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DEVELOPMENT OF AN IMPROVED MEMBRANE FOR A
VAPOR DIFFUSION WATER RECOVERY PROCESS

by

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SUMMARY

This final report covers work done by Amicon Corporation over a nine-month period on the improvement of membrane performance for the VDR process for recovery of potable water from urine on manned space missions. Kynar, Teflon, PVC, and polysulfone candidate membranes were evaluated from chemical, thermal, mechanical, and fabricating standpoints to determine their suitability for operation in the VDR pervaporation module. Pervaporation rates and other performance characteristics were determined in a breadboard pervaporator test rig. Kynar and Teflon membranes were demonstrated to be chemically stable at pervaporation temperatures in urine pretreated with the chromic acid bactericide recommended by Hamilton Standard in previous VDR work.

A modified flat-sheet pervaporator module was shown to eliminate major design flaws in the Hamilton Standard pervaporator module design. Pervaporator rates up to six times the target of 0.5 lbs./hr. ft.² specified in the RFP were obtained in tests using this improved module. Urine which had been pretreated with chromic acid was pervaporated through a Kynar 451 flat sheet membrane in an eleven-day test. Solids deposition on the membrane reduced the flux significantly over the course of the run; a water flush during the seventh day after a dump of the residual urine solids partially restored the flux but was not extensive enough to remove all the solids. Despite this reduction in flux, the average pervaporation rate over the course of the run was 1.3 lbs./hr. ft.² which is nearly twice the highest pervaporation rate (0.7 lbs./hr. ft.²) reported by Hamilton Standard in their long duration runs and significantly greater than the average flux reported by Hamilton Standard.

Improved pervaporation should result from reengineering of the flat sheet pervaporation module so as to decrease the tendency for solids deposition through use of gas recirculation to reduce the cooling effect of the gas and through use of a tighter membrane.

A pervaporation module with hollow fiber membranes was tested and shown to be suitable for VDR application and to offer the following significant advantages over the flat sheet configuration: compactness, low weight, relative insensitivity to fluid pressure balancing between the urine and sweep gas streams, and simplification of fluid seals and headers.

The chromic acid pretreatment, while effective as a bactericide, was shown to have several drawbacks:

1. it is corrosive and restricts membrane selection although both Kynar and Teflon are essentially inert to it;
2. it does not eliminate the appearance of ammonia from the pervaporate; and
3. it results in solids precipitation which deposits on the membrane. This solids deposition tended to clog the pores and thus reduce the pervaporation rate in the microporous, isotropic Teflon membrane but did not affect pervaporation with Kynar membranes significantly.

Operation at pasteurization or sterilization temperatures without chemical pretreatment proposed by Dr. Malich, NASA Ames monitor for this program, appears feasible, would reduce solids precipitation, permit use of polysulfone hollow fibers, and provide a higher water vapor driving force. Initial operation at pasteurization temperature with a tight polysulfone hollow fiber membrane without pretreatment indicates high recovery and long membrane life should be attainable with occasional water backflushes to remove deposited solids. Operation with a more open flat sheet membrane resulted in solids deposition of a more gummy, clogging nature which were more difficult to remove by water backflush. Further work in this area is indicated. Both Amicon tests and literature^(1,4) indicate either a bactericide or sterilization temperature operation will be required to prevent bacterial growth.

Principal recommendations deriving from the program are:

1. The separation of the pervaporator and condenser modules and the use of a recirculating sweep gas to conduct pervaporate to the condenser.
2. The selection of the hollow fiber membrane configuration for pervaporator module design;
3. The evaluation of polysulfone hollow fiber membranes at pasteurization or sterilization temperatures without bactericide-chemical pretreatment of the urine. Operation in the present program of these membranes in hollow fiber form at 50°C and 70°C gave encouraging results.

Polysulfone hollow fiber membranes are a commercial Amicon product and require minor modification to yield desired pervaporation rates.

4. Should unforeseen problems develop with operation at pasteurization or sterilization temperatures without pretreatment, the evaluation of Kynar 451 hollow fiber membranes and operation at 70°C with chromic acid pretreatment of urine. Kynar 451 is a high molecular weight, chemically inert, and mechanically strong resin which can be made in hollow fiber, anisotropic membrane form; and
5. The preliminary evaluation of treatment steps required for final pervaporate polishing.

I. INTRODUCTION

The vapor diffusion process (VDR) is intended for the recovery of potable water from urine on manned space missions of extended duration and utilizes a semi-permeable membrane to separate pure water vapor from the urine in a phase-change process. The feasibility of the VDR process has been demonstrated on a full-scale subsystem level in a previous NASA program by Hamilton-Standard using Amicon membranes. The hardware configuration employed by Hamilton-Standard is, however, marginal in performance and requires longer-lived, tighter and stronger membranes to meet flight standards.

Amicon was awarded Contract No. NAS 2-7649 to study improved vapor diffusion membranes and improved module configurations for the VDR process.

Analysis by Amicon had shown that the following aspects of the Hamilton-Standard design account, in part, for the problems encountered in that program and for the marginal membrane performance.

1. The liquid pressure on the inner skin side of the membrane is significantly lower at the liquid outlet to the evaporator module than at the liquid inlet. The wash water wastes undergo a significant pressure drop as they flow through a serpentine path of channels, up one channel and down the next (Figure 1).
2. Stabilization gas exerts a constant pressure on the outer membrane surface. The gas pressure outside the membrane must, therefore, differ

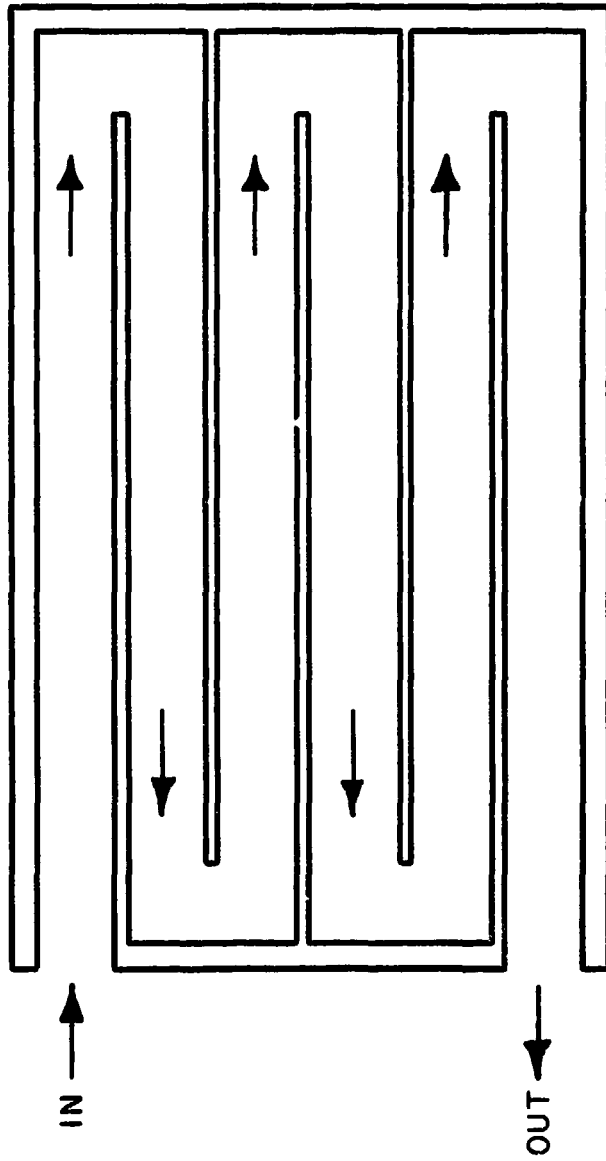


FIGURE 1

HAMILTON STANDARD MODULE

significantly from the liquid pressure inside the membrane over some region of the membrane.

3. The membrane is only spot bonded to the ribs separating the channels.
4. The hot membrane surface is separated by only a small gap from a cool condenser surface.

A. Analysis of Hamilton Standard VDR Module Design

1. Reverse Stabilization Gas Permeation

Because of the limited bonding of the membrane to the channel ribs, a liquid pressure not much greater than the stabilization gas pressure will break these bonds and cause the membrane to bow out, decreasing and possibly eliminating the necessary gap between the membrane and the porous metal condensing surface. The use of a pressurized liquid system with the Hamilton Standard design where a liquid outlet pressure is equal to or greater than the gas pressure is, therefore, not feasible since the liquid inlet pressure would then be great enough to break the membrane rib bonds and eliminate the gap between the membrane and the condensing surface.

With a fiberglass screen backing for the membrane, Hamilton-Standard was able to operate with an inlet liquid pressure exceeding the stabilization gas pressure and an outlet liquid pressure lower than the stabilization gas pressure. The pressure difference between gas and liquid at the liquid

inlet was large enough, however, that the membrane rib bonds broke in this region and the membrane bowed out, and the pressure difference at the liquid outlet was large enough that reverse permeation of the stabilization gas into the waste water side of the module occurred in this region. This permeation necessitated arrangements for separation of gas and liquid in the liquid loop and required the use of special liquid pumps which were resistant to vapor binding. A tighter membrane would decrease and, hopefully, eliminate the reverse gas permeation and simplify loop design.

2. Membrane and Module Life

The nature of the Hamilton Standard design makes likely solids deposition on the membrane surface and near the waste liquid outlet from the evaporator module. The membrane surface and the wash water concentrate circulating past it are cooled by the following three processes:

- (1) evaporation of liquid from the membrane surface;
- (2) heat conduction across the narrow gas gap separating the membrane surface from the condenser surface; and
- (3) radiation from the membrane surface to the condenser surface.

A simple analysis indicates that each of these mechanisms contributes about equally to heat loss from the circulating wash water concentrate.

Because of this heat loss, temperatures at the membrane surface will be somewhat lower than in the bulk liquid flowing past the membrane; at the same time, because of the water pervaporation, solids concentrations at the membrane surface will be somewhat higher than in the bulk liquid. Both the higher solids concentration and lower temperature will cause precipitation to occur first at the membrane surface. Similarly, since temperatures are lowest at the evaporator module outlet, solids deposition is most likely in this region.

Solids deposition on the membrane decreases its permeability to vapor and reduces the rate of vapor transmission through it.

Solids deposition near the outlet increases the flow resistance and reduces the flow rate of water waste past the membrane. This increases the temperature drop in the wash water waste, lowers the outlet temperature of the outlet liquid and fosters still greater solids deposition in this region. Thus, once solids deposition starts on the membrane or in the outlet, it will continue at an accelerated rate. The Hamilton Standard design is, in essence, a positive feedback system, inherently unstable to solids deposition.

Amicon's approach to improved membranes and VDR module was the following.

B. Membrane Selection

Requisite properties of candidate membrane materials include:

1. hydrophobicity to prevent liquid phase permeation. This requires a proper combination of low wetting and small pore size.
2. chemical resistance to urine and to the chromic acid solution added to the urine as a bactericide. This resistance is required at pervaporation temperatures ($\sim 70^{\circ}\text{C}$) for long periods and over concentrations ranging from normal urine to a solution from which 95% of the water has been pervaporated. An alternative suggested by Dr. Malich during the course of the program is operation at sterilization temperatures without a bactericide. In this case, the membrane must withstand sterilization temperatures ($\sim 100^{\circ}\text{C}$).
3. a water vapor transport capability on the order of 0.5 pounds/hour ft.² of membrane area.
4. sufficient strength and a high enough modulus to enable module design with practical dimensions and transmembrane pressure ranges; and
5. adequate membrane life.

