Development of Improved Cellulose Acetate Membranes for Reverse Osmosis

United States Department of the Interior

19960223 020

Office of Saline Water ● **Research and Development Progress Report No. 745**

Int-OSW-RDPR-72-745

PLASTEC 16875

-- 1 - AD NUMBER: D402366
-- 3 - ENTRY CLASSIFICATION: UNCLASSIFIED
-- 5 - CORPORATE AUTHOR: HERCULES INC WILMINGTON DEL
-- 6 - UNCLASSIFIED TITLE: DEVELOPMENT OF IMPROVED CELLULOSE ACETATE
--   MEMBRANES FOR REVERSE OSMOSIS.
-- 8 - TITLE CLASSIFICATION: UNCLASSIFIED
--10 - PERSONAL AUTHORS: COHEN,M.E. ;GRABLE,M.A. ;MORTON,J.W. ;RIGGLEMAN,B.
--   M. ;HARBERT ,M.B. ;
--11 - REPORT DATE: FEB   , 1972
--12 - PAGINATION: XXXXXX   MEDIA COST: $ 6.00
--14 - REPORT NUMBER: INT-OSW-RDPR-72-745
--15 - CONTRACT NUMBER: INT CONT 14-30-2527
--20 - REPORT CLASSIFICATION: UNCLASSIFIED

--27 - ABSTRACT: THE OBJECTIVE OF THIS PROGRAM WAS TO DEVELOP HIGH-FLUX
--   HOLLOW-FIBER MEMBRANES FOR REVERSE OSMOSIS DESALINATION. TWO TYPES
--   OF MEMBRANES, ASYMMETRIC AND COMPOSITE, WERE INVESTIGATED. THE

--   PROCESS OF PREPARING ASYMMETRIC MEMBRANES IN ONE STEP. THE
--   COMPOSITE MEMBRANES ARE FORMED BY COATING A POROUS NONSELECTIVE
--   SUBSTRATE WITH AN ULTRA-THIN SELECTIVE FILM. THIS APPROACH OFFERS
--   THE ADVANTAGE OF ALLOWING THE PROPERTIES OF EACH MEMBRANE LAYER TO
--   BE TAILORED FOR OPTIMUM RESULTS. THE COMPOSITE MEMBRANES STUDIED IN
--   THIS PROGRAM WERE PREPARED BY DIRECTLY COATING CELLULOSE NITRATE
--   SHOCK GELS WITH ULTRA-THIN LAYERS OF CELLULOSE TRIACETATE. (AUTHOR,
--   MODIFIED-PL)

--28 - ABSTRACT CLASSIFICATION: UNCLASSIFIED
--30 - ANNOTATION: DEVELOPMENT OF IMPROVED CELLULOSE ACETATE MEMBRANES FOR
--   REVERSE OSMOSIS.
--33 - LIMITATION CODES: 1
--35 - SOURCE CODE: 388243

Development of Improved

Cellulose Acetate Membranes for

Reverse Osmosis

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Contract No. 14-30-2527

DTIC QUALITY INSPECTED 4

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FOREWORD

This is one of a continuing series of reports designed to present accounts of progress in saline water conversion and the economics of its application. Such data are expected to contribute to the long-range development of economical processes applicable to low-cost demineralization of sea and other saline water.

Except for minor editing, the data herein are as contained in a report submitted by the contractor. The data and conclusions given in the report are essentially those of the contractor and are not necessarily endorsed by the Department of the Interior.

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SUMMARY

The objective of this program was to develop improved cellulose acetate hollow-fiber membranes for reverse osmosis desalination. Two types of hollow-fiber membranes were investigated - asymmetric and composite. Asymmetric membranes are prepared by forming a dense selective surface layer on a porous gelled substructure of cellulose diacetate or cellulose triacetate. Composite membranes are formed by coating a porous nonselective substrate with an ultra-thin selective film.

Asymmetric Membranes

Cellulose acetate (CA) hollow-fiber membranes were prepared from cellulose acetate thermal gels by spinning into a water bath and then annealing the fibers in a dilute solvent mixture. The temperature and duration of the annealing process were varied to yield hollow-fiber membranes with an initial flux rate of 6 gfd and 95% sodium chloride rejection to 8.5 gfd and 75% rejection at 600 psi. Magnesium sulfate rejection was 95% at 9.5 gfd. The membranes were found to be more suitable for brackish water treatment at 200-400 psi than for higher pressure operation.

The log-log membrane flux-decline rates of the asymmetric CA hollow-fiber membranes ranged from a slope of zero at 200 psi to -0.11 at 600 psi. These results favor an operating pressure as low as is consistent with feed concentrations and recovery levels in order to minimize compaction effects. However, more work is required to develop hollow-fiber membranes suitable for long-term use at pressures of 600 psi or greater.

The processing and performance of asymmetric membranes were improved by the development of a one-step method of preparation which eliminates the annealing procedure and simultaneously affords control over the active surface layer thickness. Asymmetric CA flat sheet membranes directly prepared by gelation from solutions in mixtures of diacetone alcohol and triethylene glycol delivered flux rates up to 66 gfd and 88% rejection from a 5000 ppm sodium chloride feed at 600 psi. In addition, short-term flux decline was negligible when measured at 600 psi.

One-step asymmetric cellulose triacetate (CTA) membranes were cast as flat sheets from CTA solutions in formic acid and sulfolane containing triethyl phosphate. This membrane produced flux of 13 gfd and rejection of 88.3% from a 28,100 ppm sodium chloride feed at 1000 psi. Further improvement in the properties might be expected by optimizing the formulations and gelling conditions.

The one-step process is well suited for producing hollow-fiber membranes because it eliminates the annealing step that is difficult to control. Further, in the one-step process, the thickness of the selective skin can be readily controlled so that membranes made by this procedure may be tailored for various applications. However, considerable work is still needed to develop, and to achieve better reproducibility in, the one-step method of preparing hollow-fiber membranes.

Composite Membranes

Studies were conducted which demonstrated the feasibility of preparing a composite hollow-fiber membrane. Membranes suitable for desalination of brackish waters were developed. However, preparation of a composite hollow-fiber membrane suitable for sea water applications depends upon the development of a substrate which can withstand the higher pressures required.

Improvements were made in the preparation of cellulose nitrate (NC) hollow-fiber shock gel substrates. The best hollow-fiber substrates produced flux data of 17.8 gfd at 200 psi; the corresponding flat sheet substrates gave fluxes of 71 gfd. However, it must be pointed out that these NC hollow fibers collapse at pressures above 200 psi. By decreasing the outside diameter/wall thickness ratio from 5 to 2.5, a fiber was prepared which could withstand 400 psi. This stronger fiber, however, exhibited a flux rate of only 3.8 gfd.

A continuous process for applying an ultra-thin CTA coating to the shock gelled NC substrate was developed. One pass through this apparatus containing a 0.25% solution of cellulose triacetate and chloroform produced a composite hollow-fiber membrane capable of rejecting 93% of the sodium chloride at a flux rate of 1.8 gfd from a 1000 ppm feed solution at 200 psi. Membranes were also prepared using the substrates which could withstand 400 psi. These membranes were given two passes through the 0.25% CTA/chloroform solution. The resulting reverse osmosis performance data were a flux of 0.34 gfd and a rejection of 98% from a 5000 ppm sodium chloride feed at 400 psi.

INTRODUCTION

The objective of this program was to develop high-flux hollow-fiber membranes for reverse osmosis. Two types of membranes, asymmetric and composite, were investigated.

The asymmetric membranes were made by annealing porous thermal gels of cellulose diacetate (CA) to produce a membrane with a unique structure consisting of a dense selective surface supported by a porous gelled substructure. Experiments were conducted to develop the process of preparing asymmetric membranes in one step.

The composite membranes are formed by coating a porous nonselective substrate with an ultra-thin selective film. This approach offers the advantage of allowing the properties of each membrane layer to be tailored for optimum results. The composite membranes studied in this program were prepared by directly coating cellulose nitrate (NC) shock gels with ultra-thin layers of cellulose triacetate (CTA).

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RESULTS AND DISCUSSION

Asymmetric Membrane Development

Two processes for developing asymmetric hollow-fiber membranes were investigated during this work period. One of these processes involved annealing a nonselective polymer gel of graded porosity to produce a membrane consisting of a thin, dense selective surface supported by a porous substructure. The other process involved preparing asymmetric membranes such as the Loeb-type in one step, i.e., without the annealing step. The latter approach also provides control over the skin thickness.

Hollow-fiber membranes prepared using the annealing process have been produced, and the performance of this type of membrane is discussed below. However, the one-step asymmetric membranes have not yet been successfully produced in the hollow-fiber form and the performance of this type of membrane as discussed below is limited to flat sheet membrane data.

Asymmetric Hollow-Fiber Membranes

Asymmetric hollow-fiber membranes were prepared from a melt consisting of 30 wt. % cellulose acetate (CA) (E400-25), 35 wt. % triethylene glycol and 35 wt. % methyl Carbitol. These hollow fibers were gelled in water and annealed in accordance with previously established procedures.[1]

The properties of asymmetric hollow-fiber membranes were investigated and improved in this program. The test results in Table I and Figure 1 show performance data for single fibers operating on brackish water feeds. Typical initial flux and salt rejection values for recent membrane lots are (1) 4 gfd and 94% rejection at 400 psi, and (2) 6 gfd and 96% rejection at 600 psi when operating on a 5000 ppm sodium chloride feed. By varying the annealing temperature (Figure 2), it is possible to trade off flux and salt rejection; for example, a flux rate of 8.2 gfd and 75% sodium chloride rejection resulted at 600 psi when the annealing temperature was reduced to 63°C from the normal 66°C level. Such a membrane would be suitable for treating brackish water containing predominantly divalent ions.

The membrane performance on magnesium sulfate is also given in Table I. Both the level of rejection and flux rate are higher on this feed than the corresponding values for a sodium chloride feed. At 600 psi, a flux rate of approximately 10 gfd and a rejection greater than 95% were observed. At 250 psi, the performance was also good, illustrating the excellent suitability of these hollow fiber membranes for treating brackish waters under a variety of operating conditions.

