CR 137546
Available to the Public

To: NASA
AMES RESEARCH CENTER
Moffett Field
California 94035
Attention: Mr. C. Malich, Tech.Mgr.

(NASA-CR-137546) WATER VAPOR DIFFUSION MEMBRANE DEVELOPMENT Final Report, 1 Jul. 1973 - 31 Mar. 1974 (Ionics, Inc.) 99 p HC $8.00 CSCL 13B
N74-34887
Unclas
G3/15 51722

FINAL REPORT
covering period
1 July 1973 to 31 March 1974

WATER VAPOR DIFFUSION MEMBRANE DEVELOPMENT

NAS 2-7651

Submitted by: IONICS, INCORPORATED
65 Grove Street
Watertown, Massachusetts 02172
Tel: (617) 926-2500

Prepared by: Michael K. Tan

Approved by: Wayne A McRae
Wayne A. McRae
Vice President, Research

OCT 1974
RECEIVED
NASA STI FACILITY
INPUT BRANCH

CR 137546

AVAILABLE TO THE PUBLIC

Water Vapor Diffusion Membrane Development

by

Michael K. Tan

April 1974

Prepared under Contract No.NAS 2-7651
by

IONICS, INCORPORATED
65 Grove Street
Watertown, Massachusetts

for

Ames Research Center
NASA

ACKNOWLEDGMENT

The author wishes to thank Mr. Samuel A. Alexander for his contributions in the initial portion of the program as well as in the area of membrane fabrication. Appreciation also goes to Mr. Robert G. Jeffery for his contributions in the laboratory work involved in this contract.

Special acknowledgment also goes to Dr. Russell B. Hodgdon, Dr.Edgardo J. Parsi, and Mr. Wayne A. McRae for many administrative and counselling assistance.

TABLE OF CONTENTS

LIST OF EXPERIMENT

LIST OF EXPERIMENTS (Continued)

LIST OF FIGURES

LIST OF TABLES

1. INTRODUCTION

The maintenance of adequate supply of potable water for astronauts on space missions of extended duration is an important problem. Limitations of launch weight and on-board storage volume preclude the carrying of large supplies of water, necessitating the recycle and reuse of waste-water produced by the astronauts.

Urine constitutes 60% of the waste water produced by a normal male (3.1 pounds water in urine, 2.0 pounds in respired air and 0.2 pound in feces are the average daily waste). Various systems have been conceived and successfully demonstrated by past investigators to recover water from urine.[1-15] In terms of energy and weight requirements, the various distillation techniques have been most successful.

Hamilton Standard, a division of United Aircraft Corp. had developed and built a prototype vapor diffusion water reclamation unit under contractual agreement with NASA-Ames Research Center.[13] The system had been successfully demonstrated on a 54 day test to be capable of reclaiming 98% of the water (with the addition of a precipitate-solids filter subsystem) and producing water of potable quality.

However, there are a few components in the system that showed marginal performance. One of these was the membrane used as a phase-separator. These membranes, polyvinyl chloride and cellophane, showed limited life and limited structural strength. The overall objective of this program is to develop membrane technology specifically for this water recovery process. Special emphasis should be given to cation-selective membranes because of their noted mechanical strength, superior resistance to acids, oxidants and germicides, and their potential resistance to organic foulants.

2. SUMMARY

(i) A thorough literature search has been performed. A total of 60 publications related to water reclamation from urine have been compiled to aid future investigators. This is listed in Appendix I. Most of them have been procured and studied under this program.

16-21

(ii) With the help of the work performed by past investigators, series of experiments have been designed and conducted to study the variables that govern the permeation process involved.

(iii) A search was also made of existing commercially available membranes, with emphasis on cation-exchange membranes; and a selection of 19 membranes was tested and compared, one to another.

All data have been reported in the International System of Units with the customary U.S. units given in parentheses, as specified by NASA SP-7012.

(iv) Two of the membranes tested were selected based on criteria deemed important to an effective water reclamation system on board spacecrafts. These were tested for over 700 hours continuously. Although flux was observed to decline with time, the rate of decline leveled off to zero after the initial 100 hours or so.

(v) Two 10 lb samples of urine were successfully processed by removing 93% of their water content in 70 hours (membrane area = 270 cm^2 of .345 ft^2).

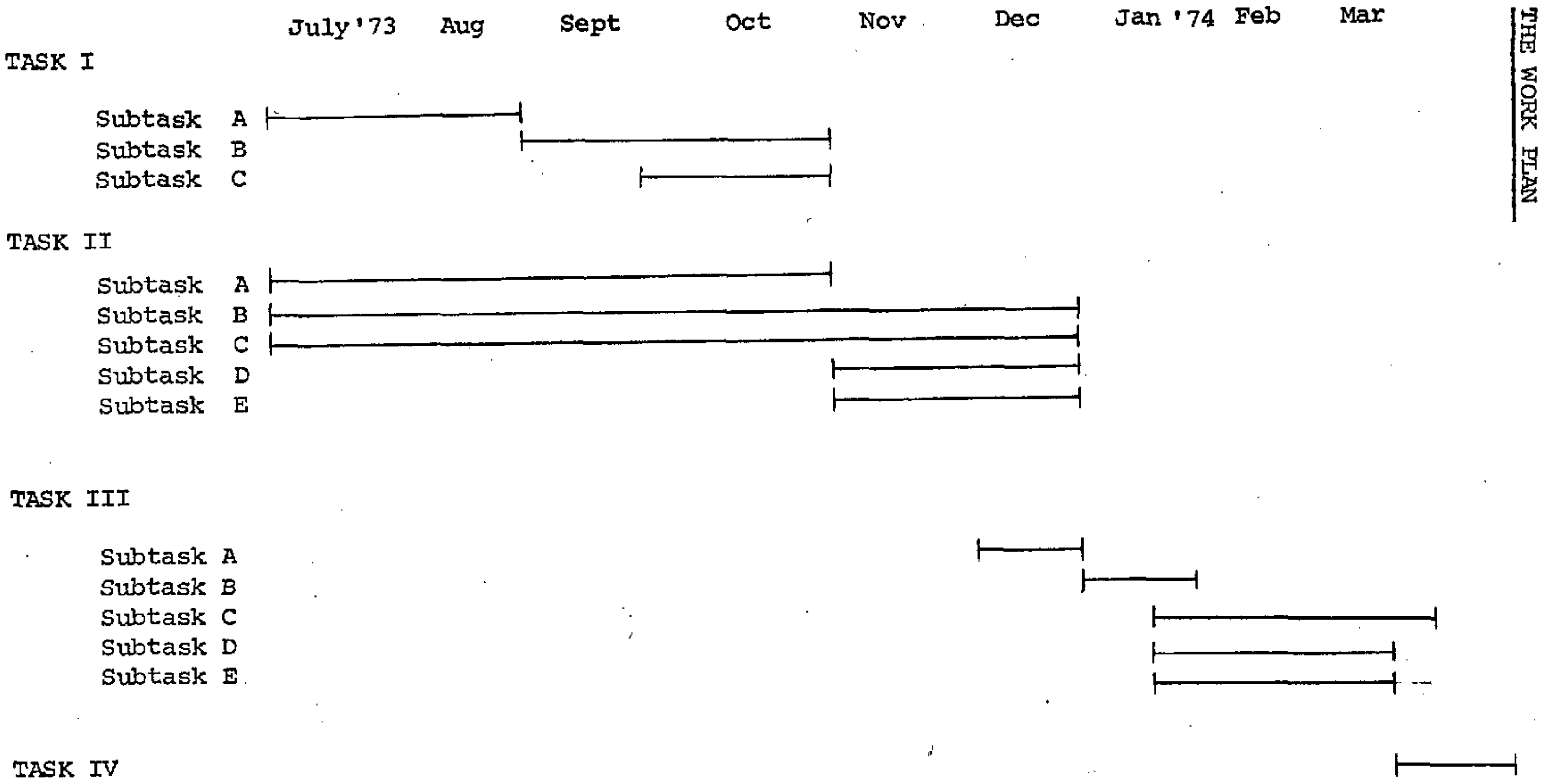
(vi) The mechanism of membrane fouling was also studied. Flushing the system with water recovered flux partially and temporarily. Acidification to redissolve precipitate did not recover flux significantly.

(vii) Literature studies and in-house experimental work have been combined to investigate the pretreatment chemistry of the urine charge. Pretreatment with an acid-oxidant formulation improved product quality. Cation exchange membranes were shown to possess superior mechanical strength and chemical resistance to cellulosic membranes.

(viii) The conclusions and recommendations for future work are summarized in Section 4 of this report (Page 80-2).

• WORK STATEMENT

THE WORK PLAN



TASK I MEMBRANE PROCESS STUDIES

Sub-Task A: Equipment Assembly

The initial portion of the program was devoted to the procurement of various equipment and membranes in order that a test system could be assembled to investigate the various parameters that influence the permeation process. A schematic diagram of the system is shown in Figure 1 .

The preheated urine charge is brought into constant contact with one surface of the membrane by means of a circulating pump. The charge species preferentially dissolve into the membrane structure, diffuse through it, and the permeated charge species are removed from the other surface of the membrane , under reduced pressure, in the vapor phase, as shown in the schematic diagram below: -

16-21

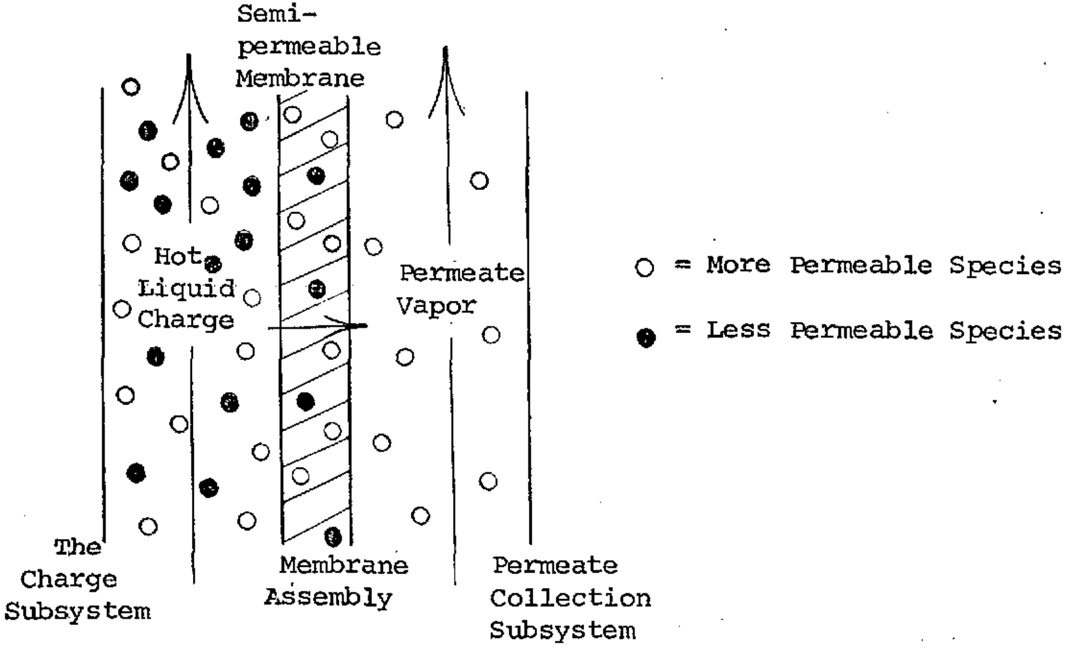
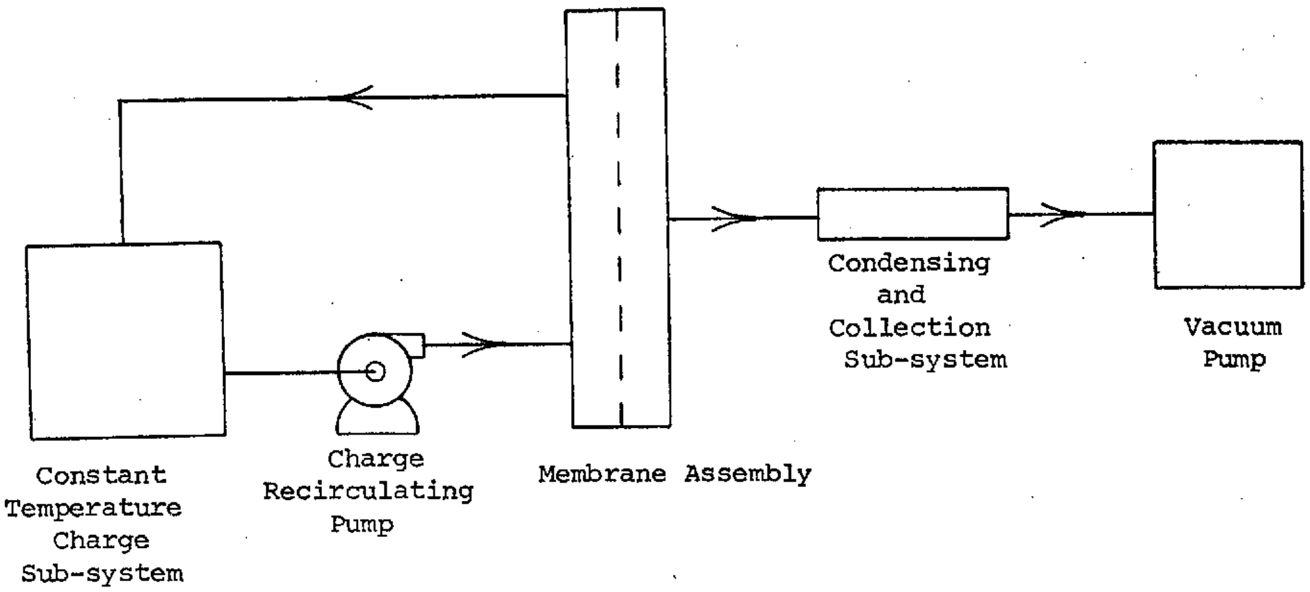


Figure 1. SCHEMATIC DIAGRAM OF A PERVAPORATION SYSTEM



The bench unit can be divided into three main subsystems which are described in greater details in the following paragraphs:

1. The Charge Subsystem

The main features of this subsystem are:

(i) charge reservoir - a three-neck 5000 ml round-bottom flask with a reflux condenser attached to its center-neck to minimize evaporation loss;

(ii) heat source - a constant temperature water-bath equipped with a heating element, a thermostat, and an agitator to maintain the urine charge at the desired temperature;

(iii) circulating pump - an oscillating laboratory pump with suitable connections to draw the charge through one closed-neck of the reservoir, push it through the membrane assembly, and return it to the reservoir through the third closed neck. This also creates sufficient agitation to maintain the charge well-mixed.

A pressure indicator and a temperature indicator are included in the feeding line to monitor initial charge pressure and temperature, respectively. Another temperature indicator and a flow indicator connected to the return line, serve to monitor the temperature drop across the membrane assembly and the flow rate of the returning charge, respectively.

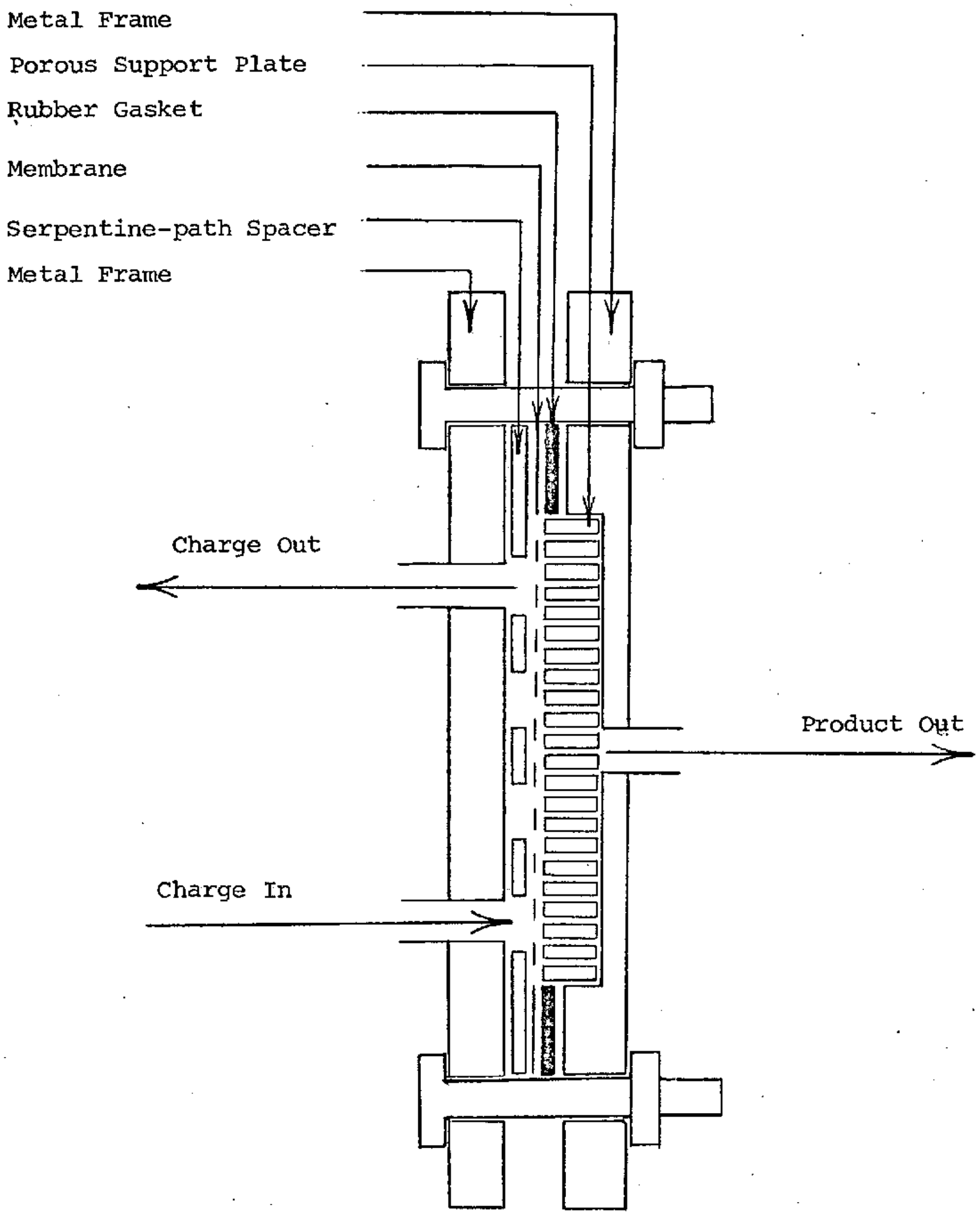
2. The Membrane Assembly

This second subsystem consists of three main components sandwiched between two insulated metal frames, held in place by 12 bolt-and-nuts as shown in Figure 2. These components are:

(i) a semi-permeable membrane situated at the center of the assembly;

(ii) A spacer with a serpentine flow-path cut out, situated at the charge-side of the membrane; (the charge is introduced at the bottom inlet port, circulated

Figure 2. Diagram of Membrane Assembly



along the tortuous path, which enhances mixing, and exited through the outlet port on top of the assembly.); and

(iii) a porous support plate, situated at the product side of the membrane. (This serves to hold the membrane tightly to the spacer and, at the same time, allows product vapor to be drawn from the product-surface of the membrane.)

A rubber gasket, situated between the membrane and the metal frame minimizes air leakage at that point. A closed-end manometer and a temperature indicator included at the product suction line monitor the processing vacuum and the product temperature, respectively.

3. The Product Collection Subsystem

The permeated charge species are removed from the membrane assembly in the vapor phase under reduced pressure and are condensed and collected in this subsystem. The three main features here are:

(i) the water condenser; (Circulating tap water provides sufficient heat exchange to condense the bulk of the product. This condensed liquid is collected in a flask by gravity);

(ii) the cold traps; (A mixture of ice and common salt, in the ratio of 2:1 yields a temperature of -30° C, which is quite sufficient to condense the residual product water. The coolant is stored in dewar flasks to minimize losses.); and

(iii) the vacuum pump; (It serves to maintain the product side of the system at reduced pressure in order that the product can be removed as a vapor.)

During the later portion of the program, three traps containing dilute sulfuric acid are added between the cold traps and the pump to entrap the highly volatile ammonia that might not have been condensed before this stage.

Sub-Task B: Processing Rate Studies

The Urine Charge. The composition of human urine has been studied by many investigators.[22-24] Some two hundred odd different constituents have been identified. One hundred fifty-eight of these are summarized in the NASA Bioastronautics Data Book.[25] The chemistry of urine is complex indeed. For this reason, a simulated urine recipe has been used for the preliminary tests investigating the parameters affecting processing rate. This recipe, shown below, accounts for 90% of the total solute species present in human urine.