Amicon selected the following materials as promising candidates from which to make membranes:

1. polyvinyl chloride. This material was selected by Hamilton Standard after trials of several others. A reevaluation of it appeared in order for the following reasons:
 - a. The hardware configurations studied by Hamilton Standard placed unnecessarily difficult requirements on the membrane to achieve operating goals; and
 - b. A more hydrophobic PVC is available than was used to make the Hamilton Standard membranes. Bulk polymerized PVC is free of dispersants whereas the material utilized to make the Hamilton Standard membranes was suspension polymerized and had a small residual concentration of aqueous dispersants and stabilizers.

2. microporous teflon. Teflon does not have a high enough solubility in appropriate solvents to make production of anisotropic membranes from it achievable with present technology. It is, however, available in an isotropic microporous thin sheet made by another process by Chemplast, Inc. of Wayne, New Jersey, and in thin sheet and hollow fiber form from Gore Associates of Newark, New Jersey, and Flagstaff, Arizona. Teflon's chemical inertness, hydrophobicity, and heat resistance make it ideally suited for the VDR process; and it may, therefore, be interesting to test even though it cannot be made in anisotropic membrane form. The Chemplast

microporous material (Zitex) can handle all corrosive liquids at temperatures as high as 500°F and down to the cryogenic range. Tensiles of 200 psi to 400 psi can be obtained depending on thickness and pore size. Zitex is available with pore size ranges of from 1 to 2 microns, from 2 to 5 microns, and so on up to 60 microns.

The Gore Associates thin sheets are available with pore sizes of from 0.2 to 5 microns and their hollow fibers are available with pores of 5 micron size and larger. The fine pore sheets can be coiled and seamed into fibers if that level of sophistication is warranted. The Gore hollow fibers are already used for gas removal from hot, corrosive, photographic solutions. Amicon developed the potting and housing system for the Gore fibers for this particular application.

Although the pores in microporous Teflon are orders of magnitude larger than those in most Amicon membranes, the microporous Teflon material is worth considering for the VDR process since two micron pores require a pressure differential of 21 psi to force room temperature water into them.

3. polyvinylidene fluoride. Fluorocarbon materials are, in general, highly hydrophobic and chemically very inert and as a result are excellent candidates for use in the VDR process. One fluorocarbon material from which Amicon has made membranes is polyvinylidene

fluoride (Pennsalt's Kynar). This high melting (340°F) crystalline polymer offers high tensile strength (7,000 psi in dense sheet form), low water adsorption (0.04%) and hence, high hydrophobicity, little degradation in 95% sulfuric acid for 30 days at 122°F, and 75,000 cycles of flex life.

4. polyvinyl fluoride. This was another fluorocarbon material felt to be of interest because of its relatively high strength due to relatively high MW. It is somewhat less inert chemically than Kynar because of the presence of both H and F atoms on a single carbon in Tedlar; it also has a slightly lower melting point and is less soluble because of its higher MW.

Amicon proposed to separate the pervaporation and condensation modules and use a sweep gas to convey water vapor between the two and proposed to study both flat sheet and hollow fiber membrane pervaporation modules. The module designs proposed for study are described in the following sections.

C. Improved VDR Module Design

1. Modified Hamilton Standard Design

Key problems with the Hamilton Standard module design are: (a) solids deposition on the membrane surface and within the evaporator module liquid loop; and (b) reverse gas permeation. These can be eliminated or at least considerably alleviated if the module is redesigned to incorporate the following features (Figures 2 and 3):

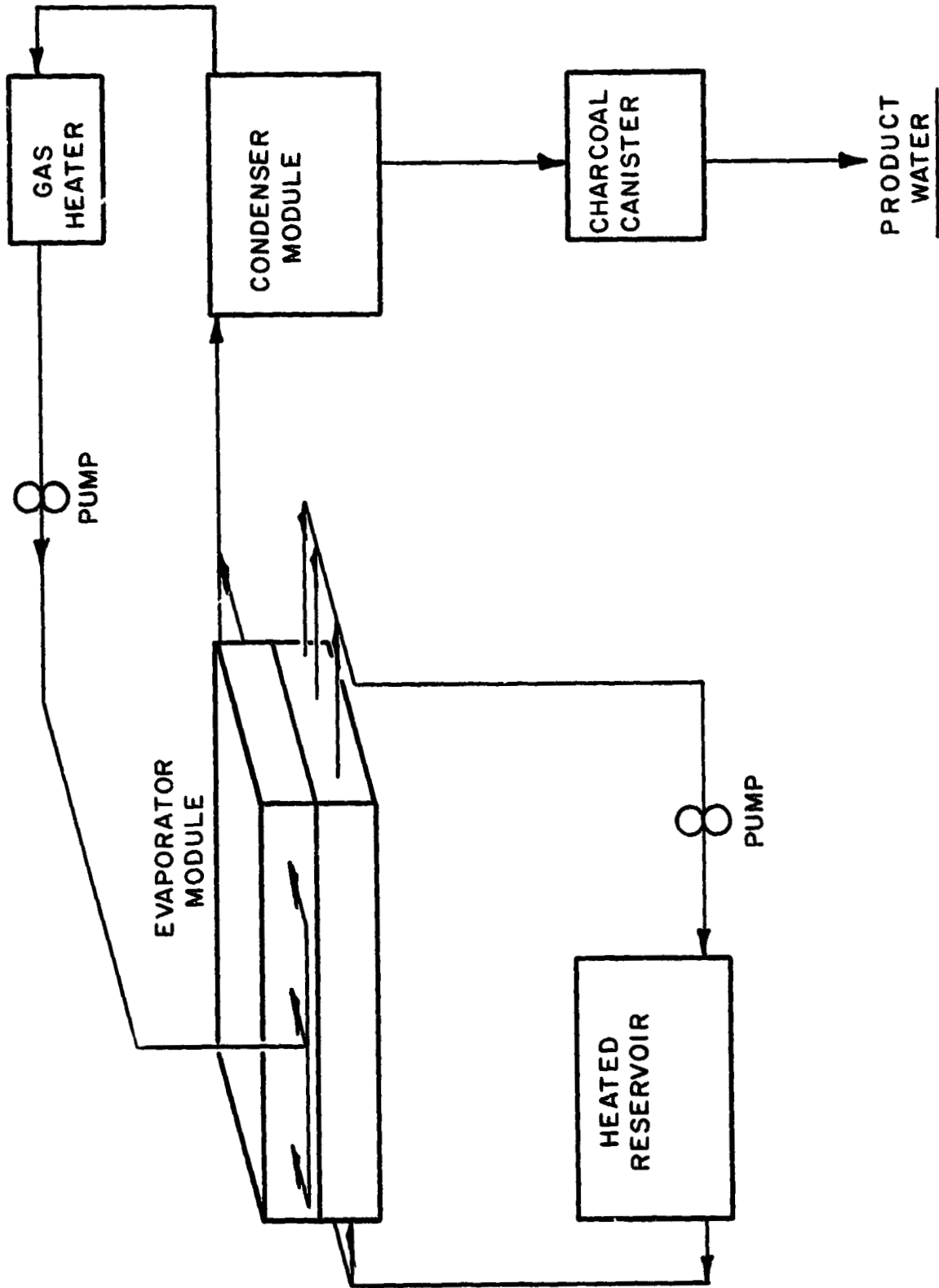


FIGURE 2
MODIFIED FLOW SCHEMATIC

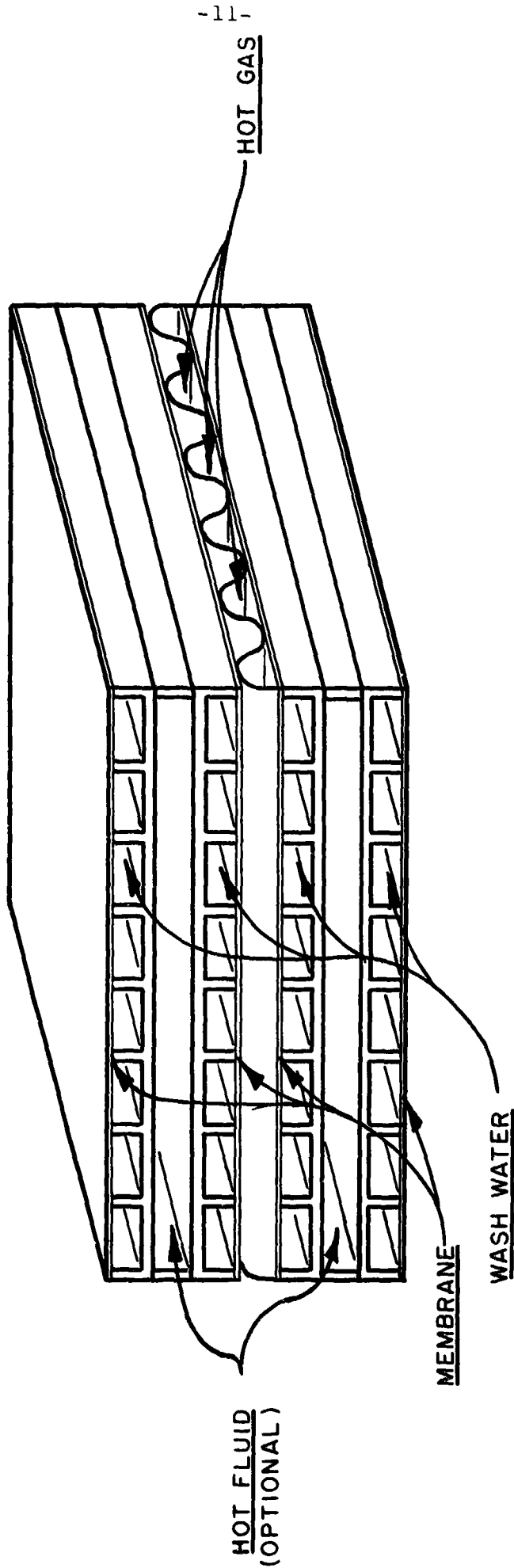


FIGURE 3
MODIFIED FLAT SHEET EVAPORATOR MODULE

- a. Placement of the evaporator and condenser in separate modules to eliminate conductive and radiative cooling of the wash water.
- b. Use of a sweep gas to transport the pervaporated water vapor from the evaporator module to the condenser module.
- c. Crossflow of wash water and sweep gas in the evaporator module.
- d. Wash water flow through channels in parallel instead of in series to reduce wash water pressure drop.
- e. Increase in wash water circulation rate through the evaporator module to reduce wash water cooling due to pervaporation.
- f. Utilization of a crimped stainless or plastic spacer to hold the membrane against the wash water flow channels and to ensure uniform flow of sweep gas past the membrane surface.

This modified evaporator module design was also utilized as the basis for a test fixture for testing flat sheet membranes in this program.

The advantages of this modification are:

- a. The cooling of the wash water by conduction and radiation to the cool condenser surface is

eliminated. The cooling of the wash water due to pervaporation is reduced because of the increase in liquid circulation rate.

- b. The reverse gas permeation is eliminated because the wash water pressure drop is significantly reduced and the pressure difference between the gas and liquid sides of the membrane can, therefore, be kept small over the entire membrane surface.