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TABLE I

LABORATORY PROPERTIES OF ASYMMETRIC CA HOLLOW-FIBER MEMBRANES

| Membrane Description | | | | Water Flux (gfd)[d] | | | Salt Rejection (%)[d] | | | Flux Decline | |
Lot[a,b] No.	Annealing[c] Temperature (°C)	Fiber OD (mils)	Feed Conc. (ppm)	200 (psi)	400 (psi)	600 (psi)	200 (psi)	400 (psi)	600 (psi)	Pressure (psi)	Log-Log Slope

Average Properties of High Selectivity Membranes on Sodium Chloride Feed

1	66	21	5000 NaCl	1.8	4.0	5.6	88.5	93.8	96.0	600	-.11
										400	-.04
										200	0

Effect of Annealing Temperature in a Flux-Salt Rejection Tradeoff - Sodium Chloride Feed

2	65	20	5000 NaCl	3.0	6.0	6.5	80	88	92	-	-
3	64	20	5000 NaCl	3.3	6.6	7.5	76.4	85.4	89.2	-	-
4	63	20	5000 NaCl	3.7	7.2	8.2	60	71	75	-	-

Properties of Membranes on Magnesium Sulfate Feed

				250 psi			250 psi				
5	66	20	5000 MgSO4	4.4	6.6	8.1	98.0	97.7	98.3	-	-
6	63	20	5000 MgSO4	5.5	8.7	9.5	89.9	92.3	95.2	-	-

(a) Full identification given in ABL Notebook No. X-209, p. 45.
(b) Membranes spun at 250°F from a 30% solution of CA (E400-25) in a 1/1 weight mixture of triethylene glycol and methyl Carbitol.
(c) Annealing carried out in a 10% solution of p-dioxane in water.
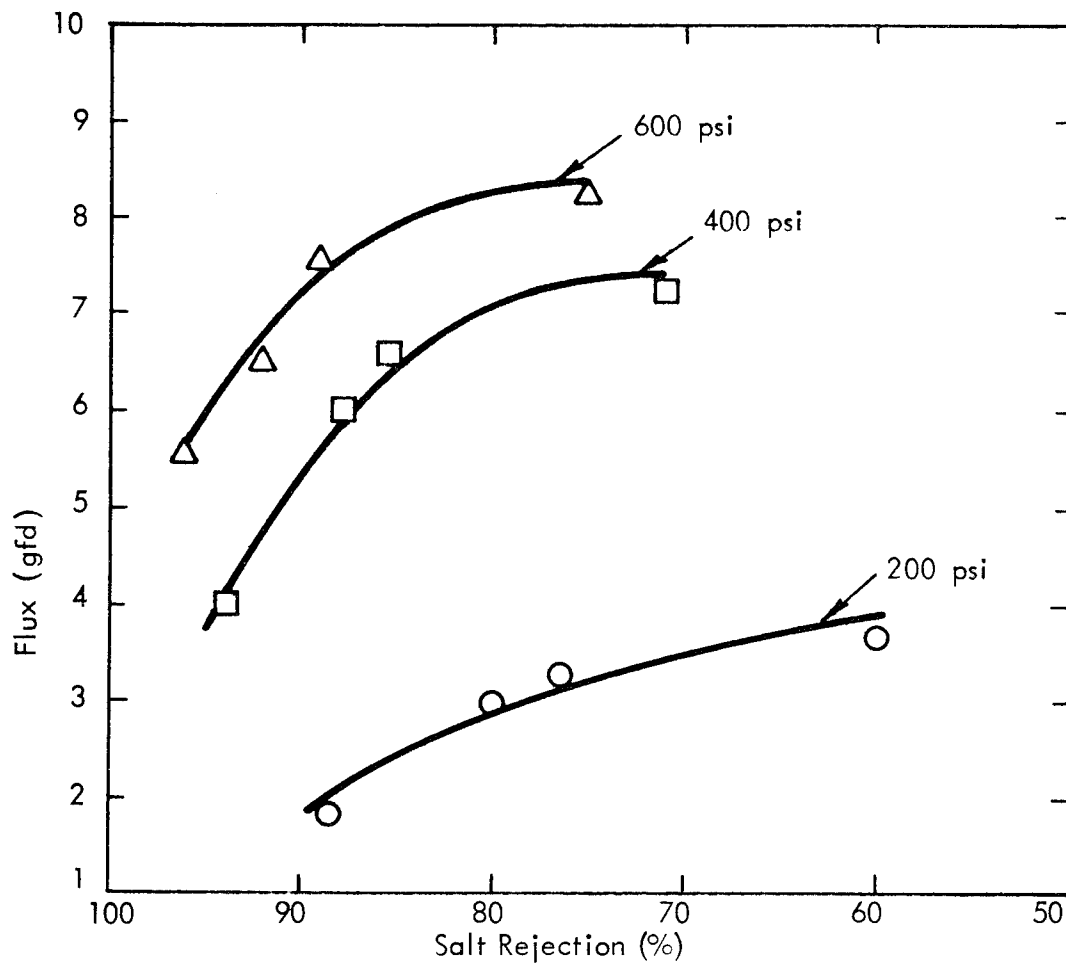(d) Initial values.

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Figure 1. Flux Versus Salt Rejection Relationship of Cellulose
Acetate Hollow-Fiber Membrane on 5000 ppm
Sodium Chloride Solution
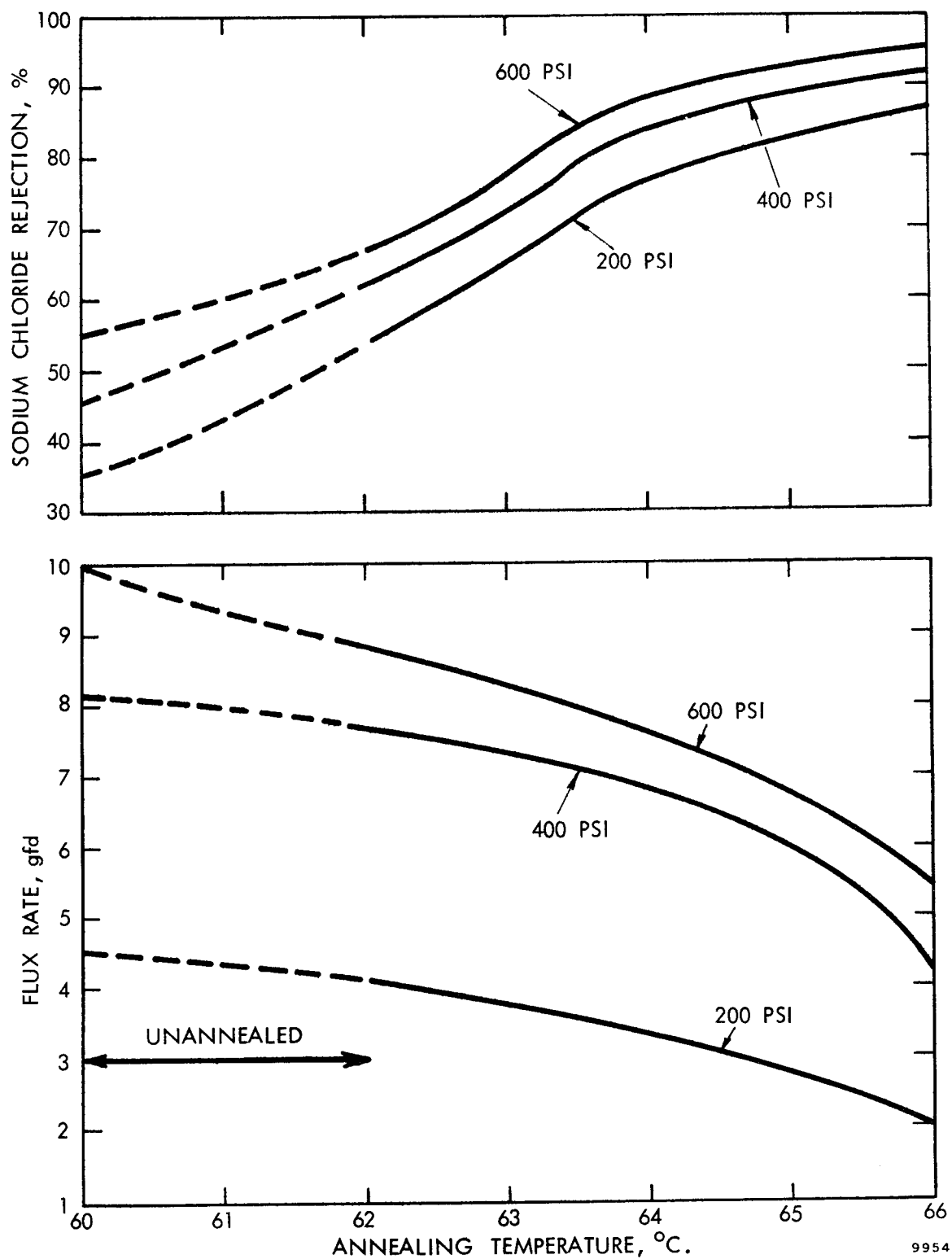
Figure 2. Performance of Asymmetric CA Hollow-Fiber Membranes
on 5000 ppm Sodium Chloride Brine

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The log-log membrane flux-decline rates ranged from a slope of zero at 200 psi to -0.11 at 600 psi when tested with a fresh water feed. These rates translate to useful module lifetimes of over 10 years at 600 psi if a lower flux limit of one gfd is established. These results favor an operating pressure as low as is consistent with feed concentrations and recovery levels in order to minimize compaction effects.

One-Step Preparation of Asymmetric Membranes

Studies on the mechanism of skinned-type membrane formation have shown, in the case of cellulose acetate, that a correlation exists between the structure of the resulting membrane and the solvation power of the casting solvent (based on the amount of water required for precipitation) as well as the direction and magnitude of the osmotic volume flows taking place during leaching.[2] Hence it was thought that a thin-skinned membrane could be prepared in one step from most polymers when the given polymer-solvent system is fairly close to the polymer precipitation point (at the casting temperature) when placed in the gelation bath and when a net diffusion of the gelation medium into gel occurs after initial skin formation.

In this way, a skin would be generated by the initial precipitation of the polymer at the surface of the cast film when the film contacts the gelation bath, and subsequently a net diffusion of the gelation medium into the film would generate a porous substructure while preventing thickening of the skin. Hence, by proper choice of polymer solvents, casting conditions, solution temperature, gelling bath composition and temperature, an asymmetric membrane should be produced having a porous substructure and a dense surface of controlled thickness.

To test this hypothesis, cellulose acetate films were cast from solutions in diacetone alcohol and in mixtures of diacetone alcohol with increasing amounts of triethylene glycol. Table II shows that as the amount of triethylene glycol in the casting solvent increases, the solvent power of the mixture decreases as expressed by the amount of water required to initiate precipitation of the cellulose acetate at 80°C. The solutions were cast at 80°C and 10-mil thickness onto glass plates and gelled in water at 60°C; gelation was followed by thorough water leaching of the solvents.

The results in Table II indicate that as the concentration of triethylene glycol in the casting solvent increases, solvation power and the tendency toward a thick, dense surface formation decrease, with the gels exhibiting high flux rates at moderately high selectivities. The gel prepared from diacetone alcohol alone (X-143-124-11) appears to possess a relatively thick active surface layer, as indicated by its low water flux rates and the moderate dye stain obtained after light scraping of the active surface. When triethylene glycol is added in the amount of 10% of the

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TABLE II

PROPERTIES OF CELLULOSE ACETATE GELS PREPARED
FROM DIACETONE ALCOHOL-TRIETHYLENE GLYCOL SOLUTIONS

Ident. Number (X143-)	CA[a] (wt-%)	DAA/TEG[a] (wt. Ratio)	Water Concentration at CA Precipitation Point at 80°C (wt-%)	Active Surface Dye Stain[b]		Water Flux (gfd) in Test With Pure Water		Test With 5000 ppm NaCl Feed at 600 psi	
				Before Light Scraping	After Light Scraping	600 psi	1500 psi	Water Flux (gfd)	NaCl Rejection (%)
124-11	25	1/0	34	Very Light	Moderate	0.85	1.9	-	-
130-5	25	9/1	27	Very Light	Intense	19	38	25.6	94.3
130-4	25	6/1	22	Light	Intense	46	88	38.7	84.8
130-1	25	3/1	20	Moderate	Intense	69	125	65.5	87.5
130-2	25	1/1	8	Intense	Intense	155	205	-	-

(a) CA = cellulose acetate (Eastman Type E400-25), DAA = diacetone alcohol, and TEG = triethylene glycol.

(b) Dye stain tests were carried out with a 0.1 wt-% aqueous solution of Rhodamine B Estra S dye, and the staining was observed under UV light. The active surface is that surface exposed to air on casting the film on a glass plate.