Recipe for Simulated Urine

Constituent	Amount
Water	960 parts
Urea	22 "
Salt	10 "
Ammonia	3.3 part as (NH_4HCO_3)
Creatinine	2 parts
Uric Acid	1 "
Hippuric Acid	.7 "

In addition, dilute hydrochloric acid is used to adjust the pH of the recipe (~ 8.5) to a level more representative of human urine (~ 5-7). Using this simulated urine as charge, the relevant operating parameters were investigated.

Table I summarizes the work performed in this section. The following paragraphs describe it in greater detail

TABLE I : Processing Rate Studies

Process Variables	Experiment Number	Expt. Date ('73)	Membrane Used *	Range of Variables Investigated	General Findings
Simulated Urine					
Time	1	9-13	RADIAN	7 hours	Stable, see Figure 3
Vacuum	2	10-16	NAFION 170	5-600 Torr	Stable, see Figure 4
Charge Rate	3	9-20	RADIAN, AMF's	200-1000ml/min	Stable, see Figure 5
Charge pH	4	9-26	RADIAN	3-8	Stable, see Figure 6
Charge Concentration	5	9-28	NAFION 170	3-11% TDS	Direct Proportion, See Figure 7
Temperature	6	10-31	NAFION 170	45-85°C	Arrhenius Type, see Figure 8
Actual Urine					
Charge pH	7	11-9	RADIAN	3-8	Stable, see Figure 6
Charge Concentration	8	11-14	NAFION 170	3-12% TDS	Direct Proportion, see Figure 7
Temperature	9	11-6	NAFION 170	45-85° C	Arrhenius Type, see Figure 8

* See Table II , page 37, for more detail.

1. Processing Time

In order to obtain a reproducible and reliable measurement of the processing rate, it is important that a steady state has been approached when the measurement is made. A sample of simulated urine is charged to the permeation system and the volume of the product collected is measured and returned to the charge. The processing rate so obtained is tabulated below and plotted against processing time as shown in Figure 3.

EXPERIMENT # 1

Membrane = RADIAN
Temperature = 80° C(175°F)
Pro.Vac = 15 Torr
Charge Rate = 900 ml/min

Processing Time, Hour	Processing Rate, gm/cm^2-hr	$(lb/ft^2$-hr)
1	.72	(1.4)
2	.83	(1.6)
3	.90	(1.8)
4	.82	(1.6)
5	.88	(1.8)
6	.83	(1.6)
7	.83	(1.6)

2. Processing Vacuum

The permeated charge species are removed as a vapor, necessitating the maintenance of a reduced pressure at the product-side of the membrane. The level of vacuum maintained could affect the permeation process. Experiment #2, summarized below, investigates this relationship. Figure 4 shows the plot of processing rate as a function of processing vacuum. At vaccum below 25 Torr processing rate seems to be dependent on processing

Figure 3. PROCESSING RATE AS A FUNCTION OF PROCESSING TIME

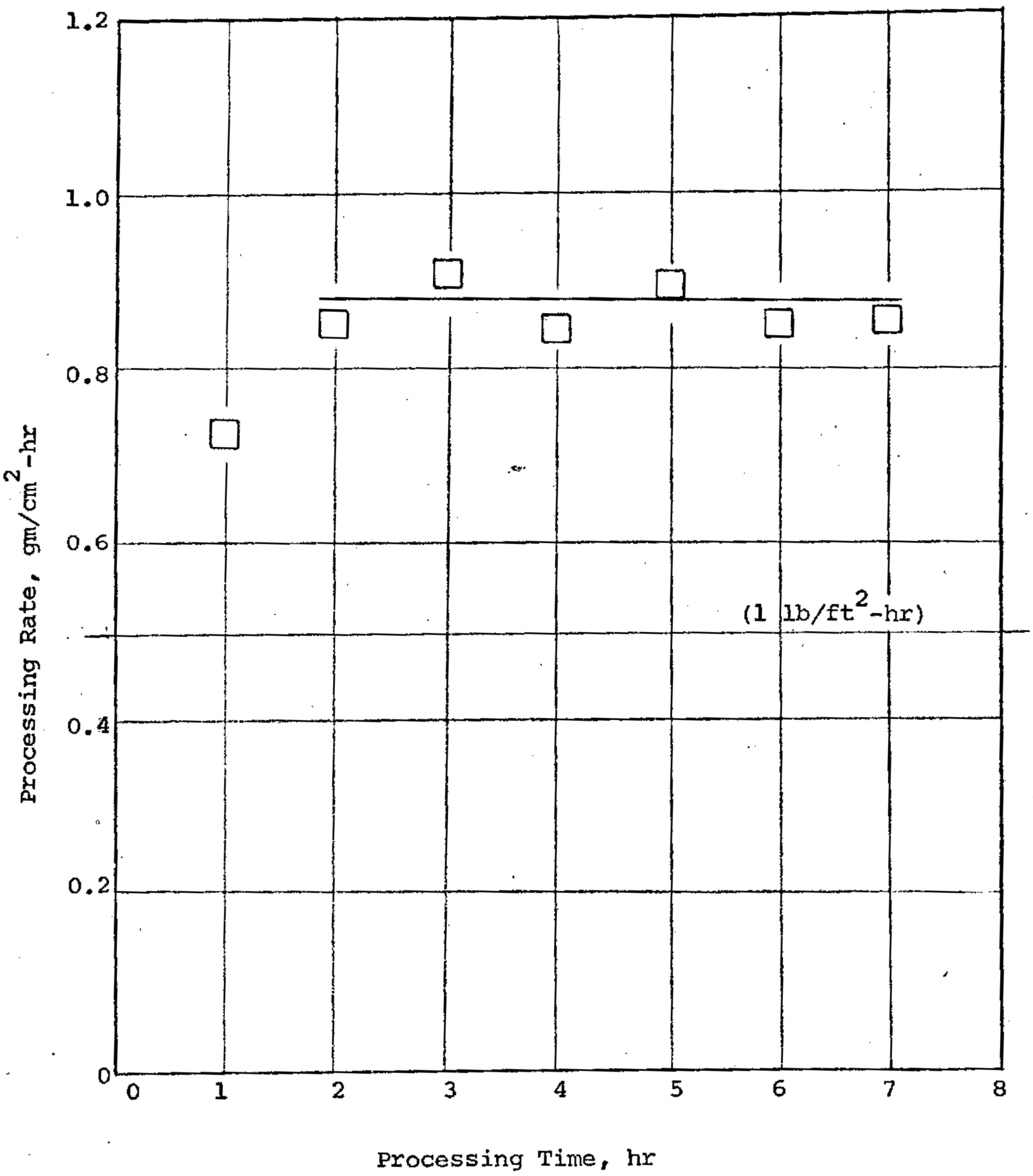
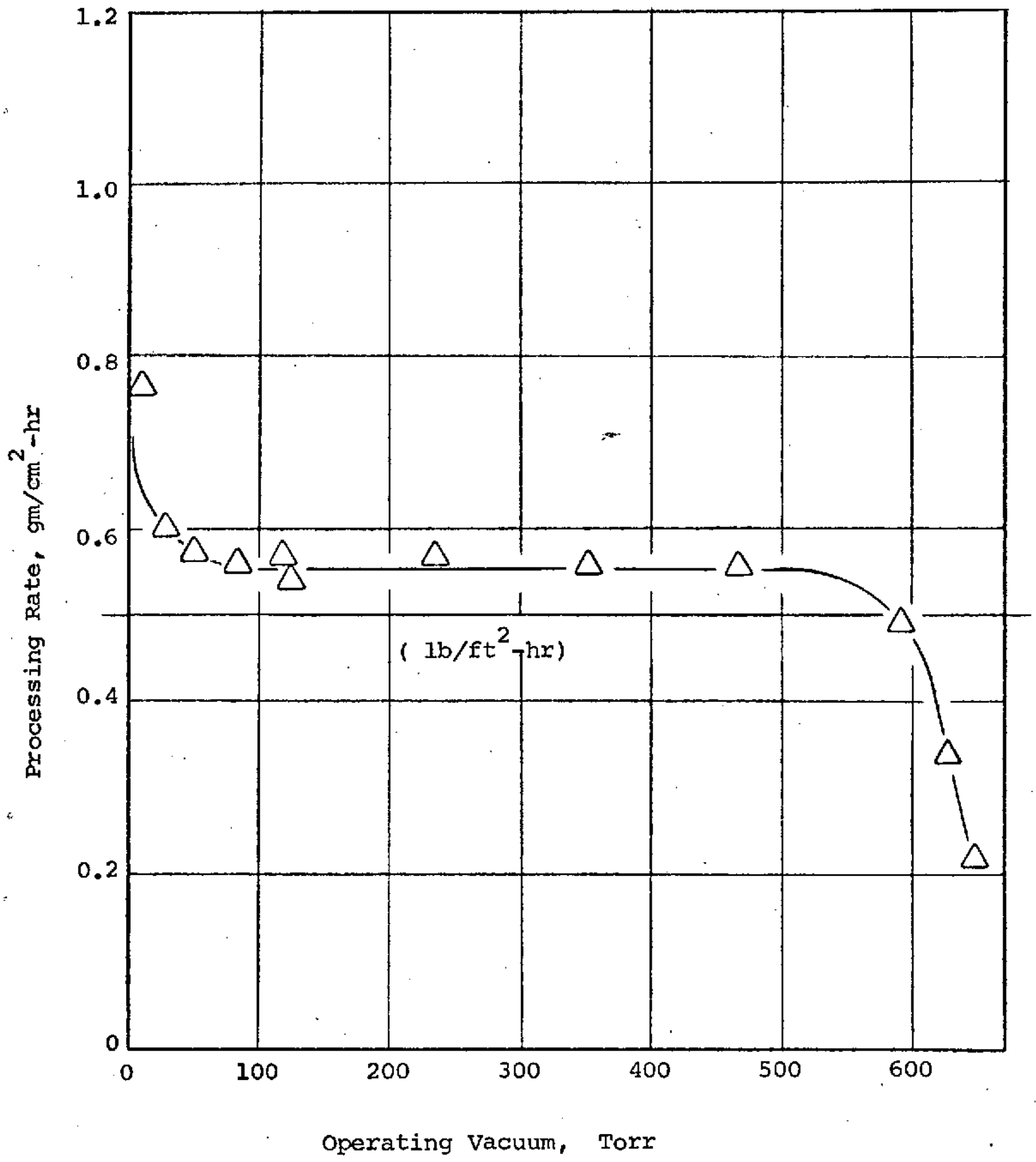


Figure 4. PROCESSING RATE AS A FUNCTION OF PROCESSING VACUUM



vacuum; but for most of the range, i.e. 25-600 Torr, the process is insensitive to the vacuum applied. Above 600 Torr processing rate drops rapidly, indicating that the product is no longer being removed as a vapor.16

EXPERIMENT # 2

Membrane = NAFION 170
Temperature = 85° C (185°F)
Charge Rate = 850 ml/min

Processing Vacuum, torr	(inch Hg)	Processing rate, gm/cm^2-hr	(lb/ft^2-hr)
2	(0.1)	.76	(1.5)
25	(1.0)	.60	(1.2)
50	(2.0)	.58	(1.2)
75	(3.0)	.56	(1.1)
125	(5.0)	.56	(1.1)
230	(9.2)	.56	(1.1)
350	(14)	.55	(1.1)
470	(17)	.55	(1.1)
590	(23)	.49	(1.0)
620	(25)	.33	(.70)
650	(26)	.21	(.40)

3. Charge Circulation Rate

The rate at which the liquid charge is brought in contact with the membrane surface affects many membrane process systems due to the phenomenon of concentration polarization. (The removal of certain charge species selectively at the membrane surface causes a disproportionately high concentration of the less permeable species at this point, leading to decline in flux and selectivity). Experiment #3 is a study of this relationship as applied to pervaporation.

The data collected are shown in the table below as well as in Figure 5. They indicate that except at charge rate below 200 ml/min (.05 gal/min) processing rate is relatively independent of charge circulation. Concentration polarization is, thus, not an important factor in this process. This is probably because the rate at which charge species dissolve into the membrane prior to diffusion through the membrane is not the rate-limiting step in this permeation process.[16]

EXPERIMENT # 3

Membrane = RADIAN
Temperature = 85°C (185°F)

Membrane = AMF's Cationic
Temperature = 80°C (175° F)

Charge rate ml/min	(gal/min)	Processing Rate gm/cm^2	(lb/ft^2-hr)	Charge Rate ml/min	(gal/min)	Processing Rate gm/cm^2-hr	(lb/ft^2-hr)
50	(.01)	.60	(1.2)	50	(.01)	.34	(.70)
150	(.04)	.89	(1.8)	200	(.05)	.45	(.90)
330	(.09)	1.0	(2.0)	450	(.12)	.46	(.91)
550	(.13)	1.1	(2.2)	700	(.18)	.45	(.90)
750	(.18)	1.1	(2.2)	950	(.25)	.48	(.93)
950	(.25)	1.2	(2.3)				

4. Charge pH

The acidity and alkalinity of a liquid charge has been known to affect the permeability of membranes by influencing their properties, such as, water sorption. (Extreme pH's are also known to aggravate the rate of hydrolysis of the membrane). This relationship is studied in Experiment #4.

As can be seen in the Table of data below and the plot in Figure 6, charge pH, within the range expected to be relevant for human urine, i.e., pH 4 - 8.5, has no effect on processing rate.

Figure 5. PROCESSING RATE AS A FUNCTION OF CHARGE RECIRCULATION

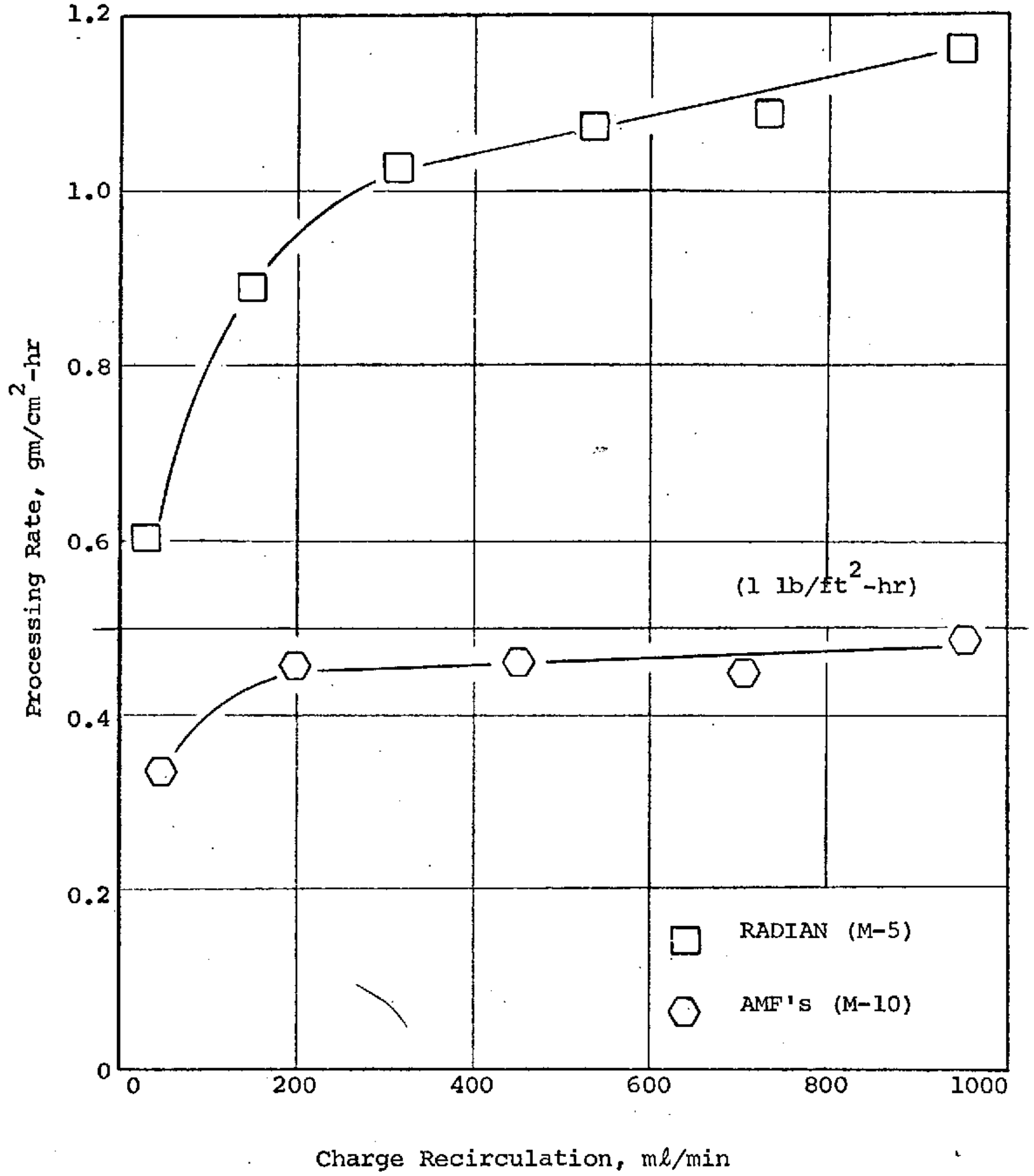
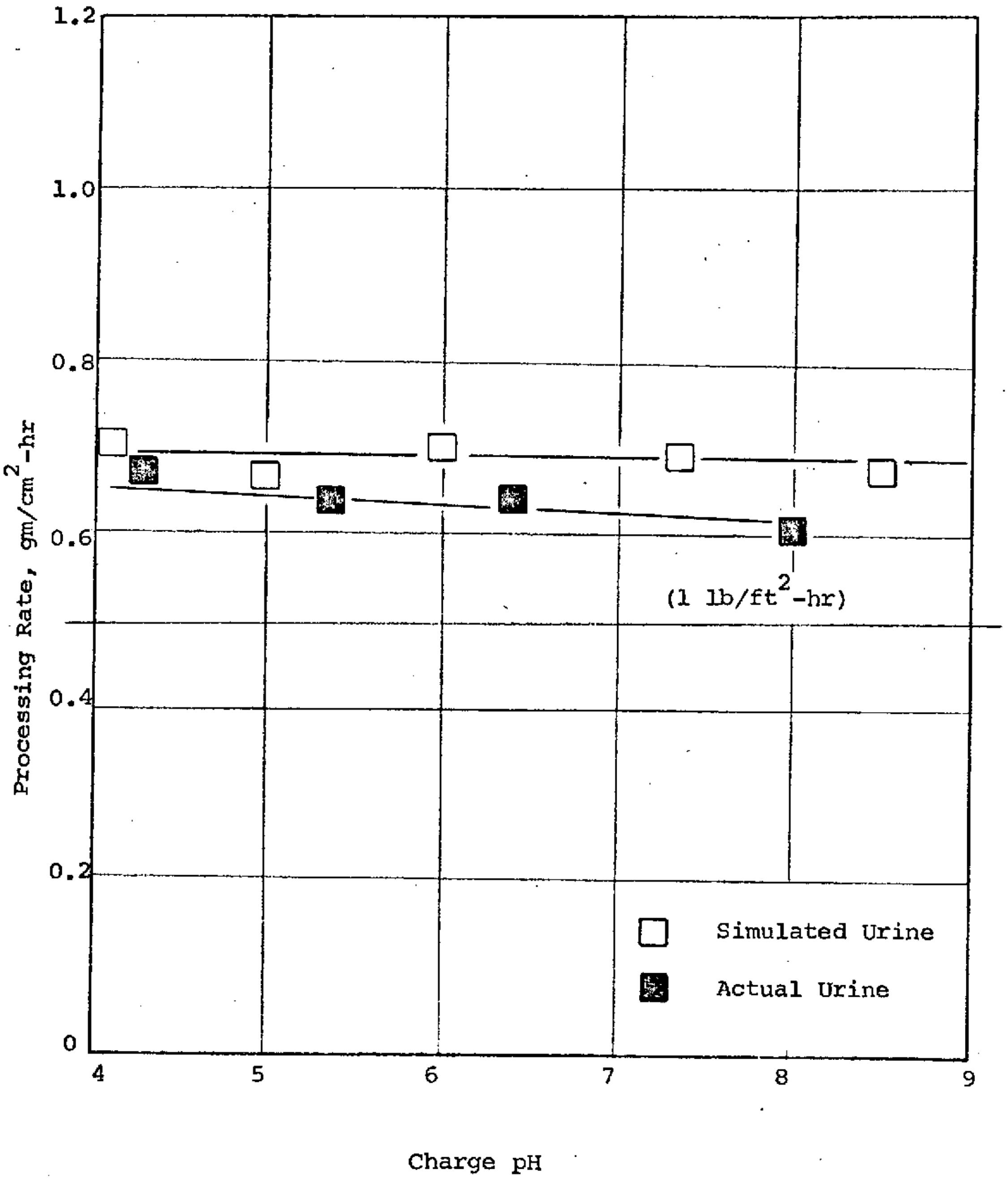


