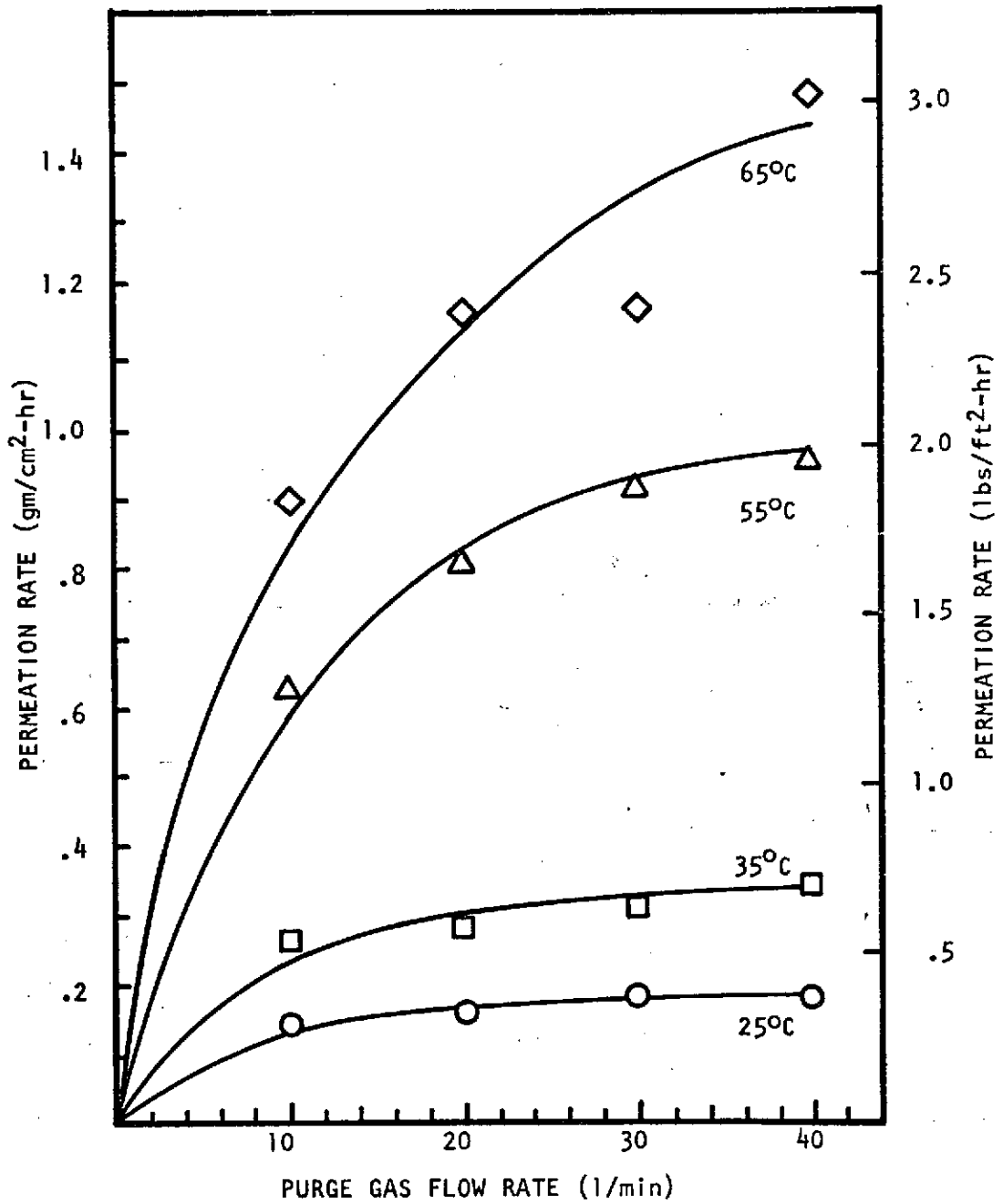


Figure 6

WATER VAPOR PERMEATION RATE AS  
A FUNCTION OF PURGE GAS FLOW RATE  
AT SEVERAL TEMPERATURES

GORE-TEX L-10272 (SINGLE BACKED FLUOROCARBON MEMBRANE)  
CELL AREA = 28.6 cm<sup>2</sup>



7 shows the observed permeation rate as a function of operating temperature for these two membranes. The permeation rate is increased nearly eightfold by increasing the operation temperature from 25°C (77°F) to 65°C (149°F). However, the efficiency of utilization of the process decreases as temperature is increased. This is displayed in Figure 8 where the normalized flux (flux divided by the vapor pressure gradient) is plotted versus the purge gas flow rate at several temperatures. The decrease in efficiency is probably the result of increased mass transfer resistance boundary layer at the higher membrane permeation rates. In other words, the increased flux causes the purge gas to become more saturated and as a result the effective pressure gradient is reduced. The net effect is that the device (cell) begins to limit the observed permeability as the operating temperature exceeds 35°C. It should be noted that this explanation of device efficiency applies only to this test device. However, this cell is specifically designed to minimize boundary layer resistances to mass transfer. Any other device designed should not be expected to improve membrane utilization significantly.

On the liquid side of the membrane both mass transfer and heat transfer resistance problems are conceivable, depending upon the membrane and liquid flow rates. For the permeation cells described above, liquid flow rates ranged from about 500 ml/min to 1200 ml/min with turbulence promoters in the channels. Temperature monitoring of both the liquid stream and purge gas stream failed to show detectable variations in inlet and outlet temperatures. The fluid dynamics of the cells were designed to minimize fluid boundary layer resistances. The fact that temperature variations were not observed in the inlet and outlet streams indicates that heat transfer is not a problem here.

Reductions in permeation rate can be expected because of a lowered water vapor pressure above a solution containing dissolved solids. However, losses in permeation rate due to water concentration gradients causing resistance to mass transfer at the liquid surface are not likely to occur except at very high dissolved solids concentrations in the liquid stream. Membrane permeation in studies done with synthetic urines\* containing up to 7¼% dissolved solids showed no reductions in flux from the pure water values even at very low liquid flow rates for porous nonwetting membranes. This is displayed in

---

\*Formulation of synthetic urine. "Clinical Diagnosis by Laboratory Methods," Todd and Sanford.

Figure 7

PERMEATION RATE AS A FUNCTION OF  
TEMPERATURE FOR GORE-TEX  
FLUOROCARBON MEMBRANES

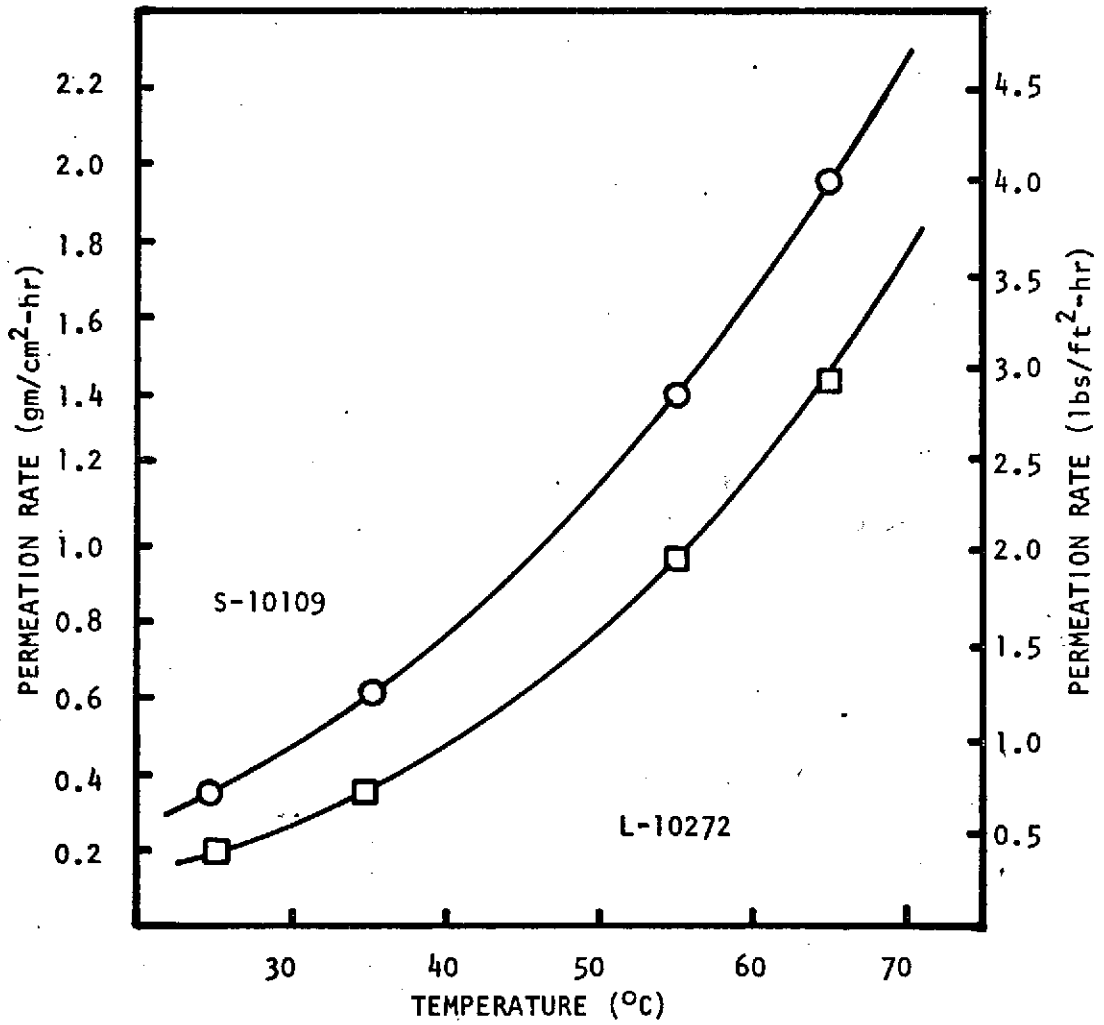


Figure 8

NORMALIZED WATER VAPOR PERMEATION RATE  
AS A FUNCTION OF PURGE GAS FLOW RATE  
AT SEVERAL TEMPERATURES

GORE-TEX S-10109 MEMBRANE  
CELL AREA = 28.6 cm<sup>2</sup>

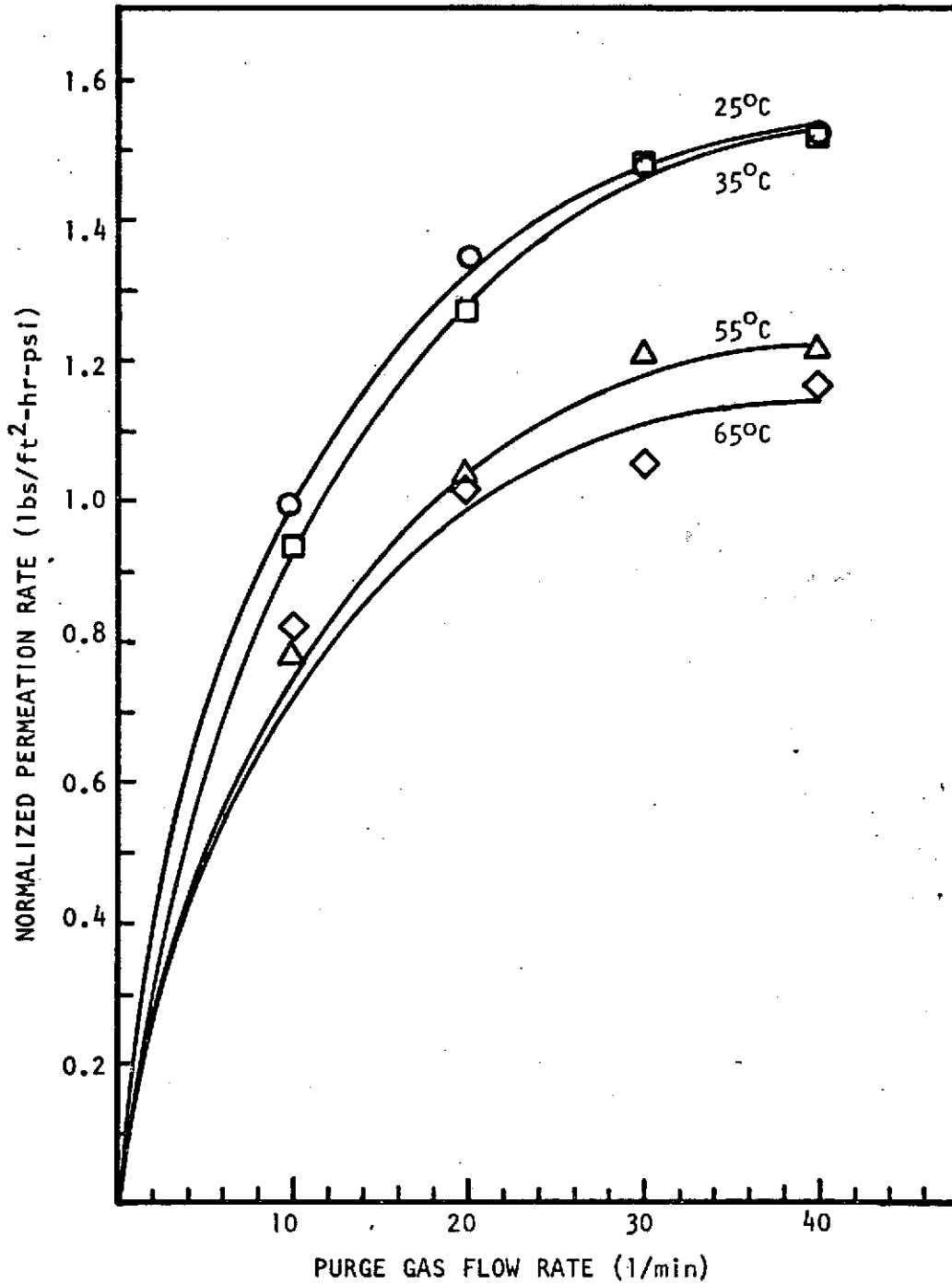


Figure 9 for the Celgard 2400 membrane.

