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USE OF IMPROVED MEMBRANES IN TERTIARY TREATMENT BY REVERSE OSMOSIS

ENVIRONMENTAL PROTECTION AGENCY WATER QUALITY OFFICE

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USE OF IMPROVED MEMBRANES IN TERTIARY TREATMENT BY REVERSE OSMOSIS

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for the

WATER QUALITY OFFICE

ENVIRONMENTAL PROTECTION AGENCY

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ABSTRACT

The purpose of this reverse osmosis study was threefold: (1) to compare tubular membranes prepared from transesterified (modified) cellulose acetate with commercially available cellulose acetate (control), (2) to evaluate the in-situ regenerable membrane reverse osmosis design on waste water and (3) to evaluate the membranes on carbon-treated secondary effluents, primary effluents and concentrated primary effluents.

The test results were: (1) tubular membranes prepared from transesterified cellulose acetate produced water fluxes slightly greater than those of membranes prepared from commercially available cellulose acetate, (2) the in-situ regenerable membranes produced fluxes below that of tubular units but showed sufficient promise for further development, (3) product water flux from operations on carbon-treated secondary effluents gradually declined from initial levels of between 15 and 25 gfd. However, product water flux could be maintained near these initial levels by periodic cleaning with enzyme-active laundry presoak solution, (4) product water flux on primary and concentrated primary effluents declined gradually from initial levels of between 15 and 25 gfd and stabilized between 4 to 5 gfd on concentrated primary effluent even with the use of enzyme-active laundry presoak solution, (5) removal of most waste water constituents was between 90 to 100% and was generally unaffected by the type of feed water or time of test. Chloride and nitrate reductions averaged approximately 70 percent.

The test results indicate that it is technically feasible to treat primary effluents with tubular reverse osmosis process. However, further development is needed to determine economic feasibility.

This report was submitted in fulfillment of Project Number 17020 DHR, Contract 14-12-417, under the sponsorship of the Water Quality Office, Environmental Protection Agency.

Key Words: Water pollution, membranes, reverse osmosis, sewage treatment, waste water treatment, cellulose acetate, carbon-treated secondary effluent, primary effluent, solid removal, organic removal, inorganic removal.

CONTENTS

Section		Page
I	CONCLUSIONS	1
II	RECOMMENDATIONS	3
III	INTRODUCTION	4
	Study Objectives	4
	Transesterified Modified Cellulose Acetate	5
	Regenerable Membrane	6
IV	MEMBRANE PREPARATION	7
	Modified Cellulose Acetate	7
	Tubular Membrane Preparation	7
	Regenerable Membrane Preparation	9
V	LABORATORY TEST RESULTS	13
VI	FIELD TESTING	16
	Description of Equipment	16
	Operating Conditions	19
	Measurements	21
	Data Reduction	23
VII	OPERATION ON CARBON-TREATED SECONDARY EFFLUENT	25
VIII	OPERATION ON PRIMARY AND CONCENTRATED PRIMARY EFFLUENT	31
IX	DISCUSSION OF RESULTS	42
	Membrane Performance	42
	Flux Decline	42
	Membrane Condition	43
	Removal Efficiency	43
	Feed Condition	43
	Regenerable Membranes	44
X	ACKNOWLEDGMENTS	45
XI	REFERENCES	46
XII	APPENDICES	47

FIGURES

		Page
1	TUBULAR MEMBRANE CASTING APPARATUS	8
2	COMPOSITE TUBULAR ASSEMBLY	10
3	CONCEPTUAL SHELL AND TUBE DESIGN (REPEATABLE UNIT) FOR REGENERABLE REVERSE OSMOSIS PLANT	11
4	REGENERABLE MEMBRANE REVERSE OSMOSIS UNIT	12
5	FLUX DECLINE USING 3,000 PPM NaCl	15
6	TEST APPARATUS SCHEMATIC	17
7	FRONT VIEW OF UNIT INSTALLED AT POMONA	18
8	REAR VIEW OF UNIT INSTALLED AT POMONA SHOWING MEMBRANE TUBES	18
9	PERFORMANCE OF TUBULAR MEMBRANES ON CARBON-TREATED SECONDARY EFFLUENT	27
10	PERFORMANCE OF REGENERABLE UNIT NO. 5 ON CARBON-TREATED SECONDARY EFFLUENT	28
11	PERFORMANCE OF MEMBRANE SET 1a OPERATED ON PRIMARY AND CONCENTRATED PRIMARY EFFLUENT	33
12	PERFORMANCE OF MEMBRANE SET 2a OPERATED ON PRIMARY AND CONCENTRATED PRIMARY EFFLUENT	34
13	PERFORMANCE OF MEMBRANE SET 3a OPERATED ON PRIMARY AND CONCENTRATED PRIMARY EFFLUENT	35
14	PERFORMANCE OF REGENERABLE UNIT NO. 6 OPERATED ON PRIMARY AND CONCENTRATED PRIMARY EFFLUENT	37

TABLES

No.		Page
I	Average Membrane Performance with Carbon-Treated Secondary Effluent Feed	26
II	Removal of Wastewater Constituents During Operating with Carbon-Treated Secondary Effluent	29
III	Average Membrane Performance with Primary and Concentrated Primary Effluent Feed	32
IV	Removal of Wastewater Constituents During Operation with Primary Effluent	38
V	Removal of Wastewater Constituents During Operation with Concentrated Primary Effluent—I	39
VI	Removal of Wastewater Constituents During Operation with Concentrated Primary Effluent—II	40

SECTION I
CONCLUSIONS

1. Tubular membranes prepared from transesterified cellulose acetate produced product water fluxes* slightly greater than those of membranes prepared from commercially available cellulose acetate (Eastman 398-10).

2. The in-situ regenerable membranes produced fluxes below that of tubular units, and solids built up severely on the membrane surfaces during operations with concentrated untreated primary effluent feeds. However, this design showed sufficient promise for further development.

3. On carbon treated secondary effluent, membranes prepared from transesterified cellulose acetate provided an overall average product water flux of 15 gfd. Membranes prepared from commercially available cellulose acetate (Eastman 398-10) exhibited an overall average flux of 10 gfd, both at 600 psig.

4. Product water flux from membranes operated on carbon treated secondary effluents could be maintained near its initial level of 25 gfd for the (transesterified) modified membranes and 15 gfd for the E-398-10 (control) membranes by periodic cleaning (approximately once every 10 days) with an enzyme active laundry presoak solution (Biz).

5. Product water flux from membranes operated with periodic (~10 day interval) Biz cleaning on primary followed by concentrated primary effluent feed decreased gradually to 4 to 5 gfd (at 600 psig). Average initial flux was the same as with the carbon treated secondary effluent.

6. Upon return to straight primary effluent feed, the flux rose to 5 to 7 gfd and continued to increase until the end of the test. Thus, average flux of an actual reverse osmosis unit would be greater than the 4 to 5 gfd observed on a concentrated primary feed.

7. Of the three cleaning procedures used (sponge ball, enzyme active laundry presoak solution, and 6M Urea solution) for membrane rejuvenation, the enzyme-active laundry presoak solution was the most effective under the test conditions employed.

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*All wastewater feeds were adjusted to a pH of approximately 5 to 6 with sulphuric acid.

8. Flux decline rate (slope of log flux-log time plot) on concentrated primary feed was the same as with pure salt solution.

9. Removal of wastewater constituents was generally unaffected by the type of feed or time on test and remained essentially constant at 90 to 100 percent during operation on carbon treated secondary, primary, and concentrated (up to 9 times the total solid concentration of primary effluent) primary effluent.

10. No degradation of any of the membranes was observed during these tests.

11. It is technically feasible to treat primary effluents with the tubular reverse osmosis process. However, further development is needed to determine the economic feasibility.

SECTION II
RECOMMENDATIONS

These results, coming from a small reverse osmosis test unit, do not completely indicate full-scale operation. The use of feed recirculation to simulate high recovery ratios may influence the test results in a way not experienced in practice.

To take full advantage of these results, operation of an appropriately sized reverse osmosis pilot plant on primary effluent at a sewage treatment facility is recommended. The pilot plant should be designed to specifically establish the necessary operating conditions and parameters for sustained performance and to provide realistic, full-scale, cost data on the process. It is estimated that the cost of this study will be about $250, 000, of which, $120, 000 would be for engineering, site preparation, laboratory supplies and procurement of a 20, 000 gfd tubular reverse osmosis unit and $130, 000 for 20 months operation, chemical and physical analyses and four months for the final report.

SECTION III
INTRODUCTION

Rapidly increasing populations and expanding industrial activities are placing greater demands on fresh water supplies. However, these supplies are relatively static in availability and in some cases even decreasing as the result of pollution. The Department of Interior has recognized the need to augment the nation's natural water resources through the desalination of brackish and marine waters. Support by the Department of Interior has produced major advances in the technology and development of suitable desalination processes. It has become apparent, however, that perhaps a much better source of water is reclamation by these methods of municipal wastewater since it contains far fewer dissolved minerals and is always available relatively near the intended use.

Of the many demineralizing processes, the comparatively low-energy reverse osmosis process appears well suited to the renovation of municipal wastewater. Processes requiring a change of phase, such as distillation and freezing, are better suited for more saline waters since their performance and costs are relatively independent of salt concentration.

Conventional wastewater treatment processes require many steps to remove wastewater constituents. Treatment processes incorporating reverse osmosis may be capable of performing a much superior treatment in fewer operations; dissolved salts, organic substances, and insoluble suspended matter are all removed in the same operation.

Basic elements of the reverse osmosis process consist of the membrane, a means for providing a high-pressure differential across the membrane, and a support for the membrane against this pressure differential. A number of different membrane materials possess the favorable osmotic properties of relatively high product water flux and low or no solute transport. However, only cellulose acetate has found extensive use in desalination.

STUDY OBJECTIVES

The purposes of this study were threefold.

(1) To compare tubular membranes prepared from transesterified (modified) cellulose acetate with Eastman 398-10 cellulose acetate (control).

(2) To evaluate the in-situ regenerable membrane reverse osmosis design on wastewater. In the regenerable unit, membranes were formed, removed and reformed in place on porous tubes in a shell and tube configuration.

(3) To evaluate the membranes on carbon treated secondary effluents, primary effluents and concentrated primary effluents. The concentrated primary effluent feed was used to simulate the near exit conditions of an operating reverse osmosis unit. Successful treatment of primary effluent by reverse osmosis would place this process in a position favorable to the economics of the overall wastewater treatment system as well as eliminate the relatively difficult to operate biological conventional secondary sewage treatment.

Both the tubular membrane and the regenerable membrane units were assembled and operated in a portable test apparatus at the Ponoma Water Reclamation Plant.

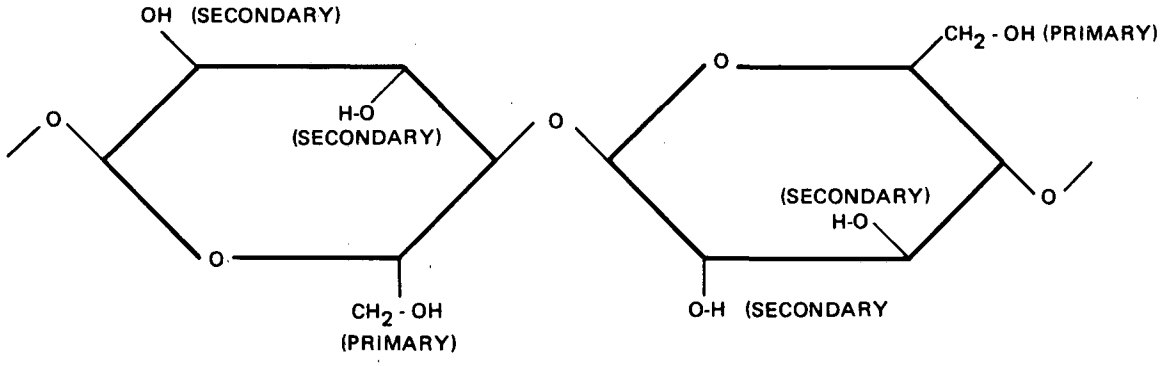
TRANSESTERIFIED MODIFIED CELLULOSE ACETATE

Since cellulose acetate is the most effective membrane material, its properties were examined and modifications were made to improve its stability, and consequently its desalination properties.

Commercially available cellulose acetate commonly used in reverse osmosis consists mainly of the diacetate (2.4 acetate); that is, 2.4 out of the three hydroxyl groups of each anhydroglucose unit are esterified. Each unit of glucose has one primary and two secondary hydroxyl groups.

For manufacturing reasons, the diacetate is made indirectly; that is, the cellulose is first completely esterified to the triacetate; enough water is then added to hydrolyze one group. The relative reaction rates are such that the primary ester linkage is hydrolyzed first, resulting in an ester having free (unacetylated) primary hydroxyl groups. This product is satisfactory for the manufacture of lacquer, which is the principal use of cellulose acetate.

Controlling the esterification process produces a cellulose acetate that contains more acetylated primary hydroxyl groups and more free secondary hydroxyl groups.



The balance between free and esterified hydroxyl groups can be shifted towards the thermodynamically more stable equilibrium distribution by dissolving the cellulose acetate in 98 to 99 percent acetic acid and maintaining it at 65 to 85°C for several hours. Malm (Ref. 1-4) has shown that under proper conditions, no further esterification and little degradation of the cellulose takes place, while the proportion of primary to secondary ester groups shifts from 1:2 to 1:4, depending on time and temperature.

Stabilized membranes prepared from this material were hoped to provide greater product water flux and be more resistant to flux decline, hydrolysis and other forms of degradation.

REGENERABLE MEMBRANE

Also evaluated in this program was a new, low-operating-cost, design concept for reverse osmosis equipment. This concept was developed with the support of the Office of Saline Water (Ref. 5) and consists of a shell and tube configuration with membranes on the outside of porous ceramic tubes. The porous ceramic tubes can be removed from the shell. Membranes are formed on the porous supports by dipping into a cellulose acetate casting solution followed by gellation with cold water and a hot water cure. Membranes are removed by dipping the membrane coated porous support tubes into a stripping solution. Membranes can then be replaced by repeating the membrane forming procedure. This design promises significant operating cost savings by eliminating most of the labor cost for membrane replacement.

SECTION IV
MEMBRANE PREPARATION

MODIFIED CELLULOSE ACETATE

Modified (transesterified) cellulose acetate was typically prepared in 400-gram lots, as described in the following procedure.

Into 1,800 ml of acetic acid was dissolved with stirring 400 gm of dried Eastman 398-10 cellulose acetate*. The mixture was heated to 85 to 87°C, then a mixture of 40 ml 10 N HCl and 400 ml acetic acid was added. The reaction mix was stirred one hour at 86 ± 1°C. The cellulose acetate was precipitated by pouring the mix into 100 liters of distilled water. The solids were filtered through a woven cloth filter and vacuum dried. Upon composite cellulose acetate batch analyses the acetyl content by weight was 39.7 percent. The hydroxyl content by weight was 3.46 percent of which 37 percent was primary and 63 percent was secondary hydroxyl groups. The remaining hydroxyl groups were converted (acetylated) to acetyl groups.

TUBULAR MEMBRANE PREPARATION

The casting solution and the tubular casting procedures were based on the procedures described by Manjikan (Ref. 6) and Loeb (Ref. 7). Casting solution was prepared by blending 25 percent cellulose acetate with 45 percent acetone and 30 percent formamide (by weight). The mix was then rolled overnight to thoroughly blend the material.

Tubular membranes were prepared in precision bore glass tubes (0.873-in. ID). The important divergence from the Loeb procedure was to raise the casting bob within the stationary casting tube and subsequently air dry the membrane 20 seconds prior to immersing the tube and membrane into a chilled water (+2°C) gellation bath. The apparatus is shown in Figure 1.

Membranes formed from the modified cellulose acetate were brittle and initially could not be fabricated into tubular units, primarily because the ends could not be flared without tearing. However, air drying the membrane prior to gellation improved the tensile strength sufficiently to allow flaring.