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diacetone alcohol content, a gel containing a highly permeable and highly selective active surface layer forms (X143-130-5). Addition of more than 10% triethylene glycol eventually results in the formation of very high flux asymmetric membranes with poor selectivity (see Table III).

Although no extensive experiments concerning flux decline have been conducted, data (Table III) obtained through approximately three hours of operation suggest a negligible flux decline rate at 600 psi as compared to the -0.11 rate observed in the membranes prepared in the conventional manner.

These results suggest that very highly permeable and highly selective asymmetric membranes can be prepared by this method from cellulose acetate as well as from other promising polymers and polymer combinations. By systematically varying polymer and solvent types and ratios, temperature of the gelling solution, and composition and temperature of the gelation bath, it should be possible to prepare asymmetric membranes having a broad range of selectivity, permeability, and useful lifetimes.

Cellulose triacetate was selected as a candidate material for preparing a one-step asymmetric membrane suitable for desalination of sea water. Some difficulty was encountered in preparing cellulose triacetate asymmetric one-step membranes by the procedure developed for its cellulose diacetate counterpart; there are only a limited number of water-miscible solvents for CTA that will permit a high enough concentration of CTA on initial precipitation of the cast film during gelation to generate a thick enough (defect-free) active surface layer. Two solvents which satisfy these criteria are formic acid and sulfolane (tetrahydrothiophene-1,1-dioxide).

Asymmetric CTA membranes could be prepared from formic acid and from sulfolane alone, but their flux rates and salt selectivities were not high (see Table IV). Also, addition of salt to the gelation bath reduced the quality of the selective layer. However, addition of pore-forming plasticizers to the casting solvent, particularly triethyl phosphate (TEP) which is slow to leach from the gel, significantly improved the performance of the CTA membrane.

Membranes X143-154-1 and X143-154-6, prepared from formic acid-TEP and sulfolane-TEP combinations, respectively, were particularly promising for use at 1000 psi in the first stage of a two-stage sea water reverse osmosis desalination system. Further improvement is to be expected by optimizing the formulations and gelling conditions.

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TABLE III

PERFORMANCE OF ONE-STEP ASYMMETRIC CA MEMBRANES*

Membrane Identification	Time (min)	Pressure (psi)	Water Flux (gfd)	NaCl Rejection (%)	Test Conditions
X143-153-1	12	200	13.0	84.9	Membrane Casting Solution
	12	400	23.8	89.8	25 wt % CA (Type E400-25) +
	12	600	33.9	91.5	75 wt % of 9 Diacetone Alcohol/
	60	600	34.6	91.7	1 Triethylene Glycol
	135	600	34.2	92.1	Feed Composition 0.5 wt % NaCl in Water
	180	600	35.3	93.1	
	12	800	44.6	92.2	Feed Flow Rate 800 cc/min
	12	1000	53.9	92.2	
	12	1200	61.4	91.9	
	12	1400	66.2	91.5	
X143-153-2	12	200	23.4	81.4	Membrane Casting Solution
	14	400	42.8	86.8	25% wt % CA (Type E400-25) +
	12	600	62.9	88.0	75 wt % of 6 Diacetone Alcohol/
	35	600	62.9	88.2	1 Triethylene Glycol
	64	600	62.9	89.2	Feed Composition 0.5 wt % NaCl in Water
	130	600	62.9	88.5	
	194	600	62.9	88.3	Feed Flow Rate 800 cc/min
	12	800	79.6	88.5	
	12	1000	93.0	88.1	
	14	1200	101.0	88.3	
X143-153-3	12	200	88.5	12.0	Membrane Casting Solution
	12	400	126	34.7	25 wt % CA (Type E400-25) +
	12	600	139	25.1	75 wt % 3 Diacetone Alcohol/
	30	600	134	22.5	1 Triethylene Glycol
	60	600	112	24.9	Feed Composition 0.5 wt % NaCl in Water
	120	600	128	21.4	
	12	800	165	25.7	Feed Flow Rate 800 cc/min
	12	1000	212	19.4	
	5	1200	223	18.4	

*All data presented were obtained from flat sheet specimens.

TABLE III (CONTINUED)

PERFORMANCE OF ONE-STEP ASYMMETRIC CA MEMBRANES

Membrane Identification	Time (min)	Pressure (psi)	Water Flux (gfd)	NaCl Rejection (%)	Test Conditions
X143-153-4	12	200	164	12.5	Membrane Casting Solution
	12	400	283	10.9	25 wt % CA (Type E400-25) +
	6	600	359	10.5	75 wt % of 2 Diacetone Alcohol/
					1 Triethylene Glycol
					Feed Composition 0.50 wt % NaCl in Water
					Feed Flow Rate 800 cc/min

TABLE IV

PROPERTIES OF ONE-STEP ASYMMETRIC CTA MEMBRANES*

Ident. No.	CTA Conc.[a] (Wt-%)	Solvent Comp.[b] (Wt-Ratio)	Temp. (°C)	Thickness (Mil)	Gelation[c] Bath Comp.	Dye Stain[d] Top Surface	Dye Stain[d] Bottom Surface	Final Thickness (Mil)	Feed NaCl Conc. (Wt-%)	Test Pressure (Psi)	Feed Flow (cc/Min)	Water Flux (Gfd)	NaCl Rejection (%)
X143-154-1	20	90FA/10TEP	25	8	Water	N/I	I	2.9	0.44 / 2.88 / 3.95	600 / 1000 / 1500	800 / 470 / 800	8.2 / 6.7 / 7.8	99.1 / 95.1 / 94.4
X143-154-2	20	80FA/20TEP	80	8	Water	N/VL	I	2.0	0.50 / 3.03	600 / 1000	650 / 550	2.8 / 2.8	98.8 / 95.0
X143-154-3A	20	79FA/15TEP / 6 Glycerin	80	8	Water	N/VL	I	1.1	0.48 / 2.88	600 / 1000	800 / 800	1.7 / 3.2	96.9 / 99.3
X143-148-2	25	90FA(90%) / 10 Water	95	10	Water	L/M	I	3.0	0.60 / 3.40	600 / 1500	600 / 552	2.5 / 10.0	- / 28.2
X143-148-2HT	Heat Treated in Water at 80°C for 10 minutes							2.5	3.03	1500	420	5.0	21.8
X143-148-3	25	90FA(90%) / 10 Dioxane	100	10	Water	N/N	I	3.5	0.80 / 3.42	600 / 1500	600 / 600	0.70 / 0.95	- / -
X143-148-6	25	90FA(90%) / 10 DMSO	100	10	Water	N/VL	I	3.0	0.80 / 3.42	600 / 1500	600 / 600	9.1 / 8.4	42.5 / 45.6
X143-148-6HT	Heat Treated in Water at 80°C for 10 minutes							3.5	3.10	1500	582	2.8	58.6
X-143-148-7	25	90FA(90%) / 10 Sulfolane	100	10	Water	N/VL	I	3.5	0.47 / 3.50	600 / 1500	600 / 522	0.75 / 1.3	- / 94.2
X-143-148-7HT	Heat Treated in Water at 80°C for 10 minutes							3.0	3.10	1500	582	0.48	-
X-143-148-8	25	90FA(90%) / 10 Glycerin	100	10	Water	N/VL	I	2.4	0.52 / 3.50	600 / 1500	684 / 522	1.1 / 3.1	68.5 / 32.3
X-143-148-8HT	Heat Treated in Water at 80°C for 10 minutes							2.8	0.52	600	684	0.28	71

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*All data presented were obtained from flat-sheet specimens.

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TABLE IV (Continued)

Ident. No.	Casting Solution CTA Conc.[a] (Wt-%)	Solvent Comp.[b] (Wt-Ratio)	Casting Cond. Temp. (°C)	Thickness (Mil)	Gelation[c] Bath Comp.	Dye Stain[d] Top Surface	Bottom Surface	Final Thickness (Mil)	Feed NaCl Conc. (Wt-%)	Test Pressure (Psi)	Feed Flow (cc/Min)	Water Flux (Gfd)	NaCl Rejection (%)
X143-146-1A	25	FA(90%) only	95	10	Water	VL/M	I	5.0	3.30	1500	450	0.85	75.0
X143-146-1B	25	FA(90%) only	95	10	2.5% Aq.NaCl	N/L	I	4.7	3.51	1500	492	2.10	24.8
X143-146-5A	25	DMSO only	140	10	Water	I	N-I/I	6.0	3.51	1500	492	2.50	70.8
X143-146-5B	25	DMSO only	140	10	2.5% Aq.NaCl	I	N-I/I	8.3	3.50	1500	480	21.0	5.7
X143-146-6A	25	Sulfolane only	160	10	Water	N/I	I	12.7	3.50	1500	480	3.7	90.1
X143-154-4	20	90 Sulfolane/10TEP	170	8	Water	VL/I	I	2.5	0.46 / 2.81	600 / 1000	800 / 600	13.0 / 13.0	93.3 / 88.3
X143-154-5	20	80 Sulfolane/20TEP	170	8	Water	N/I	I	3.0	0.49 / 2.52	600 / 1000	800 / 500	12.6 / 12.6	91.1 / 87.3
X143-154-6	20	60 Sulfolane/40TEP	170	8	Water	N/M	I	1.0	0.48 / 2.25	600 / 1000	800 / 580	11.9 / 12.6	97.1 / 96.4

a CTA was Eastman Type A432-130b, dried under vacuum at 80°C for 3 hours.

b FA = formic acid 97+%, FA(90%) = formic acid 90%, TEP = triethyl phosphate, and DMSO = dimethyl sulfoxide.

c In all cases gelation was carried out for 30 minutes at room temperature (25 ± 2°C), and was followed by four leachings with room temperature water carried out in the following sequence: 1 hr, 1 hr, 24 hr, 48 hr.

d All dye stain tests were carried out with a 0.1 wt-% solution of Rhodamine B Extra S dye, and the staining was observed under UV light. The top surface is that surface exposed to air on casting; and the bottom surface is that surface exposed to glass on casting. Results reported as surface stain or as surface stain/stain upon scraping surface with a razor blade. I = Intense, M = Moderate, L = Light, VL = Very Light, and N = No Stain.

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Other worthwhile observations are the formation of a membrane skin on the glass side surface of the CTA membrane when cast from DMSO solution (X143-146-5A) and negligible flux decline at 1000 psi during the first several hours of testing the CTA membranes prepared from sulfolane-TEP formulations.

Composite Hollow-Fiber Membrane Development

Previous work in this laboratory[1] has indicated that a composite hollow-fiber membrane capable of rejecting 99% of the salt from a 5000 ppm feed solution can be prepared by applying an ultra-thin coating of cellulose triacetate to a cellulose nitrate substrate. However, this membrane produced a flux of only 0.13 gfd and several attempts to reproduce the membrane were unsuccessful. The problems in developing a composite hollow-fiber membrane with desired properties can be divided into two fundamental areas: (1) the preparation of a suitable hollow-fiber substrate and (2) the application of the ultra-thin coating. Hence the work conducted during this year was directed toward solutions of these problems.

Cellulose Nitrate Hollow-Fiber Substrates

The shock gel process was employed to prepare both flat-sheet and hollow-fiber substrates from cellulose nitrate. This process consists of preparing a solution of NC in special solvents such as diethylene glycol and gelling the solution in water or other appropriate gelling agents. The NC solutions gel almost immediately on contact with water, thereby making the process highly suitable for spinning hollow fibers.