- c. The pervaporation rate is increased significantly because: (1) solids deposition on the membrane is decreased and the membrane resistance to pervaporation transfer is consequently decreased; (2) the use of a sweep gas sharply reduces the gas side resistance to pervaporation transfer; and (3) the wash water vapor pressure remains high because the wash water temperature drop in the evaporator module is no longer large. The driving force for pervaporation transfer is, therefore, maintained high over the entire membrane surface.

The pervaporative cooling of the wash water can be completely offset by flowing hot water between adjacent sets of wash water flow channels (or between gas flow channels) as shown schematically in Figure 3. A system incorporating this feature would be a stable one relative to solids deposition and would exhibit

"negative feedback". Solids deposition on the membrane surface would decrease pervaporation rates and would, therefore, decrease the cooling of the wash water. The wash water would rise in temperature since the hot water heating now would temporarily exceed the pervaporative cooling. The solubility of the solids would increase and the solids would redissolve.

With heating of the wash water in the evaporator module, the heater in the wash water stream external to the evaporator could be eliminated. It may, however, be desirable to keep it in the loop, both to heat the wash water at startup and to maintain the wash water at operating temperature whenever fresh wash water additions are made to the loop.

A gas pump, gas heater, and a separate condenser module have been added to the system, the phase separator in the liquid loop has been eliminated, and the pump in the wash water system has been replaced by one with larger capacity but lower head capability and without the requirement that it be able to handle two-phase flow. The overall system weight, volume, and power requirements will hopefully be reduced from those for the Hamilton Standard module because of the improvement in performance of the evaporator module. The system life and reliability will clearly be greater with the redesign.

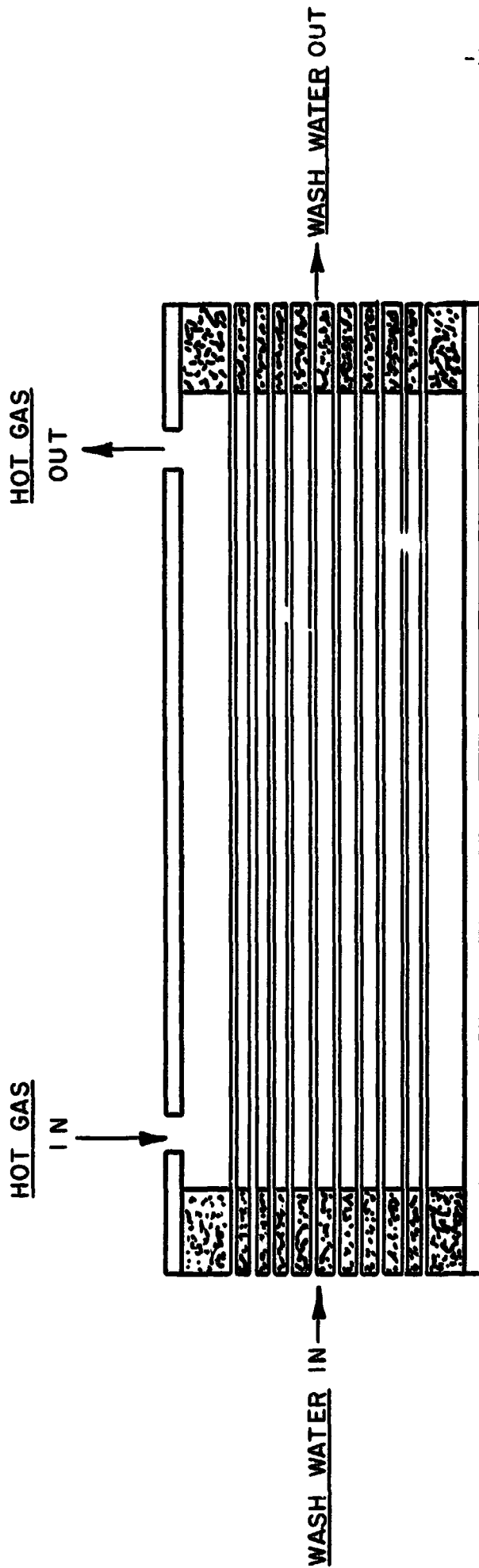
2. Hollow Fiber Module Design

Another alternative would be to use pervaporation membrane in hollow fiber form with liquid flow inside internally-skinned hollow fibers and water vapor permeating through the skin and being carried to a condenser module by a sweep gas flowing past the outside of the fibers (Figures 4).

Amicon's hollow fiber membranes are anisotropic in structure for high permeability and tubular in configuration for compactness. They may be prepared from a variety of materials and with a wide range of diameters, lengths, burst strengths, and porosities. Bundles of fibers, potted in epoxy and cut to expose the fiber ends, are placed in a suitable housing to form a module. Paints, cheese whey, sewage, sea water, blood, chrome plating wastes, and fermented by-products are examples of streams which have been processed in hollow fiber modules without difficulty.

Potential advantages deriving from the use of hollow fibers in the VDR evaporator module are:

- a. The large surface area per unit volume characteristic of hollow fiber modules permit the evaporator module to be small, compact, and light weight. A hollow fiber with the same flow area as a square channel will have four times the membrane area. Membrane surface area per unit volume is inversely proportional to hollow fiber diameter. The optimum hollow fiber diameter is apt to be smaller than that for a channel,



HOLLOW FIBER EVAPORATOR MODULE

FIG. 4

both because small fibers are easy to fabricate and because channels are more susceptible to solids deposition because of the low shear in edge regions.

- b. Operation with a pressurized liquid loop will be possible, eliminating the problem of reverse gas permeation and the requirements for a phase separator in the liquid loop and for special non-vapor binding pumps.
- c. The requirement for a membrane backup support would be eliminated.
- d. The problem of bonding the membrane to channel ribs would be eliminated.
- e. Problems due to different shrinkage of membrane and housing and support structure would also be eliminated.
- f. The hollow fiber flow geometry leads to a uniform high shear at the membrane-liquid interface. Since, for laminar flow, shear increases linearly with decrease in diameter, the smaller diameter practicable with hollow fibers will lead to a higher shear than obtained in the Hamilton Standard channels. This high shear minimizes radial temperature and concentration gradients in the liquid and reduces the likelihood of solids deposition on the membrane.

- g. Although it is not believed necessary, the hollow fibers can readily be made with an outer as well as an inner skin for greater strength and resistance to liquid and/or reverse gas permeation.

The number of fibers, their diameter and length, and the liquid and gas flows should, of course, be chosen to make the temperature drop of the liquid in traversing the evaporator module small so as to make solids deposition unlikely. Initial calculations indicate it should be simple with reasonable geometries and flows to keep the temperature drop to a fraction of a degree.

II. MEMBRANE SCREENING TESTS

A. Experimental Procedure and Results

1. Membrane Preparation

Suitable solvent systems for use in membrane preparation were determined for the candidate materials listed in Table I. Over the course of the program, no adequate solvent was found for the polyvinyl fluoride (Tedlar) which is at least partially attributable to the extremely high molecular weight of the available resin. All polymer/solvent systems require the use of water miscible solvents in order to form the anisotropic type membrane structure.

a. Preparation of flat sheet candidates

All materials, except the Teflons, were dissolved in the most suitable solvent system and cast onto glass plates using a drawdown bar. Since the solvents evaluated were not volatile, no evaporation step was incorporated prior to quenching. In all cases, except with PVC-P, a room temperature tap water quench bath was utilized. Following an overnight leaching with fresh tap water, the membranes were air dried. Some were annealed at test conditions (70°C) to pretreat the membrane for urine exposure. All membranes were capable of being dried prior to use.

Shrinkage and pinholes were the only problems experienced in flat sheet preparation. Kynar membranes shrink severely upon quenching, but remain unchanged through heat treatment. PVC changes very little on precipitation but shrinks

TABLE 1
POLYMER PROPERTIES

Polymer	Structural Properties			Thermal Properties				Moisture Properties			Trade Name
	Formula	M.W.	Specific Gravity	Melting Point °C (T _m)	Degradation Temperature °C	Tg °C	Safe Work Temp. °C	Surface Tension	WVTR		
Polytetrafluoroethylene	-{CF ₂ -CF ₂ }-	100	2.20	327	500	-113	275	18.5	5	Teflon	
Polyvinylidene fluoride	-{CH ₂ -CF ₂ }-	64	1.76	178	125	-17	135	25	1	Kynar	
Polyvinyl-fluoride	-{CHF-CH ₂ }-	46	1.40	210	355	41	93	28	46	Tedlar [®]	
Polyethylene	-{CH ₂ -CH ₂ }-	28	0.97	135	300	-125	107	31	21	--	
Polyvinyl chloride	-{CHCl-CH ₂ }-	63	1.40	125 to 310	>100	83	87	39	32	Geon	
Polyvinylidene chloride	-{CH ₂ -CCl ₂ }-	97	1.72	202	125	-17	79	40	1.5	Saran	
Polychlorotrifluoroethylene	-{CClF-CF ₂ }-	117	1.85	218	285	45	185	5.1	4.8	Kel-F	

as the membrane is annealed. To produce flat sheet material large enough to fill the pervaporation cavity in the test module, large continuous pinhole-free membranes are needed. Pinholes in the flat sheets were eventually almost completely eliminated by very carefully controlled casting procedures.

2. Soak Tests

Disks of each material were dinked out of the larger sheets and evaluated by the following tests--chemical stability, temperature stability, mechanical property determination, water vapor transmission, liquid water flux, and ease of fabrication. For chemical stability evaluation each specimen was soaked in a urine/chromic acid solution prepared as per the recipe in NASA Report No. CR-1802 on "Composition and Concentrative Properties of Human Urine" and listed in Table 2. Eighty day, thirty day, and twelve day soak tests were conducted.

a. 80-Day Soak Test

One set of relatively thick membranes was soaked at 70°C in the chromic acid/urine solution for 80 days. Results are reported in Table 3. At regular intervals during the soak cycle, membranes were removed, blotted, weighed, and liquid water flux through the membrane determined using distilled water and a 100 psig transmembrane pressure difference. The water flux data should not be taken as a measure of membrane hydrophobicity

TABLE 2

NASA Contract No. CR-1802

RECIPE FOR URINE/CHROMIC ACID PRETREATMENT

H_2SO_4	=	2.57 gm	}	per liter of urine
CrO_3	=	0.63 gm		
H_2O	=	2.56 gm		

TABLE 3

EQUILIBRIUM VALUES OF 80-DAY SOAK TESTS
Dilute Chromic Acid/Urine Solution at 70°C

Membrane	Dry Initial Weight	Wet Weight After 1 Day Soak	Wet Weight After 80 Days	Water Flux (ml/min) @ 100 psi			Membrane Thickness	Discoloration	% Decrease in Diameter	
				Days						
				26	43	57				80
Goretex	0.0875	0.0845	.1100	1.7 ^a	1.4 ^a	2.6 ^a	11	2.7	Light	0
Zitex 223/5	0.2241	0.2247	.2591	2.3	5.3	1.6	1.1	4.5	Heavy	0
Zitex 223	0.3308	0.3358	.3968	2.4	0.37	0.32	0.14	7.3	Moderate	0
Kynar 201	0.5352	0.4885	.4961	0.38	0.32	0.13	0.18	11.4	Severe	0
Kynar 201	0.2781	0.3723	.2555	0.05	0.03	0.02	0.02	5.2	Heavy	0
Kynar 201*		0.2532	.3082	0.07	0.05	0.02	0.03	6.8	Moderate	0
Kynar 201*		0.3229	.3774	0.38	0.09	0.39	0.11	8.5	Heavy	0
Kynar 451	0.3620	0.3195	.3321	--	--	--	--	7.3	Severe	15
Kynar 451*	0.2741	---	.3435	0.003	0.005	0.003	0.008	6.9	Moderate	0
PVC-B	0.4427	0.4458	.3309	0.001	0.003	0.008	0.03	10.8	Light	8
PVC-B	0.6720	0.6207	.4600	0.002	0.004	0.001	0.003	16.1	Light	15

* Heat treated 1/2 hour at 100°C in distilled water

^a measured with a 50 psi transmembrane pressure drop.

since the membranes were soaked in water prior to the flux determination. All flux, weight and color changes appeared to come to equilibrium after the first 30-day period.

b. 30-Day Soak Test

A group of thin membranes was soaked in dilute chromic acid/urine solution at 80°C for 30 days. These results are presented in Table 4. A similar group of thin membranes was soaked at 80°C for 30 days in a concentrated chromic acid/urine solution prepared by evaporating 95% of the water from the solution. These results are also presented in Table 4. Again at regular intervals, membranes were removed, blotted, weighed, and liquid water flux through the membrane determined using distilled water and a 100 psig transmembrane pressure difference.