Porous wetting membranes can show reduction in permeation rate dependent on dissolved solids content of the urine feed solution. This reduction in permeation rate is independent of liquid feed flow rate or variables which tend to eliminate mass transfer resistance on the liquid side of the membrane. This is clearly demonstrated in Figure 10 for Cuprophane membrane. In this case the decreased permeation rate is the result of the lowered water vapor pressure above the synthetic urine contained in pores of the membrane. Also contributing to the decreased permeation rate is the buildup of solids deposited on the gas side of the membrane as evaporation takes place. Warner (2) has reported similar permeation rate losses with cellophane membranes. In his studies, permeation rate losses of 50% were observed when the dissolved solids content of urine increased from 5% to 10%. These losses were recoverable, however, by simple dilution of the urine solution. Warner attributed this to a reversible coating on the membrane surface. Since this behavior is unique to the porous wetting membrane type (this is the only membrane type where urine enters the pores), it probably can best be explained as fouling caused by deposition of dissolved solids as the urine evaporates on the gas side of the membrane. Note that the loss in permeation rate is not mitigated by increased fluid velocity (See Figure 10). This indicates that the fouling problem is not attributable to any surface coating on the liquid side of the membrane. Thus the fouling must be within the membrane structure.

The results of the membrane permeation studies for the selected membranes are shown in Table II. With the exception of the nonporous diffusive membrane types and the porous nonwetting polypropylene membrane, all of the membranes have the flux required for VDR application. A considerable degree of resistance to mass transfer on the purge gas side of the membrane was observed. This resistance probably is attributable to water vapor concentration buildup at the membrane surface. Little or no liquid side mass transfer resistance was observed even for the highest flux membranes operating with synthetic urine solution of up to 7½% solids. However, the porous wetting Cuprophane (cellophane) membrane showed reductions in flux related to the dissolved solids content of the urine feed solution. This membrane fouling could limit the usefulness of cellophane as a VDR membrane choice, since the amount of water recovered from urine brines would be limited by the efficiency of this membrane.

Figure 9  
WATER VAPOR PERMEATION RATE AS  
A FUNCTION OF LIQUID FLOW  
Celgard 2400 Membrane at 23.5°C  
Purge Gas Flow 25 l/min  
Cell Area 55.5 cm<sup>2</sup>

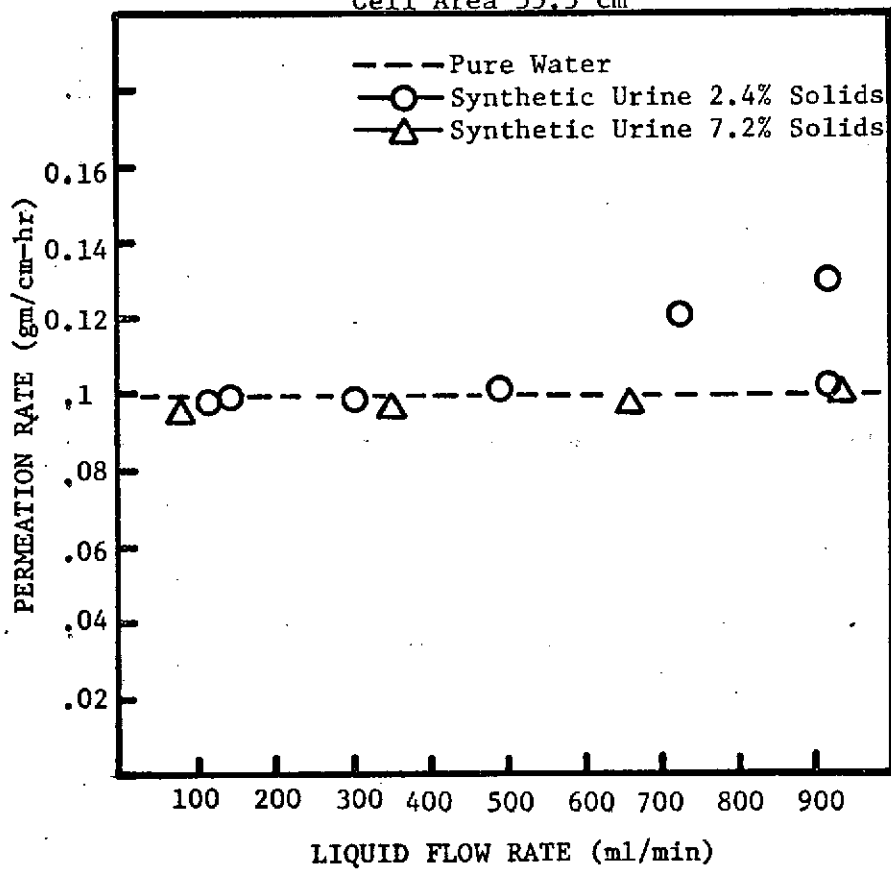




Figure 10

WATER VAPOR PERMEATION RATE  
FROM SYNTHETIC URINE (7½% DISSOLVED SOLIDS) AT  
23.5°C CUPROPHAN MEMBRANE IN  
28.6 cm<sup>2</sup> SURFACE AREA CELL

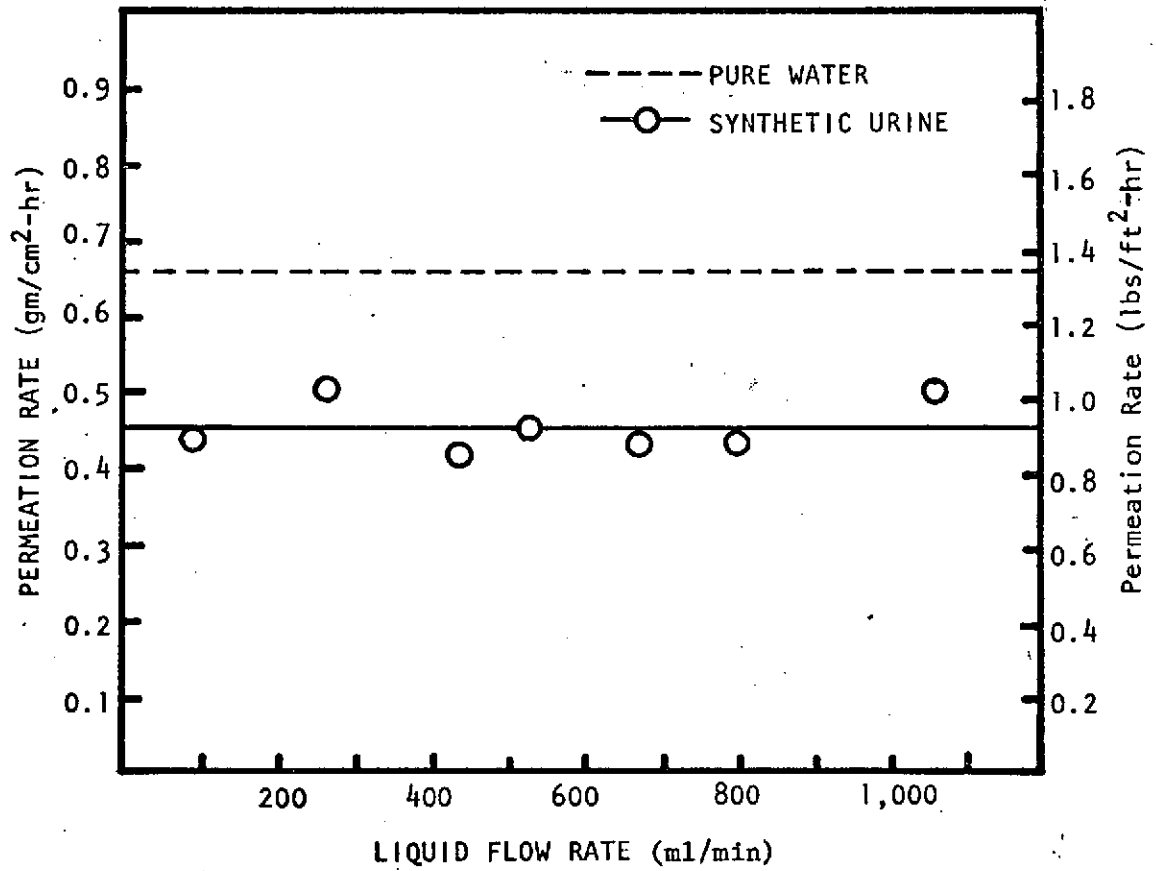


TABLE II

## WATER VAPOR PERMEATION RATE

TESTED AT 25°C

<u>Membrane</u>	<u>Permeation Rate</u>	
	gm/cm <sup>2</sup> -hr	lbs/ft <sup>2</sup> -hr
Porous Nonwetting Membranes		
Polypropylene (Celgard 2400)	0.10	0.20
Polytetrafluoro ethylene (Gore-Tex S-10109)	0.35	0.66
Polytetrafluoro ethylene single backed (Gore-Tex L-10272)	0.19	0.40
Porous Wetting		
Polypropylene (Celgard 2400W)	0.44	0.90
Cellophane (Cuprophan)	0.70	1.42
Diffusive Nonporous		
Dimethyl Silicone	0.0086	0.018
Polycarbonate / Silicone	0.0022	0.0045
Polypeptide	0.0096	0.020
Ethyl Cellulose	0.0085	0.017

## Mechanical And Chemical Stability

Experimental Method. Procedures and methods used to evaluate membranes for mechanical properties were based on methods developed under a program sponsored by NIH for the evaluation of hemodialysis membranes (4). Mechanical properties may be separated, for the purpose of tabulation, into mechanical stability properties and mechanical failure properties.

Mechanical Failure Tests. An Instron Model TM tensile tester was employed for measuring tensile strength and extension. Membrane specimens were cut in 9-inch lengths while supported on a ruled piece of paper; the backing paper made the sample visible and permitted more facile mounting of the film in the jaws of the tester. Each sample was tested using a 5.0 cm gauge length and 0.5 cm/min rate of extension. The chart speeds were adjusted to allow easy measurement of extension at failure, and to allow measurement of the initial modulus. The Instron was calibrated to provide a full scale reading of 0.2 to 2Kg. For those membranes which would undergo irreversible structural changes on wet to dry cycles, the measurements were made on wet samples which were maintained at 100% relative humidity during testing. The supported sample was placed in the upper hydraulic jaw of the tester, and sufficient preload was applied to the membrane to remove wrinkles. The lower jaw then was closed, and the backing paper was slit. Extension was carried out until the membrane failed. The work to rupture was obtained from tensile failures by measuring the area under the stress-strain curve with an Instron Model D1-53 Integrator.

The measured breaking force for ten or more replicates was reduced to tensile strength by dividing the force by the area of the original cross section of the membrane. The thickness of the actual test strips was determined by use of a dial micrometer having scale calibrations of 1 micron ( $10^{-6}$ m).

The resistance of a membrane to tear is measured as the maximum force to initiate tearing in a specially cut specimen. The method and procedures used are taken directly from the ASTM D1004-66 (reapproved 1970) Standard Method.

A simple and reliable barometer of a membrane's mechanical failure properties is a water burst test recently developed at GSRI for the evaluation of hemodialysis membranes. In this test the membrane is extended through a fixed diameter orifice by means of a pressurized fluid until it ruptures. From this test the relative burst pressure and extension at rupture are

obtained.

**Mechanical Stability Tests.** The tensile modulus (or Young's modulus) of the membrane was determined from the stress-strain curves of the failure experiments. The slope of the initial stress-strain curve gave the Young's modulus. The intercept of this line with a final slope taken after a yield region identified the yield stress. The strain at the yield stress value was labeled the yield strain. An example of a typical stress-strain curve is shown in Figure 11.