In previous NC hollow-fiber fabrications, the fiber was wound onto a drum rotating in air after passing through a gelation bath consisting of only water. It was found during the course of this work that if fiber gelation and take-up were carried out in aqueous solutions containing diethylene glycol, the fresh water water flux of the fibers could be significantly improved. The concentration of DEG in the baths investigated varied from 1 to 7% by wt, with a 5% DEG bath imparting the highest fiber flux rate (Table V). This technique produced hollow-fiber flux data of 10.3, 7.0 and 7.4 gfd at 200, 400, and 600 psi, respectively, which are significantly less than the flat sheet data of 71, 120, and 138 gfd at corresponding pressures. It should be noted that the lower flux data obtained at pressures above 200 psi indicate some collapse at those pressures.

Attempts to prepare hollow-fiber substrates which have flux properties similar to those observed in flat sheet substrates were made by preparing hollow fibers under conditions which reproduce those used in the preparation of flat sheets as accurately as possible. Several parameters in the process of spinning the fibers were varied in an attempt to reproduce the flat sheet substrate properties. The performances of the resulting fibers, as well as the different parameters varied, are described in Table VI.

TABLE V

EFFECT OF GELLING BATH COMPOSITION ON WATER FLUX RATE OF NC SHOCK GELS

| Substrate Ident. No.* | Substrate Geometry | Gelling Bath Composition | Substrate Dimensions (mil) | | | Water Flux Rate (gfd) | | |
			O.D.	I.D.	Wall	200 (psi)	400 (psi)	600 (psi)
X143-72-10D	Flat Sheet	Water	-	-	7.7	71.0	120	138
X209-39-5A	Hollow Fiber	Water	22.5	8.1	7.2	0.80	0.70	0.65
X209-39-2A	Hollow Fiber	1% Aq. DEG.	22.5	12.5	5.0	6.9	5.4	5.4
X209-40-1	Hollow Fiber	5% Aq. DEG.	25.0	12.5	6.25	10.3	7.0	7.4
X209-40-3	Hollow Fiber	7% Aq. DEG.	25.0	12.5	6.25	3.0	3.0	2.9

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*Substrates were prepared by shock gelation at 60°C of a 25 wt.-% solution of NC (RS, 5-6 sec) in diethylene glycol (DEG.)

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TABLE VI

PROPERTIES OF NC HOLLOW-FIBER SUBSTRATES

Fiber Number	O.D./Wall Ratio (In.)	Gel Bath Composition (% Deg.)	Spin Method	Dye Stain	Flux (gfd) Pressure (psi)					Comments and Observations
					200	400	500	800	1000	
X252-1-1	2.95	5	Free fall No wind	I	0.114	0.253	0.290	0.335	-	Fibers were in curls. Very difficult to handle.
X252-1-2	4.00	5	Free fall No wind	I		No	Test	Possible		Fibers were kinky.
X252-1-3	3.33	5	Wind on drum at 135 fpm	M		No	Test	Possible		Indication of low porosity.
X252-5-1	3.42	5	Free fall No wind	I	1.11	2.03	1.81	1.83	1.77	Oil in test system. Condition of fibers same as 1-1.
X252-5-2	3.14	5	Free fall No wind	I	0.58	2.64	6.30	15.96	24.21	Same as 1-2.
X252-5-3	3.50	5	Wind on drum at 166.5 fpm	M	8.43	14.78	23.30	52.37	90.93	Straight fibers.
X252-5-4	3.40	5	Wind on drum at 13.75 fpm	I						Bores closed on standing.
X252-14-1	2.75	5	Wind on drum at 17 fpm	I						Bores closed on standing.
X252-14-2	2.86	5	Wind on drum at 17 fpm	I	11.89	-	-	-	-	Fiber collapse above 200 psi.
X252-15-1	2.86	3	Wind on drum at 19 fpm	I	13.84					Fiber collapse above 200 psi.
X252-15-2	3.45	3	Wind on drum at 19 fpm	I						
X252-15-3	5.00	3	Wind on drum at 33.5 fpm	I	17.81	7.12	?.90			Fiber shows collapse above 200 psi.
X252-28-1	3.67	3	Wind at 95.5 fpm	I	4.76	7.04	7.48	6.97	6.88	Fiber shows collapse above 200 psi.
X252-28-2	3.62	3	Wind on drum at 56.5 fpm	I	7.87	?.30	8.41	-	-	
X252-54-2	2.63	5	Wind on creel at 46.5 rpm	I	-	3.80	-	-	-	Fiber collapsed above 400 psi.

NOTE: All fibers were prepared from RS 5-6 sec grade NC in a solution of diethylene glycol - concentration of the NC 25% (Deg.).

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One of the approaches used in attempting to produce fibers under the same conditions by which flat sheet substrates are produced was to allow the fibers to fall freely into the gelation bath and thus avoid fiber stretching. Examination of Table VI shows that the fibers produced in this manner yield unacceptable flux rates. These fibers were also curly and very difficult to handle without some damage. In addition, when the fibers were allowed to accumulate in the gelation bath, it was observed that they tended to form a pile and stick together in spots, resulting in damaged, unacceptable fibers.

Since the process which allowed the fibers to fall freely into the gelation bath proved to be unsatisfactory, it was decided to modify the spinning process to allow the fiber to flow freely into one gellation bath and immediately wind the fiber onto a drum rotating in another bath of the same composition. It should be noted that care was taken not to stretch the fiber in this process. The process of winding the partially gelled fiber on a drum to complete gelation is satisfactory from the standpoint of providing a fiber which is relatively easy to handle and which is reasonably free of surface defects.

Although the fibers produced by the two-step gelation process described above are easy to handle and free from surface defects, the fibers tend to acquire an oval, rather than circular, cross-sectional shape if they are stored on the drum for a few days. It is believed that the change in shape is a result of shrinkage during gelation and leaching. To overcome this difficulty a creel (Figure 3) was prepared. The creel changes diameter as the fiber shrinks, thereby producing very little if any compressive load on the fibers and reducing the fiber deformation to a negligible factor.

Examination of Table VI shows that those substrates which produce the greatest flux have a high O.D./wall thickness ratio. However, there is a significant problem of fiber collapse above 200 psi. This problem could possibly be solved by increasing the NC content of the solution from which the fibers are extruded using nitrocellulose which has a higher molecular weight than that currently used.

Preparation and Evaluation of Composite Membranes

Initial attempts to apply an ultra-thin coating of cellulose triacetate to the new, more highly permeable NC fiber substrate indicated the need for proper pretreatment of the substrate to allow uniform coating. Attempts were made to coat the fiber substrate with 0.25-0.50 wt. % solutions of cellulose triacetate in chloroform, both with and without polyacrylic acid undercoats. Ranges of dip and dry times and two coating temperatures were studied, but poor results were obtained as evidenced by moderate dye staining

A 2-End threaded 0.5 in. aluminum rod. Double-nutted holding rods.

B 1/4 In. slotted hole through 8 places: Equally spaced: Each 22.5° from C/L

C 1/4 In. Holes - 8 places equally spaced: Each 45° from C/L, Drilled 1/4 In. depth.

½ In. HIFAX

½ In.

½ In.

1/2 In. Aluminum rod threaded 1 3/4 in. both ends. Double nutted - 2 required. 11 In. Length

1/4 In. synthane 11 In. Length - 8 Required

1 In.

1½ In.

1/4 In. Synthane 1 1/4 In. Length 16 Required

± 0.002 In. Press Fit Bearing FAFNER No. S5KDD

3-5/8 In. Dia.

B

A 3 In. Dia.

B 4-1/4 In. Dia.
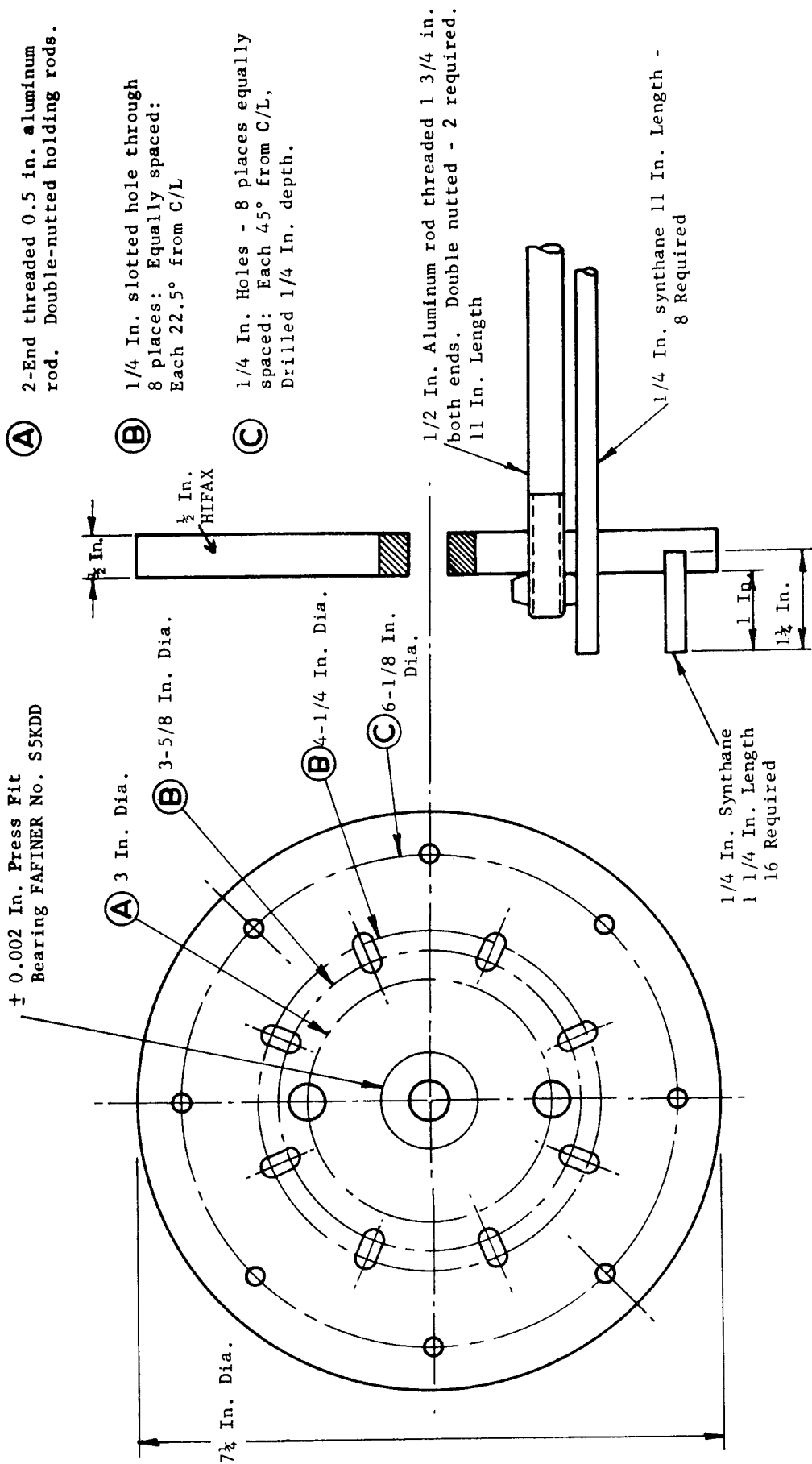
C 6-1/8 In. Dia.

7¼ In. Dia.

Figure 3. Take-up Creel for Storage of Hollow Fibers

and low salt rejections (Table VII). However, it was expected that satisfactory coating can be achieved by partially drying the substrate from a water-wet state before coating since such a procedure was successful in previous work involving the coating of very highly permeable NC flat-sheet shock gels.