The PVC membranes could not be flux tested after soaking due to shrinkage beyond the ultrafiltration cell sealing limits. Mechanical and water vapor transmission properties were determined before and after soaking as described below:

(1) Mechanical property measurement

Pieces of membrane were evaluated before and after urine/acid soaking at 80°C for tensile changes. Tensile and tear strengths were determined at room temperature on an Instron Tensile Tester at 100% elongation per minute. For tear, 1" wide strips were

TABLE 4
30-DAY SOAK TEST

Dilute Chromic Acid/Urine Solution at 80°C

Sample	Thick- ness (mil)	Weight (blotted wet) (gm)		Water Flux @ 100 psi (ml/min)		WVTR (gm/mil cm ² /hr)		Tear (lb in)	Tensile (lb/in ²)		Elongation (%)	
		t ₀	t ₃₀	t ₀	t ₃₀	t ₀	t ₃₀		t ₀	t ₃₀	t ₀	t ₃₀
Kynar 201	3.5	.1105	.1682	0.25	0.04	0.9	-	8.6	769	744	40	40
Kynar 401	3.5	.0765	.1272	0.19	(2.7)	0.5	0.2	20	1199	1381	30	30
Kynar 451	2.2	.0553	.1040	1.3	1.2	0.5	0.5	18	1512	1550	40	70
PVC-B	6.0	.1301	.0855	0.001	S*	0.06	S	9.1	917	1526	30	10
PVC-P	2.0	.0605	.0534	8.2	S	0.5	S	6.7	1133	655	50	5

Concentrated Chromic Acid/Urine Solution (95%) at 80°C

Kynar 201	3.5	.0909	.1176	0.095	0.004	0.9	0.2		769	889	40	40
Kynar 401	3.5	.0902	.0988	0.18	0.034	0.5	0.7		1199	1327	30	40
Kynar 451	2.2	.0613	.0691	0.48	0.40	0.5	0.5		1512	1545	40	45
PVC-B	6.0	.0838	.1249	0.001	S	0.06	S		917	1506	30	20
PVC-P	2.0	--	--	8.2	S	0.5	S		1133	S	50	S

*S = Shrunken

slit in half and pulled apart according to ASTM Test Designation No. D1938-67.

Reported data in the tear and tensile tests are for an average of three specimens for each material. Table 4 lists data accumulated from both dilute and concentrated 30-day soak tests.

(2) Water Vapor Transmission Measurement

Water vapor transmission was evaluated using ASTM Test Designation No. E96-63T (see Appendix B).

Membranes were placed over a cylindrical cup containing 10 ml of distilled water and clamped into place, and placed in a constant temperature (70°C) oven. Dry air was blown over the surface to pervaporate water through the membrane. Because of temperature variations in weighing the cup (the cup was initially at room temperature and had to be removed from the oven for weighing) and the insufficient water volume, the pervaporation rate never reached steady state but continued to increase with time as cup temperature increased until all the water was vaporized. These results are, therefore, only useful in a qualitative sense.

c. 12-Day Soak Tests

Two polysulfone membranes were soaked for 12 days at 85°C in urine to which the chromic acid solu-

tion described in Table 2 had been added. Eighty percent of the water in the urine/chromic acid solution was evaporated prior to the immersion of the membranes. One polysulfone membrane was dried after casting and before soak testing while the other membrane was immersed without drying. The drying step tightens the membrane considerably. Results of these tests are presented in Table 5.

B. Discussion of Membrane Soak and Screening Tests

1. Thermal Stability

Kynar and Teflon membranes have high crystalline melt temperatures, more than 100°C above the 70°C VDR pervaporation module operating temperature proposed by Hamilton Standard; and polysulfone has a heat distortion temperature of about 170°C. These materials, therefore, possess the thermal stability to operate at temperatures significantly above 70°C with a consequent increase in water vapor driving force and a decrease in membrane openness requirements. These materials even raise the possibility of operating at sterilization temperatures with the resultant elimination of the urine bactericide/chemical pretreatment requirement.

PVC, on the other hand, has a crystalline melt temperature of about 80°C, which makes the 70°C proposed by Hamilton Standard close to a maximum feasible operating temperature for it. PVC membranes,

TABLE 5

POLYSULFONE FILMS SOAKED IN 80% URINE/CHROMIC AT 85°C

	<u>Initial Weight</u>	<u>Blotted Wet Weights, g</u>			<u>Discoloration</u>	
		<u>3 Days</u>	<u>6 Days</u>	<u>12 Days</u>	<u>Skin</u>	<u>Substructure</u>
Dried before soak	0.1187 (dry)	0.3320	0.2791	0.2820	None	Tan
Wet before soak	0.2914	0.3690	0.2737	0.2704	Tan	Dark Brown

soaked in either tap water or the urine/acid solution at 70°C, were more susceptible to shrinking than Kynar or Teflon membranes, suggesting either annealing of PVC membranes prior to use or physical constraint as utilized by Hamilton Standard to prevent shrinkage. The Goretex and Zitex, Teflon membranes, underwent some dimensional change at higher temperature but not nearly as much as that for PVC. Kynar membranes shrunk during the formation procedure but were dimensionally stable subsequent to formation.

2. Chemical Stability

Discoloration, weight, and water flux changes were obtained with all membranes over the course of the soak tests. These changes occurred primarily during the initial phase of the soak tests; conditions stabilized with time with the bulk of the change occurring in the first few days and with essentially no further change occurring after 30 days.

The bulk polymerized PVC and the polysulfone membranes were the only ones exhibiting significant weight loss, indicating chemical attack of the membrane. The solution pH changes with time in the dilute urine/chromic solutions, going from acidic conditions initially to basic (pH ~ 10) after a few days of test. The significant weight loss of the bulk polymerized PVC membranes in the dilute solution may be attributable to chromic acid attack during this initially acidic condition. This tends to be corroborated by the weight gain apparent with bulk

polymerized PVC when soaked in concentrated urine/chromic solution. The concentrated solution had a basic pH throughout the test. The polysulfone weight loss in pre-concentrated urine/chromic does suggest a different mechanism of chemical attack for polysulfone than for PVC and does give credence to the Hamilton Standard conclusion that polysulfone membranes are not suitable for the VDR if chromic acid is used as a bactericide. The PVC-P control membrane does not suffer as much weight loss as the PVC-B membrane, but this may be partially attributable to greater solids deposition in the PVC-P in view of its more open structure. The tensile strength of the PVC-P membrane was significantly degraded by the acid soaking, suggesting significant chemical attack.

Some of the Kynar membranes do show some weight loss but this does not appear to result in either mechanical weakening of the membrane or opening of the skin. The higher molecular weight Kynar, Kynar 451, appears most resistant to chemical attack. The Teflon membranes appear to be completely inert to chemical attack.

Solids precipitation and deposition within the membrane pores appears responsible for discoloration, weight gain, and decrease in water flux of the membranes. The tighter the membrane skin, the less the discoloration in this area, consistent with the above explanation of discoloration; heat treated membranes discolored less because of reduced pore

size and free area of the membrane skin. A green chromate color resulted from immersion in urine/acid solutions with excess chromic trioxide and a brownish color resulted from immersion in solutions with the Table 2 stoichiometry. Less solids deposition is anticipated in long-term pervaporation tests than was obtained in these soak tests because of the shear due to fluid flow and the lack of total immersion.

3. Water Vapor Transmission

As indicated, the water vapor transmission measurements reported in Table 4 are useful primarily for qualitative comparison of candidate membrane materials. These measurements indicate that Kynar membranes can readily be made with a water vapor transmission capability comparable to that of the PVC-P control membrane. The initial PVC membranes made from bulk polymerized PVC are clearly too tight for VDR application and need to be made more open. More quantitative measures of membrane pervaporation capabilities are reported in the flat sheet pervaporation module tests (Table 5).

4. Membrane Mechanical Properties

The room temperature mechanical properties of the Kynar membranes are somewhat superior to those of the PVC membranes. This difference increases with Kynar molecular weight, progressing from the 201 through the 401 to the 451 membrane, and will become more significant as the melt temperature of the PVC is approached. It is likely to be greater when

equal thicknesses of membranes having equivalent pore size and openness are compared. Teflon has a low modulus of elasticity and is therefore more subject to distention and deformation from slight pressure imbalances across the membrane. It is also more subject to creep; but in view of its high melt temperature, its mechanical properties are much less affected by temperature than are those of PVC. Both Kynar and Teflon are essentially inert chemically to the urine and urine/chromic acid solutions as is evident from the soak test data.

The decrease in tensile strength and elongation of the PVC-P control membrane were the major apparent effects of the 30-day soak test on membrane mechanical properties.

The polysulfone membrane has a heat distortion temperature of 170°C and therefore will retain mechanical strength at sterilization temperatures.

5. Ease of Fabrication

As mentioned previously, Kynar membranes appear to shrink during precipitation while polyvinyl chloride membranes shrink during heat treatment or pervaporation at elevated temperatures. Because of the precipitating shrinkage, Kynars require larger draw-down to get the effective work area needed for the flat sheet module.

To prevent shrinkage by the PVC-B membranes, an annealing step should probably be performed although

support in the module prevents any dimensional changes during pervaporation. All membranes were capable of being pervaporated from a dried state and require no precondition' _ soak.

Pinholes are the limiting factor in the production of flat sheet membrane. The larger the sheet the greater the difficulty in obtaining defect-free sheets. This may be an important consideration in designing a prototype module for extended space flights.

III. FLAT SHEET PERVAPORATION TESTS

A. Construction of a Flat Sheet Test Module

A flat sheet pervaporation module of design similar to that described in the introduction was constructed to enable evaluation of the candidate membranes under actual operating conditions.

1. Test Cell Design (Figure 5)

The test cell was machined from two 10-inch diameter by 3/8 inch thick, 304 stainless steel plates. One half of the module required parallel channels to be machined over a 4.5 inch square area having a width of 0.25 inches and a depth of 0.030 inches. Support ridges between the channels are 0.125 inches wide. Uniform manifolding is provided at both ends to evenly distribute and collect urine flow. Feed solutions enter a 0.25 inch I.D. Swagelok fitting perpendicular to the distribution channel and leave through a similar arrangement.

The air sweep side consists of an empty 4.5 inch square cavity with flow distribution channels similar to the urine side. An "O"-ring groove provides the necessary sealing and is located 3.5 inches from center. The actual sweep channels are formed by placing a corrugated 316 stainless spacer into this cavity so as to align the channels perpendicular to the distribution cavities.