All membranes selected for the program were initially evaluated for a complete set of mechanical properties. Samples of each membrane were exposed to stabilized urine at 160°F for up to 90 days. The effect of the prolonged exposure was monitored by measuring the burst strength and hydraulic flux, if applicable, at 30-day intervals.

Finally, at the conclusion of the 90-day exposure a complete mechanical evaluation was repeated for those membranes still intact.

Results of Mechanical and Chemical Stability Tests. The initial mechanical properties of the membranes selected for the program are listed in Tables III and IV. All the membranes show good physical integrity, except for the fluorocarbon and the dimethyl silicone membranes. The fluorocarbon membrane has a very low initial modulus and elastic recovery. These properties make this material difficult to handle without introducing a permanent deformation to the membrane. This problem, however, can be overcome by use of a backed (supported) membrane. A supported fluorocarbon membrane is available and was tested for water vapor permeability. However, it was not tested for mechanical properties, as it was known to have more than adequate structural strength for VDR application. The support material is a nonwoven fibrous polypropylene mat rigidly bonded to the fluorocarbon membrane. Polypropylene is known to be chemically inert to chromic acid stabilized urine. For this reason, stability testing of the backed fluorocarbon membrane was considered unnecessary.

The dimethyl silicone membrane is such a highly elastic material that mechanical testing could not be done. A supported form of this membrane also is available but was not tested for mechanical properties. The support material is a polyester mat which would impart the necessary physical strength for the VDR application. The composite membrane was not tested for chemical stability since the membrane itself did not have the required stability.

Figure 11

Typical Stress-strain Curve

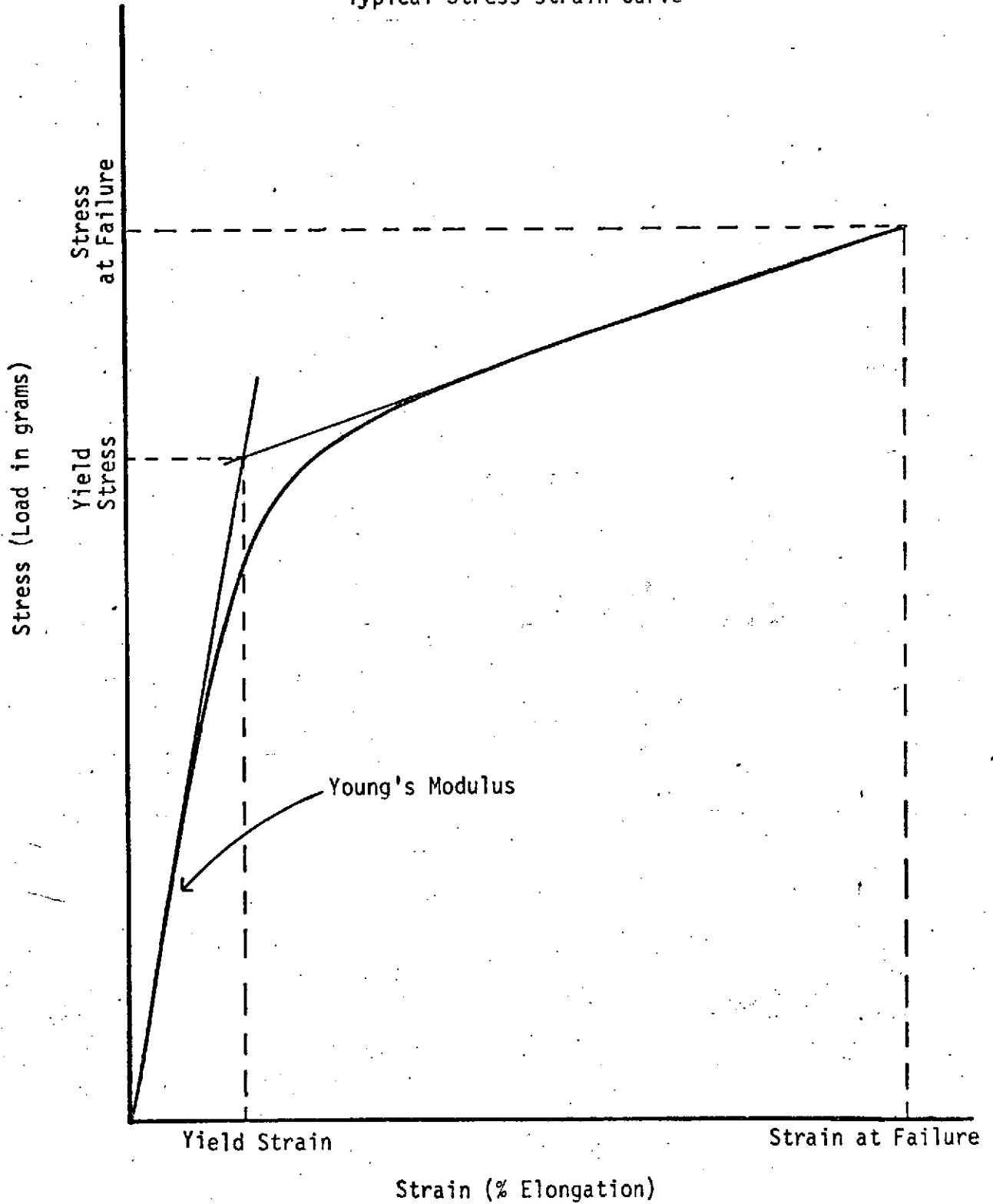


TABLE III

## MEMBRANE TENSILE PROPERTIES

## MECHANICAL STABILITY DATA

<u>Membrane</u>	<u>Initial Modulus (kg/cm<sup>2</sup>)</u>	<u>Yield Strain %</u>	<u>Yield Stress kg/cm<sup>2</sup></u>	<u>Thickness Microns</u>
Celgard 2400	4854 ± 370	2.5 ± .2	118 ± 1.1	23
Gore-Tex S-10109	125 ± 25	7.9 ± 1.1	9.5 ± .8	78
Celgard 2400W	2215 ± 261	6.3 ± .5	123 ± 3.4	22
Polypeptide 11034D	3497 ± 376	1.5 ± .1	47 ± 5.2	22
Cuprophan PM150	175 ± 11	1.2 ± .12	12 ± .5	22
Dimethyl Silicone	--	--	--	
Polycarbonate/Silicone	904 ± 145	3.9 ± .5	35 ± 1.4	28
Polypeptide (dense)	10760 ± 500	1.5 ± .08	156 ± 4.6	22

TABLE IV

## MEMBRANE TENSILE PROPERTIES

## MECHANICAL FAILURE DATA

<u>Membrane</u>	<u>Tensile Strength (Kg/cm<sup>2</sup>)</u>	<u>Elongation at Break %</u>	<u>Work to Break (Kg-M) X 10<sup>3</sup></u>	<u>Force to Initiate Tear Gm</u>	<u>Thickness Microns</u>
Celgard 2400	114 ± 1	56 ± 9	7.3 ± 1.2	277 ± 30	23
Gore-Tex S-10109	41 ± 3	454 ± 24	51.0 ± 3	579 ± 25	78
Celgard 2400W	136 ± 4	604 ± 50	33.6 ± 2.8	382 ± 26	22
Polypeptide 11034D	45 ± 3	32 ± 4	1.4 ± .2	70 ± 2.1	22
Cuprophane PM150	24 ± 2	47 ± 5	1.2 ± .12	132 ± 4	22
Dimethyl Silicone	-	-	-	-	-
Polycarbonate/Silicone	132 ± 9	369 ± 20	37.0 ± 3	218 ± 23	28
Polypeptide (dense)	166 ± 7	83 ± 2	13.9 ± .5	331 ± 27	23

Results of stability tests of the membranes in stabilized urine at 160°F are shown in Table V. The polypropylene and the fluorocarbon nonwetting membranes exhibited superior stability in the strong oxidizing chromic acid stabilized urine. The stability of these two nonwetting membranes is evidenced by their unchanging appearance and constant burst pressures (Table V). These two membranes also exhibited complete stability of mechanical properties in tests at the end of the 90-day exposure. (See Tables VI and VII.)

The nonporous membranes listed in Tables III and IV lost all mechanical integrity, as shown in Table V.

Of the porous wetting membranes, the polypeptide was eliminated after 30 days. The polypropylene wetting membrane showed only minor losses in mechanical stability (Tables VI and VII). However, data from Table V indicate sufficient changes in hydraulic permeability, appearance and burst strength to preclude use of this material. The manufacturer of this membrane warns that wetting agent leaching could be a potential problem. The data in Table V and observations during use indicate that such leaching may be occurring here.

The Cuprophan (cellophane) membrane showed only discolorations and minor burst strength and hydraulic permeability changes. However, the mechanical properties of the exposed membrane show significant increases in brittleness. Mechanical testing of the Cuprophan membrane also resulted in loss of work to break and loss of force to initiate tear. These mechanical changes probably would cause membrane failure at stress conditions under which the original membrane would survive.

Two membrane materials (fluorocarbon and polypropylene nonwetting) showed complete inertness to the stringent chemical environment of the testing program. Cellophane, although degraded in this environment, probably still shows sufficient mechanical properties for use as a supported membrane. (The permeation properties were not significantly altered during the exposure test.) The initial mechanical properties of the fluorocarbon would require that this material be supplied as a supported membrane. (Such a membrane is available.) The polypropylene membrane shows sufficient mechanical integrity for unsupported use.

#### Membrane Recommendation for 30-Day Trial

On the basis of the membrane permeation rate studies and the mechanical and chemical stability evaluations, the Gore-Tex S-10109 fluorocarbon membrane was selected for the 30-day demonstration trial. Permeation studies



TABLE V

Membrane Properties After Exposure  
to Chromic Acid Stabilized Urine at 160°F

<u>Membrane</u>	<u>Exposure Time (days)</u>	<u>Hydraulic Permeability cm/sec-atm x 10<sup>5</sup></u>	<u>Burst Pressure mm Hg</u>	<u>Appearance</u>
<u>Porous Nonwetting</u>				
Polypropylene	0	-	685	White
	30	-	533	No change
	63	-	604	No change
	90	-	531	No change
Fluorocarbon	0	-	659	White
	30	-	650	No change
	63	-	710	No change
	90	-	653	No change
<u>Porous Wetting</u>				
Polypropylene	0	102	998	White
	30	28	776	Discolored, Brown
	63	22	538	Discolored, Brown
	90	13	536	Discolored, Brown
Cellophane	0	1.9	270	Transparent
	30	1.1	244	Discolored, Brown
	63	1.7	244	Discolored, Brown
	90	2.1	248	Discolored, Brown
Polypeptide	0	6.5	220	Transparent
	30	Disintegrated		
<u>Nonporous Diffusive</u>				
Polypeptide	0	0	265	Translucent, White
	30	Disintegrated		
Polycarbonate/ Silicone	-	-	-	Transparent
	30	Disintegrated		
Dimethyl Silicone	0	0	87	Transparent
	63	0	47	No change
	90	Disintegrated		

TABLE VI  
MEMBRANE TENSILE PROPERTIES AFTER EXPOSURE TO STABILIZED URINE  
AT 160°F FOR 90 DAYS  
MECHANICAL STABILITY DATA

<u>Membrane</u>	<u>Initial Modulus</u> (kg/cm <sup>2</sup> )	<u>Yield Strain</u> %	<u>Yield Stress</u> %	<u>Thickness</u> Microns
Celgard 2400	4,333 ± 243	3.3 ± 0.3	131 ± 6.4	23
Gore-Tex S-10109	127 ± 20	10 ± 1.5	13 ± .7	82
Celgard 2400W	1,861 ± 144	3.1 ± .4	146 ± 5.4	25
Cuprophan PM150	370 ± 20	5.5 ± .4	21 ± .7	22

TABLE VII

MEMBRANE TENSILE PROPERTIES AFTER EXPOSURE TO STABILIZED URINE  
 AT 160°F FOR 90 DAYS  
 MECHANICAL FAILURE DATA

<u>Membrane</u>	<u>Tensile Strength (Kg/cm<sup>2</sup>)</u>	<u>Elongation at Break %</u>	<u>Work to Break (Kg-M) X 10<sup>3</sup></u>	<u>Force to Initiate Tear Gm</u>	<u>Thickness Microns</u>
Celgard 2400	125 ± 6.5	-	-	302 ± 9	23
Gore-Tex S-10109	47 ± 1.4	492 ± 36	63 ± 5	720 ± 21	82
Celgard 2400W	141 ± 2.5	575 ± 20	-	316 ± 33	23
Cuprophan PM150	28 ± 1	18 ± 1.6	.037 ± .04	89 ± 10	22

showed this membrane to have approximately seven times the water flux required for the VDR application at the expected temperature of operation. (Gore-Tex L-10272, the supported fluorocarbon membrane, had almost six times the required flux. See Figure 11.) This enhanced flux would allow considerable latitude in design and fabrication of the cell geometries and still insure the desired 0.5 lbs/ft<sup>2</sup>-hr flux. It was recognized that the larger demonstration cell would be much less efficient than the permeability cells.

