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April 1, 1976

NASA CR-137814

ANNUAL REPORT
GSRI Project No. 323-649-10

WATER VAPOR DIFFUSION MEMBRANES II

Prepared for:

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

Prepared by:

F. F. Holland, Principal Investigator
Elias Klein
James K. Smith
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I. INTRODUCTION

During the first year of this contract, transport mechanisms were investigated for the three different types of water vapor diffusion membranes. Membranes representing porous wetting and porous nonwetting structures as well as dense diffusive membrane structures were investigated for

a. Water permeation rate as a function of temperature.

b. Water permeation rate as a function of solids composition in solution.

c. Water permeation rate as a function of such hydrodynamic parameters as sweep gas flow rate, solution flow rate and cell geometry.

These properties were measured using nitrogen sweep gas to collect the effluent. In addition, the chemical stability to chromic acid-stabilized urine was measured for several of each type of membrane.

A technology based on the mechanism of vapor transport was developed, whereby the vapor diffusion rates and relative susceptibility of membranes to fouling and failure could be projected for long-term vapor recovery trials using natural chromic acid-stabilized urine. This study revealed that porous nonwetting membranes offer the greatest service lifetimes and highest flux with minimal loss of flux caused by fouling. This higher performance is attributed to the fact that the water is vaporized at the liquid-membrane interface, where deposited foulants can be adequately removed by adjusting the solution flow velocities. Porous wetting membranes, although having high flux rates, fouled more rapidly because the urine is evaporated at the gas/membrane interface, and solids are deposited in the membrane pores. The removal of foulants from the membrane pores is controlled by the diffusion of the foulant materials back through the membrane into the bulk solution.

Dense diffusive membranes were found to offer the greatest potential for high quality effluent. However, fluxes for such membranes are 100 to 1,000 times lower than those obtained with porous membranes.

On the basis of this technology, a 30-day vapor diffusion recovery (VDR) trial was completed using a fluorocarbon porous nonwetting membrane. During this trial, effluent water quality, urine brine properties and

fluxes were measured. The trial indicated that the fluorocarbon membrane should be tested further to investigate urine pretreatments and chemical composition of the urine as means to control effluent water quality and membrane fouling.

During the past year, work has been directed toward reducing membrane fouling by pretreating the urine brine. Several pretreatment schemes were investigated. Fouling was found to be caused by two mechanisms:

a. Calcium carbonate and magnesium carbonate are deposited on the membrane as the solubility limits of the materials are exceeded.

b. Organic deposits were found when the inorganic ions were removed by pretreatment using ion exchange resins. These deposits are thought to be protein and other complex organics which plate out on the membrane surface. Such organic deposits can reduce the surface tension on the porous nonwetting membrane and allow wetting and convective flow. To alleviate this problem, membranes of tighter pore size and/or oxidation of the foulants using chromic acid were found to be effective.

The data obtained from long-term trials carried out during this contract year suggest that a VDR process can be designed using the fluorocarbon porous nonwetting membrane and pretreated urine. Such a process should be capable of uneventful functioning for 30 days with recovery of 90% of the available water from urine.

In addition to testing VDR applications to recovery of water from urine, an effort was directed to an evaporation process to vent water vapor from waste-waters on board the space shuttler craft. The purpose here is to reduce onboard storage requirements for waste fluids and to obtain supplemental spacecraft cooling in order to conserve fuel cell water previously required for cooling. For this application, it was found that wastewaters containing soaps have surface tension too low for processing by use of available porous nonwetting membranes and hard space vacuum as the driving force. For this application, much tighter membranes are needed. Possibly dense diffusion membranes would be desirable for this application if it is not possible to chemically treat the urine-wash water mixture to maintain a critical surface tension which will allow use of the nonporous wetting membranes.

II. CELL DESIGN AND CONSTRUCTION

Previous VDR trials[1] used a commercial osmotic diffusion plate-and-frame cell. The total surface area of this cell was adjustable by inserting as many plates as desired to achieve the needed membrane surface area. Although this cell design was convenient, it suffered from several serious drawbacks:

a.   The cell had internal manifolds and the channel height was fixed by the thickness of the plates.
These factors caused large liquid side pressure drops across the cell when the liquid flow rates were increased.

b.   The channel length to width ratio was large compared to that of cells which were used to obtain basic membrane permeability data.

Because of these geometric design limitations, liquid and gas flows could not be maximized to reduce mass transfer resistances. Also, because of the relatively slow liquid side linear velocity and the long channel length, membrane fouling was a serious problem.

A new cell, similar to the diffusion cells used to characterize the VDR membranes, was designed and constructed. Its active membrane area was 194 cm^2 in two parallel plates. The gas and liquid channel heights, as well as the length to width ratio of the new cell, were similar to those of the diffusion cells. The cell is externally manifolded so that high flow rates are achievable at low pressure drops. Thus, the turbulence and the fluid boundary resistance should be similar to those of the diffusion cells at the same liquid and gas velocities. Because of the higher efficiency, larger volumes of urine could be processed with this cell. Also, measurement of test parameters and the calculation of flow characteristics should be facilitated. These factors are especially important for analyzing the solids deposition problem. A diagram of the cell cross section is shown in Figure 1. To increase turbulence, a Vexar screen is inserted in both the gas and liquid channels. A schematic of the VDR system is shown in Figure 2. This system is essentially the same as that reported last year except that it has been better instrumented and constructed entirely from type 316 stainless steel, glass, and high density polyethylene. After several tubing and pump failures, a system was developed which contained only
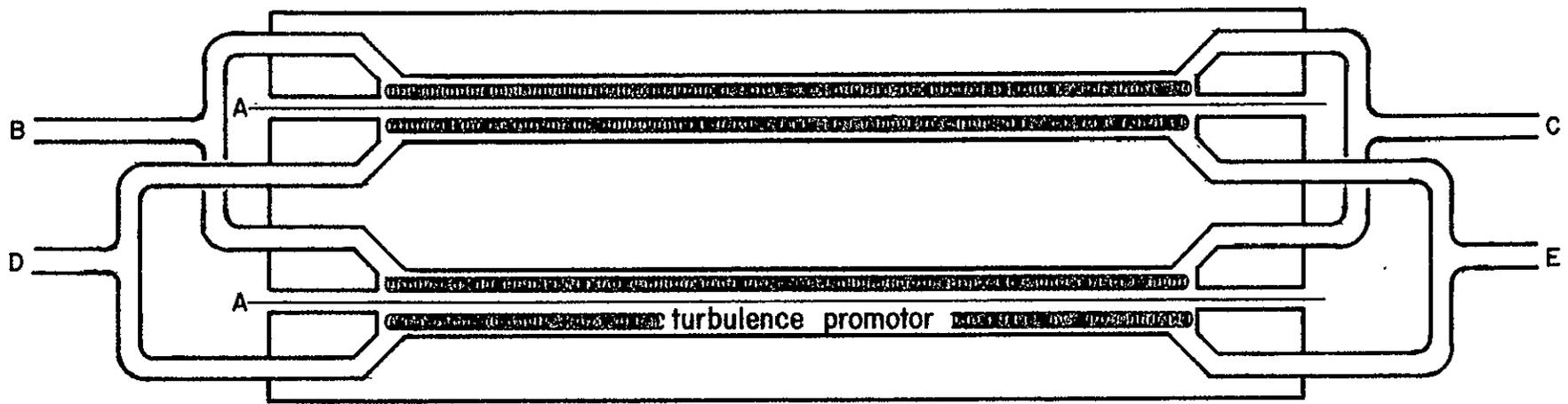
A- Membrane, B-C — Gas Channel, D-E—Liquid Channel, Membrane Area = 194 cm^2

FIG. 1.   G. S. R. I. VAPOR DIFFUSION RECOVERY CELL
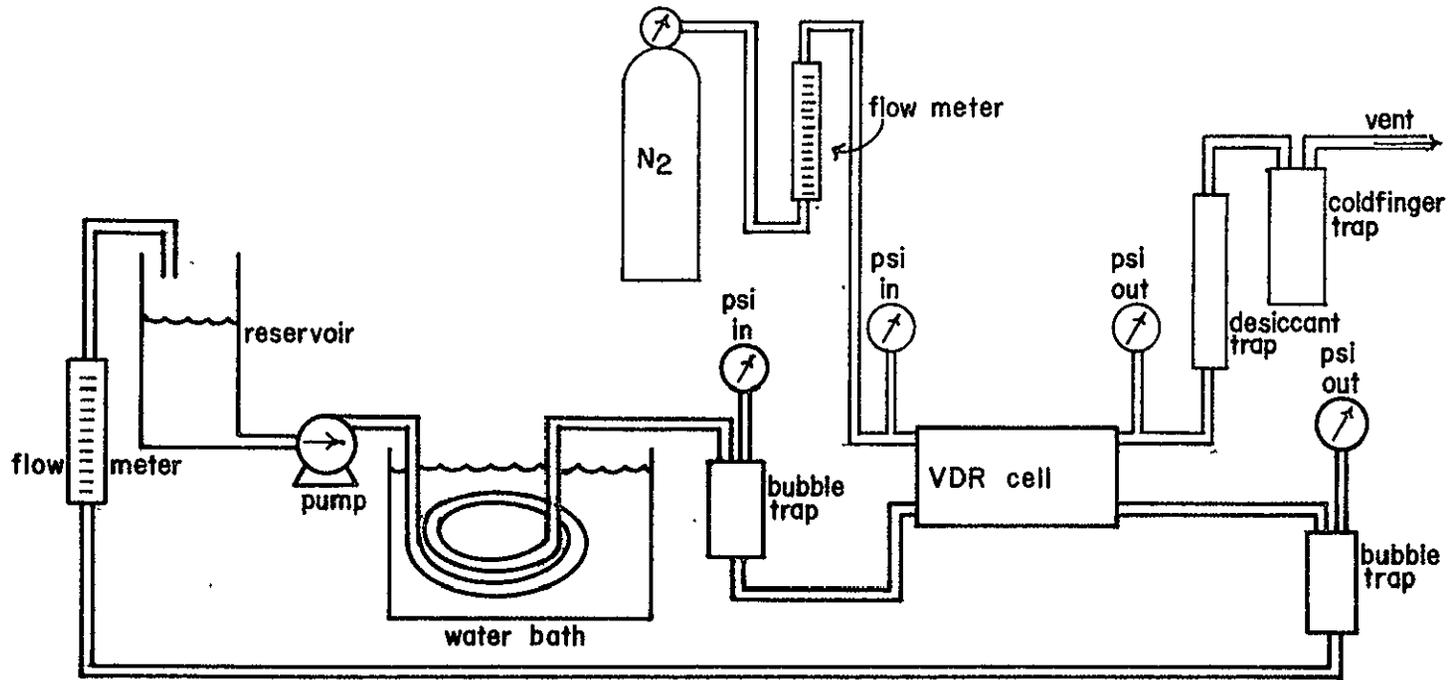
FIG. 2. SCHEMATIC DIAGRAM OF G.S.R.I. VAPOR DIFFUSION RECOVERY SYSTEM

stainless steel and propylene tubing and in which all connections used
Swagelock fittings, thus eliminating possible failure points. A magnetically
coupled Teflon gear pump having a variable output of 100 to 4000 ml/min
was installed for maintenance-free service. Instrumentations include

    a. liquid and gas flow rate measurement

    b. liquid and gas inlet and outlet pressure measurement

    c. liquid and gas inlet and outlet temperature measurement.

A preheater was added to the gas inlet to control the sweep gas temperature
to that of the liquid. The temperature also could be raised to compensate
for cooling during evaporation. Flux is measured by weighing a desiccant
column before and after a time collection interval. Effluent water is
collected using two containers, one at 0°C and the other at dry ice
acetone temperature (-78°C).

    The new VDR cell was initially characterized using distilled water
as feed solution. The water flux achievable using this cell is shown in
Figure 3 for the L-10272 membrane. The data were taken at 25°C and 60°C.
In Figure 4, these data are compared to the diffusion cell data gathered
during the previous contract year. To normalize the data for direct
comparison, the flux has been plotted as a function of the linear velocity
of the sweep gas. When the new, larger cell is used, the sweep gas linear
velocity is greatly reduced from that measured in the diffusion cell for
the same sweep gas flow rates. However, the data do agree reasonably
well, indicating that the cells have similar flow patterns.
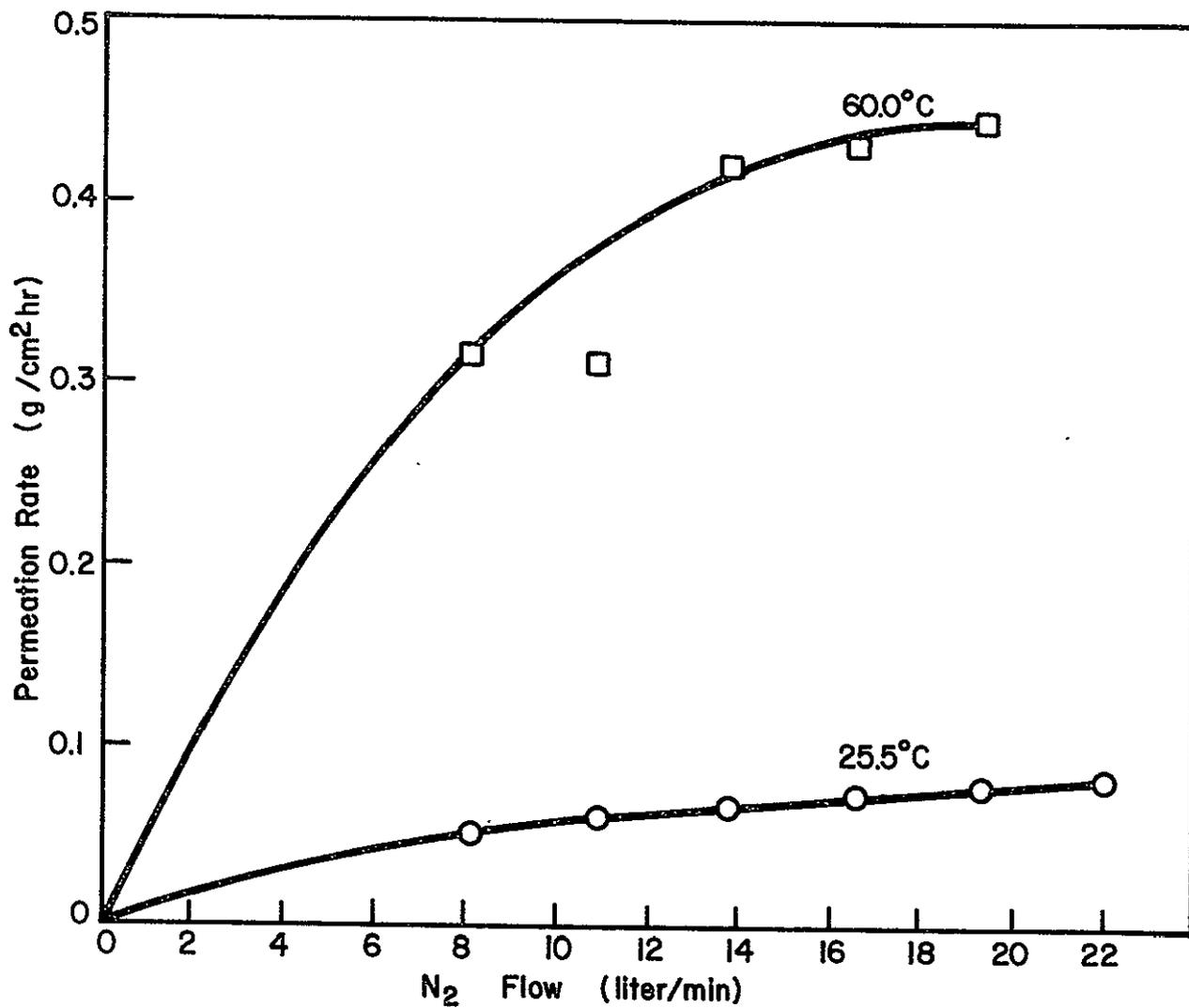
FIG. 3. Distilled water permeation rate through Gore-Tex L-10272 vs. N_2 flow rate.