In operation, the casting tube is suspended by a yoke attached by cable to a variable speed motor. A casting bob is lowered by cable through the tube. The casting tube is filled at the bottom with 80 to 150 cc of casting solution, which is held in place by the bob. The tube is lowered at a constant rate (15 ft/min) past a stationary bob, which is self-centering and wipes an even film on the tube interior. The film gels

*Eastman Chemical Products Inc., Kingsport, Tennessee.

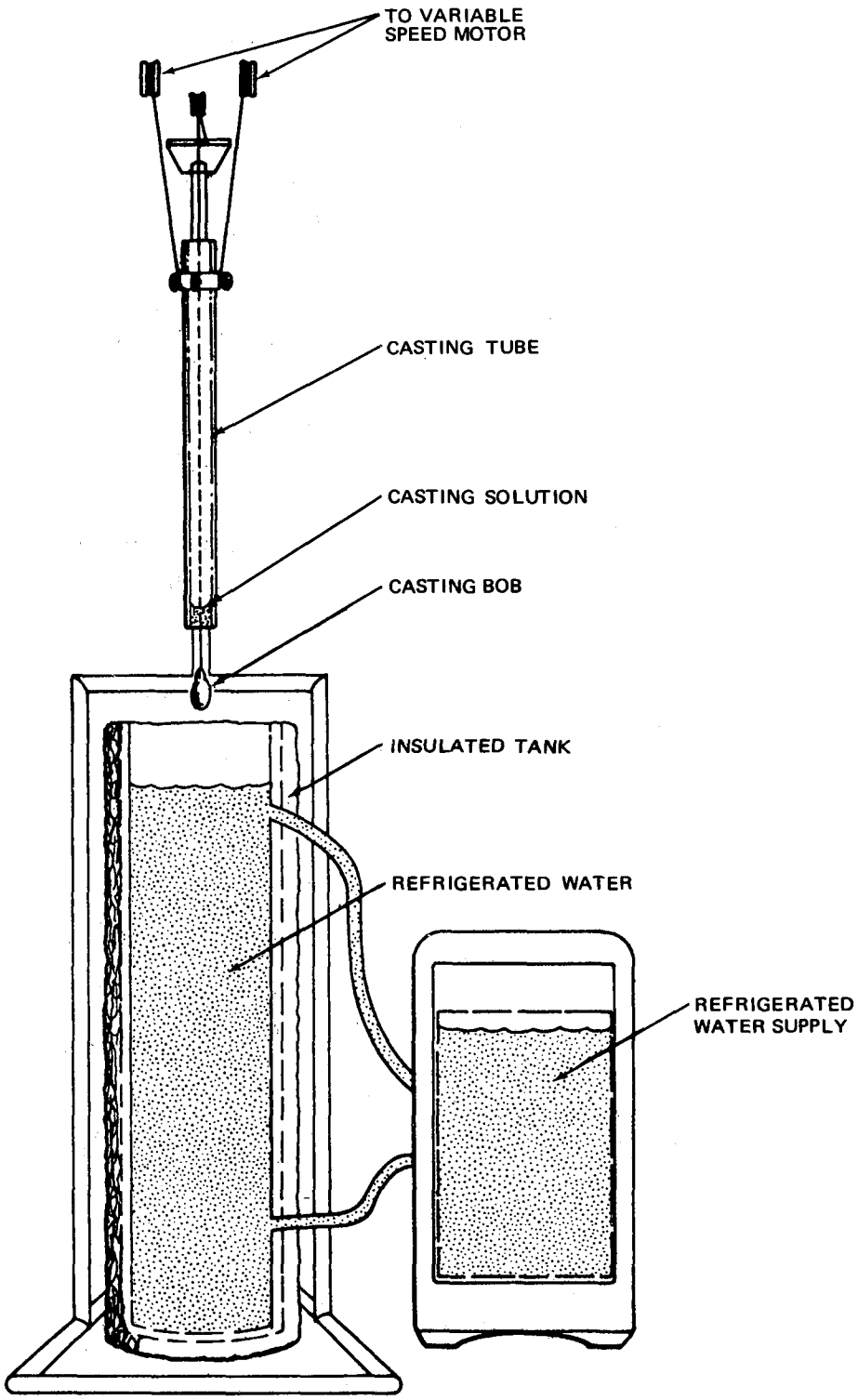


Figure 1. Tubular Membrane Casting Apparatus

into a membrane as the casting tube enters the cold water bath. The tubular membranes shrink away from the casting tube and may be removed when fully gelled.

The tubular membrane is then wrapped with nylon cloth and inserted into a type 304 stainless steel pressure tube. The membrane ends are flared to receive the end fittings. This tubular membrane construction is illustrated in Figure 2. The tube length is 4-1/2 feet and tube diameter is 1.0 inch (OD) and 0.86-inch ID to yield a membrane area of approximately 1.0 square foot per tube. After assembly, the membrane is heat annealed in the tube by circulating hot water through the tube.

REGENERABLE MEMBRANE PREPARATION

Regenerable membranes were formed directly on the outside surface of a porous support, as described in OSW Research Report No. 464 (Ref. 5). The membrane solution of E-398-10 cellulose acetate (22 percent), formamide (24 percent), and acetone (54 percent) was cast onto 1/4-inch diameter by 3-foot long porous ceramic tubes. These tubes were combined into a tube bundle and inserted into a pressure shell. Purified water flowed through the membrane and up the inside of the tube and out as illustrated in Figure 3. Figure 4 shows the tube bundle and pressure shell.

The 1/4-inch tubes were sealed into a header section with epoxy. This header section, shown as the base of the tube bundle in Figure 4, was subsequently attached to the pressure shell by a Victaulic* coupling. The opposite end of the tubes was sealed and the product water flows through the membrane, into the porous tubular membrane support and to the header section which also serves as a product collection section for the tubes.

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*Victaulic Company of America, South Plainfield, New Jersey.

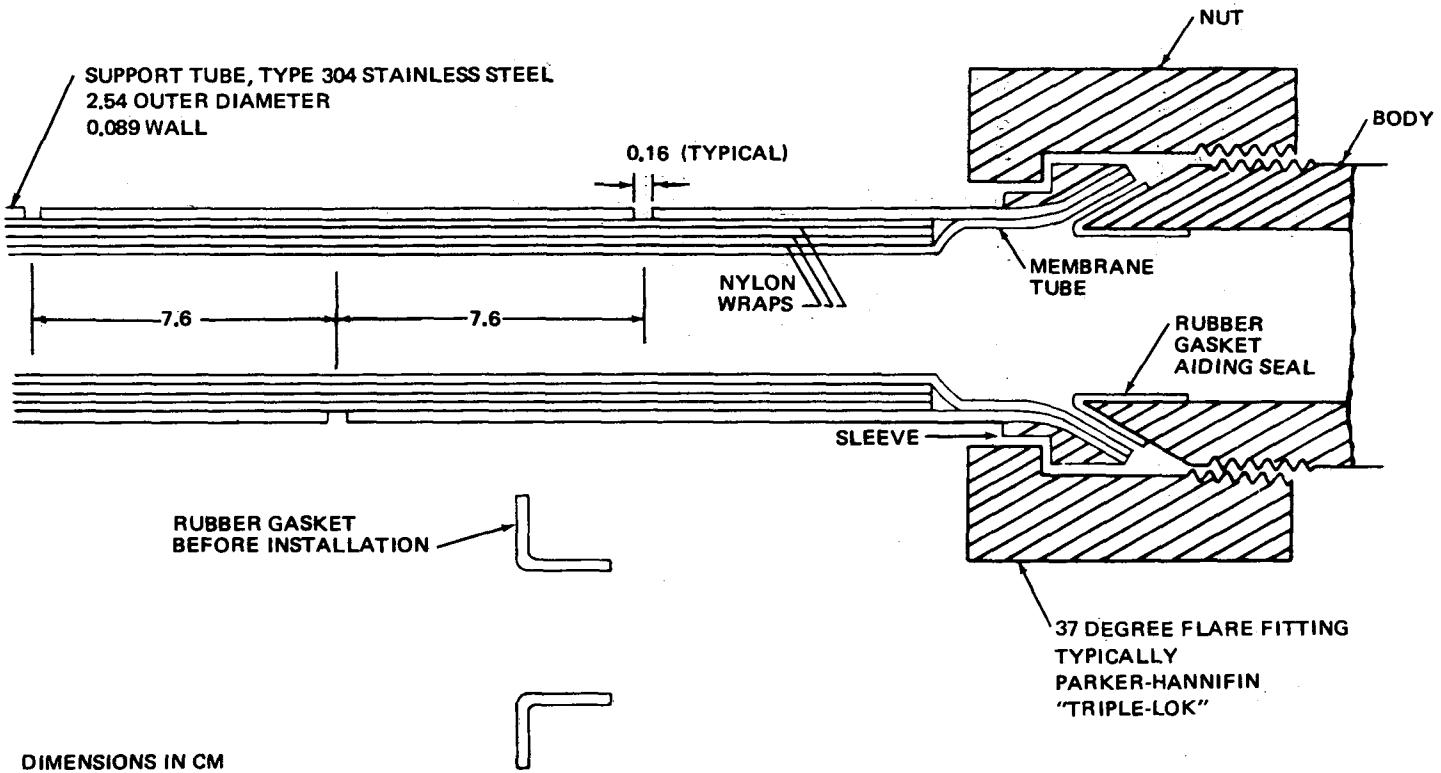

Figure 2. Composite Tubular Assembly (Ref. 1)

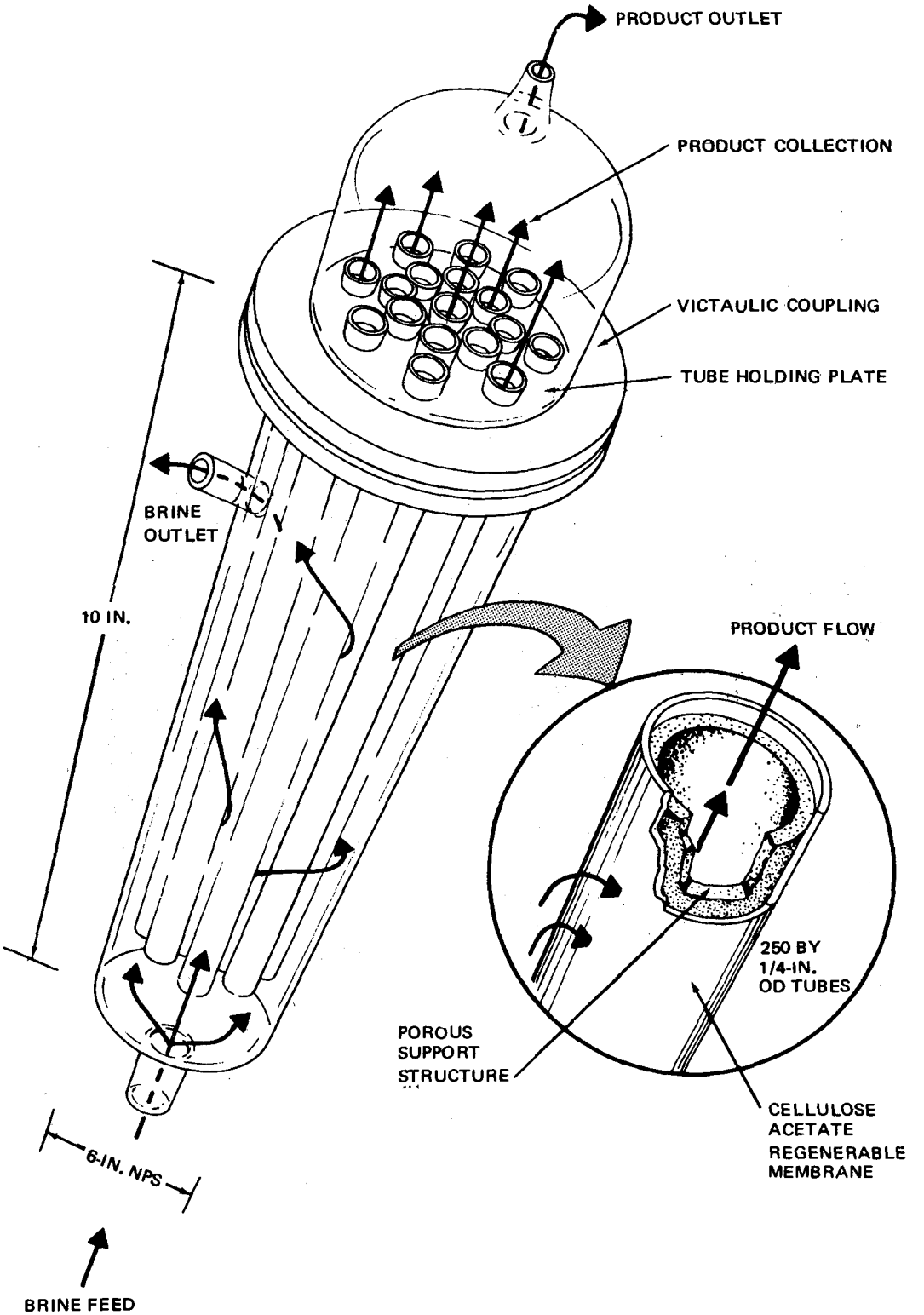

Figure 3. Conceptual Shell and Tube Design (Repeatable Unit) for Regenerable Reverse Osmosis Plant

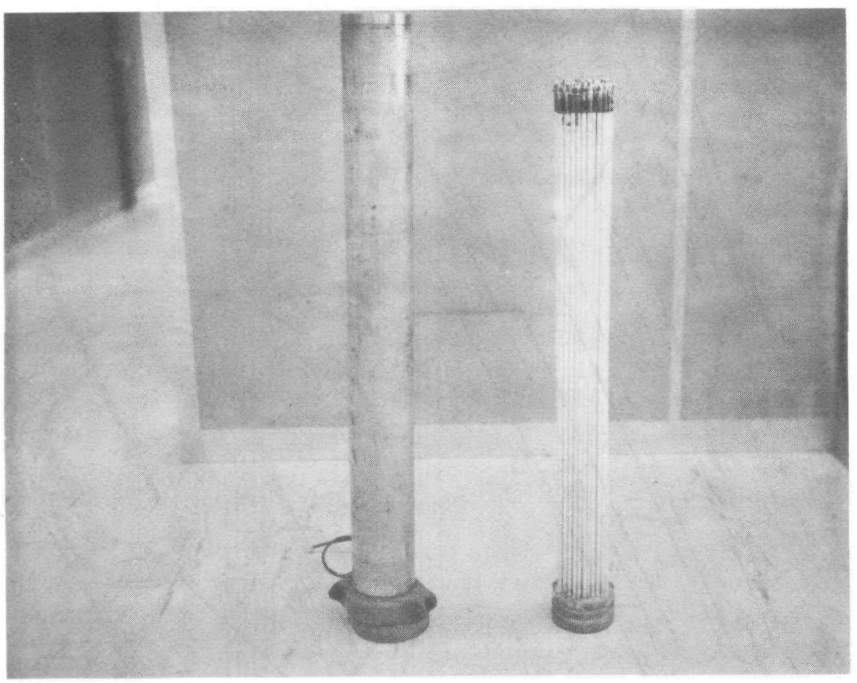

Figure 4. Regenerable Membrane Reverse Osmosis Unit

SECTION V

LABORATORY TEST RESULTS

To qualify the modified cellulose acetate, flat-sheet membranes were prepared and tested at 1,000 psi against a 1-percent NaCl solution. After 24 hours on test, the product flux was 29.1 gfd at 96.3-percent salt removal. This was considered sufficiently close to the performance target (30 gfd at 97-percent removal) to warrant using this modified cellulose acetate.

Therefore tubular cellulose acetate membranes were made and mounted into stainless steel tubes for heat treatment and initial laboratory 24-hour test. This test also included membranes made of unmodified cellulose acetate (E-398-10). The test results-control-after 24-hour testing against 3,000 mg/l sodium chloride at 600 psi were:

Set A. Modified membranes (open) 54.6 gfd at 61-percent salt removal.