As the selected membrane was of the porous nonwetting type, fouling problems were not anticipated.

Complete chemical stability in the strong oxidizing environment of the stabilized urine brine also made this the membrane of choice. The mechanical properties of the S-10109 fluorocarbon membrane would preclude its use in large surface area devices. However, a supported membrane with more than adequate properties is available. Thus this material would be consistent with eventual VDR application.

## WATER VAPOR DIFFUSION RECOVERY DEMONSTRATION TRIAL

The reliability of the Gore-Tex fluorocarbon membrane was demonstrated by a 30-day VDR trial in a 400 cm<sup>2</sup> cell using stabilized natural urine at 60°C (140°F). More than 90% of the recoverable water was removed from the urine brine during this trial. The system behaved well with only minor mechanical failures. There was some decline of the membrane flux in the course of the trial, but evaluation of this problem indicates that it can be circumvented. Product water quality, although only marginal in this test, could be expected to improve significantly with use of a better designed cell incorporating supported membranes.

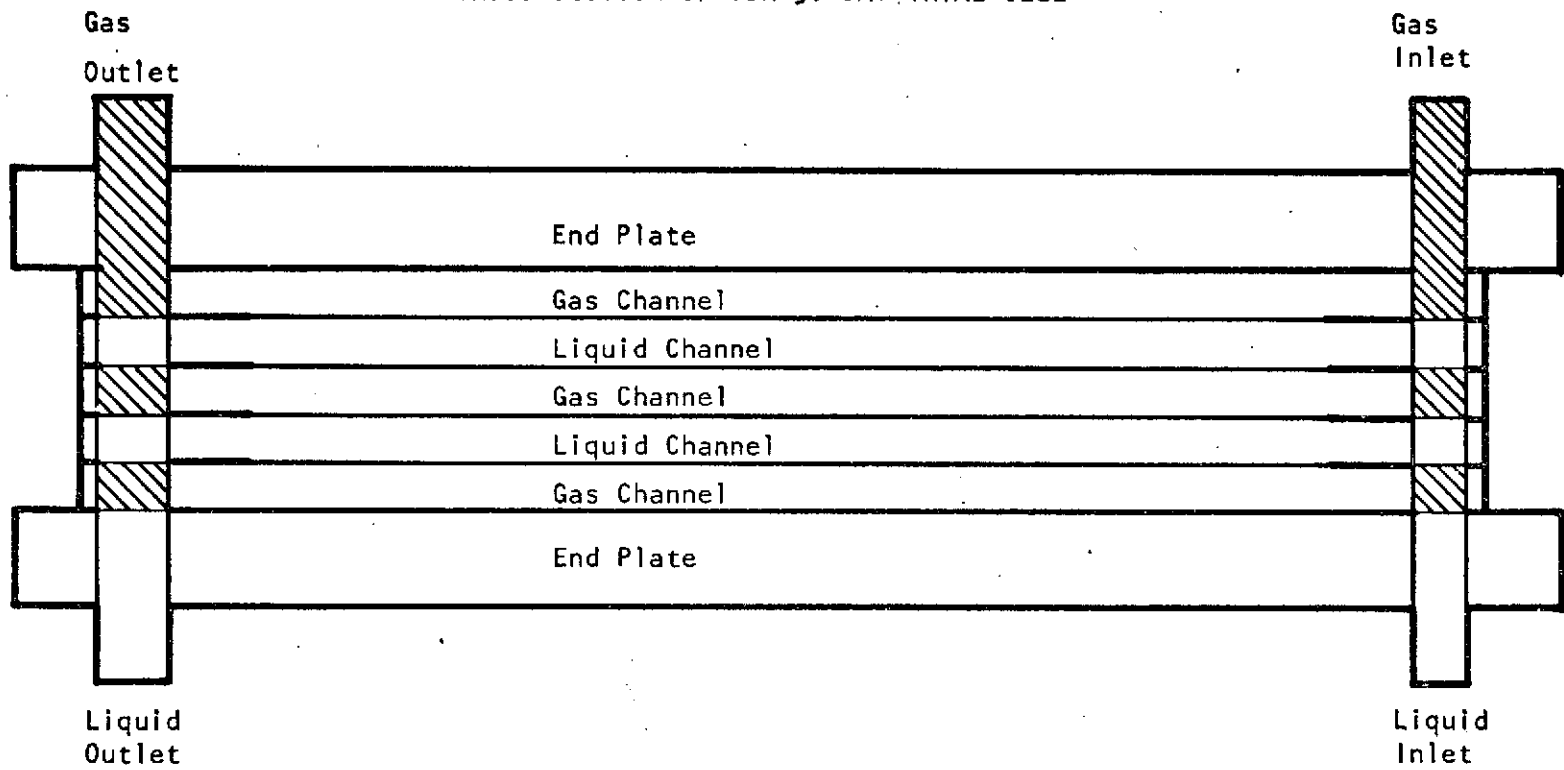
### Experimental Procedure

A commercially available cell, originally designed for osmotic diffusion, was used in the 30-day demonstration trial. A schematic of this cell is shown in Figure 12. The total membrane area was 400 cm<sup>2</sup> (.43 ft<sup>2</sup>) in four layers of parallel plates. The membranes are sandwiched between polycarbonate gasket plates. The gas and liquid streams are introduced to the selected channels by means of internal manifolds at opposite sides of the plates. Liquid and gas were flowed concurrently to reduce pressure gradients across the membrane. The cell was operated at a slightly positive pressure on the liquid side to prevent nitrogen from bubbling through to the liquid channel. The membrane used was the Gore-Tex S-10109 (thickness 78 microns). A fibrous paper support backing was added on the gas side of the membrane to reduce membrane deformation. (An insufficient quantity of the Gore-Tex L-10272 single-backed membrane was available at the time of loading.) Turbulence promoters were used only in the gas channels.

The flow schematic and instrumentation were basically the same as those used for the smaller cells. A diagram of that system is shown in Figure 1. The urine brine was pumped from a graduated reservoir via a heat exchanger to the VDR cell and back to the reservoir. The reservoir was stirred and maintained at a temperature slightly below the operation temperature. Bubble traps and gauges were used to measure the liquid pressures at the inlet and outlet ports. Liquid flow was measured by means of an inline rotometer. Flow rates of 500 to 600 ml/min were maintained. The urine temperature was maintained at 60 ± .5°C by means of the heat exchanger and water bath. Tem-

Figure 12

CROSS SECTION OF VDR 30-DAY TRIAL CELL



perature was monitored at the brine effluent from the cell. A peristaltic pump was utilized for brine circulation. Because of the limited life of the Viton pump head tubing, a 48-hour maintenance schedule was necessary to insure reliable service. The maintenance schedule usually involved the change-out of the pump and subsequent rebuilding of the head. Service interruptions of 1 to 2 minutes were required for pump change-out.

The only materials used in the system were 316 stainless steel, glass, polypropylene and Viton. All of these materials are inert to the stabilized urine, so corrosion was not a problem.

The nitrogen purge gas was supplied from a liquid nitrogen tank. It was preheated and then thermostated to operating temperature before introduction to the VDR cell. Pressures were monitored at the inlet and outlet to the cell. The normal operation pressures were adjusted so that the maximum gas pressure was slightly less than the minimum liquid pressure. The nitrogen flow rate was continuously measured, by means of a calibrated rotometer, as it exited the system.

The natural urine solution used was collected daily and refrigerated until use. It was stabilized with 4 gm/liter chromic acid just prior to addition to the system reservoir. Additions were made daily to the 6 liter reservoir, but no predetermined management program was followed.

The water vapor permeation rate was measured by the weight gain of a desiccant column, by the same procedure as described for the smaller cells. The rate was initially adjusted to 0.5 lbs/ft<sup>2</sup>-hr by control of the nitrogen purge gas flow rate. (This required approximately 16 liters/min of nitrogen.) The permeation rate was monitored during the course of the trial but not adjusted. Higher permeation rates were capable for this system when higher purge gas flow rates were employed.

The permeation rate and the other operating parameters were measured twice daily, usually in the morning when the brine was most concentrated and again several hours after the addition of fresh urine. Effluent water for analysis was collected at these times. The purge gas stream was diverted through a glass condenser, and the condensate was collected in ground-glass-stoppered bottles. An ethylene glycol-water cooling fluid at approximately 0°C was used.

The following urine brine properties were monitored:

1. pH

2. Percentage nonvolatile solids
3. Viscosity at 60°C

Accurate records of urine additions to the reservoir were kept so that the percentage of water recovery could be calculated.

The analytical tests performed on the permeate water were:

1. Conductivity
2. pH
3. Ultraviolet absorption spectra
4. Total carbon analysis
5. Total Kjeldahl nitrogen

At the conclusion of the trial the system was thoroughly flushed with demineralized water and the water permeation rate was redetermined. After the final permeation rate studies the cell was dismantled and photographed. In addition, samples of brine solution and solids found in the gas channel were sent for bacteriological analysis.

### Results

The results of the 30-day trial are illustrated in the time history charts in Figures 13 and 14. Figure 13 shows the urine brine properties during the course of the trial. The pH of the brine rose continuously during the course of the trial and had to be adjusted three times during the latter 15 days. Adjustment was made by the addition of concentrated sulfuric acid until the pH was 4.5 or less. The viscosity and percentage of nonvolatile solids increased continuously as the trial progressed. A mechanical failure on the 25th day resulted in a loss of approximately 85% of the concentrated brine. Fresh urine was added to the system and the trial was continued. Although membrane flux and effluent water properties at the very high urine concentrations were not obtained, the membrane durability was demonstrated for the full 30 days. Also, the results after 25 days are indicative of the membrane's performance at brine concentration levels high enough to be meaningful. Water recovery was calculated at 91% just before the mechanical failure. Further concentration of the brine to the estimated maximum recovery of 95% would not have substantially changed the results.

The product water properties are shown in Figure 14. The UV absorbance (of an unidentified material present in all samples), the conductivity, and the total carbon analysis responded uniformly but were not dependent on any



