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NEW MEMBRANES FOR TREATING METAL FINISHING EFFLUENTS BY REVERSE OSMOSIS

Industrial Environmental Research Laboratory
Office of Research and Development
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Cincinnati, Ohio 45268

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NEW MEMBRANES FOR TREATING METAL FINISHING EFFLUENTS BY REVERSE OSMOSIS

by

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FOREWORD

When energy and material resources are extracted, processed, converted, and used, the related pollutional impacts on our environment and even on our health often require that new and increasingly more efficient pollution control methods be used. The Industrial Environmental Research Laboratory - Cincinnati (IERL-Ci) assists in developing and demonstrating new and improved methodologies that will meet these needs both efficiently and economically.

This report is the result of a nine-month study on "New Membranes for Treatment of Metal Finishing Effluents by Reverse Osmosis" which was completed as of June 1975. These results included a successful long-term demonstration (2360 hours) of the performance of NS-100 reverse osmosis membranes for treatment of extreme pH electroplating wastes (pH 1 acid copper and pH 13 zinc cyanide rinse water effluents). Feasibility of this new membrane to commercial applications in electroplating installations was thus shown.

This project was one of several projects undertaken by IERL-C and the American Electroplaters' Society to demonstrate new techniques for purifying metal finishing waste water, a source of much water pollution throughout the country. This report will be especially interesting to individuals in the plating industry who are compelled by law to meet rather stringent effluent guidelines within the near future, and to individuals involved in industrial waste water research.

For further information on this subject contact the Metals and Inorganic Chemicals Branch, Industrial Pollution Control Division.

David G. Stephan
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ABSTRACT

Long-term reverse osmosis tests were conducted with electroplating wastes on a new membrane referred to as NS-100. This membrane consists of a polyurea layer, formed by the reaction of tolylene diisocyanate with polyethylenimine, deposited on a porous polysulfone support film. The membranes were tested as liners within 1/2-inch diameter fiber glass tubes. A total of 2360 hours of continuous reverse osmosis operation was achieved, 1220 hours on pH 1.2 acid copper rinse water and 1140 hours on pH 12.8 alkaline zinc cyanide rinse water. The membranes exhibited remarkable chemical stability during exposure to these two pH extremes. Copper and zinc rejections were generally greater than 99 percent, while cyanide rejections were typically 96 percent or greater. Membrane fluxes were in the range of 18 to 24 liters per square meter per hour (11 to 14 gfd) for acid copper, but only 8 to 15 l/m^2-hr (5 to 9 gfd) for zinc cyanide at 41.4 bars (600 psig) and 25°C. Rejection organics (including brighteners) was 60 to 78 percent for acid copper and greater than 95 percent for zinc cyanide. NS-100 membranes did not reject sulfuric acid. A modified membrane, NS-101, demonstrated twice the permeate flux of NS-100 toward zinc cyanide baths, but cyanide rejections were low at 90 percent. The serviceability of these membranes toward these pH extremes was adequately demonstrated in this test series. Difficulties of producing reproducible, high-flux tubular membranes were not fully resolved in this study. Thus, in the tubular configuration, this membrane is not yet in a stage of development for on-site demonstrations.

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ACKNOWLEDGEMENTS

This program was sponsored through a grant from the U. S. Environmental Protection Agency with Donald L. Wilson, Project Officer. The American Electroplaters' Society (AES), Inc., was the grantee co-sponsor of this program, with J. Howard Schumacher of the AES serving as Project Manager (AES Project No. 36). The support and assistance of the AES is hereby gratefully acknowledged.

The authors are grateful for the cooperation of Mr. Court Platt, Precious Metals Platers Incorporated, Mr. Roger Murnane, Superior Plating, Inc., and Mr. William Cashin, Honeywell, Inc. for providing actual plating baths used in this program.

This report was submitted in fulfillment of the requirements of Grant No. R-803264-01-0 of the U. S. Environmental Protection Agency.

SECTION I

CONCLUSIONS

The NS-100 membrane (formerly NS-1) was shown to be an excellent membrane for potential industrial use in the recycle of rinse water and plating chemicals in acid copper and zinc cyanide electroplating lines. This was demonstrated through 2360 hours of continuous operation with 1.27-cm tubular membranes, half at pH 1.2 (acid copper) and half at pH 12.8 (zinc cyanide). NS-100 membranes demonstrated stable salt rejection performance during this period, showing greater than 99 percent rejection of metals (copper, zinc) and 96 to 99 percent rejection of cyanide ion.

Test conditions were severe in that actual plating baths diluted to one-tenth full strength were used in these tests, a far higher concentration than present in conventional rinse baths. Since most membrane surfaces in a potential reverse osmosis installation would experience milder conditions, membrane lifetimes of at least 3000 hours, and probably up to 5000 hours would be a reasonable expectation based on these test results.

Water permeation rates through tubular NS-100 membranes were lower than desired, based on previous studies with flat sheet NS-100 membranes. Flux rates were 18 to 24 liters per square meter of membrane per hour (11 to 14 gallons per square foot of membrane per day) for acid copper rinsewater, but only 8 to 15 $1/m^2$-hr (5 to 9 gfd) for alkaline zinc cyanide rinse water. Continuous flux decline with time was evident, which could be restored significantly by osmotic cleaning. It was concluded that this flux decline was due in part to formation of "dynamic" membranes on the NS-100 membrane surface. No attempts were made to periodically clean membrane surfaces; industrial use of cleaning aids (detergents, osmotic cleaning) should lead to a higher level of flux values than observed in this program.

Two experimental NS-101 membranes (made with isophthaloyl chloride rather than tolylene diisocyanate) demonstrated twice the flux of NS-100 membranes toward alkaline zinc cyanide (about 27 $1/m^2$-hr, or 16 gfd). Zinc rejections were greater than 98.5 percent, but cyanide rejections were low at 90 percent. Optimization efforts on NS-101 membrane fabrication could lead to suitable salt rejection characteristics.

At the beginning of the program, optimization of the fabrication procedure for 1.27-cm tubular NS-100 reverse osmosis membranes succeeded in doubling membrane flux performance based on initial and final test comparisons. Unfortunately, attempts to fabricate NS-100 tubes late in the program by the optimized procedure gave low flux membranes with extremely high salt rejections. In fact,

throughout the program, efforts were hindered by a significant variability in the performance of individual tubes fabricated at various intervals. Variability was concluded to arise both from a very narrow set of acceptable fabrication parameters and from as yet unknown factors contributing to manufacturing nonuniformity. This membrane system, at least in the form of tubular membranes, was judged to be not yet ready for on-site demonstrations. Additional experimental studies on tube fabrication, with emphasis on the NS-101 modification, seem necessary as a next step.

SECTION II

RECOMMENDATIONS

The objectives of the program were threefold: 1) to optimize the fabrication process for NS-100 tubular reverse osmosis membranes to provide optimum performance; 2) to demonstrate sustained performance of NS-100 membranes toward highly acid and highly alkaline metal finishing waste waters; and 3) to provide sufficient data for preliminary engineering design of a possible field demonstration unit.

This program successfully demonstrated the stability and performance of NS-100 membranes to both types of plating wastes, acidic and caustic. Unfortunately, the optimization studies on the fabrication process did not lead to routinely reproducible, high-flux membranes. Thus, despite the great promise of this membrane system for field trials, on-site demonstrations would be premature at this time without a better understanding of tube fabrication parameters.

To arrive at a field demonstration phase, it is recommended that further research first be directed toward the membrane fabrication process. This task would specifically involve obtaining higher flux membranes in a reproducible manner. To achieve this goal, efforts would center on the NS-101 modification, which has been found in related seawater desalination work to demonstrate even greater durability than the NS-100 membrane. When this problem of membrane tube nonuniformity and inadequate flux is solved, the on-site demonstration phase can be realistically recommended.

SECTION III

INTRODUCTION

Midwest Research Institute, through its North Star Division, has completed the research program "New Membranes for Treatment of Metal Finishing Effluents by Reverse Osmosis" under Grant No. R-803264-01-0 from the U. S. Environmental Protection Agency (EPA) with the American Electroplaters' Society, Inc., as the grantee organization. This program was the third phase of a study initiated at North Star in 1970 on the development of reverse osmosis membranes for the treatment of metal finishing waste waters. This study was designed to help meet the needs of the metal finishing industry through improved pollution control and conservation of valuable materials.

During the first phase of this study, the treatment of metal finishing waste waters by reverse osmosis was shown to be feasible (1). A number of cellulosic membranes, both commercially available and improved derivatives synthesized at North Star, were demonstrated to be capable of treating various metal finishing effluents. The second phase of this study consisted of the fabrication and testing of membranes found most promising in the first phase into tubular configurations, and the development of new, noncellulosic, second generation membranes for improved metal finishing waste treatment by reverse osmosis (2). The third phase of this study, described in this report, consisted of a long-term test of a very promising reverse osmosis membranes, NS-100, against highly acid and highly alkaline feed solutions to demonstrate its unique level of chemical resistance and sustained performance, as a prelude to commercial utilization.

Background

The metal finishing industry has an ever-growing problem in controlling and eliminating the discharge of wastewater pollutants. The wastes that cause the problems include rinse waters from metal electroplating solutions and from acidic and alkaline cleaning and pickling solutions. The rinse water is a constantly flowing process stream generally too voluminous to impound economically, yet concentrated enough to be damaging if released to the environment without treatment. If discharged into the environment without treatment, these rinse waters can pollute our natural resources, inhibit or destroy biological activities in the natural environment and in biological sewage treatment processes, and adversely affect materials of construction. Specific examples of detrimental effects include the toxicity of heavy metals and cyanides to various forms of aquatic life (3), the deleterious effect of copper and chromium on biological sewage treatment processes (because of their toxicity to the microflora) (4), and the corrosive effects of acids and bases on sewer lines and metal and concrete structures (5,6).

Several methods presently exist whereby waste waters containing cyanide and metal ions can be treated for clean-up. Many of these techniques are aimed toward the destruction and/or removal of the contaminating species from the water. This task is often accomplished by the addition of chemicals to the effluent stream to convert the undesirable constituents to either a less harmful state or a state whereby it can be effectively removed. Although these techniques are effective in improving the quality of the water effluent, they can introduce solid waste disposal problems. Such is the case in the precipitation of potentially harmful and difficult-to-handle metal hydroxide sludges.

An attractive alternative to existing techniques in the treatment of metal finishing waste waters is reverse osmosis because it offers an opportunity to reclaim valuable chemicals from the process stream as well as to purify water for recycling purposes. In theory, all waste discharge would be entirely eliminated. The savings realized in reduced water consumption and recovered chemicals can be credited against capital and operating costs for the treatment systems. Reverse osmosis can be used in combination with other existing methods to increase their treatment efficiencies. For example, it can be used to treat water from a continuous cyanide destruction process for recycling back to the plant operations, or it can reduce the metal ion concentration prior to an ion exchange treatment process (which would then act as a polisher).

Several researchers (7-12) have examined the technical and economic feasibility of treating various waste water streams from metal finishing operations by reverse osmosis. Computations, based on laboratory test results, have shown this process to be economically viable for treatment of nickel plating streams (8,10,12). Obviously, the degree to which reverse osmosis can be adapted to a recycling process in a plating operation must be determined individually, on a case-by-case basis.

Summary of Previous Work with NS-100 Membranes

The polymer currently used most often as a membrane for reverse osmosis is cellulose acetate. Reid and Breton (13) originally showed that this material had excellent potential as a reverse osmosis membrane. Loeb and Sourirajan (14) later developed the process for fabricating asymmetric membranes for cellulose acetate, now used extensively. Second generation polymer membranes ideally suited for reverse osmosis should exhibit hydrophilicity and ease of membrane formation similar to cellulose acetate, and at the same time should have greater structural rigidity, resistance to chemical degradation and mechanical durability. The new nonpolysaccharide membrane, designated NS-100, which was originally developed as a seawater desalination membrane under contract to the Office of Saline Water (now part of the Office of Water Research and Technology, U. S. Department of the Interior), has shown considerable promise as a second-generation reverse osmosis membrane for metal finishing effluents.

In general, polysaccharide membranes, such as cellulose acetate, have been found suitable for the reverse osmosis treatment of metal finishing waste solutions only at pH's from 4 to 8. Many metal finishing effluents, however, are strongly acidic or alkaline (i.e., acid copper pH $\sim$1; zinc cyanide pH >11). Reverse osmosis membranes comprised of nonpolysaccharide polymers would offer greater

chemical resistance to a wide variety of metal finishing waste solutions. This new nonpolysaccharide membrane (NS-100), showed promise for high chemical resistance during the program funded by the Office of Saline Water. Thus, the NS-100 membrane was applied to metal finishing waste solutions during the second phase of this effort.

During Phase II, reverse osmosis tests were performed on flat-sheet and tubular NS-100 membranes using several types of electroplating rinse water solutions (copper and zinc cyanide, acid copper, chromic acid and Watts nickel). The test solutions were either actual plating solutions diluted to one-tenth full strength or simulated feed solutions that contained one-tenth the average solute concentration of their respective plating baths. High solute rejection of 99.8 to 99.9 percent were observed for copper, zinc, and nickel metal ions in all cases, during test periods ranging from 210 to 540 hours. High cyanide rejections (95.5 and 98.7 percent) were also observed for zinc and copper feed solutions, respectively.

Membrane degradation occurred when testing chromic acid waste water at pH 1.5. A substantial increase in flux accompanied by a decrease in rejection was observed within 7.5 hours of testing.

It was concluded at the end of that study that the NS-100 membrane possessed outstanding characteristics which merited further attention for treating metal finishing effluent waste waters. First, it is chemically resistant to both low and high pH extremes (pH 0.5 to 13.0). In this respect, NS-100 membranes surpass all commercial reverse osmosis membranes. With the exception of chromic acid at Ph 1.5, high membrane performances for NS-100 membranes have been reported for acid copper (pH 0.5), Watts nickel (pH 4.0), copper cyanide (pH 11.8), and zinc cyanide (pH 12.9) plating rinse waters. Cellulose acetate membranes, on the other hand, are operational only in the 2.5 to 7.0 pH range. The commercial polamide (DuPont) can withstand the high pH of cyanide solutions (pH 12), but fail in the acid region below pH 4. Thus, the NS-100 membrane greatly extends the operational pH range for reverse osmosis. It may be possible to treat plating wastewaters without pH adjustments. Second, the membrane could be fabricated into the tubular configuration (1.2 cm I.D. fiber glass-epoxy tubes lined with membrane) which demonstrated its potential for scale-up development. Third, the organic rejections for NS-100 membranes (15) exceed those of aromatic polamides membranes (16,17) and far outstrip the performance of cellulose acetate membranes (18,19,20). Therefore, organic additives to the plating solutions would be less likely to damage the membrane or interfere with a recycling system. Fourth, the membrane could be operated successfully at temperatures of up to 55°C with zinc cyanide feed solutions.

Current Research Program

The primary objective of the current program was to demonstrate the practicality of the NS-100 membrane in reverse osmosis treatment of metal finishing waste waters through long-term operation with acid copper and zinc cyanide baths on a time scale comparable to industrial usage.

Specific objectives of this effort were; to modify the fabrication process for NS-100 tubular reverse osmosis membranes to provide optimum performance toward metal finishing waste waters; to demonstrate sustained performance capabilities of the NS-100 membranes on acid and alkaline rinse waters; and to perform preliminary engineering design studies for a possible field demonstration unit utilizing data from these tests.

SECTION IV

EXPERIMENTAL PROCEDURES

Polymers

NS-100 Membrane

A schematic diagram of the NS-100 membrane fabrication process is shown in Figure 1. The actual barrier film consists of an alkyl-aryl polyurea formed by the interfacial reaction of tolylene diisocyanate (TDI) with the surface of a film of polyethylenimine (PEI) adsorbed onto a microporous support layer (polysulfone). The chemistry of the membrane is illustrated in Figure 2. The performance of the membrane is highly dependent on the thickness and density of the PEI-TDI barrier zone.

NS-101 Membrane

This NS-101 membrane also consists of a microporous polysulfone support film coated with PEI; however isophthaloyl chloride (IPC) is used as a crosslinking agent instead of TDI. Figure 3 illustrates schematic representation of the PEI-IPC crosslinked polymer network.

Tube Cast Membranes

The NS-100 membranes were fabricated in tubular form for use in 1.27-cm diameter commercial reverse osmosis tubes (obtained from Abcor, Inc.). The microporous polysulfone liner was prepared in the following manner. A 1.41-cm-I.D. stainless steel tube was filled with a 15 percent solution of Union Carbide P-3500 polysulfone resin in dimethylformamide (DMF). The tube was drained, and a 1.39-cm-diameter aluminum bob was passed through the tube to provide a uniform film of casting solution on the inside wall. The coated tube was then lowered mechanically into 1 percent aqueous DMF in a smooth, continuous motion, gelling the polysulfone coating. The seamless polysulfone tube was removed and soaked in fresh water for 30 minutes or more.

The NS-100 membrane was fabricated by immersing the seamless polysulfone tube in an aqueous solution containing 0.67 percent PEI by weight (Tydex 12, Dow Chemical Company) for 5 minutes. Upon removal from the PEI solution, the tube was immersed in 0.5 percent TDI in hexane for 1/2 to 1-1/2 minutes, then air-dried.