Assembly of the module for testing requires placement of the membrane over the urine channels skin side down. The Buna-N "O"-ring is inserted in the

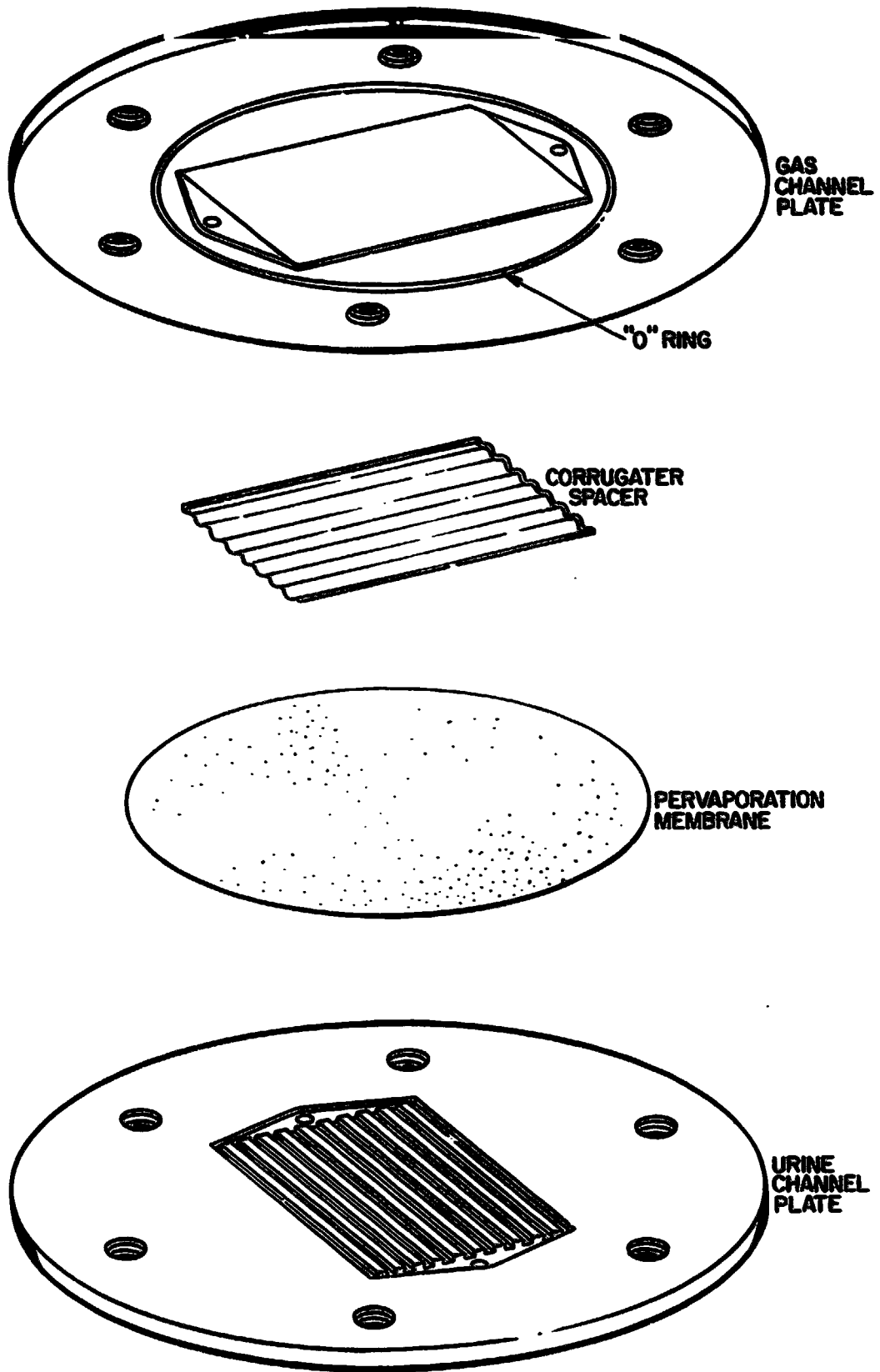


FIGURE 5: TEST CELL

groove and the sweep spacer secured in the cavity by the means of a piece of double sided tape. The gas channel plate is then placed over the membrane so as to align the sweep channels perpendicular to the urine channels. Cross flow manifolding was utilized. The plates are secured with the use of six tie-down bolts and the completed unit offers 0.1 square feet of active membrane area.

2. Instrumentation and Controls

To maintain a constant temperature environment for the test module, several methods were considered. A constant temperature liquid bath was considered but would complicate maintenance and leak detection. Heating coils would require many separate circuits and thermocouple insertions and would, therefore, be complex. The approach finally selected was to house the entire device within a small constant temperature oven.

Figure 6 schematically represents the test module, i.e., a constant temperature oven and its internal components. Nitrogen was used initially as the sweep gas but was subsequently replaced by compressed air. The sweep gas plus pervaporate was exhausted to the atmosphere through a condenser. In a true prototype system, the sweep gas would be recirculated. Gas flow and pressure are monitored prior to entrance into the test cell. The sweep gas is preheated slightly before entering the test cell. Condensation in the test cell was, however, not completely

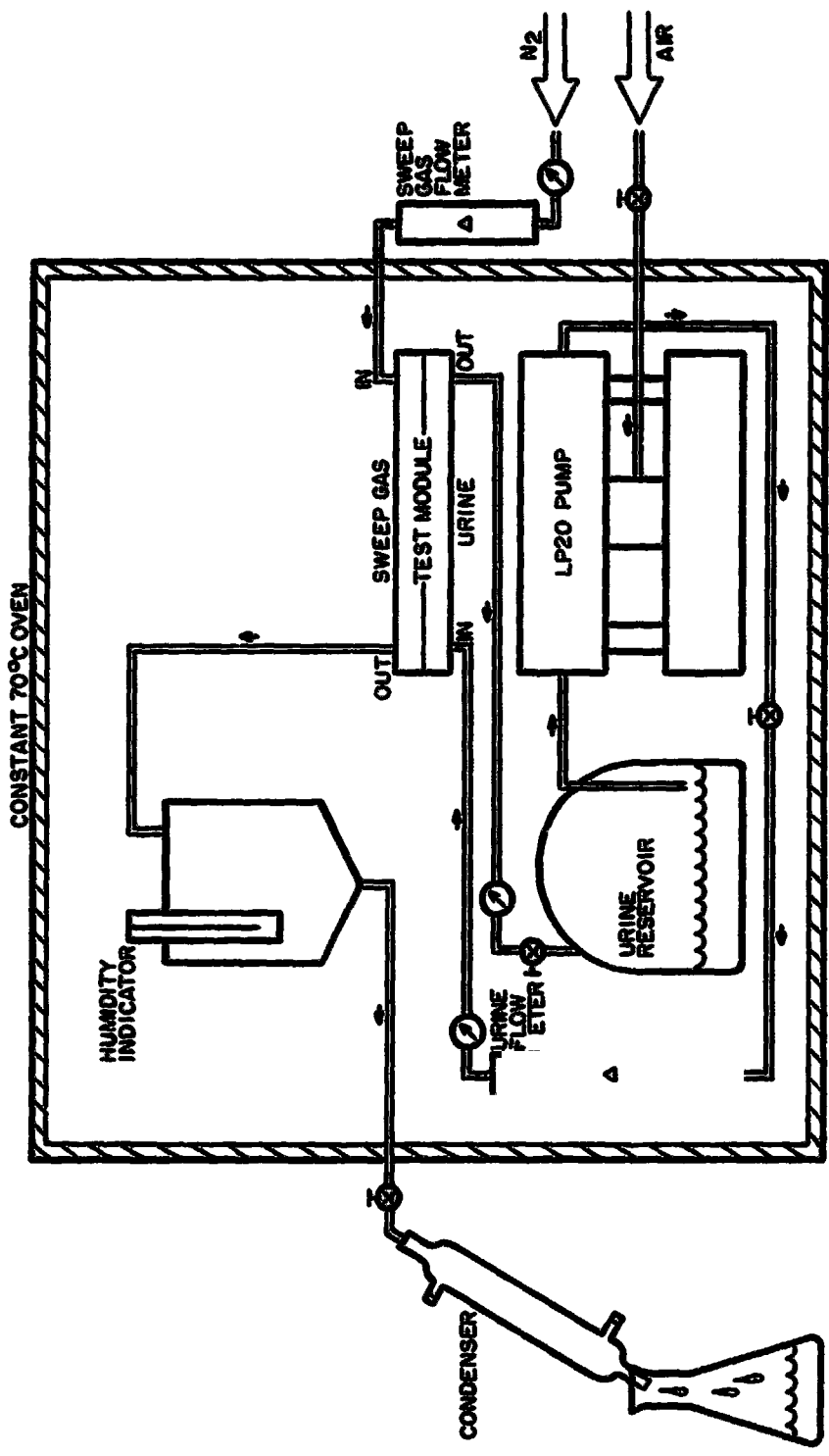


FIGURE 6: TEST MODULE

eliminated. Gas outlet is piped directly to a chamber where relative humidity and temperature are monitored to within $\pm 1\%$. A valve upstream of the condenser permits the creation of a back pressure should it be desirable. The condensation column is a glass reflux condensor maintained below room temperature with cold running tap water. Condensate or pervaporate is collected in an Erlenmeyer flask for analysis.

The urine was pumped by an Amicon LP-20 pump through a flowmeter and regulatory valve. The normal flow range of the pump exceeded the desired system flow rate so a bypass loop around the pump was installed. Even so, regular pressure surges (bumps) were characteristic of the system. The entire system from the 5 liter stainless reservoir through the LP-20 remained leak proof and resistant to chemical attack through all the runs. At the exit end of the flowmeter liquid pressure was monitored prior to entrance into the test cell. Urine samples could be withdrawn from the same location. Pressure was also monitored leaving the test cell.

System temperature was maintained at 70°C except where otherwise noted.

B. Flat Sheet Evaluation in the Test Module

The flat sheet pervaporation module was first checked out with distilled water. Pervaporation runs were then made with straight urine, then urine/chromic acid, and

finally urine/double chromic acid. All runs were performed balancing the urine inlet pressure with the sweep gas inlet pressure at 3 psig except where noted. Sweep gas flows were kept constant. Prior to pervaporation, all membranes were secured in place and the system was preheated one half hour. Three liters of urine or other feed water were placed in the reservoir and preheated two days prior to testing. Feed samples were taken before and after the preheat cycle.

The air sweep side was rinsed with distilled water prior to testing and blown through until the sweep stream had 0% relative humidity. Samples were taken throughout the run usually over ten minute periods. Prior to collecting the sample, a brief flush with distilled water was made on the condensing column.

The entire oven package was eventually installed in a hood to keep down odors. Only air regulatory valves and the condenser were not within the confines of the oven or hood.

1. Distilled Water Runs

Before urine could be run in the module, careful pretesting was carried out to find leaks and determine operating characteristics. Preliminary runs using the control PVC-P membrane on distilled water produced rips in the membrane. Sharp ridges in distribution channels and pressure surges appeared responsible for this ripping. The pressure surges were reduced by the addition of a bypass

and the sharp-ridged membrane supports in the distribution channel were machined away.