Set B. Modified membranes (tight) 20.1 gfd at 92-percent salt removal.

Set C. Standard membranes (E-398-10) 18 gfd at 96-percent salt removal.

Comparison of Set B and Set C indicated only slight difference in performance between the modified and standard membranes (control).

Additional laboratory tests were made while awaiting completion of the field test unit. The lab tests established the membrane performance using NaCl solutions over a select time period for comparison with the results obtained later with Pomona effluents. Six tubular membranes were selected at random from the 61-percent removal group (Set A). These membranes were tested for 2400 hours at 600 psi with a 3,000 mg/l NaCl solution. All product water flux and salt removal values were corrected to 77°F. The group average performance was:

24 hours	51.9 gfd	62-percent salt removal
72 hours	47.6 gfd	61-percent salt removal
1008 hours	38.7 gfd	59-percent salt removal
1680 hours	26.4 gfd	78-percent salt removal
2400 hours	21.1 gfd	84-percent salt removal

A tight tubular membrane, Set B, and a regenerable unit with 5 sq ft of surface area were also tested on a 3000 mg/l NaCl solution at 600 psig. The results of these tests are plotted in Figure 5 as log

of the product flux versus time. The flux decline coefficient, k, is expressed by

$$J = J_o \exp (kt)$$

where

J = product water flux in gallons/sq ft-day(gfd)

J_o = initial product water flux in gfd

k = flux decline coefficient in hours^{-1}

t = time on test in hours

The flux decline rate, m, is the slope of the flux decline curve on a log flux versus log time plot

$$\log J = \log J_o + m \log t$$

Both of these expressions for flux decline are tabulated below for the laboratory tests on pure saline solutions (3, 000 mg/l NaCl at 600 psig).

	k	m
Modified (loose) tubular membranes (Set A)	-0.059	-0.115
Modified (tight) tubular membranes (Set B)	-0.066	-0.083
Regenerable membranes	-0.077* -0.008**	-0.083

* Initial 600 hours of test
**Final 1000 hours of test

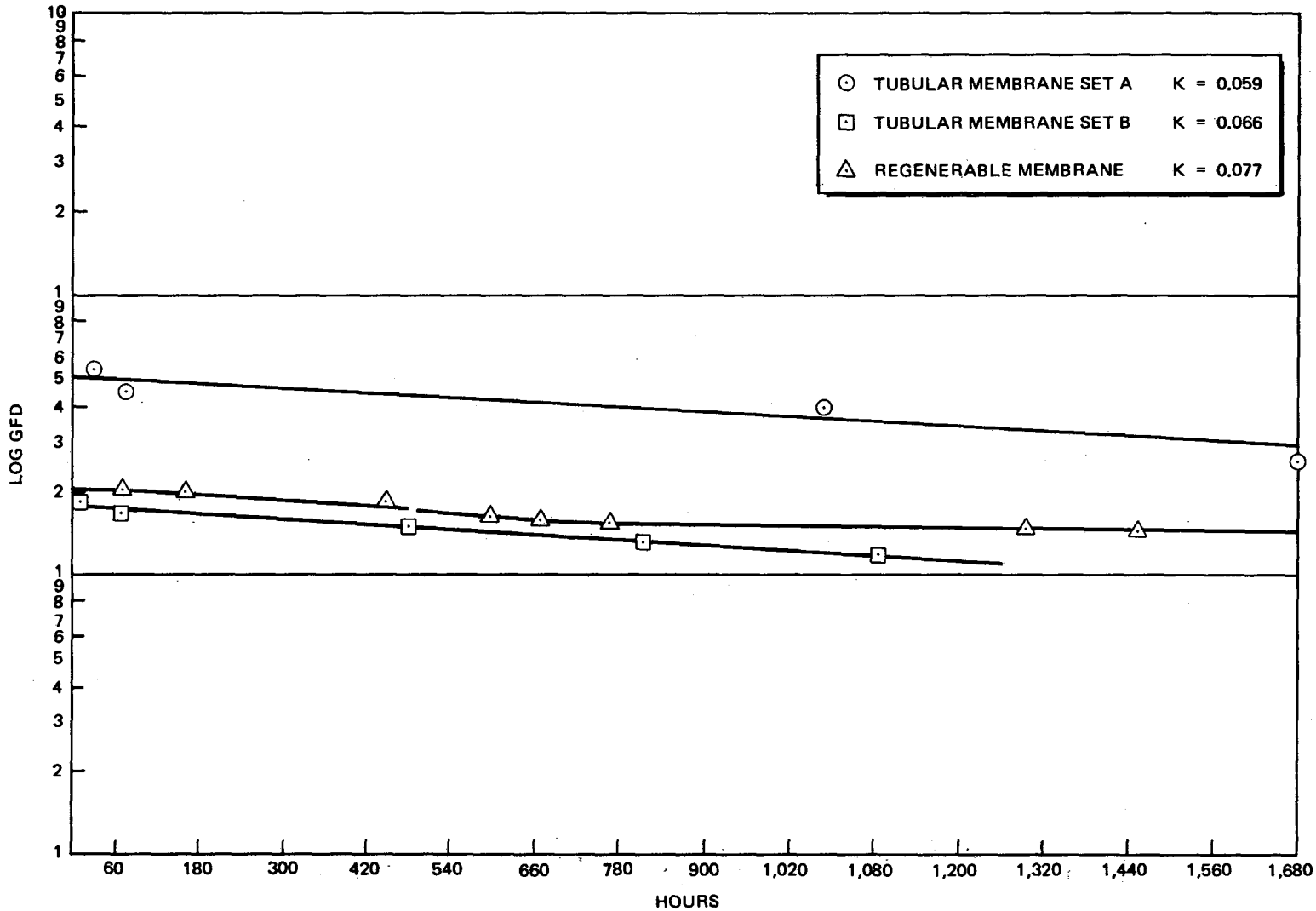

Figure 5. Flux Decline Using 3000 PPM NaCl

SECTION VI

FIELD TESTING

DESCRIPTION OF EQUIPMENT

A field test unit was built for operation at the Pomona Water Renovation Facility. A schematic of this field test unit is shown in Figure 6 and photographs in Figures 7 and 8. The major pieces of equipment are described in Appendix A.

Municipal effluent from the Pomona Water Renovation Facility flowed on demand directly into the 500-gallon feed tank. Tank level was regulated by a float valve on the wastewater inlet line.

A centrifugal priming feed pump under the feed tank provided a continuous positive head on the suction side of the high pressure feed pump. Excess flow from the priming pump not required by the high pressure feed pump was returned to the tank through a bypass line.

The pH of the effluent in the feed tank was adjusted to approximately 5 to 6 with sulfuric acid. The pH sensing unit was located in the bypass line from the centrifugal feed pump. As directed by the pH controller, sulfuric acid was injected by a metering pump at a point adjacent to the bypass return, which also provided good mixing of the acid.

Product water from the tubular units was collected in 2-in. diameter polyethylene tubes mounted around the 1-in. stainless steel membrane support tubes. These collection tubes were sealed at both ends with a one-hole (1-in. ID) rubber stopper. The collection tubes were vented to the atmosphere. The collected product water flowed by gravity to the flow meters. One-quarter-inch diameter plastic tubes attached to the bottom of the 2-in. collection tube were used to transport the product water from the individual tubular membrane units to central standpipes feeding the flow meter for each membrane set.

Initially, the test setup consisted of three sets of tubular membranes and two regenerable units as follows:

Set 1. Modified cellulose acetate tubular membranes with 60-percent removal (5 ft^2).

Set 2. Modified cellulose acetate tubular membranes with 90-percent removal (5 ft^2).

Set 3. Standard membranes (E-398-10) with 95-percent removal (5 ft^2).

Set 4. Regenerable unit No. 3 (5 ft^2) with 90-percent removal.

Set 5. Regenerable unit No. 4 (5 ft^2) with 60-percent removal.

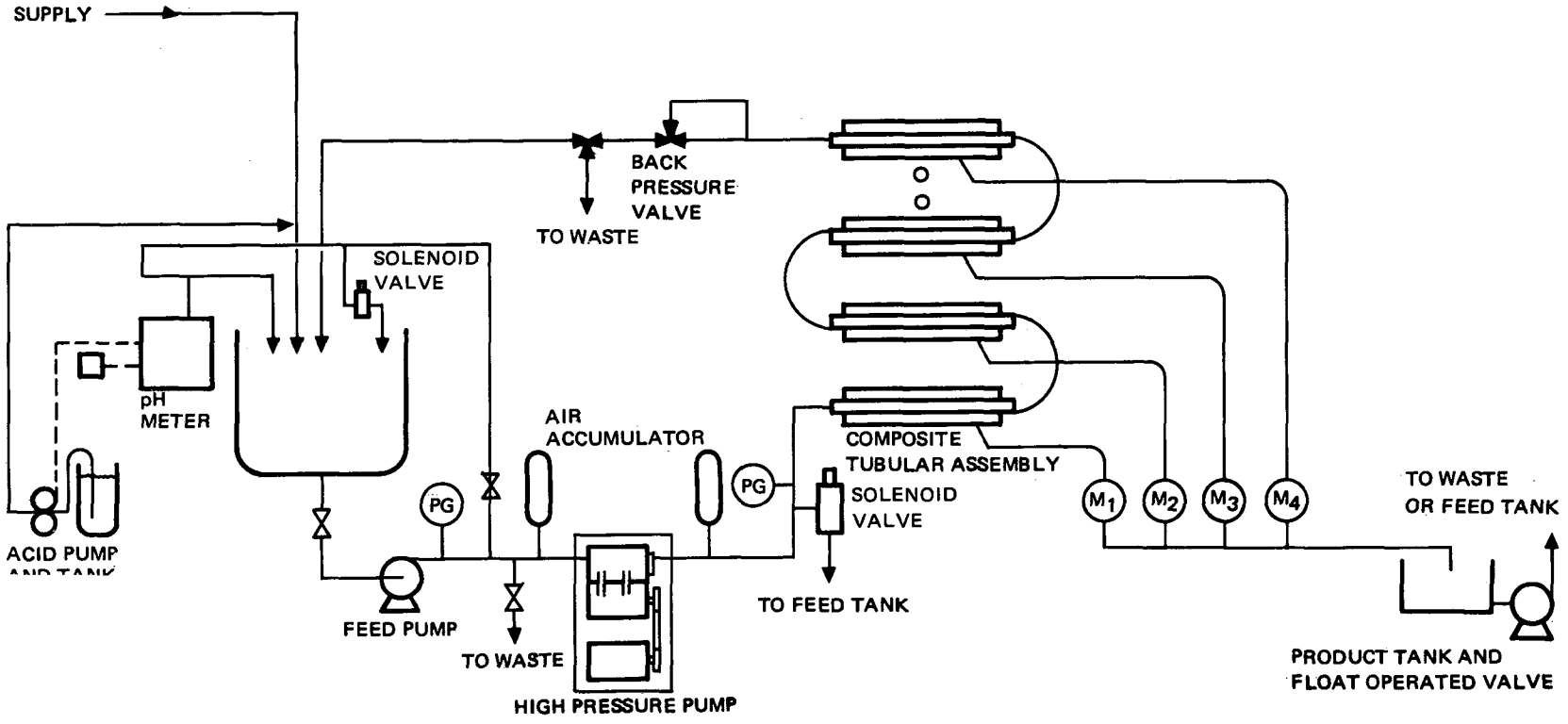

Figure 6. Test Apparatus Schematic

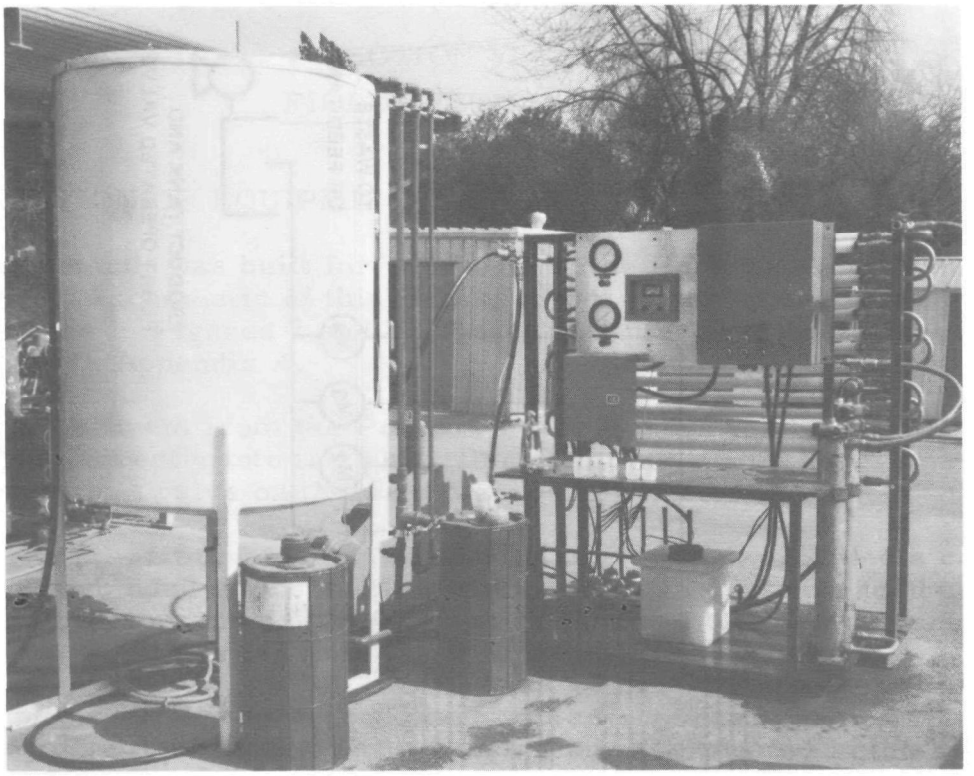

Figure 7. Front View of Unit installed at Pomona

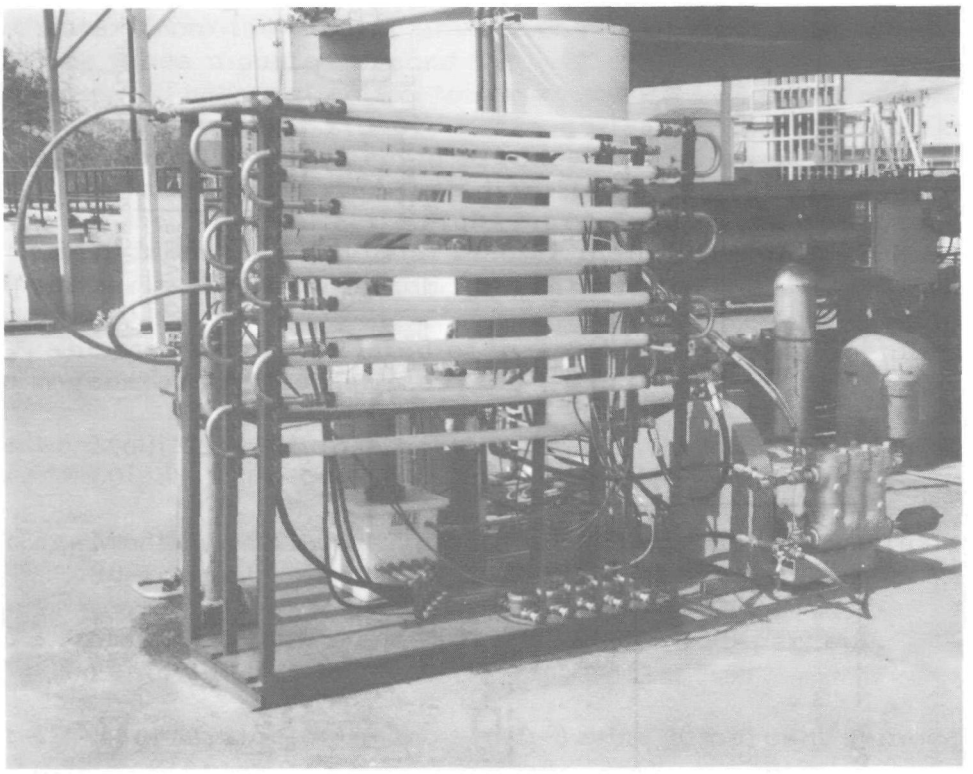

Figure 8. Rear View of Unit Installed at Pomona Showing Membrane Tubes

Each tubular membrane set consisted of five tubular units, each 4-1/2 feet long by 0.86 inches ID, 1.0 inches OD, providing a membrane surface area of approximately one square foot per tube. The three types of individual tubular units (from Sets 1, 2 and 3) were connected randomly in series so that the feed water flowed through U-bends from one tube to the next.