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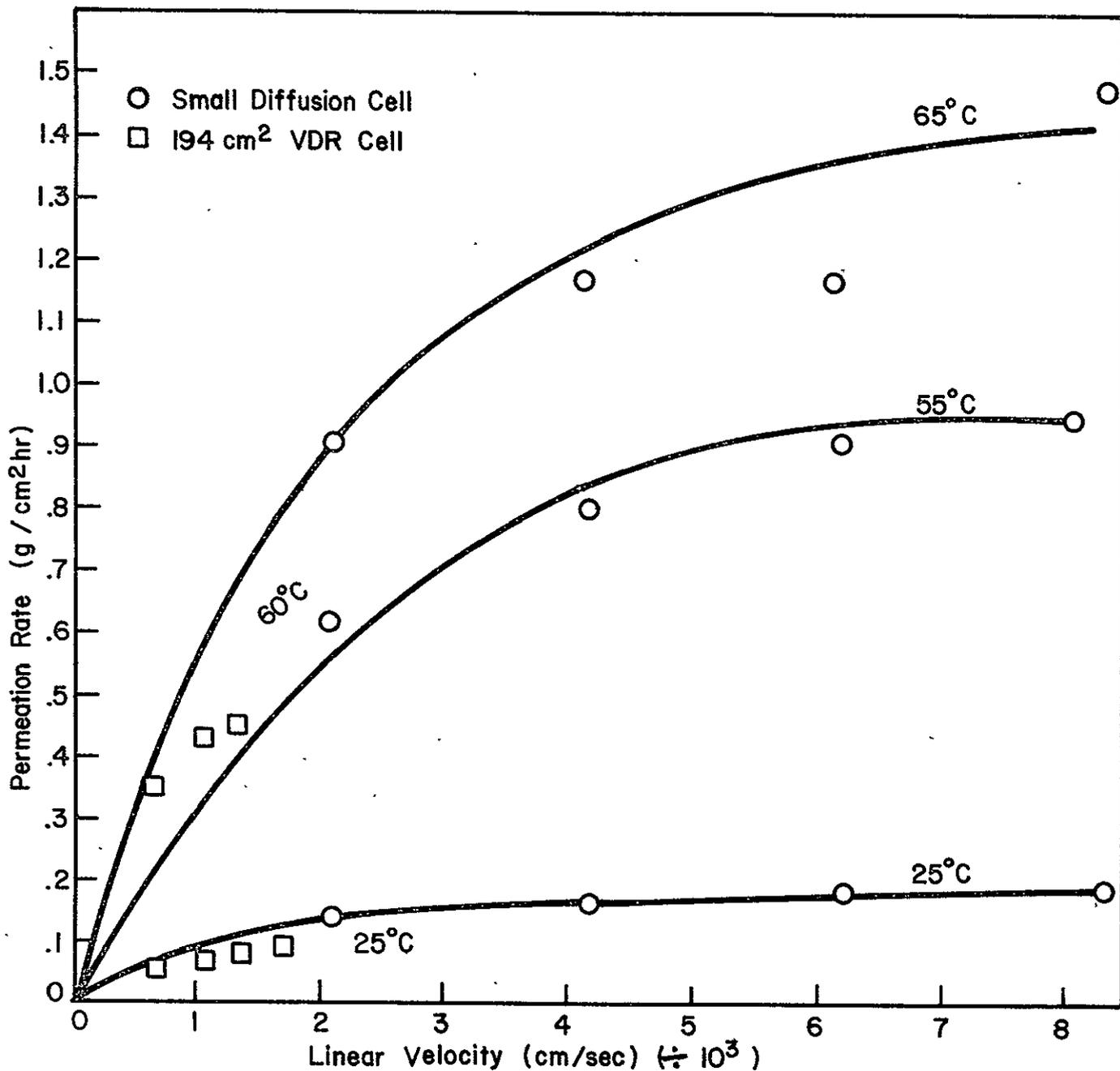
FIG. 4 Permeation rate as a function of sweep gas linear velocity at membrane surface.

III. VAPOR DIFFUSION RECOVERY TRIALS

During the recent contract year, our primary goal was to test the reliability of the porous nonwetting membranes for extended VDR trials. These trials examined several urine pretreatments for their effects upon

a. membrane flux and the rate of membrane fouling

b. water quality

c. urine brine stability

All VDR trials used the single-backed Gore-Tex L-10272 fluorocarbon membrane at 60°C unless otherwise stated. Gas and liquid inlet and outlet pressures and temperatures were monitored during the trials. Liquid and gas flow rates were fixed at about 600 ml/min (4.1 cm/sec linear velocity) and 15 liter/min (1,000 cm/sec), respectively. During the trials the water permeation rate and urine brine properties were measured twice daily. Urine properties measured were pH, kinematic viscosity at 60°C, and total solids. Effluent water was collected over a several-hour period using two traps in series at 0°C and -78°C. Quality parameters determined on the effluent included pH, color (clarity), odor, conductivity, total organic carbon (TOC), and ammonia content. Trial results will be plotted as time history graphs for the urine and effluent properties.

In addition to the measurement of effluent properties as a result of urine pretreatment, several experiments were designed to clean up the effluent using a posttreatment. Activated charcoal and polymeric absorbers were tested for this purpose. Total organic carbon and ammonia removal were the prime parameters monitored for these tests.

Membranes were loaded in the cell using Teflon tape as gasketing material. Usually several layers of tape were required to seal the L-10272 polypropylene-backed membrane. Unbacked membranes having a low modulus were self-sealing. After the membranes were loaded, the cell was pressure-tested with air. The membrane was leak tested by circulating a 1% sodium chloride solution through the liquid channel and distilled water through the gas channel. The distilled water was then checked for salt content using silver nitrate solution. A silver chloride precipitate in the distilled water indicated a membrane leak.

Table 1 summarizes the VDR trials completed during this year. Initially our concern was to develop test methods to measure effluent water quality. Trials 2-1 through 2-3, in addition to providing data showing the reliability of the Gore-Tex membrane, supplied us with sample water for these tests. Our original intention was to analyze for volatile organics by gas chromatography. However, these tests proved to be extremely time consuming and expensive. In the few chromatographic analyses that were run, the chromatographs were very complex and not easily interpreted. To get definitive data on the quantity and identity of the volatile materials present would require capillary column analyses using GC-mass spectrometry techniques. In view of the cost of such analyses, they were deferred to a later date when post VDR cleanup methods are to be investigated. For the present program, effluent quality tests should be used only to insure that any chemical pretreatment of urine or membrane system investigated does not drastically alter the effluent. For this purpose, the effluent water quality can be measured by simpler, more direct tests such as pH, conductivity, TOC, and ammonia content.

TABLE 1: SUMMARY OF VAPOR DIFFUSION RECOVERY TRIALS

Trial	Duration (days)	Membrane	Urine Pretreatment	Gas Flow Rate (1/min)	Permeation Rate Start (g/cm^2-hr)	End	Rate Loss (%)	Total Solids (%)	Water Recovered (%)	Objective of Trial
2-1	4	L-10272	4 g/1 chromic acid added to natural urine	22	0.39	0.33	14	5.73	80	Background effluent quality data
2-2	6	L-10272	"	24	0.52	0.29	44	8.81	85	"
2-3	11	L-10272	"	19	0.32	0.21	34	33	92	"
2-4	3	L-10272	30% solids urine from run 2-3, total recycle	--	----	----	--	33.8	--	Membrane fouling data at constant urine solids level; fouling determined gravimetrically
2-5	11	L-10272	no treatment	15	0.31	0.15	50	14.5	78	Effluent and fouling data
2-6	2	L-10272	pH controlled to 3.5 with H_3PO_4	14	0.38	0.31	18	5.6	55	"
2-7	4	L-10272	"	15	0.42	0.33	21	7.7	68	"
2-8	7	L-10272	"	15	0.38	0.18	53	16.4	84	"
2-9	14	L-10272	Ca depleted by ion exchange	15	0.39	0.14	65	23	93	"
2-10	14	L-10272	Ca depleted, chromic acid stabilized	15	0.33	0.24	30	30	95.5	"
2-11	5	S-10396	Urine from 2-9 trial using 55.5 cm^2 diffusion cell	15	0.66	0.68	0	23	----	membrane wetting and fouling properties
2-12	16	CAB (Ionics)	Ca depleted	15	0.47	0.10	78	14	93	effluent and fouling data

Chromic Acid-Stabilized Urine

It has been previously reported[1] that the suspended solids content of concentrated chromic acid-stabilized urine shows a dependence on pH. In an effort to determine how this relationship might affect the fouling rate of Gore-Tex membrane during a VDR trial, a more thorough investigation of this parameter was undertaken. The total solids content--both suspended (filterable) and dissolved (nonfilterable)--of a concentrated chromic acid-stabilized urine solution was measured as a function of pH. This test was accomplished by separating a nominal 30% solids urine concentrate from a VDR trial into six aliquots and adjusting the pH of each aliquot to the desired value. A pH range from 2 to 7 was chosen. The solutions were then filtered using preweighed glass fiber filters (medium porosity). The filters and the filtrates were dried in tared crucibles to constant weight at 105°C and then at 550°C. This experiment was designed to indicate the volatile and nonvolatile filterable and nonfilterable solids as a function of urine pH. The results are shown in Table 2. These data are also displayed in Figure 5 as a plot of % solids versus pH. The present data contradict previously reported data; apparently, the suspended solids content is not a fixed function of urine pH. Urine used in the latest experiment was about twice the concentration of that used in the previous experiment (33.9% compared to 16.5%). It is possible that the pH dependence is also a function of the total solids content. Within the experiment summarized in Table 2, the variation of total suspended solids with pH is relatively small (1.1 to 3.1%). The effect of total suspended solids as a function of pH on the rate of membrane fouling would be difficult to estimate, because apparently this parameter varies with the solids content of the urine, which continuously varies during a given trial as the water is evaporated. However, several trials were designed to test the pH dependence using the data obtained at 34% solids as a model.

Data for VDR trials using chromic acid-stabilized natural urine are shown in Figures 6 and 7. Trial 2-1 used chromic acid-stabilized urine without pH control. This trial was discontinued prematurely due to equipment failure. However, 80% of the available water was recovered with approximately

TABLE 2

SOLIDS CONTENT OF CONCENTRATED (30% NOMINAL) CHROMIC
ACID-STABILIZED URINE (SPECIFIC GRAVITY = 1.169 g/ml),
g/100 ml SAMPLE

Adjusted pH	Filterable Solids		Nonfilterable Solids		Total Solids (Filterable) and (Nonfilterable)
	Total	Residue (Nonvolatile)	Total	Residue (Nonvolatile)	
2	1.06	0.805	34.0	13.9	35.1
3	0.736	0.553	31.6	13.4	32.3
4	0.436	0.248	32.8·	14.1	33.2
5	0.586	0.278	32.4	13.8	33.0
6	0.356	0.204	35.6	14.1	36.0
7	1.01	0.596	33.0	14.5	34.0
					33.9

Fig. 5

SUSPENDED SOLIDS AS A FUNCTION OF URINE pH

Total Solids = 33.9%

Specific Gravity 1.169 g/ml
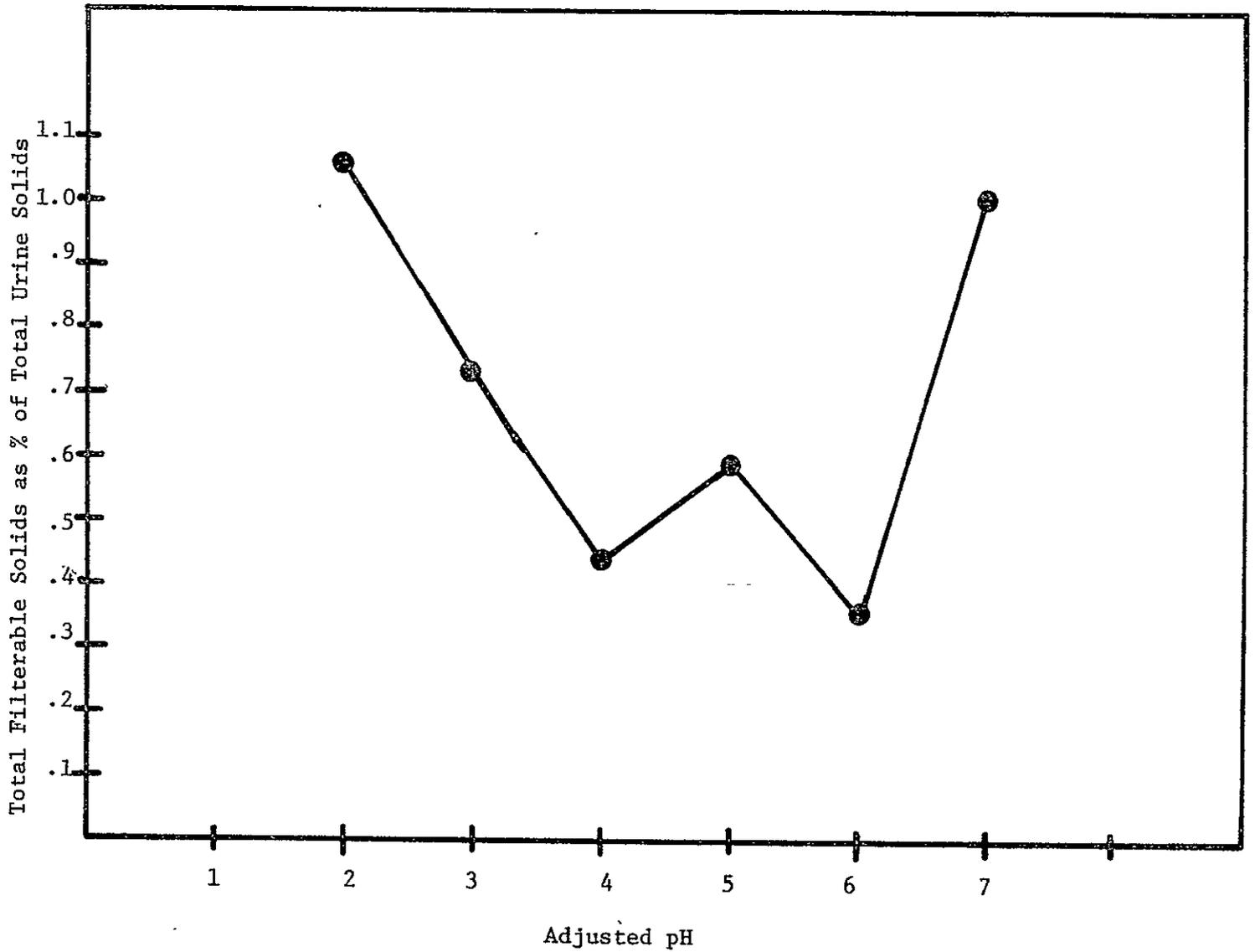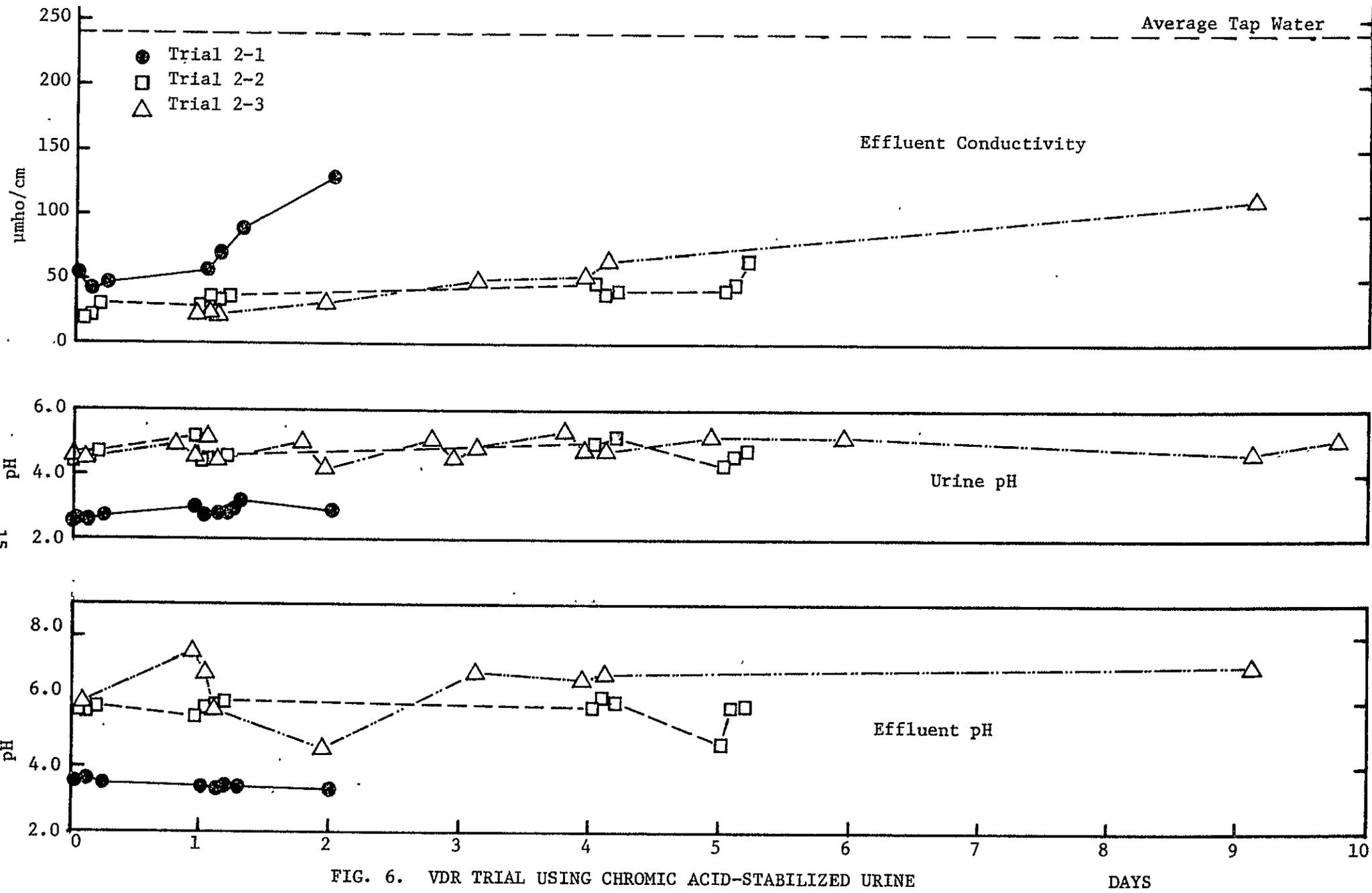
FIG. 6. VDR TRIAL USING CHROMIC ACID-STABILIZED URINE

