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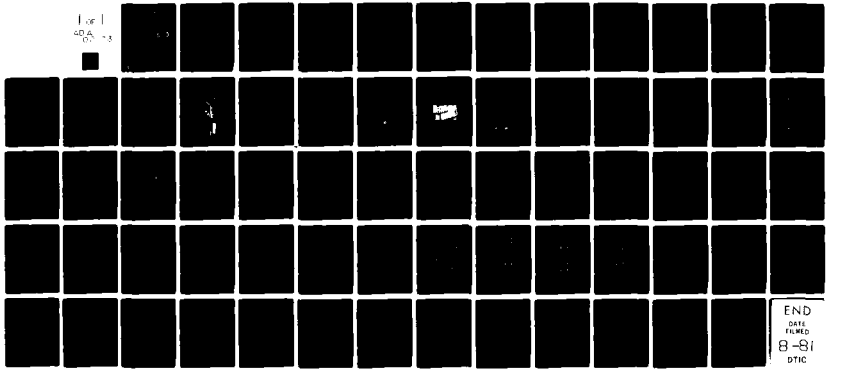

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TECHNICAL REPORT

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(6) CHLORINE RESISTANT PBI RO PERMSELECTIVE MEMBRANES.

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

A study was carried out to develop a chlorine-resistant polybenzimidazole (PBI) reverse osmosis (RO) membrane capable of desalting seawater in a single pass to yield potable water. Flux values as high as 28 gfd and rejections in the range of 94-98% were attained with unsupported flat disc specimens from membranes cast on a small laboratory apparatus. Transfer of the laboratory technology to a commercial type roll coater eventually produced satisfactory fabric supported membranes. Development of spiral wound module fabrication techniques ultimately

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yielded leak-free modules. Time and funding constraints precluded optimization of RO properties to meet the single pass seawater desalination flux and rejection targets. Chlorine sensitivity tests demonstrated that PBI is not chemically degraded. Unsupported disc samples in 5 ppm chlorine showed 90% declines in flux accompanied by increases in rejection. Fabric-supported membranes in spiral wound module configuration showed relatively stable flux values up to 1000 hours. Rejections increased somewhat at the same time.

SUMMARY

A research and development study was carried out to develop chlorine-resistant polybenzimidazole (PBI) reverse osmosis (RO) membrane capable of desalting seawater in a single pass at 800 psig operating pressure to yield potable water. Membrane casting and coating variables were first investigated on a laboratory scale with a small film casting machine. These included polymer concentration in the film casting solutions, time and temperature of drying the film in the drying chamber, and laydown thickness, among others. Annealing studies on the cast film were then carried out to establish the optimum annealing time and temperature, using ethylene glycol as the annealing medium. Unsupported and fabric-supported membranes were prepared and tested. Membrane disc samples (2-inch diameter circles) were tested in flat film test cells. In screening tests, RO properties were measured with 0.5% sodium chloride solution as the feed at 600 psig and 25°C. Fluxes as high as 28 gfd and rejections in the range 94-98% were observed. Optimum annealing temperatures in ethylene glycol were found to lie between 120°C and 140°C, depending on the specific membrane process conditions and final RO properties desired.

Major emphasis was given to the large scale, continuous fabrication of fabric-supported membrane on a three roll, reverse roll coater/dryer machine. These efforts were ultimately successful and were guided by the findings of the laboratory studies. Coating and drying parameters were investigated to establish optimum process conditions. Line speed, drying time, drying temperature, and laydown thickness, among others, were investigated and all variants were tested for RO properties. Large quantities of selected variants were prepared to permit module fabrication development and to prepare demonstration-size modules for RO evaluation and long-term chlorine resistance studies. Their RO properties,

however, did not match those of the laboratory membranes.

Membrane disc samples from selected rolls of fabric-supported membranes were evaluated for seawater desalination properties. The effects of pressure and salt solution concentration on membrane performance were studied. In simulated seawater (3.5% salt solution) tests, PBI membrane performance at 800 psig fell short of the 9 gfd and 97% rejection targets. However, optimum process conditions have not yet been identified.

PBI fibers and membranes soaked in 10 ppm free chlorine at pH 5.5 exhibited good retention of physical properties and molecular weight over 28 days. This demonstrates that PBI is not chemically degraded by chlorine and possesses a useful resistance at levels that are practiced in water pretreatment. In RO tests at 400 psig with 0.5% salt solution containing 5-8 ppm free chlorine membrane disc samples unexpectedly exhibited a sharp and rapid decline in water flux in 24 hours, but salt rejection remained high. On the other hand, spiral wound modules did not exhibit such a sharp and rapid decline. Two modules continued to function with relatively stable fluxes and rejection through nearly 1000 hours of continuous operation at 400 psig with 0.5% salt solution containing 5-8 ppm free chlorine. Time and funding constraints precluded further efforts to explain and exploit the favorable results obtained with the spiral wound modules as compared to the flat disc membranes.

It is concluded that PBI RO membranes have the potential to meet the requirements of a chlorine-resistant single pass seawater desalination membrane in the spiral wound configuration. However, further development of the roll coater process and module fabrication techniques are recommended.

PREFACE

This report was written by Howard J. Davis and John W. Soehngen, Research Associates, Celanese Research Company. The work reported herein was performed under Contract DAAK70-79-C-0232 and was sponsored by MERADCOM, Petroleum and Environmental Technology Division, Energy and Water Resources Laboratory, Fort Belvoir, Virginia 22060. Gerald R. Eskelund, Captain Thomas Broadwater and Harry Goto monitored and provided guidance to the effort during the time period from 25 September 1979 to 31 January 1981.

Besides Howard J. Davis, who served as Principal Investigator, and John W. Soehngen, the contributions of Marshall Tan, Research Engineer, are noted. The technical support of James R. Vogelsang and Arthur Schlask, Senior Technicians, is acknowledged. Joseph R. Leal, Senior Staff Associate was the Contract Administrator.

This is the Final Technical Report issued under Contract DAAK70-79-C-0232. It was submitted by the authors in February 1981.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

I. INTRODUCTION

Reverse osmosis (RO) is a pressure-driven membrane separation process for aqueous solutions in which water is transported across a semipermeable membrane to an extent much greater than that of dissolved salts (solutes). Pressure, in excess of the osmotic pressure of the solution, enhances the transport of water due to pressure-activated diffusion and high solubility of water in the membrane while solute transport (flux) is dependent on the concentration gradient across the membrane and is essentially pressure insensitive. Moreover, the thinner the active membrane layer, the greater the water flux.

In the solution-diffusion theory[1] of reverse osmosis, the transport equations for water flux, J_1, and solute flux, J_2, are as follows:

$$J_1 = A(\Delta P - \Delta\pi)$$

$$J_2 = D_2 K \frac{\Delta C}{\Delta X}$$

where ΔP is the pressure difference across the membrane; $\Delta\pi$ is osmotic pressure difference and A is a membrane constant related to the diffusion coefficient and solubility of water in the membrane. D_2 is the solute diffusion coefficient; K is the distribution coefficient for the solute between membrane and solution; ΔC is the concentration difference on the two sides of the membrane; and ΔX is the effective membrane thickness.

Polybenzimidazole (PBI), a polymer [poly-2,2'-(m-phenylene)-5,5'-bibenzimidazole] that was originally developed as a nonflammable textile fiber, was early recognized as a reverse osmosis (RO) membrane candidate.

In addition to its thermal stability, PBI possesses excellent physical and chemical stability over a wide pH range and a high affinity for water, properties that are most useful in a variety of RO applications.

RO applications were investigated in a series of government funded (Office of Saline Water and later, Office of Water Research and Technology) research studies in which it was demonstrated that asymmetric PBI membranes possessed good RO properties in both hollow fiber and flat film configurations. Long-term operational capability in brackish water and single-pass seawater desalination was demonstrated[2,3], as was high temperature (75°C) utility[4]. In another study with chromium plating rinse water, PBI membranes exhibited oxidative resistance[5].

Based on the favorable findings of these laboratory studies, it was proposed to undertake an exploratory development program for MERADCOM to develop an optimized technique for fabricating a PBI reverse osmosis membrane which was chlorine-resistant (at 5-10 ppm level of free chlorine) and capable of meeting the MERADCOM specifications for 97% chloride ion rejection and 9 gal/ft^2-day water flux at 800 psig. Complete performance specifications are set forth in Military Specification, MIL-E-52948A(ME), January 10, 1979.

There is a need for a chlorine resistant membrane in producing potable water in the field from brackish water or seawater. The RO modules currently being used in the 600 GPH water purification unit are not resistant to chlorine. This is a definite liability since the Army would like to pre-chlorinate the feedwater for disinfection, as well as to prevent undesirable biological growths and slime in the system. Furthermore, pre-chlorination would also serve to protect the membrane against microbial attack, should it be prone to such attack.

II. PROJECT OBJECTIVES AND DEVELOPMENTAL PROGRAM

The overall objective was to conduct an exploratory study directed toward optimizing a basic technique for casting a superior chlorine-resistant polybenzimidazole (PBI) reverse osmosis (RO) permselective membrane. To accomplish the overall objective, the work program was divided into the following tasks:

1. Conduct an exploratory development study directed to optimizing a basic technique for casting a superior chlorine-resistant polybenzimidazole (PBI) reverse osmosis (RO) permselective membrane.
2. Cast the experimental membranes from a "high solids" casting solution (20-25% strength) consisting principally of PBI polymer and lithium chloride dissolved in dimethylacetamide. The purpose of this procedure will be to produce a high density membrane capable of withstanding, with minimal compaction, the high pressure (900 psi) required to demineralize seawater.
3. Explore the practicality of casting a "thin" membrane (less than 2 mils thickness) to reduce overall membrane resistance and compensate for the higher density produced by the "high solids" casting.
4. Check the possibility of heating the casting solution in order to reduce the viscosity, thus maintaining the desired flow properties.
5. Consider experimenting with other variables in order to establish optimal conditions for producing a superior membrane. Include film drying

time, temperature in the casting chamber, and relevant coagulation-bath conditions.

6. Investigate the possibility of crosslinking the PBI with poly-functional agents or reacting with other functional agents in order to achieve even further improvements in membrane properties.
7. Investigate various annealing conditions with the goal of establishing ideal conditions.
8. Examine alternative post-treatment possibilities to modify and improve the membrane.
9. Although "trade-off determinations" are inevitable, make every effort to produce a membrane that is not only chlorine-resistant, but also maintains high flux and high salt rejection.
10. To measure progress and assess the results obtained, short term testing (72 hours) will be performed on cast membranes to determine performance characteristics. Selected membranes will be tested for longer periods, under simulated operating conditions, to measure flux/rejection stability and chlorine resistance.
11. Cast the large-sized membranes and fabricate the small demonstration modules using the optimum membrane identified above in 10.
12. Identify and define the variables and materials needed for the successful fabrication of a spiral-wound module for the Army's need.
13. Test the demonstration modules for the long-term operational capability of meeting performance specifications including chlorination resistance, and the wet/dry cycling capability.

III. EXPERIMENTAL

A. PBI Polymer Solution

PBI polymer solution, supplied at no direct cost to the Government by Celanese Research Company, was prepared as described by Conciatori et al.[6] It was dissolved at 230°C, under nitrogen in dimethylacetamide (DMAc) solvent containing 1.5% lithium chloride (by weight). The solution was filtered to remove gel particles and any extraneous particulate material. A 24% solution was used in initial laboratory work with the laboratory film casting unit. For membrane fabrication on the three-roll reverse roll coater, 21% solutions were prepared, from which 18% solutions were obtained by dilution with DMAc. Viscosity at 25°C of the 21% solution was about 90,000 centipoise (cps); that of the 18% solution, about 30,000 cps. Solution viscosities of less than 100,000 cps are best suited for reverse roll coating.

B. Laboratory Film Casting

A pneumatically driven laboratory film casting unit was used to prepare small (4"x12") membrane samples. The unit is shown in Figure 1. Unsupported membranes were cast onto glass plates. For supported membranes, the polymer solution was cast onto a fabric support tightly taped to the glass plate. Knife blade clearance, i.e., the laydown thickness, was controlled by micrometer screw adjustments. The glass plate, with or without fabric support, rested on the pneumatically driven bedplate and passed through the hot air drying compartment at controlled speeds ranging from a few inches per minute to 24 inches per minute. Residence times of the cast film in the drying chamber could thereby be controlled from a few seconds to about 120 seconds to find the optimum residence time. A hot air blower was used to provide drying temperatures up to about 150°C.