Additional studies were conducted to determine if the substrates could be dried, rewetted, and then serve again as effective substrates. The data presented in Table VIII show the gels to be unsuitable for use as substrates after drying, either because the porosity decreased, reflected in either excessive shrinkage or inability to absorb dye, or because the resulting gel either was brittle or possessed a surface coating that would hinder adhesion of an ultra-thin film.

Based on these results and previous experience in coating NC shock gels, the most appropriate method for preparing the substrates appeared to be wiping the surface dry with lint-free tissue. Substrates partially dried in this manner were coated with an ultra-thin CTA layer.

Composite CTA-NC flat-sheet membranes were prepared as indicated in Table IX. Of the several coating procedures and coating solution concentrations described in Table IX, the best results were obtained by dip coating in a 0.50 wt. % CTA-chloroform solution. However, the flux and salt rejection properties of hollow-fiber membranes prepared with this technique could not be consistently reproduced. The reason for the poor reproducibility in the membranes prepared using the blotting wiping methods of surface drying was the inability to maintain the required control over the process. An attempt was made to wipe dry the surface of the hollow fiber by passing it through a mercury bath prior to coating. This approach was not successful because globules of mercury tended to adhere to the surface of the hollow-fiber substrate.

The unsatisfactory results of the mercury treatment led to the investigation of two other approaches for preparing the substrate surface for coating. One of these methods involved the use of a solvent which would. dissolve the water and evaporate quickly, leaving the substrate surface ready for coating. The other method involved use of a material to wet the fiber surface and provide a base that would readily accept the CTA coating. In both of these methods it would appear that the material used in the pre-coating treatment must be able to spread on water and be inert with regard to the NC hollow fibers; hence, a series of experiments were conducted in which the ability of various materials to wet water was qualitatively evaluated. The results of the wetting experiments are provided in Table X. Most of the materials evaluated in the wetting experiments do not spread spontaneously on water. The majority of those materials that do wet water

TABLE VII

PROPERTIES OF CELLULOSE TRIACETATE-COATED NC HOLLOW FIBERS

Membrane Ident. No. (X214-)	Membrane[a,b] Substrate Pretreatment	Coating Solution[c,d] CTA Conc. (Wt.-%)	Coating Solution[c,d] Temp. (°C)	Coating Procedure Dip Time (Min.)	Coating Procedure Dry Time (Min.)	Coating Procedure Other Conditions	Dye[e] Stain	Water Flux (gfd) 200 (psi)	Water Flux (gfd) 400 (psi)	Water Flux (gfd) 600 (psi)	Salt Rejection (%) 200 (psi)	Salt Rejection (%) 400 (psi)	Salt Rejection (%) 600 (psi)
48-2	None	0.25	R.T.	2.5	2	None	L-M						
48-3	None	0.25	R.T.	3	2	None	L-M						
48-4	None	0.25	R.T.	4	2	None	L-M						
48-6	None	0.25	R.T.	5	2	None	L-M	2.8	2.1	1.7	24	25	22
48-7	None	0.25	R.T.	5	4	None	M						
48-8	None	0.25	R.T.	2	2	Fiber coated twice	L-M						
49-4	None	0.25	R.T.	30	2	None	VL-L						
57-5	Wipe dry 4 times	0.25	R.T.	0.5	1	Fiber coated 5 times	N-VL	0.14	0.33	0.35	-	74	83
49-3A	Water at 60°C for 10 min.	0.25	R.T.	3	2	None	L-M	5.6	4.5	5.1	6.0	-	2.4
49-3B	Water at 60°C for 10 min.	0.25	R.T.	5	2	None	L-M	2.0	1.6	1.8	41	39	43
50-1	Water - 60°C - 10 min. + air dry 2 min.	0.25	R.T.	5	2	None	M						
50-1A	Water - 60°C - 10 min. + air dry 5 min.	0.25	R.T.	5	2	None	M-I						
50-2	Water - 60°C - 10 min. + wipe dry 5 times	0.25	R.T.	5	2	None	M-I						
49-2	None	0.50	R.T.	5	2	None	L-M	2.2	2.1	2.3	27	28	28
49-3C	Water at 60°C for 10 min.	0.50	R.T.	5	2	None	M						
54-2	None	0.25	50	4	2	None	N-VL	0	0	0			
55-2	None	0.25	50	1.5	2	None	VL	0.29	0.42	0.26	39	71	52
48-10	PAA - Dip 1 min., Dry 2 min.	0.25	R.T.	2	2	Fiber precoated 3 times	L-M						
49-1A	PAA - Dip 5 min., Dry 2 min.	0.25	R.T.	3	2	None	L-M						
49-1B	PAA - Dip 10 min., Dry 2 min.	0.25	R.T.	3	2	None	L-M						
49-1C	PAA - Dip 15 min., Dry 2 min.	0.25	R.T.	3	2	None	L-M						
49-3D	PAA - Dip 3 min., Dry 2 min.	0.25	R.T.	3	2	Fiber preheated in water - 60°C - 10 min.	L-M	1.6	1.9	2.1	31	31	31
49-3E	PAA - Dip 1 min., Dry 2 min.	0.25	R.T.	5	2	Fiber precoated 5 times	VL-L	0.17	0.32	0.21	-	40	41
55-8	PAA - Dip 1 min., Dry 1 min.	0.25	R.T.	5	2	Fiber precoated 10 times	L	0.19	0.53	0.66	31	67	92

(a) Substrate consisted of 25 wt.-% NC (RS, 5-6 sec) shock gelled from solution in diethylene glycol in a 60°C gelation bath consisting of 5% aqueous diethylene glycol.

(b) PAA - Polyacrylic acid, Acrysol A-3, as a 3 wt.-% solution in equal weight mixture of ethanol and water.

(c) Coating solution consisted of cellulose triacetate (CTA, A432-130b) dissolved in chloroform.

(d) R.T. - Room temperature.

(e) I - Intense, M - Moderate, L - Light, VL - Very light, and N - No stain.

TABLE VIII

EFFECTS OF ENTRAINED LIQUIDS AND DRYING METHODS ON SHRINKAGE OF DRIED FLAT-SHEET NC SHOCK GELS [a]

Identification No.	Entrained Liquid	Drying Method[j]	Thickness (Mil) Original Water Wet	After Drying	Final Water Rewet	Dye Stain After Water Rewet Top	Bottom	Condition In Dried State
X243-2-1	Water	Freeze Drying (No Prefreezing)	9	3	3	-	-	Very brittle
X243-25A	Water	Freeze Drying (Prefrozen at -80°C)	8	3	2.5	None	None	Very brittle
X243-25B	Water	Freeze Drying (Prefrozen at -196°C)	9	2.6	3.2	None	None	Very brittle
X243-2-2	Tert-Butanol[b]	Freeze Drying (No Prefreezing)	8	6	5.5	-	-	Brittle
X243-12-1	Karo Syrup[c]	Freeze Drying (No Prefreezing)	9	-	8	Intense	Intense	Very brittle, much sugar on surface
X214-93-2	Karo Syrup[c]	Ambient Drying	9	-	8	Intense	Intense	Brittle
X243-12-2	Acrysol A-3[d] (25 wt.-% Aq. Soln.)	Freeze Drying (No Prefreezing)	9.5	-	9	Intense	Intense	Very brittle, sticky surface
X214-88-2B	Glycerin[e]	Vacuum Drying at Room Temp.	9.5	-	9	Intense	Intense	Flexible, slick surface
X243-26-2	Agar[f] (1 Wt.-% Aq. Soln.)	Ambient Drying	8	6.2	6.2	None	None	Flexible and curled
X243-30-1	Polyox WSRN-10[g] (5 Wt.-% Aq. Soln.)	Ambient Drying	8	2.5	2.5	None	None	
X243-26-1	Ethyl Ether[h]	Ambient Drying	8.2	5.7	5.7	None	None	Flexible
X243-28-1	Chloroform[i]	Ambient Drying	8.0	4.2	4.2	None	None	Brittle

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[a] Flat-sheet substrates were prepared by shock gelation in water at 60°C of a 25 wt.-% solution of NC (RS, 5-6 sec) in diethylene glycol.

[b] Water exchanged with tert-butanol using following sequence of solutions (wt.-% tert-butanol) for 1 hour each: 25, 50, 75, and 100.

[c] Water exchanged with colorless Karo syrup using following sequence of solutions (wt.-% syrup) for 1 hour each: 5, 25, 50, 75 and 100.

[d] Water exchanged with 5 wt.-% aq. Acrysol A-1 solution for 1 hour, then for 25 wt.-% aq. Acrysol A-1 solution for 1 hour, and finally for 25 wt.-% aq. Acrysol A-3 solution for 1 hour.

[e] Water exchanged with glycerin using following sequence of solutions (wt.-% glycerin) for 0.5 hour each: 25, 50, 75 and 100.

[f] Water exchanged directly with 1 wt.-% aq. Agar solution for 2 hours.

[g] Water exchanged directly with 5 wt.-% aq. Polyox WSRN-10 solution for 2 hours.

[h] Water exchanged first with tert-butanol using following sequence of solutions (wt.-% tert-butanol): 5, 25, 50, and 75 for 0.5 hour each and then 100 for 16 hours; then tert-butanol exchanged with ethyl ether using following sequence of solutions (wt.-% ethyl ether): 5, 25, 50, and 75 for 0.5 hour each and then 100 for 16 hours.

[i] Water exchanged first for tert-butanol using following sequence of solutions (wt.-% tert-butanol): 5, 25, 50, and 75 for 0.25 hour each and then 100 for 1 hour; then tert-butanol exchanged with chloroform using following sequence of solutions (wt.-% chloroform): 5, 25, 50, and 75 for 0.25 hour each and then 100 for 16 hours.

[j] Freeze drying was carried out at -50°C without vacuum for 1 hour, -50°C and 0.2 mm Hg for 1 hour, -50 to 10°C and 0.2 mm Hg for 4 hours, 10 to 38°C and 0.17 mm Hg for 18 hours, and finally 38 to 50°C and 0.15 mm Hg for 24 hours. Ambient conditions were 25°C and 35% relative humidity for 24 hours.