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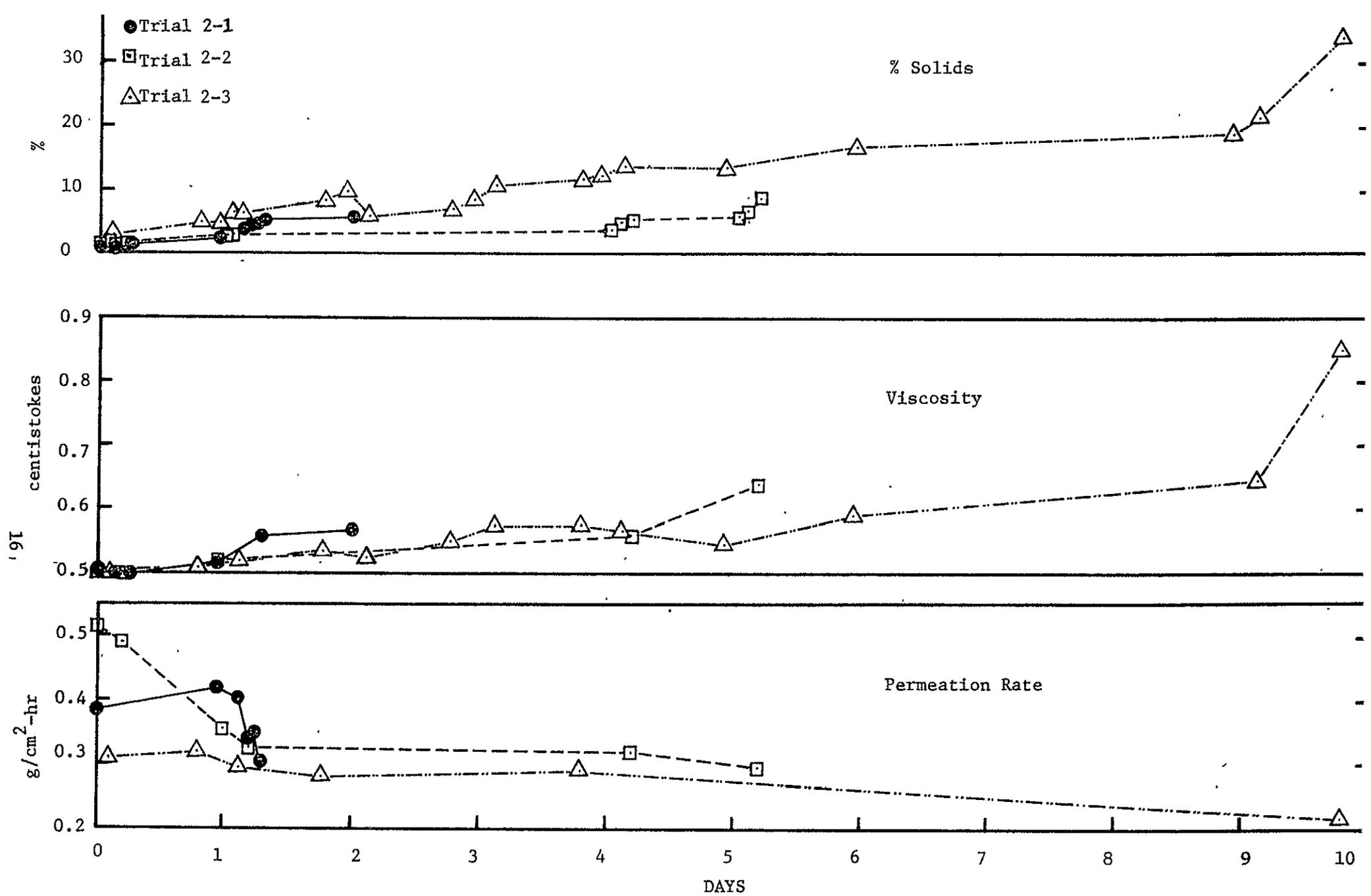
FIG. 7. VDR TRIALS USING CHROMIC ACID-STABILIZED URINE

14% loss in water permeation rate. On removal of the membrane from the cell, only moderate brown staining was evident on the membrane. In Trial 2-2, 85% of the available water was removed in six days, and the membrane flux decreased by 44%. In this trial, the urine pH was controlled at 4.5-5.0 in an effort to reduce the suspended solids concentration. Trial 2-3 was carried out at the same conditions as was 2-2. It lasted 11 days with only a 34% loss in membrane flux while 92% of the water was removed. The membranes from trial 2-3 were removed and rinsed with distilled water. After drying, the membranes were weighed. (They also had been weighed before loading.) The weight of foulant per square centimeter of membrane was calculated to be 0.08 mg/cm^2. The membranes were only slightly stained, and the weight gain was reasonable considering the amount of deposit on them. The relatively large percentage loss in flux for trial 2-2 may not be real, but rather may be the result of an inflated initial permeability measurement. If this thesis is correct, then trials 2-1 through 2-3 behaved in basically the same way. Such behavior would indicate that there is not a unique pH at which suspended solids can be minimized to reduce membrane fouling. Further, the degree of fouling and loss of flux may not be severe enough at 90% water recovery to significantly limit the usefulness of the fluorocarbon membrane. The water quality for trials 2-1 through 2-3 is shown in Figures 6 and 7. All three trials produced relatively clear, good quality water with the usual urine odor. Conductivities were lower than that of New Orleans tap water. The effluent water pH showed a dependence on urine pH. Trial 2-1 had an average pH of 3.4 (urine pH was 2.7-3.8). Trial 2-2 had an average pH of 5.3 for the effluent water from an average urine pH of 4.5. Trial 2-3 had a higher average pH (6.5) even though the urine was controlled at the same level as in trial 2-2. All effluent waters were collected in the same system at 0°C.

Trial 2-4 used the concentrated urine from trial 2-3 as feed. This trial was run at total recycle (no water removed) for 24 hr. The intent was to measure the rate of membrane fouling using a constant concentration of urine by measuring the membrane weight gain. In this trial all conditions were the same as in trial 2-3. In trial 2-4, 0.59 mg/cm^2 foulant was deposited on the membrane in 24 hr. This foulant quantity is seven times that deposited in the entire trial 2-3 (0.08 mg/cm^2) lasting ten days. Trial 2-4 was run for its entirety at 33-34% solids, whereas trial 2-3 only achieved the 33-34%

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solids level just before shutdown. Obviously, exposure to very high urine solids levels influences the amount of deposition more rapidly than does longer exposure at lower solids levels.

VDR Trials Using Natural Unstabilized Urine

Trial 2-5 used unstabilized natural urine and the same experimental operating conditions as used in the chromic acid-stabilized urine trials. This trial lasted nine days. On the ninth day, liquid flow through the cell became restricted by solids deposition. The resulting increased liquid feed pressure caused a failure in the circuit tubing with subsequent loss of feed solution. The results for trial 2-5 are displayed graphically in Figures 8 and 9. The permeation rate declined continuously during the trial, reaching 50% of the initial permeability just before failure. At that point, solids concentration of the feed was 14.5%. Previous trials using chromic acid-stabilized urine have shown only 15% flux losses at equivalent total solids concentration. During trial 2-5, 80% of the available water was removed from the urine before precipitation of solids caused the membrane channels to plug. Analysis of the precipitant showed it to be nearly 5.5% calcium, 0.3% magnesium and 0.35% sodium. The calcium and magnesium are probably precipitated as carbonates. The precipitation of these materials is dependent on the temperature, total solids level, and pH of the urine.

The condition of the liquid circuit and equipment immediately after failure indicated that there was a rapid, catastrophic buildup of solids in the system. Tubing, reservoir and membrane cell were coated with the same material that was found to be coating the membrane surface. This coating was not observed 24 hours before the system failure. Unfortunately, failure of the system allowed the solution to drain so that no adequate samples were available for further analysis.

The total and nonvolatile solids contents of the urine are tabulated as a function of time in Table 3 for the data collected. The nonvolatile solids are shown as percentages of total solids in the last column. Both the total solids and the nonvolatile solids are seen to increase, with the ratio relatively constant throughout the experiment. The nonvolatile solids are attributable to the inorganics derived from the urine.

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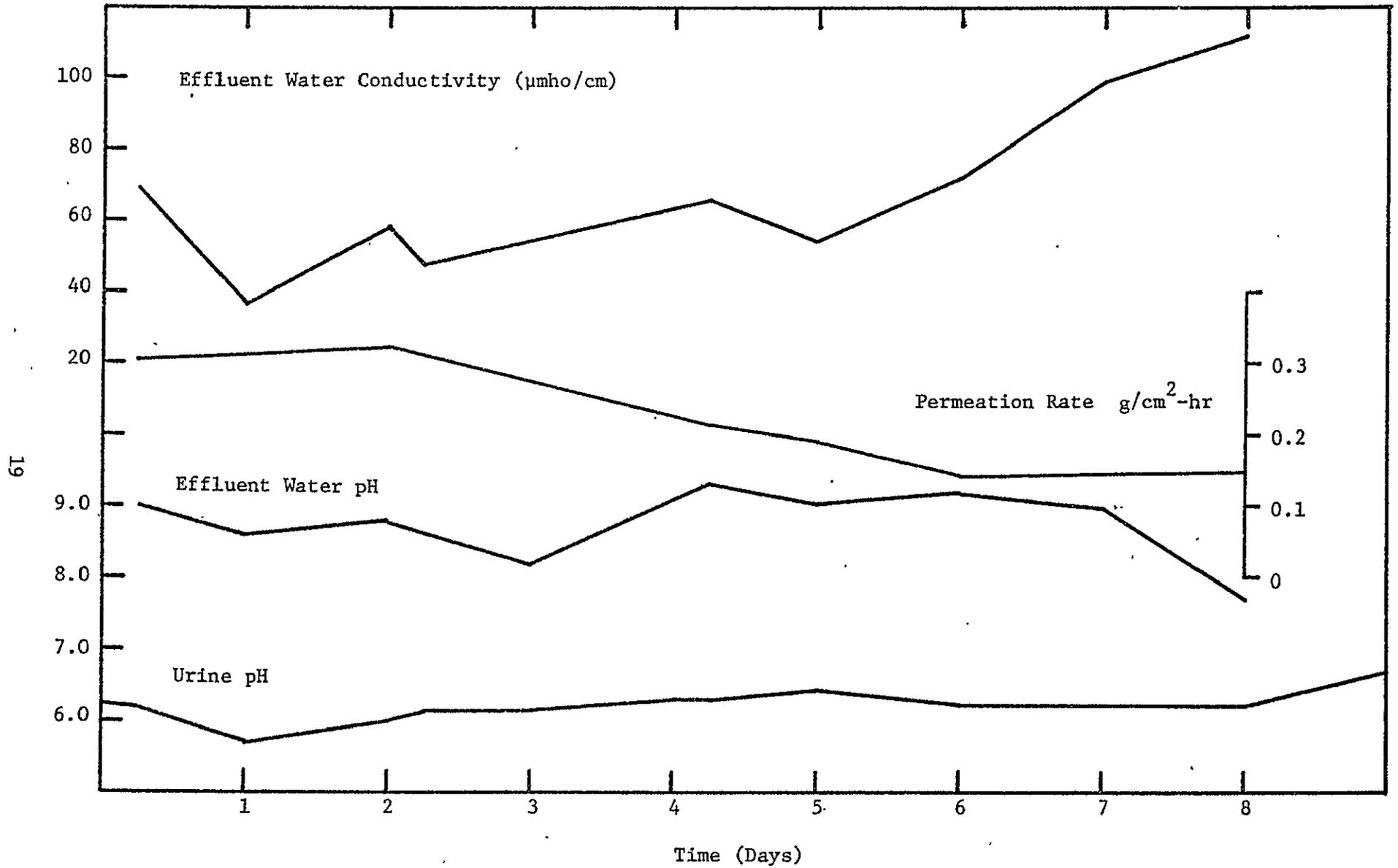
FIG. 8. NATURAL UNSTABILIZED URINE.

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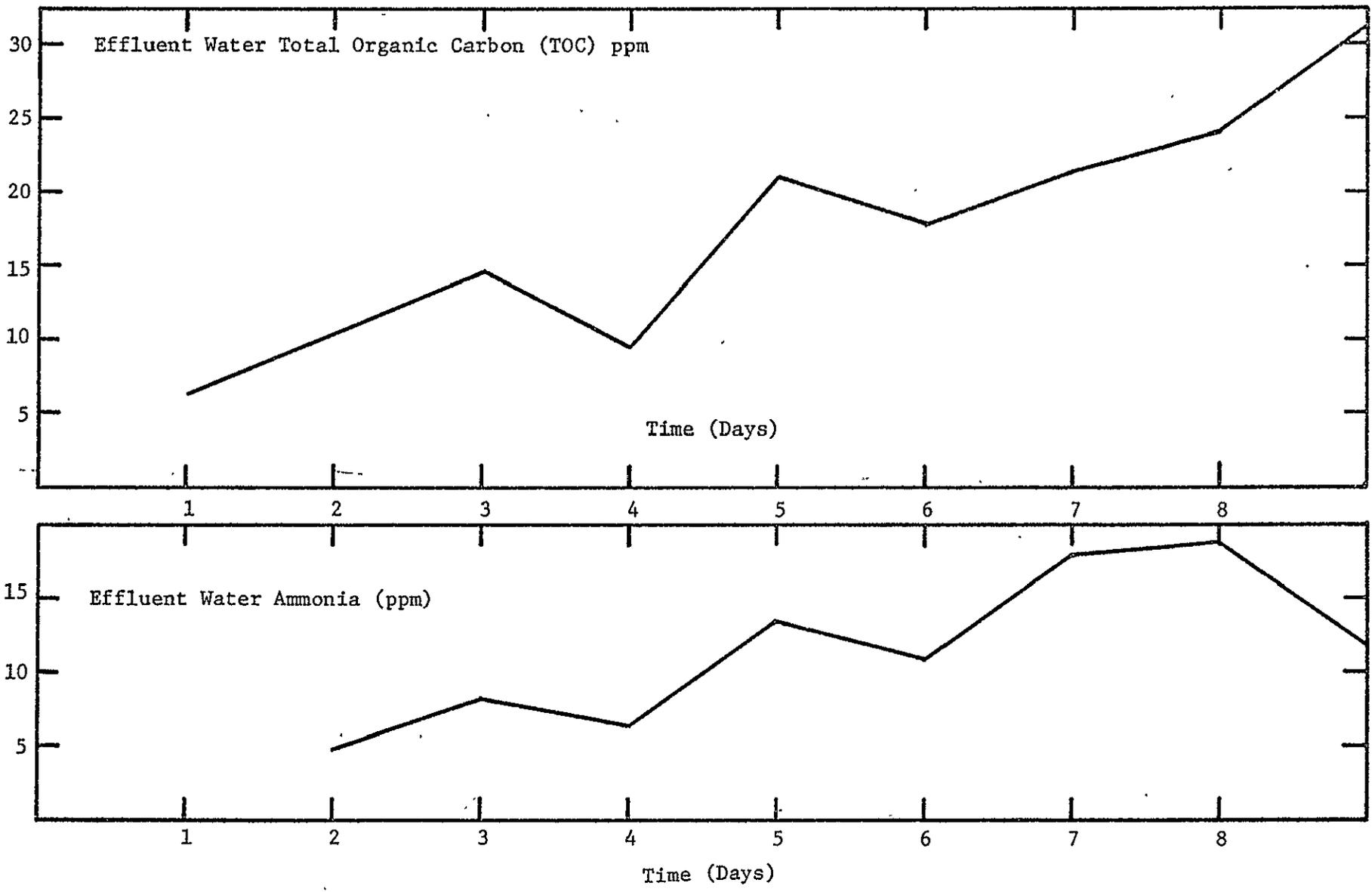
FIG. 9. NATURAL UNSTABILIZED URINE.