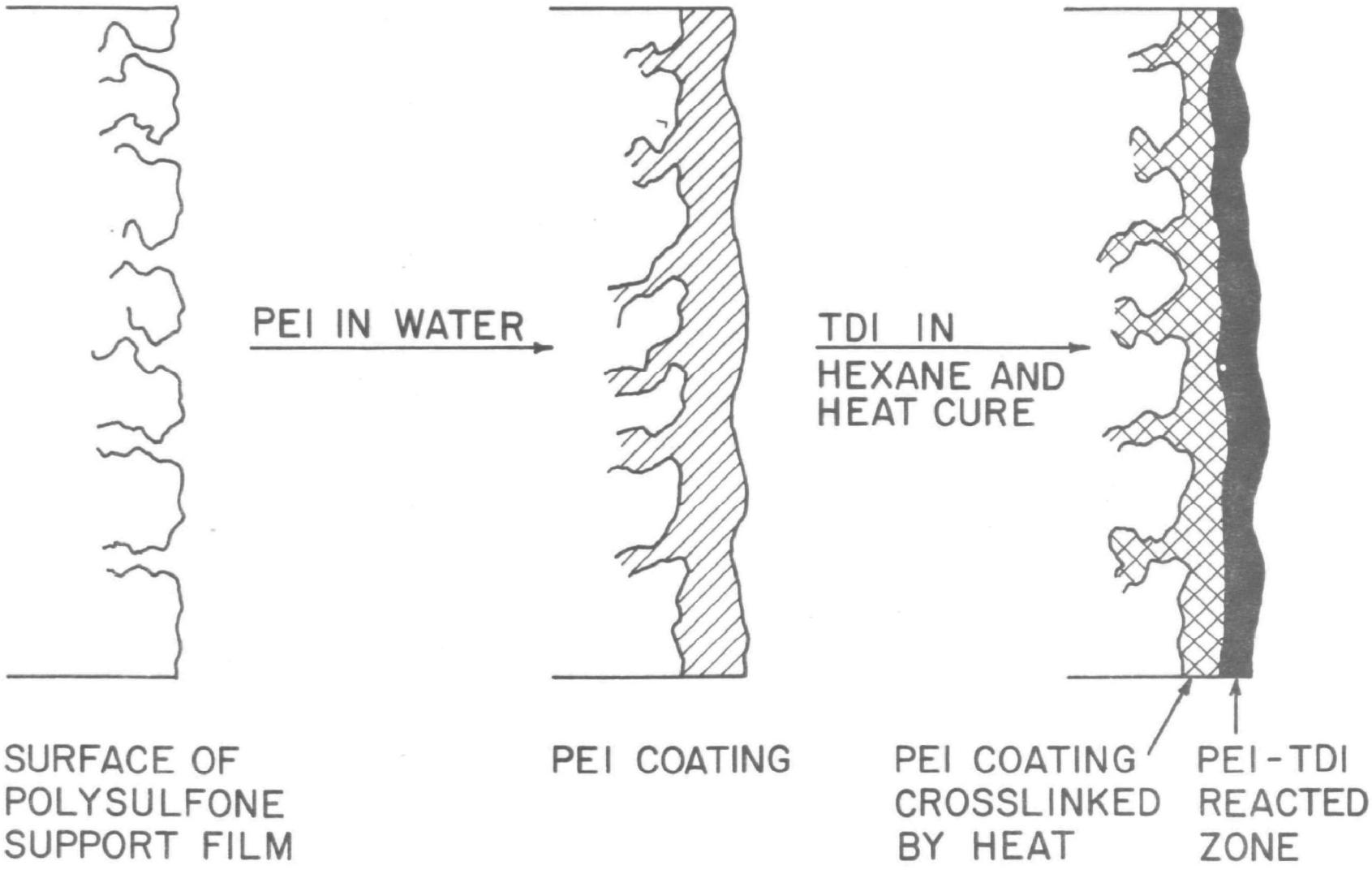


Figure 1. Schematic Representation of NS-100 Membrane

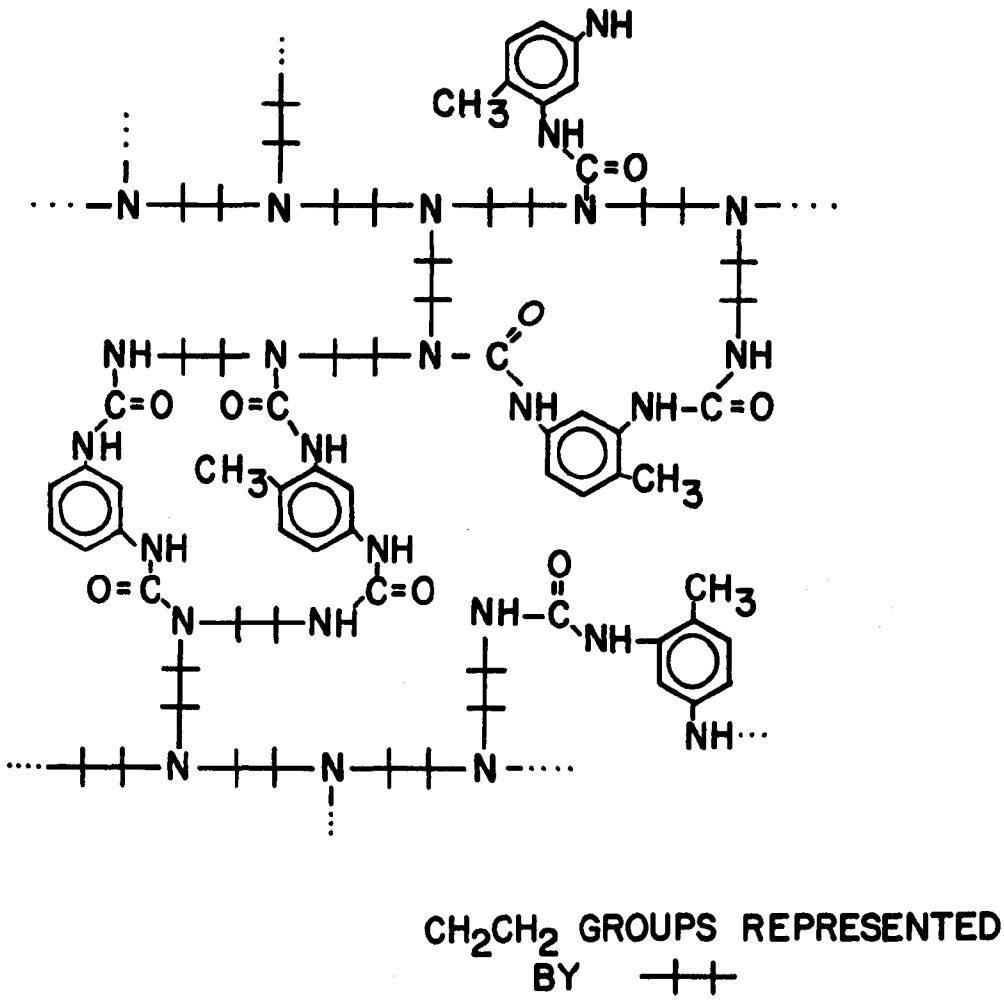


Figure 2. Idealized Structure of Polyethylenimine Crosslinked with Tolylene 2,4-Diisocyanate

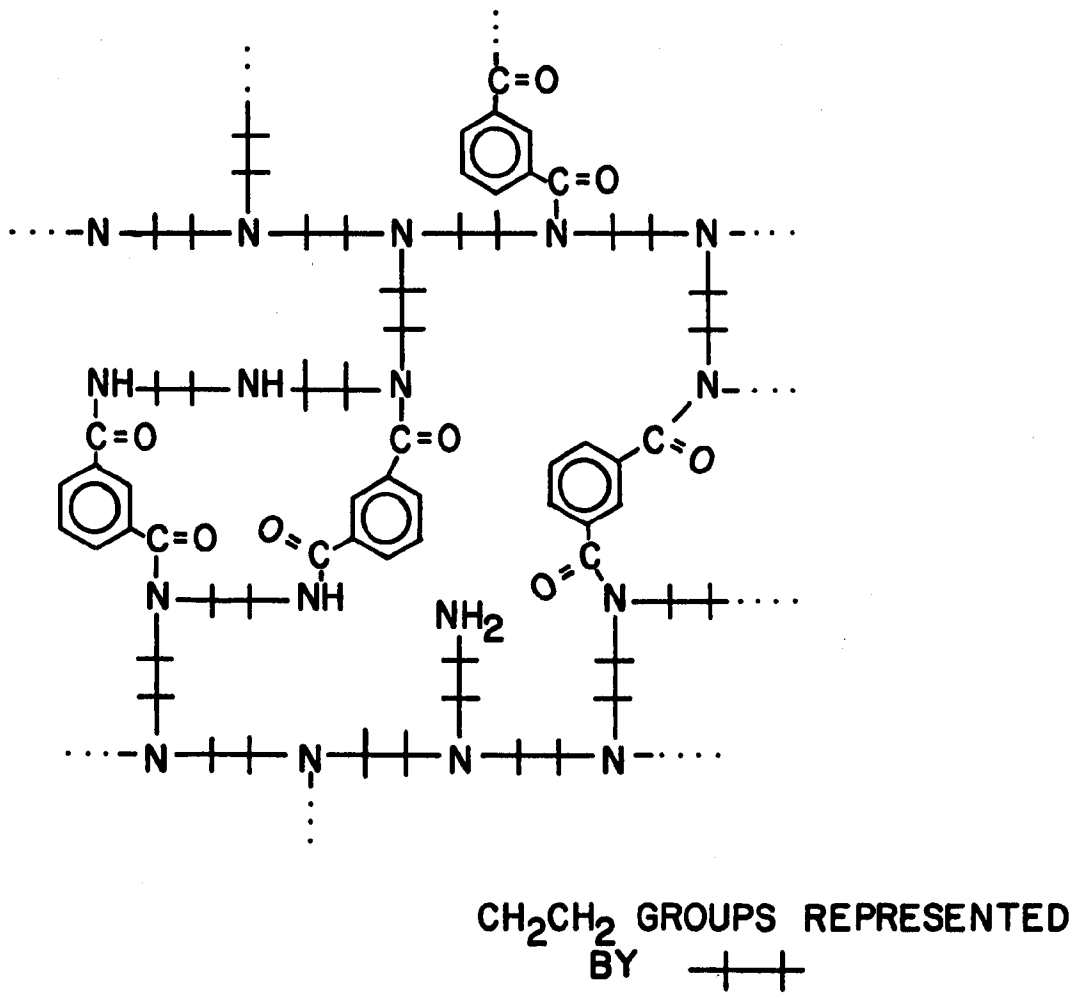


Figure 3. Idealized Structure of Polyethylenimine Crosslinked with Isophthaloyl Chloride

It was then inserted into an insulated cylindrical oven equipped with zone heating controls and thermocouples (see diagram in Appendix A) for heat curing. It was subsequently pulled into a microporous, polysulfone-coated, 1.27-cm-diameter Abcor fiber glass tube. End seals were effected by means of rubber grommets. A detailed fabrication procedure for the NS-100 tubular membranes is presented in Appendix A.

Reverse Osmosis System

The pilot-scale reverse osmosis test loop used in this program is illustrated schematically in Figure 4. The system was instrumented and equipped as follows:

1. A 115-liter brine reservoir.
2. A Moyno pump, Model 3RA-8-20, equipped with a magnetic starter. The pump had a rated capacity of 14 lpm (3.7 gpm) at 41.4 bars (600 psig) and a pressure range of 0 to 55 bars (0 to 800 psig).
3. Low- and high-pressure safety switches to disconnect the power from the magnetic starter via a relay. An operator must reset the starter.
4. A 115-liter constant-temperature bath to maintain the selected temperature of the feed. The refrigeration system was an air-cooled type and had a capacity of a 1/3-horsepower compressor.
5. Fittings and gauges for connection of standard commercial tubular-membrane modules. Lines were provided for returning product water to the feed reservoir to permit continuous operation.

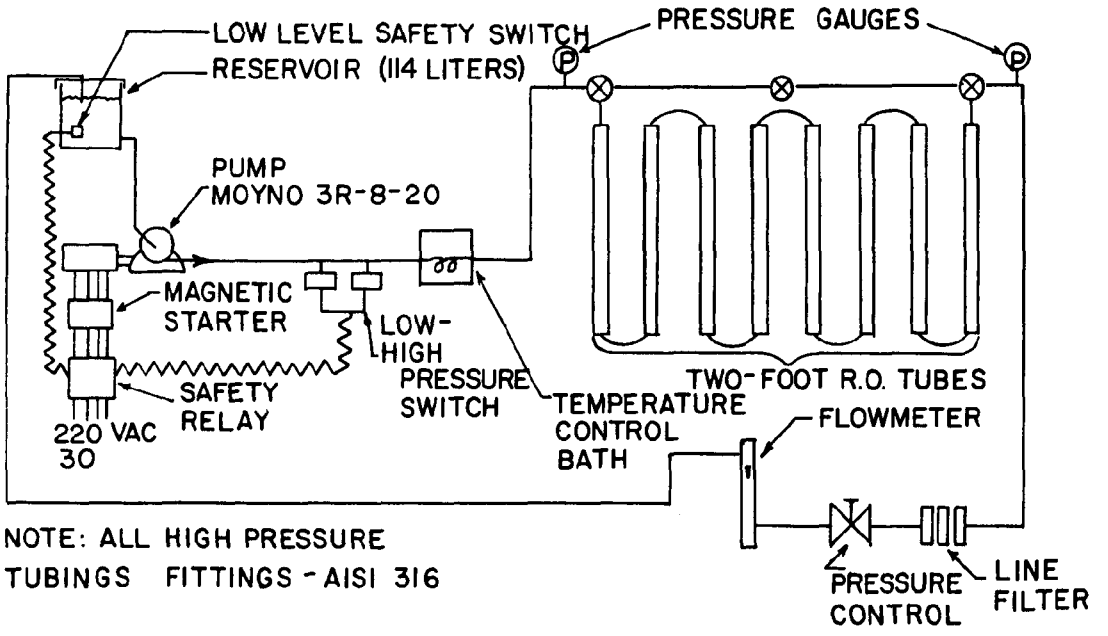


Figure 4. Flow Diagram for Reverse Osmosis Test Loop

6. A high-pressure filter to prevent contamination of the system pressure control valve.
7. A Hoke needle-type throttle valve for controlling system pressure.
8. A flowmeter to indicate system flow (Brooks rotameter).
9. A Weis thermometer for monitoring feed water temperature.

Photographs of this system in operation are shown in Figures 5, 6, and 7.

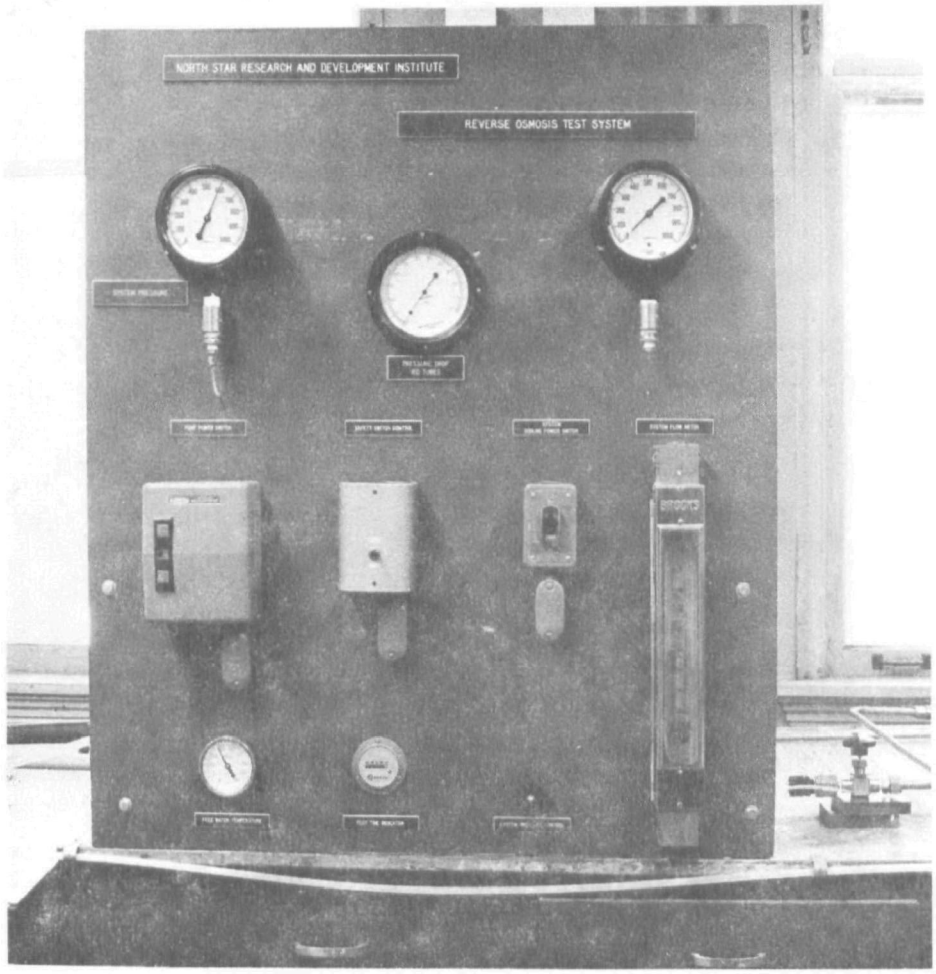


Figure 5. Photograph of Reverse Osmosis System Used in Long Term Studies, Showing the Control Panel, Flowmeter, and Throttle Valve for System Pressure Control.

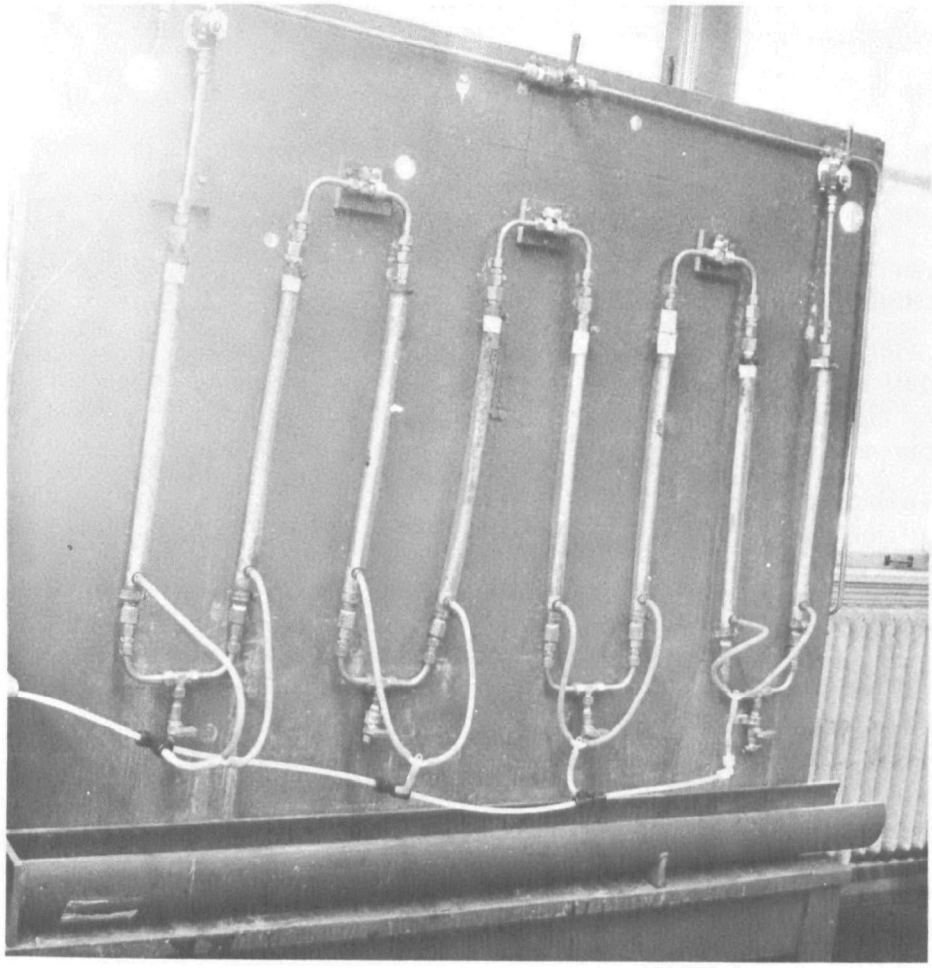


Figure 6. View of the Reverse Osmosis Board Showing Eight Tubes Connected in Series, with Product Water Collection Line Attached.