TABLE IX

PROPERTIES OF CTA-COATED NC FLAT-SHEET SHOCK GELS

Ident. No.	Substrate Pretreatment	Coating Solution CTA Conc. (Wt-%)	Coating Procedure	Coated Surface Dye Stain	Feed NaCl Conc. (Wt-%)	Test Pressure (Psi)	Time (Min)	Water Flux (Gfd)	NaCl Rejection (%)
X214-85-3	Wiped Surface Dry	0.25	Brush Coated	Very Light	3.50	1500	60	3.8	59.4
X214-86	Wiped Surface Dry	0.25	Spray Coated	Very Light	3.50	1000	60	4.9	51.1
X214-88-2B	Dried From Glycerine	0.13	Brush Coated Twice	Moderate	3.52	1500	60	48.3	5.1
X214-93-2	Dried From Karo Syrup	0.25	Brush Coated Twice	Moderate	3.52	1500	60	74.8	10.2
X243-31	Soaked in 0.125 wt-% Aq. Reten 210 Soln.	0.25	Dip Coated	Moderate	0.48	600	60	21.3	33.1
X243-34	Wiped Surface Dry	1.00	Dip Coated	None	0.51	600	60	1.3	94.3
X243-35-1	Wiped Surface Dry	0.75	Dip Coated	None	0.50	600	60	4.8	90.1
X243-35-2	Wiped Surface Dry	0.50	Dip Coated	None	0.50	600	60	5.0	93.4
X243-36	Wiped Surface Dry	0.25	Dip Coated	None	0.47	600	60	16.0	63.4
X243-37	Wiped Surface Dry	0.25	Dip Coated Twice	None	0.47	600	60	7.0	86.2
X243-39-1	Wiped Surface Dry	0.20	Dip Coated Twice	None-Moderate	0.46	600	60	8.8	84.5
X243-39-2	Wiped Surface Dry	0.10	Dip Coated Twice	None-Moderate	0.49	600	60	19.6	45.5

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TABLE X

EVALUATION OF MATERIALS FOR NC HOLLOW-FIBER
SUBSTRATE COATING PRE-TREATMENT

Material	Ability To Spread On Water	Effect on NC Substrate	Observations
Chloroform	Poor	None	
Dioxane	Poor	None	
Ethyl Acetate	Good	Dissolved fiber	
Acetic Anhydride	Good	Dissolved fiber	
Tricresyl Phosphate	Poor	None	
Allyl Alcohol	Poor	None	
2 Ethyl 1 Hexanol	Poor	None	
Cyclohexanone	Fair	Tends to close pores	Dye stain ability reduced markedly
Cyclohexanone CHCl$_3$ 1/24 by volume	Fair	Tends to close pores	Dye stain ability reduced markedly
Methylene Chloride	Poor	None	
Ethyl Ether	Good	Attacks NC Substrate	Produces CTA precipitate when a small quantity is added to 0.5% CHCl$_3$ solution, thereby permitting a nonuniform coating.
3 In 1 Oil	Fair	-	
Nujol	Poor	-	
Olive Oil	Fair	-	
Acrysol A3 25% Solution	None	-	

attack the NC hollow fiber, either dissolving the substrate completely, as indicated by the results involving ethyl acetate, or reducing the fiber porosity as indicated by the tests involving cyclohexanone.

Based upon these preliminary qualitative evaluations, it was thought that perhaps through a combination of two or more materials, an acceptable system could be discovered for the approach which employs a rapidly drying solvent. Hexane and ethanol combinations ranging from a 50/50 to a 90/10 (by weight) hexane/ethanol were evaluated. However, it was found that, even with a short exposure time (30 seconds) in the 90/10 solution, the fiber acquired a milky appearance when the cellulose triacetate was applied, indicating some damage to the substrate.

Further attempts to find a volatile solvent for water led to the evaluation of methylene chloride. Solubility and boiling point data[3] show that this material would be a good candidate. Single water-wet fibers were exposed to a methylene chloride bath, allowed to dry for a short time, and then dip coated in a 0.5% CTA/CHCl$_3$ solution. The flux and salt rejection data presented in Table XI indicate that this process is feasible and that a reasonably defect-free coating may be applied to the substrate. It is important to note that the methylene chloride treatment did not change the size of the substrate or alter the porosity of the fiber.

Continuous coating apparatus employing the methylene chloride pre-treatment was designed and assembled (see Figure 4). This apparatus was used to prepare membranes which gave flux and salt rejection data tabulated in Table XI.

It should be noted that membranes prepared using the continuous coating system and the methylene chloride pretreatment did not produce flux and rejection data as desirable as those obtained from a single fiber process. Examination of the fibers which had completed the methylene chloride pre-treatment before they were exposed to the coating solution showed a loss of porosity. This loss of porosity is attributed to attack by methylene chloride when the fiber is under a slight amount of tension.

From the data presented in Table X, it is obvious that the best method for applying the ultra-thin coating is to continuously air dry the surface of the substrate. The data presented in Table XI also indicate that more than one pass through the coating solution may be necessary to completely coat the membrane. The best membranes produced during this period were prepared by air drying the surface and then passing twice through a 0.25 wt. % CTA chloroform solution. These composite hollow-fiber membranes produced a flux rate of 0.34 gfd while rejecting 98% of the salt from a 5000 ppm sodium chloride solution at 400 psi. This membrane is capable of desalting brackish water.

The continuous coating process which employs air surface drying has shown considerable promise. However, the membranes developed during this period are not capable of sea water desalination because the substrates produced to date cannot withstand the high pressures required.

TABLE XI

PERFORMANCE OF COMPOSITE HOLLOW-FIBER MEMBRANES

| Fiber Number	Substrate Pretreatment	Coating Solution	Dye Stain	Feed (ppm) NaCl	Pressure (psi)	NaCl Rejection (%)	Flux (gfd)	Comments
X252-5-3-1	Blot dry	0.25% CTA/CHCl$_3$	N	35,000	600 / 600	6.36 / 9.54	18.0 / 70.1	
X252-5-3-2	Wipe dry	0.25% CTA/CHCl$_3$	N	35,000	800 / 1,000	- / -	0.58 / 0.59	Defective electrode
X252-15-3	Air dry after 50% Hexane/ethanol exposure	0.25% CTA/CHCl$_3$	N	5,000	600	65.27	0.36	Fibers milky in appearance
X252-28-1-2	Air dry after 70% Hexane/ethanol exposure	0.50% CTA/CHCl$_3$	N-VL	1,000	200	81.4	0.32	Fibers milky in appearance
X252-28-1-3	Air dry after MeCl$_2$ exposure	0.50% CTA/CHCl$_3$	N	1,000	200	97.18	0.25	Single fiber coat
X252-28-2-1	Air dry after MeCl$_2$ exposure	0.50% CTA	N	1,000	200	91.7	0.31	Single fiber coat
X252-44-1-1	Air dry after MeCl$_2$ exposure	0.5% CTA	N-VL	1,000	200	63.81	0.49	Continuous coating
X252-48-1-1	Air dry	0.5% CTA	N-VL	1,000	200	74.04	1.14	Continuous coating
X252-48-1-2	Air dry	0.25% CTA	N-VL	1,000	200	92.94	1.77	Continuous coating
X252-54-1-1	Air dry	0.50% CTA	N	5,000	400	94.51	0.45	Continuous coating
X252-54-2-1	Air dry	0.25% CTA	N	5,000	400	98.29	0.34	Two passes
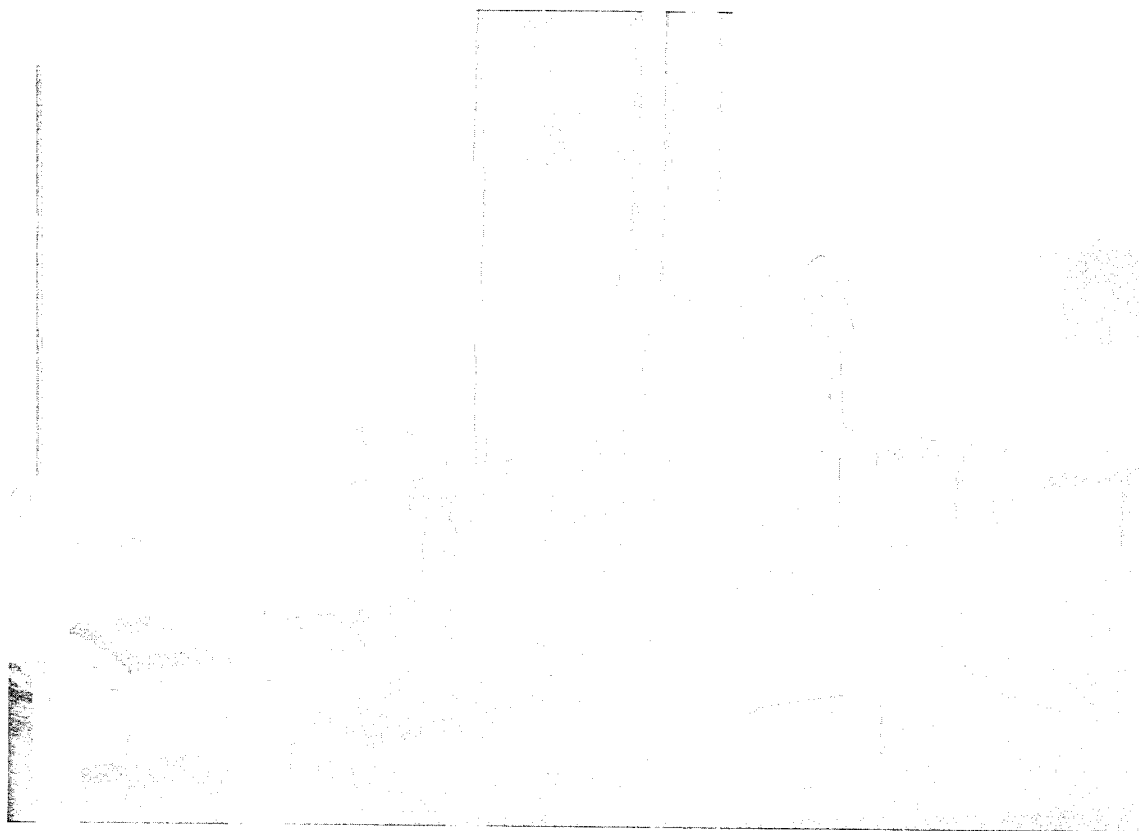
Figure 4. Continuous Coating Apparatus for Applying Ultra-Thin Selective Layer
in Preparation of Composite Hollow-Fiber Membrane

CONCLUSIONS AND RECOMMENDATIONS

1. Asymmetric hollow-fiber membranes can be tailored to give high performance (a 9.5 gfd flux rate) on brackish waters by varying the temperature at which the cellulose acetate (CA) thermal gel is annealed. The hollow-fiber flux-decline rates favor an operating pressure as low as is consistent with feed concentrations and recovery levels in order to minimize compaction effects. However, more work is required to develop hollow-fiber membranes suitable for long-term use at pressures of 600 psi or greater.

2. Asymmetric CA flat-sheet membranes can be prepared by a one-step method involving water gelation of CA from solutions in mixtures of diacetone alcohol and triethylene glycol. These membranes deliver very high flux rates (up to 101 gfd) at both low and high pressures while exhibiting low flux decline and adequate salt selectivity for use on brackish waters. Since this method of asymmetric membrane preparation does not require an annealing treatment and yet affords a means of controlling the thickness of the active surface layer, it should allow the preparation of very high flux asymmetric hollow-fiber membranes.

3. Asymmetric CTA flat-sheet membranes can be prepared in one step by water gelation of CTA from solutions in formic acid and sulfolane containing triethyl phosphate. These membranes could possibly be used in the first stage of a two-stage sea water reverse osmosis desalination system. Further improvement might be expected in the performance of these membranes by optimizing the formulations and gelling conditions. Also, these new formulations should be suitable for fabricating asymmetric CTA hollow-fiber membranes.

4. Composite CTA-NC hollow-fiber membranes can be prepared using a continuous coating process. These membranes are suitable for brackish water applications.

5. The current NC hollow-fiber substrates do not have the structural integrity required to withstand the high pressures characteristic of sea water applications.

<center>EXPERIMENTAL*</center>

Materials

The cellulose diacetate used in asymmetric membrane preparation was Eastman Grade E400-25, and the cellulose triacetate employed in composite membrane coatings was Eastman Grade A432-130b. The cellulose nitrate used in shock gel preparation was Hercules RS type of 5-6 sec. viscosity. Other reagents were either Fisher Certified Grade or Fisher Reagent Grade or, where these grades were not available, Fisher Highest Purity Chemicals.