TABLE 3

SOLIDS CONCENTRATION AS A FUNCTION OF DURATION OF THE TRIAL

Day	Percentage Total Dissolved Solids	Residue as Percentage of Urine*	Residue as Percentage of Total Dissolved Solids
1	3.6	1.3	34
2	4.9	1.9	39
3	7.0	2.2	31
4	9.7	3.0	31
5	11.7	3.9	33
6	10.2	3.3	33
7	20.1	5.2	26
8	14.4	4.9	34
9	14.5	5.0	34
10	13.4	5.4	41

* Residue after muffling at 550°C.

Apparently, the inorganic solids content increased suddenly as the solubility limits of calcium and magnesium carbonates were exceeded. As a result, the data in Table 3 show no evidence of the impending failure. The solubility of these inorganics is governed by the pH of the urine. The pH of the urine rose slowly during the course of the trial, with the final measured pH of 6.7 obtained the day before the failure.

Table 4 shows the concentration of total solids and calcium calculated for urine solution at various stages of concentration. Also shown is the pH at which calcium carbonate can be expected to precipitate. These calculations are derived in a manner similar to that used to predict reverse osmosis unit failures in saline water applications. Although other specific factors which aid calcium and magnesium solubility are involved for urine, these data indicate that for a given concentration of solids, the solution pH must be maintained below a certain value or calcium carbonate will begin to precipitate and foul the membrane or even plug the system. This behavior apparently occurred during trial 2-5. The product water pH did not show any correlation with the pH of the feed solution. The product was basic throughout the trial; although its conductivity was increasing slowly through the period it was still within acceptable levels for potable water quality at the end of the trial. The rise in conductivity paralleled the rise in pH of the feed stream, indicating that the increased product water conductivity may result from increased ammonia generation in the urine as a result of its rising pH. The ammonia content of the product water, measured with an ammonia ion specific electrode, was observed to increase. These data are shown in Figure 9. It is probable that the constant pH of the product water resulted from the buffering action of ammonium carbonate formed with the permeating ammonia.

Total organic carbon (TOC) content of the product increased throughout the trial; the data are shown in Figure 9. The value immediately prior to the system failure was 36 ppm.

Trial 2-5 has demonstrated that VDR techniques cannot be used to recover more than 75% of the available water from urine without control or removal of calcium and magnesium to preclude the formation of system-fouling precipitates. Apparently some form of urine pretreatment is necessary to control

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TABLE 4

CHANGES IN URINE CONCENTRATION AS A FUNCTION OF WATER REMOVED
NATURAL URINE COMPOSITION

Water 94.9%, Total Solids 4.9%

Ca 0.015%, Na 0.30%

K 0.15%, Mg 0.01%

% Water Removed	Buildup of Total Solids (ppm)	Buildup of Ca (ppm)	Point at which $Ca(CO_3)_2$ Precipitation Will Occur (pH)
0	49,000	150	6.2
15	57,000	174	6.1
30	69,000	211	5.9
45	86,000	263	5.7
60	114,000	349	5.4
75	170,000	520	5.1
90	340,000	1,041	4.5
95	495,000	1,515	<4

inorganic solids deposition during the VDR process. Processes by which the deposition of inorganic carbonates of the divalent cations can be controlled include the following:

a. Control of pH to a level below the minimum at which precipitation will occur.

b. Removal of divalent cations prior to the VDR process.

c. Complexation of divalent cations with strong ligands which have adequate solubility.

Urine Pretreatment with Phosphoric Acid for pH Control

Natural urine was pretreated with phosphoric acid to maintain pH at 3.5. This pretreatment was designed to maintain the calcium and magnesium carbonates in solution and thereby to retard inorganic solids deposition in the liquid channel without introducing the strong oxidizing properties of sulfuric or chromic acid. Phosphoric acid was chosen because of its low volatility and its ability to complex and aid in the solubility of many inorganics.

Three trials were run using this pretreatment. Experimental operating conditions were identical to those for previous trials. The first of these (trial 2-6) ended prematurely because of equipment failure. Trial 2-7 lasted three days, and trial 2-8 lasted seven days. Trials 2-7 and 2-8 were terminated because of apparent membrane leakage. The results for these trials are shown in Table 5 and Figure 10. The membrane leakage was later found to result from liquid wetting the membrane pores with subsequent convective liquid flow into the gas channel. Trial 2-8 was continued for seven days, at which time 84% of the water was recovered and the total solids content was 16.4%. The permeation rate declined 53% during the trial. Although the pH control was designed to retard inorganic solids deposition in the liquid circuit, by the end of trial 2-8, a coating of gray precipitate was begining to appear in the reservoir and tubing circuit. The system, however, was still functioning at 84% water recovery, whereas without pH control, the system failed at 80% recovery when using untreated urine. Thus, the benefit of pH control using H_3PO_4 was not rigorously proved but appeared to be only marginally successful in preventing solids deposition in the liquid circuit. In trial 2-8 and the previous trial (2-5) using natural

TABLE 5

VDR TRIALS USING PHOSPHORIC ACID TO CONTROL URINE pH

|	Trials		
	2-6	2-7	2-8
Urine Properties			
pH	3.2 – 3.6	3.35 – 3.75	3.1 – 3.5
% Solids	3.6 – 5.6	4.1 – 7.7	2.1 – 16.4
Viscosity	0.511 – 0.521	----	0.504 – 0.625
Permeation Rate			
g/cm^2-hr	0.388 – 0.35	0.42 – 0.33	0.38 – 0.18
% loss	8.5	21	53
Effluent Quality			
pH	4.1 – 3.9	5.2 – 4.2	3.9 – 5.6
Conductivity	44.8 – 32.6	44.7 – 38.0	25 – 30.5
TOC (ppm)	12.6 – 8.4	11.7 – 9.2	7.0 – 12.7
NH_3 (ppm)	110 – 23	51 – 64	35 – 52
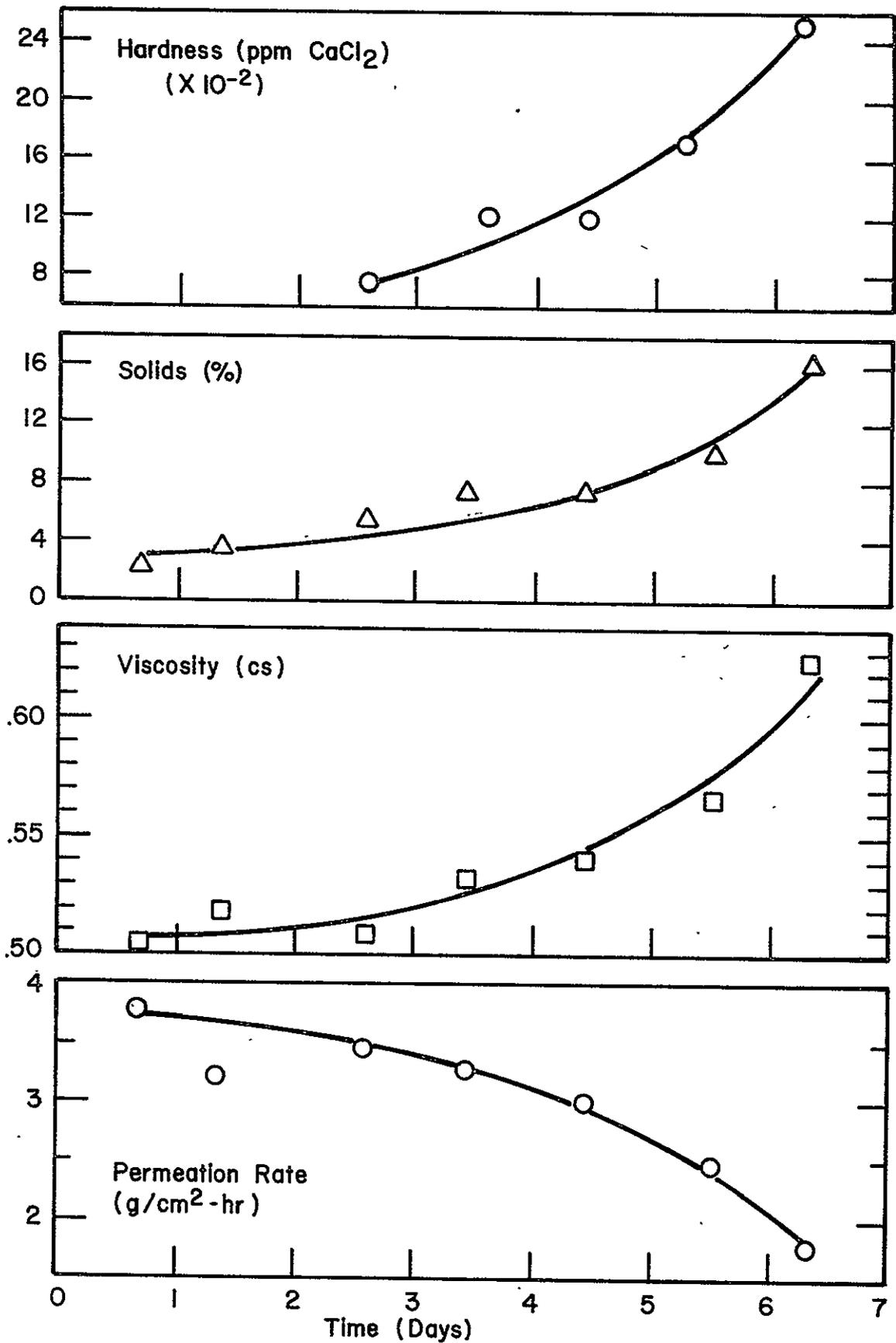
Figure 10. Urine properties for VDR trial 2-8 phosphoric acid stabilized urine.

urine without pH control, membrane fouling flux losses were similar. (Both trials had approximately 50% flux loss at 15-16% solids.) Membrane deposition was measured at 2.6 mg/cm^2 for trial 2-8, in which pH was controlled. Deposition of 6.9 mg/cm^2 was observed for trial 2-5, where no pH control was exercised.

Since calcium has been shown to be a major constituent of the fouling deposit, knowledge of its concentration at the precipitation point would be useful. To establish this information, total hardness, in addition to total solids, was measured. The total hardness analysis is an EDTA complexation titration that measures the total calcium and magnesium concentration in the urine. It is reported here as ppm $CaCO_3$. For trial 2-8 these data are reported in Figure 10. The urine hardness increased to 2500 ppm at the termination of the trial, at a total solids level of 16.4%. Precipitation on circuit tubing and in the reservoir was evident at hardness levels above 2000 ppm. Since many factors in addition to pH can contribute to the calcium and magnesium solubilities, an exact hardness concentration at which precipitation occurs cannot be defined. Such knowledge would be useful as a rough guide to predict the utility of this urine pretreatment to prevent gross precipitation and failure of the system. Unfortunately, the membrane leakage made further concentration of the urine impossible and the hardness level of the urine corresponding to the point of catastrophic precipitation could not be measured.

Effluent water properties for trials 2-6, 2-7 and 2-8 were not much different from those of the previous trials. A more serious problem which appeared for the first time during this trial was wetting of the membrane pores and subsequent liquid flow through the membrane into the gas channel. This behavior is totally unacceptable for VDR application. Evidence of wetting first appeared on the fifth day of trial 2-8 as a discoloration on the gas side of the membrane. (No effect on effluent water quality would be observed, since only vapors are transported to the collection flask.) When trial 2-8 was terminated, the entire gas channel was saturated with urine. This behavior was also observed in trials 2-6 and 2-7, but to a much lesser degree. In these trials, wetting was thought to be caused by a pinhole leak or membrane failure caused by deformation. However, three consecutive trials using phosphoric acid-treated urine produced leaking not

observed in previous trials. Trial 2-8 was continued beyond the point at
which wetting was evident. When the cell was dismantled, both membranes were
completely wetted with the urine and both gas channels were full of liquid.
It is believed that protein deposition on the membrane surface or solution
protein in the concentrated urine reduced the surface tension at the membrane
interface to allow liquid to penetrate the pores. This behavior was not
observed in previous trials where chromic acid-stabilized urine or untreated
urine was used. A more complete description of this phenomenon will be
discussed below.

Ion Exchange Treated Urine

Trial 2-9 used natural urine pretreated by removal of up to 45% of the
total hardness by ion exchange. In this process, the urine was flowed
through a weakly acidic cation exchange resin in the sodium form. Divalent
cations (Ca^{++} and Mg^{++}) are preferentially adsorbed on the resin and
exchanged for Na^+ ions, which form more soluble salts. The average total
hardness of the urine before and after ion exchange pretreatment was 525 ppm
and 294 ppm calculated as $CaCO_3$.

The results for trial 2-9 are recorded in Figures 11 and 12. The system
was operated as in previous trials, except that the natural urine was run
through the ion exchange column before it was added to the reservoir.