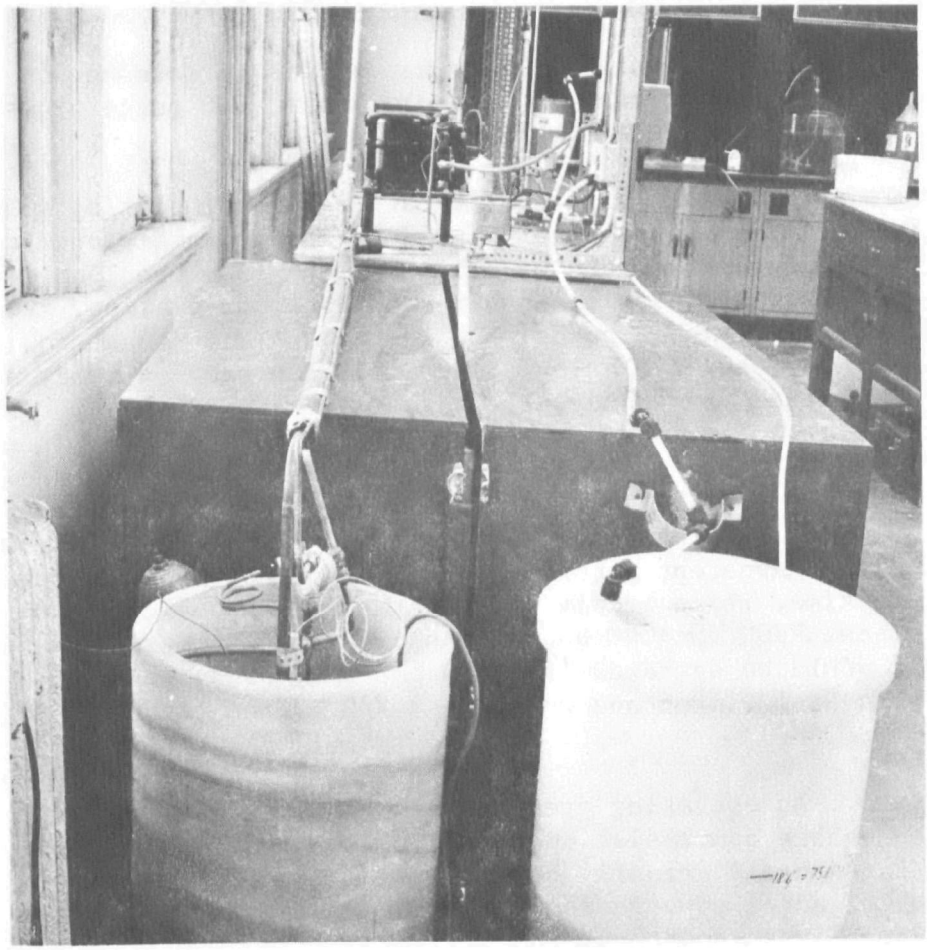


Figure 7. View of Reverse Osmosis System Showing Feed Reservoir, Heat Exchange Reservoir, and Refrigeration Unit (Reverse Osmosis Pump Located Inside Plywood Sound Shield in Foreground).

The construction of the membrane/fiber glass tube used in this test line are illustrated in Figures 8 and 9. Figure 8 depicts a longitudinal section of a fiber glass reverse osmosis tube with a polysulfone support liner. Figure 9 is a photograph showing the polysulfone liner, Abcor fiber glass tube with end fittings, and the fiber glass tube enclosed in the Tygon product water collection sleeve.

Reverse Osmosis Testing

The conditions used to measure the reverse osmosis performance of the tubular membranes during long-term testing were 41.4 bars (600 psig) pressure and 7.0 lpm (1.8 gpm) feed flow rate at a temperature of 25°C.

The feedwaters used in the long-term tests were actual plating solutions of acid copper and zinc cyanide, each diluted to approximately one-tenth full strength. Two acid copper baths were tested, one from Precious Metals Platers, Inc., Hopkins, Minnesota, and the other from Superior Plating, Inc., Minneapolis, Minnesota. Two zinc cyanide baths were tested. A mid-range zinc cyanide bath was obtained from Superior Plating, Inc. and a low-range zinc cyanide plater solution was obtained from Honeywell Inc., Golden Valley Plant, Golden Valley, Minnesota.

Test Duration. 1200 hours of continuous operation with each plating solution. Any trends in membrane performance would be noticeable in 1200 hours of testing. If no apparent deterioration or degradation were observed during this period ot time, it is likely that the membranes would perform satisfactorily for at least 2000 to 3000 hours. Assuming that a reverse osmosis purification unit would be operated 16 hours per day, 5 days a week, the expected lifetime for an NS-100 membrane would be 3-1/8 months for each 1000 hours of operation.

Pressure. An operating pressure of 41.4 bars was chosen for this program as a reasonable commercial operating range. The fiber glass-supported tubular membranes could actually be operated at pressures up to 105 bars (1500 psig). However, added power costs for high pressure pumping begin to outweigh water throughput improvements at about 55 bars (800 psig). Below 41.4 bars, savings in pump costs are lost through decreased operating efficiency of the membrane system.

Concentration. Actual plating baths (acid copper and alkaline zinc cyanide) were diluted to 10 percent of full strength. This concentration represented a 10- to 100-fold higher level than existed in plating rinse waters. However, it was considered essential in this study to demonstrate the membrane's ability to withstand concentrations which would be encountered in an actual permeate-concentrate recycling situation. These bath concentrations, at one-tenth full strength, thus represented a severe test of the membrane system. The use of actual plating baths was desirable to determine the effect, if any, of organic bath additives on the membrane that would be encountered in a pilot demonstration facility.

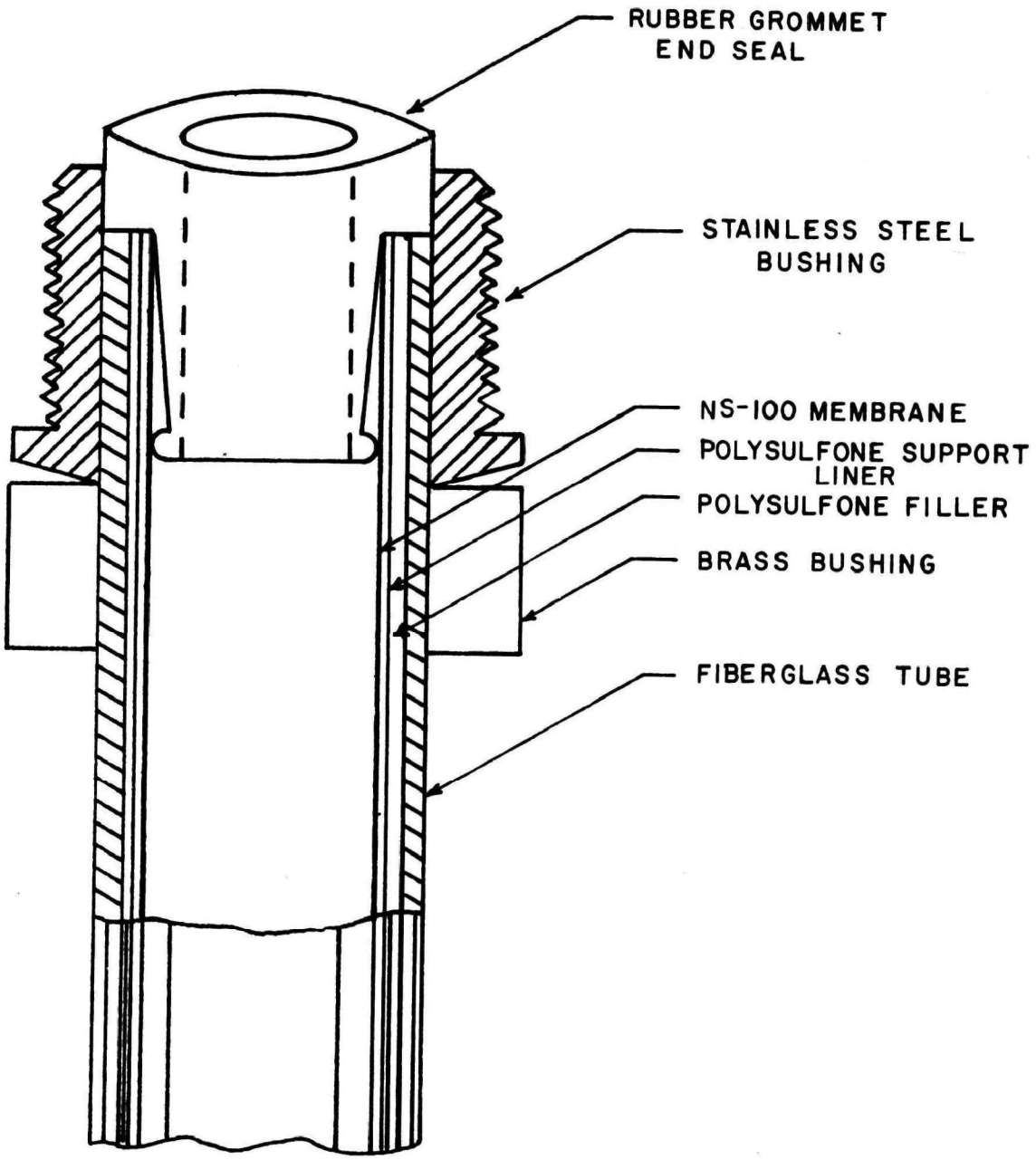


Figure 8. Longitudinal Section of a Fiber Glass Reverse Osmosis Tube with NS-100 - Polysulfone Membrane Support Composite

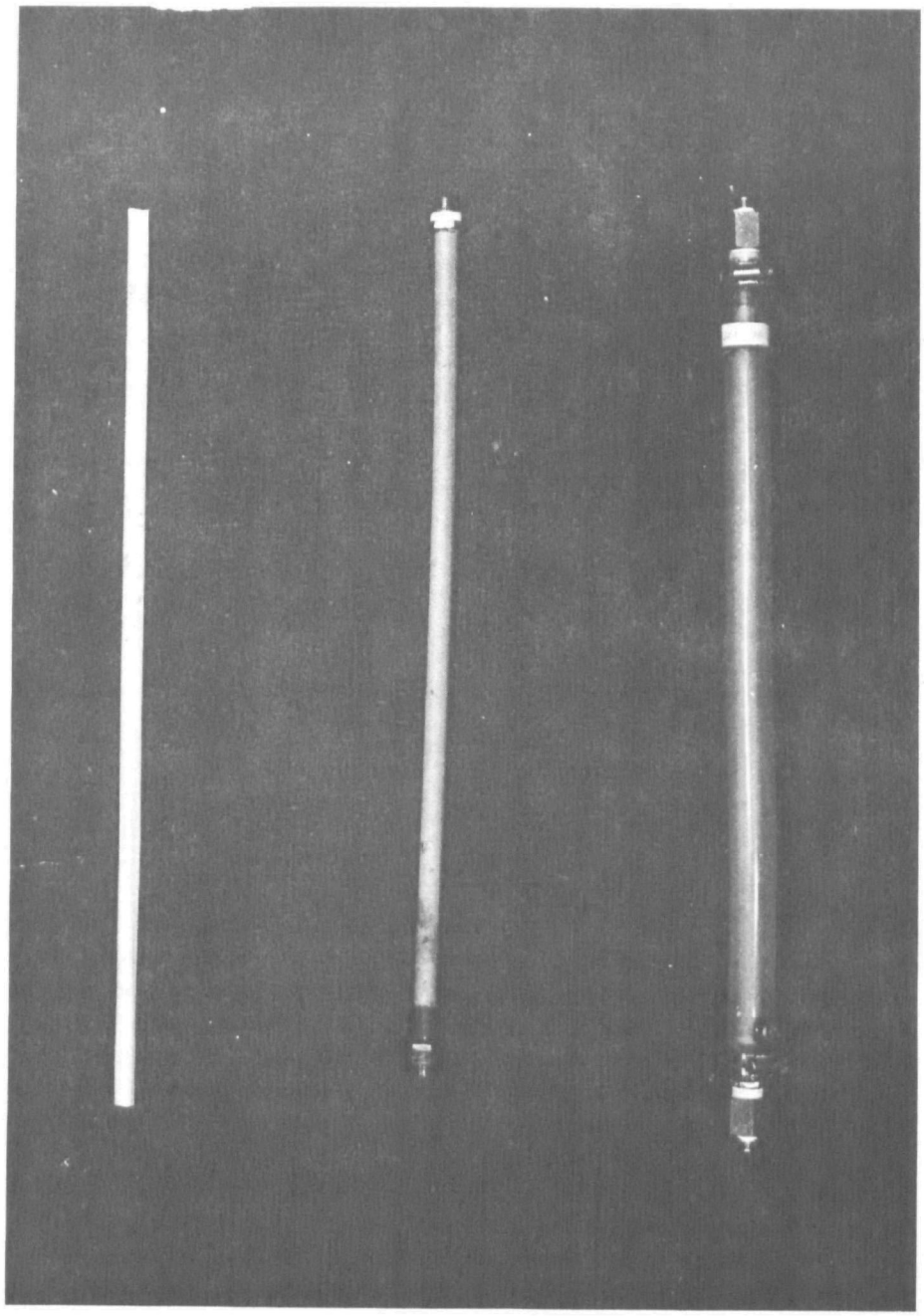


Figure 9. Photograph of Tubular Polysulfone Support Liner (left), Abcor Fiber Glass Tube with End Fittings (center), and Fiber Glass Tube Enclosed in a Tygon Sleeve (right).

Membane Evaluation

Water flux measurements were carried out by measuring the flow rate of the purified water stream from a tubular reverse osmosis unit.

Rejection measurements were made using standard analytical methods as indicated in Table 1. Assays were performed on the permeate from each tube and the the feed during each analysis. The rejection was calculated as the percent of the total chemical content in the feedwater returned by the membrane. The percent rejection, R, is defined as

$$R = \frac{C\ (feed) - C\ (permeate)}{C\ (feed)} \times 100$$

where C represents the concentration of the species being measured. More detailed feedwater make-up and analyses are given in the appropriate sections of the report.

TABLE 1. REJECTION EVALUATION TECHNIQUES FOR REVERSE OSMOSIS MEMBRANE PERFORMANCE

Constituent	Method/Equipment
Zinc	Atomic Absorption/Techtron AA 120*
Copper	Atomic Absorption/Techtron AA 120
Cyanide	Orion specific ion electrode/Orion digital pH meter model #701 (21)
	Titration (modified Liebig method using silver nitrate) (22)
Total Organic Carbon	TOC Beckman Analyzer/Model #915
Total Dissolved Solids	Gravimetric (23)
Acidity/Basicity	Orion Digital pH Meter/Model #701

*Zinc atomic absorption standard solution contained sodium cyanide and sodium hydroxide as background in the ratio of the stock plating solution (Zn:NaCN:NaOH was 1:2.4:3.5).

SECTION V

PROGRAM RESULTS

The results of this experimental program are divided into three separate parts; optimization of NS-100 tube fabrication, long-term membrane performance test results toward acid copper plating bath rinse water, and long-term membrane performance toward zinc cyanide plating bath rinse water.

Optimization of NS-100 Tube Fabrication

In earlier work, tubular NS-100 membranes with fluxes of as high as 27 $1/m^2$-hr (16 gfd) at salt rejections of 99 percent were obtained. These results, however, were more the exception than the rule. Most tubes gave fluxes in the range of 8.5 to 14 $1/m^2$-hr (5 to 8 gfd). It was reasoned that the performance of the membrane was highly dependent on the thickness and density of the PEI-TDI barrier zone (see Figure 1). Therefore, the optimization study was focused on factors which may have an effect on the thickness and density of this layer in order that high flux membranes could be consistently fabricated. Three fabrication variables were examined in the optimization study: the concentration of the TDI solution in the interfacial polymerization step, the time of exposure to the TDI solution, and the degree of heat cure employed. The first two factors determined the thickness of the alkyl-aryl polyurea barrier layer on the underlying PEI layer. The third factor affected the density of both the barrier layer and the underlying PEI layer.

Nonoptimized Membranes: Performance Towards Plating Solutions

An initial set of tubular NS-100 membranes were fabricated using conditions representative of earlier tube fabrication work. These tubes were tested under reverse osmosis conditions with an actual zinc cyanide plating solution diluted to one-tenth its strength, and with an actual acid copper plating solution, also diluted to one-tenth its strength. Table 2 lists the data obtained from these tests.

The data in Table 2 illustrated the starting point for this optimization effort. Membrane flux values were 11 to 19 $1/m^2$-hr (6.7 to 11.0 gfd) for the acid copper bath, and 5.6 to 10 $1/m^2$-hr (3.3 to 6.2 gfd) for the zinc cyanide bath. These fluxes were thus both rather low and rather variable. The higher flux rate for the acid copper bath was due to two effects: lower osmotic strength in the acid copper bath vis-a-vis zinc cyanide bath, and some swelling and opening of the crosslinked PEI matrix by salt formation between the acid and the PEI amine groups. Rejections of zinc, copper, cyanide, and total organic carbon were very good. There was fair-to-good rejection of sodium hydroxide, but apparently no rejection of acid.