Figure 6. PROCESSING RATE AS A FUNCTION OF CHARGE pH



EXPERIMENT # 4

Membrane = RADIAN
Temperature = 75°C(165°F)

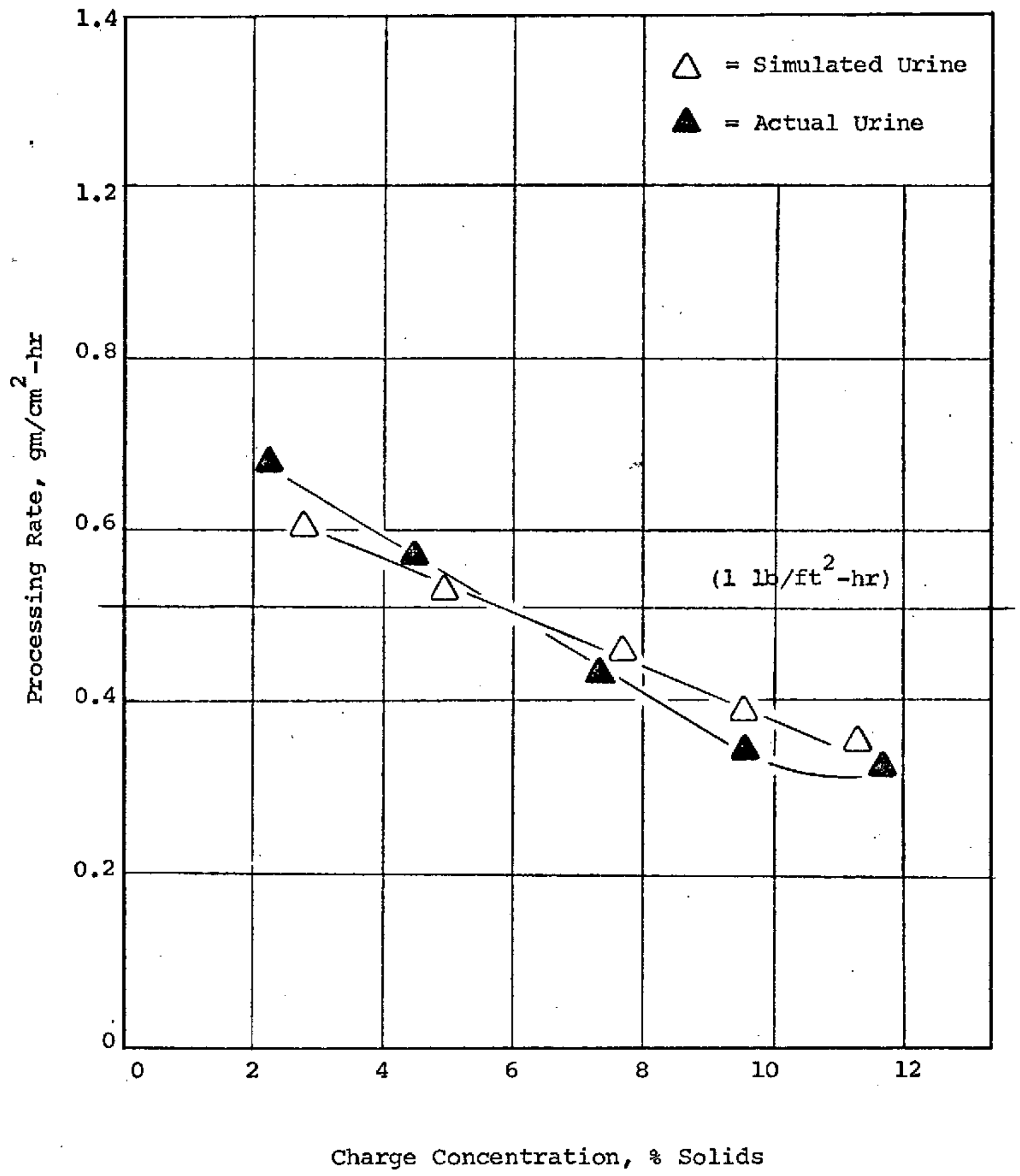
pH	Processing Rate	
	gm/cm^2-hr	(lb/ft^2-hr)
4.0	.70	(1.4)
5.0	.68	(1.4)
6.0	.70	(1.4)
7.2	.71	(1.4)
8.5	.69	(1.4)

5. Charge Concentration

The relative concentrations of the various charge species would influence their rate of solution as well as rate of diffusion through the membrane. The water solvent would be preferentially soluble and would preferentially diffuse through the membrane relative to all other charge species. As such, the main concern here is the relative concentration of water to all the other species. Thus, concentration is expressed as solute weight fraction or simply as percent total solids. (Note that "solids" here include all solutes, some of which are actually liquids.)

Figure 7 and the Table below show that processing rate decreases as the amount of total solids in the charge increases, i.e. as water is being removed from the system. Previous investigators have dealt in great detail on the changes in physical and chemical properties of human urine as it gets progressively concentrated. However, this rate decline can be simply interpreted as due to a drop in the rate determining concentration gradient in the system.[16-21]

Figure 7. PROCESSING RATE AS A FUNCTION OF CHARGE CONCENTRATION



EXPERIMENT # 5

Membrane = NAFION 170
Temperature = 85°C (185° F)

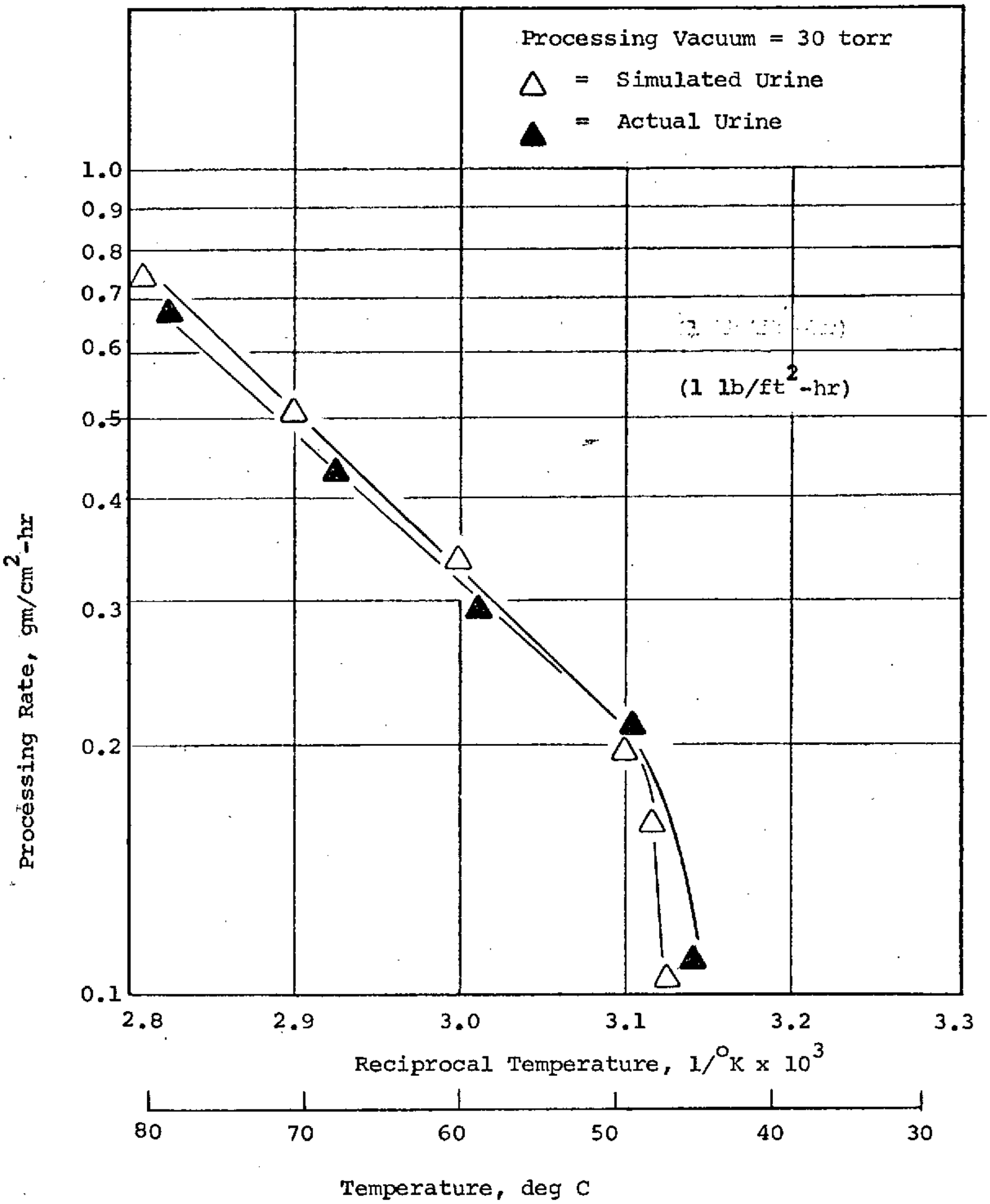
% Solids	Processing Rate	
	gm/cm^2-hr	(lb/ft^2-hr)
2.7	.60	(1.2)
5.0	.52	(1.1)
7.6	.46	(.90)
9.5	.38	(.79)
11.4	.33	(.66)

6. Processing Temperature

Experiment #6 shows that the processing temperature is singularly important in determining the processing rate. 16-21 An increase in temperature leads to a disproportionately large increase in processing rate. This Arrhenius type relationship is illustrated in Figure 8. 20,1

The findings should be no surprise since it has been established that solubility as well as diffusivity are very temperature-sensitive parameters. The data collected are tabulated below. They also show that the processing rate drops to almost zero below 50°C (120°F). This is because, at this level, insufficient amount of energy is being supplied to allow activated diffusion to occur. At the same time, the product is probably no longer being removed as a vapor at this point and beyond.

Figure 8. PROCESSING RATE AS A FUNCTION OF TEMPERATURE



EXPERIMENT # 6

Membrane = NAFION 170

Processing Temperature ^{o}C	^{o}F	Processing Rate gm/cm^2-hr	(lb/ft^2-hr)
46	(114)	.11	(.22)
48	(117)	.16	(.32)
50	(120)	.20	(.40)
60	(135)	.34	(.68)
70	(145)	.50	(1.0)
80	(175)	.73	(1.5)

7. Actual Urine Tests

In order to compare the data obtained from simulated urine to those expected of actual urine, three additional experiments have been carried out during the initial process studies period. The data from experiments 7, 8 and 9 are tabulated below. The plots have been included in Figures 6,7 and 8 for convenient comparison with simulated urine data. As can be readily seen, the differences are quite small indeed.

EXPERIMENT # 7

Membrane = RADIAN
Temperature = $80^{o}C$ (175^{o}F0

Charge pH	Processing Rate gm/cm^2-hr	(lb/ft^2-hr)
4.3	.67	(1.3)
5.4	.65	(1.3)
6.4	.65	(1.3)
8.0	.60	(1.2)

EXPERIMENT # 8

Membrane = NAFION 170
Temperature = 85°C (185° F)

EXPERIMENT # 9

Membrane = NAFION 170

% Solids	Processing Rate gm/cm^2-hr	(lb/ft^2-hr)	Processing Temp. °C	°F	Processing Rate gm/cm^2-hr	(lb/ft^2-hr)
2.2	.68	(1.4)	45	(110)	.11	(.22)
4.3	.57	(1.2)	49	(120)	.21	(.42)
7.6	.42	(.84)	58	(135)	.29	(.58)
9.5	.33	(.66)	67	(150)	.43	(.65)
11.7	.31	(.63)	79	(175)	.66	(1.3)

Discussion

1. Relevant Variables

Factors governing the processing rate and selectivity of the system may be classified into three categories: -

(i) variables inherent in the charge system, in this case, human urine (e.g. concentrations and properties of the various species, their interaction with one another, and with the membrane) which can be controlled only within the limits of chemical and physical pretreatment;

(ii) variables inherent in the membrane structure (e.g., film thickness, film density, degree of crystallinity and crosslinking, chain-packing, interstitial spaces, and presence of particular functional groups), which are not within the scope of this program; and

(iii) variables pertaining to the system - the operating conditions (e.g., temperature, pressure, means of charge introduction and permeate removal, etc.).

The first category of variables is discussed in greater detail under membrane fouling and chemical pretreatment of urine charge. The second category of variables has been widely discussed by past investigators, e.g. -

(i) permeation rate has been found to be inversely proportional to film selectivity independent of film thickness;[16-21]

(ii) degree of crosslinking has been related to water sorption which is, in turn, related to permeation rate;[21,9]

(iii) the larger and greater the amount of interstitial spaces the higher would be the permeation rate with corresponding decrease in selectivity;[21]

(iv) chain packing has been shown to be important to charge species with side chains;[16-21]

(v) crystallinity and crosslinking have been related to chain mobility and permeation rate, etc.[21]

The third category of variables has been studied and reported in the previous section. The findings, which are substantiated by those of the other investigators,[16-21] indicate a permeation mechanism as discussed below.

2. Mechanism of Pervaporation

Various past investigators have concluded that pervaporation involves three interrelated steps:[16-21]

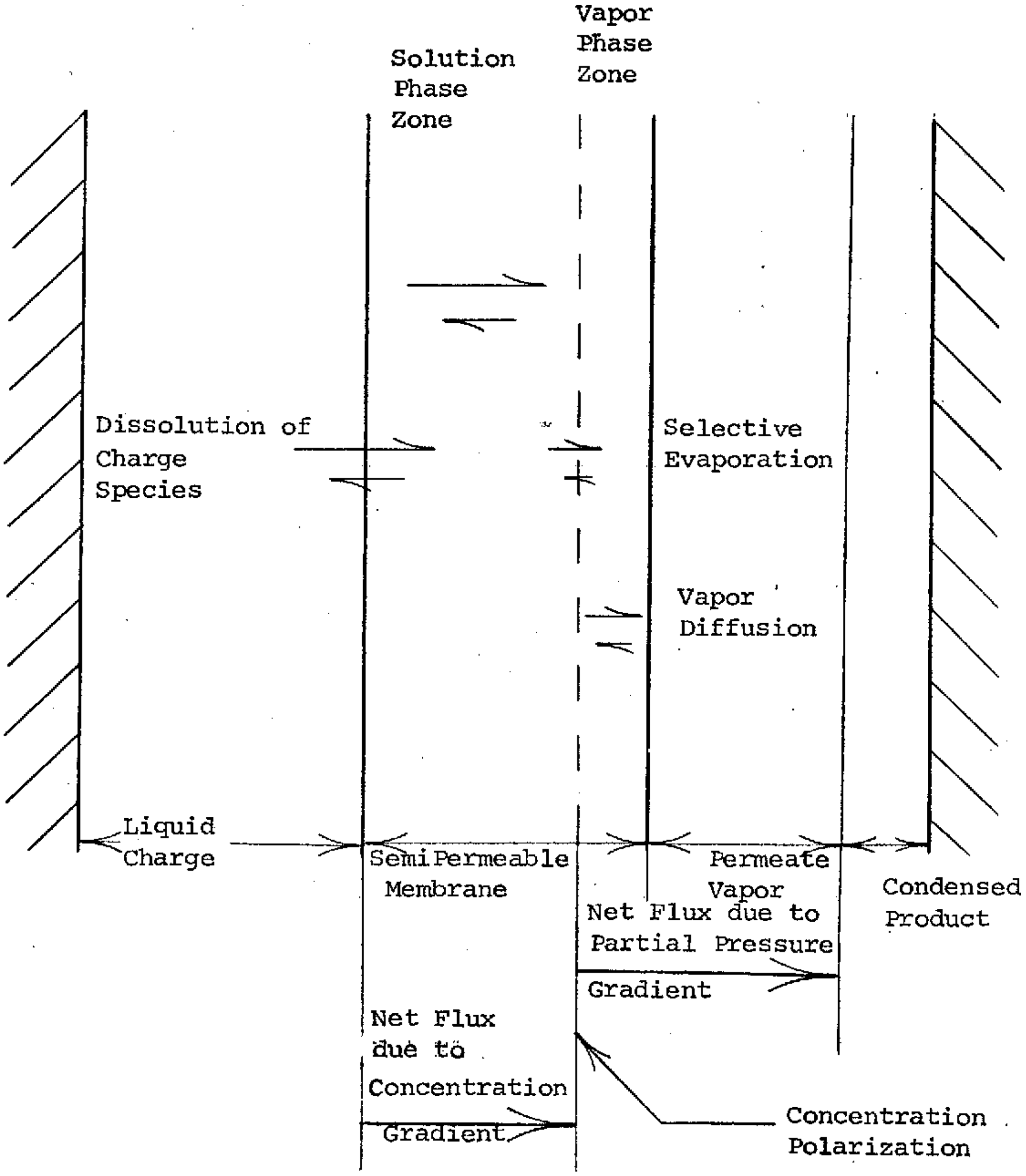
(i) the selective dissolution of the charge species into the membrane structure. (This is independent of pressure and dependent on temperature and solubility coefficient. The solvent then proceeds to "plasticize" the membrane, loosening the network of polymeric chains);

(ii) the selective diffusion of the dissolved species through the membrane (where sufficient energy of activation is available,[30] the species "wiggle" through the polymeric chain-barrier, from one position to another. The evaporation of the diffused species establishes a concentration gradient across the membrane, resulting in a net flux); and

(iii) the selective evaporation and condensation of the diffused species (evaporation occurs at the "upstream" end of the membrane structure at a rate which is a function of the temperature and the relative concentration and vapor pressure of the different species. The temperature difference between the upstream membrane surface and the condenser establishes a partial pressure gradient, resulting in a selective distillation).[1,3]

The evaporated species proceed to diffuse through the vapor phase zone at a rate several times slower than that of liquid diffusion. This, presumably, becomes the overall rate - determining step. This is illustrated in Figure 9.

Figure 9. SCHEMATIC DIAGRAM ILLUSTRATING THE MECHANISM OF PERVAPORATION 16



Sub-Task B - Product Quality Studies

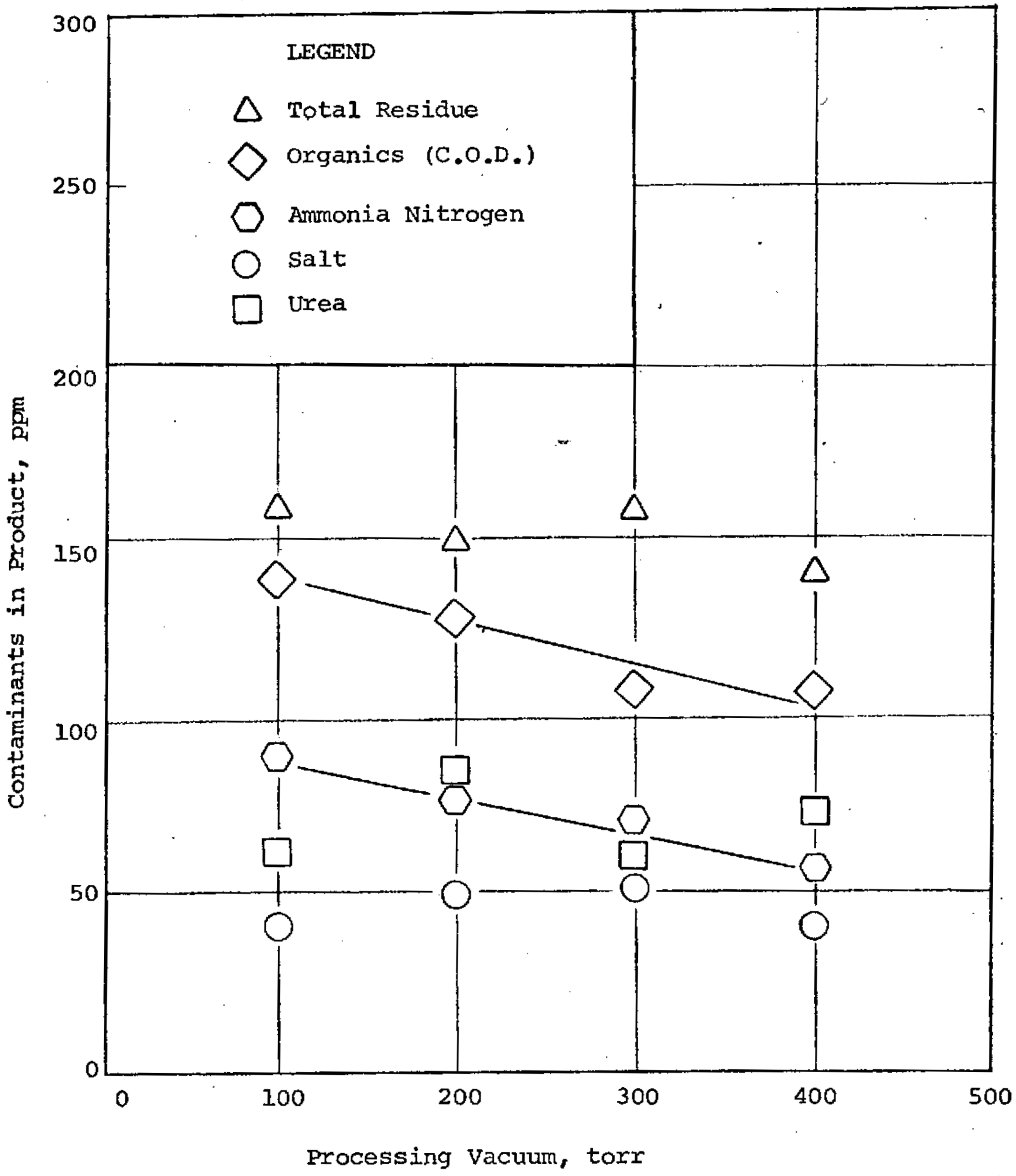
The quality of the product water cannot be over-emphasized. Ideally, the contaminants present should be well below the levels considered tolerable by the United States Public Health Service and the Space-Science-Board.[26] However, excess contaminants could be easily removed by a single-pass through activated charcoal.