Trial 2-9 lasted 14 days, during which time 94% of the available water
was removed and the permeation rate decreased by 67%. The urine solids con-
tent was 26% at the end of the trial. The total hardness (calculated as
$CaCO_3$) increased from 290 ppm to 2200 ppm. Although a small amount of
precipitate was observed on the circuit tubing near the end of the trial,
the urine remained clear. Membrane wetting was evident from the second day
of the trial. This wetting was severe enough during the latter part of the
trial that liquid collecting in the gas channel left large salt deposits on
evaporation, which eventually interfered with gas flow. Some liquid even-
tually was carried over into the collection flask, causing gross contamination
of the effluent. The wetting led to severe loss of membrane flux because of
deposition in the membrane pores. Therefore, permeation rate losses of trial
2-9 should not be directly compared to permeation rate losses of previous
trials.
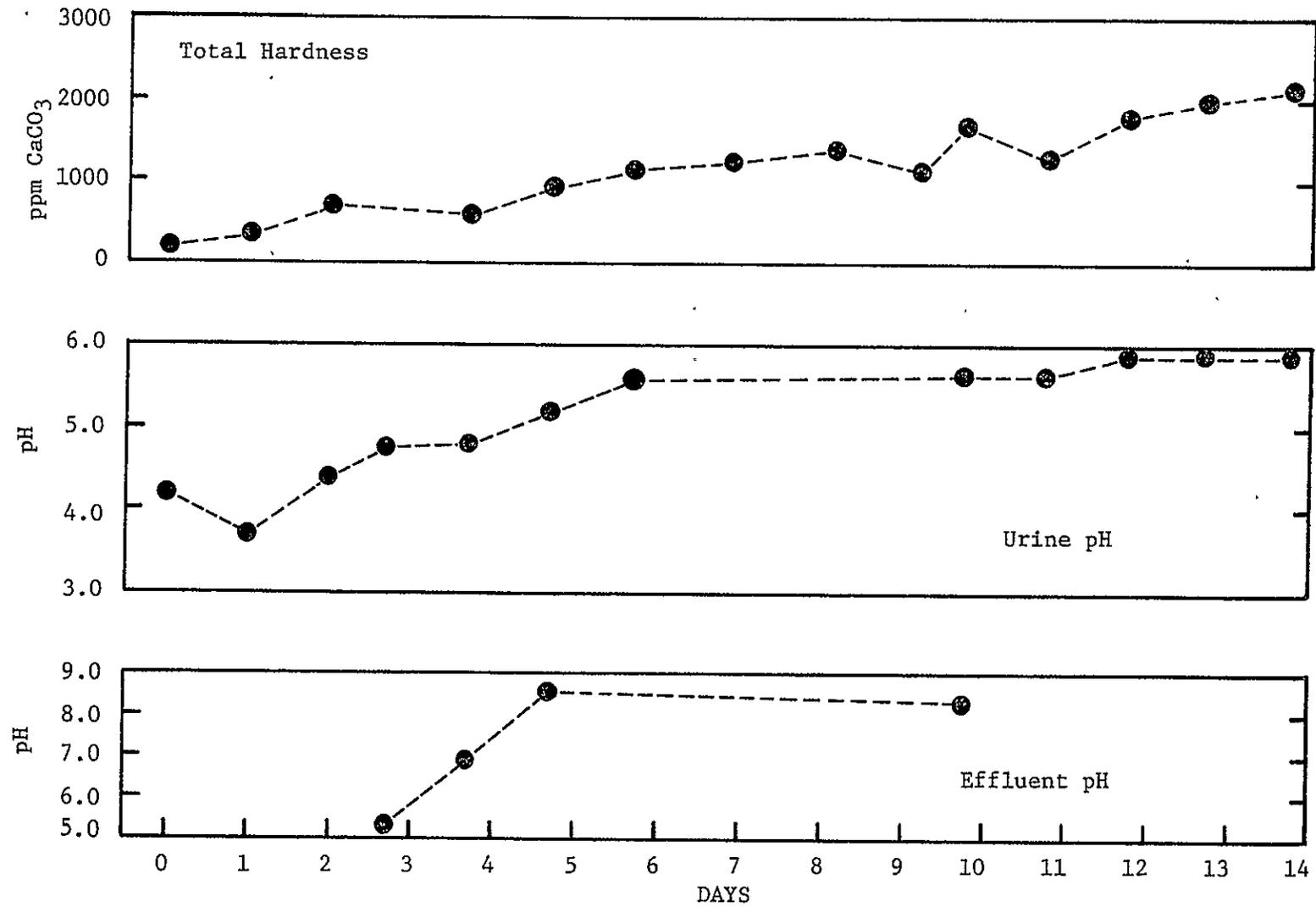
FIG. 11. CALCIUM DEPLETED BY ION EXCHANGE

29
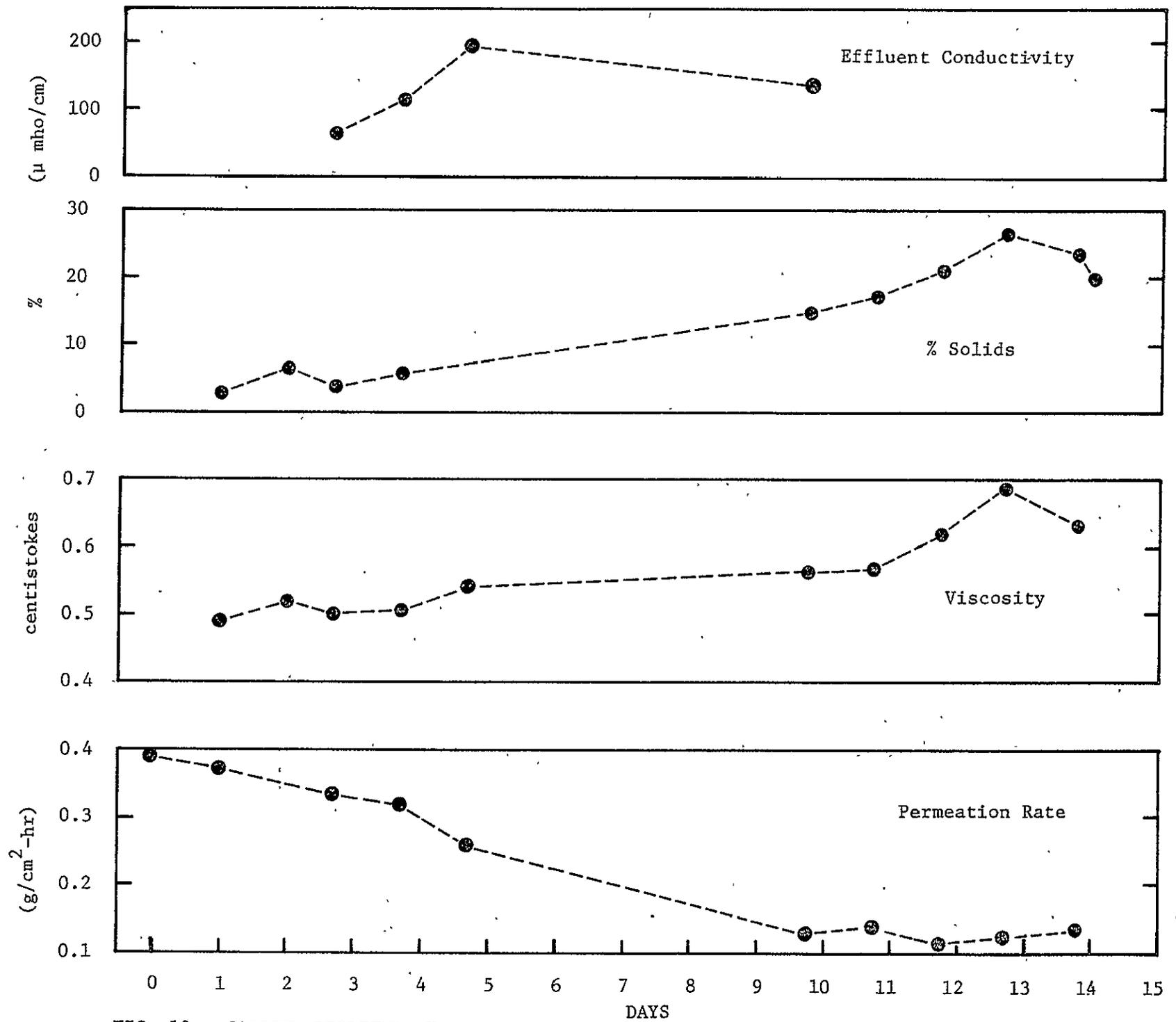
FIG. 12.   CALCIUM DEPLETED BY ION EXCHANGE

Pore wetting is thought to be related to protein layer deposition on the fluorocarbon surface and/or a gross reduction of the surface tension of the urine, caused by removal of divalent cations. The divalent cations are normally complexed to urine protein and amino acids, thus rendering these materials ineffective as wetting agents. When divalent cations are removed, the proteinaceous material is made available as a surfactant. The same thing occurs when the urine is acidified with phosphoric acid, which tends to complex divalent cations. This behavior is similar to that demonstrated in water softening and by detergent builders. Either by direct removal (ion exchange) or by complexation (phosphoric acid) the surfactant properties of the urine are enhanced.

In previous trials using natural (untreated) urine or chromic acid-stabilized urine, membrane wetting was not observed for either of the following reasons:

a. Chromic acid oxidizes proteinaceous materials to materials of lesser surfactant properties.

b. Divalent cations (Ca^{++} and Mg^{++}) which are naturally present in urine complex the proteinaceous substances, rendering them ineffective as surfactants.

To eliminate the wetting problems associated with calcium-depleted urine, two alternatives are available: (1) use of a membrane with smaller pore sizes so that a solution of lower surface tension can be used; (2) use of chromic acid as additional pretreatment to decompose proteinaceous materials. Although trial 2-9 did not give relevant data on a feasible membrane urine pretreatment system, it did reveal that removal of hardness will allow for the use of natural unstabilized urine without the fear of a catastrophic solids deposition caused by precipitation of inorganic solids. Trial 2-9 also yielded useful supportive information on the mechanism of membrane wetting.

Calcium-Depleted Chromic Acid-Stabilized Urine

Trial 2-10 was designed to test the experimental model that decomposition of proteinaceous materials, when used in conjunction with ion exchange for divalent cation removal, will decrease membrane fouling and eliminate membrane

wetting. For this trial, urine was first treated by a weakly acidic ion exchange resin in the sodium form. To this calcium-depleted urine, 4 g/liter chromic acid was added, as in previous chromic acid-stabilized trials.

The results for this trial are displayed in Figures 13 and 14. Although membrane wetting was still observed, as indicated in Figure 13, its severity was greatly reduced. Wetting did not become a problem until the urine solids reached 25%. (Wetting was severe at 5% solids content during trial 2-9, in which unstabilized calcium-depleted urine was used.) The permeation rate did not drop as fast as in previous trials, indicating that fouling was reduced. The effluent water was clear and had a mild urine odor through the course of the run. Total organic carbon (TOC) analysis of the effluent collected at 0°C is typical in all VDR trials. However, the TOC of the effluent was generally higher than in the previous trials, indicating that oxidation of organics to more volatile species may be more prevalent for this pretreatment. Water collected in a cold finger (dry ice temperature) trap in series with, but following, the main water condenser had TOC's no higher than in previous trials. These TOC's also increased as the urine solids built up. These results probably mean that oxidation products are water soluble and are not a great deal more volatile than water.

The permeation rate declined with increasing solids content. At 30% solids, the flux loss was only 30%. At this point 96% of the available water was removed from the urine. Throughout the trial, the urine was clear and there were no signs of precipitates on the circuit tubing or urine reservoir. Trial 2-10 lasted thirteen days with the final urine solids measured at 53%. At this point, 98% of the water was removed, with a 70% decline in membrane flux. Although a 32-fold concentration (98% water removal) would be impractical in actual VDR applications, this run does demonstrate the stability of the urine pretreatment system.

The extent of membrane wetting during trial 2-10 is shown in Figure 13. The extent and severity of wetting in trial 2-10 were greatly reduced compared to trial 2-9, which used calcium-depleted natural urine. Apparently, the oxidation of organics to products of lesser surfactant power by the chromic acid is sufficient to reduce the membrane pore wetting. Wetting at higher urine concentrations may be due to overall changes in the urine surface tension because of the magnitude of solids present. Alternatively, such

Figure 13. GORE-TEX L-10272 MEMBRANE
CALCIUM DEPLETED CHROMIC ACID STABILIZED URINE

33
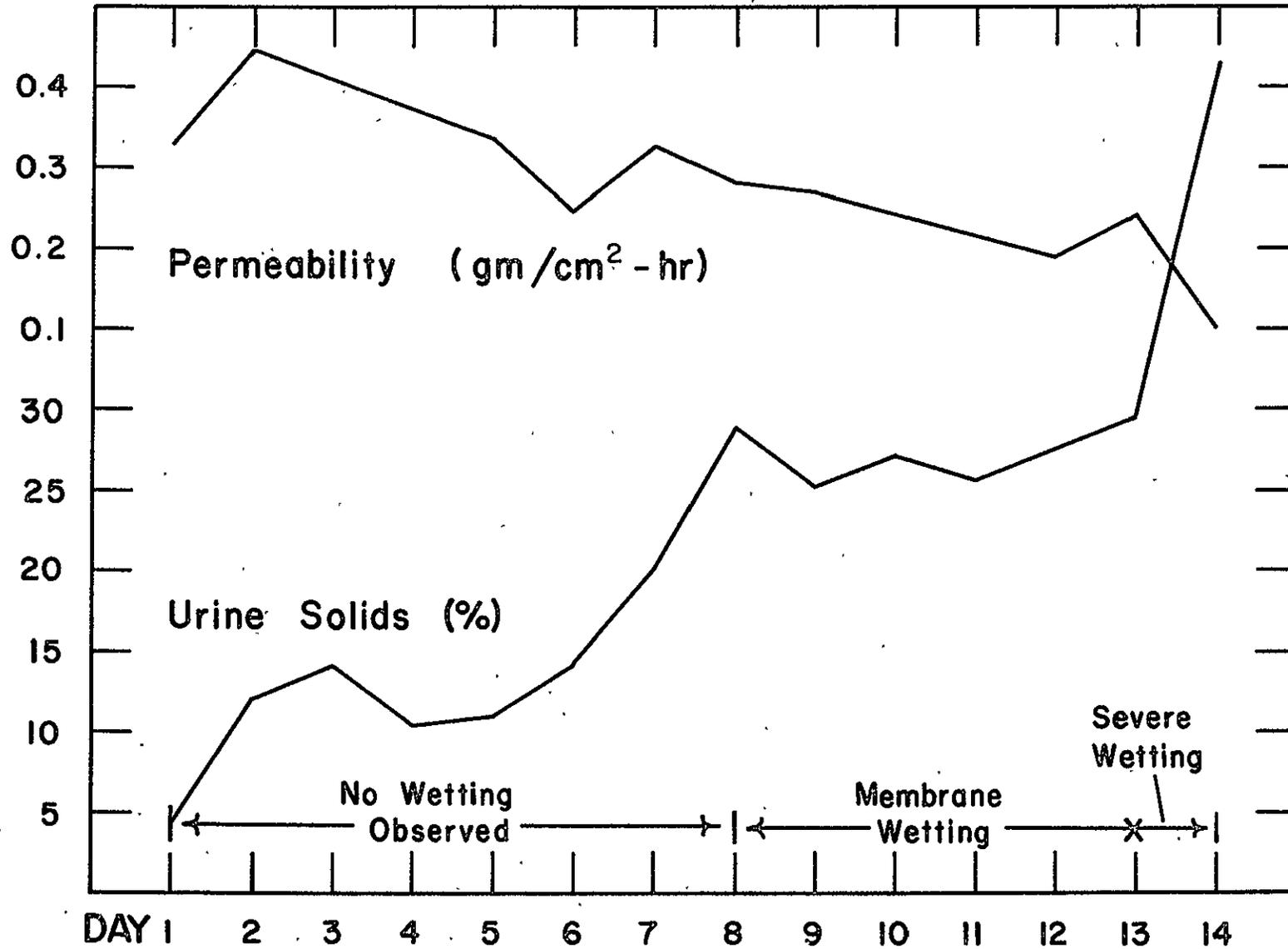
Figure 14. GORE-TEX L-I0272 MEMBRANE
CALCIUM DEPLETED CHROMIC ACID STABILIZED URINE
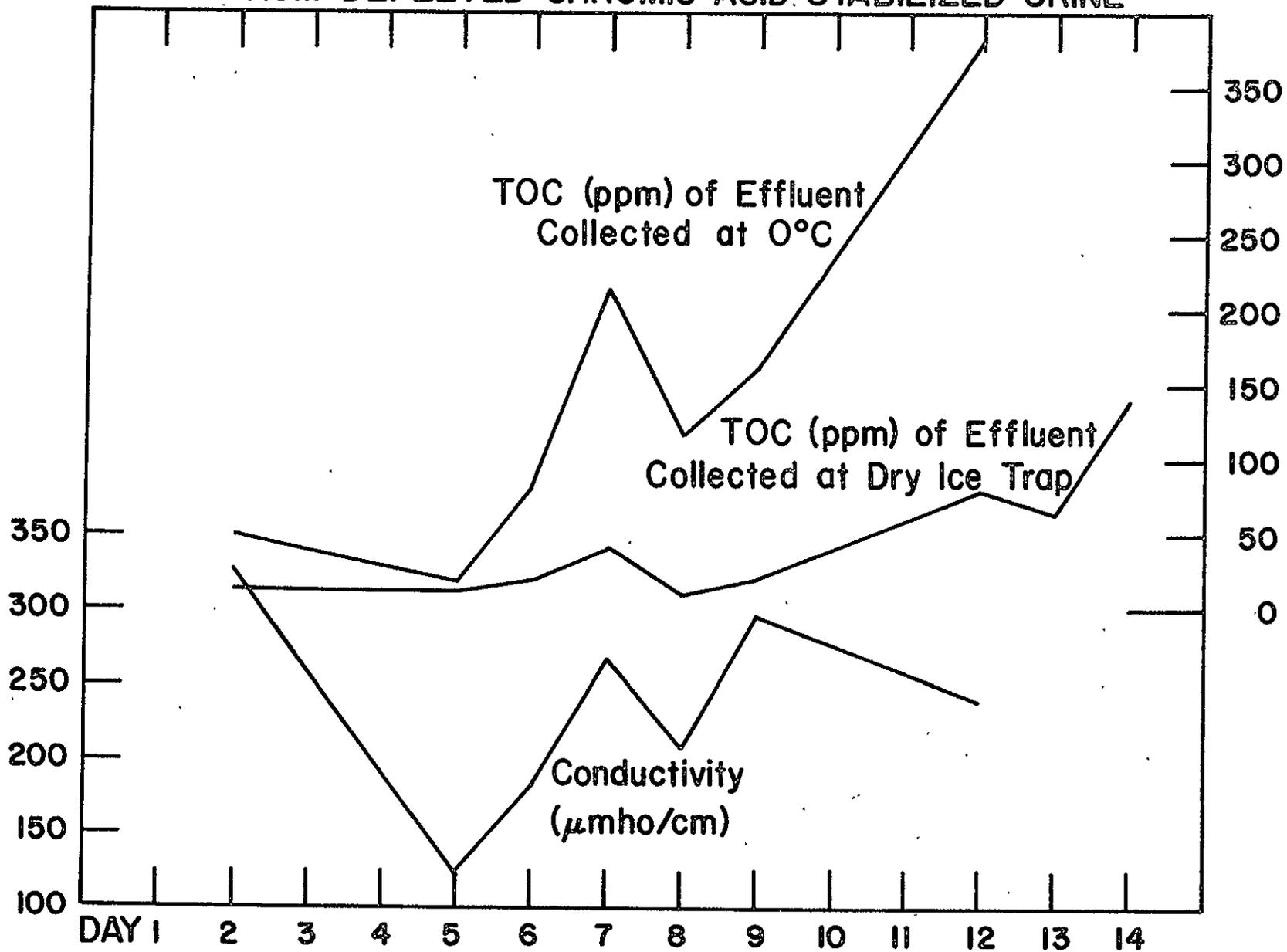
wetting may result from the presence of a nonstoichometric amount of oxidizing agent because of changes in the urine composition. Adjustment of the amount of oxidizing agent and selection of a reasonable concentration factor (such as 90% water removal) would alleviate these problems.