TABLE 2. EFFECT OF TDI CONCENTRATION ON THE PERFORMANCE OF TUBULAR NS-100 REVERSE OSMOSIS MEMBRANES WITH ZINC CYANIDE AND ACID COPPER PLATING RINSE WATERS

Tube Number	TDI Concentration in Hexane (percent)	Membrane Performance							
		Zinc Cyanide Test*					Acid Copper Test**		
		Flux*** (l/m^2-hr)	Zinc Rejection (percent)	Cyanide Rejection (percent)	TOC Rejection (percent)	Permeate pH	Flux*** (l/m^2-hr)	Copper Rejection (percent)	Permeate pH
338-T-4	0.50	6.6	>99.9	98.2	98	12.0	12.2	99.8	1.2
338-T-5	0.50	10.0	99.6	95.8	96	12.4	18.5	98.8	1.1
338-T-6	0.50	10.5	99.5	97.6	97	12.1	18.7	99.6	1.2
338-T-12	0.50	5.6	>99.9	99.5	99	11.3	11.4	>99.9	1.2

*21-hour test on 1/10th actual zinc cyanide bath, 749 ppm (0.10 oz/gal) Zn, 790 ppm (0.11 oz/gal) CN, 1840 ppm TOC, pH 13.2.

**20-hour test on 1/10th actual acid copper bath, 5025 ppm (0.67 oz/gal) Cu, 28 ppm TOC, pH 1.1.

***multiply by 0.59 to convert to gfd.

It appeared from the very high rejections of metals and cyanide that milder membrane fabrication conditions could probably be exercised. The preferred optimization approach, then, was to reduce the membrane fabrication parameters of time, concentration, and heat cure with the objective of maximizing membrane permeate flux while minimizing loss of solute rejection characteristics.

Optimization of NS-100 Membranes

Subsequent optimization studies used 1 percent sodium chloride feed instead of the actual zinc cyanide and acid copper solutions. This change in the testing procedure expedited the membrane optimization task, since the sodium chloride rejection could be conveniently determined by conductivity measurements. This allowed more tubes to be fabricated and tested in a shorter period of time. A membrane exhibiting high performance for sodium chloride would undoubtedly yield comparable results with the plating rinse water feeds.

The sodium chloride optimization data are presented in Table 3; 30 tubes were fabricated under varying conditions in this effort.

Examination of membrane heat cure conditions indicated best results at a heat cure temperature of 98°C for 5 minutes. At higher temperatures, membrane flux values dropped rapidly; at lower temperatures, salt rejection fell, indicating an incomplete cure of the PEI-TDI layer.

Examination of the effect of exposure time of the PEI-coated polysulfone tubes to the TDI reactant indicated that exposure periods of 15 seconds were sufficient to produce a good PEI-TDI reaction product layer. Attempts to lower the TDI concentration in hexane to less than 0.5 percent by weight resulted directly in significant losses in solution rejection properties.

A minimum set of fabrication conditions thus appeared to involve exposure of a PEI-coated polysulfone tube to a 0.5 percent TDI solution for 15 seconds, followed by air drying and heat curing at 98°C for 5 minutes. This minimum set of conditions was arbitrarily altered to include a 30-second dip in TDI solution rather than a 15-second dip. In examining the mechanics of smoothly immersing and removing a tubular membrane from a dip tank, a 15-second time period appeared too short and too strict an operational variable to control uniformly.

Under these conditions tubes could be fabricated with fluxes between 14 to 20 $1/m^2$-hr (8 to 12 gfd) at 98 to 99 percent salt rejection, tested against a 1 percent sodium chloride feed. This was a considerable improvement over the 4.2 to 9.3 $1/m^2$-hr (2.5 to 5.5 gfd) fluxes obtained at the start of the program with the same feed.

These results were not as good as was hoped. Flat sheet fabrication studies at North Star have consistently generated NS-100 membranes with twice this flux. A basic problem in this system appeared to be differences in microporous polysulfone films cast in 1.27-cm tubes versus those cast as flat sheets on glass surfaces. An examination of possible changes in tube

TABLE 3. OPTIMIZATION OF TUBULAR NS-100 MEMBRANES WITH ONE-PERCENT SODIUM CHLORIDE FEED

Number of Tubes Tested	Fabrication Parameter			Reverse Osmosis Performance**			
	TDI Concentration in Hexane (percent)	Heat Cure* Temperature (°C)	Exposure Time to TDI Solution (seconds)	Flux*** (l/m^2-hr) Average Value	Flux*** (l/m^2-hr) Range	Rejection (%) Average Value	Rejection (%) Range
4	0.5	110	60	7.7	4.2-9.3	99.2	98.8-99.6
3	0.5	104	60	14	10.5-16	97.6	95.2-99.1
5	0.5	98	60	16	10.5-30	98.2	96.5-98.9
3	0.5	94	60	11	8.1-14	82	50-98.5
6	0.5	98	30	14	8.1-20	98.5	97.7-99.2
2	0.5	98	15	16	15-17	98.6	98.5-98.6
3	0.5	98	10	22	15-37	93.8	88.5-97.8
2	0.45	98	15	15	12-18	94.1	92.5-95.6
2	0.40	98	15	13	11-15	89.0	86.0-93.4

*All membranes were heat cured 5 minutes in insulated cylindrical oven at their indicated temperature.

**Readings were taken after 2 hours of testing.

***Multiply by 0.59 to convert to gfd.

casting procedures for seamless polysulfone tubes to improve resulting membrane characteristics unfortunately could not be carried out within the scope of this program.

A second area of concern in this optimization study related to the tight boundaries for membrane fabrication parameters. One had to work with very dilute TDI solutions (0.5 percent solids) at very short exposure times (15 to 30 seconds), and encountered sharp dependence of flux properties on the severity of the following heat cure cycle. The high sensitivity of membrane performance characteristics to small changes in these parameters leads to considerably variability in performance between individual membrane tubes. A partial answer to this problem is the use of isophthaloyl chloride in place of TDI, as will be described in the following section.

NS-101 Membrane Fabrication

Despite concentrated efforts to optimize the NS-100 membrane system it became evident during this program that tubes of high flux and high salt rejections could not be prepared in a reproducible manner. In the meantime, related efforts on a reverse osmosis membrane contract with the Office of Water Research and Technology showed that isophthaloyl chloride (IPC) could be used in place of TDI and led to considerable flux improvement in flat-sheet membranes. These modified membranes were designated as NS-101. Late in this program the decision was made to fabricate a few NS-101 tubes and apply them toward reverse osmosis recycle of zinc cyanide plating wastes.

Fabrication of tubular NS-101 membranes, consisting of a PEI-IPC layer as the salt barrier zone instead of a PEI-TDI layer, was accomplished following the same basic procedure as was developed for the NS-100 membranes. Since time did not permit a thorough optimization study of this experimental membrane system, two procedural modifications were employed to ensure the formation of a tightly crosslinked PEI-IPC layer. First, a higher concentration (1 percent in hexane) of the crosslinking agent (IPC) was used to prepare these membranes as opposed to the 0.5 percent TDI solution. Second, the exposure time of the membrane to the hexane solution was increased from 1/2 to 1 minute.

Specifically, a tubular polysulfone support film was immersed in the aqueous PEI solution (0.67 percent PEI by weight) for 5 minutes. The membrane was subsequently exposed for 1 minute to a 1 percent isophthaloyl chloride in hexane solution, air-dried, and heat-cured at 98°C for 5 minutes.

Table 4 illustrates the reverse osmosis performance of three NS-101 membranes prepared in this manner with 1 percent sodium chloride. The NS-101 exhibited improved water fluxes, however with much variation. Salt rejections were somewhat low, ranging from 90 to 95.5 percent. Although time did not permit a thorough investigation, it may be possible to improve the reverse osmosis performance of this system by studying fabrication parameters such as IPC concentration, reaction times, and heat cure conditions.

TABLE 4. REVERSE OSMOSIS PERFORMANCE OF TUBULAR NS-101 MEMBRANES WITH ONE-PERCENT SODIUM CHLORIDE FEED

Number of Tubes Tested	Reverse Osmosis Performance*			
	Flux (l/m^2-hr)**		Rejection (percent)	
	Average Value	Range	Average Value	Range
3	30	15-31	93.0	90.0-95.5

*All tests were carried out at 41.4 bars (600 psig), 25°C, 7.0 lpm (1.7 gpm) flow rate. Readings were taken after 2 hours of testing.

**Multiply by 0.59 to convert to gfd.

Long-Term Membrane Performance Toward Acid Copper Plating Bath Rinse Water

An actual acid copper plating bath, provided by Precious Metal Platers, Inc., Hopkins, Minnesota, was diluted to approximately one-tenth of full strength and used as the feed for a set of eight 2-foot-long NS-100 membrane tubes. The test was performed for a total of 1222 hours. During this time the feed solution was changed every 2 weeks and kept fresh by frequent additions of diluted plating bath. Permeate was recycled back to the feed reservoir, except during the sampling periods, to maintain constant feed concentrations.

Samples of permeate were drawn from each tube at frequent intervals and the flux recorded. Also, pH was measured and the copper concentration determined on the permeate and feed solution. Total dissolved solids (TDS) and total organic carbon (TOC) analyses were performed on the permeate and feed at longer intervals during the study. Because of insufficient weighable residues in the sample permeate, the TDS analyses were not always reliable. Detailed performances of each tube are listed in Appendix B of this report.

Membrane Rejection

Table 5 contains performance data for eight 2-foot tubular NS-100 membranes determined at 24 hours and 1222 hours. Copper rejections were uniformly above 99 percent in six of eight tubes. Mechanical failure was apparent for one of the tubes (348-T-37C) which showed about 93 percent copper ion rejection, and was suspected for the other tube (348-T-34A) which showed about 97 percent rejection. Measurements were discontinued on 348-T037C when it became apparent that a mechanical failure had occurred. Inspection of this tube after the test revealed a large defect at one end, which accounted for its poor performance.

Table 6 illustrates the average performance of each tube during this period.

Tube Number 348-T-43A was particularly noteworthy, exhibiting an average copper rejection of >99.9 percent with an average flux of 22 l/m^2-hr (12.8 gfd). The sulfuric acid was not rejected by the membranes, however. The pH's of the

TABLE 5. INITIAL AND FINAL PERFORMANCES OF TUBULAR NS-100 MEMBRANES WITH ACID COPPER PLATING SOLUTION

Time (hours)	Measurement	Tube #348-T-								Feed Analysis*
		30B	43A	39F	22B	31A	28A	34A	37C**	
24	Flux (l/m^2-hr)***	14	23	20	34	24	26	28	30	--
24	Concentration of Copper (ppm)	7.40	4.20	17.9	53.5	27.0	35.0	184	260	3950
24	Copper Rejection (%)	99.8	99.9	99.5	96.1	99.3	99.1	95.3	93.4	--
48	TDS Rejection (%)	99.5	98.7	99.4	98.3	99.1	99.7	96.7	96.1	--
24	TOC Rejection (%)	65	70	74	70	74	65	70	78	--
24	pH	1.18	1.17	1.14	1.07	1.11	1.13	1.09	1.11	1.17
1222	Flux (l/m^2-hr)***	14	22	19	23	21	20	22	--	--
1222	Concentration of Copper (ppm)	14.3	4.70	12.4	52.0	28.0	34.0	77.5	--	5300
1222	Copper Rejection (%)	99.7	>99.9	99.8	99.0	99.5	99.4	98.5	--	--
1009	TDS Rejection (%)	99.6	99.7	99.6	98.8	99.2	99.0	97.1	--	--
1009	TOC Rejection (%)	52	63	67	76	67	65	61	--	--
1220	pH	1.39	1.41	1.39	1.34	1.35	1.35	1.34	--	1.40

*Feed Composition . . Copper Concentration . . . 3850-5850 ppm (0.514-0.781 oz/gal)
Total Dissolved Solids . . 12.4-15.5 g/l (1.65-2.07 oz/gal)
Total Organic Carbon . . . 23 ppm
pH 1.14-1.44

**Tube 348-T-37C failed at 428 hours.

***Multiply by 0.59 to convert of gfd.

TABLE 6. AVERAGE PERFORMANCE DATA FOR NS-100 TUBES DURING THE ACID COPPER TEST

Measurement	Number of Measure-ments	Tube Number							Feed Analysis
		348-T-30B	348-T-	348-T-39F	348-T-22B	348-T-31A	348-T-28A	348-T-34A	
Average Flux (1/m -hr)*	15	14	22	19	28	22	22	34	--
Average Rejection of Copper (%)	15	99.8	99.9	99.7	98.7	99.4	99.4	97.1	4940 ppm
Average Rejection of TDS (%)	5	99.6	99.3	99.1	98.7	99.2	99.2	96.8	13.83 g/l
Average Rejection of TOC (%)	3	60	66	71	69	71	69	67	23 ppm
Average pH	15	1.23	1.22	1.19	1.13	1.16	1.17	1.12	1.19

*Multiply by 0.59 to convert to gfd.

permeates were essentially identical to the pH of the feed. This may not be a drawback because acid copper plating operations are normally followed directly by other acid-based metal finishing operations. Total dissolved solids determinations confirmed the high copper rejections observed. Rejection of dissolved organic constituents, including brighteners, was in the 60 to 78 percent range. Comparing this with known rejection characteristics of NS-100 membranes towards organic compounds (15), it appears the data imply presence of low molecular weight organic species in the acid copper bath, such as ethyl alcohol.

Membrane Flux

In Figure 10, the flux and copper rejection for each tube was plotted as a function of operating time. Membrane flux varied from one tube to the next, ranging from 14 to 30 l/m^2-hr (8.3 to 17.6 gfd) at 24 hours, and 14 to 23 l/m^2-hr (8.0 to 13.8 gfd) at the end of 1220 hours. The normal operating range appeared to be in the 20 to 24 l/m^2-hr (11 to 14 gfd) range. After a rapid initial flux decline during the first 100 hours tubes leveled out to relatively constant flux readings. A flux *increase* of about 10 percent was observed for all tubes after 648 hours. At this time, due to a leak in a pipe housing on the pump shaft, the line had been stopped and tubes had been allowed to stand for 24 hours in contact with de-ionized water. Apparently, the tubes experienced osmotic cleaning during this period since subsequent water flux values were higher and remained so until almost the end of the test. These results indicated that flux loss of this system due to fouling could be restored to a significant degree by flushing with water.

Effect of Feed Concentration on Membrane Performance

During the long-term acid copper study, time was taken to gather data on the effect of higher feed concentrations on membranes flux and rejection. Thus, after 1077 hours of operation the product return line was disconnected and the feed solution was allowed to concentrate for 10 hours. Results are shown in Figure 11, where the average flux and average rejection of copper was plotted as a function of copper concentration. Average membrane flux decreased linearly with increasing copper concentration. The average copper rejection held at 99.3 percent and was not affected over this concentration range.

Plating Solution

During the last 70 hours of testing, the feed was changed to a Superior Plating acid copper rinse solution. The reason for this change was to see if the membranes would give the same performance with other acid copper solutions which may possibly contain different brightener agents. The Superior Plating acid copper solution contained Udylite UBAC #1 as the brightener additive, whereas the organic additive for the Precision Metals bath was CUE Bath. Feed analysis of this feed solution revealed approximately the same concentrations of copper and total organic carbon as the Precious Metal Platers bath. Performance results were identical for both acid copper baths. (Data are given in Appendix B.)

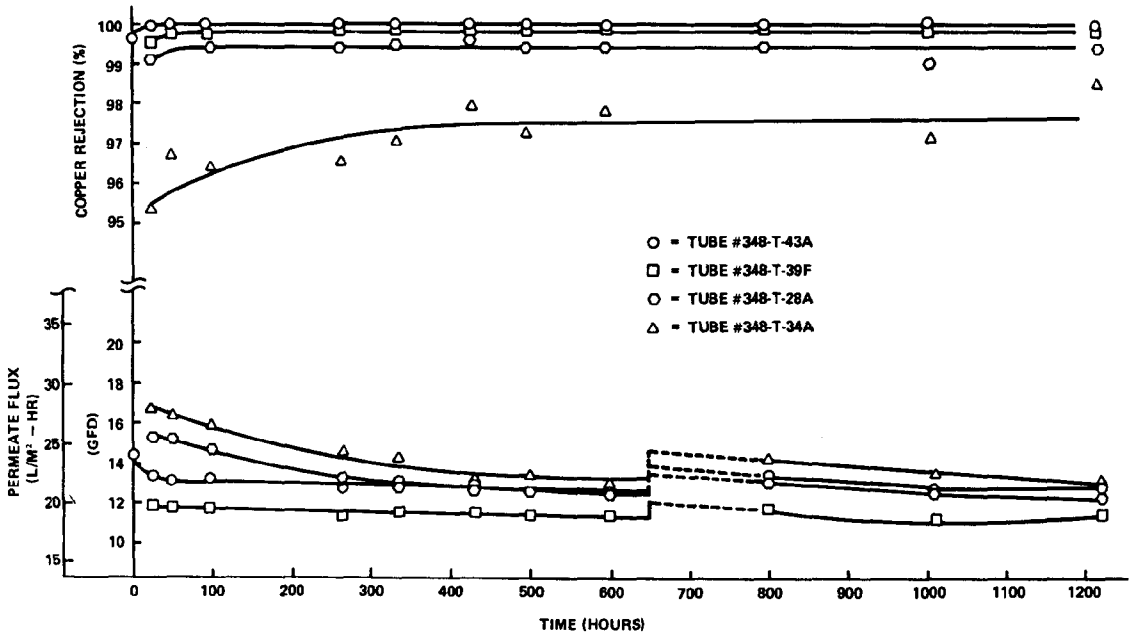
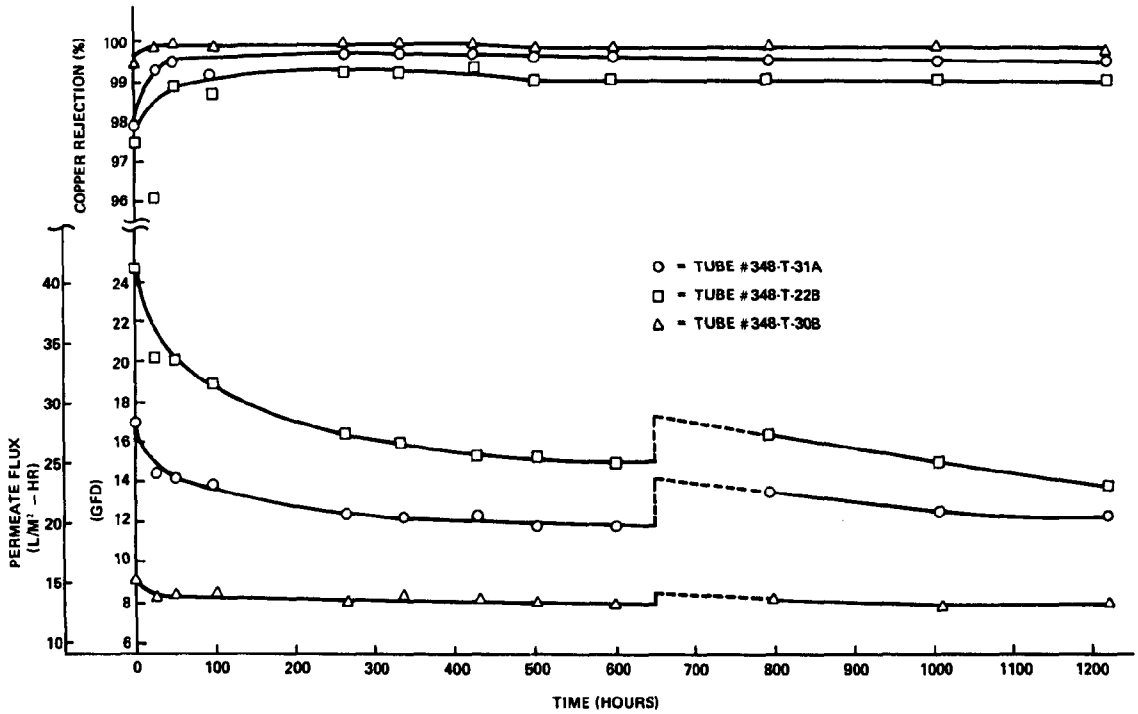


Figure 10. Plot of Reverse Osmosis Performance of NS-100 Tubular Membranes Toward Acid Copper Rinse Water. (Tubes 43A, 39F, 28A, 34A, above, and Tubes 22B, 31A, and 30B, below.)