Three preliminary experiments were performed using actual human urine to investigate the quality of the product water. Experiments # 10, 11 and 12 examined its variation with changes in processing vacuum, processing temperature, and charge concentration respectively.

1. Processing Vacuum:

As shown by the data in Experiment #10, changes in processing vacuum have no significant effect on the level of total solids, urea and salt in the product samples. However, the level of organics (as expressed by the C.O.D. values) and ammonia nitrogen seem to rise slightly but steadily, with increasing vacuum from 400 to 100 torr (Figure 10). This can be explained by the fact that ammonia and volatile organics in the urine have a significantly higher vapor pressure than either urea or salt.

Figure 10. PRODUCT QUALITY AS A FUNCTION OF PROCESSING VACUUM



EXPERIMENT # 10

Membrane = NAFION 170 Temperature = 85°C (185° F)

Processing Vacuum		Contaminants in Product (ppm)					
Torr	(inches Hg)	pH	Solids	C.O.D.	Urea	Ammonia N	Salt
100	(4)	8.2	160	140	60	80	40
200	(8)	8.4	150	130	80	70	50
300	(12)	8.3	160	110	60	60	50
400	(16)	8.2	140	110	70	70	40

2. Processing Temperature

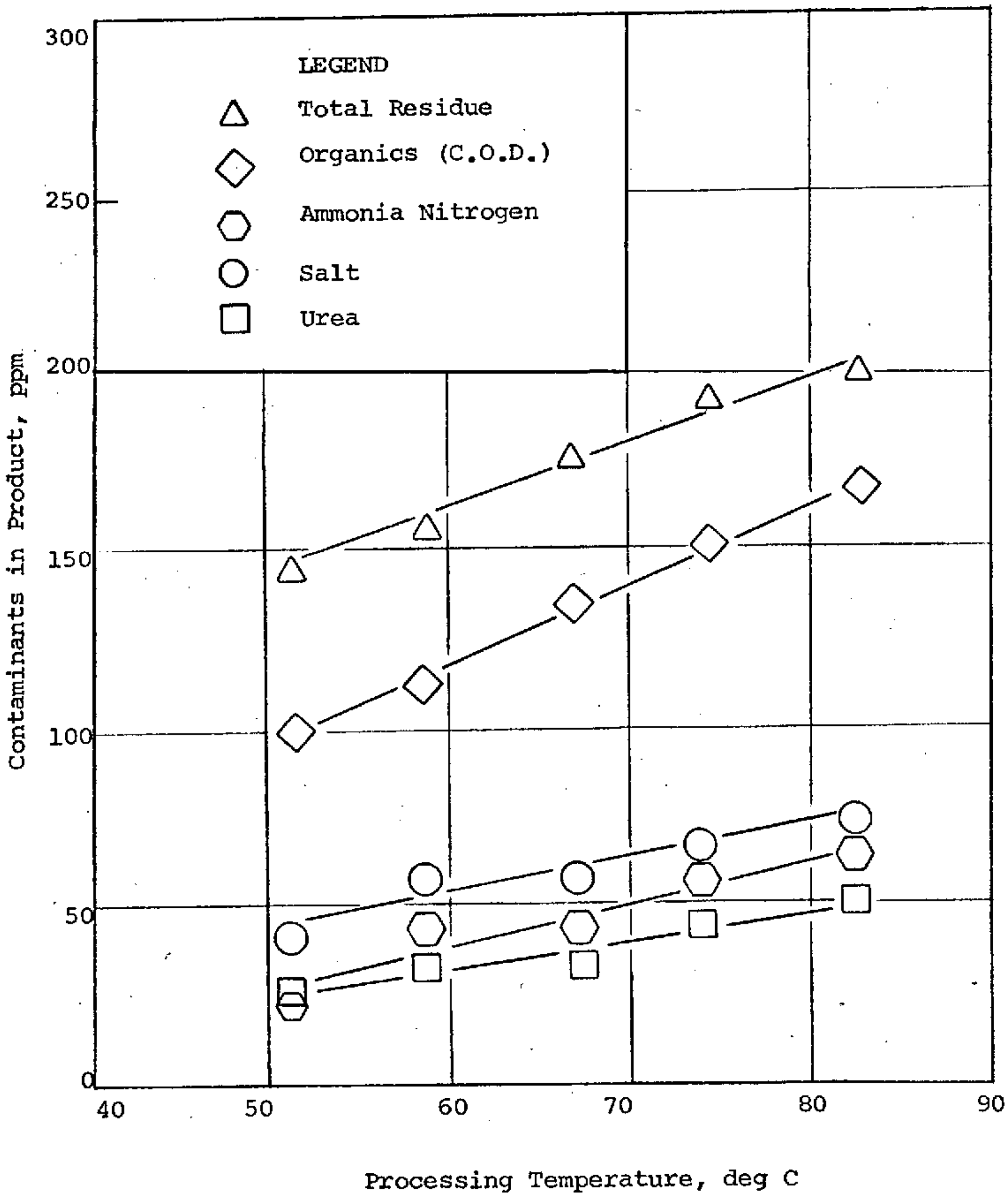
Experiment #11 shows that the level of contamination rises steadily with increasing processing temperature. This is probably caused by concentration polarization as the flux increases with temperature.

EXPERIMENT # 11

Membrane = RADIAN

Processing Temperature		Contaminants in Product (ppm)					
°C	°F	pH	Solids	C.O.D.	Urea	Ammonia N	Salt
51	124	8.1	140	100	30	30	40
59	138	8.0	160	120	30	40	60
68	154	7.9	180	140	30	40	60
74	165	8.2	190	150	40	60	70
83	181	8.0	200	170	50	70	70

Figure 11. PRODUCT QUALITY AS A FUNCTION OF PROCESSING TEMPERATURE



3. Charge Concentration

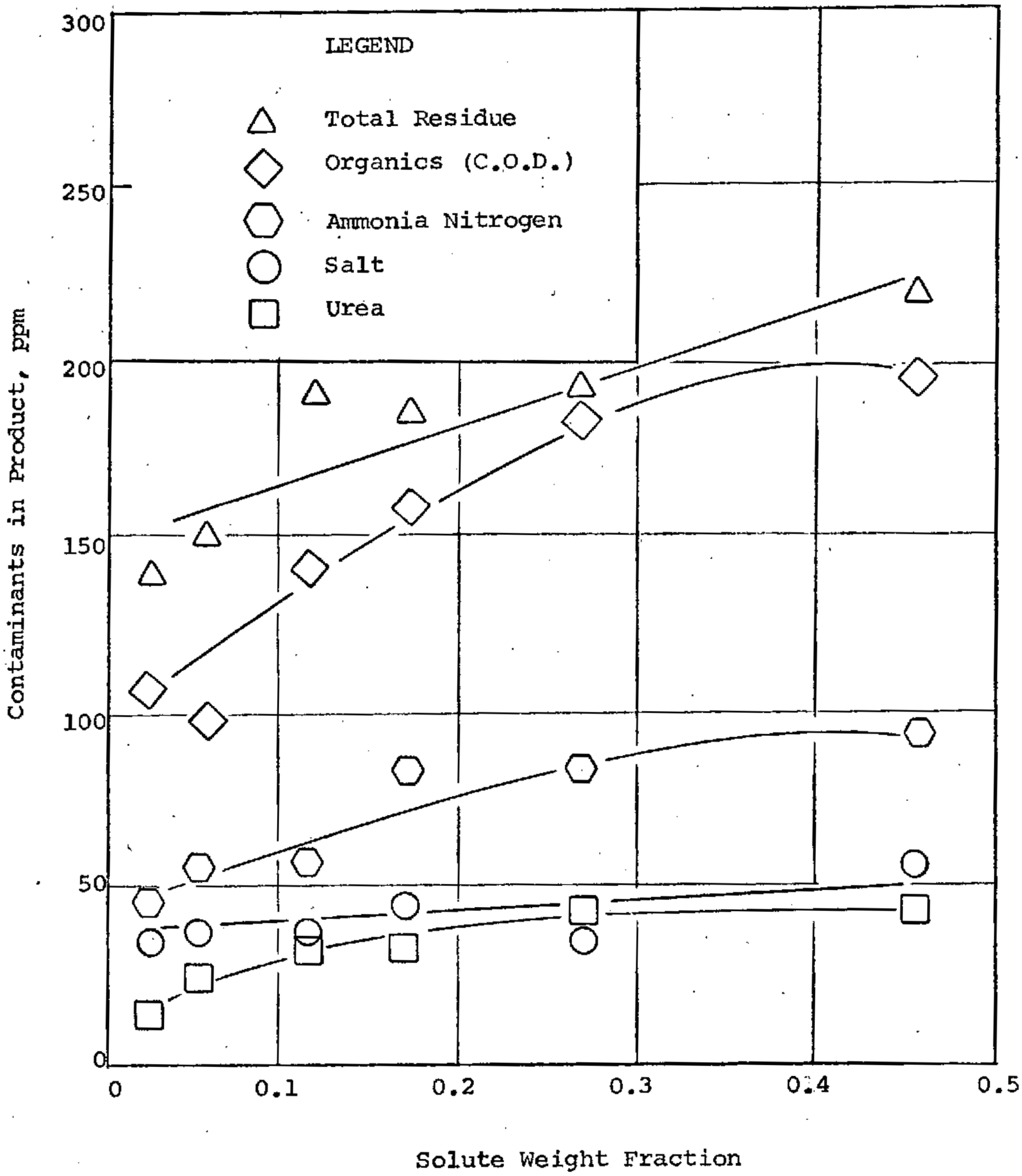
As can be seen in the tabulated data below and Figure 12, an increase in the solid-content of the urine charge leads to an increase in the level of contamination present in the product samples. This increase is especially pronounced in the case of the organic contaminants. The C.O.D. values and the ammonia nitrogen content doubled as 90% of the water was removed from the liquid charge.

EXPERIMENT #12

Membrane = NAFION 170 Temperature = 80°C (175°F)

Solute Weight Fraction	Contaminants in Product (ppm)					
	pH	Solids	C.O.D.	Urea	Ammonia N	Salt
.02	9.9	130	110	20	40	30
.05	9.7	150	100	30	60	30
.12	9.8	180	140	30	60	30
.18	10.3	180	160	30	80	40
.28	10.1	190	180	40	80	30
.46	10.2	220	190	40	90	60

Figure 12. PRODUCT QUALITY AS A FUNCTION OF CHARGE CONCENTRATION



TASK II MEMBRANE COMPARATIVE STUDIES

Introduction

The initial portion of the program was devoted to equipment assembly as well as membrane procurement. Membranes tested by previous investigators with respect to urine purification by pervaporation were reviewed. Special attention was given to two major membrane screening studies - one conducted by Ionics, Inc.[5] in 1963-64 under a contract with USAF, and the other one by Hamilton Standard of United Aircraft Corp. in the same period for NASA.[1-4]

The Ionics study involved the procurement of 28 membranes of which 23 were successfully tested at 50° C to 70° C (120° F to 160° F) using a 1X simulated urine recipe. The majority of the membranes tested were of the cellulosic variety and were quite thin (all but two had thickness less than .05 mm or 2 mils). The general findings were that the majority of these homogeneous polymeric films lacked structural strength and integrity, and exhibited low flux. (Only four films showed permeation rate of more than .05 gm/cm^2-hr).

The Hamilton Standard study involved more membranes - 43 procured and 38 tested. The testing conditions were quite similar to the Ionics case. The majority of the films were cellulosic or belonging to the polyvinyl family. The general findings were also similar - lacking structural strength and low in flux. (Less than a third of them showed processing rate above .05 gm/cm^2-hr, of which only seven had sufficient strength and integrity to be useful.)

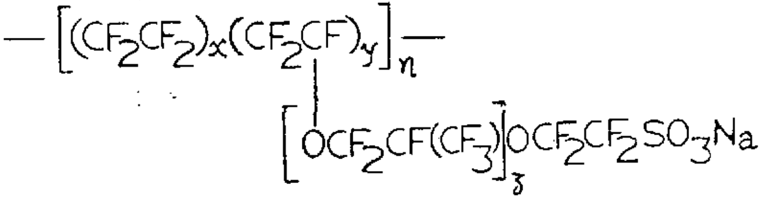
In contrast to these two studies, the present study would stress on good mechanical strength , high resistance towards acids and oxidants (to withstand any chemical pretreatment that might be needed), resistance to organic foulants and higher permeation rate. Cationic ion-exchange membranes possess all these qualities and are prime candidates. Other types of membranes would also be procured for comparison studies.

Sub-Task A. Membrane Procurement

The membranes selected for this program are summarized in Table II. A total of nineteen membranes were tested, of which 15 were cationic membranes and 16 were commercially available. The following paragraphs describe these membranes in greater details.

1. DuPont's NAFION

"NAFION" is a homogeneous film of a completely fluorinated copolymer of PTFE (polytetrafluoroethylene) and PSEPVE (polysulfonyl-fluoride vinyl ether) containing pendant sulfonic acid groups. Its basic chemical structure is as follows:[34].



$$-\left[(CF_2CF_2)_x(CF_2CF)_y\right]_n-$$
$$\left[OCF_2CF(CF_3)\right]_z OCF_2CF_2SO_3Na$$

Although the membrane is primarily designed for electrochemical applications, its hydrophilic properties and its retardation of anion passage render it suitable for pervaporation applications.

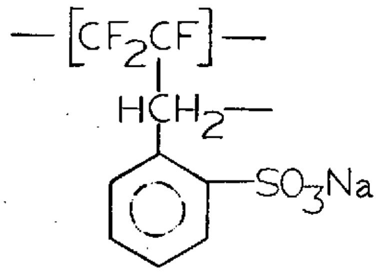
The membranes are available in four different types - one is unreinforced and the other three are reinforced with different types of teflon cloth. Its water sorption is fairly good, 15-20% in the Na^+ form at room temperature and 100% relative humidity. Annealing at high temperatures for a prolonged period of time loosens the polymeric chain packing and increases the amount of interstitial volume, leading to an increase in permeation rate. However, this effect is only temporary. And although the length of polymeric chains, the degree of chain packing, the amount of pendant groups, etc., can be tailored to the particular need, it is not within the scope of this program. The membrane was simply purchased in the four commercially available forms.

Table II. DESCRIPTION OF MEMBRANES SCREENED

Membrane Code	Manufacturer	Trade Name	Base Material	Sulfonated	Cloth Backing
M-1	du Pont	NAFION 170	PSFVE on PTFE	yes	none
M-2	du Pont	NAFION 470	" " "	yes	Teflon
M-3	du Pont	NAFION 475	" " "	yes	Teflon
M-4	du Pont	NAFION 480	" " "	yes	Teflon
M-5	Progil	RADIAN C1044	Sty. graft on PTFE	yes	none
M-6	Ionics,Inc.	61-AZL	DVB + Sty. + EVB,crosslinked	yes	Dynel
M-7	Ionics,Inc.	61-CYL	" " " "	yes	Dynel
M-8	Ionics,Inc.	61-KWL	" " " "	yes	Dynel
M-9	Tokuyama	'old' cation	DVB + Sty on PVC, "	yes	PVC
M-10	A.M.F.	-	DVB + Sty. on KELF, "	yes	none
M-11	Ionac Chem.	MC 3142	DVB + Sty. resin, + binder (Kynar)	yes	Dacron
M-12	Ionac Chem.	MC 3470	" " " " "	yes	Dacron
M-13	duPont	PB 192	Regenerated Cellulose	no	none
M-14	Envirogenics	CAB 95	Cellulose di- + tri-acetate, blended	no	none
M-15	Envirogenics	CAB 99	" " " "	no	none
M-16	Celanese	CELGARD	Polypropylene	no	none
M-17	Experimental	PPO-1	Polyphenylene oxide	yes	none
M-18	Experimental	PPO-2	" "	yes	none
M-19	Experimental	PPO-K	Polyphenylene oxide,sulf.,+Kraton	yes	none

2. Progil's RADIAN

This is a membrane in which a sheet of polymer (in the case of C1044 it is PTFE) is allowed to contact with a monomer (in this case post-sulfonated styrene) and irradiated under a vacuum. This technique of grafting produces a membrane with good chemical and mechanical stability. The basic structure of the membrane is



Since the membrane is not reinforced with a cloth backing its mechanical strengths are not as good as those of NAFION. Its dimensional stability is also lacking. However, both the NAFION and the RADIAN can be stored dry without affecting their permeability characteristics.

3. Ionics' NEPTON

These membranes are essentially copolymers of ethyl vinyl benzene, styrene and divinyl benzene, crosslinked and sulfonated. The degree of crosslinking can be controlled by adjusting the amount of divinyl benzene, and the amount of interstitial space can be tailored by using appropriate amount of the appropriate non-polymerizable solvent. The membrane thickness is controlled by using different reinforcing cloth backing.

Three of these membranes were tested - 61 CYL, 61AZL and 61KWL which use dibromoethane, diethyl benzene and diglyme (Bis-2-methoxyethyl ether), at the proportion of 40%, 48% and 70%, respectively to obtain a good range in terms of amount of interstitial spaces. The reinforcement used was Dynel, a copolymer of polyvinylchloride and polyacrylonitrile.

The membranes were commercially available in 0.5 - 0.6 mm thickness (20-23 mils). A thinner membrane would yield a higher processing rate. However, the problems of pinhole formation and cracking become progressively severe.

4. Tokuyama Soda's NEOSEPTA

This copolymer of divinyl benzene and styrene with polyvinylchloride is made by a Japanese company. It is crosslinked and sulfonated just like the NEPTON and is reinforced with a polyvinyl chloride cloth backing. Its chemical and mechanical stability is similar to that of the NEPTON family. Its water sorption, and, correspondingly, its permeability to water, is less than that of any of the aforementioned membrane.

5. AMF's Cation

The cationic membrane made by American Machine and Foundry is a homogeneous membrane of divinyl benzene and styrene grafted on a polychloro-trifluoro ethylene film, with crosslinking and sulfonation. Its chemical stability and water sorption are quite good.

6. Ionac's Membranes

These membranes consist of clusters of sulfonated divinyl benzene and styrene resins held together by a binder (kynar). The membranes are heterogeneous, certain areas being more densely packed with the resins than others. Preliminary indications are that the non-uniform distribution of the resins allows excessive passage of salt and other undesirable species, rendering the membranes unsuitable for pervaporation.

7. The Cellulosic Membranes

Cellulosic membranes are noted for their high water sorption, and therefore, high permeability to water. Both the study previously conducted by Ionics, Inc. and that by Hamilton Standard recommended cellophane, a regenerated cellulose, for high water transport. Consequently, a cellophane, similar to that employed by Hamilton Standard, was tested in the pervaporation system. The processing rate and product quality obtained were excellent. However, its resistance to high temperature and pH and chemical oxidants, especially with prolonged exposure is not promising.

A reverse osmosis type membrane made by Envirogenics Systems Co. of California was also included for testing. The membrane is interesting because of its Loeb-Sourirajan type surface, i.e. it is asymmetric or "skinned"[33]. It consists of a very dense and thin layer of a blend of cellulose di-acetate and tri-acetate supported by a much more porous and thicker layer of the same polymer. The membrane was chosen because of its proven superiority with respect to resistance to high temperatures, pressures and pH's to ordinary cellulose acetate membranes.

The water permeability in this system did prove to be far superior to that of any of the aforementioned non-cellulosic membranes. However, insufficient data are yet available to vouch for its stability to long-term exposure to high temperature and pHs and to chemical oxidants.

8. Microporous Membrane

A microporous polypropylene film by Celanese, marketed as CELGARD 2400 W, was also tested. However, the selectivity of this membrane was unacceptable - the solid content in the product water was as high as 1.6%.