Two regenerable membranes, each with five square feet of membrane area were placed in series after the tubular units.

During the first two weeks of operation the following changes were made.

1. A failure occurred in the regenerable units on the third day when a tubular membrane loosened and was transported into these units. Regenerable units No. 3 and No. 4 were replaced with another membrane bundle, Regenerable Membrane Unit No. 5, with 13 ft^2 of membrane surface area and an average salt removal capacity of 80 percent.

2. The product water meters proved to be unreliable at the low flows and pressure heads. Product water production rates were determined during the remainder of the test by measurement of the product water flow during a given time, usually one minute, whenever the units were serviced.

OPERATING CONDITIONS

The field test unit was operated continuously for 24 hours a day and 7 days a week throughout the tests. Operating pressure was maintained at 600 psig. The flow rate through the reverse osmosis unit was maintained at 12 gallons per minute. This is equivalent to a flow velocity past the tubular membranes of 1.6 feet per second. Reynold's number in the tubular units was $\sim 10^4$.

Three types of feed were tested:

1. Carbon treated secondary effluent

2. Primary effluent

3. Concentrated primary effluent.

Both the carbon treated secondary effluent and primary effluent flowed continuously into the feed tank, past the membranes, and directly to the drain. Product water also was allowed to go to the drain. Concentration changes of the feed within the test unit were negligible so that the properties of feed throughout the test unit can be assumed constant and equal to those of the incoming feed.

During the concentrating step all of the primary effluent feed was returned to the feed tank while the product water was again allowed to go to drain. This allowed the feed to become more more concentrated as the product water was removed. No blowdown of the feed tank was allowed until the total solids concentration was 9 times that of the incoming untreated primary effluent feed simulating the near exit conditions of a reverse osmosis system with approximately 90-percent water recovery.

The temperature of the carbon treated secondary and primary feed stream averaged 80°F. Product water flux values were corrected to 77°F (25°C). Temperature of the concentrated primary feed averaged 120°F (49°C) due to the heat added by the high pressure pump during recirculation of the feed stream. Product water flux values were also corrected to 77°F (25°C) using a conservative correction factor (~60 percent of the measured value). Thus, the flux values reported for 77°F are more likely lower than the actual values. To avoid this problem a heat exchanger should be used in any future studies where the wastewater feed is concentrated.

All tests were conducted at a pH of approximately 5 to 6, in order to reduce the potential for phosphate or carbonate precipitation as well as reduce the potential for membrane hydrolysis. However, pH values as high as 8 were reached during a two day malfunction of the pH controller. The sulfuric acid which was injected at the bypass return to the feed tank by the priming pump maintained the entire contents of the feed tank at a pH of 5 with the secondary advantage of stabilizing the wastewater composition.

Three different methods were experimented with to clean and rejuvenate the tubular membrane surfaces: (1) sponge flush ball, (2) enzyme-active laundry presoak (Biz) solutions, and, (3) urea solutions. The sponge flush ball consisted of a cellulose sponge formed into a 1-in. diameter ball. This ball made a tight fit in the 0.86-in. diameter membranes and was forced through the tubular membrane units under approximately 10-psig water pressure from the priming pump. However, the sponge flush ball would occasionally tear one of the tubular membranes, and was discarded in favor of a Biz flush which also gave higher flux recovery. The cleaning procedure followed for both the Biz and urea flush was to depressurize and drain the system, and then circulate the desired solution past the membranes for 30 minutes. Flow velocity was ~1 ft/sec past the membrane and flow pressure was ~10 psig. Solution temperature was 77°F (25°C). Concentration of the Biz cleaning solution was 7.1g of Biz per liter of water and concentration of the urea cleaning solution was 360g (6M) of urea per liter of water. The pH of the Biz solution was 9.2. The urea solution pH was maintained at 5.

After cleaning the system was drained and repressurized with the normal feed. After 30 minutes of operation the product water flux was determined. Any sampling for chemical analysis was done prior to cleaning.

MEASUREMENTS

Grab samples representing point values were taken for chemical analysis. The following constituents were monitored and analyzed in accordance with procedures outlined in the Twelfth Edition of Standard Methods for the Examination of Water and Wastewaters, American Public Health Association, Inc., or FWQA approved alternate methods – pH, electrical conductivity, total dissolved solids, total solids, total chemical oxygen demand, filtered chemical oxygen demand, and ammonia.

Electrical conductivity was determined by using a conductivity bridge, Beckman Model RD 125J with temperature correction, with a 4.5-ml capacity cell, Beckman Model G2.

Total dissolved solids were measured by weighing the residue from a filtered and evaporated sample. A 0.45μ membrane filter was used. Total solids were determined in the same manner using an unfiltered sample.

Total chemical oxygen demand (COD) was determined by potassium dichromate-sulfuric acid digestion for two hours and ferrous ammonium sulfate titration to the ferroin indicator endpoint; any chloride present in the sample was complexed with mercuric sulfate. Filtered chemical oxygen demand was determined in the same manner from a sample filtered through a 0.45μ membrane filter. Initially, a disposable plastic filter unit (Nalgene No. 245) was used. However, increases in the COD value, attributed to preservatives in the filter, were observed. Subsequent filtering was done with a pressure filter (Millipore No. 4004700) and 0.45μ membrane filter (Millipore HA).

Ammonia contained in samples was distilled from Kjeldahl flasks and collected in boric acid solution. The amount of ammonia in the distillate was determined colorimetrically at 425μ wavelength in a spectrophotometer following Nesslerization.

Samples were taken early in the morning and refrigerated so that the chemical oxygen demand measurements could be made the same day since changes in the COD values were observed in samples held overnight, even under refrigeration. Samples taken for ammonia or nitrogen analysis were fixed with sulfuric acid (~2 ml/l) immediately after they were taken.

Product water flux was measured before and 30 minutes after membrane cleaning to allow the flux to stabilize. The product water flux only was measured after membrane cleaning because of possible residues of the cleaner used. All other parameters such as salt, solids and COD removal were measured prior to membrane cleaning.

Four samples were taken during these tests for a complete chemical analysis as follows.

Sample 1. At the end of the carbon treated secondary effluent test.

Sample 2. At the end of the primary effluent test.

Sample 3. In the middle of the concentrated primary effluent test.

Sample 4. At the end (prior to use of urea for membrane cleaning) of the concentrated primary effluent test.

The following analyses were made on these samples:

MBAS	Methyl blue active substances minimum detectable level 0.001 mg/l
Total Alkalinity	mg/l as $CaCO_3$ using methyl orange indicator and comparing against a standard curve.
Total Hardness	mg/l as $CaCO_3$ using Eriochrome Black T indicator and comparing against a standard curve.
Phosphorus	mg/l of P by the stannous chloride method in which all phosphorus is converted to orthophosphate and analyzed colorimetrically using a factor of 0.3263 to convert to phosphorus.
Total Nitrogen	mg/l of free ammonia and organic nitrogen by the Kjeldahl method.
Chloride	mg/l of Cl by the Mohr titration method using silver nitrate.
Sulfate	mg/l of SO_4 measured gravimetrically after precipitation with barium chloride
Calcium	mg/l of Ca by titration with disodium dihydrogen using muroxide as an indicator.
Magnesium	mg/l of Mg determined by difference between calcium and total hardness.
Volatile Matter	Suspended material - filtrate from Gooch filter and dried for 1 hour at 500°C sensitivity 0.01 mg/l.

In order to present comparable product water flux measurements a plot of temperature versus water flux was prepared and all flux values corrected to 77°F (25°C).

For the carbon treated secondary and primary effluents which were discharged after passing through the test unit the average feed temperature was 80° and the necessary temperature correction was 0.97. The average feed temperature during recirculation (concentrated primary effluent test) was 120°F (49°C) requiring a temperature correction factor of 0.60.

DATA REDUCTION

Initial examination of the data on product water fluxes indicated that most test results may be presented as exponential functions of time. Therefore flux decline data were calculated using all the data points presented and are given in the form of coefficients J_o and k to fit the general equation:

$$J = J_o e^{kt} \tag{1}$$

where J is product water flux in gal/(sq ft) (day), J_o is initial flux upon attainment of specified concentration, k is the flux decline coefficient in hours^{-1}, and t is expressed in hours of operation at desired wastewater concentration condition. The fluxes were converted to their logarithms and the line of best fit for the data was determined by least-square regression methods. Average product water flux for this period was calculated from this line of best fit.

An alternative method of representing the data is by a log-log plot of product water flux vs time. Using this representation the product water flux decline may be expressed by the general equation:

$$\log J = \log J_o + m \log t \tag{2}$$

where J, J_o and t have the same connotation as above. In this equation m is the slope of the product water flux decline curve.

Both the flux decline coefficient, k, and the slope of the product water flux decline curve on a log-log plot, m, were calculated using the least square regression methods and are presented in this report.

A semi-logarithmic plot of log flux vs time, following equation (1), was chosen to represent the data because it presents the changes occurring during the test in a simple chronological manner with each portion of the test given equal representation.

Membrane performance with respect to constituent removal was calculated on the basis of the feed to the reverse osmosis unit. However, at the flow rate used in this test unit (12 gpm) the changes in feed concentration as it passes through the unit are negligible. Thus the composition of the feed entering the unit can be considered representative of the entire unit.

A membrane coefficient, μg/(sq cm) (sec) (atm) was calculated and plotted along with the standard flux units of gfd. The membrane coefficient corrects or normalizes the flux values for operating pressure, thus allowing direct comparison of product water flux measured at different operating pressures. Several normalizing coefficients have been used by other workers (Ref. 5, 6 & 7), but this one has the advantage of yielding numerical values almost identical to gfd in the very commonly used 600 to 700 psig operating pressure range.

SECTION VII

OPERATION ON CARBON-TREATED SECONDARY EFFLUENT

The tubular membranes described in Section VI were operated on carbon-treated secondary effluent with and without periodic cleaning for 1,185 hours.* The overall performance of these membranes on carbon-treated secondary effluent is summarized in Table I. The changes in product water flux with time are presented in Figure 9 as a plot of log J (flux) vs time.

During the first 400 hours of operation (Stage I with no membrane cleaning) the product water flux from membranes based on modified cellulose acetate (Set 1 & 2) dropped from an initial value of 30 gfd to a more-or-less equilibrium value of 10 to 15 gfd. During the same period product water flux from control membranes based on E-398-10 (Set 3) declined from an initial value of 20 gfd to an equilibrium value of 7 gfd.

However, subsequent periodic cleaning with an enzyme-active laundry presoak solution (Biz) restored and maintained the product water flux at very near its initial value.

Salt (conductivity), COD, and total solids removed (rejected by the membranes) remained fairly constant throughout the test. Average values for Set 3 were 95 to 98 percent. Sets 1 and 2 were lower (68 to 85 percent), although Set 2 rose to 96 percent during the latter portion of the test. The lower rejection observed with Set 1 was attributed to small mechanical leaks and was corrected in subsequent work with primary effluent.

Changes in product water flux with time for the regenerable membrane followed the same pattern as the tubular units, Figure 10. Although flux and salt rejection were somewhat lower, the flux decline coefficients, k and m, were also lower.

The detailed data for Table I and Figures 9 and 10 are tabulated in Appendix B.

Near the completion of the operation on carbon-treated secondary effluent a complete analysis was made of the feed and product streams. The results are tabulated in Table II.

The carbon treated secondary effluent used in this test was obtained from the Pomona Reclamation Plant. Just prior to this study, secondary effluent was treated in four consecutive activated carbon

*All carbon-treated secondary effluent feeds were adjusted to pH of approximately 5 to 6 with sulfuric acid.

Table I

AVERAGE MEMBRANE PERFORMANCE WITH CARBON-TREATED SECONDARY EFFLUENT FEED

	Tubular			Regenerable
Membrane Set No.	1	2	3	5
Flux Decline Coefficient*, k (hr^{-1})	-0.00258	-0.00084	-0.00334	-0.00178
Slope, m,**	-0.403	0.295	0.482	0.215
Average Flux, gfd (Stage I, No Cleaning)	22	17	11	8
Average Flux, gfd (Stage II, Periodic Cleaning)	29	21	16	10
Average Percent Removal (Total Solids)	76	83	97	77
Average Residual Total Solids., mg/l	130	100	25	130
Average Percent Removal (Total COD)	85	84	97	85
Average Residual COD, mg/l	3	3	1	3
Average Percent Removal (Total Salts based on conductivity)	68	80	95	73

*Calculated for the first 400 hours of test and prior to any cleaning.

**Slope of the flux decline curve on a log-log plot of flux vs time. Also calculated for the first 400 hours of test.

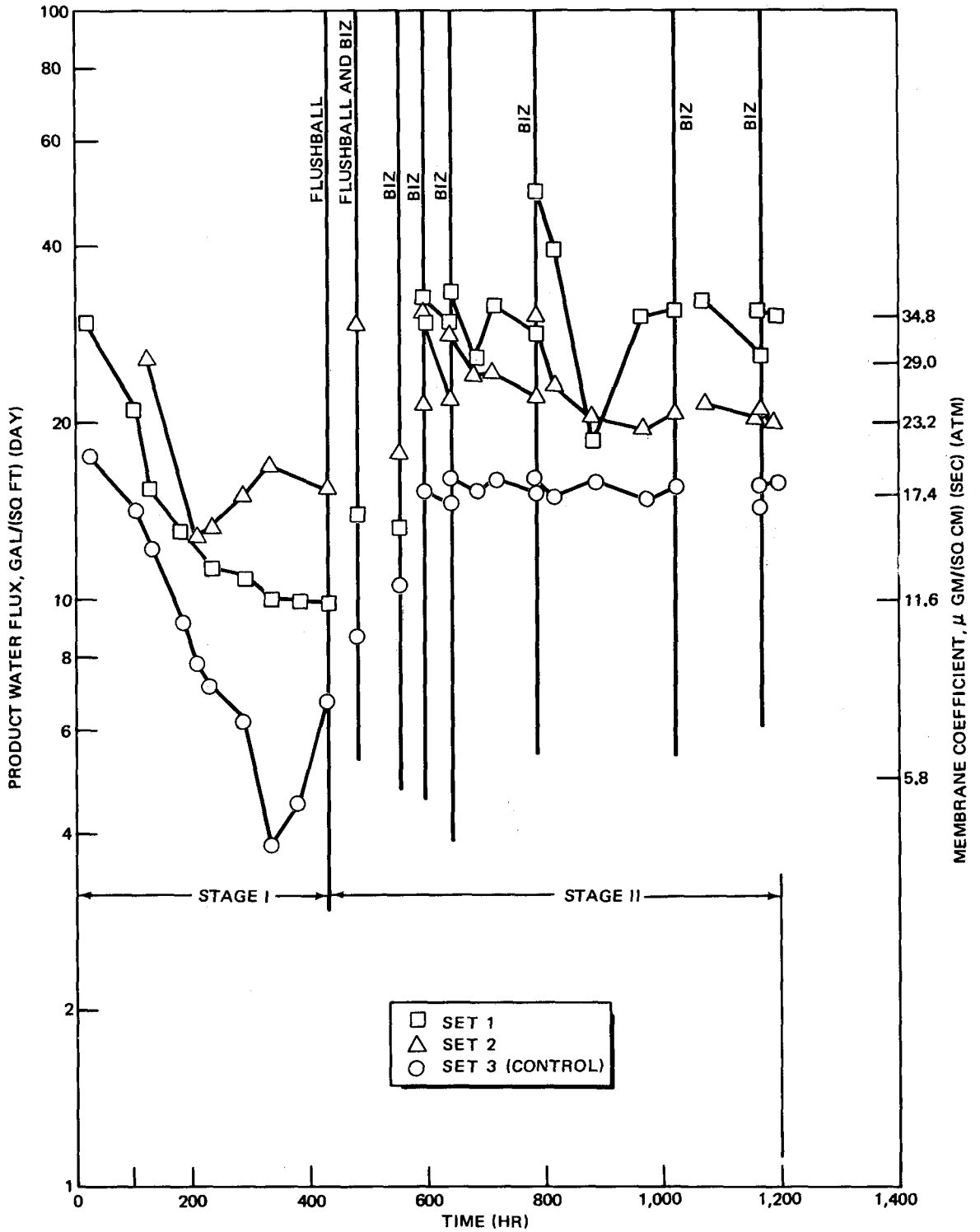

Figure 9. Performance of Tubular Membranes on Carbon-Treated Secondary Effluent (600 psig)