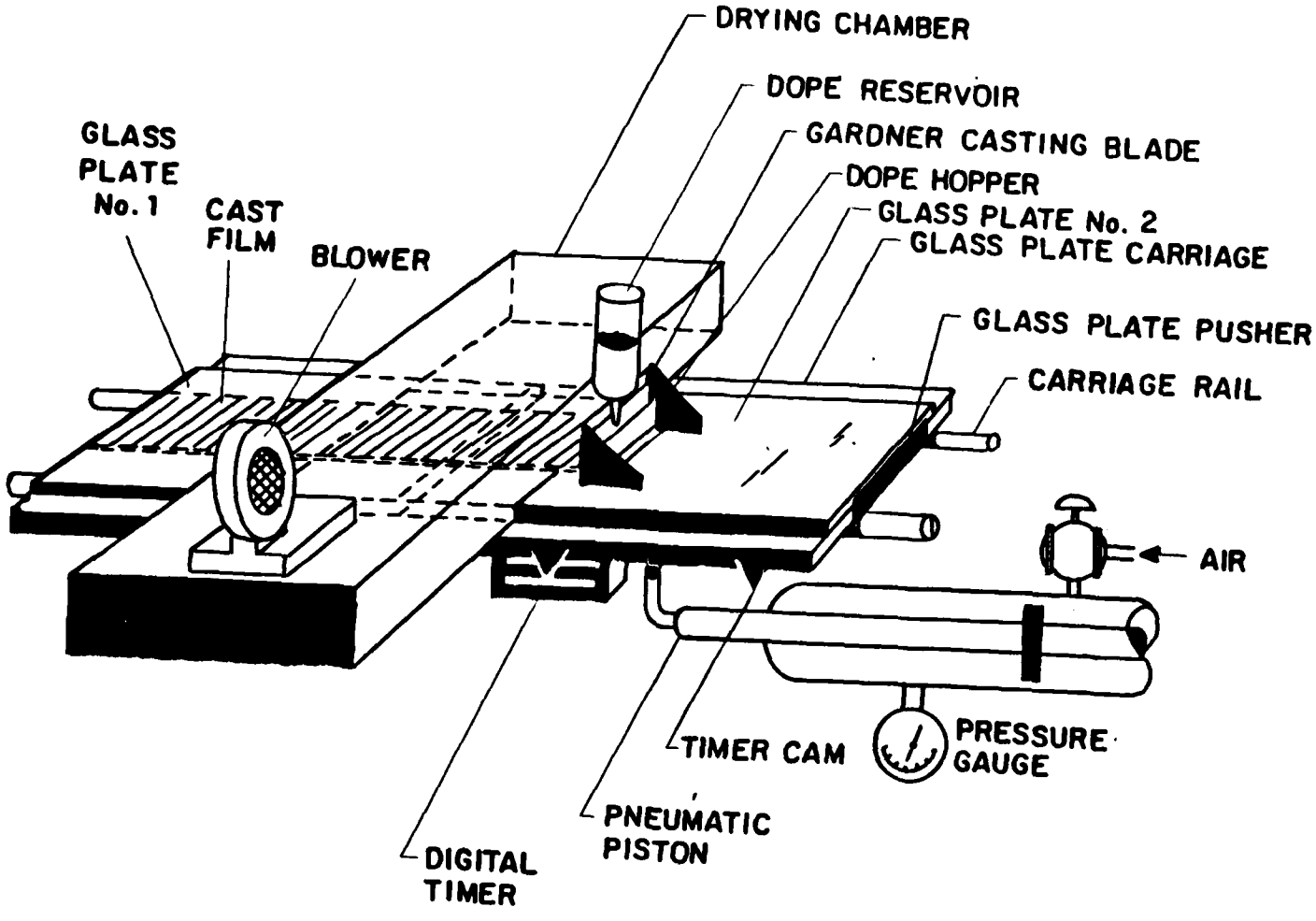

FIGURE 1. LABORATORY FILM CASTER

Air velocity of about 400 cfm was employed in a cross-flow pattern over the membrane surface. On emerging from the drying chamber, the glass plate was immersed in water at room temperature and thereafter stored in water. An asymmetric (monolithic) membrane was thereupon obtained, as depicted in Figure 2, consisting of a very thin dense barrier layer over a much thicker, porous layer. Void volume was about 60%.

C. Membrane Testing

Membrane disc (coupon) samples were tested for RO properties according to ASTM Method D 3736-39 on a high pressure, circulating flow system shown diagramatically in Figure 3 and photographically in Figure 4. Two-inch (actually 1 31/32") diameter discs were tested in stainless steel flat film test cells (Figure 5). For screening test purposes and to simulate brackish water, 0.5% sodium chloride solution was used as the feed. To simulate seawater, a 3.5% sodium chloride solution was used. Operating pressure when using 0.5% salt solution was 400 psig or 600 psig. In testing the small spiral wound modules, 400 psig was used. However, simulated seawater tests were carried out at 800 psig operating pressure with disc samples.

Ten membrane cells in the test system were connected in series. Type 316 stainless steel was used throughout. All lines were 3/8" inside diameter. Valves on each test cell were of the Whitey (Whitey Co., Oakland, CA) "PD" series of straight-through, rising plug design. The filtration system for the feed solution utilized a Pall Ultipore® 0.9μ filter cartridge (Pall Trinity Micro Corporation, Cortland, NY) in a Pall stainless steel filter housing. A positive displacement Lapp Pulsafeeder CPS-4 diaphram pump (Interpace Corp., Leroy, NY) rated for 1500 psi service maintained the feed flow at about 22 gallons per hour. Linear feed flow rate was about 65 ft/min. over the membrane surface in each cell with chamber clearance at 0.090 inches.