Subtask B -- Membrane Fabrication

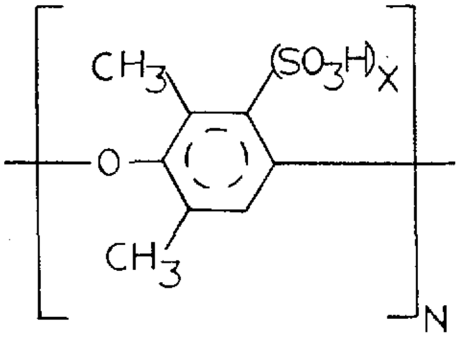
While searching for commercially available membranes for testing, it was suspected that membranes which possessed good mechanical strength, such as NAFION, might exhibit inadequate water permeability. At the same time, several membrane systems, notably polyphenylene oxide and styrene-divinyl benzene membranes, while possessing high water permeability, lack mechanical strength. As such, a series of experiments was planned in which these membranes would be fabricated in a strengthened system.

KRATON is a commercially available thermoplastic rubber. It is essentially a block polymer with an elastomeric polybutadiene segment ended by two thermoplastic polystyrene segments. Where the thermoplastic end-blocks are in minor proportion, they associate together to form discrete particles. These particles act as crosslinks for the elastomeric center-blocks. The result is a network held together by reversible physical bonds (suitable for dissolution and molding), while possessing the excellent strength of rubber vulcanizates.

It is thought that if this KRATON polymer could be added to the aforementioned two polymeric systems, membranes with superior mechanical strength could be fabricated.

1. Sulfonated Polyphenylene Oxide Membranes.

General Electric has developed a membrane of sulfonated 2,6 -dimethyl polyphenylene oxide:[32]



This membrane has been demonstrated in reverse osmosis system to exhibit water permeability surpassing that of cellulose acetate. G.E.'s fabrication procedure involves combining a thin active PPO-SO_3H layer with a microporous substrate (polypropylene) to form composite membranes.

In the procedure developed under this contract, the PPO (obtained in a powdered form from G.E.) is first reacted with chlorosulfonic acid ($ClSO_3H$) in a chloroform solution at room temperature. The extracted and purified PPO-SO_3H is then combined with 6% its weight of KRATON and dissolved in a 1:1 methanol-chloroform mixture (10% by weight solution). The polymer is then cast on glass, allowed to dry at controlled conditions, and released from glass plate by immersion in water.

Comparing with the PPO-SO_3H membranes fabricated without KRATON, the KRATON-strengthened membrane exhibits superior Mullen Burst strength while retaining similar water sorption and water permeability characteristics. There is also noted, a significant improvement in terms of fabricating pinhole-free membranes and in the ease of handling fabricated membranes.

2. Styrene-Divinyl Benzene Membranes

The membranes fabricated by Ionics, Inc. are of this variety.[35] Although the water passage of these membranes is good, their inadequate mechanical strength necessitates that they be fabricated with reinforcing cloth and in relatively thick form. (A disadvantage considering that permeation rate is inversely proportional to membrane thickness.) As such, if KRATON could be added in the way similar to the aforementioned PPO-SO_3H system, a membrane with good mechanical strength (and not brittle when dried) and even greater water passage (because of the decreased thickness) would be obtained.

The procedure attempted involves the bulk polymerization of styrene (100 parts), 55% divinyl benzene (3 parts), KRATON (23 parts) and Benzoyl peroxide as catalyst (1 part). The reaction is allowed to reach completion at 65° C for 17 hours. Sulfonation is performed with Ionics, Inc. special formulation of ethylene dichloride, benzoic acid and sulfur trioxide.

The membranes obtained exhibit good water sorption (over 50%). Unfortunately, it is difficult to obtain pin-hole-free and uniformly thick pieces of sufficient size to be tested in the pervaporation system.

Since the complete development of these membrane systems is not within the scope of this contract, the fabrication experiments were discontinued at this point.

Sub-Task C Membrane Characterization

In addition to permeation data, various other relevant physical properties of the membranes are measured for characterization and comparison purposes. These are:

Film Thickness
Specific Gravity
Burst Strength
Ion-exchange capacity
Dimensional stability
and Water sorption

The measurements obtained are summarized in Table III. The following paragraphs discuss these measurements in greater detail

1. Film Thickness

Previous data obtained by other investigations have established that permeation rate is inversely proportional to and selectivity is independent of membrane thickness.[16-21] Permeation data are incomplete without the accompanying data on film thickness. Furthermore, permeation rate can be increased by decreasing the film thickness. The latter usually means a sacrifice in mechanical strengths and ease of handling and fabrication. Often, a trade-off point is required.

Film thickness is simply measured with a micrometer equipped with a vernier. Since some of the membranes have to be stored wet to prevent irreversible changes when dried, the thickness of all membranes is measured only after equilibrating them in distilled water at room temperature. The units are given in millimeters as well as mils.

Table III. PHYSICAL PROPERTIES OF MEMBRANES SCREENED

Membrane Code	Thickness mm (mils)	Specific Gravity	Burst Strg. torr (psi)	Ion-exchange capacity (m eq/g)	% Swelling when wet	Water Sorp. % H_2O/wet wt.
M-1	.089 (3.5)	2.0	2100 (40)	.83	9	15
M-2	.30 (12)	1.2	8800 (170)	.82	3	9
M-3	.38 (15)	1.3	7300 (140)	.82	2.5	12
M-4	.48 (19)	1.3	6200 (120)	.82	3	11
M-5	.076 (3.0)	1.5	2300 (45)	1.3	10	15
M-6	.51 (20)	1.3	6800 (130)	2.7	n.a.	38
M-7	.55 (22)	1.3	5700 (110)	2.1	n.a.	32
M-8	.58 (23)	1.1	5700 (110)	2.3	n.a.	40
M-9	.20 (8)	1.0	4700 (90)	1.9	3	10
M-10	.23 (9)	1.6	3600 (70)	.96	5	22
M-11	.15 (6)	1.2	9900 (190)	1.1	2	10
M-12	.33 (13)	1.2	9900 (190)	1.1	2	10
M-13	.033 (1.3)	1.1	1300 (25)	n.a.	2	37
M-14	.089 (3.5)	1.1	1600 (30)	n.a.	n.a.	64
M-15	.089 (3.5)	1.1	1600 (30)	n.a.	n.a.	64
M-16	.020 (8)	.9	1800 (35)	n.a.	3	25
M-17	.18 (7)	1.3	520 (10)	1.6	n.a.	40
M-18	.10 (4)	1.3	300 (6)	2.0	n.a.	56
M-19	.12 (5)	1.5	620 (12)	2.2	n.a.	50

n.a. = not applicable

As can be seen from Table III, membrane thickness ranges from .020 mm (.8 mils) to 0.58 mm (23 mils). It might be pointed out that the effective thickness of membranes #M-14 and #M-15, i.e. the Cellulose Acetate Blend membranes with the Loeb surface, is actually of the magnitude of a few microns.[33]

Membrane permeation data are often expressed as permeation rate per unit thickness of the membrane to better express the membrane properties. However, for all practical purposes, the membrane thickness is not within the control of the present investigator. At the same time, actual thickness of the membrane cannot be readily and accurately measured when the polymer of the membrane is encapsulating a cloth backing, thus giving it a non-uniform surface. For these reasons permeation data are given as unit weight processed per unit area and time, and the membrane thickness is given separately.

2. Specific Gravity

This is also measured after the membrane has equilibrated in water at room temperature. The membrane thickness is measured with a micrometer-vernier, and the linear dimensions, with a ruler. The weight of the membrane is measured after excess water has been wiped off. The weight in grams divided by the volume in cc yields this reading.

3. Burst Strength

The Mullen burst strength is measured for membrane samples equilibrated in water at room temperature, accoding to ASTM method #D774. The membrane is held in place with a clamp, and a steady hydraulic pressure is applied by means of a motor-driven piston arrangement until the membrane bursts. The maximum pressure required is then recorded as the burst strength. This is given in terms of psi as well as torrs (mm mercury) in Table III, and is accurate to within .25 - .50 psi. The measurement reflects the mechanical strength of the membranes.

4. Ion-Exchange Capacity

The (scientific) weight capacity of the ion-exchange membranes is measured to further characterize the membranes.[28] The measurement shows the number of ionogenic groups contained in unit weight of the membrane in its H^+ form devoid of sorbed solutes and solvents and reinforcing cloth backing. The procedure simply involves conversion to the H^+ form, exchanging the H^+ with Na^+, and performing an acid-base titration to determine the amount of the H^+. This measurement would reflect the anion passage retardation of the membranes and is given in terms of milliequivalent per unit dry weight of polymer.

5. Dimensional Stability

This measurement is simply made with a ruler and is applicable only to membranes that can be stored dry. The linear dimensions of a dry piece of membrane are first measured. The membrane is then allowed to equilibrate in water at 85° C (185°F). The new dimensions are then measured. The percent increment reflects the dimensional stability of the membrane. Where the swelling is great, the membrane cannot be installed in the system dry without resulting in blockage of the serpentine flow path later, when it becomes wet and, consequently, swelled. It has also been observed that where the swelling is great, cracks tend to form at the junction between the wet portion (where the membrane sorbs the charge) and the dry portion (where the membrane is clamped in place) of the membrane. Reinforced membranes have significantly better dimensional stability and are preferred.

6. Water Sorption

The water sorption of a membrane has been shown to be directly related to the water permeability of the membrane by various investigators.[21,29] Water sorption is dependent on the charge species present, the charge temperature and the particular form the cation membrane is in (e.g. H^+ or Na^+ form, which is pH dependent). A large water sorption means a great increase in interstitial spaces, a looser chain-packing and, consequently, a greater ease for permeating species to "wiggle" through the polymeric chains of the membrane. This generally means an increase in processing rate and a corresponding decrease in selectivity.

Table III shows the sorption of the various membranes expressed in terms of amount sorbed per unit wet weight of the membrane. The equilibration is conducted in urine samples at 85° C (185° F). A direct comparison of the various membranes is not readily available because some of them are reinforced with cloth backing and some are not. However, there is a definite trend associating high water sorption with high water permeability.

Sub-Task D   Comparison of Membrane Processing Rate

The nineteen membranes selected have been tested in the permeation unit, using actual human urine as the charge. (Experiments #13a through 13s). The processing rate was measured after two hours of operation to insure that steady state had been reached. Samples of the product water collected were analyzed for total solids, C.O.D., salt, urea, ammonia nitrogen, and acidity.[27] The data collected are summarized in Table IV .

In terms of processing rate, the cellulosic membranes rank high with the cellophane, M-13, showing a processing rate of 1.7 gm/cm^2-hr (3.5 lb/ft^2-hr), the "loose" CAB membrane, M-14, showing a rate of .90 gm/cm^2hr (2.0 lb/ft^2-hr). (Although the polypropylene membrane, M-16, shows an excellent rate of 2.6 gm/cm^2-hr, it is microporous and the contamination in the product water is high indeed - 1.6% total solids. The membrane is, thus, unacceptable for this process.)

The ion-exchange membranes that have comparable processing rate are M-8, Ionics' KWL; M-18, the experimental PPO-2; and M-5, Progil's RADIAN. (The values are 1.7, 1.6, and 1.2 gm/cm^2-hr, respectively.) M-6, Ionics' AZL and M-1, duPont's NAFION also exhibit good processing rate - .75 and .73 gm/cm^2-hr, respectively.

The remainder of the membranes exhibit rather low permeation rate and do not appear promising. These include the Ionac membranes (M-11 and M-12), Tokuyama's NEOSEPTA(M-9) and A.M.F.'s cation membrane (M-10).

TABLE IV. PERMEATION DATA ON MEMBRANES SCREENED

Membrane Code	Charge Concentration (% TDS)	Charge Temperature	Proc. Rate $\left(\frac{g}{cm^2\text{-}hr}\right)$	$\left(\frac{lb}{ft^2\text{-}hr}\right)$	PRODUCT QUALITY (ppm) solids	C.O.D.	NaCl	Urea	AMM. M	pH
M-1	3.1	93 (200)	.73	(1.5)	200	110	15	45	30	8.3
M-2	2.1	88 (190)	.29	(0.59)	120	80	15	50	35	7.9
M-3	3.2	93 (200)	.51	(1.0)	200	90	25	40	40	7.6
M-4	2.5	88 (190)	.36	(0.73)	250	100	25	50	40	8.2
M-5	3.1	88 (190)	1.2	(2.4)	200	120	30	30	45	8.2
M-6	3.1	93 (200)	.75	(1.5)	300	220	45	100	70	8.4
M-7	3.1	93 (200)	.50	(1.0)	270	180	15	80	50	8.2
M-8	3.0	93 (200)	1.6	(3.2)	870	400	70	270	90	7.9
M-9	2.9	93 (200)	.46	(0.93)	130	70	10	80	25	8.4
M-10	3.0	93 (200)	.46	(0.93)	180	90	40	70	40	8.1
M-11	3.7	93 (200)	.65	(1.3)	530	220	220	160	130	9.6
M-12	3.7	93 (200)	.43	(0.87)	470	180	300	120	130	8.9
M-13	2.6	93 (200)	1.7	(3.5)	160	80	25	50	30	8.4
M-14	3.9	77 (170)	1.7	(3.5)	280	80	30	60	35	10.1
M-15	3.9	82 (180)	.90	(2.0)	180	50	10	30	20	10.1
M-16	2.7	93 (200)	2.6	(5.0)	16000	-	-	-	-	8.3
M-17	2.4	93 (200)	.54	(1.1)	160	100	10	35	35	8.1
M-18	2.9	93 (200)	1.7	(3.5)	180	90	20	40	40	9.2
M-19	3.3	88 (190)	.97	(2.0)	210	80	20	40	50	9.4

Sub-Task E Comparison of Membrane Selectivity

The quality of the product samples is of primary importance even when post-treatment with activated charcoal is feasible. However, as previously discussed, product quality is related to, but not synonymous with membrane selectivity. The studies here shall be two-fold -- the examination of product quality, and the monitoring of membrane true selectivit

1. Product Quality

Table IV summarizes the quality of the product samples obtained from different membranes using actual urine as the charge. In terms of meeting the standards established by the USPHS[26] for the level of total solids acceptable[27], only two membranes failed - the microporous polypropylene membrane (M-16) and Ionics' KWL (M-8). Both of these membranes exhibit good flux and poor product samples (16,000 and 870 ppm solids as opposed to the 500 ppm standard.)

The Ionac membranes while exhibiting poor processing rate, yield product samples that are, at best, marginal in terms of the level of total solids and chloride. The explanation probably lies in the heterogeneous structure of the membranes. Since these membranes are essentially clusters of resins held together by a binder, it is not difficult to see that there exist loosely structured regions where the sodium and chloride ions can pass through with relative ease. The high salt content in this small fraction of the total permeate sample in turn causes a disproportionately large contamination level to appear in the remainder of the otherwise "pure" permeate sample.

Aside from the Ionac membranes (M-11 and 12), all the other membranes yield product samples that are low in salt contamination - 10 to 45 ppm as compared to the 250 ppm level set by USPHS and the 450 ppm deemed acceptable by NASA's SSB.

On the other hand, the C.O.D. level appears to be relatively high - 70 to 120 ppm for most of the samples - especially in the case of the Ionics and Ionac membranes - 180 to 400 ppm. Unfortunately, neither USPHS nor SSB specifies the requirement for total organics. Passage through activated charcoal will remove these as well as the accompanying disagreeable odor.

Both USPHS and SSB also left out the specification for the level of urea and ammonia nitrogen. Although they do not appear to be toxic to human beings, a high level of these contaminants could result in a disagreeable taste or some side effects as obscure as , e.g. tooth decay. The level of urea and ammonia nitrogen, like the level of C.O.D., is highest for the Ionics and Ionac membranes (100 to 270 ppm) and is actually as low as 50 ppm or less for all the other membrane systems.

In conclusion, it may be added that the pH level of the samples is also within the < 10.5 level set by USPHS.

2. Membrane Selectivity

As the charge species selectively permeated the membrane layer, they are selectively removed, in the vapor phase, under the reduced pressure established. The latter selectivity is a function of permeate temperature, the relative concentration of the different species present, and, most of all, the vapor pressure of the component involved.

As the process continues, the more volatile organics, the ammonia, and the water would distill over and accumulate in the collector due to the temperature gradient which, in turn, results in a partial pressure gradient, established by the hot urine charge and the condenser.[1,3] At the same time, the low-vapor-pressure components, notably, urea and salt, would accumulate in the vicinity of the product-side membrane surface. This build-up would result in changes of the composition of the 'permeate', which would, in turn, cause a drop in the rate of distillation of the high-vapor-pressure components, and, even, result in the distillation of the low-vapor-pressure components.

This build-up of urea and salt would also affect the concentration gradient established between the liquid charge and the permeate vapor, in particular, the concentration gradient between the extremeties of the vapor-phase zone.[16] This might result in a significant reduction of the processing rate, as well as, the selectivity. Furthermore, the accumulation could conceivably cause an actual, physical 'plugging' of the downstream membrane surface, resulting in further reduction in rate and selectivity.

For these reasons, it was decided, at the beginning of the program, that the monitoring of the undistilled permeated components should be carried out.

Experiments #14a through 14h were carried out for this investigation. In these experiments, the permeation was allowed to proceed for 4 to 5 hours. The volume and composition of the distillate samples were monitored. At the end of the experiment, the vacuum lines were disconnected, and the downstream chamber was carefully flushed with a known quantity of distilled water. Presumably, this 'washing' would dissolve the bulk of the resident, permeated species. This flush-water was then assayed for total solids, C.O.D., urea, salt and ammonia nitrogen. A material balance calculation would determine the amount of the various components permeated.

The data are summarized in Table V. The solids retention ranges from 88 to 97%. Urea retentions are in the same range. Except for the Ionac membrane, the salt retention is high for all membranes - above 97%. Retentions of ammonia nitrogen and the organics are also in the nineties.

Also can be found in Table V are the data correlating the amount of the different species permeated with the amount of contamination found in the product samples. In general, it can be stated, that, the level of permeated species is directly proportional to the level of contamination found in the product. Furthermore, the percent of the permeated species that distills over to be collected is reflective of the vapor pressure of the particular species. Urea and salt have low vapor pressure. As such, only 8.5 and 17% , respectively, of the total amount of these species that have permeated the membrane are collected in the product samples. The corresponding percentage figures for the volatile ammonia and organics are 42% and 71%, respectively.

Table V. SELECTIVITY STUDIES

1. Total Solids

	CONCENTRATION (ppm)			Membrane % Retention	% Distilled
Membrane	Charge	Permeate	Product		
M-1	31,000	1,300	180	96	14
M-5	30,000	1,050	160	97	15
M-6	29,500	2,500	350	92	14
M-8	29,800	3,100	590	90	19
M-10	27,400	780	170	97	22
M-11	32,000	3,700	500	88	14
M-14	28,500	840	180	97	21
M-19	27,000	910	190	97	21

2. Urea

M-1	18,900	690	50	96	7
M-5	17,500	510	35	97	7
M-6	21,000	1,900	100	91	5
M-8	19,500	2,200	280	89	13
M-10	19,000	370	30	98	8
M-11	17,100	2,400	190	86	8
M-14	17,400	630	60	96	10
M-19	18,300	300	30	98	10

3. Salt

M-1	9,100	100	15	99	15
M-5	9,400	90	15	99	17
M-6	9,700	180	35	98	19
M-8	8,900	290	55	97	19
M-10	11,000	100	20	99	20
M-11	8,900	1,700	270	81	16
M-14	9,000	160	20	98	13
M-19	9,500	170	30	98	18

Table V - SELECTIVITY STUDIES (Continued)

4. Ammonia N

Membrane	CONCENTRATION (ppm)			Membrane % Retention	% Distilled
	Charge	Permeate	Product		
M-1	3,200	150	45	95	30
M-5	3,500	80	45	98	56
M-6	3,000	170	80	94	47
M-8	2,600	240	100	91	42
M-10	2,850	90	30	97	33
M-11	2,650	170	100	93	59
M-14	3,100	140	45	95	32
M-19	2,700	100	40	96	40

5. C.O.D.

M-1	8,800	200	110	98	55
M-5	8,600	190	120	98	63
M-6	9,500	280	220	97	79
M-8	9,000	400	360	96	90
M-10	8,050	160	90	98	50
M-11	7,100	250	200	96	80
M-14	9,100	100	80	99	80
M-19	6,850	110	80	99	73

TASK III -- MEMBRANE LIFE TEST

Subtask A. Membrane Selection

Comparison of membrane processing rates and product contamination has been performed in the previous section. In accordance with the contractual agreement, two membranes were selected for prolonged testing. The selection of the membranes has been based on five criteria which are believed to be relevant for effective water-recovery. These are:

a) Easy Handling - the membrane should be relatively rugged, easy to store and transfer, and exhibit dimensional stability after it has been transferred from storage to permeation unit. Membranes that are cloth-backed, that can be stored dry and that swell minimally linearly when immersed in hot urine would be preferred.

b) High Flux - the higher the flux is the smaller the unit would need to be. Membranes that exhibit highest flux (without sacrificing distillate quality) and minimal decline in the flux with time and concentration would be preferred.

c) Chemically Resistant - the membrane should be stable in hot urine. However, in anticipation of the possible need for pretreating urine, membranes with good resistance towards acids, oxidants, germicides, etc., would be preferred.

d) Availability vs Flexibility - while low cost and easy availability would be relevant parameters, they would be balanced against the flexibility of the membranes in terms of modification to achieve higher flux, better resistance, lower passage of particular components, etc.

e) Membrane Selectivity - the effect of non-volatile solids building up on the downstream surface of the membrane is not known. However, higher retention of solids, volatile and non-volatile, should be preferred since there is the indication that the level of contamination of product is related to the amount of permeated species.