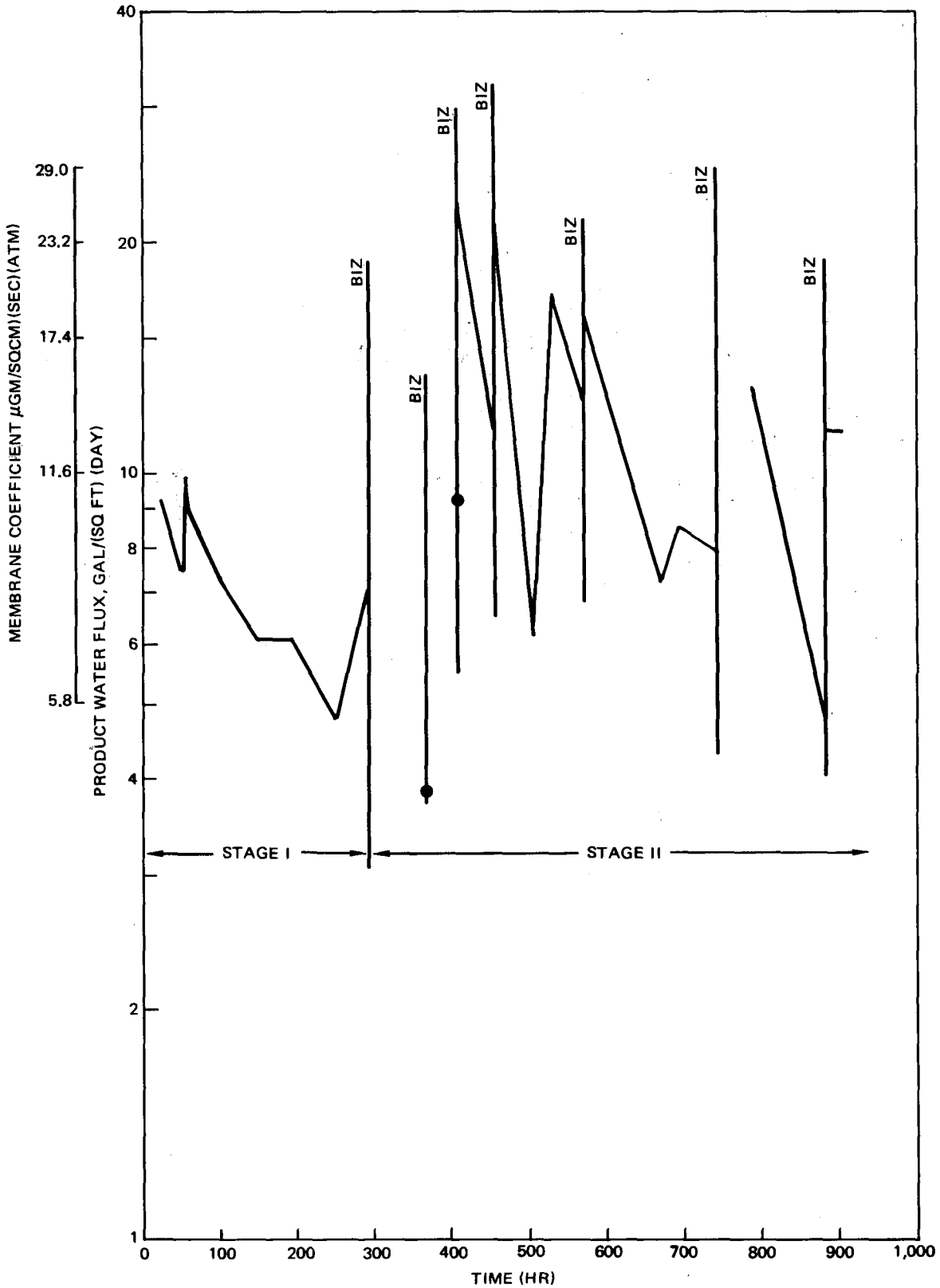

Figure 10. Performance of Regenerable Unit No. 5 on Carbon-Treated Secondary Effluent (600 psig)

Table II

REMOVAL OF WASTEWATER CONSTITUENTS DURING OPERATION WITH CARBON-TREATED SECONDARY EFFLUENT*

Wastewater Constituent	Tubular Membrane Set No. 1	2	3	Feed**
MBAS (mg/l)	<0.00	<0.001	<0.001	0.25
Percent Removal	100	100	100	
Total Alkalinity (mg/l as Ca CO_3)	7.50	15.00	10.00	30.00
Percent Removal	75	50	60	
Total Hardness (mg/l as Ca CO_3)	32.5	32.50	2.50	210.00
Percent Removal	85	85	99	
Phosphorus (mg/l)	3.26	3.58	0.97	11.55
Percent Removal	72	69	92	
Total Nitrogen (mg/l)	8.40	6.30	4.20	14.80
Percent Removal	43	57	72	
Chlorides (mg/l)	49.6	17.72	3.54	106.35
Percent Removal	53	83	97	
Sulfates (mg/l)	36.6	31.68	Trace	281.89
Percent Removal	87	89	99	
Calcium (mg/l)	10.0	10.00	0.95	66.00
Percent Removal	85	85	99	
Magnesium (mg/l)	1.81	1.85	Trace	10.89
Percent Removal	83	83	99	
Volatile matter (mg/l)	<0.0	<0.01	<0.01	<0.01

*Sample taken after 1, 185 hours of operation on carbon-treated secondary effluent.

**After pH adjustment with sulfuric acid

columns, operated in series, for the removal of dissolved organics and suspended matter. However, during the first portion of this R.O. study, from 0 to 431 hours (February 3, 1970 until March 11, 1970), the secondary effluent was treated in a single column followed by additional treatment in a small auxiliary column that acted as a polishing unit. As a result of this mode of activated carbon treatment, the carbon effluents were of relatively poorer quality with total COD concentrations ranging from 10 to 30 mg/l as compared to 7 mg/l to 11 mg/l (after normal activated carbon operations were resumed) and total solids averaging 650 mg/l as compared to 613 mg/l (after normal activated carbon operations were resumed Table BV appendix). Thus the R. O. test results during the 0 to 431 hour period were probably adversely affected by the relatively poorer carbon effluent, especially the product water flux decline. After March 11, 1970, the secondary effluent was again treated by the four-column group, but modified to operated as two 2-stage units in parallel. However, detention time in each of the two 2-stage units was the same as in the four-stage consecutive series operation, thus carbon effluent quality was approximately equivalent. Carbon effluents from the two 2-stage units were used from 431 hours until the end of the carbon effluent test period.

SECTION VIII

OPERATION ON PRIMARY AND CONCENTRATED PRIMARY EFFLUENT

A new set of tubular membranes of the same dimensions was prepared from modified cellulose acetate and commercially available cellulose acetate, Eastman 398-10. Regenerable membranes using Eastman 398-10 were reformed directly on the surface of porous ceramic support tubes. These membranes, identified as follows, were installed on a portable test stand at the Pomona Water Reclamation Plant and operated on primary and concentrated primary effluent.*

Set 1a. Modified cellulose acetate tubular membranes with 60-percent removal (5 ft^2).

Set 2a. Modified cellulose acetate tubular membranes with 90-percent removal (5 ft^2).

Set 3a. Standard tubular membranes with 90-percent removal (5 ft^2).

Set 6. Regenerable unit No. 6 (5 ft^2) with 90-percent removal.

The overall performance of these membranes is summarized in Table III. The changes in product water flux with time are presented in Figure 11 for tubular membrane set 1a, Figure 12 for tubular membrane set 2a and Figure 13 for tubular membrane set 3a.

The product water flux declined slowly during the first half of the test (Stage I) period from an initial value of 22 to 27 gfd to 2 to 3 gfd (Figure 11, 12, and 13). Flux then rose and appeared to stabilize at 5 to 6 gfd, in Stage II.

Stage I and Stage II correspond approximately to the period of primary and concentrated primary feed respectively. Although recycling of the feed was instituted during Stage I, higher feed concentrations were not reached until the end of Stage I. Total solids content of the feed to the reverse osmosis test unit at the end of Stage I was five times that of the incoming primary effluent. During Stage II the total solids content of the feed continued to rise reaching a maximum of nine times that of the incoming primary effluent. This concentration simulates the exit conditions of a reverse osmosis unit operating near 90-percent water recovery.

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*Primary and concentrated primary effluent feeds were pH adjusted to approximately 5 to 6 with sulfuric acid.

Table III

AVERAGE MEMBRANE PERFORMANCE WITH PRIMARY AND CONCENTRATED PRIMARY EFFLUENT FEED

Membrane Set No.	Tubular 1a	Tubular 2a	Tubular 3a	Regenerable 6
Flux Decline Coefficient, k, hr^{-1}	-0.00234	-0.00254	-0.00277	-
Slope, m* (Stage I)**	-0.438	-0.428	-0.540	-
Flux Decline Coefficient, k, hr^{-1}	-0.00057	-0.00042	-0.000129	-
Slope m* (Stage II)***	-0.080	-0.101	-0.021	-
Average Flux, (gfd) (Stage I)*	14	17	9	3
Average Flux (gfd) (Stage II)**	6	6	5	-
Average Percent Removal (Total Solids)	92	94	92	73
Average Percent Removal (Total COD)	95	97	96	-
Average Percent Removal (Total Salts)	86	97	89	66

*Slope of the flux decline curve on a log-log plot of flux versus time.
**Primary effluent.
***Concentrated primary effluent, 5 times the average total solids concentration of untreated primary effluent.

Other performance parameters such as the salt (conductivity) removal, the COD removal and the total solids (TS) removal changed very little during the 2,500-hour test period including Stage I and Stage II. Average salt (conductivity) removal was 94 percent for the tight modified cellulose acetate membrane (Set 2a) and the standard cellulose acetate membrane (Set 3a), and 87 percent for the high-flux modified cellulose acetate membranes (Set 1a). The COD removal averaged 98 percent

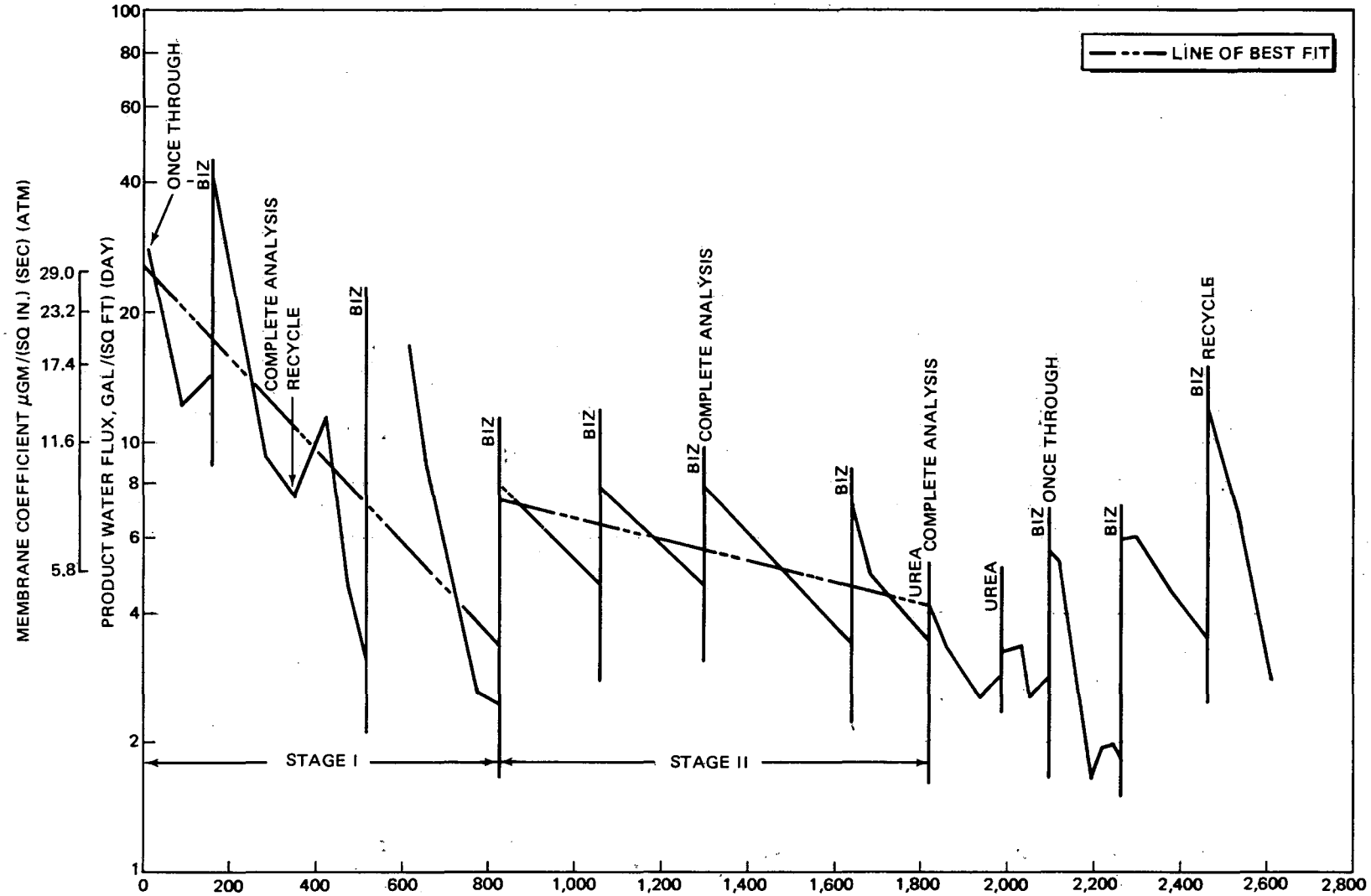

Figure 11. Performance of Tubular Membrane Set 1a Operated on Primary and Concentrated Primary Effluent (600 psig)