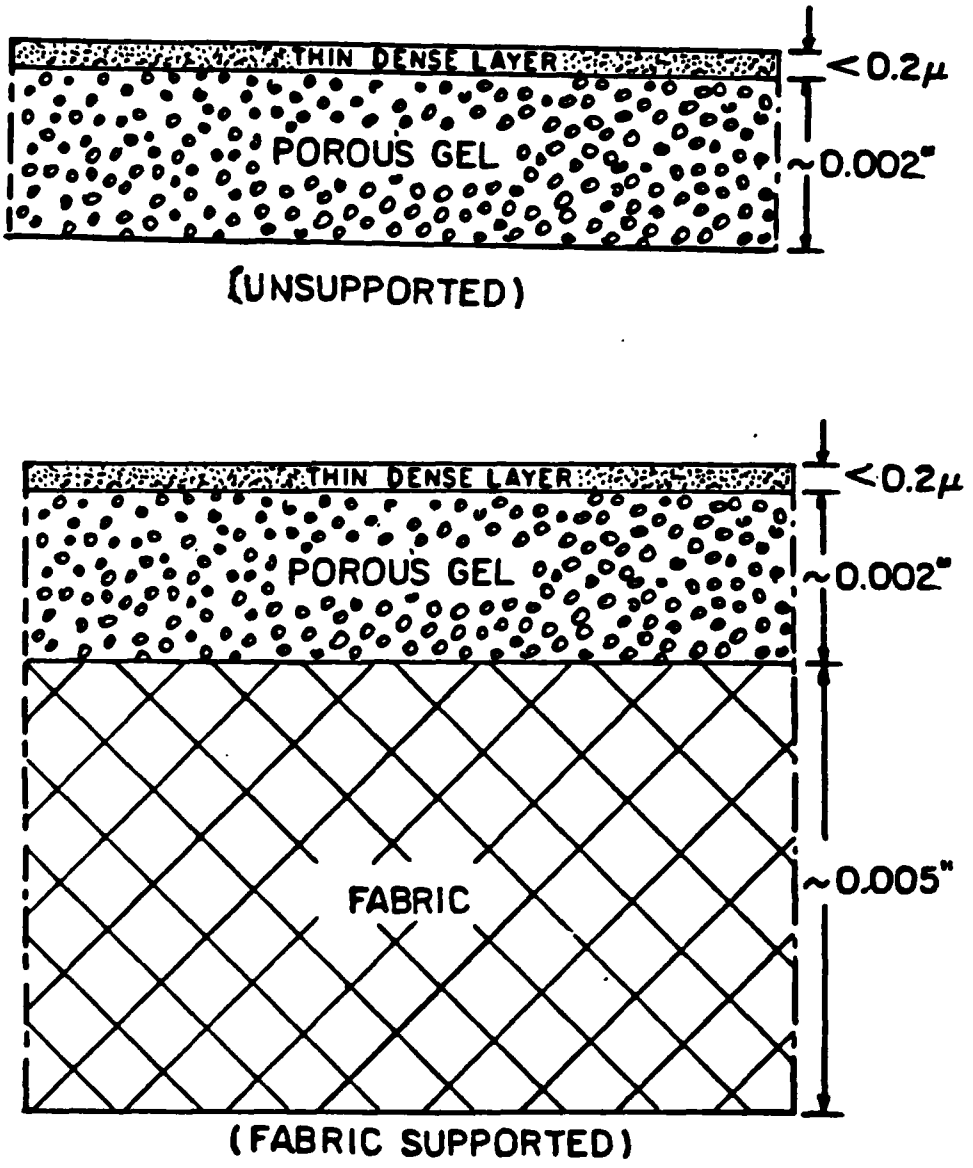

FIGURE 2. PBI ASYMMETRIC MEMBRANE

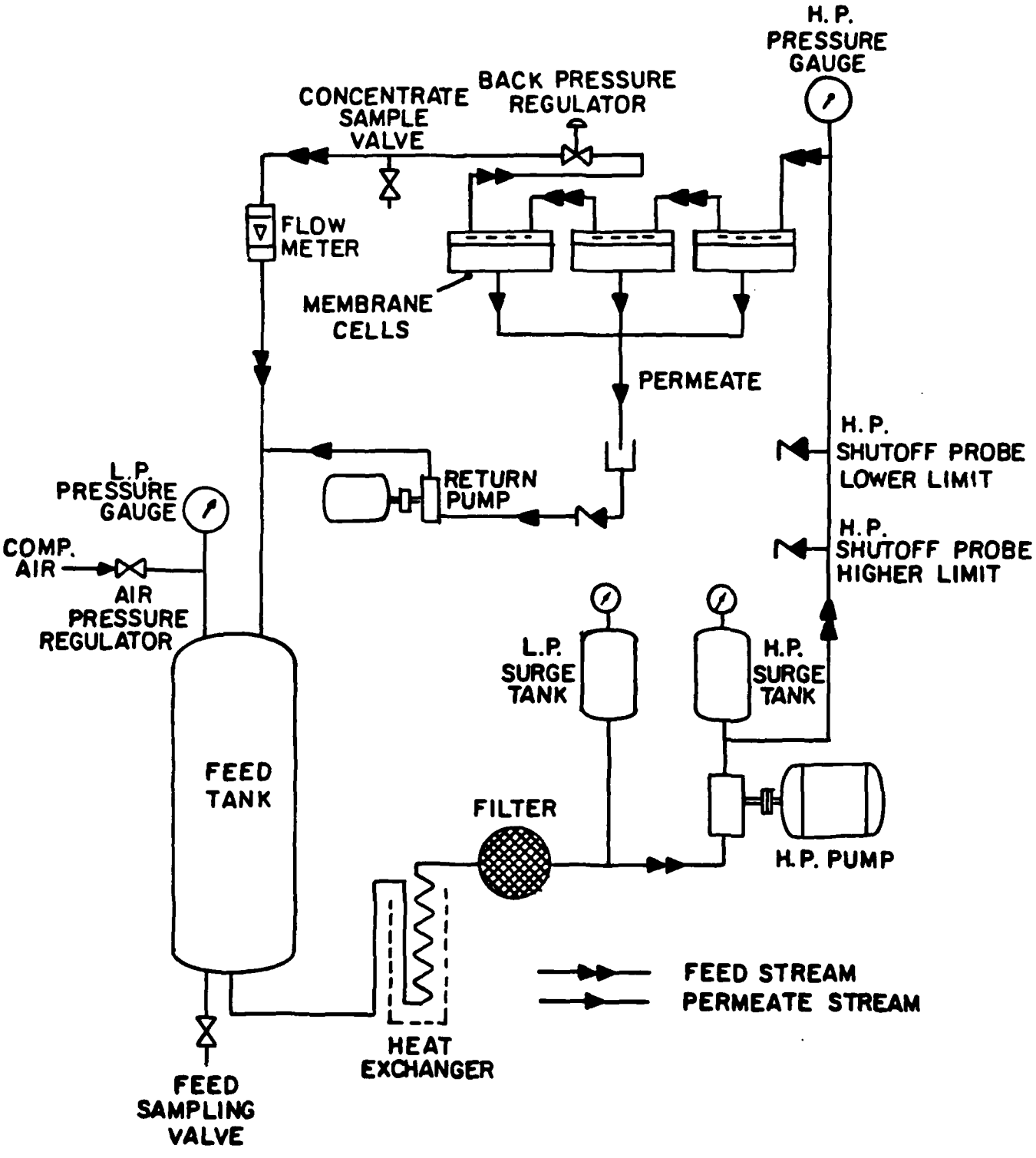

FIGURE 3. CIRCULATING HIGH PRESSURE TEST SYSTEM

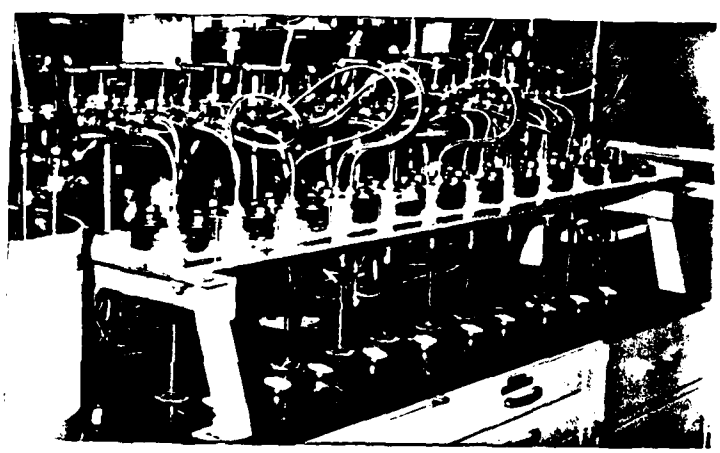

FIGURE 4. MEMBRANE TEST STAND

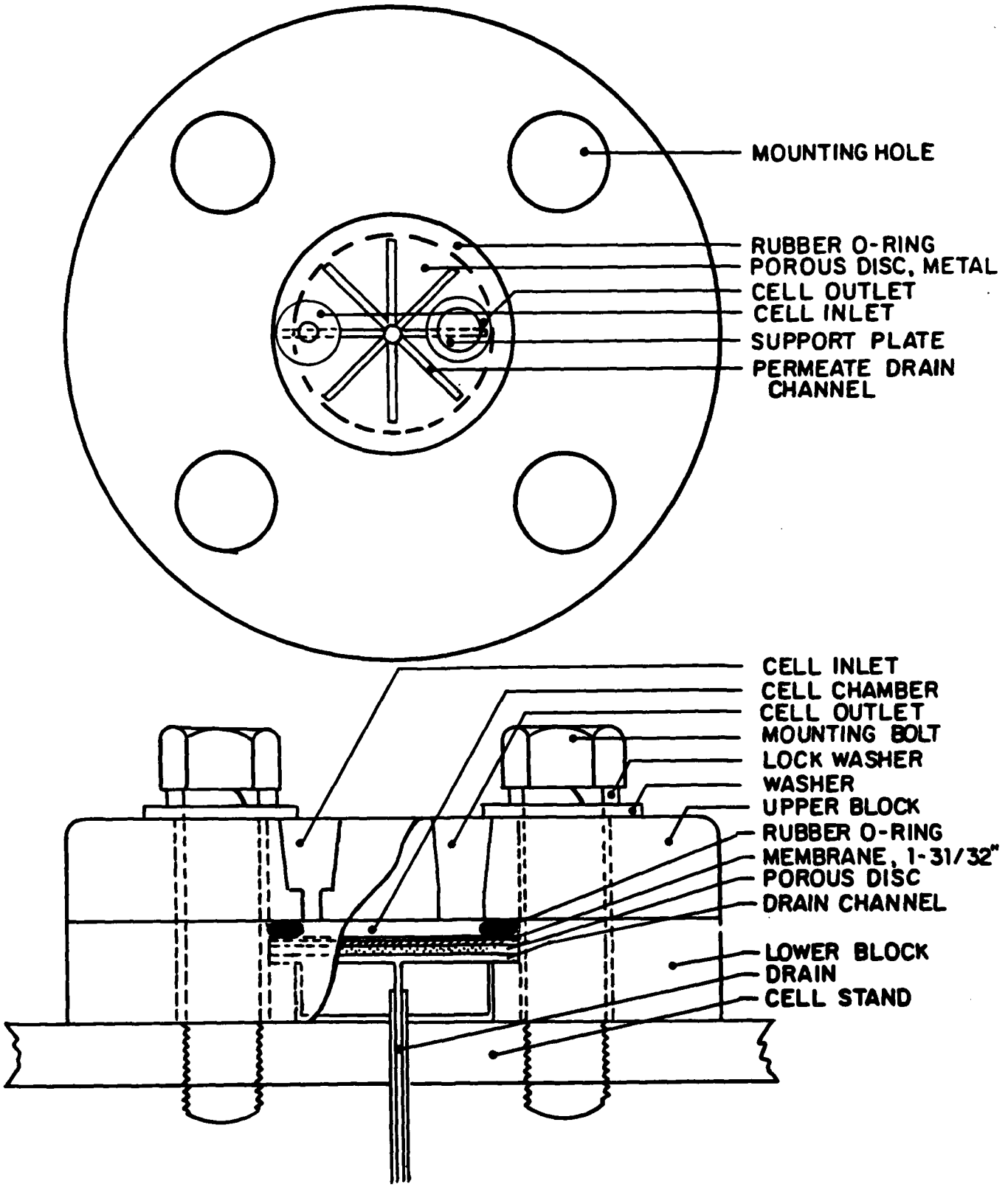

FIGURE 5: MEMBRANE TEST CELL

Operating pressure was controlled by a back-pressure regulator. (100 psi - 2000 psi range, Model S-91-W, Grove Valve and Regulator Co., Oakland, CA). Permeate return pump was a Lapp Hydracone® diaphram pump rated at 2.3 gal/hr. at 185 psi. All permeate, except for the small, insignificant amounts removed for analysis, was returned to the feed tank. Under these conditions, percent conversion was zero.

Water flux, expressed as gallons-per square foot-per day (gfd) was determined by collecting a measured volume of permeate in a graduated cylinder over a measured time period. The active membrane area in a test cell was 0.0156 ft^2. Salt rejection, % R, was determined by measuring the salt concentration in the permeate relative to that of the feed. Both conductivity (for 0.5% salt solution), ASTM D 1125-77 and titrimetric, ASTM D 512-67 (for 3.5% salt solution) methods were employed. Percent salt rejection was calculated as follows:

$$\%R = \frac{\text{Feed concentration-permeate concentration}}{\text{Feed concentration}} \times 100$$

Concentrations were expressed as ppm. Conductivities were measured with a Radiometer meter, Model CDM2d (Copenhagen, Denmark). The titration method was based on the mercurimetric titration of chloride ion with mercuric nitrate to a diphenylcarbazone indicator end point (colorless to wine-red).

D. Module Fabrication

Modules were fabricated for test using the standard spiral wound configuration utilizing a polyurethane adhesive as described in a previous study[7]. A 9" x 35" membrane sheet was folded over so that the active layer faced inwards and a polypropylene net was inserted between the two membrane surfaces. This then

was laid onto a melamine coated polyester tricot fabric previously bonded at one end to a 3/4" diameter perforated Noryl permeate tube and tensioned at the other end by a set of negators. In use, the polypropylene net functions as a channel for the feed solution after the complete assembly is wound around the core, with the tricot becoming the permeate channel.

Polyurethane adhesive was applied to the membrane backing along previously determined "glue" lines to provide a seal between the membrane backing and the tricot to isolate feed and permeate flows. The entire assembly was then wound up to give alternate layers of tricot/membrane/net/membrane/tricot, etc., resulting in about 3 spiral turns of the membrane. Adhesive tape was then wound about the finished assembly and the adhesive was allowed to cure at room temperature as specified by the adhesives manufacturer.

Some adhesive spreading occurs as the assembly is wound up resulting in some encroachment of the adhesive into the membrane area thus reducing the effective transfer area. It is estimated from examination of modules that the true area in these small test modules is of the order of 0.7 ft^2 although this might vary somewhat from module to module. Larger width and length membrane sheets used in fabricating large area modules of course will result in a very much smaller percentage area lost to the adhesive.

E. Module Testing

Small spiral wound modules were tested on the membrane test system but because of the limited permeate return volume available, no more than two modules could be tested at one time. In order to test larger numbers of modules and modules with larger membrane areas, a skid-mounted test system was purchased, at no direct cost to the Government, from Osmonics, Inc., Hopkins, MN. Operating pressures up to 1000 psi are attainable.

F. Continuous Membrane Preparation

To scale-up membrane fabrication from the laboratory film casting scale to continuous commercial scale needed to generate large quantities of membrane to support spiral wound module fabrication efforts, Celanese purchased, at no direct cost to the Government, a three-roll reverse roll coater, a hot air impingement dryer and a water coagulation or quench tank, as shown in Figures 6 and 7. The coating trials were preceded by laboratory film casting studies to guide the large scale efforts. Initial coating trials were devoted to a statistical study of main effect variables, such as line speed, oven drying temperature, laydown thickness, etc. The coating line consisted of a coating stand capable of coating up to 12 inches in width, an 8-foot air impingement dryer and a large water coagulation tank. Fabric-supported membranes and some unsupported membranes were prepared. A non-woven polyester fabric, Hollytex ® 3329 (Eaton-Dikeman, Mount Holly Springs, PA) was used as the support for supported membranes. Unsupported membranes were cast onto Mylar ® film and then lifted off.

Laydown thickness, usually 4 or 5 mils, was controlled by the metering gap clearance. The slot openings, 10 inches apart, were fixed at 3/8" and the air gap distance, i.e., the distance from the slot to the membrane surface in the dryer, was kept constant at 6 inches. Each sample from the continuous coater was collected on 3-inch plastic cores at the windup position and thereafter was stored in water. Several hundred feet of each sample was usually collected to insure an ample supply for fabrication of spiral wound elements.

G. Annealing

All membranes were annealed under restraint in ethylene glycol to develop RO properties to the maximum permitted by the

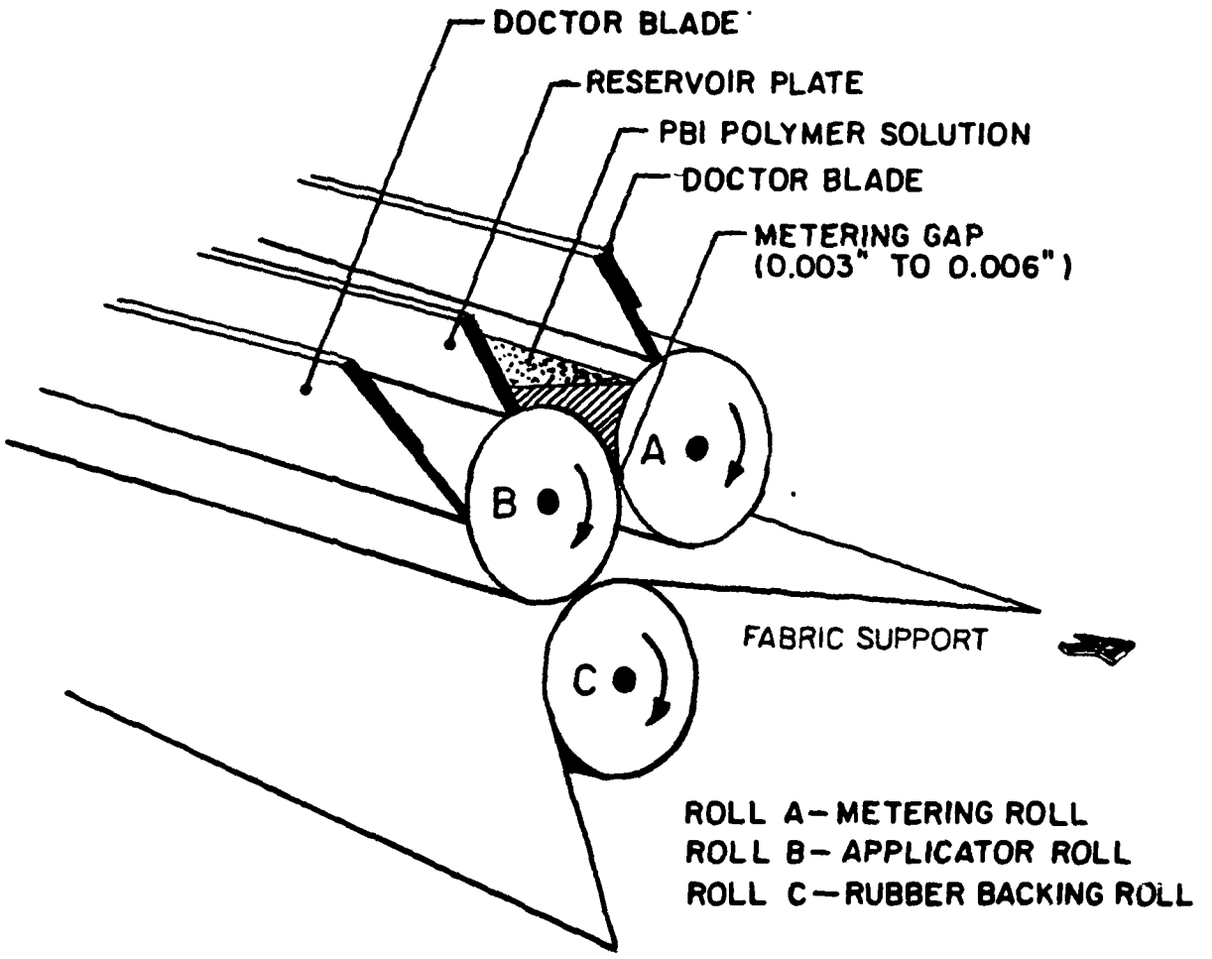

FIGURE 6. THREE-ROLL REVERSE ROLL COATING

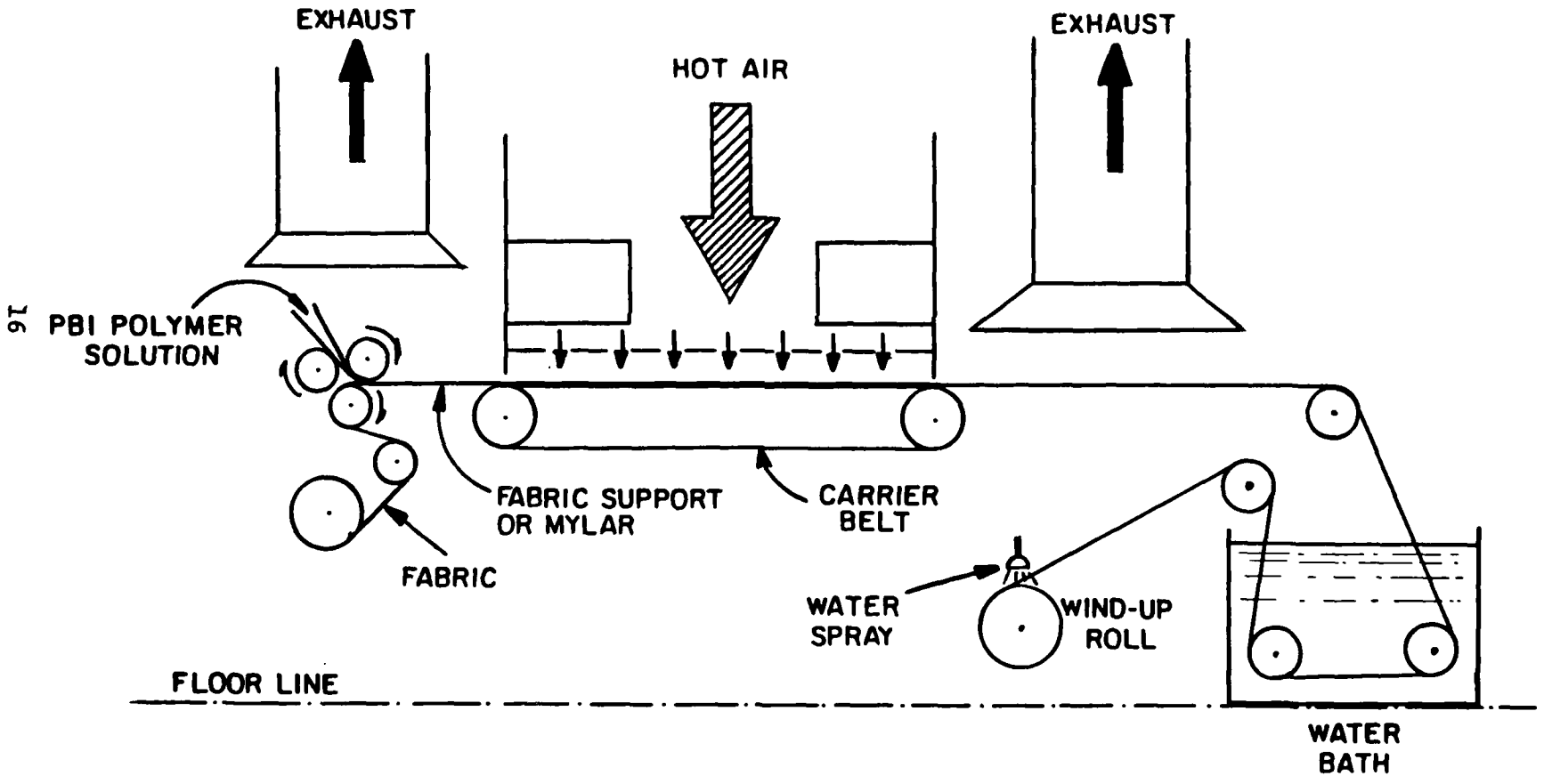

FIGURE 7. PBI MEMBRANE COATING PROCESS

casting or coating conditions used in preparing the membranes. Small (4" x 12") membrane samples were mounted in flat metal (aluminum or stainless steel) clip frames to maintain constant dimensions as shown in Figure 8 and annealed in hot ethylene glycol at temperatures ranging from 110°C to 140°C, depending on the membrane preparative conditions. Annealing time in all cases was 10 minutes. Large membrane sheets (12 inches wide) needed for spiral wound elements were taken from sample rolls from the continuous reverse roll coater unit and annealed on large perforated frames as shown in Figure 9. The 13-inch diameter frame provided 40-inch lengths of membrane and the spiral frame was used to anneal 8½-foot lengths. Bar clamps at both ends were used to maintain constant length. The large sheets were also annealed in ethylene glycol for ten minutes at 120°C - 140°C. The optimum annealing temperature for the large sheets was first determined with small samples annealed in the clip frame.