Table VI summarizes the membrane selection procedure. The membranes selected for prolonged testing are the NAFION 475 (M-3) and the NEPTON-AZL (M-7).

1. NAFION 475

The mechanical strengths of NAFION 475 are excellent. The reported values are:[34]

Tensile strength	(ASTM-D882)	4000	psi
Elongation	(" ")	140	%
Tensile Modulus	(" ")	35,000	psi
Tear strength	(" -D689)	12	gm/mil
Burst strength	(" -D774)	150	psi

Its chemical resistance has been proven in a 40-day static tolerance test conducted under this program. Literature also claims that it is stable with prolonged exposure to:[34]

25-40%	KOH	at	150°C
70%	HNO_3	at	100°C
30%	H_2O_2	at	80°C
85%	H_3PO_4	at	150°C
50%	H_2SO_4	at	150°C

These superior properties are supported by its ease in handling — it can be stored, shipped and installed dry; it does not swell too much when wetted by the urine charge, and it is rugged indeed.

Unfortunately, although NAFION-475 has great preference to water passage compared with the passage of the other charge components, its

Table VI -- MEMBRANE SELECTION FOR LIFE TEST

	CRITERIA FOR SELECTION					
Membranes	Handling	Permeation Rate	Chemical Resistance	Flexibility	Membrane Selectivity	Final Action
M-1	ab	D	EFG	HI	K	Rejected-inadequate strength
M-2,3,4	AB	d	EFG	HI	K	M-3 chosen for best flux
M-5	ab	C	EFG	ij	K	Rejected-inadequate strength
M-6	AC	D	EFG	HJ	k	Rejected,M-7 preferred
M-7	AC	C	EFG	HJ	k	Accepted despite fair selectivit
M-8	AC	C	EFG	HJ	l	Rejected, very poor selectivity
M-9	AC	d	EFG	ij	K	Rejected,inferior in general
M-10	ab	d	EFG	hj	K	Rejected, inferior in general
M-11,12	AB	d	EFG	Hj	l	Rejected,very poor selectivity and flux
M-13	ab	C	efg	Hj	K	Rejected, poor resistance and strength
M-14,15	ac	C	Efg	HI	K	Rejected, poor resistance, wet storage
M-16	ab	C	efg	Hj	l	Rejected, very poor selectivity and strength
M-17,18	ac	C	efg	hJ	K	Rejected, experimental
M-19	ac	C	efg	hJ	K	Rejected, experimental

CODE:

A = Good mechanical strength
B = Minimal swelling when wetted
C = Excellent permeation rate
D = Fairly good permeation rate
E = Good resistance to acids
F = Good resistance to alkalis
G = Good resistance to oxidants
H = Easily available
I = Modification claimed by manufacturer
J = Modification available to this investigator
K = Good membrane selectivity

a = Lacking mechanical strength
b = Excessive swelling when wetted
c = Requires wet storage at all time
d = Low permeation rate
e = Poor or questionable resistance to acid
f = Poor or questionable resistance to alkalis
g = Poor or questionable resistance to oxidants
h = NOT commercially available
i = Problems in procurement, imported
j = Modification possibility unknown or none
k = Inadequate membrane selectivity
l = Very poor selectivity

permeation rate is not as good as that of the other membrane screened. (.51 gm/cm^2-hr as compared to 1.7 gm/cm^2-hr for the cellulose acetate blend membrane and 1.6 gm/cm^2-hr for NEPTON KWL.) However, the membrane can be modified, within limits, to increase its water passage, although this is not within the scope of this program. (It should be noted that the membrane was not primarily designed for high water passage.)

2. NEPTON-AZL

The NEPTON-AZL has been used in more than 150 electrodialysis installations involving various kinds of waste streams, subjected to various rough handling. Its stability to solutions up to pH 11 and 95° C is well established. Higher pH's and temperatures are not expected to affect the membrane. Its mechanicsl strengths are not as good as those of the NAFION. However, its burst strength, which is certainly the most relevant measurement for the particular type of system involved here, of 120-140 psi is excellent for the system.

The AZL also has significantly higher water permeability than the NAFION. Unfortunately, the product water quality is correspondingly worse. AZL also has to be stored wet. Otherwise, cracking of the membrane would occur.

Sub-Task B -- Equipment Modifications

After the membranes had been selected, the equipment was modified to operate continuously and automatically. The modifications involved the following : -

(i) replacement of the distillate collection glassware with a stainless steel container for the purpose of providing sufficient strength and rigidity for (ii);

(ii) installation of three solenoid valves and a distillate delivery pump such that the container is evacuated and collects the condensed distillate in the normal position; and is vented to atmosphere and emptied of its content in the activated position;

(iii) installation of a timer-relay subsystem to activate and deactivate the components mentioned in (ii) according to a carefully calculated time sequence to provide a continuous operation;

(iv) installation of a level control safety subsystem to shut off all operating components in case of an accidental leakage in the charge subsystem or the membrane assembly;

(v) modification of the charge reservoir to minimize loss due to evaporation; and

(vi) installation of a level-control float in the constant temperature bath such that fresh water is added when necessary, to compensate for loss due to evaporation.

A parallel system was also installed such that two membranes could be tested simultaneously

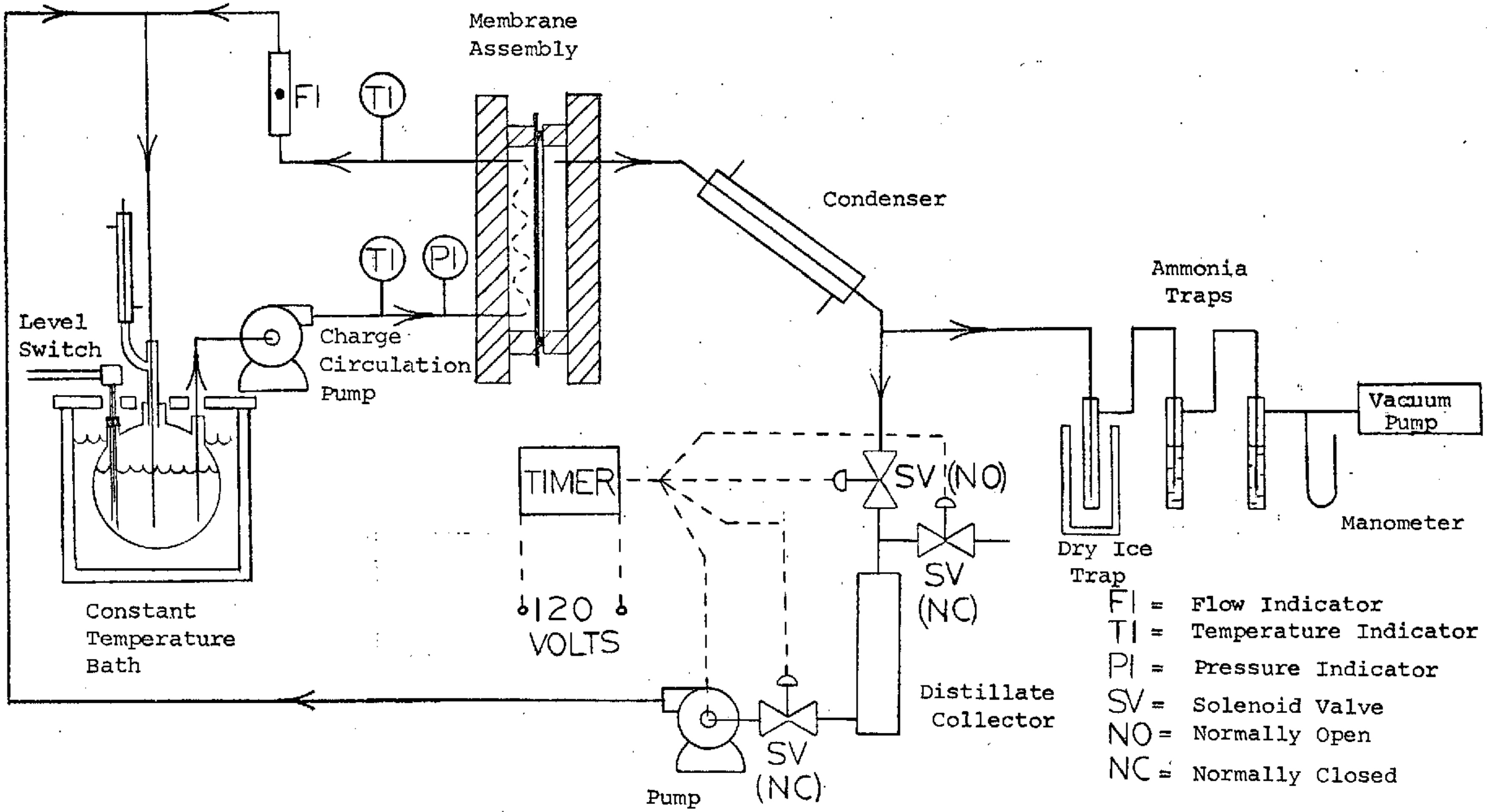


Figure 13. SCHEMATIC DIAGRAM OF A CONTINUOUS OPERATION PERVAPORATION SYSTEM

Sub-Task C -- Studies of Membrane Processing Rate

1. Experimental Data

Initially, the processing rate was studied as a function of time for three membrane systems, using actual urine as charge. The experiment (#15) was conducted in a differential mode, i.e. the permeated liquid was periodically recycled back to the charge reservoir, such that the charge was essentially concentration invariant. Processing rate was monitored periodically and tabulated below. Figure 14 illustrates the relationship between processing rate and processing time.

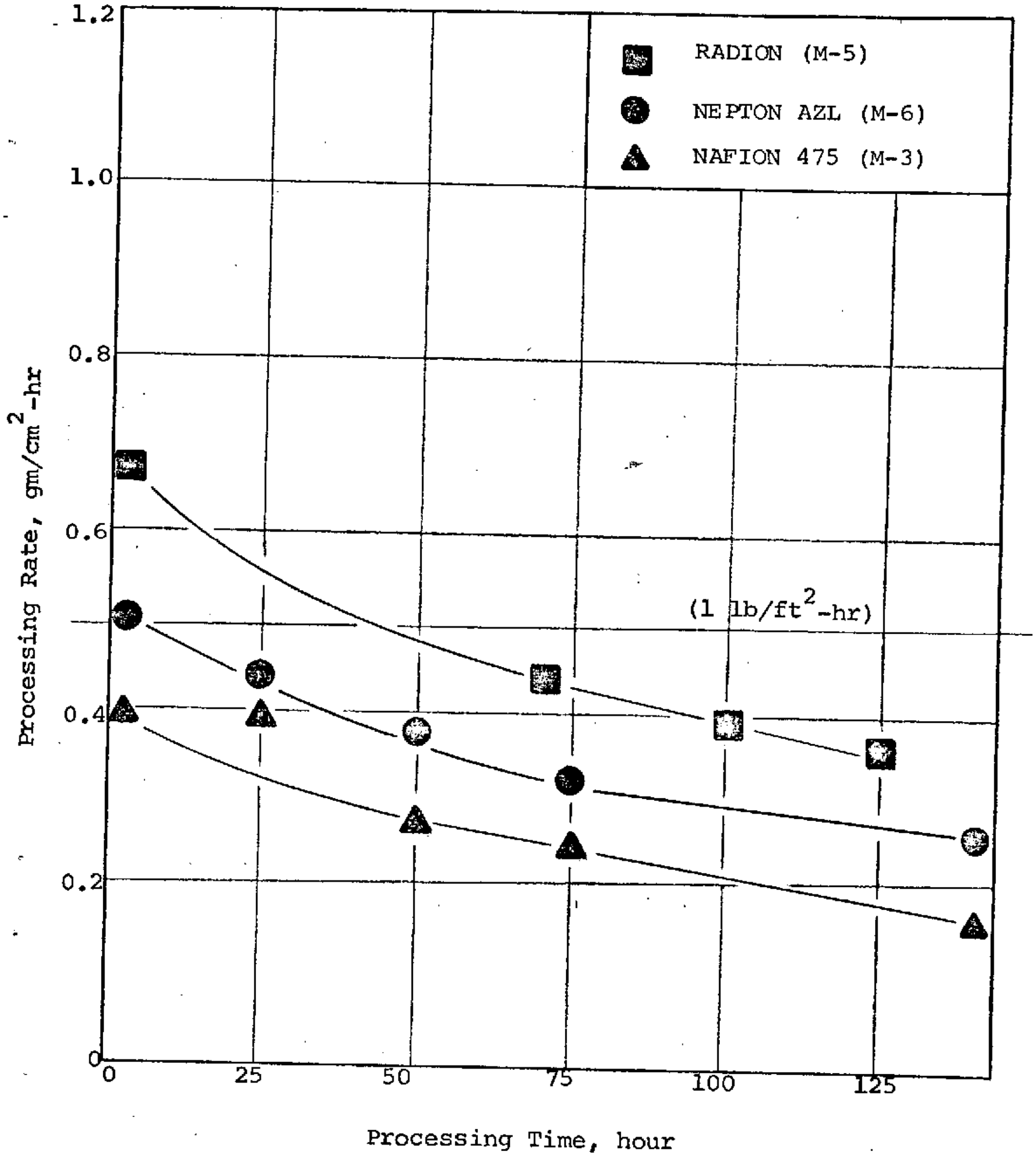
EXPERIMENT # 15

Membranes = RADIAN (M-5)
= NEPTON AZL(M-6)
= NAFION 475 (M-3)

Processing Time, hr.	Processing Rate, gm/cm^2-hr (lb/ft^2-hr)					
	RADIAN		NEPTON		NAFION	
2	.67	(1.4)	.50	(1.0)	.40	(.82)
25	—	—	.45	(.90)	.40	(.80)
50	—	—	.39	(.80)	.27	(.55)
70	.44	(.88)	—	—	—	—
75	—	—	.32	(.65)	.23	(.50)
100	.39	(.80)	—	—	—	—
125	.36	(.70)	—	—	—	—
140	—	—	.26	(.50)	.17	(.35)

In contrast to the data presented earlier in this report which showed processing rate to be stable with time for simulated urine, the data from Experiment #15 showed that this was true only for the initial 10 hours or so. After that flux underwent a steady decline.[5] The rate of decline for all three membranes studied was remarkably similar, amounting to approximately

Figure 14. PROCESSING RATE AS A FUNCTION OF PROCESSING TIME



0.6 gm/cm^2-hr (1.2 lb/ft^2-hr) for each 24 hour operating period. On disassembling the equipment, it was found that a beige color precipitate has deposited on the charge-side membrane surface.

The precipitate was carefully removed from the NAFION and analyzed.[36] The membrane system was reassembled. The processing rate recovered somewhat, but proceeded to decline as shown in Figure 15.

A new piece of NAFION was tested for 72 hours. After the processing rate has declined, the system was flushed with hot water at the rate of 1000 ml/min (.26 gpm) for two hours. The flux recovery was significant, but decline occurred as previously observed (Figure 15).

Acidification of "denatured" urine charge caused the precipitate to redissolve, but flux improvement was probably not significant (Figure 15).

A further experiment was conducted in which the fresh urine charge was pretreated with a combination of copper sulfate, chromium trioxide and sulfuric acid in accordance with the formulation developed by David F. Putnam of McDonnell-Douglas.[37] The processing rate declined with time but at a somewhat slower rate. At the same time, the rise in the pH level of the charge that was previously observed did not occur.

A second series of experiments (#16) was conducted in which the permeated liquid was removed from the system instead of returned to the charge, i.e. in the integral mode. The processing rate decline was more severe than in the case of the differential runs (Figure 16). The contribution to flux decline was, of course, twofold - the increase in processing time as well as the increase in charge concentration. However, over ninety percent

Figure 15. EXPERIMENTS TO RECOVER PROCESSING RATE

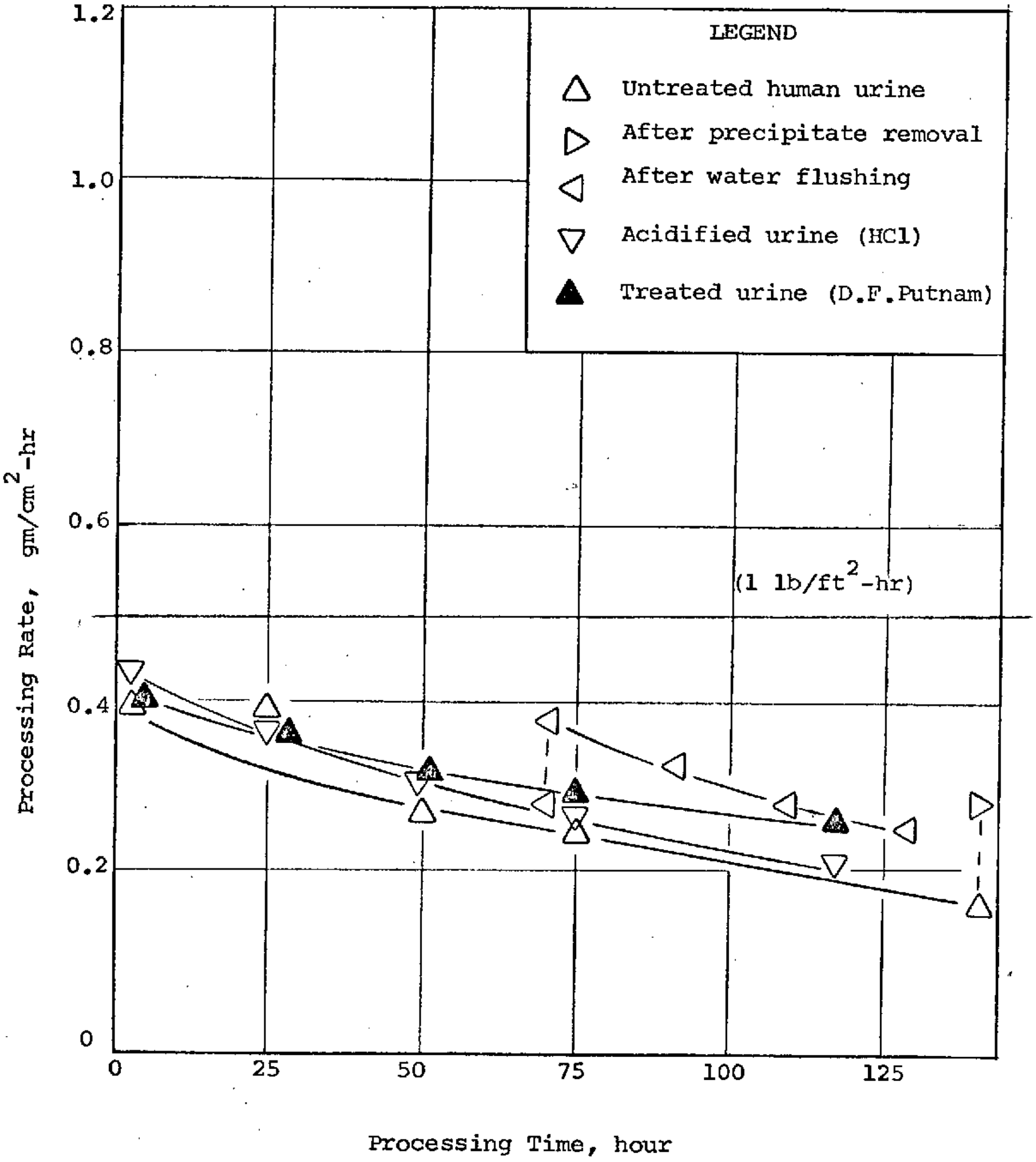
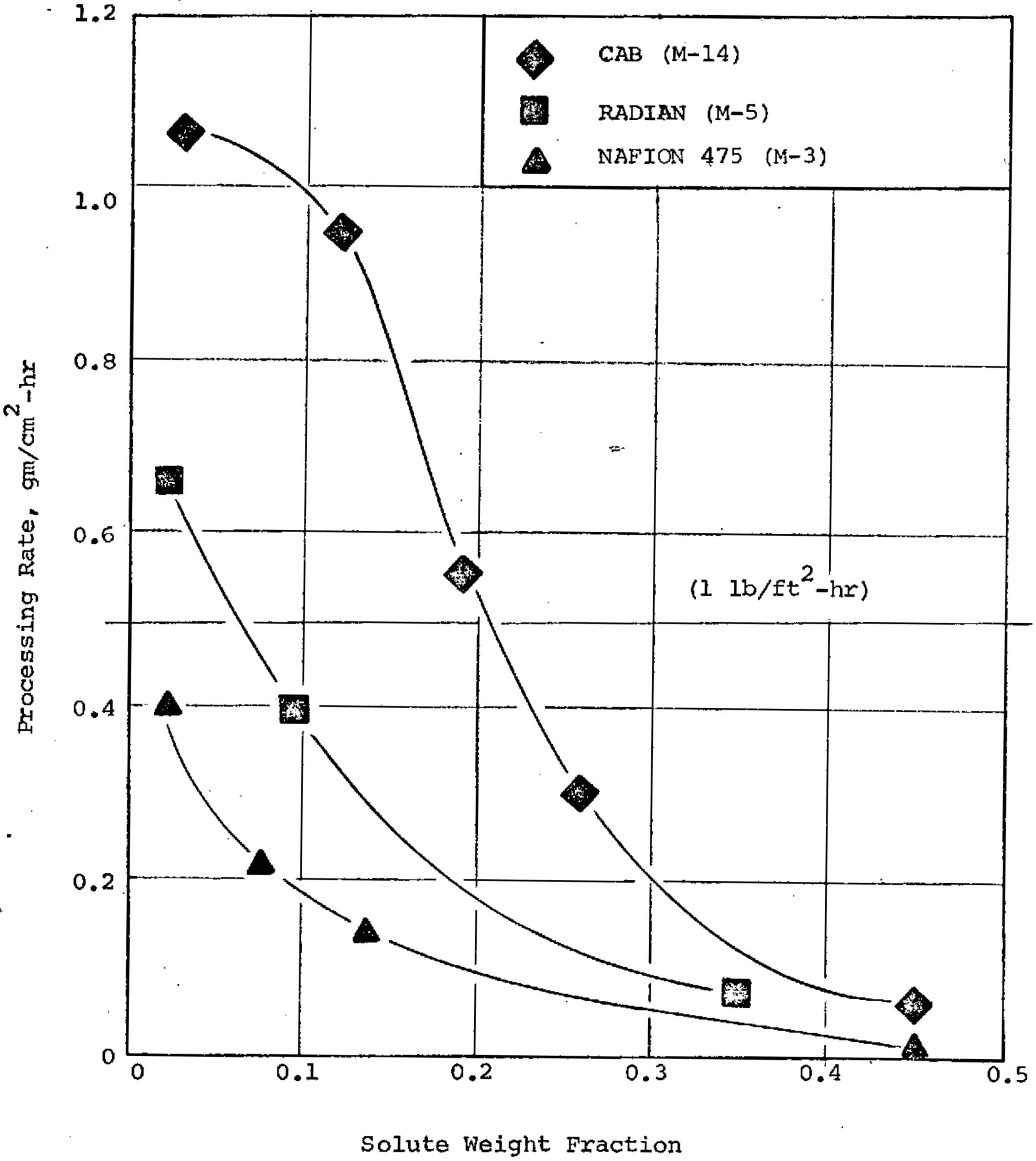