Figure 13

Time History Chart - Brine Properties

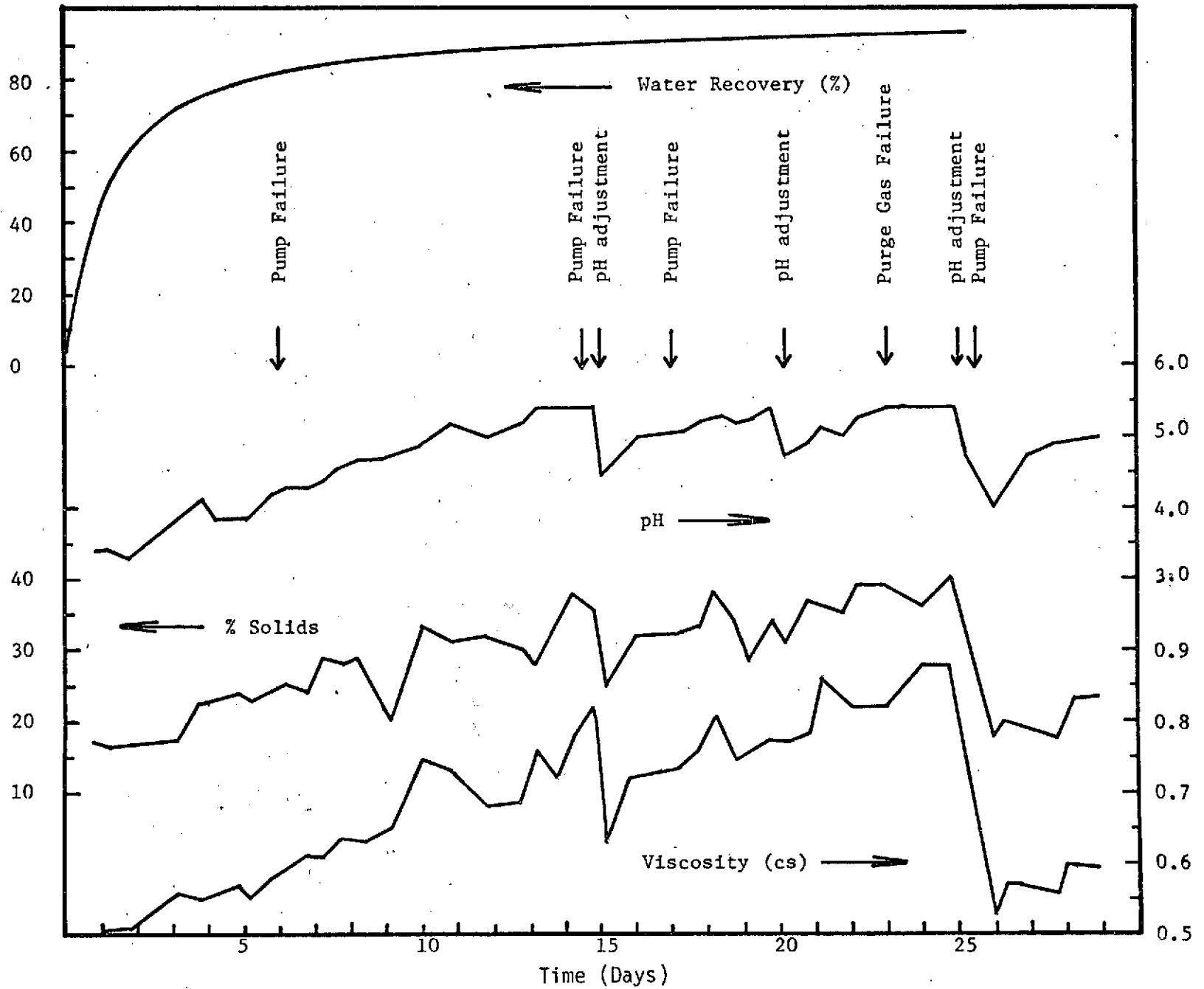
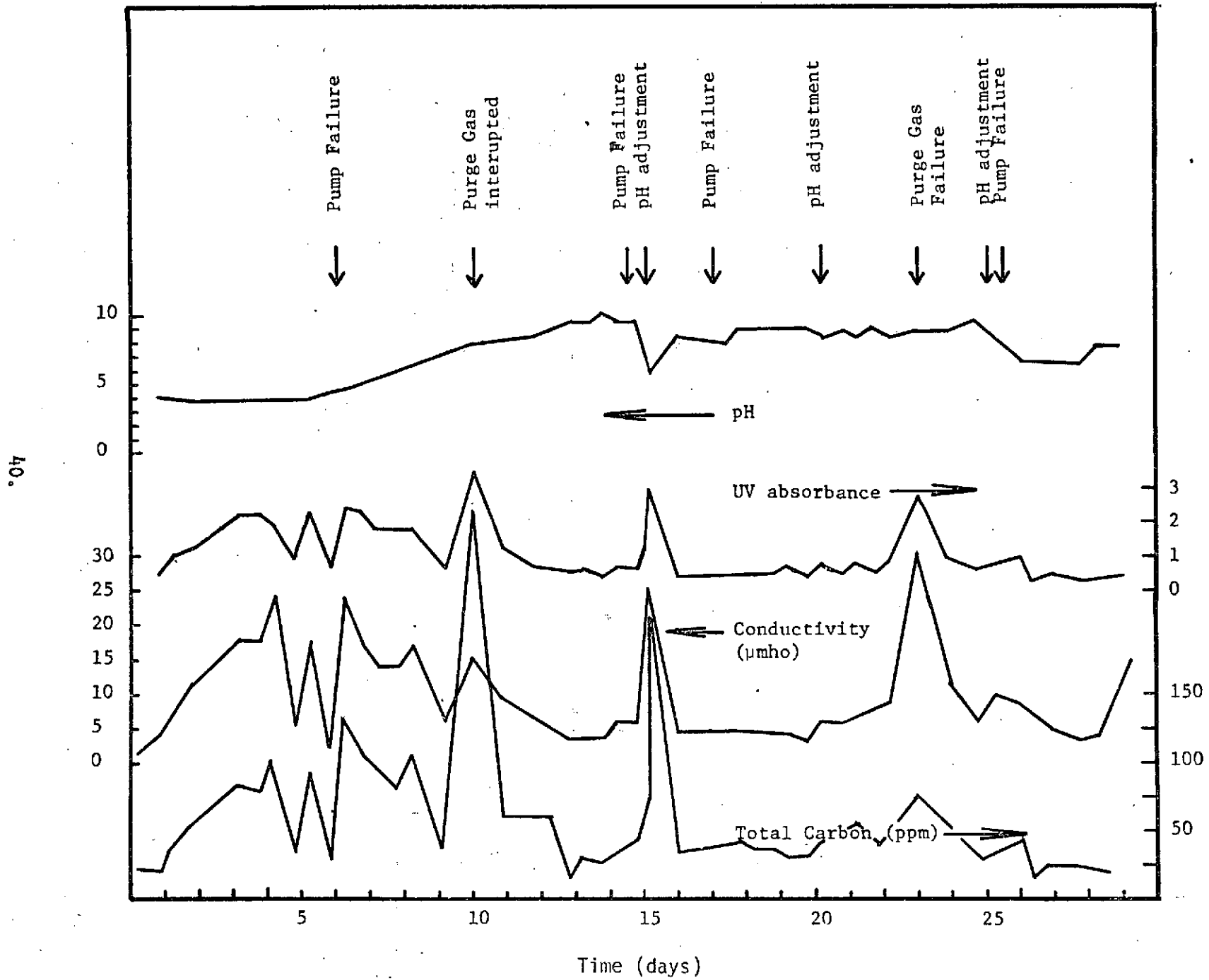


Figure 14  
Time History Chart - Effluent Water Quality



of the brine properties. The only property of the product water which showed definitive dependence on brine properties was pH. When the brine was controlled at pH 4.5, the product water pH was generally 7.5 to 8.5.

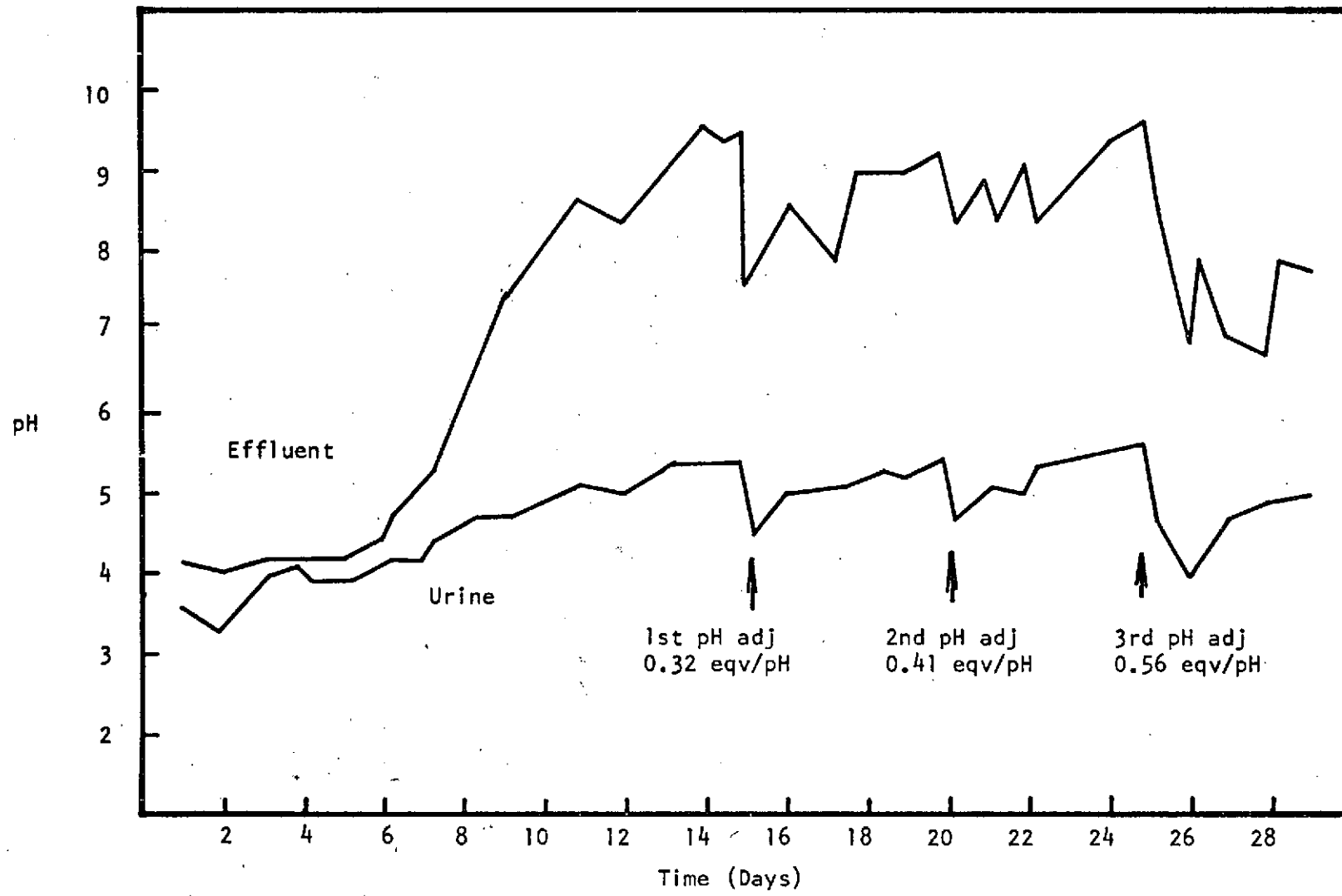
During the first six days of the trial the brine pH remained stable and low. (See Figure 15.) However, after this period the brine pH began a slow, steady increase from about 4.2 to about 5.5. This increase caused a rapid increase in effluent water pH from an initial value of 4.5 to about 9.5. A pH adjustment of the brine back to 4.5 was neutralized within 24 hours to pH 5. Eventually without further adjustment the pH of the brine would level off at 5.5. Two subsequent pH adjustments of the brine produced similar results.

Apparently a buffer system, with an equilibrium pH of about 5.5, is produced in the brine and becomes stronger as the brine concentrates. This is demonstrated by the increasing equivalents of sulfuric acid required to adjust the pH. (See Figure 15.) Of even more importance is the fact that the brine pH rises so rapidly following adjustment. This can only be caused by decomposition of urea to ammonia followed by neutralization to the ammonium salts. The buffering action is probably produced by an ammonium salt. The chemical pretreatment (4 gm/liter chromic acid) was designed to neutralize any free ammonia in the fresh urine by forming the thermally stable ammonium chromate salt (3). This quantity of the pretreatment chemical could not be expected to neutralize ammonia produced by thermal decomposition and/or bacterial decomposition of urea. At the operation temperatures of this trial, thermal decomposition was not expected to be important. Enzyme decomposition as a result of bacterial contamination could not be expected to occur at these operating conditions (acidic pH, temperature of 140°F, and strong oxidizing atmosphere of the chromic acid). Apparently, in the concentrated brine the production of ammonia by thermal decomposition does become significant even at operating conditions used, and additional acid is needed to neutralize it.

The rapid increase in pH of the product water is the apparent result of ammonia distillation. Total Kjeldahl nitrogen analysis on samples from the latter stages of the trial indicate sufficient quantities of ammonia to justify the effluent water pH (See Table VIII). Further increases in pH above approximately 9 are not likely, since an ammonium carbonate buffer system will control the pH and additional ammonia production could not be measured by pH of the product water.

The product water quality was variable. However, it was found to vary

Figure 15  
pH OF URINE AND EFFLUENT WATER AS  
A FUNCTION OF TIME



42.

REPRODUCIBILITY OF THE  
ORIGINAL PAGE IS POOR

TABLE VII.

AVERAGE QUALITY FOR SAMPLES COLLECTED  
DURING PERIODS OF CONTINGENCY OPERATION

	<u>New Orleans Tap Water</u>	<u>VDR Trial Water</u>
Conductivity ( $\mu$ mho)	14	10
Total Carbon (ppm)	10-20	40
pH	9.7	8.5
Total Kjeldahl Nitrogen (TKN) (reported as ppm $\text{NH}_3$ )	1	10
Appearance	clear	clear
Odor	none	distinct noxious organic odor

more in response to periods of interrupted flow due to equipment failure than it varied in response to any of the brine properties measured. This is illustrated in Figure 14. Sharp peaks occur simultaneously in all the quality indicators. Each of the peaks occurs immediately following an equipment failure. However, when the system was run continuously for long periods without failures, water quality progressively improved. The average water quality from samples collected during periods of continuous operation was not bad in comparison to New Orleans tap water (See Table VIII). The conductivity, pH and color are certainly acceptable. The total carbon analysis is only slightly higher than that of the tap water. However, total dissolved carbon is not a criterion by which drinking water quality could be judged, since it does not reflect on the nature of the contaminants or their toxicity. A value of 40 ppm may be perfectly acceptable. Total Kjeldahl nitrogen (reported in Table VIII as ppm  $\text{NH}_3$ ) would report all nitrogenous compounds in the sample. Ammonia and/or volatile amines at the concentration levels found in the effluent would influence the pH to the levels found in the samples. The relative toxicity of ammonia if present as ammonium ion at this level (10 ppm) is not severe (5). At the pH of the product water 50% of the ammonia will exist as ammonium ion. The remainder would be converted to ammonium ion immediately on ingestion. Potable water at this level (10 ppm ammonium ion) would be acceptable for intermittent use. A concentration of less than 5 ppm would be required for continuous use. (5)

The distinct organic odor of the effluent water could be eliminated by an aftertreatment with activated carbon. Should the basic nitrogen constituents be volatile amines or amides, etc., they also would probably be removed.