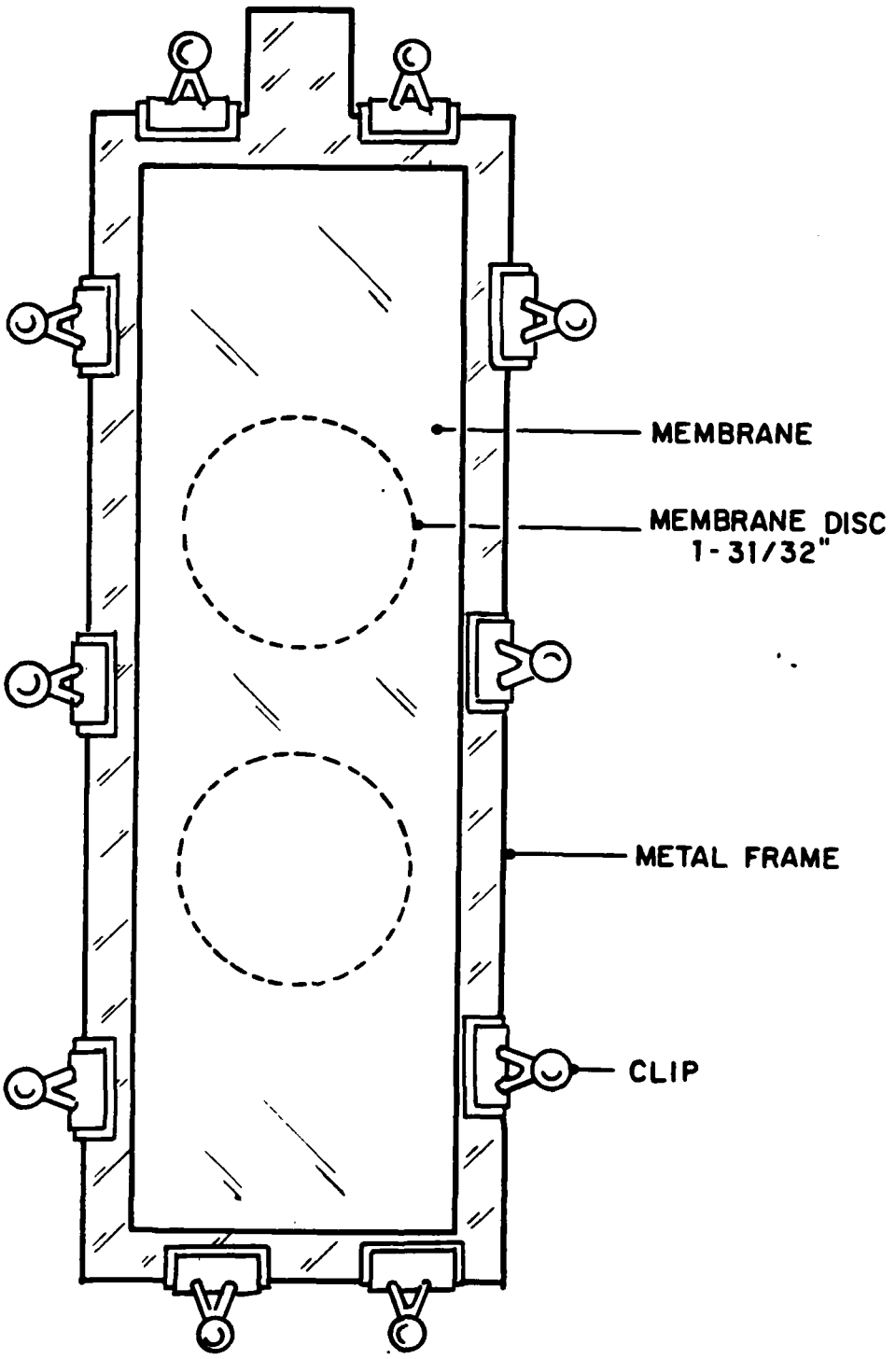

FIGURE 8. MEMBRANE ANNEALING CLIP FRAME

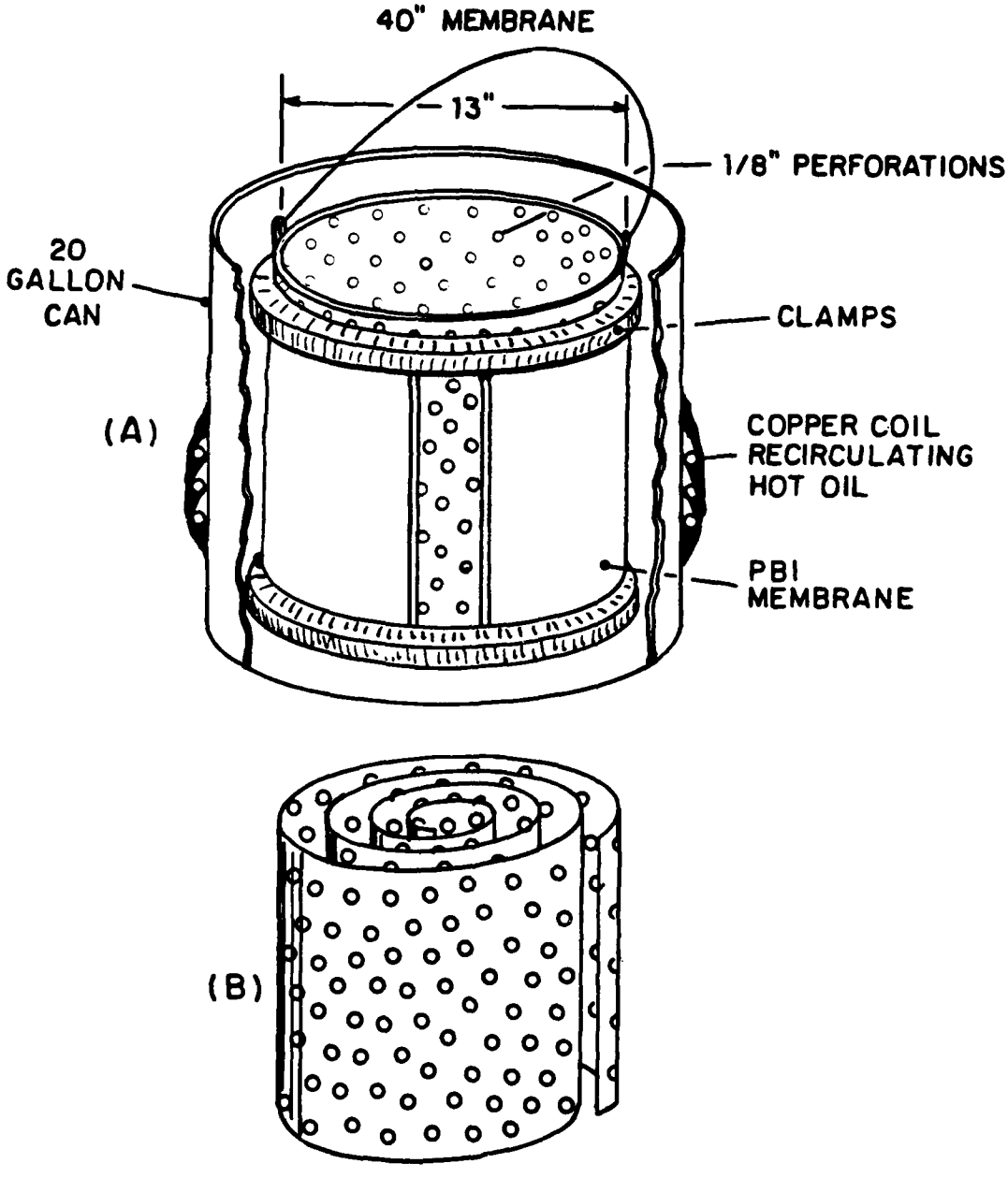

FIGURE 9. ANNEALING FRAMES AND BATH FOR LARGE MEMBRANES

IV. TECHNICAL DISCUSSION

A. Membrane Optimization - Laboratory Membrane Preparation and Testing

A major objective was to optimize the membrane fabrication process to produce membranes capable of meeting Army performance requirements. The first approach was a laboratory scale study of membrane casting variables to identify conditions leading to superior membrane properties and then to translate this technology to a continuous membrane fabrication process. Unsupported membranes were cast from 24% polymer solutions on the laboratory casting unit. It was reasoned that, using higher polymer concentrations, denser and stronger membranes would be obtained. At the same time, it was expected that these membranes would have good RO properties as well as being better able to withstand pressure-induced compaction. Membranes with thicknesses ranging from 0.8 to 6.9 mils were prepared. Air drying times in the casting chamber of 30 seconds and 60 seconds were investigated, based on the results of an earlier study[7]. All 4"x12" samples were annealed in clip frames for 10 minutes in ethylene glycol at 140°C. Duplicate membranes were prepared for each set of conditions and two membrane discs were taken from each sample for testing. The membranes were tested with 0.5% salt solution at 600 psig operating pressure.

The RO test results are given in Table 1. The average of the two discs from each sample is reported. The best RO properties were obtained with the membranes that were 2.8 and 2.9 mils in thickness and cast at a 4-mil doctor blade setting. Through 72 hours, high salt rejections were obtained with these samples ranging from 95% to 98%. Although water flux values were variable, at least two samples retained high fluxes (24.1 and 22.6 gfd) along with high rejection (95-97%) after 72 hours. These were selected

TABLE 1. RO PROPERTIES OF MEMBRANES PREPARED FROM A 24% SOLIDS CASTING SOLUTION
(5,000 ppm NaCl, 600 psi, 25°C)

DOCTOR BLACE READING	MEMBRANE THICKNESS (mils)	DRYING TIME (sec)	24 HOURS		48 HOURS		72 HOURS	
			FLUX (gfd)	REJECT. (%)	FLUX (gfd)	REJECT. (%)	FLUX (gfd)	REJECT. (%)
6 mil	6.9	30	13.3	96.0	8.7	96.3	-	-
		30	13.3	96.7	8.6	98.0	-	-
	6.9	60	9.9	97.8	6.1	98.1	-	-
		60	7.2	98.8	5.0	98.3	-	-
4 mil	2.9	30	11.9	97.5	10.9	95.9	10.9	98.0
		30	23.2	94.7	21.7	95.7	24.1	94.7
	2.8	60	22.1	97.5	20.6	97.7	22.6	96.9
		60	16.0	96.1	14.8	96.0	15.9	97.9
2 mil	1.6	30	14.1	96.7	9.0	94.5	-	-
		30	16.3	94.9	9.1	93.9	-	-
	1.4	60	37.5	36.8	26.1	43.9	-	-
		60	54.7	16.3	46.5	24.5	-	-
1 mil	0.8	30	29.7	32.6	21.7	39.3	22.6	41.0
		30	26.1	79.1	21.4	78.7	23.5	89.8
	0.8	60	11.9	98.2	11.7	98.3	12.6	97.9
		60	7.8	83.6	5.9	77.5	5.6	87.2

for further long-term testing to evaluate flux stability.

A possible explanation for the variability in flux, in otherwise similarly prepared membranes, is uneven tension during annealing in the clip frame. The membranes do shrink during annealing if unrestrained and loose clips could permit slippage of the membrane held between the two flat frames. The high shrinkage forces and any slippage would result in tightening up of the membrane, hence lower water flux. The other membranes in this series exhibited unsatisfactory flux values and/or salt rejections.

The two membrane samples with flux/rejection values of 24.1/94.7 and 22.6/96.9 after 72 hours were subjected to further long-term testing. Testing was continued to 418 hours (22 days) and the flux and rejection values measured during this period. The test results are plotted in Figure 10. The membranes exhibited good flux stability. The logarithemic flux decline factor, m, (the slope of the log-log plot) averages -0.018 for these samples. This is as good as or better than the values of -0.02 to -0.05 reported for commercial membranes[8]. Salt rejection remained high throughout, averaging about 96%. In comparison to the less favorable long-term results obtained previously with membranes cast from 18% solids[7], this series would indicate that high solids solutions lead to improved flux stability.