Figure 16. PROCESSING RATE AS A FUNCTION OF CHARGE CONCENTRATION



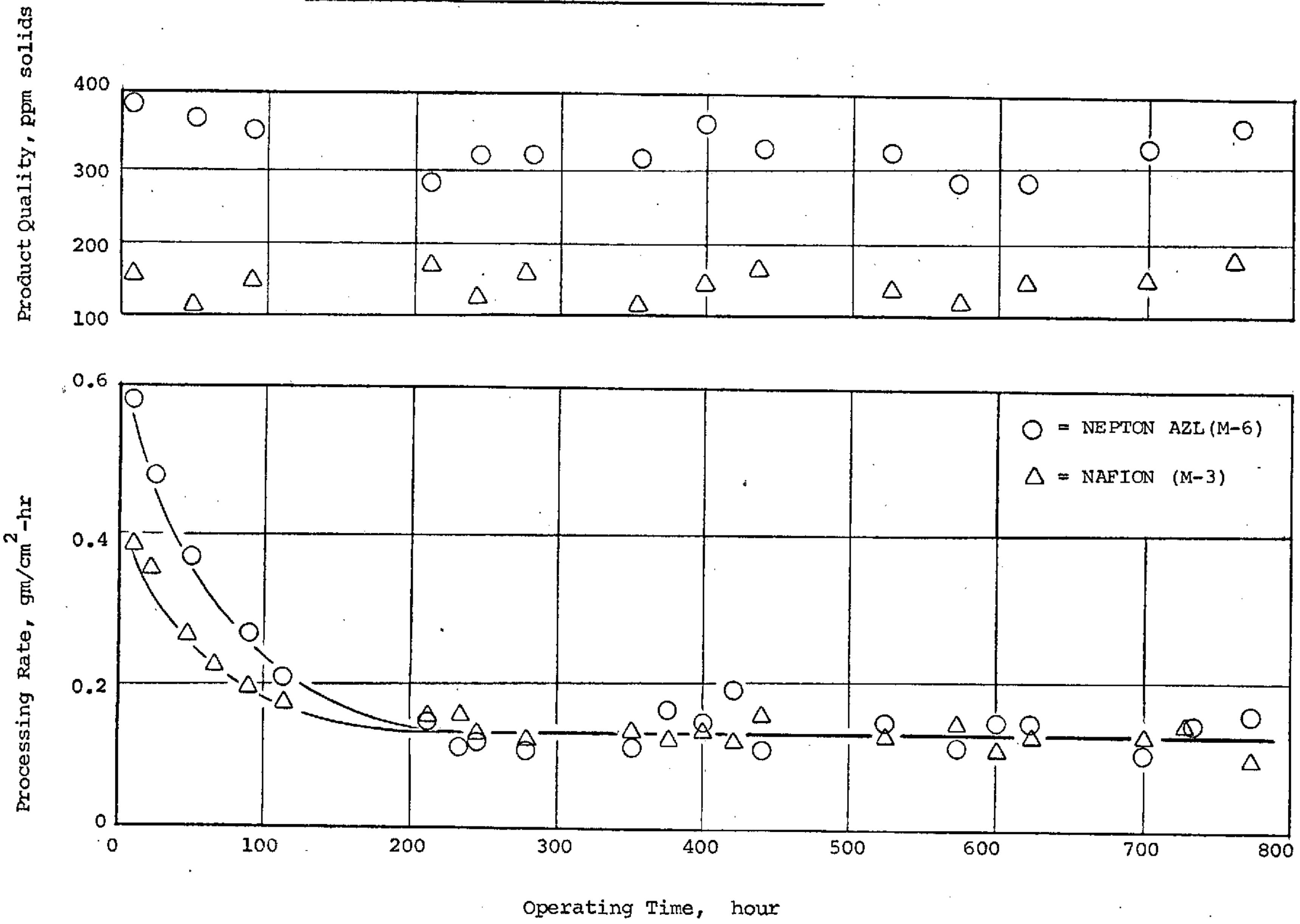
of the water was successfully removed from two samples of urine using the NAFION membrane and the CAB membrane, respectively. For a starting sample of 5 liters human urine, it took 40 hours to remove 93% of the water for the CAB membrane, and 70 hours to remove 92% of the water for the NAFION membrane, the area of permeation being 480 cm^2 (.346 ft^2).

A third experiment was performed (#17) for long-term testing of two membranes - the NAFION and the AZL. Data were collected periodically and plotted as a function of time in Figure 17. It is interesting to note that after the decline of the processing rate during the initial 150 hours or so the rate of decline quickly tapered off. This stability of the processing rate seemed to indicate that an equilibrium was reached. Furthermore, the experiment was interrupted after 300 hours of operation and the system flushed with water. There was no flux recovery!

2. Discussion

The decline in processing rate is two-fold -- a decline due to increase in the concentrations of the charge species other than water, relative to water, and, hence, a decrease in the concentration gradient of the system; and a phenomenon summarily called "membrane fouling." The former has been discussed in a previous section of this report. The exact mechanism of membrane fouling is not understood. However, it is, at least partially, attributable to the formation of precipitate when human urine is exposed to a certain level of heat and the accompanied rise in alkalinity. The precipitate deposits on the membrane surface, blocking the entrance of permeating species. A plausible process is underlined below:

Figure 17. SUMMARY OF MEMBRANE LIFE TEST



(i) Human urine contains urea, the enzyme urease, acidity, alkalinity, and proteins;[22-24]

(ii) Urea can decompose to form ammonium carbonate, as well as, ammonia in the presence of

a) heat
b) urease
c) heat + H^+, or
d) heat + OH^- [24]

e.g.

$$2\,CO(NH_2)_2 \xrightarrow{\text{heat}} NH_3 + (NH_2CO)_2NH$$

$$CO(NH_2)_2 + H_2O \xrightarrow{\text{urease}} 2\,NH_3 + CO_2$$

$$CO(NH_2)_2 + 2\,H_2O \xrightarrow{>65^{\circ}C,\ H^+} (NH_4)_2CO_3 \longrightarrow 2\,NH_3 + CO_2 + H_2O$$

$$CO(NH_2)_2 + NaOH \longrightarrow NH_3 + Na\,HCO_3$$

(iii) Urea decomposition leads to an increase in alkalinity of the urine charge (this increase in alkalinity was observed).

(iv) The heat, as well as the increase in alakalinity denatures certain proteins causing them to be insoluble; e.g. histones are insoluble in alkalis, but soluble in acids.[38]

(v) The precipitate (analyzed to be 48% Lowry protein) deposits on the membrane surface, reducing the accessibility of the membrane to the different permeating species.

This mechanism is substantiated by the following observations:

(i) Flushing with water temporarily removes the protein deposit, leading to flux recovery. As permeation continues, the protein is redeposited, causing flux decline.

(ii) Acidification with HCl redissolves protein, leading to flux recovery. Decomposition of urea neutralizes acidity until pH becomes high enough for further precipitation and subsequent flux decline. (The increase in pH of acidified urine was also observed).

(iii) Treatment with acid-oxidant combination was observed to stabilize the pH level of the urine charge, maintaining precipitation at a low level. (This precipitate was observed to be greenish, probably some hydroxides of copper or chromium; e.g. $CuSO_4 \cdot 3\,Cu(OH)_2$, $Cr(OH)_3$.) The stability of pH is probably due to the formation of the heat stable ammonium sulfate or chromate,

$$CO\,(NH_2)_2 + 2\,H_2O \xrightarrow{>65^{\circ}C,\ H^+} (NH_4)_2CO_3$$

$$(NH_4)_2\,CO_3 + H_2SO_4 \longrightarrow (NH_4)_2SO_4 + H_2O + CO_2$$

$$(NH_4)_2\ CO_3 + H_2O + CrO_3 \longrightarrow (NH_4)_2CrO_4 + H_2O + CO_2$$

The fouling is probably also partially attributable to a more severe type of "clogging", e.g. the larger charge species could have dissolved into the membrane and become physically trapped among the polymeric chains or bonded through hydrogen bonding. This is supported by the observation that the flux recovery through water flushing is exposure-dependent. Experimental data showed that repeated flushing with distilled water recovered 85% of the flux after running for 48 hours, 55% after 96 hours and 22% after 150 hours for the NAFION system. And, the long-term test showed that after 300 hours, flux recovery was zero. This last observation indicated that certain fouling phenomena were completed after the system had been in operation for some 300 hours, as though certain functional groups available for bonding were saturated at that point.

Sub-Task D -- Studies of Product Quality

Two experiments were performed to study the variation of the product quality - one as a function of processing time and the other as a function of charge pretreatment.

1. Processing Time

Experiment #18 showed that there was no significant variation in product quality with prolonged exposure to untreated human urine. As shown in Figure 17, the total solid contents of the product samples fluctuated between 110 and 180 ppm for the NAFION system, and between 290 and 390 ppm for the AZL. This indicated that the total contamination of the product samples was independent of processing time.

During Experiment #18, the concentration of the other components in the charge and the product samples was monitored weekly and summarized in Table VII. While alkalinity of the charge was observed to increase with exposure to heat, no general trend was observed for the other components in the charge or the product samples. Thus, it can be concluded that product quality is independent of processing time.

2. Charge Pretreatment

Experiment #18 was conducted to investigate the effect various pretreatment of the urine charge might have on the quality of the product water samples. The data collected are summarized below:

TABLE VII. PRODUCT QUALITY

CHANGE AS A FUNCTION OF TIME

Processing Time	URINE CHARGE Urea	Salt	C.O.D.	Ammonia	pH
1st Week	17,600	10,900	9,700	3,200	5.7
2nd Week	16,900	9,800	8,600	3,500	6.4
3rd Week	15,400	10,000	8,500	3,000	7.4
4th Week	15,900	11,100	8,100	2,800	8.6
5th Week	14,800	9,700	7,800	2,750	8.9

	PRODUCT FROM NAFION 475				
1st Week	40	30	90	70	8.9
2nd Week	50	25	110	80	9.4
3rd Week	35	30	120	100	9.1
4th Week	40	25	120	80	9.3
5th Week	30	25	130	110	9.2

	PRODUCT FROM NEPTON AZL				
1st Week	100	40	250	80	8.7
2nd Week	90	30	210	70	9.4
3rd Week	120	35	200	80	9.4
4th Week	80	45	190	90	9.4
5th Week	100	35	180	70	9.4

EXPERIMENT # 18

Membrane = NAFION 475
Temperature = 85°C (185° F)

Charge Pretreatment	CONTAMINANTS IN PRODUCT (ppm)						
	Solids	Urea	Salt	COD	Ammonia N	pH	Odor
None	120	40	30	90	70	8.9	highly objectionable
HCl (pH=1.8)	130	35	25	50	50	3.9	some disagreeable odor
CrO_3, H_2SO_4 and $CuSO_4$ (Putnam's formulation)	130	30	30	30	40	2.8	very faint odor

While the experimental findings are not conclusive, they indicate that pretreatment with an acid or combination of an acid and an oxidant would lead to a substantial decrease in the organic and ammonia contamination of the product water samples. This decrease is also accompanied by a large drop in the pH level of the samples (from 8.9 to 2.8-3.9).

This observation is in agreement with findings by various past investigators.[22-24]

a. Stabilization of Ammonia : Human urine contains ammonia in the forms of ammonium carbonate and ammonium bicarbonate. Ammonia and/or ammonium carbonate may also be formed by the decomposition of urea when stimulated by heat, enzyme urease, acids or alkalis. The ammonium carbonate and bicarbonate are unstable when heated. Conversion to an ammonium salt which has good thermal stability such as the chloride or sulfate would avoid the release of ammonia gas. The table below list some of the ammonium salts and their decomposition or sublimation temperatures.[24]

Ammonium Salt	Temperature of Decomposition or Sublimation °C	(°F)
Carbonate	58	(136)
Bicarbonate	36-60	(97-140)
Acetate	114	(237)
Chromate	180	(356)
Nitrate	210	(410)
Chloride	350	(662)
Bisulfate	490	(914)
Sulfate	513	(955)

b. Sterilization of Urine: The heat supplied to maintain the urine charge at 85° C(185°F) precludes the survival of most of the bacteria, and, as such, the enzymatic decomposition of urea. The semipermeable membrane also acts as a retainer of most bacteria. A sample of untreated urine charge after the 30-day operation at 85° C showed zero total bacteria count as well as zero coliform count . A sample of the product water after sanitization of the system also showed zero level on both counts.

Furthermore, many bacteria do not survive extreme pH's as well as heavy metals. As such, the system studied is very much free from microbiologically contaminations.

c. Stabilization of Volatile Organics: It has been well established by previous investigators that most of the odoriferous volatile organics present in human urine could be converted to less volatile or non-odoriferous form by the action of an oxidant. Hydrogen peroxide and chromium trioxide are two excellent examples of an oxidant that can be used in this system. Experiment actually showed a lower level of odoriferous materials as well as total organic contents in the product samples when the urine charge had been pretreated with an oxidant.

Sub-Task E -- Chemical Stability of the Membranes

As a result of the potential need of pretreating the urine charge so as to optimize processing rate and product quality, the chemistry of urine pretreatment has been investigated. The work of some past investigators is summarized in Table VIII. In addition, Experiment #19 has been designed to investigate the stability of the different membranes in different solutions of acids and oxidants.

Seven membranes with comparatively high flux than the others were chosen for this test. They were: -

DuPont's NAFION 170
DuPont's NAFION 475
Progil's RADIAN C1044
Ionics' NEPTON 61-AZL
DuPont's Cellophane PD192
Envirogenic's CAB 95
G.E.'s PPO-2

These membranes were cut into uniform pieces of 3" x 3/4" and immersed in eight different solutions of acids, germicides and oxidants for 40 days:

H_2SO_4 , pH = 1
H_2SO_4 , pH = 3
H_2SO_4 , pH = 5
$CuSO_4$, 10X Putnam's formulation[24]
CrO_3 , 10X Putnam's formulation[24]
H_2O_2 , 10X Putnam's formulation[24]
$H_2SO_4 + CrO_3$, Putnam's patent[39]
$H_2SO_4 + CrO_3 + CuSO_4$, Putnam's revision of patent[37]

Table VIII Urine Pretreatment Work by Past Investigators[24]

		SUCCESS OBTAINED			
Chemicals	Function	Fixing Ammonia	Stabilizing Organics	Others Mentioned	Major Problems Arisen
1. H_2SO_4	acid	good	inadequate	-	Organic volatiles
2. $K_2Cr_2O_7$ + H_2SO_4	oxidant acid	good	fair	-	Organic volatiles
3. CrO_3	acid,oxidant germicide	fair	good	no bacteria	Precipitate developed $Cr(OH)_3$. Some ammonia
4. CrO_3 + H_2SO_4	acid, oxidant Acid	good	good	-	Mold developed in long-term test[37]
5. $CuSO_4$ + H_2O_2	acid germicide oxidant	good	good	no bacteria	Precipitate formed $CuSO_4 \cdot 3\ Cu(OH)_2$
6. $CuSO_4$ + H_2SO_4 + CrO_3	germicide acid oxidant	good	good	no bacteria	None
7. P_2O_5 + CrO_3	acid, oxidant acid,oxidant germicide	good	good	-	High weight requirement. P_2O_5 deliquescent
8. Cl_2	oxidant,germicide	fair,pH dependent	inadequate	no bacteria	Cl_2 handling
9. Urease + citric acid	reactant acid	good	not known	-	N.B. Increased urea & Na Rejection in RO system[7]
10. HCl	acid	good	inadequate	-	H_2SO_4 and Cl_2 superior
11. SO_3, S_2O_7, $H_2S_2O_7$ or $H_2S_2O_8$	acid	good	fair	-	H_2SO_4 superior

The cellophane and the sulfonated polyphenylene oxide membranes demonstrated the least stability to oxidants. Their structure was so weakened that they separated into several pieces on shaking after immersion in CrO_3, H_2O_2, and the other two CrO_3-acid combinations. The other membranes were apparently stable in the acid-oxidant solutions, demonstrating no significant change in the physical properties measured at the beginning and the conclusion of the 40-day test. The properties monitored were -- specific gravity, thickness, water sorption, and ion-exchange capacity.

4. CONCLUSIONS AND RECOMMENDATIONS FOR FUTURE WORK

(i) High Processing Temperature. The work performed under this contract and the data presented in the literature show that a high processing temperature is singularly important in obtaining good processing rate, for this system.[16-21] All experiments, therefore, were conducted at the elevated temperature of 85° C(185° F), instead of the lower temperatures (below 145° F) recommended by previous investigators (to avoid urea decomposition).

It has not been determined whether the conversion of urea to ammonia at this temperature is a serious problem in the final design of the waste treatment system. Although a rise in alkalinity and the level of precipitation was observed to occur simultaneously with flux decline, a causal relationship has not been established.

It would seem that the trade-off between high processing temperature (its advantages of not requiring a germicide and yielding higher flux, and, thus, requiring less membrane area and the resultant hardware) and the problems it entails (higher energy requirement, ammonia handling, etc.) has to be studied in greater detail to determine what the optimum processing temperature should be.

(ii) Urine Pretreatments. Although many past investigators involved themselves with urine pretreatments, no solid data establishing their relationship to processing rate, product quality and membrane life could be found. Some experimental data have been presented in this report on this subject (e.g. addition of an oxidant and an acid improved product quality, certain membranes found to be stable with exposure to concentrated solutions of oxidants and acids for 40 days, etc.). However, much work still needs to be done in terms of comparing chemical pretreatments to charcoal post-treatment to improve the odor of the product water, studying the effect of pretreatment chemistry on membrane flux, etc.

(iii) Membrane Fouling. Various past investigators have dealt with this subject in other types of separation systems. However, no data were available for pervaporation. This project has dealt with membrane fouling in some detail (e.g. fouling has been related to precipitate formation, shown to be exposure-dependent, and partial flux recovery has been shown to be, at least temporarily, possible). However, before the optimum conditions can be determined for this system, a more detailed study of the mechanism of membrane fouling is necessary.