VDR Trial Using a Fluorocarbon Membrane of Reduced Pore Size

An alternative means to eliminate membrane wetting is to reduce the average pore size of the nonwetting membrane. As a test of this thesis, a Gore-Tex S-10396 membrane was tested (trial 2-11) over a four-day period using calcium-depleted natural urine. The concentrated urine feed was taken from trial 2-9, in which severe membrane wetting was demonstrated with the L-10272 membrane. The urine solids content was approximately 25% when trial 2-11 was initiated. The trial was conducted in a 55.5 cm^2 diffusion test cell. This cell was employed because of the limited quantity of membrane available. Water was evaporated throughout the day and was replaced in the evening so that the reservoir would not run dry overnight. The solids content cycled between approximately 25% and 35% for the duration of trial 2-11. The membrane flux was measured daily but did not change appreciably over the course of the trial (the change in flux was less than 5%).

Direct visual observation during trial 2-11 revealed that there was no membrane wetting. At the conclusion of the trial, the membrane was removed and rinsed with distilled water. A very slight brown stain on the liquid side was all the deposition that remained.

VDR Trial of Ionics Cellulose Acetate Membrane

Ionics Corporation[2] has adopted an approach to vapor diffusion recovery of water from urine, which uses an asymmetric reverse osmosis membrane having a relatively high rejection of urea. The membrane is tested in a cell utilizing a high vacuum to evaporate the water from the downstream surface. Solute rejection occurs at the liquid-membrane (dense side) interface. Those solutes not rejected and having low volatility collect in the membrane's porous backing or in the membrane support plate. In VDR trials utilizing this system, membrane fouling can be severe, but fluxes are recoverable by rinsing the membrane with hot water.

This membrane was tested with sweep gas recovery methods employed at GSRI for porous nonwetting membranes. Trial 2-12 used the Ionics cellulose acetate membrane and calcium-depleted natural urine. The system was operated in the same manner as previous VDR trials using the fluorocarbon porous non-wetting membranes. The results from this cellulose acetate trial are displayed graphically in Figures 15 and 16. The most obvious difference between this membrane and the fluorocarbon membranes is the rapid fouling as the urine solids built up. Figure 17 is a plot of membrane flux as a function of urine solids for the two membrane types. The relative difference in flux loss is obvious. Observation during trial 2-12 revealed that a large quantity of dark brown liquid collected in the gas channel. This is the result of convective liquid flow through the membrane caused by capillary condensation. Condensate collected for analysis would not reflect the quality of this water since redistillation occurs before the vapor reaches the collection flask. Effluent water quality as measured by conductivity and TOC analysis is similar to that obtained using the Gore-Tex L-10272 fluorocarbon membrane with the same urine pretreatment. It is possible that higher effluent water quality would have been obtained if the membrane had been operated in a vacuum evaporation system, but the rate of membrane fouling would not have been altered.

The greatest disadvantage of the cellulose acetate membrane is the speed at which it fouls. This is due to the membrane structure (porous wetting) and the mechanism by which water permeates. Any porous wetting membrane can be expected to foul more rapidly than the nonwetting membrane, since nonrejected urinary solutes permeate the pore structure and deposit on the evaporation side of the membrane. Also, membrane contact with support surfaces must be avoided to eliminate capillary condensation and subsequent buildup of solids in the gas channel. Another disadvantage of this membrane is its limited stability. Urine pretreatments involving strong oxidizing agents and strong acids would cause degradation of the cellulose acetate polymer. Data in this report indicate that such pretreatments are necessary if high water recovery rates are to be obtained.

Posttreatment of VDR Water for Removal of Volatile Organic Materials

A sample of the combined effluents from trial 2-5 was treated by slow percolation through an excess of granulated activated charcoal. The charcoal

Figure 15. CELLULOSE ACETATE MEMBRANE
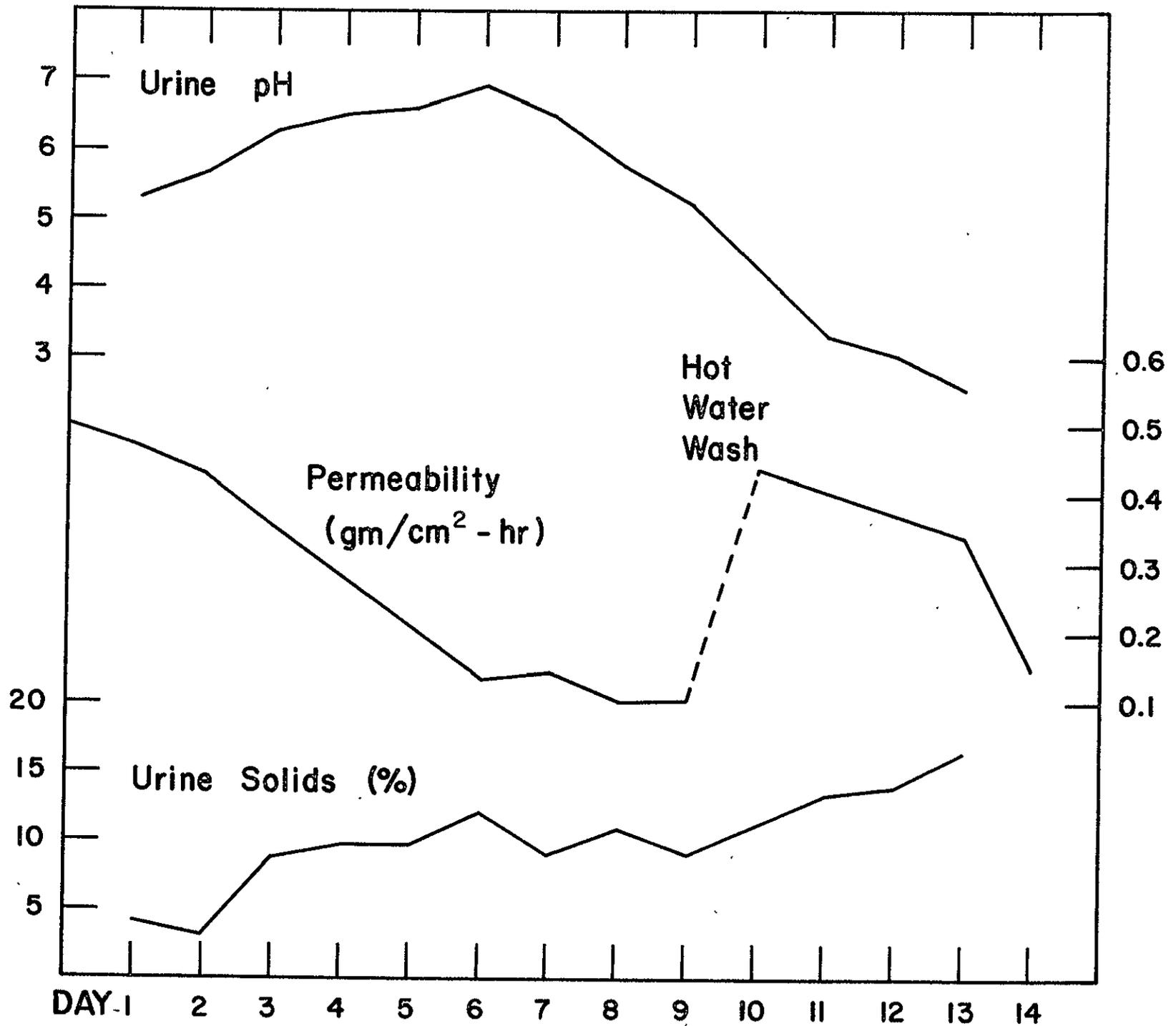
Figure 16. CELLULOSE ACETATE MEMBRANE
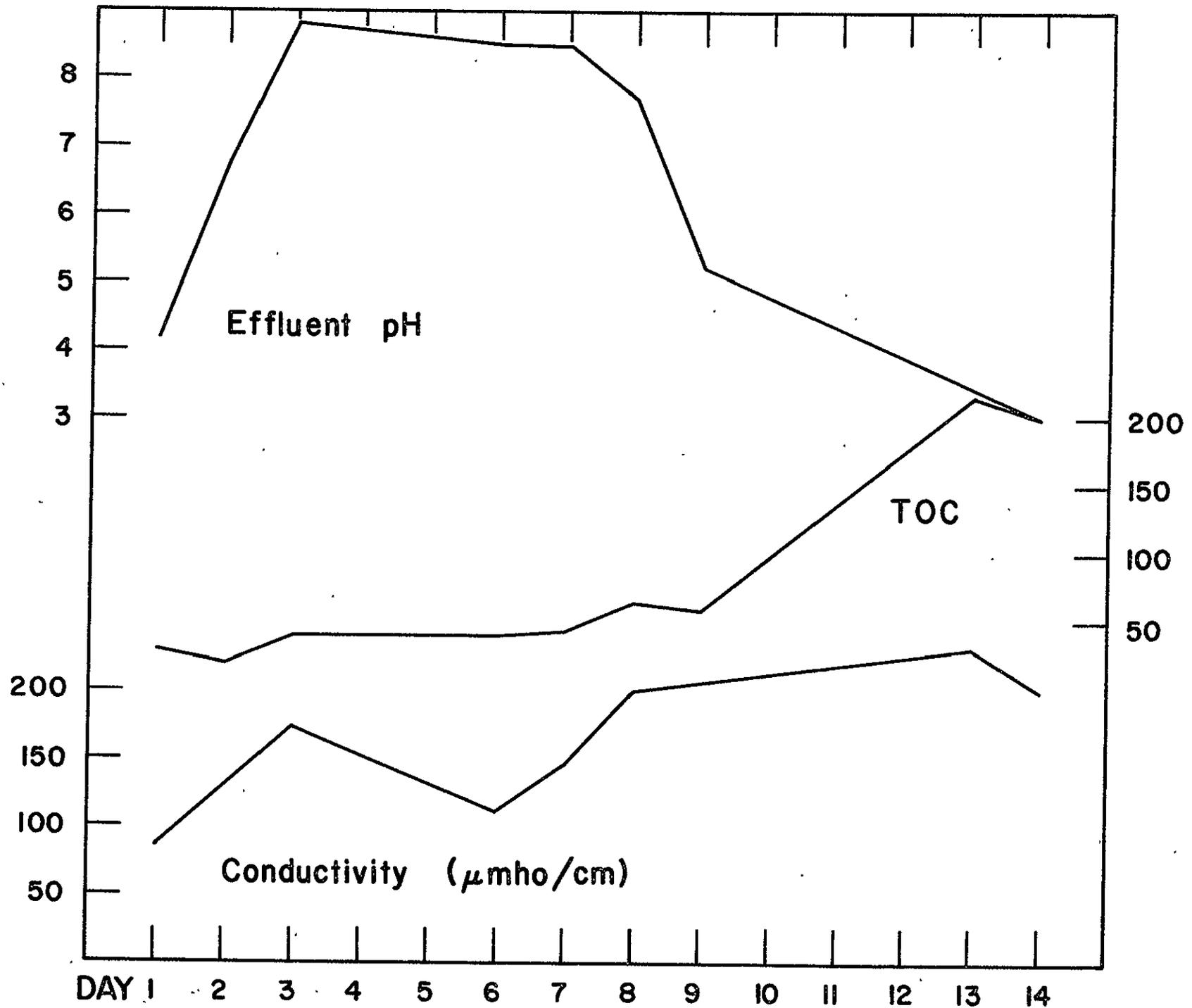
Figure 17. PLOT OF MEMBRANE FLUX AS A FUNCTION OF URINE SOLIDS
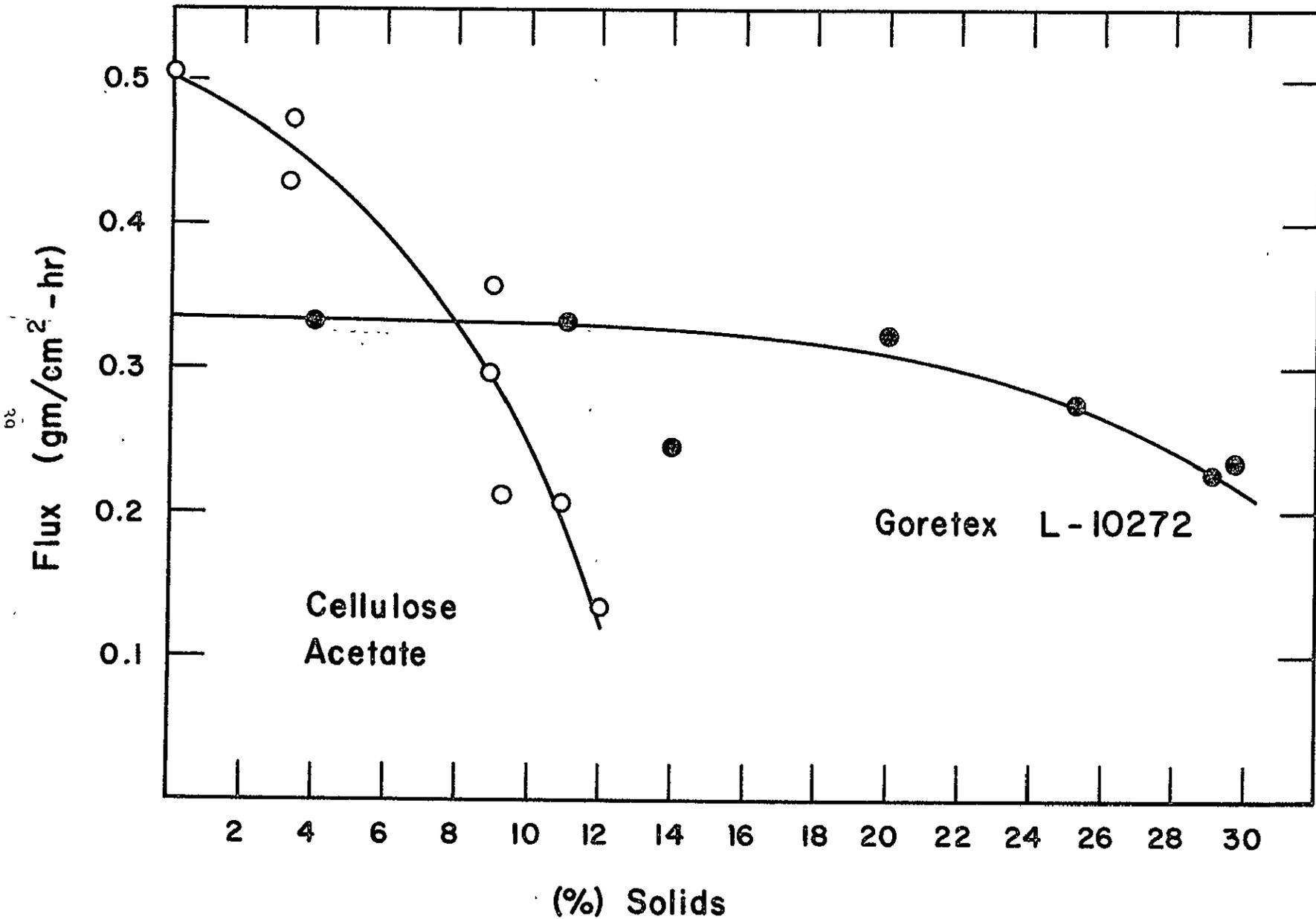
was activated just prior to the treatment by heating 1 hr at 350°C. An additional effluent sample was treated with excess of polymeric resin (Rohm and Haas XAD-2). Before and after treatment, the following tests were performed on the effluent: Total Organic Carbon (TOC), ammonia, and threshold odor number (TON). The TON measurement indicates the dilution factor required for a trained panel to judge the water as odor free. Results for these tests are shown in Table 6. The activated carbon reduced the TOC and ammonia to approximately 50% of their initial values. However, the odor-contributing components were reduced much more dramatically. The VDR product water required a dilution factor of 1172 to make it odor free; after carbon treatment it required only a sixfold dilution. The results for the XAD-2 resin treatment were not conclusive. Apparently, the resin was not completely washed before the experiment and additional TOC demand was leached from the resin. This problem is not uncommon to sorbents of this type. Although a thorough washing protocol based on available literature was followed, it was apparently inadequate. No further work was done using this resin.