Some of the other membrane samples were also subjected to long-term testing along with the two best samples discussed above. These data are given in Table 2. The thin (0.8 mils) membranes also exhibited good flux stability over the long term.

The RO properties for duplicate membrane samples prepared in a repeat fabrication of membranes from the same high solids,

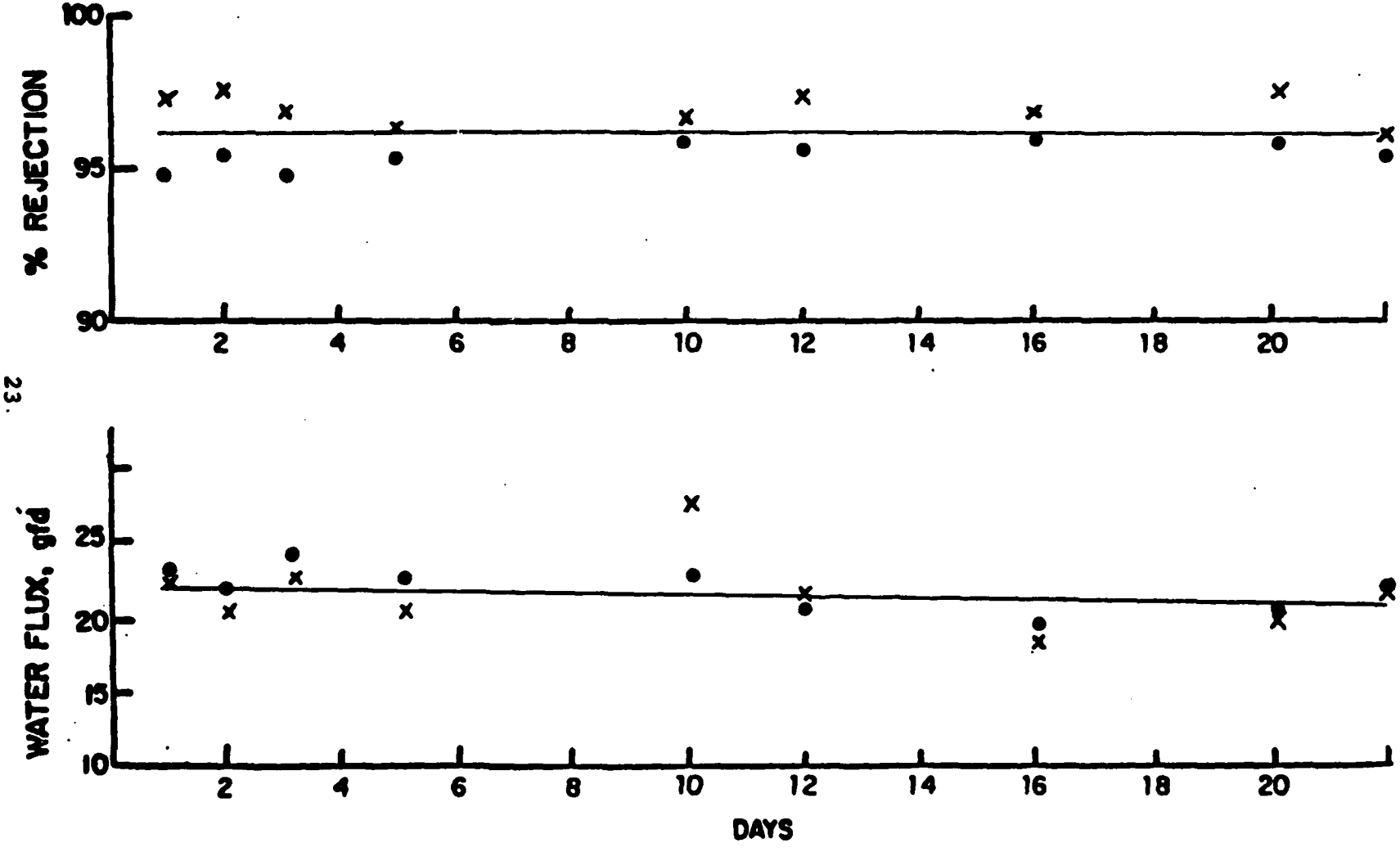

FIGURE 10. LONG TERM RO PROPERTIES OF MEMBRANES PREPARED FROM A 24% SOLIDS CASTING SOLUTION (5,000 ppm NaCl, 600 psi, and 25°C)

TABLE 2. LONG-TERM RO PROPERTIES OF MEMBRANES PREPARED FROM A 24% SOLIDS CASTING SOLUTION (5,000 ppm NaCl, 600 psi, 25°C)

TIME (Hrs)	MEMBRANE SAMPLE A(1) Flux (gfd)	A(1) Reject. (%)	A(1) Flux (gfd)	A(1) Reject. (%)	B(2) Flux (gfd)	B(2) Reject. (%)	B(2) Flux (gfd)	B(2) Reject. (%)	C(3) Flux (gfd)	C(3) Reject. (%)	D(4) Flux (gfd)	D(4) Reject. (%)
24	11.9	97.5	23.3	94.7	22.1	97.5	16.0	96.1	-	-	11.9	98.2
48	10.9	95.9	21.7	95.7	20.6	97.7	14.8	96.0	21.4	78.7	11.7	98.3
72	10.9	98.0	24.1	94.7	22.6	96.9	15.9	97.9	23.5	89.8	12.6	97.9
120	10.9	96.6	22.6	95.3	20.4	96.8	15.9	97.4	20.9	89.0	11.7	98.9
240	10.2	97.9	22.7	96.0	27.9	97.2	13.8	91.5	19.5	90.1	10.3	98.8
288	9.7	98.1	20.4	95.7	21.7	97.3	13.1	95.8	21.9	90.1	13.1	98.6
360	9.9	98.0	19.3	96.1	18.6	97.0	12.1	98.0	17.1	90.4	11.4	98.7
408	10.9	97.8	20.5	96.0	19.9	97.4	13.2	97.9	19.9	91.2	10.5	98.7
528	11.2	98.1	21.9	95.5	21.9	96.1	14.1	97.8	18.5	90.0	11.7	98.0

(1) Laydown thickness = 4 mils, drying time = 30 seconds, membrane thickness = 2.9 mils.
(2) Laydown thickness = 4 mils, drying time = 60 seconds, membrane thickness = 2.8 mils.
(3) Laydown thickness = 1 mil, drying time = 30 seconds, membrane thickness = 0.8 mils.
(4) Laydown thickness = 1 mil, drying time = 60 seconds, membrane thickness = 0.8 mils.

24%, casting solution are given in Table 3 and show that good flux/rejections values were again obtained for the unsupported membranes. Flux values, after 96 hours, were 18.5 and 22.5 gfd with salt rejection values at 97% and 98% for 4-mil laydown thickness (2.8 mil membrane).

Fabric supported membranes prepared from the same casting solution also exhibited good RO properties for 4-mil laydown thickness. Flux values ranged from 18.5 to 30 gfd and salt rejection, 90% to 96% after 96 hours. The fabric-supported membranes were prepared to demonstrate translatability of unsupported membrane RO properties to the fabric-supported structure since ultimately, in spiral wound element fabrication, supported membranes must be used. From the standpoint of experimental ease and convenience in laboratory studies, the unsupported membranes are easier to prepare.

The 2-mil membrane in Table 3 also showed excellent RO properties after 96 hours. This result indicates the feasibility of preparing thinner overall thickness membranes with less resistance to water transport.

B. Membrane Optimization - Continuous Coating

Guided by the results of the laboratory studies of film casting variables for supported and unsupported membranes, a scouting membrane coating trial was conducted on a reverse roll coater. Conditions used were as follows:

Polymer Concentration: 18%
Line Speed: 6 ft/min
Air Gap Distance: 6 inches
Slot Width: 3/8 inches
Dryer Air Velocity: 600 ft^3/min
Water Bath: 25°C, Unstirred
Fabric Support: Non-woven polyester, 5.5 mils thick

TABLE 3. RO PROPERTIES OF MEMBRANES FROM A 24% SOLUTION (5,000 ppm NaCl, 600 psi, 25°C)

Membrane	Casting[1] Conditions	Flux/Rejection[2] Hours 24	48	72	96
UNSUPPORTED; REPEAT	4/140/30	28/96	27/98	-	22.5/97
	4/140/60	21.5/97	21.4/98	-	18.5/98
FABRIC-SUPPORTED	4/140/30	36/87	36/89	-	30/90
	4/140/60	21/95	21.5/96	-	18.5/96
	2/140/60	27.5/94	27.5/98	-	24.5/96

(1) Laydown thickness, mils/drying temp., °C/drying time, secs.
(2) Flux, gal/ft^2-day/Rejection, %.

Sample rolls containing several hundred feet each of membrane on 3-inch plastic cores were collected, representing different drying temperatures and laydown thicknesses. Sections of each sample were mounted in clip frames and annealed in ethylene glycol for 10 minutes at 140°C. A two-inch membrane disc was punched out from each of two clip frame samples and tested for RO properties with 0.5% sodium chloride at 600 psig. The flux/rejection values after 24 hours are given in Table 4.

The coating operation proceeded smoothly without any processing difficulties. The results in Table 4 indicated that drying temperatures well below 90°C are suitable and that in this trial the lower laydown thickness, 5 mils (smaller metering gap between metering roll and transfer roll), was preferred. In general, the flux values and rejection values were encouraging for a first coating effort, but it was apparent that these values were much inferior to those obtained for laboratory cast membranes from the high solids solution.

Major emphasis continued on the optimization of the continuous membrane fabrication process. "Low" (18%) and "high" (21%) polymer concentrations were investigated, as well as different levels of coating and drying conditions. Process conditions and RO properties of each sample roll produced in the coating trials are given in Table 5.

RO tests were carried out with 0.5% salt solution at 600 psig operating pressure. Duplicate sections from each sample roll were annealed in the 4 x 12-inch clip frame and one membrane disc (2-inch diameter) was tested from each clip frame. RO properties were determined after 24 hours. Samples 4-4, 4-9, 5-5 and 5-10 exhibited the highest salt rejection, 98% or better, but flux values were generally low.

TABLE 4. RO PROPERTIES OF FABRIC SUPPORTED MEMBRANES
(5,000 ppm NaCl, 600 psi, 25°C)

Membrane Number	Laydown Thickness mils	Drying Temp., °C	Flux/Rejection (1) 24 Hours
1-1	7	40	(a) 14.4/70
			(b) 10.6/88
1-4	7	40	(a) 4.4/88
			(b) 4.7/95
1-8	7	70	10.8/85
1-9	5-5.5	50	(a) 11.5/83
			(b) 6.4/98
1-A	7	90	Membrane too dry and dense

(1) Flux, gal/ft^2-day/Rejection, %.

TABLE 5. FABRIC-SUPPORTED MEMBRANES - PROCESS CONDITIONS AND RO PROPERTIES

Smp. No.	Conc. %	Laydown Thickness mils	Line Speed fpm	Oven Temp. °F	Slot Width inches	Anneal. Temp. °C	RO Properties Flux gfd	RO Properties Rejection %
4-3	18	4	12	120	3/8	120	15.0	93.5
4-4	18	4	9	112	3/8	120	7.1	99.6
4-4	18	4	9	112	3/8	140	2.7	-
4-5	18	4	9	112	3/8	120	6.8	96.8
4-6	18	4	10.5	112	3/8	120	13.4	93.5
4-7	18	4	10.5	112	3/8	120	10.9	93.3
4-8	18	4	12	120	3/8	120	12.9	92.2
4-9	18	4	12	120	3/8	120	14.0	99.3
4-9	18	4	12	120	3/8	140	2.3	98.0
4-10	21	4	12	120	3/8	120	7.6	97.7
4-11	21	4	16	120	3/8	120	6.6	97.2
4-12	21	4	24	120	3/8	120	10.5	93.5
4-12	21	4	24	120	3/8	140	6.3	97.0
4-13	21	4	24	120	3/8	120	12.1	91.5
4-14	21	4	30	128	3/8	120	12.5	93.5
4-15	21	4	30	120	3/8	120	12.8	90.5
4-16	21	4	40	120	3/8	120	14.1	86.5
4-17	21	4	50	120	3/8	120	13.0	88
4-17	21	4	50	120	3/8	140	8.5	97.5
5-1	18	4	12	122	3/8	140	17.8	95.5
5-1	18	4	12	122	3/8	120	34.4	64.6
5-2	18	4	16	122	3/8	140	25.1	91.4
							15.4*	90.5*
5-3	18	4	24	122	3/8	140	23.4	87.4
5-4	18	4	30	122	3/8	140	28.1	82.5
5-5	18	4	12	130	7/8	140	10.8	98.0
5-5	18	4	12	130	7/8	120	24.3	87.0
5-6	21	3	12	130	7/8	120	9.0	95.5
5-6	21	3	12	130	7/8	140	2.1	94.0
5-7	21	3	12	122	7/8	140	5.7	98.3
5-7	21	3	12	122	7/8	120	8.0	95.1
5-8	21	3	24	130	7/8	140	13.7	95.8
5-8	21	3	24	130	7/8	120	14.2	96.3
5-9	21	3	30	130	7/8	140	0.7	93.6
5-10	21	3	24	130	3/8	140	10.4	98.3
5-10	21	3	24	130	3/8	120	13.7	93.5
5-11	21	3	24	122	3/8	120	9.8	98.7

* Used 8"x12" annealing clip frames. All other samples used 4" x 12" frame.
Fixed Conditions: Air velocity, 600 cfm.
Air gap distance, 6" (slot to membrane surface).
Fabric support, Hollytex 3329, except for 4-8 and 4-9 which is #3361.
Polymer batch, #2137-138-139.

Refinement of annealing conditions disclosed that different optimum annealing temperatures were needed for each trial sample. Annealing was carried out for 10 minutes in ethylene glycol. The different annealing temperatures, 120° and 140°C, are ascribed in part to relative humidity conditions, which affect the rate of evaporation of solvent from the developing film surface, i.e., polymer skin formation.