(iv) Membrane Fabrication. Various commercially available membranes have been studied in this and other investigation. The present study has demonstrated the superiority of ion-exchange membranes to cellulosic membranes in terms of mechanical strength and chemical resistance. However, the water passage of the existing ion-exchange membranes can be improved upon. (It should be remembered that ion-exchange membrane technology is not designed for high water permeability.) This project has devoted some effort in improving the mechanical strength of two existing membrane systems. Further investigation is warranted in terms of modifications of existing membrane systems (e.g. increasing interstitial spaces, decreasing membrane thickness, replacement of cloth type reinforcement with the KRATON type system, etc.), as well as, developing new membrane systems (e.g. styrene-butadiene).

REFERENCES

1. Kolnsberg, H.J. and Stoltz, M., "A Study to Analyze and Develop Design Criteria for Flight-Concept Prototype Vapor Diffusion Water Reclamation System." NASA CR-66637, prepared under NAS 1-7170 by Hamilton Standard, August 1968.

2. Kolnsberg, H.J. and Dudarevitch, M.D., "Water Reclamation by Membrane Vapor Diffusion," J.Eng. Ind. #90 (4), pp. 569-76,1968.

3. Kolnsberg, H.J. and Coe, W.B., "An Improved Water Reclamation System Utilizing a Membrane Vapor Diffusion Still Concept." NASA CR-66154 prepared under NAS 1-5312 by Hamilton Standard, July 1965.

4. Kolnsberg, H.J. and McCann, D.R., "Design and Fabrication of a Flight-Concept Prototype Vapor Diffusion Water Reclamation System," NASA CR-111932, Hamilton Standard, August 1971.

5. Warner, A. W., Brown, D.L., Glass, W., "Recovery of Potable Water from Urine by Membrane Permeation," AMRL-TDR-64-73, prepared for AF 33(657)-11353 by Ionics, Inc., September 1964.

6. Hendel, F.J., "Recovery of Water During Space Missions," ARS Jour., #32(12), pp.1847-1859, 1962.

7. Meier, E. A. and Everett, R., Jr., "The Feasibility of Using Membranes for Urine Purification," AMRI-TDR-63-113, prepared for AF33(657)-9347 by Radiation Applications, Inc., New York.

8. Tuwiner, S.B., "Research, Design and Development of an Improved Water Reclamation System for Manned Space Vehicles," NASA CR-66323, prepared for NAS 1-4373 by RAI Research Corp., New York.

9. Presti, J.B. et al, "A Laboratory Model of an Integrated Water Recovery System," AMRL-TDR-63-88 prepared for AF 33(657)-9310 by General Dynamics/Electric Boat, Connecticut.

10. Sendroy, J. and Collison, H.A., "Potable Water Recycled from Human Urine," Aerospace Med., #30, pp.640-9, 1959.

11. Bentel, J., "Water Recovery by Reiterative Freezing," AMRL-TDR-62-14.

12. Konikoff, J. and Okomoto, A., "Study of the Purification of Water from Biological Waste," NASA CR-16776.

13. Putnam, D. F. and Thomas, E.C., "Recovery of Potable Water from Human Urine," Aerospace Med., July 1969.

14. McRae, W. A., et al "Manned Orbital Space Station - Water Reclamation," Report No. SID 63-36-9, prepared by Ionics, Inc. for North American Aviation, Inc.

15. Bambenek, R.A. and Zeff, J.S., "Development of a Unit for Recovery of Water......", WADC Report #58-562, 1958.

16. Binnings, R.C. et al, "Separation of Liquid Mixtures by Permeation," Ind. and Eng. Chem., #53, p.45, January 1961.

17. Sanders, B.H. and Choo, C.Y., "Latest Advances in Membrane Permeation," Petroleum Refiner, June 1960.

18. Choo, C.Y., "Membrane Permeation," Chapter 2 in Vol. 6, Advances in Petroleum Chemistry and Refining, Interscience.

19. Choo, C.Y., "Structurally Modified Polymers as Permselective Membranes," D. Sc. Thesis, MIT, 1960.

20. McRae, W.A., "Liquid-Phase Permeation Through Membranes," Report, Ionics, Inc.

21. Rogers, C.E., Fels, M and Li, N.N., "Separation by Permeation Through Polymeric Membranes," Recent Developments in Separtion Science, pp.107 to 156, CRC Press.

22. Putnam, D.F., "Composition and Concentrative Properties of Human Urine," NASA-CR-1802, prepared for NAS 1-8954 by McDonnell Douglas Astronautics Co., California, July 1971.

23. Putnam, D.F., "Chemical and Physical Properties of Human Urine Concentrates," NASA CR-66612 prepared for NAS 1-7104 by Douglas Aircraft Company, California, April 1968.

24. Putnam, D.F., "Chemical Aspects of Urine Distillation," ASME #65-AV-24. Presented at Aviation and Space Conference, L.A.

25. See Appendix II, this report.

26. See Appendix III, this report.

27. See Appendix IV, this report.

28. Helfferich, F., Ion Exchange , Chapter 4, McGraw-Hill Book Company, Inc.

29. McBain, J.W. and Stuewer, R.F., "Ultrafiltration Through Cellophane of Porosity Adjusted Between Colloidal and Molecular Dimensions," presented at the 13th Colloidal Symposium, St. Louis, June 1936.

30. Barrer, R. M., "Permeability in Relation to Viscosity and Structure of Rubber".

31. Barrer, R.M., "The Zone of Activation in Rate Processes".

32. La Conti, A.B., "Development of Sulfonated Polyphenylene Oxide Membrane for the Reverse Osmosis.....", ASME #73-ENAs-16, 1973.

33. Lawrence, R. W. and Saltonstall, C.W., "The Application of Reverse Osmosis to Wash-Water Renovation," ASME #73-ENAs-12, 1973.

34. Technical Notes from duPont.

35. Eisenmann, J.L. and Roach, E.T., "Electrodialysis Membranes", presented at AIChE symposium, Washington, D.C., November 1969.

36. Analysis of precipitate yields - 48% Lowry protein, 23% salt, 9% urea, 20% unknown.

37. Anon. "Conference on Nutrition and Space and Related Waste Problems," NASA-SP-70, April 1964.

38. Fieser, L.F. and Fieser, M., "Organic Chemicstry", Chapter 16, D.C.Heath & Co., Publishers.

39. Putnam, D.F., et al "Recovery of Water from Urine by Chromium Ion Treatment and Distillation," U.S. Patent # 3,556,949, January 1971.

40. "Standard Methods for the Examination of Water and Wastewater," published by APHA, AWWA, WPCF.

41. Analytical Chemistry, #27 (3), p.454.

APPENDIX I

Literature Studies Performed Under This Contract

A. Literature pertaining to Pervaporation - see References 16-21.

B. Literature pertainint to Urine, see References 22-24, 38,39.

C. Literature pertaining to Water Recovery from Urine by Pervaporation, see References 1-5.

D. Literature pertaining to Competing Processes, see References 6-15, 24, 37; also,

Bambnek, R.A., Zeff, J.S., "Life Systems Designed for Maintainability," Space Aeronautics, Vol.37, No. 1, pp.54-59, 1962.

Metzger, C.A. et al, "Applications of Radioisotope for Aerospace Waste Reclamation and Water Systems," U.S. Government Research Development Rep. #68(8), 37, 1968.

Behls, H.F., Zeff, J.D., "Preliminary Test Report for AMF Model 08-062 Water Reclamation System," American Machine and Foundry Company Report, 1962.

Wallman, H., Barnett, S.A., "Water Recovery Systems (Multi-Variable)", WADD Tech. Rep. #60-243, 1960.

Nau, R.A., "Environmental Control Systems for Space Vehicles," ASME paper #59-AV-V,1959.

Bambenek, R.A., Zeff, J.A., "Water Recovery in a Space Cabin," Astronautics, Vol. 4, 1959.

Bambenek, R.A., Zeff, J.S., "Development Status of Advanced Life-Support Systems" ARS Journal, October 1961.

Collins, V.G., Popina, D.C., "Water Reclamation and Conservation in a Closed Ecological System," presented at Ecological Technology Symposium, Washington, D.C., February 1966.

McRae, W. A., McGriff, S.G., "Waste System for Aerospace Stations," Proposal by Ionics, Inc., October 1962.

McRae, W.A., et al,"Self-Deploying Space Station Water Reclamation System," Ionics, Inc., Report, September, 1962.

Slonim, *et al.*, "Water Recovery from Physiological Sources for Space Applications," Final Report for MRL-TDR-62-75.

Ginwala, K., "Engineering Study of Vapor Cycle Cooling Equipment for Zero-Gravity Environment", WADD Tech. Rep. #60-776.

Sandage, C.N., "Techniques for the Sterilization of Wastes," ASD Tech. Rep. #61-575.

Bentel, J., "Water Recovery by Reiterative Freezing", Tech. Rep. #MRL-TDR-62-14.

Wallman, H., Steele, J.A., "Water Reclamation Subsystems for a Space Station," presented Am.Inst.Chem.Eng., 53rd National Meeting, March 1964.

Anon. "Preliminary Research from an Operational 90-day Manned Test of a Regenerative Life Support System," pp.35-98, 251-8.

Anon. "NASA Life Sciences Data Book", June 1962, pp.117-121.

Bates, J.H., "Recent Aspects in the Development of a Closed Ecologic System," *Aerospace Med.* 32, 12-24, January 1961.

E. Latest Relevant Literature: presented at the Intersociety Conference on Environmental Systems, July, 1973:

Houck, O.K., Symons, J.J., "Laundering in Space - A Summary of Recent Developments," ASME Paper No. 73-ENAs-43.

Sofios, M., "Microbial Contamination of Water-Traditional and Space-Age Problems and Approaches," ASME Paper No. 73-ENAs-33.

Singer, G.A., Hanlon, W.H., Senator, F.E., "Advanced Trash Mangement System", ASME Paper No. ENAs-31.

Ingelfinger, A.L., Murray, R.W., "Waste Management Systems Overview for Future Spacecraft", ASME Paper No. 73-ENAs-18.

Behrend, A.F., Swider, J.E., "Zero Gravity and Ground Testing of a Waste Collection Subsystem for the Space Shuttle", ASME Paper No. 73-ENAs-42.

Manning, M., Reid, R.C., "Adsorption of Spacecraft Contaminants on Bosch Carbon," ASME Paper No. 73-ENAs-15.

Gibb, J.W., Lauback, G.E., Stoll, O.T., "Space Shuttle Orbiter Environmental Control and Life Support Systems (EC/LSS)," ASME Paper No. 73-ENAs-23.

Wells, G.W., Wong, W., Putnam, D.F., "Design Considerations for Spacecraft Wash-Water Processing by Reverse Osmosis," ASME Paper No. 73-ENAs-3.

LaConti, A.B., "Development of Sulfonated Polyphenylene Oxide(PPO) Membrane for the Reverse Osmosis of Wash Water at Sterilization Temperature (165° F)" ASME Paper No. 73-ENAs-16.

Lawrence, R.W., Saltonstall, C.W., "The Application of Reverse Osmosis to Wash Water Renovation," ASME Paper No. 73-ENAs-12.

F. U.S. Patents

Putnam, et al., "Recovery of Water from Urine by Chromium Ion Treatment & Distillation" at United Aircraft #3,556,949, approved January 19,1971.

Guter, G.A., et al., "Water Purification" at McDonell-Douglas #3,582,485, approaved June 1, 1971.

Zeff, J.D., "Method of Purifying Waste Water by Catalyctic Oxidation," at Arde Inc., #3,487,016, approved July 14, 1967.

Putnam, "Process of Extracting Potable Water from Urine," at United Aircraft #3,428,535, approved February 18, 1969.

Hayes, L.W., Cross, J.T., "Urine Recovery Process by Thermo-Electnz Distillation & Filtration" at Whirlpool Corp. #3,506,543, approved April 14, 1970.

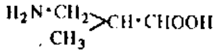
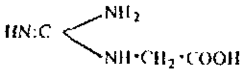
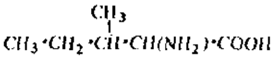
Lindstrom, R.W., "Water Recovery by Electrodialysis," at Ionics, Inc., #3,268,441, approved August 23, 1966.

APPENDIX II

CONSTITUENTS OF HUMAN URINE EXCEEDING 10 mg/l.[22]

Item	Formula	Formula Weight	Range		Solubility Limit In A Binary Solution
			mg/l	mg/l	g/100g H_2O
Total Solutes			36,700	46,700	---
Urea	H_2NCONH_2	60.1	9,300	23,300	119
Chloride	Cl^-	35.5	1,870	8,400	---
Sodium	Na^+	23.0	1,170	4,390	---
Potassium	K^+	39.1	750	2,610	---
Creatinine	$C_4H_7N_3O$	113.1	670	2,150	8.7
Sulfur, Inorganic	S	32.1	163	1,800	---
Hippuric Acid	$C_6H_5CO\cdot NHCH_2\cdot CO_2H$	179.2	50	1,670	0.367
Phosphorus, Total	P	31.0	470	1,070	---
Citric Acid	$HOC(CH_2CO_2H)_2CO_2H$	192.1	90	930	208
Glucuronic Acid	$C_6H_{10}O_7$	194.1	70	880	S.
Ammonia	NH_3	17.0	200	730	---
Uric Acid	$C_5H_4O_3N_4$	168.1	40	670	0.00645
Uropepsin (as Tyrosine)	$HO\cdot C_6H_4\cdot C_2H_3(NH_2)\cdot CO_2H$	181.2	70	560	0.04
Bicarbonate	HCO_3^-	61.0	20	560	---
Creatine	$HN{:}C(NH_2)N(CH_3)\cdot CH_2\cdot CO_2H\cdot H_2O$	149.2	0	530	1.4
Sulfur, Organic	S	32.1	77	470	---
Glycine	$NH_2\cdot CH_2\cdot CO_2H$	75.1	90	450	23
Phenols	$C_6H_5\cdot OH$	94.1	130	420	8.2
Lactic Acid	$CH_3\cdot CHOH\cdot CO_2H$	90.1	30	400	∞
Calcium	Ca^{+2}	40.1	30	390	---
Histidine	$C_3H_3N_2\cdot CH_2\cdot CH\cdot (NH_2)\cdot CO_2H$	155.2	40	330	S.
Glutamic Acid	$HO_2C\cdot CHNH_2\cdot (CH_2)_2\cdot CO_2H$	147.1	<7	320	1.5
Androsterone	$C_{19}H_{30}O_2$	290.5	2	280	i.;S.
1-Methylhistidine	$C_3H_3N_2CH_2CH(NH\cdot CH_3)\cdot COOH$	169.2	30	260	
Magnesium	Mg	24.3	20	205	---
Imidazole Derivatives	$C_3H_4N_2$	68.1	90	200	S.
Glucose	$C_6H_7O_6(COCH_3)_5$	390.4	30	200	0.15
Taurine	$NH_2\cdot CH_2\cdot CH_2\cdot SO_3H$	125.2	5	200	6.4
Aspartic Acid	$C_4H_7O_4N$	133.1	<7	170	2.71
Carbonate	CO_3^{-2}	60.0	100	150	---
Cystine	$[HO_2C\cdot CH(NH_2)\cdot CH_2S\cdot]_2$	240.3	7	130	0.01
Citrulline	$NH_2CONH(CH_2)_3\cdot CH\cdot (NH_2)\cdot CO_2H$	175.2	0	130	S.
Threonine	$C_4H_9O_3N$	119.1	10	120	S.
Lysine	$(NH_2)_2C_5H_9\cdot CO_2H$	146.2	5	110	V.S.
Indoxylsulfuric Acid	$C_8H_7ON\cdot H_2SO_4$	231.2	3	110	
m-Hydroxyhippuric Acid	$C_4H_4COHC(CONH\cdot CH_2COOH)$	195.2	1	100	
p-Hydroxyphenyl-Hydrocrylic Acid			1	100	

CONSTITUENTS OF HUMAN URINE EXCEEDING 10 mg/1.

Item	Formula	Formula Weight	Range		Solubility Limit In A Binary Solution
			mg/l	mg/l	g/100g H_2O
Aminoisobutyric Acid	 $H_2N{\cdot}CH_2 > CH{\cdot}CHOOH$, CH_3	103.1	3	120	
Inositol	$C_6H_{12}O_6$	180.2	5	100	
Formic Acid	$H{\cdot}CO_2H$	46.0	20	90	∞
Urobilin	$C_{33}H_{40}O_6N_4$	588.7	7	90	
Tyrosine	$HO{\cdot}C_6H_4{\cdot}C_2H_3(NH_2){\cdot}CO_2H$	181.2	10	70	0.04
Pyruvic Acid	$CH_3{\cdot}CO{\cdot}CO_2H$	88.1	2	70	∞
Albumin			7	70	
Asparagine	$HO_2C{\cdot}CH(NH_2){\cdot}CH_2{\cdot}CONH_2$	132.1	20	70	3.1
Tryptophan	$\underbrace{C_6H_4{\cdot}NH{\cdot}CH{:}C}{\cdot}C_2H_3(NH_2)CO_2H$	286.8	5	60	25
Ketones (as Acetone)	CH_3COCH_3	58.1	10	50	∞
Serine	$HO{\cdot}CH_2{\cdot}CHNH_2{\cdot}CO_2H$	105.1	20	50	4
Alanine	$H_2N{\cdot}CH(CH_3){\cdot}CO_2H$	89.1	15	50	20.5
Purine Bases	$C_5H_4N_4$	120.1	0	50	i.
Glycocyamine			15	45	
Proline	$H\underbrace{N{\cdot}(CH_2)_3{\cdot}C}H{\cdot}CO_2H$	115.1	<7	40	V.S.
Arginine	$H_2N{\cdot}C(:NH){\cdot}NH{\cdot}(CH_2)_3{\cdot}CH(NH_2){\cdot}CO_2H$	174.2	<7	40	15
Ascorbic Acid	$C_6H_8O_6$	176.1	3	40	V.S
Oxalic Acid	$HO_2C{\cdot}CO_2H$	90.0	1	30	10
Bilirubin	$C_{33}H_{36}N_4O_6$	584.7	3	30	i.
Valine	$(CH_3)_2CH{\cdot}CH(NH_2){\cdot}COOH$	117.2	<7	30	
Phenylalamine	$\beta{\cdot}C_6H_5{\cdot}CH_2{\cdot}CH(NH_2){\cdot}COOH$	165.2	6	30	
Allantoin	$C_4H_6O_3N_4$	158.1	2	25	0.76
Oxoglutaric Acid	$C_5H_6O_5$	146.1	13	25	
Leucine	$(CH_3)_2CH{\cdot}CH_2{\cdot}CH(NH_2){\cdot}COOH$	131.2	8	25	
Guanidinoacetic Acid	 $HN{:}C<\begin{matrix}NH_2\\ NH{\cdot}CH_2{\cdot}COOH\end{matrix}$	117.1	9	25	
Isoleucine	 $CH_3{\cdot}CH_2{\cdot}\overset{\overset{CH_3}{\vert}}{CH}{\cdot}CH(NH_2){\cdot}COOH$	131.2	4	22	
Urobilinogen			0	17	
Ethanolamine	$NH_2{\cdot}CH_2{\cdot}CH_2OH$	61.1	3	15	∞
Guanidine	$(H_2N)_2C{:}NH$	59.1	7	13	V.S.
Methionine Sulfoxide			0	13	
Dehydroascorbic Acid	$C_6H_6O_6$	174.1	3	13	
Other Organics				285	

PRECEDING PAGE BLANK NOT FILMED

APPENDIX III

Concentration of Contaminants in Product Water Compared to Established Potability Standards

Contaminants	Sample from NAFION 475	Ham. Std.'s (Cellophane)	US PHS Limits	SSB-NAS Limits
Total Solids	120	76	500	1000
Volatile Solids	ND	20	NS	NS
Total Nitrogen	82	15	NS	NS
Ammonia Nitrogen	50	14	NS	NS
Urea	30	ND	NS	NS
C.O.D.	80	8	NS	200
Chloride	25	.5	250	450
Sulfate	ND	10	250	250
Phosphate	2.4	ND	100	150
Sodium	14	ND	200	200
Potassium	7	ND	100	100
Iron	.3	.01	.3	NS
Copper	0	.06	1.0	3.0

NS = Not specified

ND = Not determined

APPENDIX IV

CHEMICAL ASSAYS

Contaminants Monitored	Methods Used
Total Solids	STANDARD METHODS[40] # 164
C.O.D.	" " # 220
Salt	" " # 112
Ammonia Nitrogen	" " # 132 (Cross checked with ORION's electrode)
pH	" " # 144
Urea	p-dimethyl aminobenzaldehyde reaction[41]
Protein	Lowry Assay
Metals	Atomic Absorption (performed by Metcalf and Eddy, Boston)
Total Nitrogen	STANDARD Methods #135(M&E)
Bacteria	" " #408 A & 408B