PVC-B membranes were placed in the module and found not to pass water even with 15 psi transmembrane pressure. At that pressure, the membrane ripped on the edge of the sweep channel spacer. In addition to the sharp edges on the sweep spacers, pressure balancing seemed difficult. The sweep gas channels were further extended into the manifold area and the spacer was permanently mounted in the cavity with the use of RTV silastic to prevent movement and sweep gas bypassing on the back side. Ripping and pressure balancing problems were eliminated with these modifications. The PVC-B membrane did pervaporate at 15 psi prior to ripping but was clearly too tight a membrane.

2. Urine Runs

Three liters of urine were collected in the men's laboratory and placed in the reservoir without addition of any chromic acid. The density and pH (1.022 and 6.0 respectively) were recorded prior to heating. Pervaporation data are summarized in Table 6; feed solution information is presented in Table 7.

Urine pervaporation was performed using PVC-P and Kynar 451 membranes. Thirty-six percent of the water initially present was pervaporated. Most of the pervaporation was performed on the Kynar 451 membrane which yielded a pervaporation rate better

TABLE 6: TYPICAL PERVAPORATION DATA
 Collected in 0.1 ft.² Flat Sheet Test Module @ 70°C

Membrane	Test Solution	Thick- ness (mil)	Conductivity (x 1000µv)	Ammonia (mg/l)	pH	Pervaporation Rate		Solids Deposition
						Initial (ml/min)	Equilibrium (lb/hr-ft ²)	
PVC-P	Urine	2.8	1.2	224	10.2	1.2	1.8	None
	Urine/Chromic @ 50°	2.5	1.0	156	9.6	0.8	1.2	Slight
	Urine/Chromic (2X)	2.5	2.1	352	8.1	0.6	2.4	Moderate
Kynar 201	Urine/Chromic @ 50°	4.3	0.4	8	5.0	0.5	1.0	Slight
	Urine/Chromic	4.3	---	50	10.1	0.7	1.0	Slight
	Urine/Chromic (2X)	5.3	2.3	264	7.7	0.5	1.5	Moderate
Kynar 451	Urine	6.4	1.8	108	10.1	3.0	3.0	Moderate on air side
	Urine/Chromic	4.7	1.9	614	10.0	2.8	3.3	Moderate
	Urine/Chromic (2X)	5.2	3.4	493	7.1	2.0	3.0	Heavy
Goretex (S10183)	Urine/Chromic (2X)	4.0	1.8	614	7.6	3.2	2.7	Heavy
	Urine/Chromic (2X)	4.0	1.8	101	7.9	4.0	3.0	Heavy

*Final Value

TABLE 7
FEED SOLUTIONS OF RUNS ON TABLE

<u>Solution</u>	<u>Chromic Acid Conc. (mg/l)</u>	<u>Room Temperature Initial Ammonia</u>		<u>2 Days @ 70°C Ammonia</u>		<u>After Pervaporation</u>			<u>Comments</u>	
		<u>pH</u>	<u>(mg/l)</u>	<u>pH</u>	<u>(mg/l)</u>	<u>Time (hrs)</u>	<u>% Water Evaporated</u>	<u>pH</u>		<u>Ammonia (mg/l)</u>
Urine	---	6.0	---	9.2	1710	4.5	36	8.7	2510	Bacterial Growth
Urine/ Chromic	5.8	2.3	---	---	2770	8.8	23	8.7	2690	
Urine/ Chromic (2X)	11.6	1.8	548	6.4	2820	14.3	49	5.5	2350	Green Precipitate

than twice that of the PVC-P control. Pervaporation rates significantly exceeded the 0.5 lbs./hr. ft.² target specified in the RFP. Although the conductivity of the PVC-P pervaporate was lower than that of the Kynar 451, the Kynar produced less ammonia. Discoloration was nonexistent on the urine side of either membrane but was produced on the sweep side of the Kynar 451 following a brief imbalance in urine and sweep gas pressures. Bacteria was observed to collect in the urine reservoir following the several days at ambient conditions.

3. Urine/Chromic Acid Runs

Three liters of urine were treated according to the recipe in Table 2 and placed in the module reservoir. After several hours preheat, the urine/acid system was evaluated at 50°C to determine the effect of lower temperature on ammonia release and pervaporation rate. PVC-P and Kynar 201 were evaluated at these conditions as well as at the elevated temperature (70°C) with Kynar 451.

Pervaporation rates again significantly exceeded the 0.5 lbs./hr. ft.² target specified in the RFP. Over the course of six hours, pervaporation with the Kynar 201 and PVC-P membranes yielded the lowest conductivities and ammonia contents of all pervaporates taken. The Kynar 201 (Table 5) pervaporate had only 8 ppm of ammonia at 50°C pervaporating at the same rate as the PVC-P control.

The low ammonia concentration in the pervaporate is doubtless attributable to the low feed pH which stayed below 3 throughout the run.

Elevating temperature increased pH and the evolution of ammonia. Kynar 201 continued to yield a higher pervaporation rate than the PVC-P, but pervaporation rate did not increase as much with temperature as anticipated. The incidence of discoloration increased with temperature indicating more solids deposition on the membrane; the interference these solids present to pervaporation may account for the failure of the pervaporation rate to increase more with temperature. Kynar 451 gave three times the pervaporation rate as did the Kynar 201 or PVC-P but also gave a 10-fold increase in ammonia at the same pH. A final feed pH of 8.7 was reached after nine hours of pervaporation with 23% removal of water from the urine solution.

The addition of chromic acid to the urine appears to increase wetting of the membranes by the solution, increasing pervaporation slightly initially but also increasing the extent to which solids deposit in the membrane and clog its pores. The wetting may also result in an increase in the ammonia content and conductivity of the pervaporate.

4. Urine/Double Chromic Acid

The chromic acid pretreatment recipe in Table 2 was doubled and added to determine the effects of acid on the feed solution and membranes. Initial pH was decreased from 6.0 to 1.8 but increased to 6.4 after two days at 70°C. PVC-P, several Kynar 201's, Kynar 451, and two Goretex membranes were evaluated starting with three liters of this solution. The higher acid concentrations generally gave higher ammonia levels for the same membranes at low acid levels, although pH was kept lower. Pervaporation remained unchanged for all the membranes except the PVC-P which doubled in pervaporation as ammonia levels increased. This may indicate some attack of the membrane skin. The Goretex membranes pervaporated at rates comparable with the Kynar 451 at equivalent ammonia levels. Goretex pervaporation rates decreased rapidly over the few hours of the test period and severely discolored. This discoloration appeared to be on the urine side of the membrane. The discoloration was more severe than the Kynar 451 and does indicate that solids deposition progressively clogs the pores and decreases the pervaporation rate. The nominal pore size of the two Goretex membranes was 0.2 microns and the thicknesses were 2 and 4 mils. Due to the elasticity of the Teflon materials, deformation of the thinner membrane into either the sweep gas or urine channels could not be prevented due to unavoidable slight imbalances in the urine and sweep gas pressures.

C. Longer Duration Flat Sheet Tests

A longer duration flat sheet pervaporation run was attempted using a Kynar 451 membrane. Initial efforts were unsuccessful because pressure surges ruptured the membrane. Design modifications were carried out to overcome this problem. The LP-30 pump was replaced with an LP-1 tubing pump located outside the heated enclosure to prevent motor overheating. Improved operation resulted but membranes were still subject to rupture due to pressure imbalances in the inlet and outlet flow plenums. The corrugated stainless spacer terminated at the plenums and tended to cut through the membrane when pressure differences forced the membrane down over the spacer.

Operation with straight urine (no chromic acid added) at pasteurization temperatures resulted in solids deposits on the membrane and in the flow channels which were of a dark brown gummy nature and tended to clog the membrane and the flow passages. Water flushes were not as effective in cleaning the membrane as they were in the previous straight urine pervaporation runs described under the section on "Hollow Fiber Pervaporation Tests." It was surmised in part that the solids penetrated and clogged the more open flat sheet membrane more easily; and that the better results obtained with hollow fibers were attributable to the tightness of the membrane.

To further reduce the tendency for membrane rupture, two additional modifications to the pervaporation module were made: (1) the stainless steel corrugated

spacer was used to mold a silicone rubber spacer which would be less apt to cut through the membrane; and (2) metal supports for the membrane in the plenum areas were machined so that transmembrane pressure imbalances in these regions would not bow the membrane.

A long duration pervaporation run with urine, to which the standard chromic acid solution had been added, was started. The run lasted a total of eleven days and was terminated because the project engineer was going on vacation. The results are presented in Table 8. The run was conducted in two parts: in the first part, a total of 17 liters of urine were charged and 10.9 liters of water were pervaporated over a period of six days, 18 hours, and 15 minutes. The 10.9 liters of pervaporate represents the sum of condensate collected plus uncondensed water vapor leaving with the sweep gas. A liquid material balance indicates a water loss of 14.5 liters. The difference between the two numbers is probably attributable to leaks. The pervaporation rate had fallen at the end of this first part of the run and 75% of the water added had been recovered so it was decided to dump and flush the urine side of the system with distilled water. After dumping, several liters of water were added and flushed through the urine side of the system for 15 minutes at 70°C. The flush water was then dumped and the system recharged with urine and chromic acid and pervaporation again started. In this second part of the run, a total of 6.5 liters of urine were charged and 2.7 liters of water were pervaporated over a period of two days and 17 hours. The 2.7 liters of pervaporate is derived from the sum of condensate

TABLE 8: LONG-TERM FLAT SHEET PERVAPORATION TESTS (Kynar 451 Membrane - 5 mil thick)

Time (hrs)	Comments	Urine Flow Rate	Sweep Gas Flow Rate	Temp (°C)	Sweep Gas Humidity (% RH)	Condensate Rate-A	Uncondensed Water Vapor in Sweep Gas-B	Total Pervaporate (A+B)	Product Water Quality
		(gal/hr)	(l/min)	(°C)	(% RH)	(lbs/hr ft ²)	(lbs/hr ft ²)	(lbs/hr ft ²)	Conductivity X100 μ
0	Startup								
4	4 liters straight urine	18	23	70°	1%	3.7	---	---	--
18	Pump surge ripped membrane	18	23	60°	--	---	---	---	--
After several attempts to rerun on urine, lines plugged and pump ruptured membrane; LP-30 pump replaced by LP-1. System flushed and reservoir filled with 4 liters of urine/chromic system. Pressures balanced.									
0	Startup	12	22	70°	19%	1.7	0.5	2.2	10.9
18		11	22	70°	8%	1.6	0.5	2.1	11.8
42		11	22	70°	8%	1.5	0.5	2.0	10.9
66		11	23	70°	8%	0.9	0.5	1.4	10.5
94	Add 1.5 ml H ₂ SO ₄ /l	14	23	70°	8%	1.2	0.5	1.7	10.8
140		12	23	70°	8%	0.5	0.5	1.0	9.9
163	Shutdown pervap. too low	12	23	70°	8%	0	0.5	0.5	--
Avg. -1.45 over 163 hrs									
0	Startup	11	12	70°	29%	0.8	0.2	1.0	--
65	Membrane ruptured	8	12	70°	13%	0.3	0.2	0.5	--
Avg. -1.32 over entire 228 hrs.									