The results from this study indicate that posttreatment cleanup using activated charcoal or carbon should be adequate to obtain potable quality water. No attempt was made in this study to optimize this process. An off-the-shelf granular charcoal was used. As a broad spectrum of charcoal carbons are available, more suitable sorbents undoubtedly can be found.

TABLE 6

WATER QUALITY OF THE COMBINED EFFLUENT

	Before Activated Carbon Treatment	After Activated Carbon Treatment	After XAD-2
TOC (ppm)	19.3	9.9	29.3
NH$_3$ (ppm)	8.6	4.3	8.1
Threshold Odor Dilution Level	1,172	6.0	—

IV. APPLICATION OF VDR PROCESS TO THE VENTING OF WASTEWATER VAPOR FROM
SHUTTLER-ORBITER SPACECRAFT

As an additional task during the recent contract year, NASA requested
that we investigate the possibility of using VDR technology for venting
water vapor from wastewater storage tanks onboard the shuttler-orbiter
spacecraft. The disposal of wastewater by venting to space vacuum can signifi-
cantly reduce onboard storage requirements and provide supplemental spacecraft
cooling for the shuttler-orbiter space mission. Fuel cell water which would
otherwise be required for cooling can then be made available for other uses.
Direct dumping of wastewater into space is not possible because of inter-
ferences caused by the accumulation of contaminants around and on the
spacecraft. However, dumping of water vapor and volatile compounds that will
diffuse away from the spacecraft is acceptable.

Initially, the fluorocarbon membrane system developed for VDR application
was to be adapted to use space vacuum for the evaporation process. Fluoro-
carbon hollow tube devices were chosen because they present a large surface
area with respect to total weight and size. The hollow tubes were thought to
have a pore size similar to that of the L-10272 fluorocarbon membranes which
have been used successfully in VDR trials. However, direct comparison was not
possible, as pore size data were not available for either the fluorocarbon
hollow fibers or the flat sheet membranes.

In initial trials using distilled water as feed solution through the
hollow tube lumens and hard vacuum to evaporate the water on the exterior
of the tubes, gross convective liquid flow was observed. Microscopic examina-
tion of the tubes revealed much larger pore sizes than expected. Since the
pore sizes of these tubes could not restrict pure water, they would not be
able to retain a wastewater containing soap.

Further work concentrated on testing the flat sheet fluorocarbon
membranes. A test unit was set up to begin extended trials using the
S-10109 fluorocarbon membranes which have a nominal 0.2 μ pore size.

A diagram of the test setup is shown in Figure 18. A reverse osmosis
cell with an area of 42.32 cm^2 was used as the evaporator (Fig. 19). The
wastewater reservoir is maintained at room temperature, and the fluid is
heated to 43.5°C (110°F) just before it enters the evaporator. After leaving

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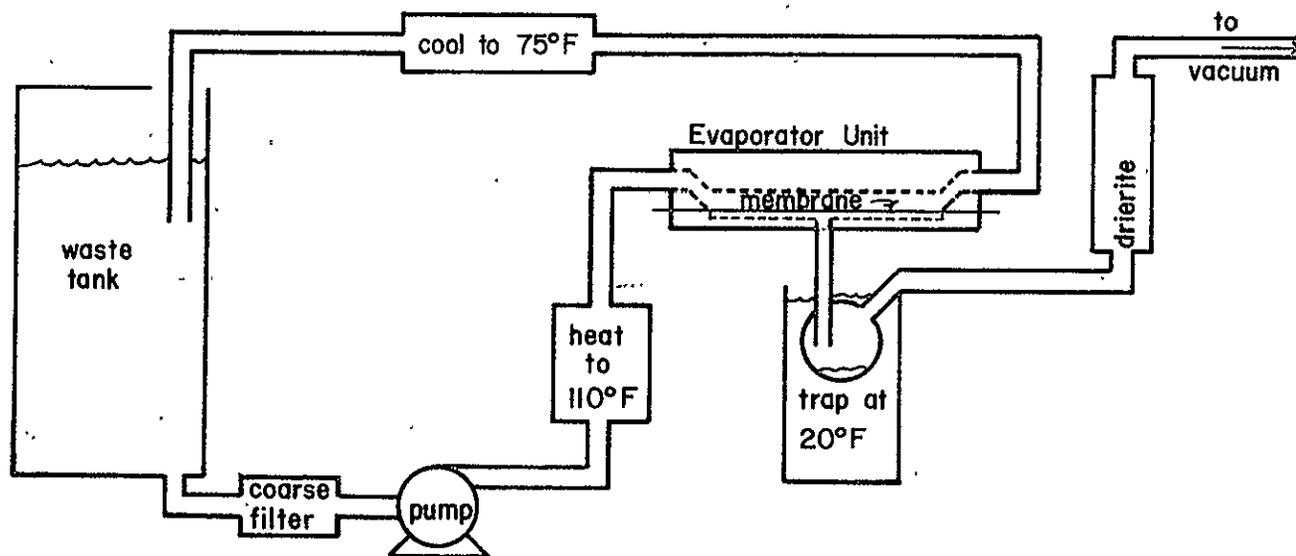
SPACE SHUTTLE·-ORBITER EVAPORATOR TEST RIG

FIG. 18.

Fluid in

Turbulence Promotor

Fluid out

Membrane →

← O Ring

Sintered Stainless Steel

Support Filter

to
Vacuum
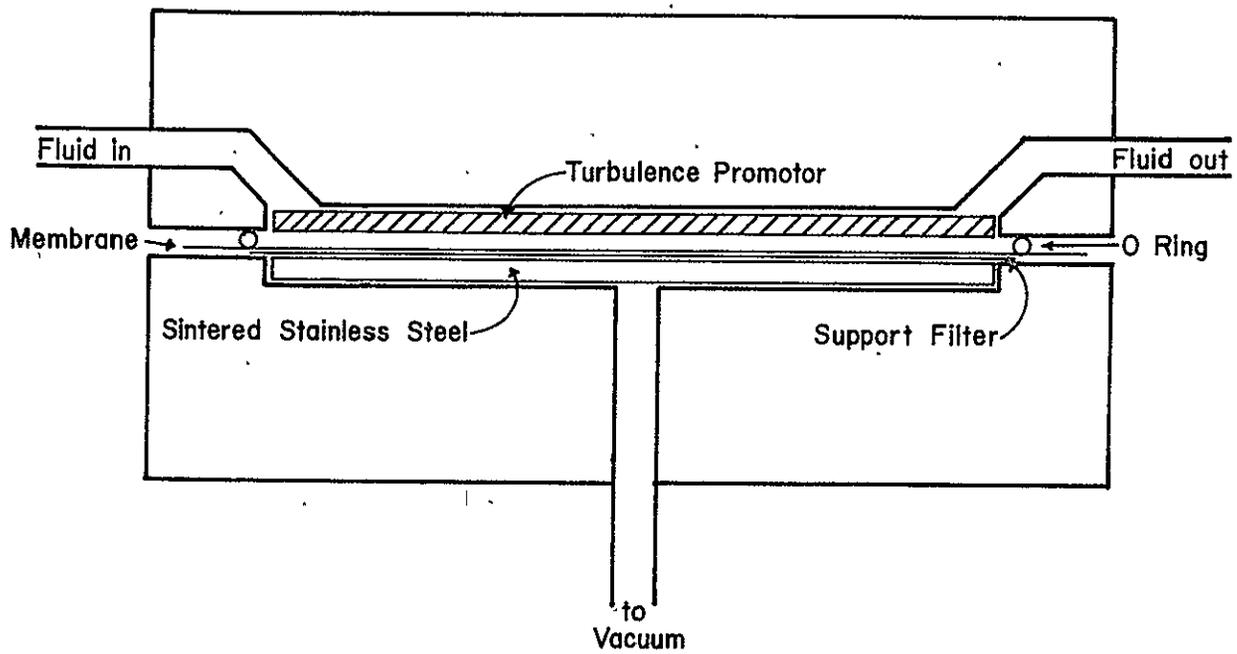
G. S. R. I. VACUUM RECOVERY VDR CELL

FIG. 19.

43.

the evaporator, the fluid is cooled to 23.5°C (75°F). This system was designed to minimize precipitation in the evaporator. Presumably, any precipitation is limited to the wastewater reservoir, where it can be filtered out. Also, the evaporator temperature can be varied to obtain flux and heat loss data as a function of temperature. The evaporator is operated by vacuum, and the condensate is collected at -6°C (20.2°F). The wastewater used in these tests is composed of 2 parts urine, 1.2 parts washwater (0.2% olive leaf soap* in demineralized water) and 0.8 parts demineralized dilution water. Membranes were loaded in the cell and leak tested by flowing 1% saline through the cell. The evaporate was collected and tested for chloride content using silver nitrate ($AgNO_3$) solution. Only if the $AgNO_3$ test was negative was the membrane used. Permeability rates were measured at various temperatures using demineralized water as the feed solution. These data are shown in Figure 20, compared to the nitrogen sweep gas recovery method. On the basis of these data, we could process about 2.5 liters per day using the S-10109 membrane. The 42 cm^2 cell would be about 10% scale of the anticipated requirement for the craft.

However, wastewater processing was not possible with the S-10109 fluorocarbon porous nonwetting membranes. The urine-soap mixture had surface tension too low to be contained by the S-10109 fluorocarbon membrane. A nonwetting porous polypropylene membrane having a smaller pore size (0.1 μm) was also tried, but it also was unable to retain the wastewater mixture. These experiments show that the surfactant quality of the soap was not being destroyed by the divalent cations in the urine. In an effort to correlate wastewater surface tension to a usable membrane system surface tension, measurements were made using a du Noüy tensiometer. The results are shown in Table 7. The surface tension of the wastewater was reduced significantly by the soap and could not be raised by adding divalent cations to precipitate the fatty acid soap. Attempts were also made to raise the surface tension by adding various concentrations of chromic acid and by raising the temperature to 185°F to oxidize any organics present. These efforts also failed, as shown by the data in Table 7.

In order to obtain some background information on processing wastewater, we proceeded to test diffusive membranes, since leakage would not be a problem with them. The wastewater mixture forms a nonfilterable colloid. In a trial

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*The olive leaf soap solution was supplied by NASA, Houston. It was diluted to 0.2% solution to make the wash water component of the wastewater.

FIG. 20.

PERMEATION RATE
AS A FUNCTION OF TEMPERATURE

O — S-10109 (vacuum)
□ — L-10272 (nitrogen)
◇ — TA16 tube (nitrogen)

Flux $(g/cm^2\ hr)$

Temperature (°C)
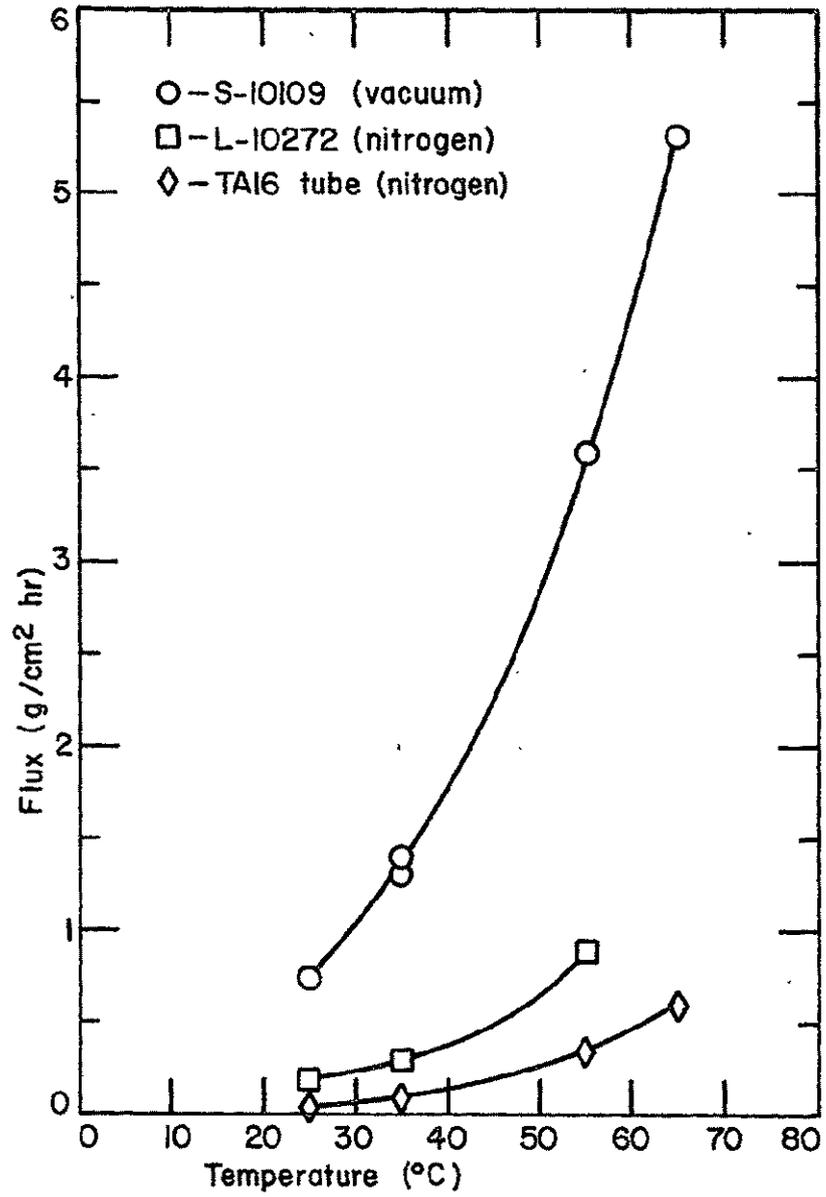
TABLE 7

SURFACE TENSION DATA FOR VARIOUS SOLUTIONS

Sample	Surface Tension (dyne/cm)
Distilled water	76.3
Urine	58.9
Urine:water (1:1)	61.5
Wastewater (pH 6.8)	32.4
Wastewater + 5 g $CaCl_2$/100 ml	31.5
Wastewater + 1 g $CaCl_2$/100 ml	31.7
+ 0.5 g $CaCl_2$/100 ml	31.8
+ 0.01 g $CaCl_2$/100 ml	32.2
+ 0.4 ml Chromic Acid/100 ml	37.5
+ 1.0 ml Chromic Acid/100 ml	38.6
+ 2.0 ml Chromic Acid/100 ml	38.8
Wastewater pH = 4	37.4
pH = 5	31.3
pH = 6	33.2
pH = 7	33.8
pH = 8	36.2
pH = 9	39.5
pH = 10	42.0
pH = 11	42.1
Wastewater Fe (OH)$_3$ flocced and filtered	54.0

which lasted 66 hours using the single-backed dimethyl silicone membrane, solid deposits formed throughout the system, eventually plugging the liquid channel in the evaporator but not the membrane. Even though no significant concentration was accomplished during this period, the deposition problem became quite severe. This filtration, using a commercial fiber-wound depth filter, was essentially useless in removing the finely dispersed colloidal materials. Further long-term testing was considered unfeasible until a flocculation and filtration technique could be worked out.