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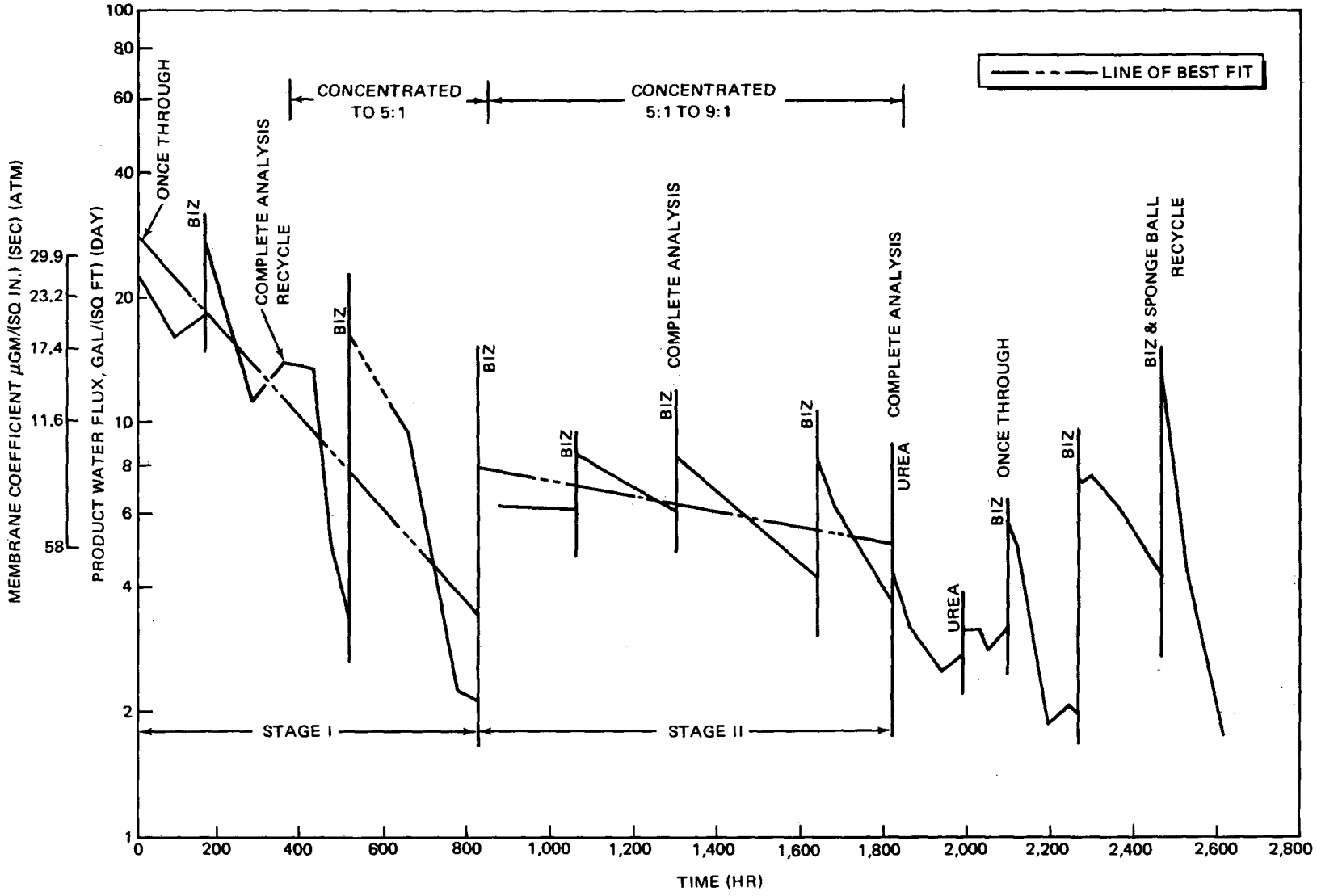

Figure 12. Performance of Tubular Membrane Set 2a Operated on Primary and Concentrated Primary Effluent (600 psig)

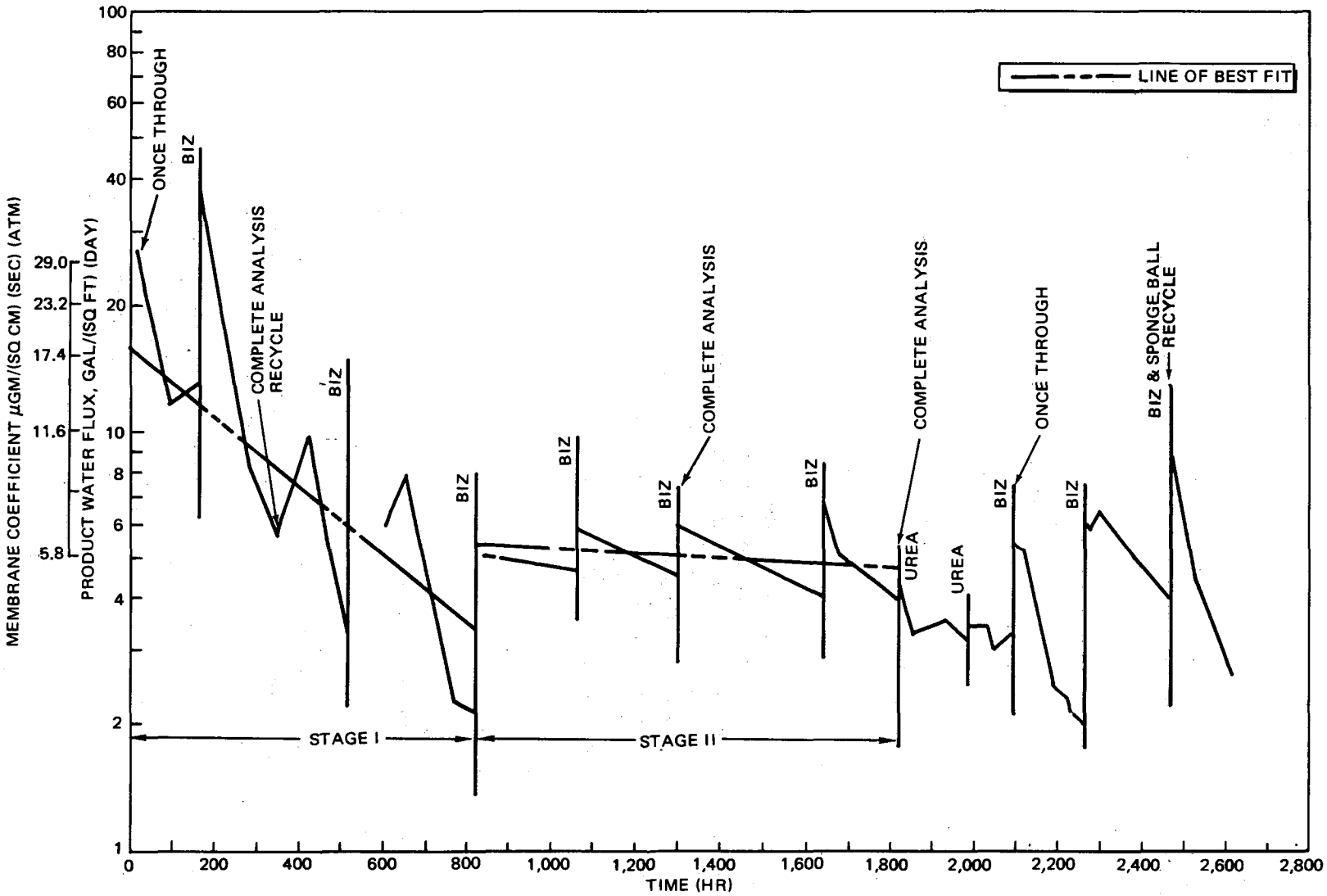

Figure 13. Performance of Tubular Membrane Set 3a Operated on Primary and Concentrated Primary Effluent (600 psig)

for all tubular membranes. The total solids removal averaged 97 percent for the tight modified cellulose acetate membrane and 91 percent for both the standard and the high-flux modified cellulose acetate membrane.

Again, membranes were cleaned using (1) a sponge flush ball, (2) enzyme-active laundry presoak (Biz) solutions and (3) urea solutions. Initially the sponge flush ball was used, but it would occasionally tear a membrane. The flux recovery after cleaning with the laundry presoak solution was higher than with the sponge ball so most subsequent membrane cleanings were made with Biz. To determine the performance of urea solutions, two successive flushes were made with a 6M solution of urea in ambient temperature water (~26°C). The urea solution pH was adjusted to 5. Flux recovery after membrane cleaning with 6M urea solutions was approximately one half that achieved with Biz solutions, Figures 11, 12 and 13. However, the use of the urea solutions at ambient temperatures (26°C) rather than with heated solutions probably contributed to its reduced effectiveness.

Performance of the regenerable membrane system on primary effluent followed the same pattern as the tubular membrane systems. However, the solids built up severely on the surface of the membranes during operation with concentrated primary effluents, Figure 14. Examination of this unit after the test showed the presence of loose organic material on the membrane surface. This loose material could be washed away easily with a water jet, but a brown film remained on the membrane surface.

The average membrane performance is summarized in Table III. Detailed data for this table and Figures 11 through 14 are tabulated in Appendix C.

A complete analysis of the product and feed was made at the conclusion of operations on primary effluent and in middle and at the conclusion of operations on concentrated primary effluent, Table IV, V, and VI. As with the carbon-treated secondary effluent, the membranes were effective (85 to 100 percent) in removing most of the MBAS, hardness, phosphorous, sulfates, calcium, and magnesium. Nitrogen, nitrate and chlorides removal was somewhat lower, ranging from 66 to 93 percent.

At the conclusion of the urea cleaning tests, the feed was switched back to primary effluent for two weeks, followed by approximately two weeks of concentrated primary effluent feed (5 times the total solids concentrations of primary effluent). After the two-week untreated primary effluent test, a sponge ball was forced through the tubular membrane units. The solids loosened by the sponge ball, amounting to approximately 100 grams, were collected and analyzed spectrographically, Appendix D.

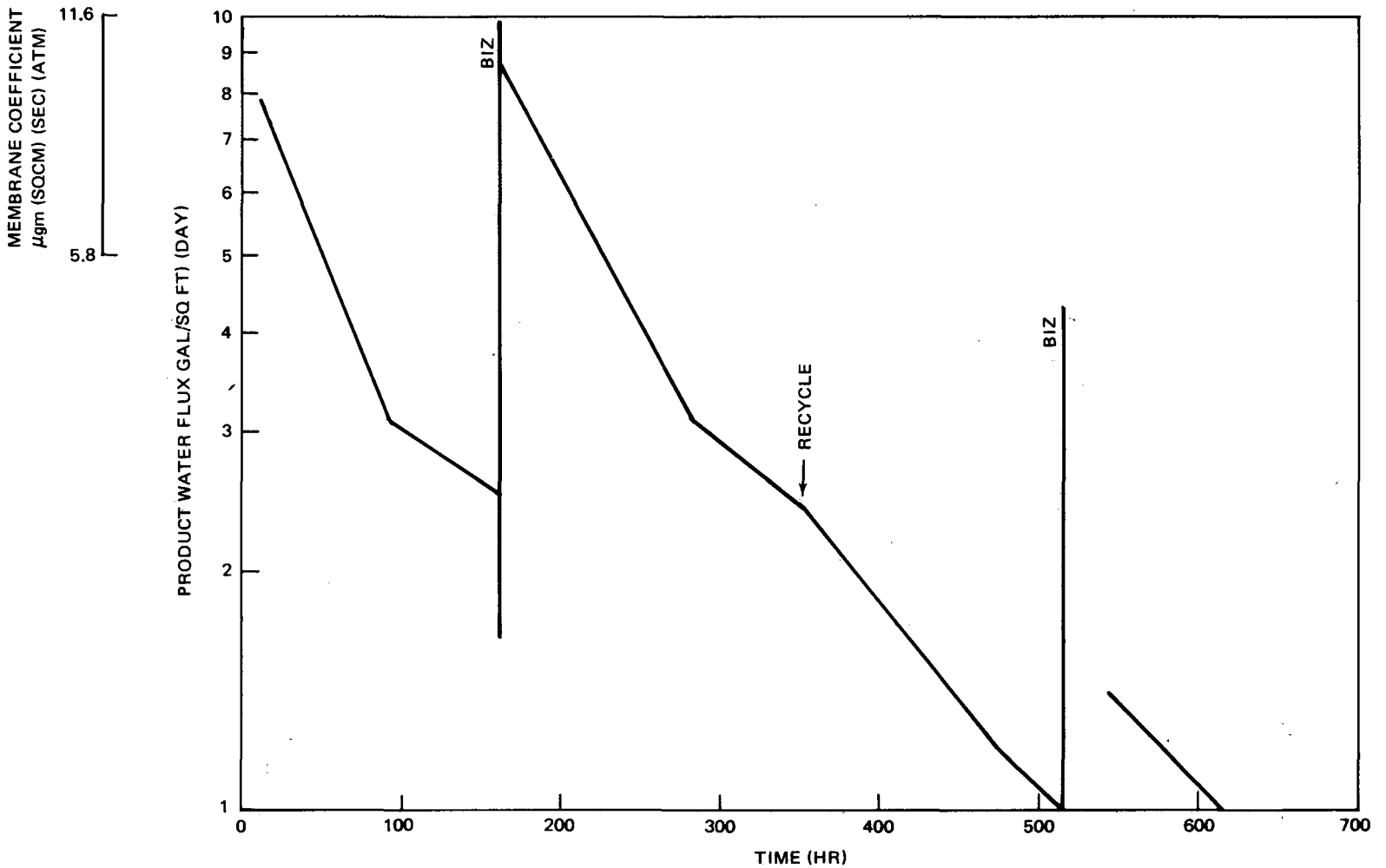

Figure 14. Performance of Regenerable Unit No. 6 Operated on Primary and Concentrated Primary Effluent (600 psig)

Table IV

REMOVAL OF WASTEWATER CONSTITUENTS DURING OPERATION WITH PRIMARY EFFLUENT*

Wastewater Constituents	Tubular Membrane Set No. 1a	2a	3a	Feed**
MBAS (mg/l)	<0.001	<0.001	0.001	0.43
Percent Removal	100	100	100	
Total Alkalinity (mg/l as $CaCO_3$)	35.00	20.00	45.00	85.00
Percent Removal	59	76	47	
Total Hardness (mg/l as $CaCO_3$)	22.50	2.50	20.00	230.00
Percent Removal	90	99	91	
Phosphorus (mg/l)	0.94	0.98	1.92	12.92
Percent Removal	93	92	85	
Total Nitrogen (mg/l)	7.00	9.10	14.00	40.60
Percent Removal	83	78	66	
Chlorides (mg/l)	44.21	8.86	51.40	187.43
Percent Removal	76	95	73	
Sulfates (mg/l)	5.34	Trace	6.99	294.47
Percent Removal	98	99	97	
Calcium (mg/l)	6.00	0.95	7.00	85.00
Percent Removal	93	99	92	
Magnesium (mg/l)	1.81	Trace	1.21	18.10
Percent Removal	90	99	93	
Volatile Matter (mg/l)	<0.01	<0.01	<0.01	0.10
Percent Removal	100	100	100	

*After 350 hours of operation - end of run on primary effluent (once through).

**After pH adjustment with sulfuric acid.

Table V

REMOVAL OF WASTEWATER CONSTITUENTS DURING OPERATION WITH CONCENTRATED PRIMARY EFFLUENT–I*

Wastewater Constituents	Tubular Membrane Set No.			Feed To Membrane** (Concentrated)	Feed To Tank*** (Unconcentrated)
	1a	2a	3a		
MBAS (mg/l)	0.15	<0.001	<0.001	0.45	0.21
Percent Removal	66	100	100		
Total Alkalinity (mg/l as $CaCO_3$)	10.00	10.00	10.00	42.50**	300.00
Percent Removal	76	76	76		
Total Hardness (mg/l as $CaCO_3$)	100.00	25.00	40.00	1,800.00	200.00
Percent Removal	94	99	98		
Phosphorus (mg/l)	6.69	2.93	3.10	29.36	10.31
Percent Removal	77	90	89		
Total Nitrogen (mg/l)	26.60	11.20	16.80	161.00	32.20
Percent Removal	83	93	90		
Chlorides (mg/l)	129.39	46.08	101.03	382.86	170.16
Percent Removal	66	88	74		
Sulfates (mg/l)	225.50	57.84	3.10	2,990.37	127.56
Percent Removal	92	98	99		
Calcium (mg/l)	27.00	8.00	13.00	448.0	52.0
Percent Removal	94	98	97		
Magnesium (mg/l)	7.86	1.21	1.81	164.56	16.94
Percent Removal	95	99	99		
Volatile Matter (mg/l)	<0.01	<0.01	<0.01	0.70	0.45
Percent Removal	100	100	100		

*After 1,300 hours of operation--middle of Stage II.
**After pH adjustment with sulfuric acid.
***Not pH adjusted.