Asymmetric Membrane Preparation

The CA asymmetric hollow-fiber membranes were prepared from porous CA thermal gels. The thermal gel precursor was prepared by cooling, to its gelation point, a melt of 25-30 wt. % CA and 70-75 wt. % plasticizer. Flat-sheet and hollow-fiber thermal gels were gelled rapidly in a water bath followed by thorough leaching with distilled water. These gels were stored in room-temperature distilled water before use.

The CA hollow-fiber and flat sheet thermal gels were leached in water and then stored in water containing a bactericidal agent. Before testing, the porous thermal gels were crystallized by heat treatment in 60-80°C water. Annealing, the final step in the preparation of asymmetric membranes, was carried out with a 10% aqueous dioxane solution at 60-70°C.

The one-step asymmetric CA and CTA membranes were prepared by casting onto preheated glass plates the appropriate solution at the minimum temperature necessary to achieve the desired casting viscosity and then gelling the cast film for 0.5 hr in water at 60°C in the case of the CA membranes and in water at room temperature in the case of the CTA membranes. Gelation was followed by thorough water leaching of the solvents using room temperature water baths in the following sequence: 1 hr, 1 hr, 24 hr, and 48 hr. The membranes were stored in water before use.

Composite Membrane Preparation

Composite hollow-fiber and flat-sheet membranes were prepared by applying an ultra-thin cellulose triacetate coating to a shock gel substrate of cellulose trinitrate. These cellulose nitrate shock gels were prepared from 25 wt. % solutions of Hercules RS (5-6 sec.) cellulose nitrate in diethylene glycol. These solutions at 70-80°C were shock gelled in distilled water,

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*Experimental data are recorded in ABL Research Notebooks X143, X214 and X252.

both with and without diethylene glycol, at 60°C followed by thorough leaching with distilled water. The resulting porous gels, in flat-sheet or hollow-fiber form, were transparent and extremely flexible. These gels were stored in room-temperature distilled water before use.

The ultra-thin coating was applied by two processes. One involved immersing partially dried single fibers or flat sheets into a 0.25-0.50% cellulose triacetate chloroform bath followed by a brief period of air drying. The other technique employed was a continuous coating process in which the substrate was removed from a creel rotating in water, surface air dried, passed through a cellulose triacetate chloroform solution, again air dried, and finally wound onto a drum rotating in water. The membranes produced by both techniques were stored in water until they were tested.
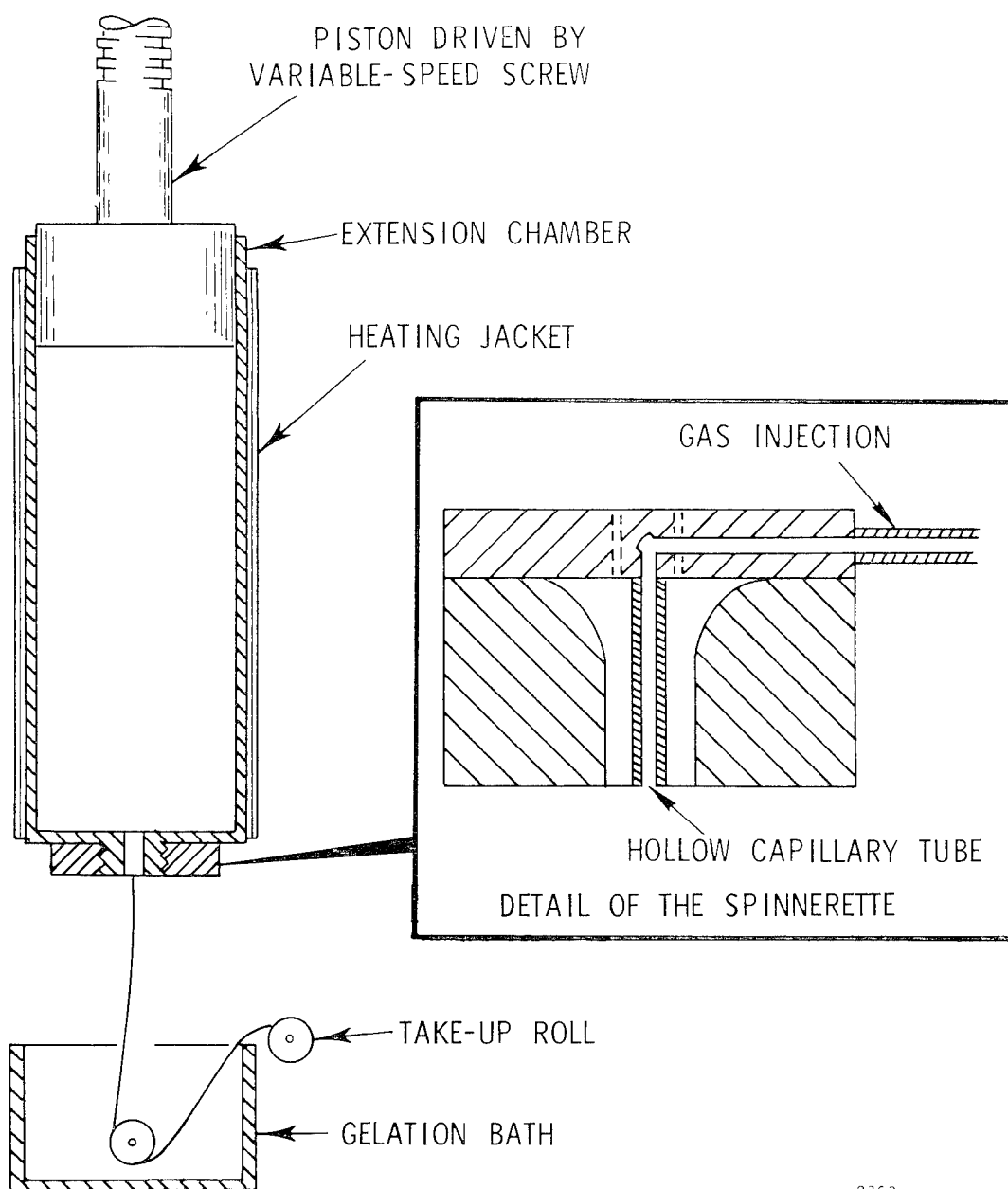
Dye Staining

The membrane specimen was leached in water to remove plasticizer and then dipped into a 0.1% aqueous solution of Rhodamine B Extra S dye and held for 1 minute. After removal and rinsing with water, the dye-stained specimen was visually observed under ultraviolet light.

Hollow Fiber Spinning

A schematic diagram of the hollow-fiber spinning apparatus is given in Figure 5. This apparatus consists basically of the following components:

1. Stainless steel extrusion chamber 1-inch I.D. x 10-inch long.

2. Piston capped with Teflon head machined to fit inside the extrusion chamber to close tolerances.

3. Screw jacket connected directly to piston.

4. Variable-speed drive to provide precise control of ram movement.

5. Specially designed spinnerette, including a hollow capillary tube for injecting gas (or liquid) into the center of the strand.

6. Heating jacket surrounding extrusion chamber.

7. Thermocouple.

8. Gas source for fluid injection.

9. Micro-flow meter (0-0.1 cc/sec).

PISTON DRIVEN BY
VARIABLE-SPEED SCREW

EXTENSION CHAMBER

HEATING JACKET

GAS INJECTION

HOLLOW CAPILLARY TUBE

DETAIL OF THE SPINNERETTE

TAKE-UP ROLL

GELATION BATH

9363

Figure 5. Schematic Diagram of Hollow-Fiber Spinning Apparatus

10. Teflon strand guides.

11. Cooling bath.

12. Variable-speed take-up roll.

This spinning apparatus has a capacity of about 6 in^3 and may be used to extrude either low- or high-viscosity slurries, including solutions or melts. A maximum temperature of 400°F can be obtained in the extrusion chamber by using the heating jacket in combination with heating tape and insulation on the outside of the extrusion chamber. The temperature can be regulated by a Variac. Piston movement can be adjusted precisely over the range 0 to 2.8 in/min. Depending upon fiber dimensions, spinning speeds up to several thousand inches per minute can be achieved at the die exit.

A variety of dies and hollow pins may be used with the spinnerette assembly. In practice, only the 47-mil die and the 22-mil insert were used. By controlling gas injection rate, extrusion rate, and drawdown ratio, it was possible to use this die combination to produce hollow fibers having ultimately a wide range of dimensions and wall thickness-to-diameter ratios. The hollow fibers were wound on Teflon spools with the linear take-up rate adjustable from essentially zero to about 1000 in/min.

Membrane Testing Procedures

Test Equipment

Flat sheet membrane testing was conducted using a commercially available high-pressure filter holder (millipore XX45-04700). Figure 6 illustrates the assembly of the test cell which had an effective filtering diameter of 43 mm.

A schematic diagram of the test setup is shown in Figure 7. High pressures are developed by an electrically operated or an air-operated positive displacement Sprague pump. Circulation rates were adjusted by high-pressure needle valves on the downstream side of the test cell.

The hollow-fiber test cell and a fiber bundle assembly are shown in Figure 8. Single strands of hollow fibers 10-14 in. in length or bundles of 10 to 50 fibers were tested in this high pressure cell. Both ends of each fiber were cemented into a thin plate with fast-curing adhesive (Eastman 910), and the plate was forced against an O-ring seal in the test cell. The test cell was filled with water or salt solution and pressurized with a nitrogen cylinder or installed into the system described in Figure 7. Effluent was collected from the ends of the fibers in a small vial. Extending the fiber ends through the cell wall into the atmosphere ensured that back-pressure inside the fibers did not affect the test.

Water Flux

Water flux, in gal-ft^{-2} day^{-1}, was calculated by collecting the effluent water in a tared vial and determining, for a given time period, the weight of water collected. From this weight, the volume of water collected was calculated. With the volume of water collected over a given period of time and the exposed membrane surface area known, the water flux could then be calculated directly. Calculation of the membrane surface area was based on the outside diameter of the fiber in all cases.