Some permeation rates were measured using the diffusive membranes in short trials. These data are shown in Table 8.

The dimethyl silicone membrane tested here is a single backed 0.0025 cm (1 mil) film. This type of diffusive membrane has a homogenous structure. Even though it has the highest specific water permeability for any polymer reported, its net flux is 100 to 1000 times lower than that of porous membranes. The data reported in Table 8 for pure water and the wastewater mixture were obtained using the vacuum recovery technique. Although the dense structure of the diffusive membrane retards the water permeation rate, it also completely retards the diffusion of nonvolatile solutes into the membrane. As a result membrane fouling does not occur.

As a means of improving permeation rates, asymmetric membranes have been developed. These membranes employ very thin diffusion barriers (0.01 μm) supported on a porous backing. The NS-1 membrane is a polysulfone-backed polyamide membrane. As reported in Table 8, this membrane has an excellent water permeation rate and should have good resistance to fouling. The water permeation rates for the NS-1 membrane at various temperatures, using a vacuum receiver are reported in Table 8. In a five-hour trial using wastewater, no loss of flux was observed for the NS-1 membrane.

In an effort to eliminate the buildup of colloidal materials in the liquid circuit, two techniques were examined briefly.

One procedure requires only the addition of a base to change the pH of the solution from its initial value of 6 to 10.5-11.0. At this point, additional insoluble species precipitate and combine with the colloids present to generate a large, voluminous floc whose particles trap and enmesh the suspended matter in the water. After filtration, a clear solution is obtained that would be amenable to concentration by water evaporation across

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TABLE 8

PERMEATION RATES FOR DIFFUSIVE MEMBRANES

Membrane	Feed Solution	Temp.	Time of Trial	Permeation Rate g/cm^2-hr
Dimethyl Silicone 1 mil single backed with polyester fiber mat	Demineralized Water	44°C		0.014
	Wastewater	44°C	66 hr	0.013
NS-1 Membrane	Wastewater	41°C	5 hr	0.45
NS-1 Membrane	Demineralized Water	22°C		0.19
		35°C		0.49
		40°C		0.59
		45°C		0.89
		50°C		0.99
		55°C		1.09
		60°C		1.22

a vapor barrier membrane. While the large voluminous floc is easily filtered, the large adjustment in pH is undesirable both from the quantity of material required, and from the pH of the resulting solution and its possible effect on the membrane and materials of construction.

A second procedure appears to provide an attractive alternative for coagulating the solution colloids. The procedure is based on the theory that the surface charge of the colloidal material in suspension must be essentially neutralized to optimize floc formation and filtration. We have found it possible to destabilize the colloidal suspension by using salts of iron and aluminum. Destabilization in these treatments is related to the zeta potential of the coagulant. The chemistry of the coagulants is complicated; however, the zeta potential is predictable as a function of pH. For iron salts, the zeta potential decreases in positive charge as the pH increases until the isoelectric point is reached at about pH 8, where the charge reverses. The isoelectric point for ferric hydroxide coincides with the region of minimum solubility. Thus, the desired operating regions for destabilization of wastewater colloid, when treated with ferric salt and neutralized to pH 7 or 8, produces a hydrolyzed coagulant with a desirable, positive zeta potential. Alum (aluminum salts) also has similar zeta potential-pH relationships and solubility properties.

This method of coagulation and flocculation is attractive because only low levels (10-50 mg/liter) of additives are required, and the final pH of the solution remains essentially neutral. Additional benefits are recognized in the filtrability of the floc. Also of interest is the fact that flocculation and filtration yield clear solution, but also raise the surface tension. This phenomenon is highly important if porous nonwetting membranes are to be used, since it allows for use of membranes of larger pore size. These techniques have been investigated briefly in the laboratory as a means to minimize suspended solids, as measured by visual detection methods. The effects of flocculation and filtration upon processing ability and long-term stability of the wastewater during concentration trials have not been established.

V. POROUS NONWETTING MEMBRANES

Mechanism of Transport

The usefulness of the porous nonwetting membrane is due to the mechanism by which water vapor is transported. Vaporization takes place at the liquid/membrane interface. As a result, only volatile solutes can penetrate the porous nonwetting membrane structure. This mechanism may be contrasted to that of porous wetting membranes, in which evaporation occurs at the gas/membrane interface. The porous nonwetting membrane is characterized by reduced fouling rates yet still possesses the high permeation rates, as do the highly water swollen porous wetting membranes.

The mechanism by which liquid intrusion is restricted is based upon the interfacial tension between the liquid and membrane polymer. For a surface to be nonwetting, the contact angle (θ) between the fluid and polymer must be greater than 90 degrees, measured in the customary manner. At equilibrium, the free energy of interface which must be maintained in order to prevent wetting of the pore is given by:

$$F^s_{s/1} = F^s_{s/a} - \gamma_{1/a} \cos \theta$$

where the superscript s refers to the solid phase, and the subscripts refer to the interface with air, a, or with liquid, 1. Thus, the free energy of the surface in contact with air must be equal to the free energy of the surface in contact with liquid, plus the product of the contact angle cosine and the surface tension of the fluid between itself and air.

The solid-air surface tension is a characteristic of the membrane polymer. It cannot be measured directly, but is conveniently determined by wetting experiments with fluids of known surface tension. For a nonwetting condition to be maintained, the contact angle θ should be as large as possible or $\cos \theta$ should be a minimum. Therefore, $F^s_{s/a}$ should be small and $\gamma_{1/a}$ should be large. Polytetrafluoroethylene having a surface tension of 18.5 dynes/cm is the best possible polymer for this application. Surface tensions for liquids of interest in VDR and the space shuttler application are reported in Table 7. By use of these these data, together with literature calibration of

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contact angles as a function of surface tension, the interfacial tension can be calculated and related to the membrane pore size.

The relationship between the previously listed variables and the intrusion pressure of the liquid is given by

$$P = \frac{\beta(\gamma_{s/a} - \gamma_{l/a} \cos \theta)}{d}$$

where P is the pressure in psi to force intrusion of the liquid, β is a proportionality constant, d is the diameter of the pore in microns, and the surface tensions are as indicated previously. This is the basis of the bubble point method for measuring pore size (ASTM F-316, 1970)[3]. In Table 9, we have calculated the pore size required to prevent wetting by various solutions having surface tensions from 72 to 24 dyne/cm at a driving pressure of 1 to 15 psig.

The contact angles and surface tensions are taken from J.R. Dann[4]. From these calculations, it appears that, to maintain the nonwetting properties of the membrane, we must have pore sizes no greater than 0.22 microns for applications to the space shuttle program. (In the space shuttle, the system operating conditions are transmembrane pressures of 15 psig and low surface tension liquids.) However, VDR applications where liquid surface tension of the urine may not drop below 50 dynes/cm, and maximum pore sizes of 0.9 μm and 4.5 μm may be adequate for vacuum and nitrogen sweep gas recovery methods, respectively.

The liquid surface tension and the applied pressure thus define the maximum pore size that can be tolerated and still restrict liquid penetrations into the pore. The S-10109 membrane, which has a nominal 0.2 μm pore size, will suffice for VDR applications where the transmembrane pressure is less than 5 psig (assuming that the largest pore is less than ten times the nominal pore size) but for space shuttle application, a membrane with much tighter pore structure is needed.

TABLE 9

CRITICAL PORE SIZE (μm) TO PREVENT LIQUID INTRUSIONS
IN EXPANDED POLYTETRAFLUOROETHYLENE MEMBRANE
$$\gamma^s_{s/a} = 18.5 \text{ dynes/cm}$$

	Liquid Surface Tension $\gamma_{\ell/a}$	Pressure PSIG			
		15	5	3	1
Pure Water	72.0	1.2	3.8	6.3	18.9
	51.3	0.93[1]	2.8	4.6	13.9
	36.1	0.39	1.2	1.9	5.9
	30.0	0.22	0.64	1.1	3.2
	28.0	0.067	0.20	0.34	1.0
	25.6	0.066	0.19	0.33	0.99
	24.0	0.042	0.13	0.21	0.63

VI. SUMMARY OF RESULTS AND CONCLUSION

During this contract year, twelve VDR trials were carried out. These
trials were directed toward understanding the membrane fouling mechanism
and ways in which urine pretreatments could help to reduce membrane fouling.
Water effluent quality was also monitored during these trials. These efforts
were directed at understanding the gross effect which urine pretreatments
might have on the effluent water quality. The results of these trials for
the porous nonwetting fluorocarbon membranes are summarized in Table 10. For
each urine pretreatment, the flux loss is shown for urine solutions with
various percentages of solids. The effluent water conductivity and TOC,
membrane solids deposition, and membrane wetting are also reported. From
these data a fouling mechanism has been proposed. This mechanism considers
fouling as the result of two processes:

a. Inorganic carbonates of divalent cations (Ca^{++} and Mg^{++}) are
deposited as the solubility limits of these materials are exceeded. This
type of fouling is characterized by a rapid buildup of inorganic solids in
the liquid circuit. Large losses of membrane flux and/or complete plugging
of the liquid circuit may be caused by such solids buildup. Factors which
influence the calcium and magnesium solubilities, such as lowering the urine
pH or complexing with ligands to form more soluble products, greatly increase
the urine's stability to inorganic precipitation. Removal of calcium and
magnesium by ion exchange also decrease inorganic precipitation.

b. Organic deposits, believed to be proteinaceous materials, are
deposited on the membrane surface. This deposition is enhanced if Ca^{++} and
Mg^{++} are removed either by ion exchange or by complexation by stronger ligands
such as phosphate. In addition, release of proteinaceous materials previously
bound to divalent cations (calcium and magnesium) can grossly reduce solution
surface tension, or reduce interfacial tension at the membrane surface caused
by deposited materials on the membrane. These factors can then cause liquid
intrusion into the membrane pores, breaking down the transport mechanism of
the porous nonwetting membrane.

Effluent water quality from VDR trials is relatively invariant with
urine pretreatment tested in this program, but does vary with degree of
urine concentration. As urine solids increase, the TOC and conductivity

TABLE 10

SUMMARY OF DATA

POROUS NONWETTING MEMBRANE APPLICATIONS TO VAPOR DIFFUSION RECOVERY OF WATER FROM URINE

URINE PRETREATMENT	SOLIDS (%)	FLUX LOSS (%)	CONDUCTIVITY (µmho/cm)	TOC (ppm)	WETTING	DEPOSITION (mg/cm^2)
4 g/1 Chromic Acid	5	2.6	25	---	none	
Trial 2-3	10	5.2	32	---	none	
	20	12.2	99	---	none	
	30	24.8	110	---	none	0.08
Natural Urine	5	9.9	50	10	none	
Trial 2-5	10	27	65	12	none	
	15	56	110	20	none	6
Phosphoric Acid-	5	14.3	30	8	none	
Stabilized Urine	10	30.3	--	--	slight	2.6
pH=3.5, Trial 2-8	15	49.5	--	---	severe	
Calcium-Depleted	5	15	65	20	slight	--
Urine	10	36	194	50	severe	
Trial 2-9	15	56	135	61	severe	
	20	73	--	4000	severe	
Calcium-Depleted,	5	0.6	100	49	none	--
Chromic Acid-	10	2.9	100	49	none	
Stabilized	15	6.0	100	49	none	
Trial 2-10	20	10	100	49	none	
	25	20	100	49	slight	
	30	32	300	600	severe	

of the effluent increase. Effluent water quality from a VDR trial using a cellulose acetate membrane was similar to that found for the porous nonwetting membrane. These results indicate that for these two membranes there was little difference in selectivity of solute rejection. Posttreatment studies using charcoal have been shown to reduce TOC and odor.

As a result of these experiments some kind of urine pretreatment is indicated to improve urine stability and reduce membrane fouling. The choice of pretreatment, however, will depend to some extent on the membrane and the evaporation and condenser system chosen. For all membrane systems, regardless of the membrane's ability to reject solutes, a urine pretreatment is necessary to control inorganic precipitation in the liquid circuit if water recoveries above 80% are desired. Inorganic deposition can be controlled by

    a.   Chromic acid stabilization.

    b.   Depletion of divalent cations by ion exchange pretreatment.

    c.   pH control using nonoxidizing acid.

If membranes other than the chemically inert porous nonwetting fluorocarbons are used, then pretreatments involving divalent cation removal or pH control using nonoxidizing acids would be indicated. Control of pH using nonoxidizing acids is not as effective as ion exchange pretreatment to control inorganic deposition. Since no mechanism is available to control ammonia evolution using ion exchange pretreatment alone, a combination of both treatments would be needed unless a highly selective membrane is found. Membranes capable of processing such urine would probably have to be diffusive, since extremely small pore sizes would be required for porous nonwetting membranes to exclude these liquids. An appropriate urine pretreatment for use of porous nonwetting fluorocarbon membranes is chromic acid stabilization, which provides the necessary acidity to control the solubility of Ca^{++} and Mg^{++} salts, and helps to decompose proteinaceous materials. This pretreatment is also very effective in controlling ammonia volatility. VDR trials using chromic acid-stabilized urine and Gore-Tex fluorocarbon membrane system have been shown to perform reliably with water recoveries up to 95%. Chromic acid stabilization has been shown previously to be compatible with VDR applications. Its cost and weight requirements and its materials compatibility have been investigated[5].

Applications of the fluorocarbon porous nonwetting membrane have relied on use of nitrogen sweep gas vapor recovery techniques. These techniques require only small transmembrane pressure differentials. Calculations developed in this report show that the applied liquid pressure and surface tension determine the required pore size for an effective porous nonwetting membrane phase separator. Porous nonwetting membranes tested in this program (Goretex L-10272 and S-10109) do not have the necessary small pore size for application using vacuum recovery techniques. Hence any application using the fluorocarbon porous nonwetting membranes would necessitate water recovery techniques utilizing minimum effective transmembrane pressures, such as the sweep gas recovery method. Whereas evaporator-condenser designs have not yet been established for VDR applications, the ultimate choice of a membrane system would depend on that design. Porous nonwetting membranes, as compared to other membranes tested for VDR application, offer the following advantages:

a. Complete chemical inertness, which allows any type of chemical pretreatment.

b. High water permeation rate.

c. Longer service life as a result of slower membrane fouling rates.

Only commercially available porous nonwetting membranes have been tested. Development of a fluorocarbon membrane with smaller pores may be possible. If such a membrane becomes available, the limitation of applied pressure and surface tension might be eliminated. Since no effort has been directed toward developing such a membrane, its availability cannot be predicted.

Efforts at applying porous nonwetting VDR membranes for venting water vapor for the space shuttler program have not been encouraging. As discussed above, applied membrane pressure and reduced surface tension of liquids required by space shuttle applications cause membrane pore penetration by the liquid. The liquid penetration breaks down the mechanism by which the membrane serves as a phase separation barrier and allows convective liquid flow with no rejection of dissolved solutes. Therefore, for applications in this program, available porous nonwetting membranes would be inadequate without reducing applied transmembrane pressure and chemically treating the wastewater to maintain a minimum surface tension above which membrane wetting would not be a problem.

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