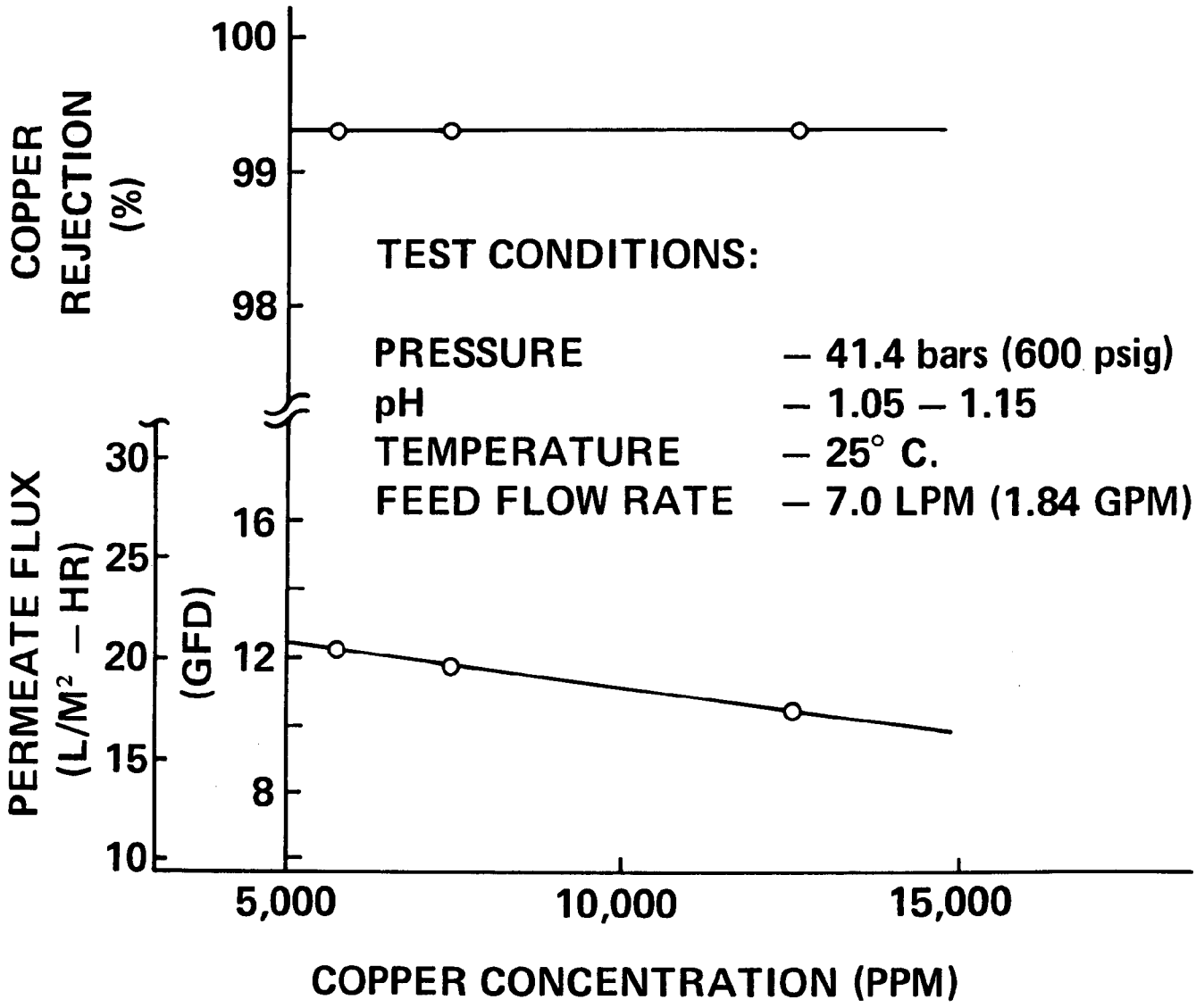


Figure 11. Effect of Acid Copper Rinse Water Concentration on NS-100 Flux and Copper Rejection

Summary of Results: Acid Copper Test

Results of the reverse osmosis study with acid copper feedwater may be summarized as follows:

1. The NS-100 membrane demonstrated long-term stability in treating highly acidic pH (1.1 to 1.4) copper rinse water over 1220 hours.

2. Copper rejections for six NS-100 tubes were greater than 99 percent during most of the test.

3. High rejections of TDS (greater than 99 percent) were observed throughout the test for the high copper-rejecting membranes. Rejection of dissolved organic constituents, including organic brighteners, was in the 60 to 80 percent range.

4. Sulfuric acid was not rejected by the NS-100 membranes.

5. Normal water flux performance was in the 20 to 24 l/m^2-hr (11 to 14 gfd) range. Large variations in flux were observed from tube to tube, especially at start-up.

6. Flux decline was minimal after the first 100 hours of testing. Substantial flux could be restored by osmotic cleaning.

7. Water flux decreased linearly with increasing feed concentration; however, copper rejection remained constant over the concentration range studied (5,000-15,000 ppm).

8. The NS-100 membrane was equally effective in treating acid copper baths from two different plating sources.

Long-Term Membrane Performance Toward Zinc Cyanide Plating Bath Rinse Water

An actual zinc cyanide plating bath was provided by Superior Plating, Inc., Minneapolis, Minnesota, and diluted to one-tenth full strength. Ten 2-foot tubes were tested with this solution whose pH was 12.8 at 41.4 bars, 25°C, 7.0 lpm flow rate for 1143 hours. Six tubes (30B, 43A, 39F, 22B, 31A, and 28A) were the same tubes that had already passed 1220 hours exposure toward acid copper rinse water. Two new NS-100 tubes were prepared and were added to the reverse osmosis zinc cyanide test after 238 hours to replace two failed tubes. Two tubes (46A and 47B) contained the modified NS-101 experimental membrane, in which isophthaloyl chloride (IPC) was employed as the crosslinking agent instead of tolylene diisocyanate (TDI).

Permeate was collected at various times throughout the test. Membrane performance parameters such as flux, permeate pH, cyanide rejection, and zinc rejection were determined after each measurement. Total dissolved solids and TOC analyses were performed twice on the permeate and feed, once at the beginning and once near the end of the test. Detailed performance data for each tube is presented in entirety in Appendix C.

Data summarizing the reverse osmosis performance of each tube during the zinc cyanide long-term study are illustrated in Tables 7 and 8. Table 7 illustrates the initial and final performances of each tube at 24 and 1143 hours, while Table 8 presents the average overall performance for each parameter for the respective tubes during the entire test. In addition to these data, membrane flux and solute rejection data are plotted as a function of time in Figures 12 and 13. Figure 12 graphically illustrates flux, zinc rejection and cyanide rejection data for the NS-100 membranes. Plotted in Figure 13 are the flux and rejection performance of the experimental NS-101 membranes (46A and 47B).

TABLE 7. INITIAL AND FINAL PERFORMANCES OF TUBULAR NS-100 MEMBRANES WITH ALKALINE ZINC CYANIDE PLATING SOLUTION*

Time (hours)	Measurement	Tube Number 348-T- 30B (NS-100)	43A (NS-100)	39F (NS-100)	22B (NS-100)	31A (NS-100)	28A (NS-100)	54A* (NS-100)	53A* (NS-100)	46A (NS-101)	47B (NS-101)	Feed Analysis*
24	Flux (l/m^2-hr)**	10	18	14	29	18	25	7.8	5.1	24	40	--
24	Concentration of Zinc (ppm)	110	2.32	20.3	5.40	12.0	9.50	4.50	1.70	42.5	10.7	1550 ppm
24	Zinc Rejection (%)	92.9	99.9	98.7	99.7	99.2	99.4	99.8	>99.9	97.3	99.3	--
24	Concentration of Cyanide (ppm)	170	19.7	48.8	67.6	44.9	54.1	66.9	24.4	236	229	2380 ppm
24	Cyanide Rejection (%)	92.9	99.2	97.9	97.2	98.1	97.7	97.6	99.1	90.0	90.4	--
24	pH	12.04	11.54	11.73	12.06	11.83	11.97	12.15	11.55	12.55	12.58	12.74
304	TDS Rejection (%)	92.9	98.3	97.0	93.8	96.4	95.5	92.8	97.3	76.2	73.9	2.621 (wt.%)
304	TOC Rejection (%)***	94.2	98.7	97.3	95.7	96.6	96.3	95.3	97.9	83.3	84.8	1250 ppm
1143	Flux (l/m^2-hr)**	8.1	14	12	20	15	14	8.7	5.2	23	20	--
1143	Concentration of Zinc (ppm)	66.3	1.40	11.8	4.50	45.5	38.5	4.50	1.60	19.8	15.3	1650 ppm
1143	Zinc Rejection	96.0	>99.9	99.3	99.7	97.2	97.7	99.7	>99.9	98.8	99.1	--
1143	Concentration of Cyanide (ppm)	159	19.3	46.3	111	120	129	119	22.9	276	291	2910 ppm
1143	Cyanide Rejection (%)	94.5	99.3	98.4	96.2	95.9	95.6	95.9	99.2	90.5	90.0	--
1143	pH	11.85	11.41	11.58	12.01	11.79	11.92	12.00	11.53	12.56	12.62	12.71
1044	TDS (wt.%)	0.1429	0.0365	0.0622	0.1545	0.0808	0.1506	0.1382	0.0537	0.5720	0.6467	2.198 (wt.%)
1044	TDS Rejection (%)	93.5	98.3	97.2	93.0	96.3	93.1	93.7	97.6	74.0	70.6	--

*Test Conditions:
Feed Composition . . . . . Zinc Concentration . . . . 1400-2100 ppm (0.187-0.281 oz/gal)
Cyanide Concentration . . 2120-3430 ppm (0.283-0.458 oz/gal)
Total Dissolved Solids . . 2.198-2.621 (wt. percent)
Total Organic Carbon . . . 1250 ppm
pH 12.71-12.82

Tubes 348-T-54A and 348-T-53A are fresh NS-100 tubes. The initial data presented for these tubes were taken after 66 hours of testing and final test time was 905 hours.

**Multiply by 0.59 to convert to gfd.

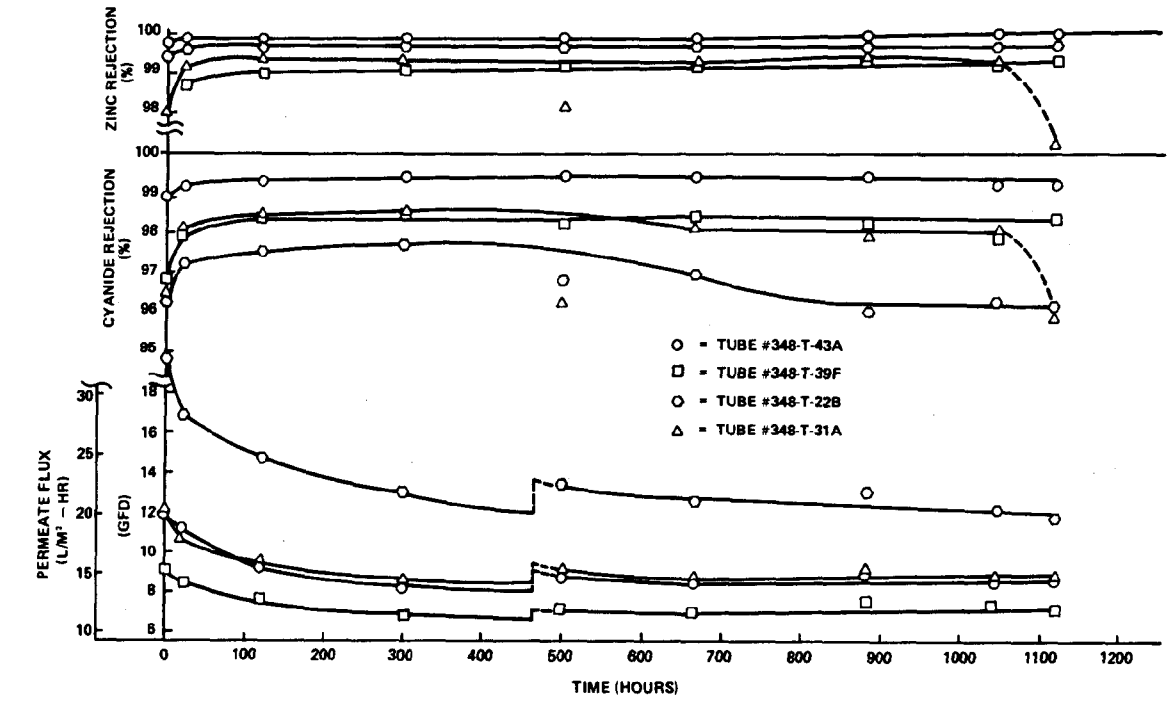
***Total organic carbon measurements taken after 1044 hours of operation were erroneous due to instrumental problems.

TABLE 8. AVERAGE REVERSE OSMOSIS PERFORMANCE OF NS-100 TUBES DURING ZINC CYANIDE LONG-TERM TEST

Membrane Parameter	Number of Measurements	Tube Number 348-T-30B (NS-100)	348-T-43A (NS-100)	348-T-39F (NS-100)	348-T-22B (NS-100)	348-T-31A (NS-100)	348-T-28A (NS-100)	348-T-54A* (NS-100)	348-T-53A* (NS-100)	348-T-46A (NS-101)	348-T-47B (NS-101)	Feed Analysis
Average Flux (l/m^2-hr)**	9	8.7	16	13	24	16	17	8.5*	5.2*	24	29	--
Average Rejection of Zinc (%)	9	94.8	99.9	99.1	99.7	98.8	97.2	99.7*	99.9*	98.1	99.1	1670 ppm
Average Rejection of Cyanide (%)	9	93.8	99.3	98.1	96.8	97.5	95.8	96.7*	99.2*	90.5	90.3	2750 ppm
Average Rejection of TDS (%)	2	93.5	98.3	97.1	93.4	96.4	94.3	93.3*	97.5*	75.1	72.3	2.410 (wt.%)
Rejection of TOC (%)	1	94.2	98.7	97.3	95.7	96.6	96.3	95.3*	97.9*	83.3	84.8	1250 ppm
Average pH	9	11.97	11.50	11.67	12.07	11.80	11.97	12.07*	11.54*	12.58	12.64	12.77

*Tubes 348-T-54A are fresh NS-100 tubes. These tubes were added to the line after 238 hours of testing had been completed on the other tubes. Data designated by asterisk for these tubes represents average of six readings.