The most reasonable explanation for the water quality variation is leakage of liquid through membrane areas which have undergone deformation due to pressure surges. These deformations can cause increases in pore size to such an extent that wetting may occur. The urine feed solution could then wick through the membrane and accumulate in gas channels during shut downs. When gas flow was then re-established, a slug of impure product would be swept from the cell with entrained moisture. Also, a slight loss of water quality was found immediately following addition of fresh urine to the reservoir. Apparently some volatile materials are quickly stripped from the urine and appear in the product water. This is particularly noted in the odor of the

samples, although some of the UV absorbence data also reflect this.

The membrane permeation rate during the trial is shown in Figure 16. A decline in flux is apparent from approximately day 8 until day 25, when the system lost the concentrated feed brine as a result of a mechanical failure. The permeation rate at this time was 0.21 lbs/ft<sup>2</sup>-hr, or approximately 58% loss in flux. The percentage nonvolatile solids and viscosity were 30% and 0.909 cs, respectively (See Figure 13).

At the end of the trial the system was thoroughly flushed with demineralized water and the permeation rate was redetermined with water at 140°F to determine if a permanent loss of flux (membrane fouling) had occurred. Approximately 26% of the initial water flux could not be regained. This is illustrated in Figure 17. When the cell was dismantled, considerable deposits were noted on the liquid side membrane surface. This deposition undoubtedly is the cause of the membrane permeability loss. It should be pointed out that no filtration for suspended solids was done during this trial. The effect of the solid content is further illustrated in Figure 17, where the membrane flux is plotted against total nonvolatile solids in the brine feed solution. The data has been analyzed with the assumptions that vapor pressure decline and solid deposition both contribute to the decline in flux of the membrane. In the initial portion of the trial the reduction in flux occurs primarily due to lowering of the vapor pressure as the concentration of salts in solution builds up. But from the point when the solution contains approximately 15% total solids, membrane flux is reduced more rapidly. This more rapid reduction in flux may be the result of solids deposition as well as vapor pressure decline as the solubility limits of various salts are exceeded. Figure 17 illustrates that approximately 26% of the flux is not reclaimed due to solids deposition on the membrane surface, and that approximately 26% of the initial flux (or about 50% of the lost flux) would be recoverable by backwashing.

Further tests on the brine removed from the system at the conclusion of the trial revealed that the amount of dissolved solids versus suspended solids is very dependent on the brine pH. This is illustrated in Figure 18, where the percentage of filterable solids from the brine is plotted versus brine pH. During this trial the brine pH was not controlled closely to minimize the suspended solids. The most favorable conditions for solids deposition were actually used most frequently.

Figure 16

Time History Chart - Membrane Permeability

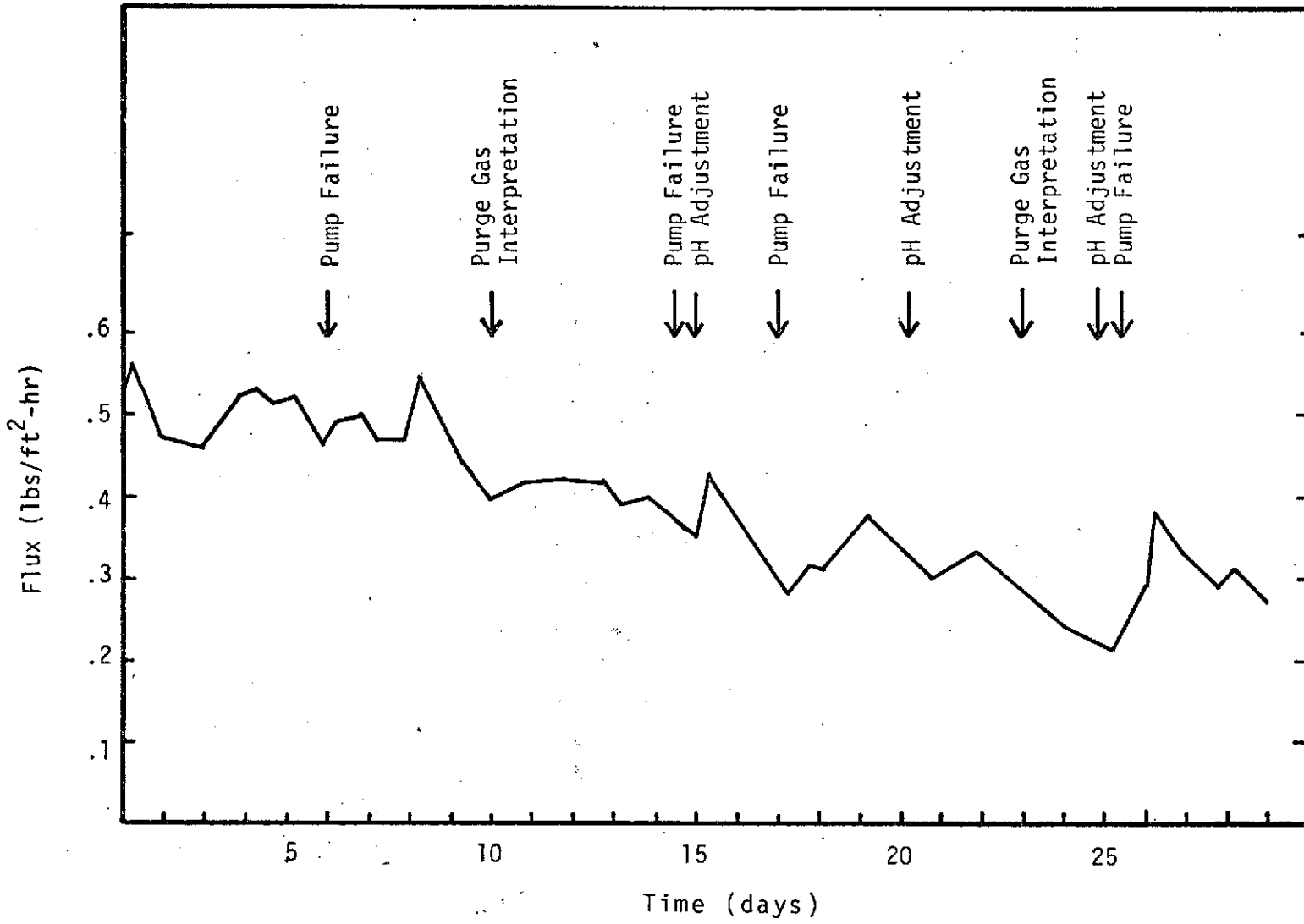




Figure 17  
Membrane Flux as a function of brine total solids content

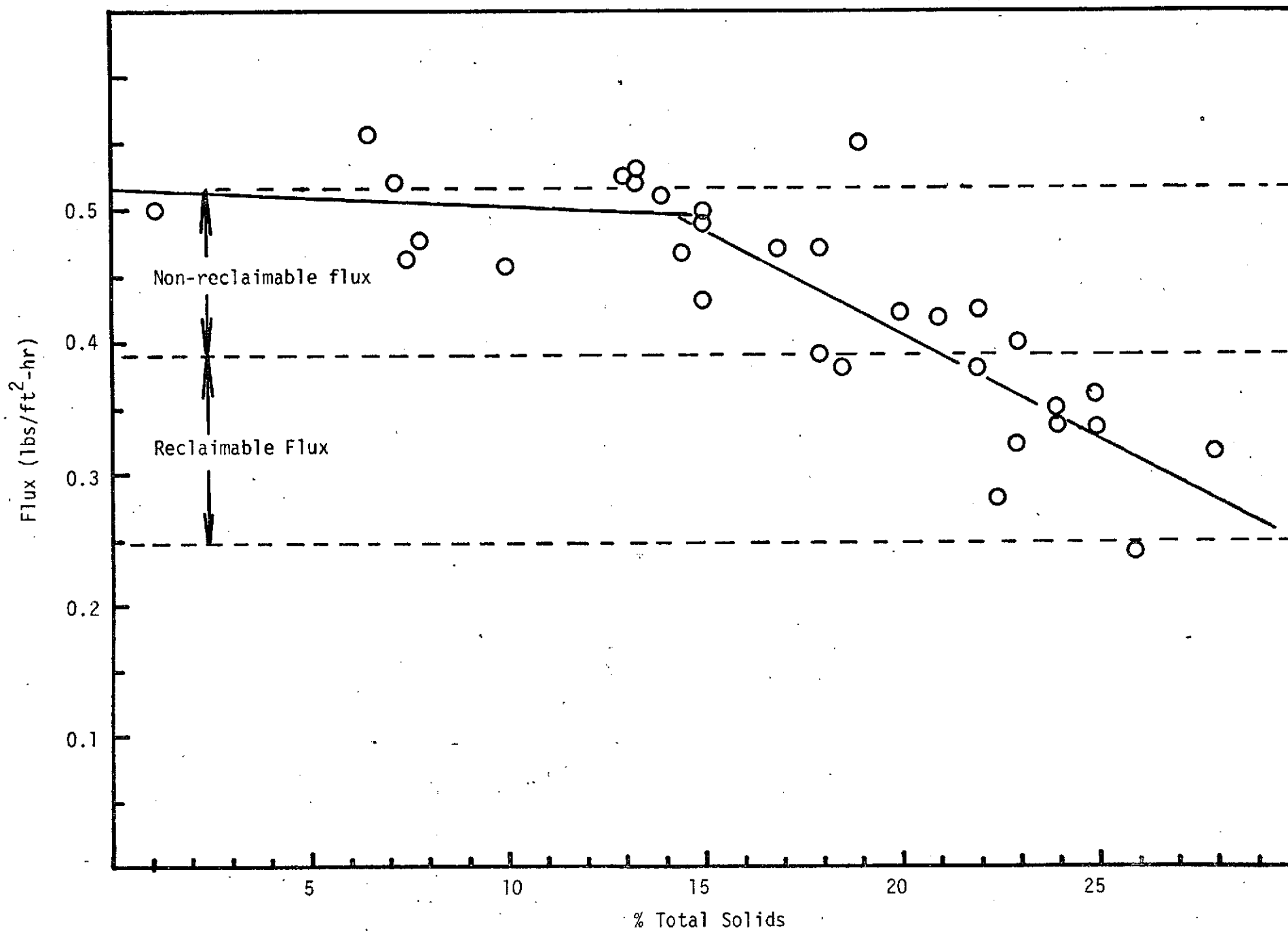
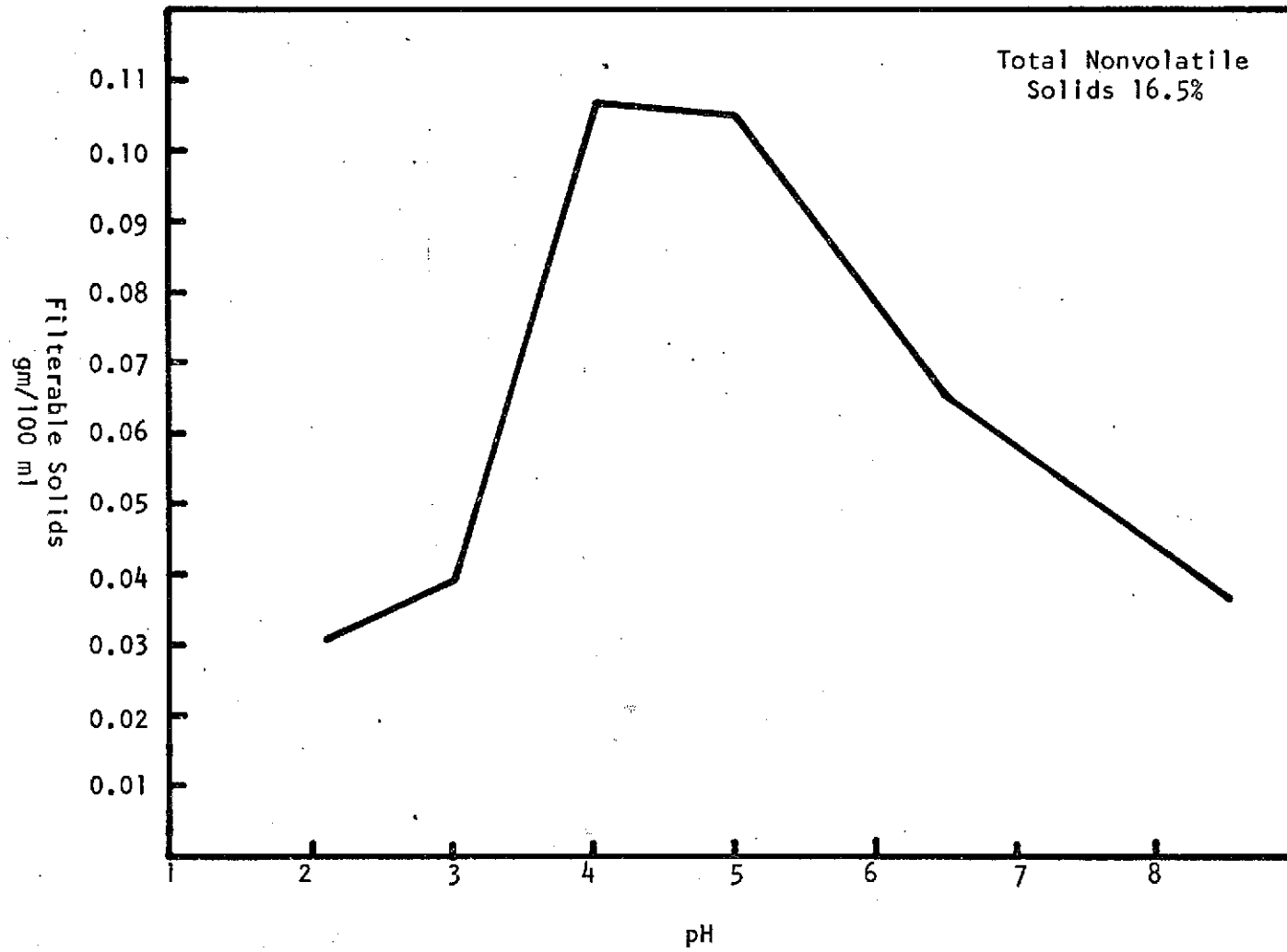