Sample 4-4, 4-9, 5-5, and 5-10 exhibited the highest salt rejection in testing with 0.5% salt solution at 600 psig. However, flux ranged only from 4 to 14 gfd. Performance requirements for single-pass seawater desalination, 97% or better chloride ion rejection at 800 psig, are far more demanding in that the net effective pressure is lower, about 400 psig, (i.e., the difference between 800 psig and seawater osmotic pressure of about 400 psi) than is the net effective pressure of about 550 psig when using 0.5% salt solution as the feed. Samples 5-2, 5-3, 5-4 and 5-5 exhibited high flux values, but with unacceptably low salt rejections.

The different flux values reported for sample 5-2 reflect the variability associated with annealing of small membrane sections in different size annealing clip frames. Tension control of the small shrinkage is known and recognized as being important to membrane properties. Except for sample 5-2 as noted, all samples in Table 5 were annealed in the same size (4" x 12") clip frames. Better dimensional and tension control are achieved with the annealing of larger membrane sections, e.g., 9 ft. x 1 ft. To this end, a new large annealing frame and annealing bath will be constructed. Such large membrane sections are needed for the fabrication of demonstration size modules.

The results of the coating trials and preceding laboratory film casting studies indicate that the "high," 21%, polymer concentration is preferred to the "low," 18%, level for better long-term flux stability and stronger membranes. On the other hand, solids levels over 21% possess too high a solution viscosity, in excess of 100,000 cps, for the reverse roll coating process to work properly. Line speeds (coating speed) between 9 fpm and 16 fpm are preferred. The preferred laydown thickness (metering gap) is 4 mils. This yields a membrane of about 2.5 mils thick on top of the 5 mil fabric support. Optimum drying temperature is 50°C (122°F) at an air velocity of 600 cfm in the dryer when the slot widths are 3/8" and the air gap distance is 6 inches.

These initial oating trials served as the basis for the acquisition (at no direct cost to the Government) of a new and fully instrumented reverse roll coater/dryer. Upon installation of the new 12-inch reverse roll coater/dryer, trials were carried out, utilizing, as far as possible, the process conditions established previously on the other coater. As before, several hundred feet of each sample variant was collected on 3-inch cores. Duplicate sections of each sample were then annealed in 4" x 12" clip frames and one membrane disc from each clip frame was tested for RO properties, using 0.5% salt solution feed and 600 psig operating pressure. The flux and rejection values were determined after 24 hours.

Process conditions and RO properties are given in Table 6. Included are the RO properties obtained at different annealing temperatures. Annealing was carried out for 10 minutes in ethylene glycol.

The effect of increasing annealing temperature is to tighten up the membrane so that rejection increases and flux decreases

TABLE 6. FABRIC-SUPPORTED MEMBRANES
NEW COATER PROCESS CONDITIONS AND RO PROPERTIES

Sample	Laydown Thickness mils	Line Speed fpm	Annealing Temperature °C	RO Properties			
				Flux gfd		Rejection %	
CRC-1	4	12	120	15.1	13.4	92.3	94.0
			140	11.3	10.2	96.6	97.6
CRC-2A	4	10	110	13.6	14.3	91.3	90.5
			120	10.5	11.1	97.2	97.1
			130	6.0	5.3	98.7	99.0
CRC-2B	4	15	130	14.9	14.9	95.6	95.5
CRC-2F	5	20	120	21.9	19.5	82.0	89.6
			130	17.6	17.1	92.5	91.2
			140	5.1	10.8	94.5	96.5
CRC-2L	3	20	120	24.4	21.7	88.1	88.8
			130	18.5	17.3	92.9	93.3
			140	11.8	10.9	96.0	95.7

Fixed Conditions: Polymer concentration, 21%.
Oven temperature, 50°C (122°F).
Air velocity, 600 fpm.
Slot width, ¼".
Air gap distance, 6".
Fabric support, Hollytex 3329.

over the temperature range studied. Sample CRC-2L, for example, exhibited a water flux value of about 23 gfd and 88% salt rejection when annealed at 120°C. At 130°C, flux decreased to 18 gfd while rejection improved to 93% and at 140°C, flux declined to 11 gfd while rejection improved further to 96%. Sample CRC-2A exhibited the highest salt rejection, 99%, but an unsatisfactory flux value, 5-6 gfd, when annealed at 130°C. In general, the results of the coating trials on the new machine were promising, but further optimization is clearly indicated before single-pass seawater desalination can be achieved.

C. Membranes from Solvent/Non-solvent Mixtures

In an approach to improve RO properties as well as to increase mechanical strength, a solvent/non-solvent casting solution was employed in a laboratory film casting experiment. The solvent, as usual, was dimethylacetamide (DMAc). Ethylene glycol (EG) was selected as the higher boiling non-solvent. Unsupported membranes were cast onto glass plates from an 80/10/10 DMAc/EG/LiCl solution, dried and coagulated in water as previously described. The membranes were mounted in clip frames and annealed for 10 minutes in ethylene glycol at 140°C. Two-inch membrane discs were tested for RO properties with 0.5% salt solution at 600 psig operating pressure and the test results are given in Table 7.

The RO properties were similar, 24 gfd and 94% salt rejection, to those cast from DMAc solvent alone. Longer drying times (120 seconds vs. 30-60 seconds), at 140°C were found to be necessary to develop the good RO properties, however, and the membranes were weaker and more brittle. At higher levels of ethylene glycol non-solvent, the solution was not homogeneous. Higher non-solvent levels are desirable and this approach to membrane formation merits further study with other non-solvents as well as with DMAc and other solvent systems such as dimethylsulfoxide. Constraints of time and cost prevented further study in this direction.

TABLE 7. RO PROPERTIES OF MEMBRANES CAST FROM SOLVENT/NON-SOLVENT MIXTURES

Membrane[1]	Conditions[2]	Flux/Rejection[3] Hours	
		24 Hours	72 Hours
Unsupported	4/140/60	46.1/74.4	38/87
Unsupported	4/140/120	25.2/94.0	24.1/94.0

(1) 18% solids dope in 80/10/10 Dimethylacetamide/ethylene glycol/LiCl.
(2) Laydown thickness, mils/drying temp., °C/drying time, secs.
(3) Flux, gal/ft^2-day/Rejection, %.

D. Simulated Seawater Test

In order to assess the potential of supported RO membranes in seawater desalination, four fabric-supported membrane samples were selected for testing with simulated seawater (3.5% sodium chloride) as well as with more dilute salt solutions, to observe the effect of salt concentration and operating pressure on membrane properties. Samples 4-4, 4-14, 5-5 and 5-10 (see Table 5) were annealed in metal clip frames to maintain constant dimension. Samples 4-4 and 4-14 were annealed for 10 minutes in ethylene glycol at 120°C. Sample 5-5 and 5-10 were annealed at 140°C. Duplicate sections were annealed for each sample and one disc from each clip frame was tested in the circulating, high-pressure test system with 0.5%, 2.9% and 3.5% sodium chloride feed solutions at 600 psig, 800 psig and 900 psig. The concentration of sodium chloride in the 2.9% feed solution more closely approximates the uni-univalent ionic species (largely sodium chloride and potassium chloride and potassium bromide) content of seawater than does 3.5% sodium chloride. The unibivalent and bivalent salts (sodium sulfate, magnesium chloride and calcium chloride) are far more easily rejected because of their much larger hydrated ion size.

Samples were tested in duplicate at 25°C. In the sequential pressure level testing for each salt solution, water flux and salt rejection were determined after 24 hours at the lower pressure level, followed by 4 hours at the higher pressure level. The latter was adequate to assess pressure effects on flux and rejection. Feed flow rate was 18-20 gal/hr at zero percent conversion. Concentration polarization was considered to be negligible in the test cells under these conditions. Conductivity measurements were used for the 0.5% salt solution tests to determine salt rejection while for the 2.9% and 3.5% feed solutions, chloride ion concentrations were based on titration of the chloride ion with standard mercuric nitrate solution in the presence of

diphenylcarbazone indicator.

The RO properties, water flux (gfd) and salt rejection (%R) are given in Table 8 for the duplicate samples and the average values are graphically presented to show the effects of salt concentration and pressure upon flux and rejection in Figures 11, 12, 13 and 14.

In Figure 11, both flux and rejection are observed to decrease with increasing salt concentration at a fixed operating pressure. The decline in flux is largely attributable to a decreasing net effective pressure at the constant 800 psi operating pressure. The net effective pressure (NEP) is 742, 460 and 388 psig, respectively for 0.5%, 2.9% and 3.5% sodium chloride. Salt passage is pressure insensitive for a truly semi-permeable membrane. The observed decline in salt rejection is largely the direct consequence of the reduction in water flux and the increasing salt concentration gradient, which is the driving force for salt flux. The contribution of salt flux coupled to the convective transport of water is not known but it can be said that these membranes are not yet ideal semi-permeable membranes.

The membrane with the best combination of RO properties is no. 5-5, with an average flux of 7.0 gfd and 92% rejection at 800 psig for a 2.9% feed solution. Sample 5-10 shows a higher average salt rejection, 93.7, but a lower flux, 5.5 gfd. These properties fall short of the target 97% chloride ion rejection and 9 gfd at 800 psig. Although short of target values, the observed flux and rejection values suggest that with further optimization of membrane processing conditions, target properties can be achieved.

Figures 12, 13 and 14 show the effect of operating pressure on flux and rejection for different concentrations of sodium chloride in the feed solution. For a fixed concentration, both flux

TABLE 8. EFFECT OF SALT CONCENTRATION AND PRESSURE ON RO PROPERTIES OF FAERIC-SUPPORTED MEMBRANES

Sample		Flux/Rejection[1] 0.5% NaCl 600 psig 24 Hrs.	Flux/Rejection[1] 0.5% NaCl 800 psig 4 Hrs.	Flux/Rejection[1] 2.9% NaCl 800 psig 24 Hrs.	Flux/Rejection[1] 2.9% NaCl 900 psig 4 Hrs.	Flux/Rejection[1] 3.5% NaCl 800 psig 24 Hrs.	Flux/Rejection[1] 3.5% NaCl 900 psig 4 Hrs.
4-4	1.	12.5/94.1	18.2/97.4	10.8/83.2	12.8/84.3	9.1/80.0	10.9/81.5
	2.	9.9/96.8	15.2/97.0	7.7/86.4	9.3/87.6	6.3/83.6	7.6/85.5
4-14	1.	7.2/97.7	10.3/94.4	6.0/83.4	5.1/84.3	4.9/79.0	6.2/81.1
	2.	5.2/96.4	8.0/96	4.3/88.0	7.0/88.6	3.5/84.6	4.1/86.5
5-5	1.	8.7/96.8	14.6/96.4	6.3/92.3	7.4/92.4	4.7/89.0	4.7/91.1
	2.	9.0/96.6	14.6/97.0	7.7/91.6	9.5/92.4	6.3/89.3	8.0/90.7
5-10	1.	8.0/97.5	11.5/98.3	5.7/93.0	6.6/93.2	4.6/89.2	5.6/90.7
	2.	7.8/98.7	12.1/98.9	5.2/94.4	6.2/94.7	3.8/91.6	5.3/92.6

Standard Deviations (based on Ranges for n = 2): 0.5% Feed: 1.2 gfd, 1.3%R
2.9% Feed: 1.6 gfd, 2.1%R
3.5% Feed: 1.7 gfd, 2.6%R

(1) Flux, gal/ft^2-day/Rejection, %.