**Multiply by 0.59 to convert to gfd.



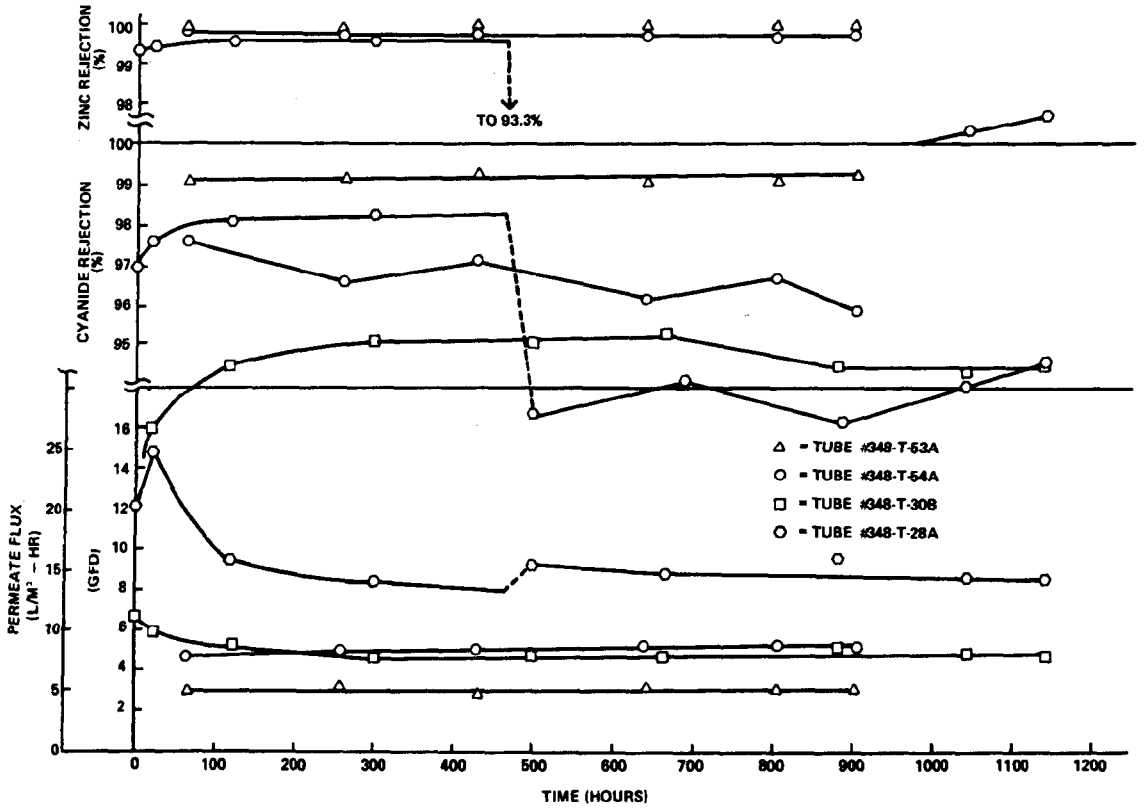


Figure 12. Plot of Reverse Osmosis Performance of NS-100 Tubular Membranes Toward Zinc Cyanide Rinse Water

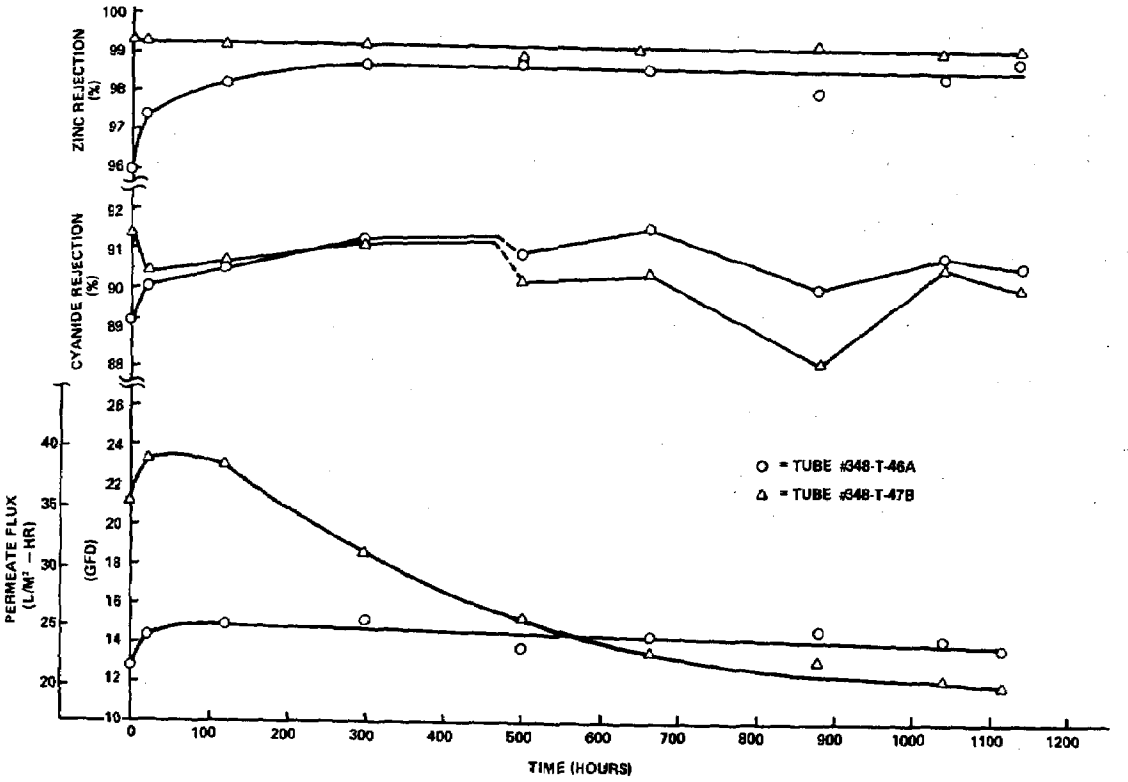


Figure 13. Plot of Reverse Osmosis Performance of NS-101 Tubular Membranes Toward Zinc Cyanide Rinse Water

Membrane Rejection

High rejections of zinc (greater than 99 percent) were observed for six of the eight NS-100 tubes (43A, 39F, 22B, 31A, 53A, and 54A) during most of the test. Cyanide rejections generally ranged between 96 and 99.4 percent, except for two tubes (30B and 28A), whose cases will be examined later in this report. Average rejections of zinc and cyanide at the conclusion of the test (1140 hours) for the eight standard NS-100 membranes were 98.8 and 96.9 percent respectively.

Membrane rejection of alkalinity followed cyanide rejection in that high rejection membranes gave lower pH permeate than low cyanide rejection membranes. For example, tubes exhibiting cyanide rejections of 99 percent or greater exhibited lower pH readings of 11.5 to 11.6 while other tubes whose cyanide rejection were 96 percent demonstrated pH values near 12.0. The overall permeate pH for the standard NS-100 membranes was 11.8, which indicates an average alkaline rejection of approximately 90 percent. Trends in the total organic carbon (TOC) and total dissolved solids (TDS) rejections also followed the cyanide rejections closely, and were generally above 95 percent. Rejections of TDS ranged from 92.9 to 98.3 percent for the NS-100 membranes, while TOC rejections ranged from 94.2 to 98.7 percent. Total organic carbon measurements taken after 1044 hours of operation were erroneous, due to instrumental problems, and are not included in the data in Table 7.

One tube carried over from the acid copper test was apparently damaged at the start of the test. Tube #30B demonstrated low rejections for cyanide and zinc during the entire test. Rejections of 95 percent for these two species were not observed until 300 hours had elapsed. Failure of a second NS-100 membrane (28A) was observed after a power failure shutdown at 466 hours. This tube had also been carried forward from the acid copper test. Rejections of cyanide and zinc for this tube both dropped to 93.3 percent after the incident and remained low for the rest of the test.

The power failure also caused noticeable changes in several NS-100 tubes. Most dramatically affected were tubes 31A and 22B. Both tubes exhibited at this time a sharp decrease in cyanide rejection (from 0.9 to 2.7 percent) and in zinc rejection. Resulting rejection data corresponded approximately to their initial readings taken at 1 hour. At the same time a slight increase in flux was observed. Both tubes quickly recovered their zinc rejections while only 31A recovered its former cyanide rejection. Tube 31A later lost its zinc and cyanide rejection performance after 1044 hours of use against zinc cyanide (and 1220 hours against acid copper). This loss on solute rejections was not accompanied by an increase in water flux, and may indicate, instead, contamination of the permeate by feedwater leakage through an adjacent mechanical connection.

Membrane Flux

Permeate flux was considerably lower with alkaline zinc cyanide feed than experienced with acid copper solution. This reflects, in part, the much higher solids content of the zinc cyanide bath, and consequently its higher osmotic pressure. Membrane flux ranged from 5.1 to 29 $1/m^2$-hr (3.0 to 16.9 gfd) (average 16 $1/m^2$-hr) at 24 hours and from 5.1 to 30 $1/m^2$-hr (3.0 to 11.8 gfd) (average 12 $1/m^2$-hr) at the end of 1140 hours of testing. The average flux was considerably lowered by the low fluxes of the two new NS-100 tubes prepared for this test. For unknown reasons, attempts to make tubes of high flux following the optimum fabrication conditions established earlier in the program failed.

NS-101 Membranes

The two experimental NS-101 membranes (46A and 47B) demonstrated substantially improved flux (overall average fluxes of 24 and 29 $1/m^2$-hr (14.2 to 16.9 gfd) respectively) compared to the regular NS-100 membranes. Although these tubes rejected zinc quite well (98.6 to 99.3 percent), cyanide rejections were not too satisfactory at 91 percent. Rejections of TDS and TOC were also low at 75 and 87.5 percent, respectively. Permeate pH measurements revealed very low rejections of alkalinity for these membranes. Improvement in these performance characteristics would seem possible through optimization of fabrication variables.

Discussion

The results of this study seem to indicate that a dynamic membrane was formed on the surface of the NS-100 membranes during reverse osmosis testing. This layer was apparently active in facilitating high solute rejections, especially

that of cyanide. Low flux rates accompanied by high rates of flux decline (average 15 percent) experienced by the NS-100 membranes also lends substance to this view. The higher flux membranes were more sensitive to this effect since they experienced higher rates of flux decline and greater changes in rejection performance during the first 24 hours of testing. The decrease in rejection values and concurrent flux increases observed after shut-down were most likely the result of osmotic cleaning, which would have occurred after the feed pressure was released. The dynamic layer was apparently removed when the flow of water was reversed, driven by the normal osmotic pressure gradient.

The formation of this dynamic layer on the surface of the NS-100 membrane may arise from two possible sources: deposition of colloidal metal hydroxide impurities, and adsorption of organic additives present in the plating solution. Analysis on the feed solution during the test revealed total organic carbon concentrations as high as 1250 ppm (excluding cyanide). The charged nature (cationic) of the NS-100 membranes may act to facilitate deposition of organic materials on its surface. This effect would likely be more significant in a feed stream which is highly concentrated with respect to charged ionic and organic species, such as the one used in this test.

Summary of Results: Alkaline Zinc Cyanide Test

Results of the reverse osmosis study with alkaline zinc cyanide feedwater may be summarized as follows:

1. The NS-100 membrane demonstrated long-term stability in treating this highly alkaline (pH 12.8) zinc cyanide waste solution. Four NS-100 membranes demonstrated high zinc and cyanide rejections for (1140) hours after completing 1220 hours of testing with acid copper at pH 1.1 to 1.4.
2. Five of the eight NS-100 membranes demonstrated zinc rejections of greater than 99 percent during most of the test. Two tubes demonstrated rejections of 99.6 and 99.9 percent during the entire study.
3. Cyanide rejections were generally greater than 96 percent, with one tube as high as 99.4 percent.
4. High rejections of organic species were observed and closely followed the cyanide rejection trend. Rejection of total organic carbon and total dissolved solids were generally above 95 percent.
5. Alkaline rejection also resembled the pattern set by the cyanide rejection. High rejecting cyanide membranes yielded permeate with lower pH values.
6. Typical flux operation range for the NS-100 membrane during the zinc cyanide study appeared to be in the 8.5 to 15 $1/m^2$-hr (5 to 9 gfd) range.
7. NS-101 membranes also demonstrated high zinc rejections and at twice the permeate flux,but cyanide rejections, at about 90 percent, needed improvement.

SECTION VI

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SECTION VII

APPENDICES

APPENDIX A

Fabrication Procedure for Tubular NS-100 Membranes for Reverse Osmosis

The general procedure for the NS-100 membrane tubular fabrication is outlined in Figure A1. The tubular fabrication process is divided into three basic areas: the modification of Abcor fiber glass tubes to accommodate the NS-100 membrane, the fabrication of the tubular NS-100 membrane, and the assembly of the reverse osmosis tube containing the NS-100 membranes.

Each of these steps are discussed in detail in the procedures section, below.

Safety Precautions

Tolylene 2,4-Diisocyanate

Vapors of tolylene 2,4-diisocyanate (TDI) are very toxic. Extreme care must be exercised at all times to avoid inhalation of TDI fumes. The handling of this compound should be restricted to a well-ventilated area such as a walk-in hood.

EPI-CURE 8494 (Celanese)

This composite blend consists of a variety of aromatic amines which are irritants to the skin as well as being carcinogens. This curing agent should be handled with protective gloves.

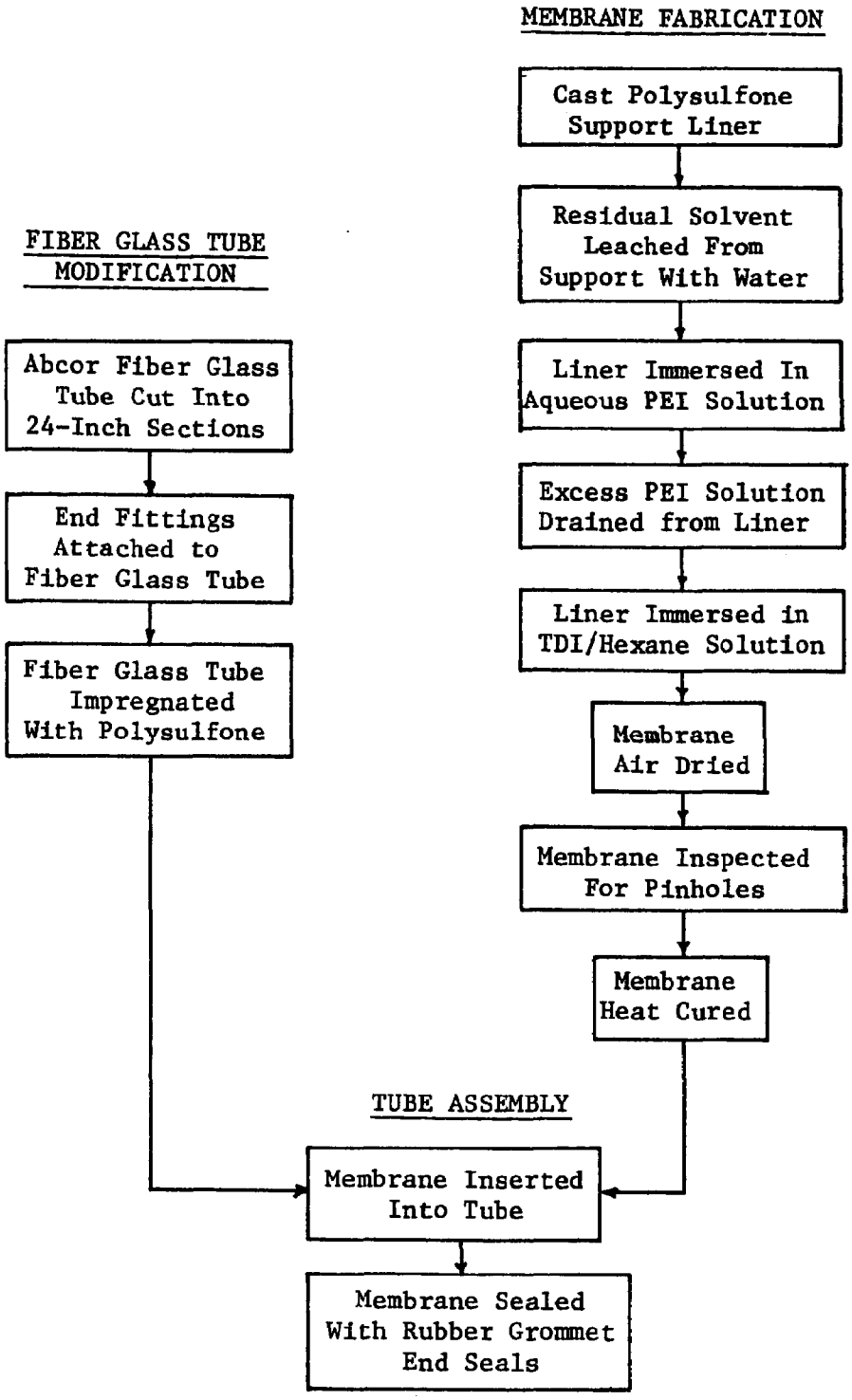

Figure A1. General Outline of NS-100 Reverse Osmosis Tube Fabrication

TABLE A1. APPARATUS AND REAGENTS FOR TUBE FABRICATION

EQUIPMENT

Item	Number	Dimensions	Purpose
Aluminum bob	1	I.D. - 1.33 cm	Impregnating fiber glass tube with polysulfone
Aluminum bob	1	I.D. - 1.39 cm	Casting polysulfone liner
Stainless steel tube (inside polished to near mirror finish)	1	Length - 91.4 cm I.D. - 1.41 cm	Casting polysulfone liner
EC Motomatic Motor Control (Model #E550M)	1	--	Casting polysulfone liner
ED Motomatic D.C. Servo Motor-Generator (Model #5503)	1	--	Casting polysulfone liner
Metal tube	1	Length - 1.02 m I.D. - 3.49 cm	Immersion tank for polysulfone liner casting
Glass tube	2	Length - 91.4 cm I.D. - 3.49 cm	PEI and TDI immersion tanks
Oven	1	Length - 76.2 cm	Membrane heat cure
Dry-Air Drier	1	--	Humidity control for polysulfone liner casting room

CONSTRUCTION MATERIALS

Item	Number	Dimensions	Purpose
Fiber glass tube (Abcor, Inc., Cambridge, Mass.)	1	Length - 1.52 m I.D. - 1.35 cm O.D. - 1.55 cm	R.O. tube housing unit for membrane
Abcor rubber grommet and plastic inserts	2	--	Membrane end seal with R.O. tube
Brass bushing	2	Length - 1.27 cm I.D. - 1.59 cm O.D. - 2.54 cm	Allows attachment of sleeve for permeate collection
Stainless steel (316) reducing bushing	2	Male NPT Pipe Size - 1.27 cm Inside bored out to 1.59 cm I.D.	Tube end fittings

TABLE A1. (Continued)

Item	Number	Dimensions	Purpose
Tygon tubing	1	Length - 54.6 cm I.D. - 2.54 cm	Collects product water
Adjustable hose clamps	2		Fastens permeate collection sleeve to brass bushing

REAGENTS

Item	Grade	Purpose
Polysulfone (Union Carbide P-3500	--	Liner preparation
Tydex 12 (Dow polyethylenimine)	--	NS-100 membrane formation
Epon 828 (Shell)	--	Epoxy ingredient
DER 736 (Dow)	--	Epoxy ingredient
EPI-CURE 8494* (Celanese)	--	Epoxy ingredient
Tolylene 2,4-Diisocyanate (TDI)*	Practical	NS-100 membrane formation
N,N-Dimethyl formamide	Reagent	Solvent for polysulfone
Hexanes	Reagent	Solvent for TDI
De-ionized water	--	Solvent for polyethylenimine

* See "SAFETY PRECAUTIONS" Page 41.