Figure 18

FILTERABLE SOLIDS AS A FUNCTION OF URINE pH  
URINE SOLUTIONS TAKEN FROM 30 DAY TRIAL



Further, no systematic brine management program was followed. The system was initially charged with urine, and additional urine was added as needed. It is possible that the same degree of water recovery could have been achieved with less solids deposition on the membrane simply by control of the fresh urine input to avoid temporary excursions in solids content. Improved liquid flow dynamics such as higher flow rates with increased turbulence would tend to minimize solids deposition. In this trial no special flow precautions were taken.

Bacteriological examination of the samples taken from feed urine and solids found in the cell showed contamination from yeast, bacillus subtilis, staphylococcus epidermidis and other common bacteria. Since the system was not sterilized before start-up and sterile procedures were not followed on disassembly of the cell, no conclusions could be reached regarding the source of contamination. Previous work (See Appendix I) using bacteria seeded feed streams has shown no contamination of product water with use of the Gore-Tex S-10109 membrane in the VDR application.

### Additional VDR Trials Using Natural Urine

At the conclusion of the 30-day trial two shorter VDR runs were made using the supported dimethyl silicone membrane and the supported fluorocarbon membrane (Gore-Tex L-10272) which were described earlier in this report. The purpose of these additional trials was to evaluate water quality and to determine if other operating conditions could effect water quality improvements. Because of membrane deformation experienced during the 30-day trial using the unbacked S-10109 fluorocarbon membrane, water quality was variable and below expected standards. (A support material was used in the cell but the membrane was not bonded to it. Therefore deformation could still take place in one direction.) This trial was intended to determine to what extent water quality could be improved by use of a fluorocarbon membrane capable of withstanding the operating pressure surges without structural damage. For both of these additional trials, all operating conditions and cell set-up were maintained as for the 30-day trial. The one exception was the feed brine.

In the dimethyl silicone membrane trial unstabilized natural urine was used as the feed solution. The trial was continued for two days so that sufficient permeant could be collected for analysis. The results for this trial are shown in Table IX. The water permeation rate for this membrane is in the range anticipated for the nonporous diffusive type. Flux measurements during the course of the trial were constant and equal to the permeation rate for pure water which was measured before the trial began. The effect that brine solids content might have on the permeation rate could not be obtained during the two days of the trial.

The water quality was of primary interest, since the nonporous diffusive membrane type has the potential of greater selectivity in solute transport. Little or no improvement in water quality over the fluorocarbon membrane was observed. In fact, total carbon analysis and UV spectra data indicate a greater percentage of the unidentified materials in the product water. This could be the result of the natural chemical composition of the urine. That is, some components of the urine may have a volatility dependent on the pH of the urine feed stream. The transport of these materials through the membrane could have been avoided by a pH adjustment to the urine feed.

Other diffusive membranes could have substantially different transport properties for volatiles in urine. Such properties are totally dependent

TABLE IX

VDR TRIAL USING DIMETHYL SILICONE MEMBRANE  
AND UNSTABILIZED NATURAL URINE

<u>Permeation Rate*</u>	<u>gm/cm<sup>2</sup>-hr</u>	<u>lbs/ft<sup>2</sup>-hr</u>
Water	0.014	0.030
Urine	0.013	0.026

<u>Water Quality</u>	
Color	clear
Odor	strong organic
pH	8.6
Conductivity	15 $\mu$ mho/cm
Total Carbon Analysis	143 ppm
UV Absorption	three distinct peaks at 281, 242 and 218 nm. Absorbance approximately 5 times greater than 30-day trial samples

\* Operation conditions: 60°C, 10 l/min purge gas flow rate. The permeation rate showed no dependence on purge gas flow rate.

on the solubility of these materials in the membrane. Identification of the suspected volatiles would aid in the development of membranes possessing the necessary properties to give better water quality from the VDR process.

Additional VDR trials using the Gore-Tex L-10272 supported fluorocarbon membrane were done using unstabilized natural urine and stabilized natural urine at two pH levels as the feed brine. The results of these experiments are reported in Table X and XI. During these trials the membrane flux which was adjusted to approximately  $0.60 \text{ lbs/ft}^2\text{-hr}$  at the start of the trial did not vary significantly. The effect solids deposition might have on the flux could not be obtained for the limited duration of these trials.

Product water quality from both the unstabilized and stabilized urine trials exceeded that obtained during the 30-day trial. This confirmed the observation that product water quality during the 30-day trial was influenced by brine leakage through deformed membrane areas. And that a considerable improvement in water quality could be expected from the fluorocarbon membrane.

Effluent water quality did not show dramatic differences with stabilized urine or unstabilized urine as feed. The pH of the effluent water responded as expected to the change in brine pH. However, Kjeldahl nitrogen analysis showed that a brine pH near neutral is needed before appreciable ammonia distillation to the product water is observed. Other water quality indicators (total carbon, UV spectra, odor and color) showed no dependence on the brine pH or the presence of chromate ions.

It should be noted that the duration of these trials was not extensive and that water quality properties might vary significantly with the age of the brine and the concentration of the dissolved solids.

TABLE X  
 VDR TRIAL USING GORE-TEX L-10272  
 (SINGLE-BACKED FLUOROCARBON MEMBRANE)  
 UNSTABILIZED NATURAL URINE AT 60°C  
 PURGE GAS FLOW RATE 20 l/min

<u>Time (hrs)</u>	0	3	8	9.5	11
<u>Brine Properties</u>					
viscosity (cs)	0.497	0.498	0.514	--	--
% solids	3.0	3.0	4.2	--	8.0
pH	5.8	5.8	5.7		5.7
% dehydration	0	25	50	68	75
<u>Permeation Rate</u>					
gm/cm <sup>2</sup> -hr	0.32	0.27	0.29	0.28	0.28
lbs/ft <sup>2</sup> -hr	0.64	0.55	0.60	0.56	0.56
<u>Effluent Water Quality</u>					
pH	8.7	8.9	9.1	--	9.0
color	clear	clear	clear	clear	clear
odor	present	present	present	present	present
total carbon	--	14	11	29	20
UV spectra (209 nm)	0.96	0.82	0.76	0.80	0.80
total Kjeldahl nitrogen (ppm as NH <sub>3</sub> )	2.8	1.2	3.6	2.1	--

TABLE XI

VDR TRIAL USING GORE-TEX L-10272 (SINGLE-BACKED FLUOROCARBON MEMBRANE)

STABILIZED NATURAL URINE AT 60°C -- PURGE GAS FLOW RATE 20 l/min

<u>Time (hours)</u>	0	2.5	5	6.8	7.5	7.5	10	12.8
<u>Brine Properties</u>								
viscosity	0.490	--	--	0.536	0.536	0.536	--	0.589
% solids	3.1	--	5.0	--	5.7	5.7	--	10
pH	3.4	3.0*	6.7*	6.7	6.5	3.9*	--	--
% dehydration	--	--	--	35	37	37	74	80
<u>Permeation Rate</u>								
gm/cm <sup>2</sup> -hr	0.29	--	0.25	0.27	0.25	0.27	0.23	0.24
lbs/ft <sup>2</sup> -hr	0.59	--	0.51	0.56	0.51	0.56	0.47	0.49
<u>Effluent Water Quality</u>								
pH	4.6	4.2	9.8	--	9.8	4.9	4.9	4.6
color	clear	clear	clear	--	clear	clear	clear	clear
odor	slight	slight	slight	slight	slight	slight	slight	slight
total carbon	21.8	19.8	12.8	--	--	9.8	14.8	17.8
UV spectra (abs. at 206 nm)	0.62	0.65	0.69	--	--	0.71	0.70	0.70
total Kjeldahl nitrogen as ppm NH <sub>3</sub>	1.5	1.5	7.7	--	--	--	1.7	0.2

\*Adjusted to given pH



## CONCLUSIONS AND RECOMMENDATIONS

This program has demonstrated that a mechanistic approach to the transport of water vapor across semipermeable membranes can lead to improved membrane processes for recovery of water from human urine. A membrane process based upon the convective transport of water vapor across a porous nonwetting membrane can satisfy most of the criteria for VDR application. On the basis of this technology a selected membrane was evaluated for VDR feasibility during an extensive 30-day trial demonstration. Results of this trial indicate that the technology developed has merit and can provide the basic background for future VDR developments.

Results of this program indicate that additional efforts in the following areas are needed:

1. The Gore-Tex fluorocarbon membrane has been shown to have adequate properties for VDR applications. The quality of product water from VDR applications appears to be good. However, more detailed analysis on product water quality is needed. This will require additional VDR trials where water quality is analyzed as a function of operating conditions and various urine brine properties.

In addition, studies of permeation rate as a function of brine properties should be continued. Programs to minimize solids depositions on the membrane surface should be investigated. Control of brine pH, liquid flow dynamics, and brine management should be evaluated as means to mitigate the solids deposition problems.

2. The investigation of stabilized versus unstabilized urine needs additional study. This study indicates that the merits of chromic acid stabilization are doubtful. Control of product water ammonia through the use of chromic acid solution alone has not been demonstrated. Perhaps other methods to remove ammonia from product water or to block its formation in the urine should be investigated.
3. In this program use of a nonporous diffusive membrane for VDR application has not shown marked improvements in product water quality over other membrane types. Because transport of solutes is directly related to their solubility in these membranes, the potential exists for development of a membrane with the selectivity necessary for

VDR application. Ultrathin membranes recently developed for reverse osmosis applications enable greatly enhanced fluxes. This technology offers the possibility of obtaining both required fluxes and membrane selectivity needed for high quality and product water.

## APPENDIX 1

The Gore-Tex S-10109 membrane was evaluated for its ability to retain bacteria. Two bacterium species were tested.

1. Escherichia Coli, a rod shaped bacterium with dimensions of about 0.5 by 1.0 to 3.0 microns.
2. An unidentified spherical bacterium specie with about a 1.0 micron diameter. While the bacteria was not classified according to its specific class it did provide a good marker species for study and will be referred to as bacterium X.

The experiments were conducted by first treating the disassembled cell and membrane with a 2% formaldehyde solution for at least one hour. All units were washed with several rinses of sterile water and the permeation cell containing the Gore-Tex membrane was assembled employing sterile conditions. After assembling, the cell was given a one-hour wash with absolute ethyl alcohol followed with additional sterile water rinses. The system was checked for bacteria by performing a permeation run for fifteen minutes with sterile water. The gas stream employed in all tests was nitrogen which had been filtered through a tenth micron filter. After the permeation run the gas side of the membrane was washed with sterile water, and the wash water analyzed for bacteria. No evidence of bacterial contamination could be found employing these procedures.

Subsequent to the sterile water test, the same procedure was repeated for a pre-sterile phosphate buffer solution seeded with either E. Coli or bacterium X. The results shown below show that no bacterial colonies were observed from samples taken from the water recovery side of the membrane and confirm that this membrane is not permeable to these bacteria.