Table VI

REMOVAL OF WASTEWATER CONSTITUENTS DURING OPERATION WITH CONCENTRATED PRIMARY EFFLUENT–II*

Wastewater Constituents	Tubular Membrane Set No.			Feed To Membrane** (Concentrated)	Feed To Tank*** (Unconcentrated)
	1a	2a	3a		
MBAS (mg/l)	1.03	0.12	1.25	3.12	2.60
Percent Removal	67	96	60		
Total Alkalinity (mg/l as $CaCO_3$)	10.00	5.00	15.00	20.00**	295.00
Percent Removal	50	75	25		
Total Hardness (mg/l as $CaCO_3$)	80.00	20.00	30.00	2,000.00	250.00
Percent Removal	96	99	99		
Phosphorus (mg/l)	7.01	3.10	3.59	63.62	14.57
Percent Removal	89	95	94		
Total Nitrogen (mg/l)	19.60	14.00	11.20	85.00	35.00
Percent Removal	77	84	87		
Chlorides (mg/l)	102.80	46.08	81.53	354.50	132.93
Percent Removal	71	87	77		
Sulfates (mg/l)	176.94	50.61	72.01	2,658.70	88.7
Percent Removal	93	98	97		
Calcium (mg/l)	22.00	7.00	9.00	640.00	53.00
Percent Removal	97	99	99		
Magnesium (mg/l)	11.49	0.60	1.81	96.80	28.43
Percent Removal	88	99	98		
Volatile Solids (mg/l)	<0.01	<0.01	<0.01	92.00	48.67
Percent Removal	100	100	100		
Nitrates (mg/l)	0.97	0.88	1.77	5.31	2.65
Percent Removal	82	83	67		

*After 1,825 hours of operation, end of Stage II.
**After pH adjustment with sulfuric acid.
***Not pH adjusted.

At the conclusion of the test program (following operation with concentrated primary feed) one tubular membrane was removed for examination prior to any cleaning. Very little residual material was found on the membrane. This residual material was removed and amounted to a little over one tenth of a gram. This material was also analyzed spectrographically, Appendix D. The large sample collected with a sponge ball cleaning following the test with primary feed probably came from solids lodging in fittings and bends of the plumbing since such a small amount of material was actually found on the membrane following disassembly. The major cation constituents of the residue on the membrane were iron and sodium. Silicon, lead, barium and calcium were also present in considerable amount (>1 percent). Phosphorus was also present in considerable quantity.

SECTION IX

DISCUSSION OF RESULTS

MEMBRANE PERFORMANCE

Performance (flux and removal efficiency) of tubular membranes prepared from modified cellulose acetate was slightly better on primary and concentrated primary feed than that of tubular membranes made from Eastman E-398-10 cellulose acetate control. The results from earlier tests made with carbon treated secondary effluent were inconclusive because of problems in sealing the ends of the modified membranes; some of the tubular membranes prepared from the modified membranes apparently developed small leaks which did not change the product water flux, but by allowing a small quantity of feed water to pass through, substantially reduced constituent removal efficiency. Five of these tubular membranes constituted a membrane set and the product water was combined so that a leak in any membrane would change the removal efficiency of the entire set.

Membranes formed from the modified cellulose acetate were mechanically weaker and more brittle than membranes prepared from E-398-10 (control). The ends of the modified membranes could not be flared for accepting the end fitting seals without cracking. Modifying the casting cycle to provide a 20-second air dry allowed the tubular membranes made from modified cellulose acetate to be flared and sealed if done carefully.

The first set of membranes (used for carbon treated secondary effluent) were made before this procedure was completely developed. Also initially sponge balls were used to clean the membranes and the mechanical abrasion occasionally tore the more brittle modified membranes.

Comparison of results between the high-flux and low-flux transesterified cellulose acetate membranes indicate that on carbon-treated secondary effluent the high flux membrane produced a greater product water flux on the average. However, the flux decline rate was also greater for the high flux membrane. On primary and concentrated primary effluents, comparison shows little difference between the two types of membranes. The type and quantity of membrane foulants were probably different for the different wastewaters. On carbon treated secondary effluent, the product water flux was maintained near its initial level using the enzyme-active, laundry-presoak solution. On primary and concentrated primary effluents, the product water flux declined even with the use of the enzyme-active, laundry-presoak solution. However, regardless of the wastewater used, substantial flux decline was observed on the once through (less than 2 percent product recovery) tests indicating that membrane fouling is the most important factor in reducing membrane productivity.

FLUX DECLINE

With a carbon treated secondary effluent feed and no membrane cleaning the product water flux declined at 4 to 5 times the rate, based on the slope of a log flux log time plot, of membranes with a pure salt solution feed. However with periodic membrane cleaning the flux could be maintained at near its initial level.

With a primary effluent feed and periodic membrane cleaning the flux declined at a rate (m = 0.4 to 0.5) 4 to 5 times that of pure salt solution. However, during the transition from primary to concentrated primary effluent feed the flux decline rate, m, abruptly changed to equal that observed with pure salt solution (m = 0.08 to 0.10). However, the product water flux for treating concentrated primary effluents was relatively low, approximately 5 to 6 gfd. During the final portion of the test when the feed was changed back to primary effluent the flux rose by approximately 10 percent and was still increasing up to the end of the test. This means the average flux obtained in an actual reverse osmosis system with near 90-percent recovery would be higher than the 5 to 6 gfd observed with the concentrated primary effluent feed. These test results are encouraging in that they indicate long term stability of the membranes when operated at high recovery ratios on primary effluents.

MEMBRANE CONDITION

Very small quantities of residual solid materials were found on tubular membrane surfaces following testing with concentrated primary effluent. This suggests that product water flux decline is due to deposition of colloidal, dissolved organic and dissolved inorganic materials in the membrane pores rather than gross, easily settled, particulate matter on the membrane surface.

REMOVAL EFFICIENCY

The removal efficiency of all the membranes was most encouraging, generally exceeding 90 percent for most constituents in the wastewater. Even more encouraging was the ability of the cellulose acetate membranes to maintain this high removal rate with exposure to concentrated primary effluent, high-feed water temperature (49°C), occasional feed-water pH of 8, and periodic flushing with a strong enzyme-active laundry presoak solution.

Among the wastewater constituents the nitrates and chlorides were the most difficult to remove. But even for these materials the average removal efficiency was over 70 percent.

FEED CONDITIONS

During concentration of the primary effluent almost the entire feed

was recirculated and the energy introduced by the high-pressure feed pump increased the temperature to 49°C. A temperature correction curve was prepared in which the product water flux at the higher temperature was compared to that at 25°C (77°F). In view of the substantial temperature correction factor (0.6) the product water flux reported is believed to be conservative.

Concentration of the wastewater constituents could lead to a separation and partial segretation of the suspended solids. However the high recirculation rate, 12 gpm, and conical feed tank bottom make this unlikely. Sulfuric acid was used to adjust the pH of the feed in the feed tank to approximately pH 5 to 6. This produced a sulfate concentration as high as 3 g/l during the concentration phase, and a correspondingly low alkalinity.

REGENERABLE MEMBRANES

The regenerable membrane concept provides a low cost reverse osmosis system. A simple tube and shell configuration was used in which the feed was put into the shell side. Thus flow velocities past the membrane coated tubes were generally much lower and more variable than with the tubular membranes. On carbon treated secondary and primary effluent feed this resulted in somewhat lower product water flux. However, during operation on concentrated primary effluent feed the solids deposition on the membrane surface was severe and could not be removed by flushing with Biz solution.

As a result of this test, inexpensive flow directors will be incorporated into the tube and shell design. These flow directors will provide a constant high-velocity flow of the feed past the membrane. The addition of these flow directors adds less than a penny per thousand gallons to the cost of waste water treatment by this reverse osmosis system.

SECTION X

ACKNOWLEDGEMENTS

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The complete cooperation and assistance of the County Sanitation Districts of Los Angeles County and the WQO personnel at Pomona in providing the municipal wastewaters, space, and service for operation of the reverse osmosis test unit used in this program are gratefully appreciated and acknowledged.

SECTION XI

REFERENCES

1. Malm et al. JACS 70, 2740

2. Malm et al. JACS 72, 2674

3. Malm et al. JACS 74, 4105

4. Malm et al. JACS 75, 80

5. Bishop, H. K., Belfort, G. and G. A. Guter, "In-situ Formation of Regenerative Cellulose Acetate Membranes on Porous Supports," Office of Saline Water Research & Development Report No. 464, Dec 1969

6. Manjikian, S., Loeb, S., and McCutchan, J. W., "Improvement in Fabrication Techniques for Reverse Osmosis Desalination Membranes," Proc. First Intl. Symp. Water Desalination, U. S. Dept. of Interior, Office of Saline Water, Wash. D. C. 2: 159, 1965.

7. Loeb, S., "Sea Water Demineralization by Means of a Semipermeable Membrane, "Univ. of California, Dept. of Engr., Los Angeles, Progr. Rept. No. 6142, Aug 1961.

SECTION XII
APPENDICES

		Page No.
A.	Description of Equipment	49
B.	Performance of Membranes Operated on Carbon-Treated Secondary Effluent	50
	Table BI: Performance of Tubular Membrane Set 1 Operated on Carbon-Treated Secondary Effluent	51
	Table BII: Performance of Tubular Membrane Set 2 Operated on Carbon-Treated Secondary Effluent	52
	Table BIII: Performance of Tubular Membrane Set 3 (Control) Operated on Carbon-Treated Secondary Effluent	53
	Table BIV: Performance of Regenerable Membrane Set 5 Operated on Carbon-Treated Secondary Effluent	54
	Table BV: Properties of Carbon-Treated Secondary Effluent Feed	55
C.	Performance of Membranes Operated on Primary and Concentrated Primary Effluent	56
	Table CI: Performance of Tubular Membrane Set 1a Operated on Primary and Concentrated Primary Effluent -- Measured Values	57
	Table CII: Performance of Tubular Membrane Set 1a Operated on Primary and Concentrated Primary Effluent -- Calculated Values	58
	Table CIII: Performance of Tubular Membrane Set 2a Operated on Primary and Concentrated Primary Effluent Feed -- Measured Values	59

Page No.

Table CIV: Performance of Tubular Membrane Set 2a Operated on Primary and Concentrated Primary Effluent — Calculated Values 60

Table CV: Performance of Tubular Membrane Set 3a Operated on Primary and Concentrated Primary Effluent — Measured Values 61

Table CVI: Performance of Tubular Membrane Set 3a Operated on Primary and Concentrated Primary Effluent — Calculated Values 62

Table CVII: Properties of Primary and Concentrated Primary Feed 63

Table CVIII: Performance of Membrane Set 6 (Regenerable Unit 6) Operated on Primary and Concentrated Primary Effluent 64

D. Spectrographic Constituent Analysis of Deposits on Membrane Surfaces 65

APPENDIX A

DESCRIPTION OF EQUIPMENT

FEED TANK - 500 gallon fiberglass tank 48 by 72 inches manufactured by Century Fiberglass Company, Santa Ana.

HIGH PRESSURE PUMP - Gardner-Denver (Denver, Colorado), Model P-Q-2, triplex piston pump with aluminum-bronze body, stainless steel valves and colmonoy plungers.

pH SENSOR AND CONTROLLER - Universal Interloc (Santa Ana, California), Model 1000 M with flow cell.

pH RECORDER - Rustrack millivolt recorder.

ACID PUMP - Precision Chemical Pump Corporation (Waltham, Massachusetts) Series 1200 pump.

BACK PRESSURE REGULATOR - Marotta Valve Corporation (Santa Ana, California), Model PRV-533.

MOUNTING RACK - Astropower Laboratory.

PRIMING PUMP - Flotec Model C3P5-1100 with PVC head.

APPENDIX B

PERFORMANCE OF MEMBRANES OPERATED ON CARBON-TREATED SECONDARY EFFLUENT

Table BI

PERFORMANCE OF TUBULAR MEMBRANE SET 1 OPERATED ON CARBON-TREATED SECONDARY EFFLUENT

(Values presented are properties of the product water.)

Time (Hr)	gfd[a]	Conductivity[a] ($\frac{\mu mho}{cm^2}$)	pH	Total COD (mg/l)	Total Solids (mg/l)	Percent Conductivity Removal	Percent COD Removal	Percent TS Removal
00 Start								
22	29.4	410				62		
104	21.3	220			127.	79		80
130	15.4	280	6.0	2.1	148.	73	93	78
185	13.1	310		2.9	132.	72	84	81
240	11.5	375	5.7		190.	65		72
290	11.1	280	5.9		149.			
335	10.1	400				54		
381	10.0	260						
431[b]	9.9	320				68		
481[b, c]	14.0	750				66		
554[c]	13.4	350				68		
595	29.6	300				70		
596[c]	32.3	425				68		
642	29.6	410			215.	65		69
645[c]	33.3	280				71		
688	25.3	290			136.	70		74
716	31.6	195			107.	77		80
790	28.6	260		1.5	125.	77	85	81
791[c]	49.6	600				46		
818	39.4	520				53		
883	18.3	350		4.9	168.	65	57	72
973	30.8	300	5.8		148.	72		76
1,024[c]	31.4	340	5.9	4.5	164.	70	33	75
1,075	32.3	325				70		
1,164	26.2	310				72		
1,165[c]	30.9	325				71		
1,185	29.5	350				72		

(a) Adjusted to 77°F (25°C).
(b) Cleaned with sponge ball.
(c) Flushed for 30 minutes with a solution of Biz in water (7.1 g/l) at 25°C and pH 9.2.

Table BII

PERFORMANCE OF TUBULAR MEMBRANE SET 2 OPERATED ON CARBON-TREATED SECONDARY EFFLUENT

(Values presented are properties of the product water.)

Time (Hr)	gfd[a]	Conductivity[a] ($\frac{\mu mho}{cm^2}$)	pH	Total COD (mg/l)	Total Solids (mg/l)	Percent Conductivity Removal	Percent COD Removal	Percent TS Removal
00 Start								
104		150		6.2	90.	87	32	87
130	25.5	210	6.0	8.7	128.	80	71	81
185		250		5.5	113.	75		
208	13.0							
232	13.4							
290	15.0	390	6.0		231.			
335	17.0	490				44		
431[b]	15.6	220				88		
481[b, c]	29.3	620				72		
554[c]	17.7	230				79		
595	21.7	250				75		
596[c]	30.4	480				52		
642	22.2	330			188.	67		73
645[c]	28.7	425				55		
688	24.1	270			150.	73		71
716	24.3	260			159.	69		70
790	22.2	330		6.3	170.	71	38	74
791[c]	30.4	500				54		
818	23.3	400				64		
883	20.1	180		2.5	78.	82	78	87
973	19.5	220	5.8		102.	80		83
1,024[c]	20.8	200	5.7	1.1	125.	83	84	81
1,075	21.4	110	6.3		50.	90		93
1,164	20.5	50	7.2		22.	96		96
1,165[c]	20.9	85				92		
1,185	20.0	80				94		

(a) Adjusted to 77°F (25°C).
(b) Cleaned with sponge ball.
(c) Flushed for 30 minutes with a solution of Biz in water (7.1 g/l) at 25°C and pH 9.2.

Table BIII

PERFORMANCE OF TUBULAR MEMBRANE SET 3 (CONTROL) OPERATED ON CARBON-TREATED SECONDARY EFFLUENT

(Values presented are properties of the product water.)

Time (Hr)	gfd[a]	Conductivity[a] $\left(\frac{\mu mho}{cm^2}\right)$	pH	Total COD (mg/l)	Total Solids (mg/l)	Percent Conductivity Removal	Percent COD Removal	Percent TS Removal
00 Start								
22	17.7							
104	14.2	50			32.	95		95
130	12.4	55	6.0	1.0	38.	95	97	95
186	9.2			0.3	16.		98	98
208	7.8							
232	7.2							
290	6.3	55	5.9		34.			
335	3.8	50				94		
381	4.5							
431[b]	6.8	70				93		
481[b, c]	8.7	110				95		
559[c]	10.6	45				96		
595	15.4	50				95		
596[c]	15.4	40				96		
642	14.7	50			25.	95		96
645[c]	16.1	20				93		
688	15.2	75			13.	92		98
716	16.2	45			2.	95		99
790	15.3	60		3.3	32.	95	67	95
791[c]	15.7	55				95		
818	15.0	60				95		
883	16.0	45			1.	96		99
973	14.8	50	5.7		12.	95		98
1,024[c]	15.6	60	5.7		26.	95		96
1,075	16.0	65	6.0		28.	94		96
1,164	14.5	60	6.8		25.	95		96
1,165[c]	15.6	70				94		
1,185	16.0	80				94		

(a) Adjusted to 77°F (25°C)
(b) Cleaned with sponge ball.
(c) Flushed for 30 minutes with a solution of Biz in water (7.1 g/l) at 25°C and pH 9.2.