System was drained and flushed with water and a heating coil installed in sweep side; fresh urine/chromic added. Membrane was not replaced or removed.

collected plus uncondensed water vapor leaving with the sweep gas. A liquid material balance indicates a water loss over the course of this second part of the run of 4.0 liters. Once again, the difference between these two numbers is probably ascribable to leaks. The membrane cleaning after the first part of the run was not sufficient to bring the pervaporation flux back to its original value, but did significantly increase the pervaporation flux. The flux was, however, falling continuously through the second part of the run. At the end of the test the pervaporation module was disassembled and the pervaporation membrane was removed and inspected. It was still intact and chemically unaltered but was saturated with a deposit of green chromate solids and a brown material. The deposit was clearly responsible for the decline in flux.

One reason for the solids deposition is the fact that the sweep gas flow is unheated and completely dry entering the pervaporation module. As a result, it is apt to exert a strong cooling effect as it flows past the membrane. This is accentuated by the relatively high rate at which the sweep gas is circulated. This cooling effect on the liquid adjacent to and in the pores of the pervaporation membrane lowers the solubility of the solids in solution. Since they are in highest concentration at the membrane surface and the solubility is lowest there because of the cooling effect, the solids are most likely to precipitate there. In an attempt to reduce the magnitude of this effect, before the second part of the run the inlet gas was piped through a stainless coil located in the heated chamber to warm it before it

entered the pervaporation module. The sweep gas flow rate was at the same time cut in half in a further effort to reduce the cooling effect. These measures doubtless helped but, as indicated, did not prevent further solids deposition and flux decline.

More extensive system changes should bring about a significant alleviation of the solids deposition problem. Recirculating the gas with a relatively high relative humidity and a high gas rate and a modest increase in humidity across the pervaporation module should decrease the cooling effect. Use of a tighter membrane will decrease the pervaporation rate and hence the cooling rate and will decrease the tendency for the liquid to penetrate the membrane and for solids to precipitate in it.

The pervaporation rates obtained in this long duration run are significantly higher than those obtained by Hamilton-Standard in comparable runs. The highest rate they report in their final report is 0.7 lbs./hr. ft.² while the average pervaporation rate obtained in the long duration run reported here is 1.3 lbs./hr. ft.².

IV. HOLLOW FIBER PERVAPORATION TESTS

A. The Preparation of Hollow Fiber Candidates

Many of the shortcomings mentioned in the preparation of flat sheet candidates are not problems in the preparation of hollow fibers. Except for the addition of a few extrusion variables, spinning hollow fibers follows the same precipitation scheme as used in the preparation of flat sheet membranes.

Kynar and PVC hollow fibers produced in initial studies have skin defects and inadequate mechanical properties but demonstrate the feasibility of hollow fiber production from these materials. Formulational and nozzle adjustments will be required to produce hollow fibers with the desired skin integrity, pore size, and mechanical strength, but this should be a straightforward activity based on prior Amicon work in this field. Past experience suggests that hollow fibers with appropriate properties are apt to have slightly lower pervaporation rates than the corresponding flat sheet membranes, but this should be more than compensated for by the high interfacial area of the hollow fiber modules per unit volume.

B. Evaluation of Hollow Fiber Candidates in Test Module

Polysulfone, which had been ruled out in previous work by Hamilton Standard for its lack of chemical durability, was considered as a useful membrane should chromic acid not be involved and thermal sterilization used instead. A typical unit designed specifically for use as a "hollow fiber artificial dialyzer" and having a tighter membrane

skin than desired for pervaporation was evaluated on the test module as a possible candidate.

1. Urine Runs

Pure urine was collected as before and charged to the test module reservoir to preheat to 50°C. After two days of preheating, the three liters of urine were pumped through lumens of the 10,000 fibers (10 square feet of surface area) at 14 gallons per hour. Air sweep gas was circulated at a rate exceeding 20 liters per minute through a water-cooled condenser to enable pervaporate collection as in the flat sheet pervaporation module experiments. Table 9 lists the pervaporate collected at both 50 and 70°C using a urine feed solution. Although the run only reached 17% water removal, pervaporate conductivity was low throughout the test. At 50°C no ammonia was evolved whereas some was found in the 70°C pervaporates. Pervaporation rate per unit area was lower than desired as was anticipated in view of the tight dialyzer membrane skin and the lack of sweep gas baffling in the extracapillary region. The hollow fiber geometry is much more stable to transmembrane pressure drop than the flat sheet pervaporation module, and balancing of urine and sweep gas pressures is therefore not nearly as critical a requirement.

The polysulfone hollow fibers did not discolor during the straight urine pervaporation and appear to be well suited for operation at sterilization temperatures

TABLE 9

PM-30 HOLLOW FIBER UNIT
(10 square feet - 10,000 fibers)

% Conc.	Urine		Air Sweep		Pervaporation		Feed						
	Temp °C	Inlet Press	Outlet Press	Flow (gph)	Press (cc/min)	Flux (ml/min)	pH (x 1000 μV)	Cond. (mg/l)	Ammonia (mg/l)				
0	50	2.5	0.5	14	5.0	>20,000	3.0	7.7	2.1	0	6.4	30	1312
2.5	50	2.5	0.5	14	7.5	"	3.0	7.8	1.3	0	---	--	---
5	70	2.5	0.5	14	5.0	"	7.0	9.7	5.1	170	7.3	--	---
9	70	2.5	0.5	14	5.0	"	7.0	9.3	4.1	87	---	--	---
16	70	2.5	0.5	14	5.0	"	4.0	8.8	2.0	27	---	--	---
17	70	2.5	0.5	14	7.5	"	5.0	8.9	2.2	38	9.2	60	1920
Urine/Chromic Solution (add appropriate amount of chromic acid)													
30	50	3.0	0.5	20	7.5	"	3.0	9.8	2.5	63	---	--	---
43	50	3.0	0.5	20	7.5	"	2.4	9.6	1.6	36	---	--	---
48	50	3.0	0.5	20	7.5	"	2.0	9.5	1.8	23	---	--	---
72	70	4.0	0.5	20	7.5	"	3.0	9.2	1.1	23	---	--	---
90	70	5.0	0.5	14	7.5	"	2.4	8.8	1.2	11	6.6	60	1633

without chromic acid. The increased driving force for water vapor transport at sterilization temperatures should markedly decrease the extent to which the membrane has to be opened to keep the pervaporation module volume and weight small.

2. Urine/Chromic Acid Runs

Using the setup described above, chromic acid was added to the urine and the temperature readjusted to 50°C to enable the collection of data on the lower half of Table 8. Starting at 30% water removal, the PM-30 hollow fiber device was pervaporated to 48% water removal. Pervaporation rate was lower than experienced with straight urine with higher levels of ammonia. Elevating the temperature to 70°C did not improve the pervaporation rate or alter the ammonia concentration in the pervaporate. Urine inlet pressure had to be increased to compensate for increasing solids deposition. A brown stain appeared after 40% recovery on the urine exit end (air entrance port) of the device. The stain enlarged throughout the run and propagated down the fiber. A rupture in a tubing line in the flow circuit (not in the hollow fiber module) terminated the run at about 50% recovery. Following this, pure water was pumped through the unit on the air side. The stain was easily and rapidly dissolved confirming its deposition nature. A quick leak check of the unit revealed no leaks or apparent degradation.

These results suggested a review of the Hamilton Standard findings concerning the chromic acid attack of polysulfone membranes; but subsequent soak tests in concentrated chromic acid at 85°C (Table 5) do confirm slow membrane attack in this environment.

V. PERVAPORATION TESTS - DISCUSSION OF RESULTS

A. Temperature Effects on Urine and Pervaporate Composition

Increase in pervaporation temperature increases the ammonia content, odor, and conductivity of the pervaporate but, of course, also increases the pervaporation driving force.

B. Bacterial Growth

Literature searches⁽¹⁾ indicate untreated urine decomposes by microbial action to form ammonia and carbon dioxide. Amicon's work with raw urine test solutions does show evidence of microbial growth. This growth is probably unacceptable since it may clog the urine flow circuit; may induce growth on the hollow fibers; and if the urine wets the membrane, growth may enter the product stream. The need for a bactericide of some sort or for operation at sterilization temperatures is clearly evident.

C. Ammonia

Literature⁽²⁾ also indicates the presence of dissolved ammonia as organo-acid salts in urine. Our titrimetric evaluations of urine solutions confirm this and indicate that additional ammonia produced by heating urine solution. This ammonia is the decomposition product of urea and other nitrogenous material. In untreated urine microbial decomposition of urea is a principal source of ammonia. The literature⁽³⁾ also indicates that urea is slowly hydrolyzed to ammonia, especially at elevated temperatures.

According to Putnam⁽⁴⁾, chromic acid is added to the urine solution to act as both bactericide and to tie up initially free ammonia present in urine. Amicon's test runs show that the quantity of chromic present is not adequate to handle additional levels of ammonia created during pervaporation due to the decomposition of urea and other nitrogenous compounds. Independent of whether chromic acid is used as a bactericide or not, some ammonia will be evolved on heating and will appear in the pervaporate (ion exchange resins or charcoal adsorption may well be required to remove this). Decreased ammonia evolution may result from using more acid and less chromic oxide in the pre-treatment.

D. Effects of Chromic Acid

As with the chromic acid/urine soak tests, the immediate consequence of chromic acid in urine is the generation of precipitates (green and brown deposits). The green precipitate, which is probably calcium and magnesium chromates, collects in the channels and on the skin of the membrane. Meanwhile, a brown precipitate seems to accumulate in the membrane as chromic levels are increased.

The green precipitate appeared on the surface of the membrane which was in contact with the liquid (the skin side) for all pervaporation runs with chromic acid added to urine. The brown precipitate, in the case of PVC-P, the control membrane, was slight and appeared to be localized in the pores judging from the discoloration it generated. Kynar 201 and 451 were discolored only slightly more than the PVC-P but contained more dark

brown staining. This discoloration microscopically appears to result from a precipitate in the membrane structure localized near the skin (liquid side) of the membrane. Kynar, over the short-term run (up to 50% concentration of urine), showed no effects of the precipitate on pervaporation rate or membrane performance. Teflon (Goretex), run at high chromic levels, shows a significant decrease in pervaporation rate with time. This is presumably due to precipitation of solids clogging the pores.

Chromic acid appears to increase the ease of membrane wetting. Although the mechanism is not completely clear, transmembrane pressure differentials, sufficient to wet and cause urine to flow through the membrane, are smaller with chromic acid pretreated urine than with untreated urine.

No effect of chromic acid on pervaporate conductivity is apparent except when transmembrane pressures are not balanced.

E. Pervaporation Rate

1. Flat Sheet

The highest pervaporation rate of 5 pounds/hr. ft.² was obtained with the Goretex Teflon membrane, but the Teflon pervaporation rate declined rapidly, presumably due to solids precipitation in the Teflon pores. Teflon membranes have thus far only been run with double the Hamilton Standard chromic acid pretreatment, which does generate a relatively large volume of

precipitate. Runs have not been long enough to determine whether the flux stabilizes at some level or continues to decline.

Kynar 451 membranes gave an equilibrium pervaporation rate of 3 pounds/hr. ft.² at 70°C, but the rate was relatively constant with time and independent of chromic acid addition over the test period. Solids deposition does not appear to clog the tighter pores of the thin Kynar skin.

The Kynar 201 membranes are tighter and gave a pervaporation rate of about 1.3 pounds/hr. ft.², also independent of time or whether chromic acid was present.

The PVC-P membrane gave a pervaporation rate intermediate between the Kynar 201 and 451 membranes. This rate also was not affected by time or chromic acid addition.

b. Hollow Fiber

Hollow fiber pervaporation results were highly encouraging. Urine without chromic acid was used since under the Hamilton Standard contract, polysulfone membrane was shown to be degraded by chromic acid. A pervaporation rate of 3 ml/minute was obtained at 45°C and of 7 ml/minute at 70°C.