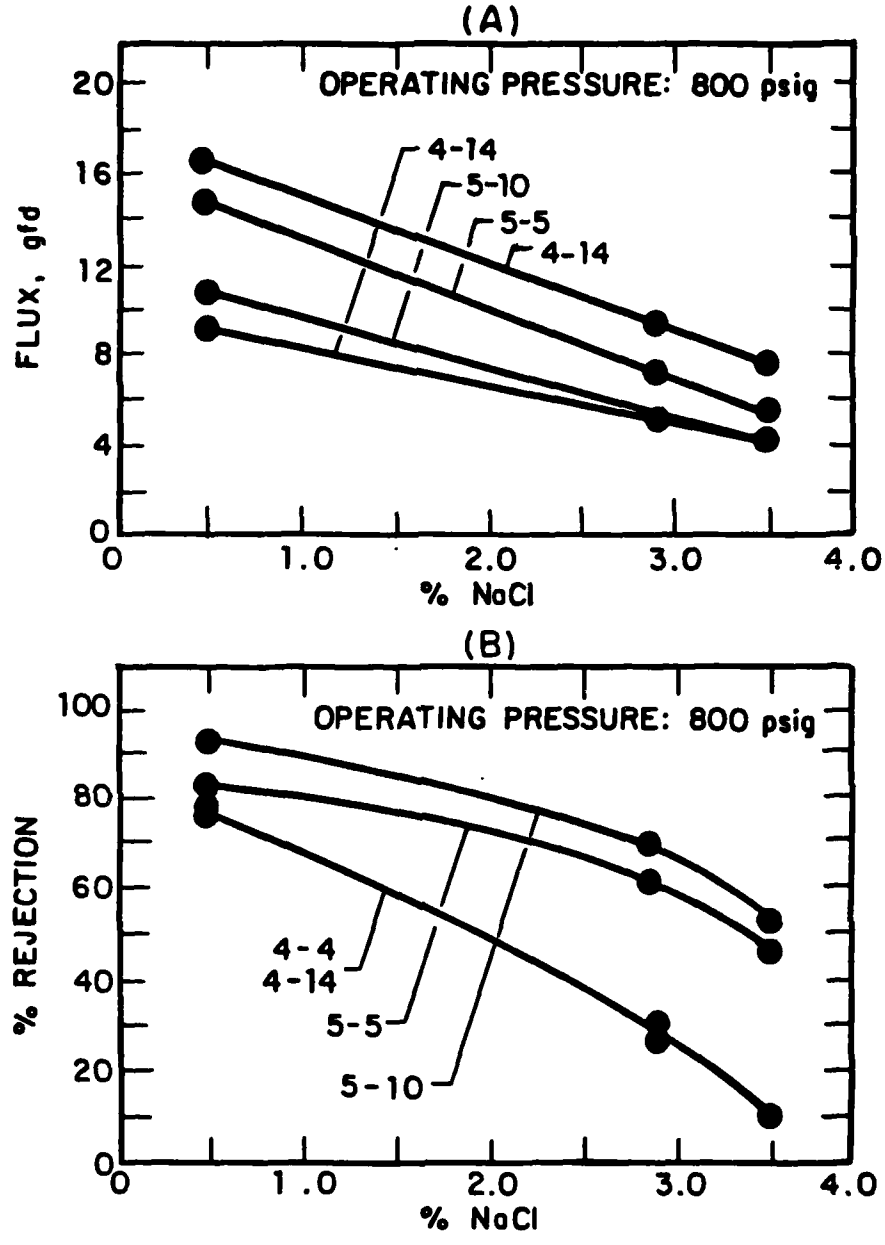

FIGURE 11. EFFECT OF SALT CONCENTRATION ON FLUX AND REJECTION AT 800 psig OPERATING PRESSURE

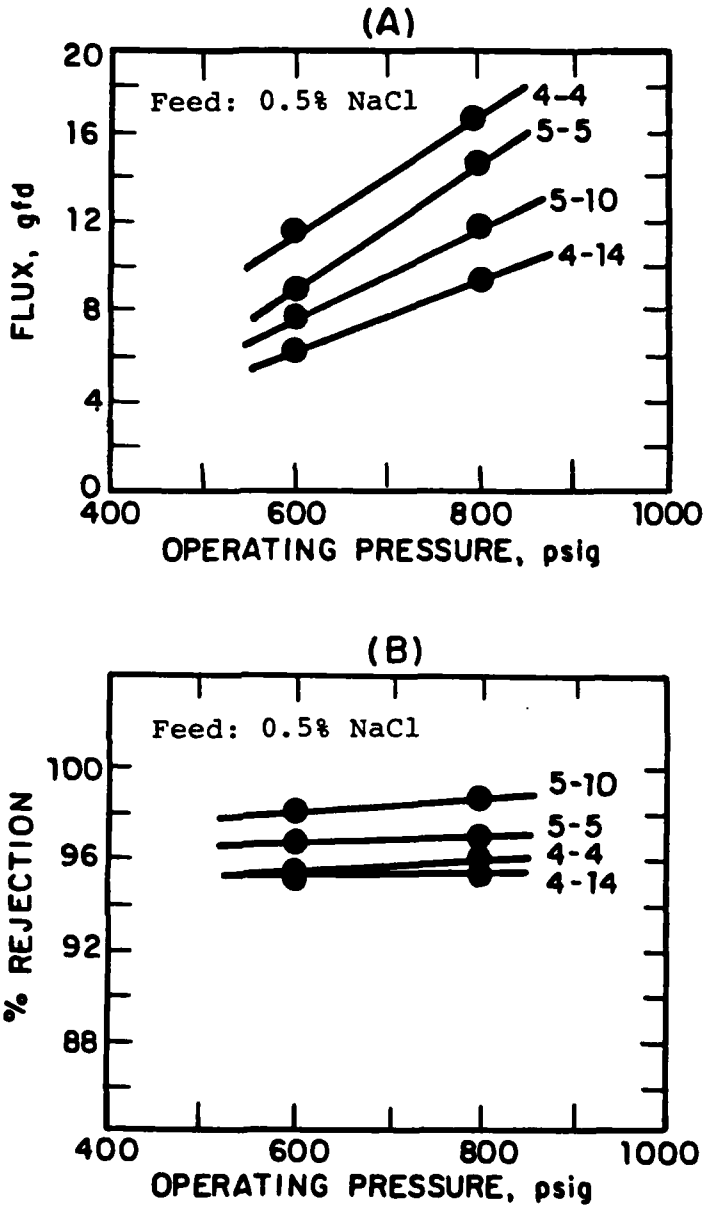

FIGURE 12. EFFECT OF PRESSURE ON FLUX AND REJECTION (0.5% NaCl FEED)

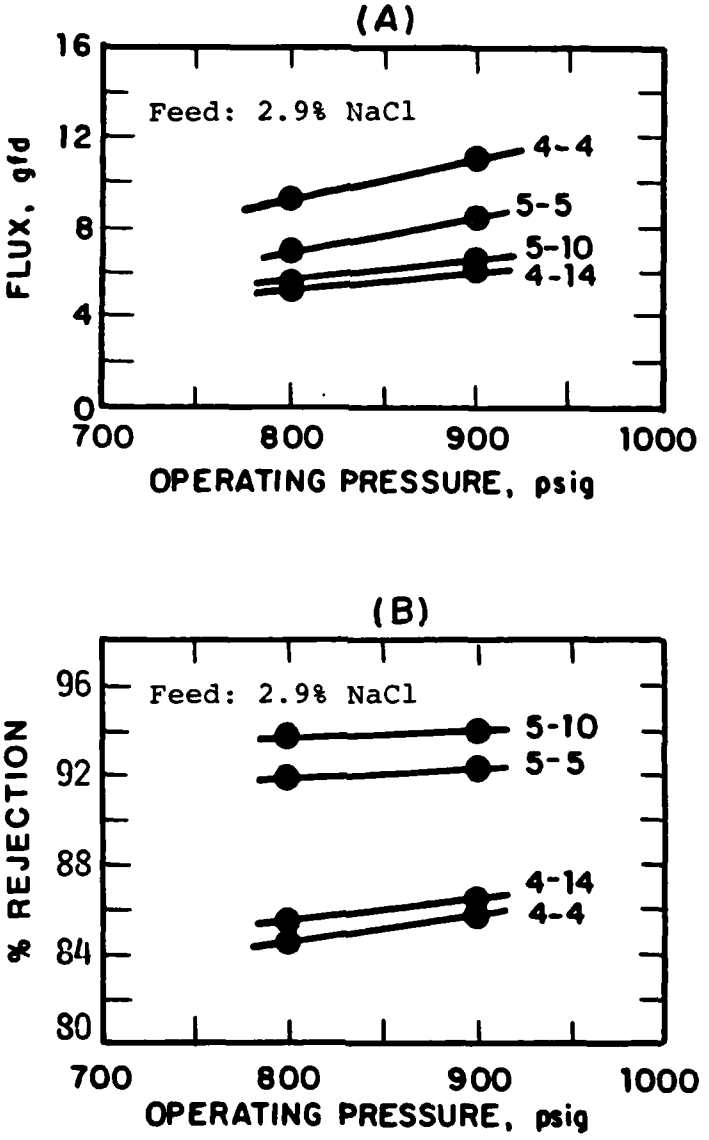

FIGURE 13. EFFECT OF PRESSURE ON FLUX AND REJECTION (2.9% NaCl FEED)

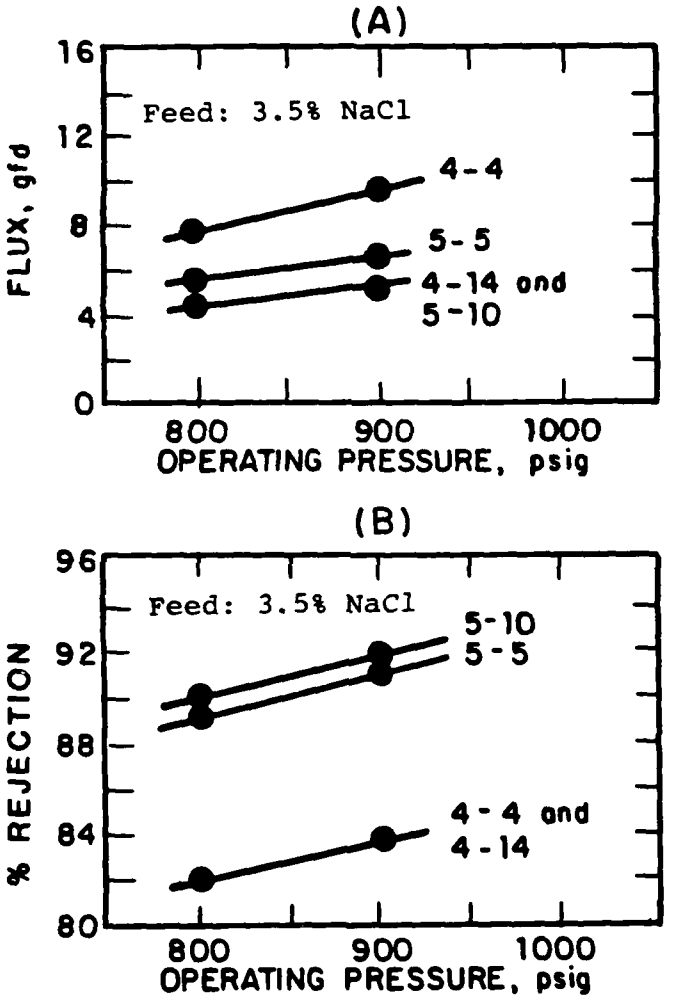

FIGURE 14. EFFECT OF PRESSURE ON FLUX AND REJECTION (3.5% NaCl FEED)

and salt rejection increase as pressure is increased, as expected from the direct dependence of volumetric flux on pressure. With solute flux being essentially independent of pressure, the percent salt rejection increases as a consequence of the increased volumetric flux, as observed.

Estimates of the variability of test results are given by the standard deviation values at the bottom of Table 8 calculated from the ranges of duplicate measurements. The four membrane samples had been tested previously with 0.5% salt solution (Table 5), with different sections from which 2-inch test discs were punched out. It is seen that on comparing the older values for samples 4-4 and 4-14 with those in Table 8 for 0.5% salt solution at 600 psig there is considerable variability between different annealed sections from the same parent sample roll.

An assessment of disc-to-disc variance was made by determining the RO properties of four 2-inch discs punched out at 1½-foot intervals along an 8-foot length of annealed membrane sample, 5-1. On testing with 0.5% salt solution at 600 psig, the flux values for the four discs ranged from 16.2 to 19.9 gfd and salt rejection, from 87.1% to 92.9%. The average values were 17.8 gfd and 91.2% salt rejection and are not statiscally different from 17.8 gfd and 95.5% reported in Table 5. Standard deviations, calculated from ranges for n=4, are 1.7 gfd and 2.8%, respectively, for flux and rejection, therein showing considerable disc-to-disc variability and pointing out the virtue of testing large membrane areas, say, in a spiral wound module, to average out the disc-to-disc variability.

E. Chlorine Resistance of PBI

A major program objective was to develop a chlorine resistant membrane that would permit chlorination of feed water for

disinfection and slime control in the field water purification unit. To meet this objective, a definitive assessment of the chlorine sensitivity of PBI was undertaken in which the physical properties of fiber and membrane as well as the RO properties of membrane discs and spiral wound modules were monitored in long-term exposure to chlorine. Changes in the tensile properties reflect changes in polymer structure due to degradation or depolymerization. This one property, then, affords a quick, sensitive measure of any such structural damage, which if substantial, would make it pointless to proceed with RO tests against chlorinated feed water. A demonstrated retention of physical properties under chlorine exposure, on the other hand, would favorably reflect on the polymer's resistance which, in RO membrane application, could translate to a useful and practical resistance to chlorine in water pretreatment.

Samples of drawn and undrawn PBI textile yarn were immersed at 25°C in distilled water containing 10 ppm free chlorine at 7.4 pH. Household bleach (5.25%), sodium hydrochlorite, was used as the source of chlorine. Frequent monitoring and additions of bleach were made daily to maintain the free chlorine at 10±2 ppm. Yarn samples were removed at intervals over a 48-day period and single filament tensile properties (according to ASTM D 2101-72) were measured on an Instron tester at 72°F and 65% relative humidity. Gauge length was 1.00 inch and strain rate was 100%/minute. Ten filaments were tested and the average values of the 10 breaks were recorded. The properties measured were denier-per-filament (dpf), percent elongation at break, tenacity (grams/denier) and initial modulus (grams/denier). Denier is the weight in grams of a 9,000 meter length of filament. Samples were removed from the 10 ppm chlorine bath at 10, 20 and 48 days. Tensile properties are given in Table 9.

TABLE 9. EFFECT OF CHLORINE ON PBI FIBER PROPERTIES*

Sample	dpf (1)	Elongation %	Tensile Strength g/d (2)	Initial Modulus g/d (2)
A. Undrawn PBI Yarn 7-4-14-78-49 (Control, 0 days)	2.60	88.3	1.42	44.6
10 days	2.74	65.7	1.23	41.7
20 days	2.74	50.4	1.13	46.7
48 days	2.93	7.7	0.75	33.8
B. Drawn Yarn 5-3-78-44 (Control, 0 days)	1.50	27.2	3.13	71.8
10 days	1.66	29.9	2.54	56.6
20 days	2.01	38.0	2.73	61.1
48 days	1.56	20.7	2.06	49.6

* Soaked in 10 ppm free chlorine solution at pH 7.4.

(1) Denier per filament (grams in 9000 meters of filament).
(2) Grams per denier.

Under the conditions of the chlorine resistance test, PBI fiber showed excellent retention of properties through 20 days in 10 ppm free chlorine at pH 7.4. Tenacity and modulus values showed little change from the control values. Even after 48 days, both yarn samples exhibited good retention of tensile properties. The undrawn sample did show a considerable loss in elongation, but otherwise it possessed useful tensile properties.

Chlorine soak tests were next run on PBI RO membranes and mechanical properties were monitored as was done for the fiber samples. An unsupported membrane, mounted in stainless steel clip frames, was immersed in a 30°C water bath maintained at pH 5.5 and containing 10 ppm free chlorine. The pH was selected as being typical of that of acid treatment as practiced in water pretreatment. Mechanical properties were determined according to ASTM D 882-67. Breaking stress (in pounds), percent elongation at break and initial modulus were determined on an Instron tester. Sample gauge length was 2 inches at a specimen width of 15 mm. The testing speed was set at 0.4 inches/minute. The membranes were tested wet.