PERMEABILITY OF GORE-TEX S-10109 MEMBRANE TO ESCHERICHIA COLI  
AND BACTERIUM X

Run	Sample	Time (mins)	Total Coliform Counts	Other Bacterial Colonies
Sterilization Preparation	Feed Water Sample	0	0	0
	Wash samples from the device liquid side	0	0	0
	Gas side	0	0	0
	Gas side	15	0	0
E. Coli	Feed sample (1)	0	$2.3 \times 10^7/500$ ml	$1.2 \times 10^8/500$ ml
	Gas side	15	0	0
Bacterium X	Feed sample	0	Total colonies (2) $1.3 \times 10^6/500$ ml	
	Gas side	15	0	

1. Feed samples were prepared with a 7.2 pH phosphate buffer seeded with the appropriate bacteria.
2. No specific identifications were made.

These are in agreement with the solute transport experiments where it was found that no urea permeated the membrane in pervaporation trials.

## APPENDIX II

### CHROMIC ACID STABILIZATION OF URINE

Chromic acid stabilization was initially developed for recovery of water from urine by distillation techniques. It was designed to be operated at low temperatures (below 150°F). It was not designed for membrane vapor permeation systems where solution contact with a membrane is necessary. Because there are differences between straight distillation and evaporative distillation across a membrane barrier, a better understanding of the urine stabilization process was needed. A study of natural and synthetic urine was performed to define: (1) the decomposition rate of urea, (2) the decomposition mechanism of urea, and (3) the difference between the decomposition of a chromic acid stabilized system and the decomposition of an unstabilized system.

Natural and synthetic urine decomposition rates were determined both with and without chromic acid stabilizer. The synthetic urine solutions were prepared as previously described. Natural urine samples were collected from multiple donors in an 8-hour period prior to initiation of the test. Duplicate samples of each solution were placed in a constant temperature bath at 160°F. Each sample was fitted with a condenser to minimize water loss. The solutions were continuously swept with a very low flow rate of wet nitrogen. The gas effluent containing the entrained CO<sub>2</sub> generated during the decomposition was passed through the condenser and trapped at the outlet in a small volume of NaOH. Trace amounts of carbon 14-labeled urea were added to each solution. The change in urea concentration in the urine solutions and the amount of CO<sub>2</sub> generated were monitored by normal radiotracer techniques. This analysis of both the remaining urea and the gas effluent provided the necessary mass balance check to assure reliability of the data.

The results are shown in Figures 1 and 2. The synthetic urine solution decomposition should reflect the chemical stability of the system at the test temperature. The natural urine could decompose both chemically (thermal decomposition) and by attack of enzymes produced by bacteria. It was found that the decomposition of the natural and synthetic solutions were similar. The synthetic urine decomposition rate was found to be linear when plotted as a semilog function of the urea concentration, indicating pseudo first order decomposition kinetics. The natural urine solutions followed the same pattern

after 30 or 40 hours of reaction. The deviation in the initial test period may be due to decomposition of the urea by enzyme producing bacteria that are not destroyed immediately on exposure to the chromic acid system. After the first 50 hours of exposure the decomposition rate of the natural urine is slightly less than that of the synthetic urine. At this time we can only speculate on the reason for this difference. It could be related, however, to the buffer capacity of the two systems. The slowest rate of urea decomposition was found in the unstabilized urine. This may be due to differences in the pH and/or percentage of ammonia present in the test samples.

At the temperature used in these experiments (160°F) the hexavalent chromium does not appear to be necessary to stop bacterial action. The acid may serve a useful function in binding the ammonia generated. The combination of the hexavalent chromium and sulfuric acid provide a highly acid oxidizing environment which accelerates the decomposition of organic material present in the source solution and also attacks the membrane and device.

It was not possible, in this limited study, to elucidate fully the decomposition that occurs in a continuous water recovery system. If it is correct that bacterial and/or enzymatic activity are not immediately stopped on contact with the chromic acid system, then in a continuous extractive system, where fresh urine is added routinely, urea would be decomposed both chemically and biologically. The concentration of solids that occurs in the continuous system may also effect the kinetics. The data indicate that the highly oxidizing acid system employed for solution stabilization is not necessary in a recovery system operated at 160°F. If it is desirable to bind ammonia as it is generated in the solution, it may be advantageous to seek methods other than a straight acid addition to remove the ammonia.

Figure I

Thermal Decomposition of Stabilized Urine

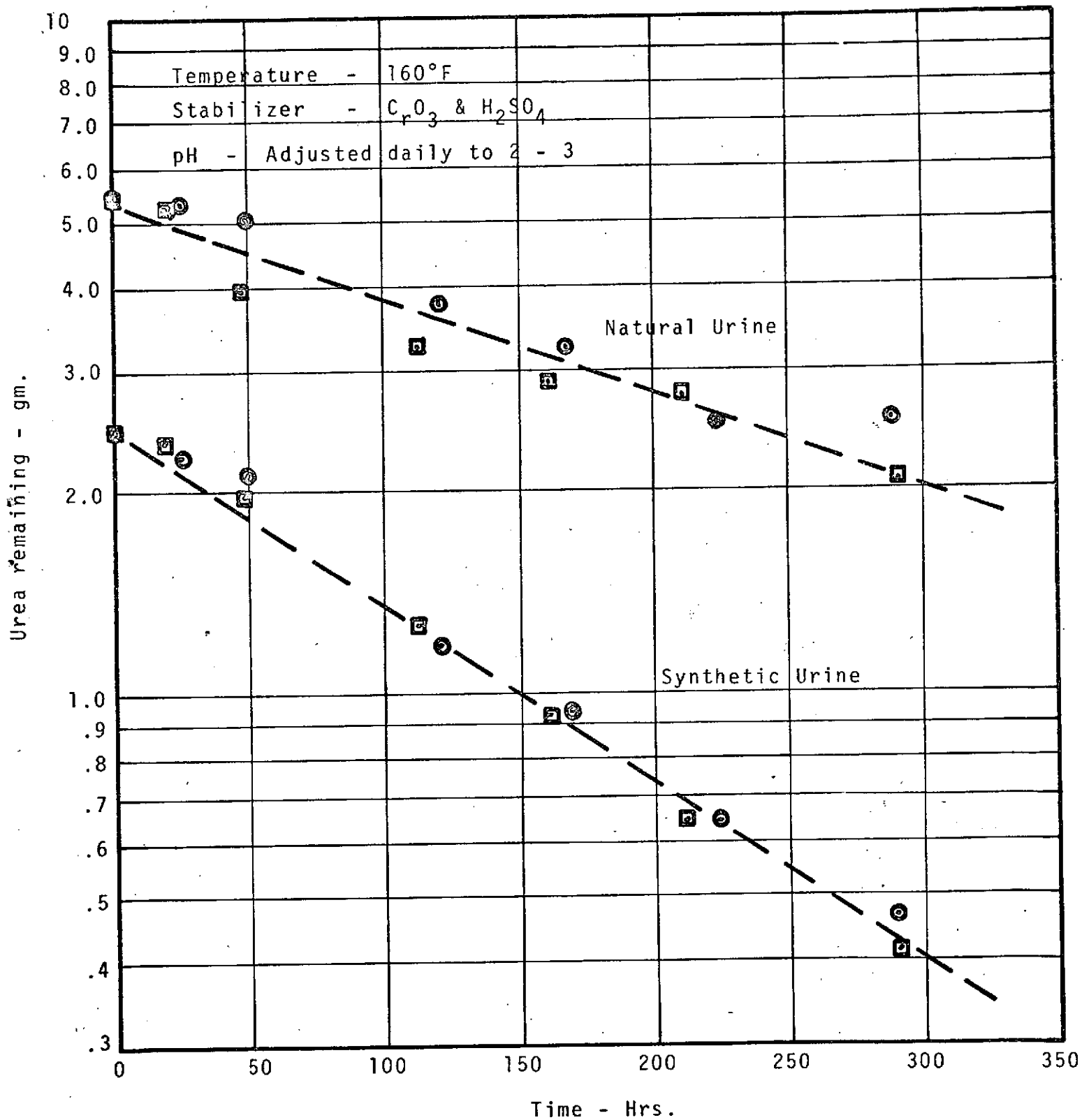
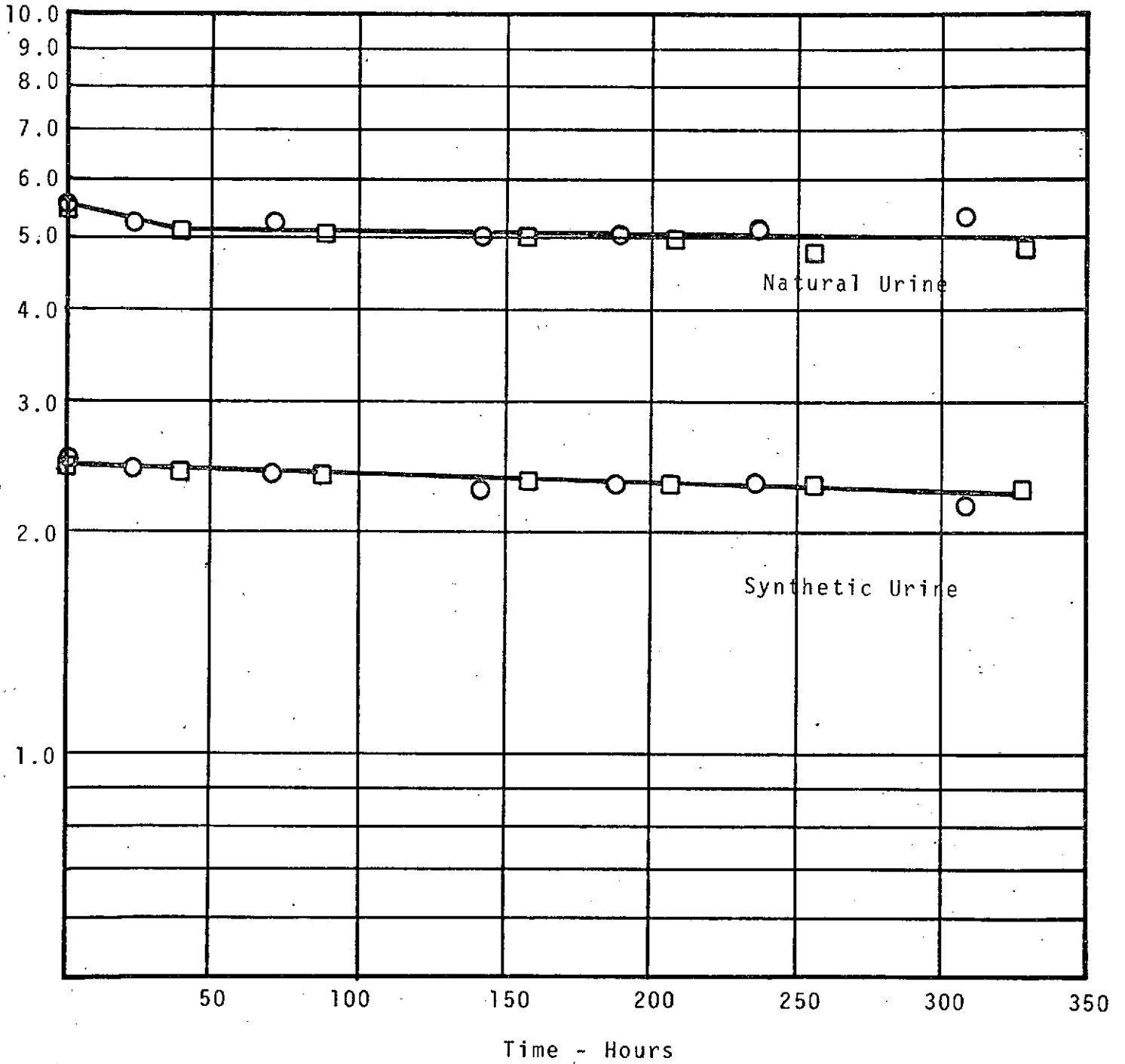


Figure 2

Thermal Decomposition of Unstabilized Urine at 160°F.





## REFERENCES

1. Kolnsberg, H.J., et al., *Design and Fabrication of a Flight Concept Prototype Vapor Diffusion Water Reclamation System*, NASA Contractor's Report No. 111932, (1971).
2. Warner, A.W., Brown, D.L. and Glass, W., *Recovery of Potable Water From Urine by Membrane Permeation*, Clearinghouse for Federal Scientific and Technical Information Accession No. AD607759, (September 1964).
3. Putnam, D.F., et al., *Chemical Aspects of Urine Distillation*, ASME Paper No. 65-AV-24. The American Society of Mechanical Engineers, New York, New York, (January 1965).
4. Klein, E., Smith, J.K. and Holland, F.F., *Membrane and Material Evaluation; Cuprophane 150-PM Artificial Kidney Reference Membrane - Evaluation and Experimental Procedures*, Annual Report AK-2-72-2221, (1974).
5. National Academy of Sciences - National Research Council, Committee on Toxicology, *Report of the Panel on Potable Water Quality in Manned Spacecraft*, (August 1972).