PROCEDURE

Fiber Glass Tube Modification

Operation	Comments
1. End fittings for the tubes are made by boring out stainless steel threaded reducing bushings (1/2-inch Male NPT pipe size) to 1.59 cm in diameter.	1. This allows a smooth, snug fit between the tube and fittings.
2. Abcor fiber glass tubes (1.55 cm in diameter) are cut into sections 61 cm in length.	2. The ends of the tube may have to be sanded in order to fit the brass and stainless steel bushings.
3. An epoxy blend for sealing the metal bushings to the tube is prepared by mixing 7.0 grams Shell Epon 828, 3.0 grams Dow DER 736 and 4.5 grams Celanese EPI-CURE 8494.	3. The epoxy formulation can be mixed in disposable aluminum trays. Ingredients are thoroughly mixed and allowed to stand for about 1 hour at room temperature.
4. The metal bushings are epoxied onto the ends of the fiber glass tube in the manner shown in Figure 8 of the text. The brass fitting is placed into position first, followed by the threaded stainless steel bushing.	4. Epoxy solution should be applied liberally to the area of the fiber glass tube where the bushings are to be positioned. It is also applied to inside surfaces of the bushings themselves. Special care must be taken to insure that the epoxy adhesive is applied to all surface areas in contact between the stainless steel bushing and the fiber glass tube. Excess epoxy is wiped from the tube before it sets so it will not interfere with the positioning of the rubber gommet end seals later in the fabrication process. The stainless steel bushing is allowed to extend 0.32 cm over the end of the fiber glass tube. This creates a shelf onto which the rubber grommet end seal can rest.

Operation	Comments
5. Impregnation of the fiber glass tube with polysulfone is accomplished by plugging one end of the tube with a rubber stopper and filling the tube with a 20 percent solution of polysulfone in N,N-dimethyl formamide (DMF). The tube is allowed to stand in the vertical position until the solution seeps through the walls of the tube (from 1 to 10 minutes, depending on porosity of the fiber glass tube). Once the polysulfone has seeped through the walls of the tube over all areas in the bottom half of the tube, a rubber stopper is placed at the top of the tube. The tube is then inverted. Polysulfone solution is added to replenish the solution which seeped out. When the solution has penetrated all areas of the tube the rubber stopper is removed from the bottom and the solution is allowed to drain into a collection pan. An aluminum bob 1.33 cm in diameter is passed through the tube. The tube is then immersed at a uniform rate into a de-ionized water quench bath. [This operation can be performed by hand.] After soaking 15 minutes the tube is removed from the first quench bath and placed in a fresh de-ionized water bath for 4 hours. The modified fiber glas tube is then air-dried and ready for use.	5. The polysulfone is applied to the fiber glass tube to provide a smooth uniform surface of even porosity. The tube should be held at a tilted angle so the solution can be poured slowly down the side of the tube. This avoids the entrapment of air bubbles.

Membrane Fabrication

Operation	Comment
1. Prepare a 15 percent polysulfone in DMF solution. Filter the solution through a Seitz filter to remove any particulate matter.	1. Time can be minimized by adding the polysulfone pellets to hot DMF while stirring rapidly. The mixture is stirred at approximately 110°C to 120°C for about 1 hour (until solution occurs). The hot solution is easily filtered. If heated, the polysulfone solution must be cooled to room temperature before use.
2. A polysulfone liner is cast in a polished stainless steel tube (1.41 cm in diameter). One end of the stainless steel tube, thirty-six inches in length, is plugged with a rubber stopper. The filtered polysulfone solution is poured slowly down the side of the tube through the open end. After the solution settles (one minute) it is drained through the bottom of the tube. An aluminum bob 1.39 cm in diameter passed through from top to bottom at the same time. The stainless steel tube is immediately lowered at a uniform rate 10.2 to 15.2 cm/second (4 to 6 inches/second) into an aqueous 2-percent DMF bath. The polysulfone is gelled immediately as it contacts the water solution.	2. This step must be carried out under low humidity conditions. The polysulfone solution can be used several times. The solution becomes cloudy after exposure to moisture in the air over long periods of time (1 to 2 days); however, it can be restored by heating at 110°C to 120°C for about 1 hour Erratic immersion rates will produce liner defects. Uniform immersion rates can be accomplished mechanically by the use of an EC Motomatic Motor Control and an EC Motomatic D.C. Servo Motor-Generator set-up.
3. The freshly prepared polysulfone liner is allowed to stand in the aqueous DMF quench bath for 1/2-hour. It is then removed and thoroughly rinsed by soaking in de-ionized water for at least 1 hour.	3. It is important that all DMF is removed from the polysulfone support film. Residual DMF adversely affects later fabrication steps.
4. The polysulfone liner is removed from the stainless steel tube and immersed for 5 minutes in an aqueous solution of polyethylenimine (PEI) that is 0.66 percent solids by weight.	4. The operation must be performed on a wet support film. Once the polysulfone is dried it is not receptive to water and cannot be adequately coated by PEI.

Operation	Comment
5. The polysulfone support is removed from the PEI solution and excess water allowed to drain off.	5. The support cannot be dried at this point because the water within the pores protects the polysulfone from TDI attack during the subsequent steps. The aqueous PEI solution is stable for periods up to 2 to 3 weeks; however, the solution has to be kept clean by frequent filtrations.
6. The PEI coated support is immersed in a 1/2 percent TDI in hexane solution for 1/2 minute.	6. Caution must be exercised when working with TDI, which is very toxic. This step should be carried out under a properly ventilated hood. Fresh TDI-hexane solutions must be prepared each day. In the presence of water TDI reacts slowly with itself to form an insoluble urea.
7. Membrane is air dried.	7. --
8. Membrane is inspected for pin holes by holding it next to a strong fluorescent lamp in a dark room and siting through it.	8. Thorough liner inspection cannot be accomplished unless the liner is dry, since pinholes do not show up when liner is wet.
9. Membrane is heat cured at 98°C for 5 minutes.	9. The cylindrical oven used for membrane heat cure during this program is illustrated in Figure A2. Other oven designs may be equally practical.

Assembly of NS-100 Reverse Osmosis Tube

1. The NS-100-polysulfone composite membrane is pulled into the modified Abcor fiber glass tube by taping to a wooden dowel and pulling the dowel through.	1. The membrane is pulled into the tube slowly to avoid damage resulting from tearing.
2. The reverse osmosis tube is pulled into a 1-inch diameter Tygon sleeve (for water collection). The ends of the sleeve are fastened to the brass bushings with adjustable hose clamps. A small hole (0.64 cm I.D.) is punched near one end of the tube to allow drainage of product water.	2. --

Operation	Comment
A small Tygon hose (0.95 cm O.D.) is inserted into this hole and fastened to the sleeve by solvent fusion with cyclo-hexanone.	
3. The membrane is fastened to the fiber glass tube with Abcor rubber grommet end seals. The membrane seal is made when a plastic expander is inserted into the rubber piece. Hollow metal spacers inserted into stainless steel fitting on reverse osmosis line hold the plastic expanders in place.	3. A trace of Vaseline lubricant is applied to the grommet where contact is made with the membranes.
4. The reverse osmosis tube containing the NS-100 membranes is stored in de-ionized water until testing.	4. High performance NS-100 membranes will suffer degradation when exposed to air for long periods of time.

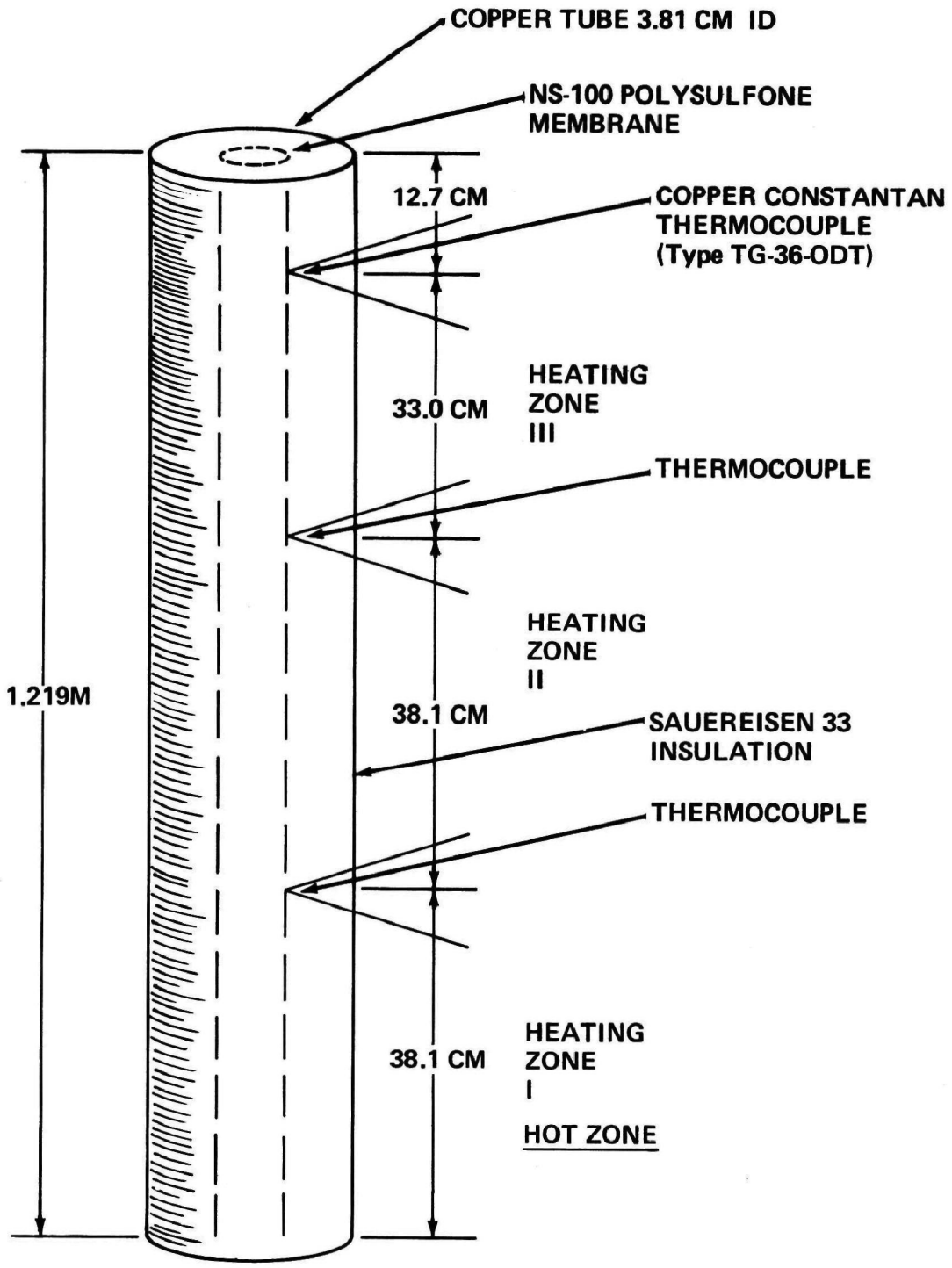

Figure A2. Cylindrical Oven

APPENDIX B

Individual Membrane Performance Data with Acid Copper Plating Bath Rinse Waters and Feed Analyses

Test Conditions: Pressure . . . . . 41.4 bars (600 psig)
Temperature . . . . 25°C
Feed Flow Rate . . . 7.0 lpm
Feed . . . . . One-tenth actual acid copper plating bath

Table B1. Acid Copper Feed Analysis

Time (hours)	Copper Concentration (ppm)	pH	Total Dissolved Solids (Wt. %)	Total Organic* Carbon (ppm)	Bath Source	Comments
1.0	3850	1.24	---	---	Precious Metal Platers, Inc.	---
24	3950	1.17	---	23.0	"	---
48	4950	1.18	1.320	---	"	---
96	4450	1.16	---	---	"	---
144	---	---	---	---	"	Shut-down to change line filter
263	5850	1.16	1.548	---	"	
309	---	---	---	---	"	Changed feed
335	4850	1.14	1.244	---	"	
428	5150	---	1.263	---	"	
502	4650	1.17	---	22.5	"	
602	5000	1.20	---	---	"	
649	---	---	---	---	"	Shut-down due to equipment failure (22 Hours)
797	4700	1.27	---	---	"	Changed feed
890	---	---	---	---	"	Changed feed
1009	5500	1.18	1.420	23.0	"	
1077	5750	1.15	---	---	"	Feed solution allowed to concentrate
1081	7500	1.13	---	---	"	"
1088	12600	1.05	---	---	"	"
1152	---	---	---	---	Superior Plating, Inc.	Changed feed
1222	5300	1.40	---	18.0	"	

*Precious Metal Platers stock plating solution contained CUE Bath as the organic brightening agent.
Superior Plating stock plating solution contained Udylite UBAC #1 as the organic brightening agent.

TABLE B2. INDIVIDUAL MEMBRANE PERFORMANCES WITH ACID COPPER PLATING BATH RINSE WATER

Tube Number	Position On R.O. Board	Time (Hours)	Permeate Flux (l/m^2-hr)	Permeate Copper (ppm)	Cu Rejection (%)	Permeate pH	Permeate TDS (Wt. %)	TDS Rejection (%)	Permeate TOC (ppm)	TOC Rejection (%)	Bath Source
348-T-											Precious Metal
30B	1	1.0	15.4	23.2	99.4	1.22	---	---	---	---	Platers, Inc
		24	14.1	7.4	99.8	1.18	---	---	8	65	"
		48	14.3	7.1	99.9	1.22	0.0063	99.5	---	---	"
		96	14.4	8.8	99.8	1.23	---	---	---	---	"
		263	13.7	8.0	99.9	1.23	0.0090	99.7	---	---	"
		335	14.1	5.7	99.9	1.20	0.0038	99.7	---	---	"
		428	13.9	6.5	99.9	---	0.0092	99.3	---	---	"
		502	13.6	8.5	99.8	1.24	---	---	8	64	"
		602	13.4	8.5	99.8	1.24	---	---	---	---	"
		797	13.9	9.2	99.8	1.32	---	---	---	---	"
		1009	13.3	11.2	99.8	1.24	0.0062	99.6	11	52	"
		1077	13.1	22.6	99.6	1.21	---	---	---	---	"
		1081	12.8	12.7	99.8	1.20	---	---	---	---	"
		1088	11.2	21.8	99.8	1.10	---	---	---	---	"
		1152									Superior Plating, Inc.
		1222	13.6	14.3	99.7	1.39	---	---	9.0	50	"

Tube Number	Position On R.O. Board	Time (Hours)	Permeate Flux (l/m^2-hr)	Permeate Copper (ppm)	Cu Rejection (%)	Permeate pH	Permeate TDS (Wt. %)	TDS Rejection (%)	Permeate TOC (ppm)	TOC Rejection (%)	Bath Source
348-T-											Precious Metal
43A	2	1.0	24.4	15.9	99.6	1.21	---	---	---	---	Platers, Inc.
		24	22.8	4.2	99.9	1.17	---	---	7	70	"
		48	22.2	4.1	>99.9	1.19	0.0172	98.7	---	---	"
		96	22.4	4.2	>99.9	1.21	---	---	---	---	"
		263	21.5	4.0	>99.9	1.21	0.0032	99.8	---	---	"
		335	22.2	4.6	>99.9	1.20	0.0138	98.9	---	---	"
		428	21.7	3.7	>99.9	---	0.0064	99.5	---	---	"
		502	21.4	4.2	>99.9	1.23	---	---	8	64	"
		602	21.2	4.8	>99.9	1.23	---	---	---	---	"
		797	22.6	4.5	99.9	1.32	---	---	---	---	"
		1009	21.4	5.1	>99.9	1.24	0.0047	99.7	8.5	63	"
		1077	21.4	5.5	>99.9	1.21	---	---	---	---	"
		1081	20.4	6.3	>99.9	1.19	---	---	---	---	"
		1088	18.0	11.4	>99.9	1.09	---	---	---	---	"
		1152									Superior Plating, Inc.
		1222	21.5	4.70	>99.9	1.41	---	---	6.5	64	"

Tube Number	Position On R.O. Board	Time (Hours)	Permeate Flux (l/m^2-hr)	Permeate Copper (ppm)	Cu Rejection (%)	Permeate pH	Permeate TDS (Wt. %)	TDS Rejection (%)	Permeate TOC (ppm)	TOC Rejection (%)	Bath Source
348-T-39F	3	24	20.2	17.9	99.5	1.14	---	---	6	74	Precious Metal Platers, Inc.
		48	19.9	13.0	99.7	1.17	0.0073	99.4	---	---	"
		96	19.9	12.0	99.7	1.17	---	---	---	---	"
		263	19.2	8.8	99.8	1.17	0.0066	99.6	---	---	"
		335	19.5	6.8	99.8	1.18	---	---	---	---	"
		428	19.5	8.0	99.8	---	0.0260	97.9	---	---	"
		502	19.2	9.4	99.8	1.23	---	---	6	73	"
		602	19.2	10.8	99.8	1.19	---	---	---	---	"
		797	19.7	9.7	99.8	1.27	---	---	---	---	"
		1009	18.7	9.8	99.8	1.21	0.0063	99.6	7.5	67	"
		1077	19.0	12.7	99.8	1.16	---	---	---	---	"
		1081	18.2	3.2	>99.9	1.16	---	---	---	---	"
		1088	16.4	20.2	99.8	1.06	---	---	---	---	"
		1152									Superior Plating, Inc.
		1222	19.2	12.4	99.8	1.39	---	---	6.5	64	"

Tube Number	Position On R.O. Board	Time (Hours)	Permeate Flux (l/m^2-hr)	Permeate Copper (ppm)	Cu Rejection (%)	Permeate pH	Permeate TDS (Wt. %)	TDS Rejection (%)	Permeate TOC (ppm)	TOC Rejection (%)	Bath Source
348-T-22B	4	1.0	41.7	95.0	97.5	1.13	---	---	---	---	Precious Metal Platers, Inc.
		24	34.3	53.5	96.1	1.07	---	---	7	70	"
		48	34.1	52.0	98.9	1.11	0.0226	98.3	---	---	"
		96	32.1	58.5	98.7	1.11	---	---	---	---	"
		263	27.8	48.5	99.2	1.11	0.0187	98.8			"
		335	27.0	35.5	99.2	1.14	0.0196	98.4			"
		428	26.0	36.5	99.3	---	0.0167	99.0			"
		502	25.8	45.0	99.0	1.16	---	---	9	60	"
		602	25.3	50.0	99.0	1.14	---	---	---	---	"
		797	27.7	48.0	99.0	1.23	---	---	---	---	"
		1009	25.3	52.5	99.0	1.15	0.0176	98.8	5.5	76	"
		1077	25.0	59.0	99.0	1.09	---	---	---	---	"
		1081	24.4	67.5	99.1	1.07	---	---	---	---	"
		1088	20.9	134	98.9	0.98	---	---	---	---	"
		1152									Superior Plating Inc.
		1222	23.4	52.0	99.0	1.34	---	---	7.5	58	"