The test results are presented in Table 10. Through 28 days, the duration of the test, the PBI membrane sample showed excellent, 93% retention of strength, as measured by the breaking stress. The membrane became stiffer, as indicated by the increase in modulus and decrease in elongation. The intrinsic viscosity, a polymer solution property directly related to molecular weight, dropped only to 0.50 dl/g from an initial value of 0.71 dl/g. These results, as did those from the single filament tests, indicated that PBI may possess sufficient resistance to chlorine as an RO membrane.

TABLE 10. EFFECT OF CHLORINE ON MEMBRANE PHYSICAL PROPERTIES

Sample (3-M2)	Thickness mils	Break Stress lbs	Elongation at Break %	Modulus x 10^6	Intrinsic Viscosity dl/g
Annealed Control	1.9	5.36	9.5	0.179	0.71
10ppm @ pH 5.5:					
7 days	2.75	5.30(100%)	8.5(86%)	0.115	-
14 days	2.6	5.40(100%)	4.9(51%)	0.153	0.71
28 days	2.0	5.00(93%)	3.6(38%)	0.242	0.50

Test Standard Deviations:

Breaking Stress: 0.12 for Annealed Control
0.31 for Test Samples

% Elongations: 0.55 for Annealed Control
1.9 for 10ppm Sample
0.75 for 50ppm Sample

Values in parentheses are percent property retention relative to the control.

The effect of chlorine on membrane and module RO properties was next investigated with chlorinated feed water containing 5-8 ppm free chlorine in 0.5% sodium chloride at 25°C. Feed pH range was 6.8 to 7.4. Operating pressure was 400 psig instead of 600 psig to accommodate the small spiral wound modules, not rated for higher pressure operation. The ratio of water flux at 400 psig relative to that at 600 psig was experimently established to be 65%, i.e., directly proportional to the operating pressure.

Test results of the first chlorinated feed test for two membrane samples, tested in triplicate, are given in Table 11. After first testing for 72 hours with unchlorinated feed water, 5-8 ppm of chlorine was added to the feed and the test continued without interruption. After 24 hours with chlorinated feed, an unexpected and steep decline in flux was observed. After 48 hours, the flux for both samples declined even more, down to about 10% of the original value. Salt rejection, on the other hand, remained high and, in fact, showed some improvement. This suggests that the membrane was not chemically damaged by the chlorine as is the case with chlorine sensitive membranes. In such cases, flux usually increases and rejection decreases. At this time, an explanation for this behavior is not at hand.

Two small modules that were tested simultaneously with the membrane disc samples exhibited drops in both flux and rejection. In this case, the possible failure of the adhesive cannot be ignored. Even a small break in the glue line would permit enough leakage of the feed to show up as a large decrease in rejection. On the other hand, the modules were not taken apart or otherwise inspected after the test so that the exact cause for the change in flux and rejection is not at all established.

In view of the puzzling results obtained in this series of tests, it was decided to go back to the annealing step. It had

TABLE 11. EFFECT OF CHLORINE ON RO PROPERTIES*
(5000 ppm NaCl, 400 psi, 25°C)

		FLUX/REJECTION[1]				
		UNCHLORINATED FEED			CHLORINATED FEED	
Sample		4 Hours	24 Hours	72 Hours	24 Hours	48 Hours
Membrane CRC-2M	a.	13.9/86.9	11.7/91.0	9.9/93.4	1.7/92.4	0.9/ -
	b.	12.0/86.7	10.4/91.0	8.8/92.9	1.5/94.4	0.8/96.2
	c.	14.4/88.4	12.4/91.1	9.6/92.8	2.2/93.0	1.4/96.4
	Average	13.4/87.3	11.5/91.0	9.4/92.9	1.8/93.4	1.0/96.3
Membrane CRC-1	a.	10.5/92.2	8.1/94.6	7.3/95.9	1.1/93.3	0.6/96.6
	b.	8.9/93.4	7.6/95.3	6.6/96.7	1.0/96.4	- /98.1
	c.	12.2/92.8	9.1/95.1	8.5/96.3	1.2/94.9	0.9/97.2
	Average	10.5/92.8	8.3/95.0	7.5/96.3	1.1/94.9	0.7/97.3
Module A[2]		6.3/94.6	6.0/95.4	5.5/96.7	2.1/39	2.4/24
Module CRC-1[2]		2.1/93.0	1.80/92.4	1.65/95.0	1.20/15	1.75/<1

* 5 to 8ppm free chlorine in feed water.

(1) Flux, gal/ft^2-day/Rejection, %.
(2) Module flow in cc's/minute.

been shown in some earlier work, that the PBI can undergo crosslinking reactions. It is also possible to react the membrane with various acids that bind or associate with sites that could be interacting with chlorine and thereby causing the drop in flux.

Additional samples of the two membranes used in the chlorinated feed test (CRC-2M and CRC-1) were annealed in clip frames for 10 minutes in ethylene glycol at 130°C. CRC-2M was an unsupported membrane while all others were fabric-supported. After annealing, the samples were immersed in 10% aqueous sulfuric acid to crosslink the membrane. The intent here was to crosslink the membrane to make it more resistant to compaction and to block sites that might be reacting with chlorine so as to overcome the observed decrease in transport properties.

A high flux, unannealed membrane, CRC-2L, was selected to assess the magnitude and extent of flux decline and the final stabilized value. This was to be compared with the annealed CRC-2L. In addition, two small modules containing annealed CRC-1 membrane were included. These membrane sheets were annealed for longer times at 140°C to further "harden" the membrane.

The membranes and modules were first tested with unchlorinated feed for 120 hours, at which point 5-8 ppm of chlorine were added and testing continued. The flux and rejection data are given in Table 12.

All of the membrane disc samples, except for the unannealed sample CRC-2L, again showed sharp drops in flux when the feed was changed as was observed previously. Salt rejection, in general, remained high. Acid treatment of the annealed membranes did not seem to have any appreciable effect. Strangely enough, the unannealed sample (unannealed CRC-2L) did not exhibit such a propor-

TABLE 12. EFFECT OF CHLORINE ON RO PROPERTIES
(5000 ppm NaCl, 400 psi, 25°C)

		FLUX/REJECTION[1]								
		Unchlorinated Feed			→ Chlorinated Feed					
Sample		24 Hours	48 Hours	120 Hours	24 Hours	48 Hours	72 Hours	96 Hours	168 Hours	336 Hours
CRC-1	a.	7.1/96.4	7.0/96.1	6.4/96.5	0.7/95.8	0.5/93.6	0.3/92.4	0.3/89.4		
Acid Treated	b	7.3/94.3	7.1/95.2	6.9/95.1	0.8/96.5	0.5/95.9	0.4/95.2	0.3/94.6		
CRC-2M	a.	9.0/91.5	9.2/91.5	8.8/91.5	1.2/96.8	0.7/95.9	0.6/93.6	0.4/94.3		
Acid Treated	b.	7.0/91.5	6.9/91.5	6.6/91.6	1.0/92.0	0.8/62	0.5/57	0.5/55		
CRC-2L	a.	9.4/95.6	9.4/95.6	10.2/93.2	1.0/95.4	0.7/93.6	0.5/92.9	0.4/91.8		
	b.	7.5/95.8	7.3/95.4	7.3/93.8	1.0/93.2	0.7/92.1	0.6/91.6	0.5/90.3		
CRC-2L	a.	-	-	34.1/9.1	21.1/20	19.8/24	19.3/22	18.9/24		
(Unannealed)	b.	-	-	40.5/9.1	25.9/15	24.7/21	23.7/19	21.9/21		
Module 1* (CRC-1)		11.0/59.5	10.5/56.2	7.6/65.5	5.8/73	5.4/81.3	4.2/80.4	4.2/81.3	3.6/89.0	2.6/88.1
Module 2* (CRC-1)		10.3/84.5	9.2/82	6.6/64	5.0/76	3.9/82	3.2/80.5	3.2/72	0.9/56	-

*Module flow in cc's/minute.

(1) Flux, gal/ft^2-day/Rejection, %.

tionately large drop in flux. After 96 hours with chlorinated feed, the average flux value had dropped only about 50% from the 120 hour unchlorinated feed value. Because the membrane was unannealed, the rejection was low. However, the introduction of chlorinated feed was accompanied by a measurable increase (nearly 100%) in the rejection.

The modules did not exhibit the same degree of flux decline seen with the membrane disc samples. After 96 hours with chlorinated feed, the flux value for Module 1 had dropped only about 45% as compared to the flux after 120 hours exposure to unchlorinated feed. Salt rejection improved considerably, up to 81% after 96 hours, compared to an original value (at 120 hours of unchlorinated feed) of about 66%. Module 2 showed similar flux retention of about 50% and improvement in flux through 96 hours with chlorinated feed, after which, for unknown reasons, performance declined and the module was removed. Module 1 continued to improve in rejection through 336 hours.

In view of the more favorable response and behavior observed for the modules, testing with chlorinated feed was continued and a third module, Module 3, was installed for the long-term test. Long-term test data for Module 1 are given in Table 13. Table 14 shows the results obtained with Module 3.

The observed long-term flux decline includes that which would have occurred as a result of pressure-induced membrane compaction, regardless of whether or not the feed water was chlorinated. Therefore the long-term flux retention of these two modules exposed to the chlorinated feed water is actually better than the direct comparison of the values before and after testing with chlorinated feed. The significantly better performance of the

TABLE 13. LONG-TERM CHLORINATED FEED TEST RESULTS FOR MODULE 1
(5000 ppm NaCl, 400 psi, 25°C)

Test Hours	Permeate Flow cc/min.	Rejection %
24 - no chlorine	11.0	59.5
48 - no chlorine	10.5	56.2
120 - no chlorine	7.6	65.5
Added 5-8ppm chlorine to feed.		
24	5.8	73.3
48	5.4	81.3
96	4.2	81.3
166	3.55	89.0
213	3.25	88.2
260	3.3	90.1
332	2.9	89.3
Shutdown for repairs.		
336	2.65	83.1
502	3.45	86.5
547	3.2	89.4
571	3.1	87.4
713	2.9	86.8
738	2.9	85.9
761	2.85	86.3
836	2.65	85.5
856	2.6	85.7
Changed feed solution.		
860	3.2	87.0
879	2.85	87.3
883	3.25	86.4
903	3.25	86.5
929	3.2	85.2
998	2.95	81.3

TABLE 14. LONG-TERM CHLORINATED FEED TEST RESULTS FOR MODULE 3
(5000 ppm NaCl, 400 psi, 25°C)

Test Hours	Permeate Flow cc/min.	Salt Rejection % R
6.5 - no chlorine	5.8	86.9
71 - no chlorine	5.9	85.2
Shutdown to install baffle in module.		
72 - no chlorine	8.1	95.3
89 - no chlorine	6.6	96.6
96 - no chlorine	6.2	96.9
137 - no chlorine	5.3	97.3
168 - no chlorine	5.0	97.5
233 - no chlorine	4.6	98.6
Shutdown, transferred module to chlorinated feed test system, 5-8ppm free chlorine.		
5	3.8	91.1
22	3.5	90.0
29	3.0	92.0
46	2.8	92.6
72	2.7	92.3
92	2.65	93.1
164	2.25	93.2
Shutdown to repair test system.		
166	1.9	91.1
262	2.5	90.7
334	2.35	91.6
355	2.20	92.0
379	2.25	91.5
403	2.2	91.7
504	2.2	91.9
569	2.0	91.6
644	1.75	91.3
664	1.7	92.0
Changed feed solution.		
668	2.0	93.7
687	1.8	94.2
691	2.15	94.0
711	2.2	94.3
737	2.25	94.0
806	1.95	93.7
809	1.92	92.4
831	2.0	92.5
900	Shutdown to repair leak in feed tank.	
986	1.96	88.5
1011	1.96	88.5
1058	1.71	88.2
1077	1.91	77.1

modules relative to the disc samples is believed to be due, in part, to the difference in configuration of the test membrane and supporting materials. This being so, then there needs to be a reexamination made of the membrane preparation processes to optimize module properties instead of depending entirely on disc-test performance.

V. CONCLUSIONS AND RECOMMENDATIONS

RO tests on 2-inch membrane discs have shown that unsupported PBI membranes can be laboratory-cast which have high flux and rejection against 0.5% salt solution at 600 psig. With flux values as high as 28 gfd and rejections ranging from 94-98%, attempts were made to transfer the laboratory technology to a continuous roll coater to yield fabric-supported membranes in a quantity sufficient to fabricate spiral wound modules. While ultimate success was realized in producing membranes on the large equipment, it took longer to do so than originally anticipated. On the other hand, the level of RO properties seen with laboratory-cast membranes was not reached. The same can be said for the fabrication of spiral wound modules. It took longer than expected to get leak-free modules and the RO properties fell below the targets. Moreover, a high pressure module test stand was not available until much later than planned.

One consequence of the delays and difficulties is that there was not enough time to demonstrate a module with RO properties at least equivalent to those that had been cast in the laboratory. Moreover, unexplained differences between disc tests and module tests were recognized at a point when it was too late to permit reexamination of the polymer preparation, casting and annealing steps.

Chlorine resistance tests have shown that the PBI polymer is not chemically degraded by the presence of chlorine. RO performance, however, has not been consistent. Thus, although disc tests showed a 90% reduction in flux after 24 hours exposure to 5 ppm chlorine, module tests approaching 1000 hours showed a relatively stable flux after an initial drop that is typically observed against an unchlorinated feed. Contrary to the usual case with

chlorine sensitive RO membranes, the rejections have gone up somewhat with time instead of down.

Because the potential of PBI RO membranes was indicated but not fully exploited, it is recommended that the membrane casting steps be further developed as required for the continuous roll/coater machine. It is further recommended that module fabrication and testing be continued in order to demonstrate single pass seawater desalination at a flux that is comparable to the current 600 gph unit.

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