Salt Rejection

Salt rejection was calculated by dividing the difference between the initial and the final salt concentrations by the initial salt concentration. Salt concentrations of both feed and effluent waters were determined with a Thomas Dipping Type Micro Conductivity Cell, No. 3980-D60, and a Thomas-Serfass Conductivity Bridge, No. 3965-A. The bridge was standardized with the conductance cell, and a calibration curve was constructed from the specific conductances of 30 standard NaCl solutions, the concentrations ranging from 0.01 to 5.50 wt. % NaCl. Calibration of this conductivity system was checked periodically.
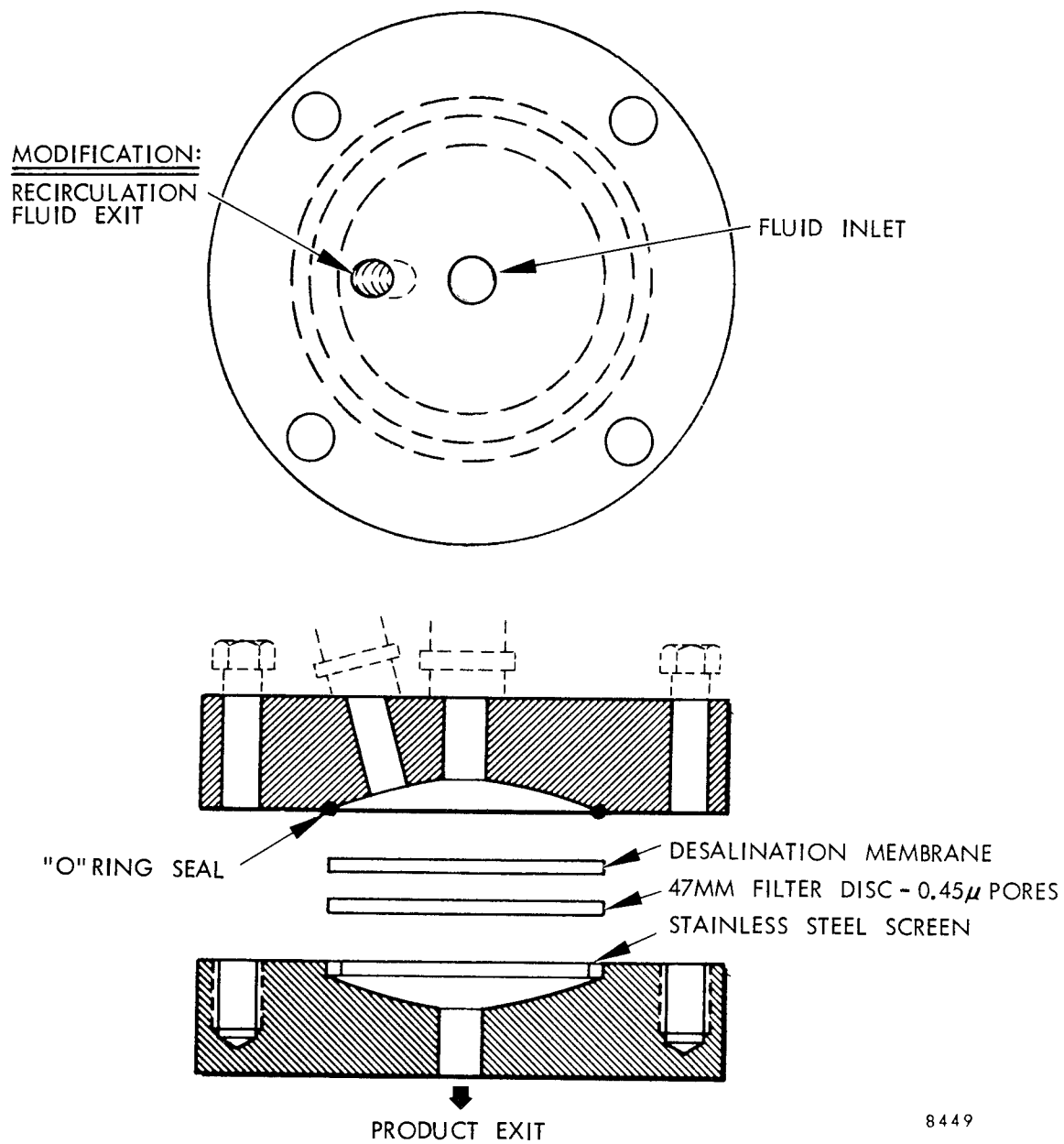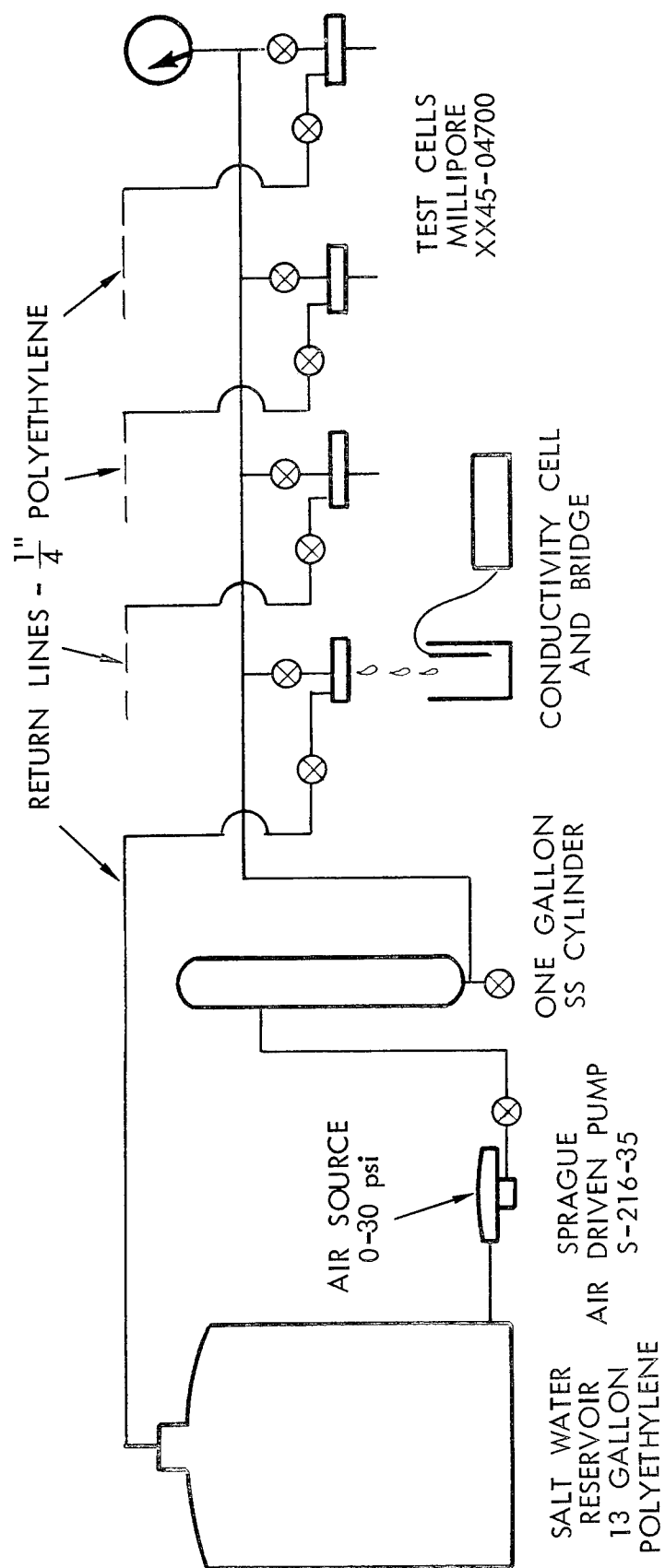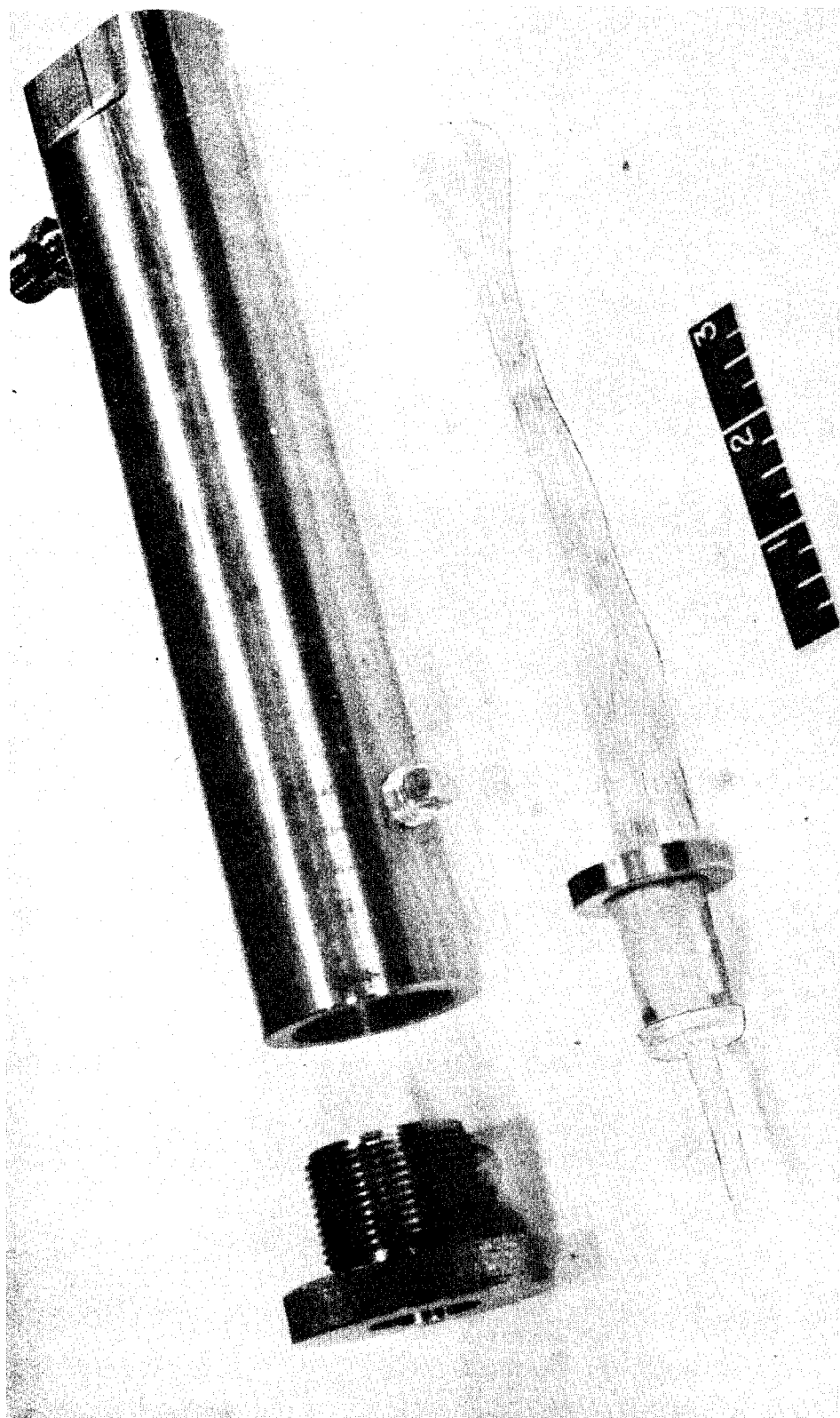
MODIFICATION:
RECIRCULATION
FLUID EXIT

FLUID INLET

"O" RING SEAL

DESALINATION MEMBRANE
47MM FILTER DISC - 0.45μ PORES
STAINLESS STEEL SCREEN

PRODUCT EXIT

8449

Figure 6. Modification and Assembly of Millipore Filter Holder for Membrane Testing

33

RETURN LINES – $\frac{1}{4}''$ POLYETHYLENE

TEST CELLS
MILLIPORE
XX45-04700

CONDUCTIVITY CELL
AND BRIDGE

ONE GALLON
SS CYLINDER

AIR SOURCE
0-30 psi

SPRAGUE
AIR DRIVEN PUMP
S-216-35

SALT WATER
RESERVOIR
13 GALLON
POLYETHYLENE

8448

Figure 7. Desalination Test Set-up

G-2393

Figure 8. Fiber Bundle Assembly and Test Cell Apparatus

REFERENCES

(1) Cohen, M. E., Grable, M. A., and Riggleman, B. M., "Development
     of Improved Cellulose Acetate Membranes for Reverse Osmosis,"
     R&D Progress Report No. 608, Office of Saline Water, U. S.
     Department of the Interior (September 1970).

(2) Bloch, R., Frommer, M. A., Kedem, O., Feiner, I., Kedem, A.,
     and Lancet, D., "The Mechanism for the Formation of a Skinned-Type
     Membrane," R&D Progress Report No. 499, Office of Saline Water,
     U. S. Department of the Interior (December 1969).

(3) Handbook of Chemistry and Physics, 48th Edition, The Chemical Rubber
     Company, Cleveland, Ohio, 1967.