Tube Number	Position On R.O. Board	Time (Hours)	Permeate Flux (l/m^2-hr)	Permeate Copper (ppm)	Cu Rejection (%)	Permeate pH	Permeate TDS (Wt. %)	TDS Rejection (%)	Permeate TOC (ppm)	TOC Rejection (%)	Bath Source
348-T-31A	5	1	28.7	80.5	97.9	1.17	---	---	---	---	Precicus Metal Platers, Inc.
		24	24.4	27.0	99.3	1.11	---	---	6	74	"
		48	23.9	26.3	99.5	1.14	0.0117	99.1	---	---	"
		96	23.6	36.5	99.2	1.15	---	---	---	---	"
		263	21.1	20.3	99.7	1.19	0.0100	99.4	---	---	"
		335	20.9	14.8	99.7	1.16	0.0084	99.3	---	---	"
		428	20.9	17.0	99.7	---	0.0143	98.9	---	---	"
		502	20.0	18.8	99.6	1.17	---	---	6	73	"
		602	20.0	22.0	99.6	1.17	---	---	---	---	"
		797	22.8	23.3	99.5	1.25	---	---	---	---	"
		1009	21.2	26.8	99.5	1.20	0.0108	99.2	7.5	67	"
		1077	21.7	30.0	99.5	1.12	---	---	---	---	"
		1081	20.5	38.3	99.5	1.10	---	---	---	---	"
		1088	18.0	65.5	99.5	1.00	---	---	---	---	"
		1152									Superior Plating, Inc.
		1222	20.9	28.0	99.5	1.35	---	---	6.0	67	"

Tube Number	Position On R.O. Board	Time (Hours)	Permeate Flux (l/m^2-hr)	Permeate Copper (ppm)	Cu Rejection (%)	Permeate pH	Permeate TDS (Wt. %)	TDS Rejection (%)	Permeate TOC (ppm)	TOC Rejection (%)	Bath Source
348-T-28A	6	24	26.0	35.0	99.1	1.13	---	---	8	65	Precious Metal Platers, Inc.
		48	25.8	37.0	99.5	1.14	0.0043	99.7	---	---	"
		96	25.0	28.8	99.4	1.15	---	---	---	---	"
		263	22.4	30.8	99.5	1.16	0.0092	99.4	---	---	"
		335	21.9	22.3	99.5	1.17	0.0145	98.8	---	---	"
		428	21.4	22.5	99.6	---	0.0099	99.2	---	---	"
		502	21.4	27.5	99.4	1.20	---	---	5	78	"
		602	21.1	30.5	99.4	1.18	---	---	---	---	"
		797	22.1	29.3	99.4	1.26	---	---	---	---	"
		1009	21.2	36.3	99.3	1.17	0.0143	99.0	8.0	65	"
		1077	21.5	34.0	99.4	1.12	---	---	---	---	"
		1081	20.5	46.5	99.4	1.11	---	---	---	---	"
		1088	18.7	82.0	99.3	1.01	---	---	---	---	"
		1152									Superior Plating, Inc.
		1222	20.5	34.0	99.4	1.35	---	---	5.5	69	"

Tube Number	Position On R.O. Board	Time (Hours)	Permeate Flux (l/m^2-hr)	Permeate Copper (ppm)	Cu Rejection (%)	Permeate pH	Permeate TDS (Wt. %)	TDS Rejection (%)	Permeate TOC (ppm)	TOC Rejection (%)	Bath Source
348-T-34A	7	24	28.2	184	95.3	1.09	---	---	7	70	Precious Metal Platers, Inc.
		48	27.7	142	97.1	1.08	0.0432	96.7	---	---	"
		96	26.8	160	96.4	1.10	---	---	---	---	"
		263	24.6	178	97.0	1.12	0.0544	96.5	---	---	"
		335	24.1	126	97.0	1.11	0.0411	96.7	---	---	"
		428	22.4	106	97.9	---	0.0360	97.1	---	---	"
		502	22.8	132	97.2	1.12	---	---	7	69	"
		602	21.7	112	97.8	1.13	---	---	---	---	"
		797	23.9	---	---	1.21	---	---	---	---	"
		1009	22.8	128	97.7	1.14	0.0412	97.1	9.0	61	"
		1077	23.2	140	97.6	1.08	---	---	---	---	"
		1081	27.2	183	97.6	1.06	---	---	---	---	"
		1088	19.9	300	97.6	0.96	---	---	---	---	"
		1152									Superior Plating, Inc.
		1222	21.5	77.5	98.5	1.34	---	---	5.5	69	"

Tube Number	Position On R.O. Board	Time (Hours)	Permeate Flux (l/m^2-hr)	Permeate Copper (ppm)	Cu Rejection (%)	Permeate pH	Permeate TDS (Wt. %)	TDS Rejection (%)	Permeate TOC (ppm)	TOC Rejection (%)	Bath Source
348-T-37C**	8	1	31.7	335	91.3	1.15	---	---	---	---	Precious Metal Platers, Inc.
		24	29.9	260	93.4	1.11	---	---	5	78	"
		48	28.5	---	---	1.15	0.0519	96.1	---	---	"
		96	29.4	190	95.7	1.11	---	---	---	---	"
		263	28.5	465	92.1	1.14	0.1808	88.3	---	---	"
		335	27.8	315	92.1	1.15	0.0874	93.0	---	---	"
		428	29.5	685	86.4	---	0.1986	84.3	---	---	"

Testing was discontinued after 428 hours of operation because of membrane failure.

APPENDIX C

Individual Membrane Performance Data with Alkaline Zinc Cyanide Plating Bath Rinse Waters and Feed Analyses

Test Conditions:
- Pressure . . . . . 41.4 bars
- Temperature . . . . . 25°C
- Feed Flow Rate . . . . 6.8 lpm
- Feed . . . . . One-tenth actual zinc cyanide plating bath

TABLE C1. ZINC CYANIDE FEED ANALYSIS

Zinc Cyanide Feed Analysis

(Hours)	Cyanide Concentration (ppm)	Zinc Concentration (ppm)	pH	Total Organic* Carbon (ppm)	Total Dissolved Solids (Wt. %)	Comments
1.0	2120	1400	12.80	---	---	---
24	2380	1550	12.74	---	---	---
120.5	2520	1750	12.75	---	---	---
304	2820	2100	12.74	1250	2.621	---
362	---	---	12.80	---	---	Changed feed
466	---	---	---	---	---	Shut-down due to power failure
499	3280	1800	12.82	---	---	---
666	3430	1650	12.80	---	---	---
827	---	---	---	---	---	Changed feed and line filter
881	2510	1550	12.77	---	---	---
1044	2750	1550	12.73	---	2.198	---
1143	2910	1650	12.71	---	---	---

*Stock plating solution contained Enthone Q-540 as the organic brightener bath additive.

TABLE C2. INDIVIDUAL MEMBRANE PERFORMANCES WITH ALKALINE ZINC CYANIDE PLATING BATH RINSE WATER

Tube Number	Position on R.O. Board	Time (hours)	Permeate Flux (l/m^2-hr)	Permeate Cyanide (ppm)	CN Rejection (%)	Permeate Zinc (ppm)	Zn Rejection (%)	Permeate pH	Permeate TOC (ppm)	TOC Rejection (%)	Permeate TDS (Wt. %)	TDS Rejection (%)
30B	1	1	11.3	260	87.7	172	87.7	12.23	---	---	-----	---
		24	9.8	170	92.9	110	92.9	12.04	---	---	-----	---
		120.5	8.8	138	94.5	102	94.2	12.03	---	---	-----	---
		240	---	---	---	---	---	---	---	---	-----	---
		304	7.8	138	95.1	90	95.7	11.96	71.3	94.2	0.1871	92.9
		498.6	8.1	160	95.1	65.0	96.4	11.95	---	---	-----	---
		666.0	8.0	150	95.6	55.0	96.7	11.96	---	---	-----	---
		881	8.5	139	94.5	49.5	96.8	11.86	---	---	-----	---
		1044	8.2	153	94.4	50.0	96.8	11.88	**	**	0.1429	93.5
		1143	8.1	159	94.5	66.3	96.0	11.85	---	---	-----	---
43A	2	1	20.0	25.6	98.8	3.40	99.8	11.67	---	---	-----	---
		24	18.0	19.7	99.2	2.32	99.9	11.54	---	---	-----	---
		120.5	15.9	18.3	99.3	2.00	99.9	11.53	---	---	-----	---
		304	14.1	17.5	99.4	2.40	99.9	11.51	16.4	98.7	0.0448	98.3
		498.6	14.9	20.6	99.4	1.80	99.9	11.48	---	---	-----	---
		666.0	14.4	20.2	99.4	1.65	99.9	11.52	---	---	-----	---
		881.2	15.3	16.2	99.4	1.30	>99.9	11.41	---	---	-----	---
		1044	14.7	18.8	99.3	1.35	>99.9	11.41	**	**	0.0365	98.3
		1143	14.3	19.3	99.3	1.40	>99.9	11.41	---	---	-----	---

Tube Number	Position on R.O. Board	Time (hours)	Permeate Flux (l/m^2-hr)	Permeate Cyanide (ppm)	CN Rejection (%)	Permeate Zinc (ppm)	Zn Rejection (%)	Permeate pH	Permeate TOC (ppm)	TOC Rejection (%)	Permeate TDS (Wt. %)	TDS Rejection (%)
39F	3	1	34.7	65.1	96.9	---	---	11.86	---	---	-----	---
		24	14.4	48.8	97.9	20.3	98.7	11.73	---	---	-----	---
		120.5	12.9	42.5	98.3	18.0	99.0	11.71	---	---	-----	---
		304	11.5	44.7	98.4	19.3	99.1	11.70	33.4	97.3	0.0790	97.0
		498.6	12.1	58.2	98.2	14.0	99.2	11.69	---	---	-----	---
		666.0	11.9	54.3	98.4	14.3	99.1	11.68	---	---	-----	---
		881.2	12.7	46.3	98.2	11.3	99.3	11.56	---	---	-----	---
		1044	12.3	56.9	97.9	11.8	99.2	11.59	**	**	0.0622	97.2
		1143	12.0	46.3	98.4	11.8	99.3	11.58	---	---	-----	---
22B	4	1	33.8	77.7	96.3	6.64	99.5	12.20	---	---	-----	---
		24	28.7	67.6	97.2	5.40	99.7	12.06	---	---	-----	---
		120.5	25.3	63.5	97.5	4.40	99.7	12.06	---	---	-----	---
		304	22.2	65.0	97.7	5.40	99.7	12.06	54	95.7	0.1625	93.8
		498.6	22.6	106	96.8	4.90	99.7	12.10	---	---	-----	---
		666.0	21.2	103	97.0	5.10	99.7	12.11	---	---	-----	---
		881.2	22.1	100	96.0	3.90	99.7	12.00	---	---	-----	---
		1044	20.7	103	96.3	4.60	99.7	12.04	**	**	0.1545	93.0
		1143	20.0	111	96.2	4.50	99.7	12.01	---	---	-----	---

Tube Number	Position on R.O. Board	Time (hours)	Permeate Flux (l/m^2-hr)	Permeate Cyanide (ppm)	CN Rejection (%)	Permeate Zinc (ppm)	Zn Rejection (%)	Permeate pH	Permeate TOC (ppm)	TOC Rejection (%)	Permeate TDS (Wt. %)	TDS Rejection (%)
31A	5	1	20.7	73.5	96.5	2.60	98.1	11.97	---	---	-----	---
		24	18.2	44.9	98.1	12.0	99.2	11.83	---	---	-----	---
		120.5	16.1	40.3	98.4	10.3	99.4	11.83	---	---	-----	---
		304	14.5	42.3	98.5	12.3	99.4	11.80	43.0	96.6	0.0946	96.4
		498.6	15.5	125	96.2	32.5	98.2	11.80	---	---	-----	---
		666.0	14.8	65.3	98.1	12.0	99.3	11.79	---	---	-----	---
		881.2	15.9	52.0	97.9	9.6	99.4	11.70	---	---	-----	---
		1044	15.2	52.5	98.1	10.5	99.3	11.73	**	**	0.0808	96.3
		1143	15.1	120	95.9	45.5	97.2	11.79	---	---	-----	---
28A	6	1	20.7	62.5	97.0	10.0	99.3	12.04	---	---	-----	---
		24	25.1	54.1	97.7	9.50	99.4	11.97	---	---	-----	---
		120.5	15.9	48.2	98.1	7.75	99.6	11.94	---	---	-----	---
		304	14.1	48.9	98.3	9.10	99.6	11.73	45.9	96.3	0.1181	95.5
		498.6	15.6	221	93.3	120	93.3	12.11	---	---	-----	---
		666.0	14.9	202	94.1	100	93.9	12.09	---	---	-----	---
		881.2	15.8	172	93.1	77.5	95.0	12.00	---	---	-----	---
		1044	14.7	137	95.0	43.5	97.2	11.95	**	**	0.1506	93.1
		1143	14.4	129	95.6	38.5	97.7	11.92	---	---	-----	---

Tube Number	Position on R.O. Board	Time (hours)	Permeate Flux (l/m^2-hr)	Permeate Cyanide (ppm)	CN Rejection (%)	Permeate Zinc (ppm)	Zn Rejection (%)	Permeate pH	Permeate TOC (ppm)	TOC Rejection (%)	Permeate TDS (Wt. %)	TDS Rejection (%)
54A	7		---	---	---	---	---	---	---	---	-----	---
		64	7.8	66.9	97.6	4.50	99.8	12.15	59.1	95.3	0.1889	92.8
		260.5	8.5	111	96.6	6.10	99.7	12.14	---	---	-----	---
		428	8.4	100	97.1	5.0	99.7	12.09	---	---	-----	---
		643	8.9	94.4	96.2	4.10	99.7	12.02	---	---	-----	---
		806	8.8	89.7	96.7	4.30	99.7	12.02	**	**	0.1382	93.7
		905	8.7	119	95.9	4.50	99.7	12.00	---	---	-----	---
53A	8	66	5.1	24.4	99.1	1.70	>99.9	11.55	26.2	97.9	0.0697	97.3
		260.5	5.2	25.4	99.2	1.60	>99.9	11.53	---	---	-----	---
		428	5.1	25.4	99.3	1.35	>99.9	11.56	---	---	-----	---
		643	5.3	22.4	99.1	1.35	>99.9	11.47	---	---	-----	---
		806	5.1	24.3	99.1	1.30	>99.9	11.60	**	**	0.0537	97.6
		905	5.2	22.9	99.2	1.60	>99.9	11.53	---	---	-----	---

Tube Number	Position on R.O. Board	Time (hours)	Permeate Flux (l/m^2-hr)	Permeate Cyanide (ppm)	CN Rejection (%)	Permeate Zinc (ppm)	Zn Rejection (%)	Permeate pH	Permeate TOC (ppm)	TOC Rejection (%)	Permeate TDS (Wt. %)	TDS Rejection (%)
46A	9	1	21.7	229	89.2	55.5	96.0	12.51	---	---	-----	---
		24	24.1	236	90.0	42.5	97.3	12.55	---	---	-----	---
		120.5	25.3	240	90.5	31.3	98.2	12.60	---	---	-----	---
		304	25.6	247	91.2	27.5	98.7	12.53	209	83.3	0.6228	76.2
		498.6	23.4	299	90.0	24.3	98.7	12.63	---	---	-----	---
		666.0	24.4	291	91.5	23.1	98.6	12.64	---	---	-----	---
		881.2	25.0	251	90.0	30.3	98.0	12.58	---	---	-----	---
		1044	23.9	251	90.8	25.0	98.4	12.58	**	**	0.5720	74.0
		1143	23.2	276	90.5	19.8	98.8	12.56	---	---	-----	---
47B	10	1	36.0	181	91.5	10.3	99.3	12.57	---	---	-----	---
		24	39.5	229	90.4	10.7	99.3	12.58	---	---	-----	---
		120.5	39.0	234	90.7	14.2	99.2	12.65	---	---	-----	---
		304	31.6	250	91.1	16.0	99.2	12.63	190	84.8	0.6832	73.9
		498.6	26.0	320	90.2	19.0	98.9	12.70	---	---	-----	---
		666.0	23.1	328	90.4	15.5	99.1	12.73	---	---	-----	---
		881.2	22.1	299	88.1	13.0	99.2	12.69	---	---	-----	---
		1044	20.4	260	90.5	15.0	99.0	12.60	**	**	0.6467	70.6
		1143	20.0	291	90.0	15.3	99.1	12.62	---	---	-----	---

TECHNICAL REPORT DATA
(Please read Instructions on the reverse before completing)

1. REPORT NO.	2.	3. RECIPIENT'S ACCESSION NO.
EPA-600/2-76-197		

4. TITLE AND SUBTITLE	5. REPORT DATE
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7. AUTHOR(S)	8. PERFORMING ORGANIZATION REPORT NO.
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15. SUPPLEMENTARY NOTES	

16. ABSTRACT Long-term reverse osmosis tests were conducted with electroplating wastes on a new membrane referred to as NS-100. This membrane consists of a polyurea layer, formed by the reaction of tolylene diisocyanate with polyethylenimine, deposited on a porous polysulfone support film. The membranes were tested as liners within 1/2-inch diameter fiber glass tubes. A total of 2360 hours of continuous reverse osmosis operation was achieved, 1220 hours on pH 1.2 acid copper rinse water and 1140 hours on pH 12.8 alkaline zinc cyanide rinse water. The membranes exhibited remarkable chemical stability during exposure to these two pH extremes. Copper and zinc rejections were generally greater than 99 percent, while cyanide rejections were typically 96 percent or greater. Membrane fluxes were in the range of 18 to 24 liters per sq. m. per hr. (11 to 14 gfd) for acid copper, but only 8 to 15 l/m^2 -hr (5 to 9 gfd) for zinc cyanide at 41.4 bars (600 psig) and 25°C. Rejection of organics (including brighteners) was 60 to 78 percent for acid copper and greater than 95 percent for zinc cyanide. NS-100 membrandes did not reject sulfuric acid. A modified membrane NS-101, demonstrated twice the permeate flux of NS-100 toward zinc cyanide baths, but cyanide rejections were low at 90 percent. Difficulties of producing reproducible, high-flux tubular membranes were not fully resolved in this study.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Copper, Cyanides, *Electroplating, Industrial Waste Treatment, Industrial Water, *Membranes, *Osmosis, *Semipermeability, Water Pollution, Zinc	Polymer membranes, Reverse osmosis, Electroplating waste water	13B, 13H, 13K

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