Significant increases in pervaporation rate should result from use of more open membranes and from baffling of the sweep gas flow past the hollow fibers.

A pervaporation rate of 15 ml/minute was the target set for the Hamilton Standard pervaporation module, and this rate should be readily achievable with a hollow fiber pervaporation module smaller than a can of tennis balls.

One advantage the hollow fiber module configuration has over the flat sheet is that balancing of the transmembrane pressure differential is not as critical. With a flat sheet module, too high a transmembrane pressure differential forces the membrane into the liquid or sweep gas channels depending on which stream is under higher pressure. This problem does not occur with hollow fibers. In addition, hollow fiber modules can be made more compact and of lower weight and with simplified header and fluid seal design.

F. Odor

The lower the test temperature, the lower the pervaporate odor. Urine without chromic acid gave low odor pervaporates but odor becomes extremely noticeable if the membrane leaks. Chromic acid gave the least odor obtained, especially with the low temperature runs. Double chromic seems to give a stronger odor. The odor varies from that of latrines to definite ammonia.

VI. CONCLUSIONS

The following conclusions may be derived from this program:

1. Polysulfone meets VDR pervaporation module requirements provided operation at sterilization temperatures is used without chromic acid addition. Polysulfone has the advantage of being commercially available in hollow fiber form and of requiring only minor modification to make it suited for VDR use. Polysulfone is, however, slowly attacked by chromic acid and may not give adequate pervaporator module life and reliability where chromic acid is used.
2. Polyvinylidene fluoride (Kynar) appears to meet all the requirements for a VDR pervaporation module membrane. It is hydrophobic and can be produced in anisotropic membrane form with a fine enough pore size skin to prevent liquid permeation against a driving force of at least several psi. This same membrane is sufficiently open to pervaporate water at up to five times the target of 0.5 lbs./hr. ft.² specified in the RFP. It will withstand the chromic acid biocide recommended by Hamilton Standard. Kynar's high melt temperature should make readily feasible operation at sterilization temperatures without chromic acid or other biocide-chemical pretreatment. Experimental work of a straightforward nature is required to produce Kynar membranes with preferred properties, particularly in hollow fiber configuration.

Of the three Kynar resins, the high molecular weight polymer, Kynar 451, appears to be the most chemically inert and to have the best mechanical properties.

3. Microporous Teflon also meets VDR pervaporation module membrane requirements. It is obtainable in suitable membrane form, is hydrophobic, chemically inert and thermally stable. Considerations which favor the selection, however, of Kynar over Teflon are:
 - a. to obtain Teflon in fine pore size ($<5 \mu\text{m}$) in hollow fiber configuration, expensive fabrication from flat sheet is required;
 - b. the finest-pored microporous Teflon has pores order of magnitude larger than those in the skin of an anisotropic Kynar membrane with suitable pervaporation characteristics. The larger pores and isotropic pore structure of the Teflon makes it more susceptible to solid deposition and pore clogging; and
 - c. the low elastic modulus of the Teflon and low creep resistance requires use of a thicker membrane to achieve desired mechanical properties.

Considerations which argue in favor of Teflon selection over Kynar are:

- a. Teflon is immediately available in the desired configuration; and
 - b. Teflon is chemically more inert.
4. Polyvinyl chloride does not appear as promising a candidate for VDR application as the above materials. PVC is chemically attacked by chromic acid solution, raising doubts about pervaporation module reliability and life where chromic acid is used. The relatively low (80°C)

crystalline melt temperature of PVC precludes its consideration for pervaporation module operation at sterilization temperatures.

5. Polyvinyl fluoride (Tedlar) is unsuited for pervaporation module application because the high polymer molecular weight range available has thus far precluded finding a suitable solvent for it.
6. Significantly improved flat sheet VDR pervaporator module performance can be obtained through suitable modification of the Hamilton Standard design. Pervaporation rates up to six times those specified in the RFP have been obtained. The concept of a sweep gas and separate pervaporation and condensation modules appears sound and able to circumvent the solids deposition, reverse gas pervaporation, and temperature variation problems experienced by Hamilton Standard.
7. The suitability of the hollow fiber membrane configuration for the VDR pervaporation module has been demonstrated. A hollow fiber pervaporation module requires less careful balancing of pressures than flat sheet and can readily be operated with high liquid flows and high shears which keep solids from depositing. It can be made more compact and of lighter weight than a flat sheet module with simpler liquid and gas seal problems.
8. Operation at sterilization temperatures has been suggested as an alternative to the use of chromic acid or other bactericide-chemical pretreatment by

Dr. Charles Malich of NASA Ames, monitor of this program. Such operation has the following potential advantages:

- a. The water vapor driving force will be higher due to the higher operating temperature. This, in turn, will reduce pervaporation membrane area requirements or permit use of a tighter membrane;
- b. Polysulfone hollow fibers could be used in the pervaporation module; and
- c. Solids deposition in the membrane would be reduced both because of decreased solids precipitation and because of decreased membrane wetting in the absence of chromic acid.

Ammonia generation and volatilization of undesirable organic impurities at sterilization temperatures need evaluation but appear to be acceptable.

9. Ammonia and some other impurities will be present in the pervaporate at low concentrations independent of whether chromic acid is used as a bactericide. Their removal by treatment of the pervaporate with ion exchange resin and/or charcoal adsorption and/or other appropriate treatment should not be difficult and may well be desirable.
10. Bacteria will grow in urine if a bactericide or sterilization temperatures are not used.

VII. RECOMMENDATIONS

The following recommendations are made for the further development of the VDR process:

1. The separation of the pervaporator and condenser modules and the use of a recirculating sweep gas to conduct pervaporate from the pervaporator to the condenser module.

The present program has demonstrated the feasibility of this approach and its superiority relative to the Hamilton Standard design.

2. The selection of the hollow fiber membrane configuration for pervaporator module design. Advantages of this configuration over flat sheet include greater compactness and lower weight, simpler fluid pressure balancing requirements, simpler header design, and simpler fluid seal design.
3. The evaluation of polysulfone hollow fiber membranes and operation at sterilization temperatures without bactericide-chemical pretreatment of the urine. Operation at sterilization temperatures without chromic acid pretreatment offers the advantages of a less corrosive environment, decreased solids deposition, and increased pervaporation rate due to higher operating temperatures. Polysulfone hollow fiber membranes are a commercial Amicon product and require only minor modification to open the membrane skin and increase the pervaporation rate. Polysulfone hollow fibers will

withstand sterilization temperatures and the urine environment in the absence of chromic acid.

4. Should unforeseen problems arise with operation at sterilization temperatures (e.g., excessive ammonia and/or other impurity contamination of the pervaporate or complications in fluid handling due to high temperatures and possible pressurization requirements), the evaluation of Kynar 451 hollow fiber membranes and operation at 70°C with chromic acid pretreatment or urine. Although both Kynar and Teflon membranes will withstand chromic acid, the Kynar anisotropic hollow fiber membrane is less subject to solids deposition and pore clogging than the microporous Teflon, will be mechanically stable with a thinner wall, and will be less expensive. The higher molecular weight Kynar resin, Kynar 451, is recommended because of its somewhat greater chemical inertness and mechanical strength. If this approach is investigated, the utilization of higher operating temperatures will be evaluated as a secondary consideration. Kynar hollow fiber membranes are capable of operating at temperatures considerably in excess of sterilization temperatures.

Another area for secondary evaluation will be operation at higher sulfuric acid and lower chromic oxide levels to lower ammonia evolution and solids deposition.

5. The preliminary evaluation of treatment steps (e.g., ion-exchange and/or charcoal adsorption) required for final pervaporate purification and elimination of taste and odor.

6. Modification of the breadboard VDR pervaporation loop constructed in the present program to accommodate:
 - a. provision for sweep gas recirculation;
 - b. improved temperature, humidity, pressure and flow instrumentation and controls;
 - c. better matching of pervaporation module size and liquid recirculation pump capacity; and
 - d. baffling of the hollow fiber extracapillary region to improve mass transfer of pervaporate into the sweep gas.

APPENDIX A

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APPENDIX B

ANALYSIS OF WATER VAPOR TRANSMISSION MEASUREMENTS

The water vapor transport cup has a mass of 132 g empty, a specific heat of about 0.11 BTU/pound °F, and a surface area (including the membrane surface) of about 90 cm². Taking the sum of the radiation and convection heat transfer coefficients, h_c and h_r , to be about 2 BTU/ft.² °F, the minimum time (ignoring vaporization) required to heat the cup to 60°C when placed in an oven at 70°C will be

$$(h_c + h_r)(A)(T_{\text{oven}} - T_{\text{cup}}) = (mC_{P_{\text{cup}}} + mC_{P_{\text{water}}}) \frac{dT}{d\theta}$$

$$\ln \frac{(T_{\text{oven}} - T_{\text{cup}})_{\text{initial}}}{(T_{\text{oven}} - T_{\text{cup}})_{\text{final}}} = \frac{(h_c + h_r)(A)}{(mC_{P_{\text{cup}}} + mC_{P_{\text{water}}})} \theta$$

$$\therefore \theta = \left[\ln \left(\frac{90}{18} \right) \right] \frac{132 \times .11 + 10}{2 \times \frac{90}{900}} = 0.43 \text{ hours}$$

When the cup has come to a steady state temperature, the heat con-
 vected and radiated to it will be absorbed in the vaporization of
 water.

Conduction from the cup to the water will be sufficient to maintain
 the water essentially at cup temperature. Hence, the steady state
 cup temperature may be estimated by equating the heated convected
 and radiated to the cup to that absorbed in vaporizing the water.
 If 10 grams of water are vaporized in five hours, then

$$(h_c + h_r)(A)(\Delta T) = \left(\frac{\Delta W}{\Delta \theta}\right) \Delta H$$

where $\frac{\Delta W}{\Delta \theta}$ is the vaporization rate and

ΔH is the heat of vaporization

$$(2)\left(\frac{90}{900}\right)\Delta T = \frac{10}{454} \times \frac{1000}{5}$$

$$\dots \Delta T \approx 22^\circ\text{F} \approx 12^\circ\text{C}$$

Maximum anticipated water vapor transport rate

$$F = \frac{DA}{t} \left(\frac{P_2 - P_1}{RT}\right)$$

where D is the diffusivity of water vapor in air, cm^2/sec .

t is the membrane thickness, cm

P is the partial pressure of water vapor, atm

R is the gas constant = $82 \text{ cm}^3\text{atm/g mole, } ^\circ\text{K}$

T is the temperature, $^\circ\text{K}$

A is the membrane area.

For a membrane surface temperature of about 60°C

$$F = \frac{0.2 \text{ cm}^2/\text{sec} \times 10.2 \text{ cm}}{.003 \times 2.54 \text{ cm}} \left(\frac{0.19 \text{ atm} \times 18 \text{ g}}{82 \times 333 \frac{\text{cc atm}}{\text{g mole}}} \right) (\text{g mole} \times 3600 \text{ sec/hr.})$$

$$= 120 \text{ g/hour}$$

This is about 60 times the observed rate, suggesting that only a small fraction of the membrane skin is available for water vapor transport. Thus, higher water vapor transport rates should be obtainable with more open membranes. A trade-off or optimization will be involved since a more open membrane will not be as strong or as liquid retentive and may be more subject to solids deposition in the pores.