Table BIV

PERFORMANCE OF REGENERABLE MEMBRANE SET 5 OPERATED ON CARBON-TREATED SECONDARY EFFLUENT

(Values presented are properties of the product water.)

Time (Hr)	gfd[a]	Conductivity[a] $\left(\frac{\mu mho}{cm^2}\right)$	pH	COD (mg/l)	TS (mg/l)	Percent Conductivity Removal	Percent COD Removal	Percent TS Removal
00 Start								
24	9.3							
48	7.5							
56	9.9							
60	9.1							
106	7.3	150			83.	85		87
152	6.1	250	5.6					
198	6.1	115				87		
248	4.8	200				80		
297[b]	7.1	480				78		
370[b]	3.7	370				66		
411[b]	9.0	250				75		
412	23.0							
459[b]	11.4	300			163.	73		76
460	21.1							
504	6.2							
533	17.3	210			122.	75		77
578[b]	12.1	310		3.3	154.	73	70	76
606	12.6	290				74		
671	7.2			0.35			97	
695	8.5	240	5.6		113.	78		82
746[b]	8.0	300	5.6		150.	74		77
797	12.8	380			174.	65		83
887[b]	4.6	425	7.1		194.	61		66
908	11.4	380				70		

(a) Adjusted to 77°F (25°C).
(b) Flushed for 30 minutes with a solution of Biz in water (7.1 g/l) at 25°C and pH 9.2.

Table BV

PROPERTIES OF CARBON-TREATED SECONDARY EFFLUENT FEED

Time (Hr)	Conductivity[a] $\left(\frac{\mu mho}{cm^2}\right)$	Total Solids (mg/l)	Total COD (mg/l)	pH
00 Start				
22	1,040			5.5
104	1,040	669.	9.6	
130	1,040	687.	29.5	6.0
185	1,100	685.	17.9	5.6
208	950			7.4
240	1,070	678.	22.3	5.7
335	870			7.8
381	950	528.		7.7
431	1,020	660.		6.0
481	2,200			
554	1,100			
559	1,100			
595	1,000			
642	1,000	684.		
688	980	516.		
716	840	537.		
790	1,150	642.	10.1	
818	1,100			
883	990	603.	11.3	
973	1,075	607.		5.9
1,024	1,150	660.	6.6	5.8
1,075	1,075	690.		6.3
1,164	1,100	577.		7.7
1,185	1,250			

[a] Adjusted to 77°F (25°C)

APPENDIX C

PERFORMANCE OF MEMBRANES OPERATED ON PRIMARY AND CONCENTRATED PRIMARY EFFLUENT

Table CI

PERFORMANCE OF TUBULAR MEMBRANE SET 1a OPERATED PRIMARY AND CONCENTRATED PRIMARY EFFLUENT--MEASURED VALUES

(Values presented are properties of the product water)

Time (Hr)	gfd[a]	Conductivity[a] $\left(\frac{\mu mho}{cm^2}\right)$	pH	COD (mg/l)	Filtered COD (mg/l)	Total Solids (mg/l)	TDS (mg/l)	NH_3 - N mg/l
00 Start								
11.0	27.8	140	5.6			54		
91.0	12.3	210	4.3			94		
163.5	14.5	170	6.2			102		
164.5[b]	40.7							
282.0	9.3	550	3.5			121		
351.0[c]	7.4	260	6.6			100		
424.0	11.6	220	6.0			96		
471.0	4.8	400	6.3			192		
517.1	3.15	480	6.3			248		
614.5[b]	16.7	480	6.4			230		
658.6	9.0	610	6.3			295		
779.0	2.6	890	6.5	34.2		458		
827.2	2.45	700	6.8					
868.0[b]	7.2	850	6.4			454		
1,061.1	4.6	680	6.6			352		
1,062.0[b]	7.8							
1,300.9	4.6	1000						
1,301.5[b]	2.8							
1,641.4	3.4	980	6.8	23.9		551		
1,642.5[b]	7.1							
1,686.5	4.9		6.7	39.8		553		
1,825.1	3.4	750	5.8	35.9		434.	352	
1,826.0[d]	4.15							
1,867.0	3.3	690	6.3			380		
1,939.0	2.55	600				376		
1,990.5	2.85	460	6.7	8.1		250		8.8
1,991.5[d]	5.65							
2,035.0	3.35	165	6.6	8.1		79		
2,056.0	2.55	160	6.6			96		
2,100.0[e]	2.8	180	6.6	15.9		141		
2,101.0[b]	3.65							
2,124.0	5.3	170	6.2	2.8		109		
2,196.0	1.65	210	6.3			145		
2,220.0	1.95	160	6.1			66		
2,244.0	1.99	170	6.3	5.1		49		
2,267.0	1.81							2.5
2,268.0[b]	5.95							
2,279.0	6.0			17.4	8.0	95	92	
2,300.0	6.05							
2,370.0	4.7	165	6.8			80		1.85
2,469.9[c]	3.5	240	7.4			120		
2,470.5[b]	11.4							
2,537.0	7.0	400	3.6			206		
2,616.6	2.8	450	5.8					

Notes:

(a) Adjusted to 77°F (25°C).
(b) Flushed for 30 minutes with a solution of Biz in water (7.1 g/l), pH 9.2.
(c) Feed recycled.
(d) Flushed for 30 minutes with a 6M solution of urea adjusted to pH 5.
(e) Returned to one-pass flow.

Table CII

PERFORMANCE OF TUBULAR MEMBRANE SET 1a OPERATED ON PRIMARY AND CONCENTRATED PRIMARY EFFLUENT--CALCULATED VALUES

(Based on properties of product water)

Time (Hr)	gfd[a]	Percent Conductivity Removal	Percent COD Removal	Filtered Percent COD Removal	Percent TS Removal	Percent TDS Removal	Percent NH_3 Removal	Feed Concentration Ratio (TS)
00 Start								
11.0	27.8	91			93			
91.0	12.3	86			90			
163.5	14.5	86			88			
164.5[b]	40.7							
282.0	9.3	81			90			
351.0[c]	7.4	81			88			
424.0	11.6	87			92			
471.0	4.8	84			89			
517.0	3.15	83			88			
614.5[b]	16.7	89			93			
658.6	9.0	86			92			
779.0	2.6	82	95		89			5.1
827.2	2.45	84			91			5.1
868.0[b]	7.2	83			88			4.5
1,061.1	4.6	88			92			5.6
1,062.0[b]	7.8							
1,300.9	4.6	83						
1,301.5[b]	7.8							
1,641.4	3.4	83	98		90			7.4
1,642.5[b]	7.1							
1,686.5	4.9		95		89			9.1
1,825.1	3.4	86	96		92	93		7.2
1,826.0[d]	4.15							
1,867.0	3.3	87			93			8.3
1,939.0	2.55	88			92			6.7
1.990.5	2.85	89	99		94		91	5.5
1.991.5[d]	3.25							
2,035.0	3.35	89	96		93			1.6
2,056.0	2.55	87			90			1.7
2,100.0[e]	2.8	86	91		83			1.3
2,101.0[b]	5.65							
2,124.0	5.3	83	98		86			
2,196.0	1.65	75			75			
2,220.0	1.95	83			90			
2,244.0	1.99	82	97		93			
2,267.0	1.81						80	
2,268.0[b]	5.95							
2,279.0	6.0		90	84	86	85		
2,300.0	6.05							
2,370.0	4.7	81			86		86	
2,469.9[c]	3.5	82			85			
2,470.5[b]	11.4							
2,537.0	7.0	82			88			
2,616.6	2.8	72						

Notes:

(a) Adjusted to 77°F (25°C).
(b) Flushed for 30 minutes with a solution of Biz in water (7.1 g/l), pH 9.2.
(c) Feed recycled.
(d) Flushed for 30 minutes with a 6M solution of urea adjusted to pH 5.
(e) Returned to one-pass flow.

Table CIII

PERFORMANCE OF TUBULAR MEMBRANE SET 2a OPERATED ON PRIMARY AND CONCENTRATED PRIMARY EFFLUENT-- MEASURED VALUES

(Values presented are properties of the product water)

Time (Hr)	gfd[a]	Conductivity[a] $\left(\frac{\mu mho}{cm^2}\right)$	pH	Total COD (mg/l)	Filtered COD (mg/l)	Total Solids (mg/l)	TDS (mg/l)	Nessler NH_3 - N mg/l
00 Start								
11.0	21.9	95	5.5			22		
91.0	16.1	80	4.1			4		
163.5	18.5	50	5.7			34		
164.5[b]	27.2							
282.0	11.3	200	3.9			35		
351.0[c]	14.0	80	5.9			15		
424.0	13.6	75	6.3			26		
471.0	5.1	130	6.2			55		
517.0	3.45	170	6.6			81		
614.5[b]	11.3	160	6.5			73		
658.6	9.45	220	6.3			101		
779.0	2.25	520	6.7	27.9		251		
827.2	2.15	360	6.7					
868.0[b]	6.3	330	6.5			169		
1,061.1	6.2	290	6.7			147		
1,062.0[b]	8.4							
1,300.9	6.15	380						
1,301.5[b]	8.35							
1,641.4	4.3	390	6.2	19.9		210		
1,642.5[b]	8.2							
1,686.5	6.25		6.3	15.9		197		
1,825.1	3.7	280	6.2	47.8		150	114	
1,826.0[d]	4.45							
1,867.0	3.2	230	6.2			114		
1,939.0	2.55	220						
1,990.5	2.8	200	6.7	12.1		108		3.9
1,991.5[d]	3.2							
2,035.0	3.2	65	6.4	8.1		34		
2,056.0	2.85	70	6.0			35		
2,100.0[e]	3.25	80	6.6	6.0		83		
2,101,0[b]	5.85							
2,124.0	5.0	80	6.0			55		
2,196.0	1.90	120	6.0			90		
2,220.0	2.0	90	6.3			28		
2,244.0	2.1	100	5.9	2.4		14		
2,267.0	2.03							1.6
2,268.0[b]	7.4							
2,279.0	7.25			13.5	11.5	45	36	
2,300.0	7.6							
2,370.0	6.3	60	6.2			18		0.65
2,469.9[c]	4.3	110	6.4			58		
2,470.5[b]	13.0							
2,537.0	4.25	150	3.7			73		
2,616.6	1.80	100	6.3					

Notes:

(a) Adjusted to 77°F (25°C).
(b) Flushed for 30 minutes with a solution of Biz in water (7.1 g/l). pH 9.2.
(c) Feed recycled.
(d) Flushed for 30 minutes with a 6M solution of urea adjusted to pH 5.
(e) Returned to one-pass flow.

Table CIV

PERFORMANCE OF TUBULAR MEMBRANE SET 2a OPERATED ON PRIMARY AND CONCENTRATED PRIMARY EFFLUENT--CALCULATED VALUES

(Based on properties of the product water)

Time (Hr)	gfd[a]	Percent Conductivity Removal	Percent COD Removal	Filtered Percent COD Removal	Percent TS Removal	Percent TDS Removal	Percent NH_3 Removal	Feed Concentration Ratio (TS)
00 Start								
11.0	21.9	94			97			
91.0	16.1	95			99			
163.5	18.5	96			96			
164.5[b]	27.2							
282.0	11.3	93			97			
351.0[c]	14.0	94			98			
424.0	13.6	96			98			
471.0	5.1	95			97			
517.0	5.45	94			96			
614.5[b]	11.3	96			98			
658.6	9.45	95			97			
779.0	2.25	90	96		94			5.1
827.2	2.15	92			96			5.1
868.0[b]	6.3	93			96			4.5
1,061.1	6.2	95			97			5.6
1,062.0[b]	8.4							
1,300.9	6.15	94						
1,301.5[b]	8.35							
1,641.4	4.3	93	98		96			7.4
1,642.5[b]	8.2							
1,686.5	6.25		98		96			9.1
1,825.1	3.7	95	95		97	98		7.2
1,826.0[d]	4.45							
1,867.0	3.2	96			98			8.3
1,939.0	2.55	96						6.7
1,990.5	2.8	95	99		97		96	5.5
1,991.5[d]	3.2							
2,035.0	3.2	96	96		97			1.6
2,056.0	2.85	94			96			1.7
2,100.0[e]	3.25	94	97		90			1.3
2,101.0[b]	5.85							
2,124.0	5.0	92	99		93			
2,196.0	1.90	86			85			
2,220.0	2.0	90			96			
2,244.0	2.1	89	99		98			
2,267.0	2.03						87	
2,268.0[b]	7.4							
2,279.0	7.25		92	77	93	94		
2,300.0	7.6							
2,370.0	6.3	93			97		95	
2,469.9[c]	4.3	92			93			
2,470.5[b]	13.0							
2,537.0	4.25	93			96			
2,616.6	1.80	92						

Notes:

(a) Adjusted to 77°F (25°C).
(b) Flushed for 30 minutes with a solution of Biz in water (7.1 g/l), pH 9.2.
(c) Feed recycled.
(d) Flushed for 30 minutes with a 6M solution of urea adjusted to pH 5.
(e) Returned to one-pass flow.

Table CV

PERFORMANCE OF TUBULAR MEMBRANE SET 3a OPERATED ON PRIMARY AND CONCENTRATED PRIMARY EFFLUENT--MEASURED VALUES

(Values presented are properties of the product water)

Time (Hr)	gfd[a]	Conductivity[a] ($\frac{\mu mho}{cm^2}$)	pH	COD (mg/l)	Filtered COD (mg/l)	Total Solid (mg/l)	TDS (mg/l)	NH_3 - N mg/l
00 Start								
11.0	27.2	190	5.8			80		
91.0	11.7	200	5.2			96		
163.5	13.1	180	6.2			102		
164.5[b]	39.2							
282.0	8.4	460	3.7			168		
351.0[c]	5.6	510	6.4			118		
424.0	9.9	230	6.2			106		
471.0	5.4	310	6.3			151		
517.1	3.25	450	6.5			236		
614.5[b]	6.0	400	6.4			206		
658.6	8.1	500	6.4			248		
779.0	2.25	590	6.9	32.1		302		
827.2	2.15	480	6.9	24.3		232		
868.0[b]	5.0	540	6.5			284		
1,061.1	4.7	550	6.6		0.2788			
1,062.0[b]	5.9							
1,300.9	4.65	630						
1,301.5[b]	5.95							
1,641.4	4.1	550	6.9	15.9		312		
1,642.5[b]	6.85							
1,686.5	5.1		6.7	19.9		277		
1,825.1	3.9	440	6.0	35.9		256	204	
1,826.0[d]	4.45							
1,867.0	3.3	440	6.5			204		
1.939.0	3.55	360				225		
1,990.5	3.2	280	6.3	16.2		167		5.3
1,991.5[d]	3.45							
2,035.0	3.45	95	6.4	8.1		56		
2,056.0	3.0	110	6.4			74		
2,100.0[e]	3.35	110	6.5	6.0		76		
2,101.0[b]	5.45							
2,124.0	5.2	150	6.2			84		
2,196.0	2.50	155	6.2			118		
2,220.0	2.35	140	6.0			62		
2,244.0	2.1	150	6.1	7.3		58		
2,267.0	2.03							2.2
2,268.0[b]	6.15							
2,279.0	5.85			10.0	8.8	82	71	
2,300.0	6.45							
2,370.0	5.25	120	6.9			60		1.10
2,469.9[c]	4.00	220	7.1			123		
2,470.5[b]	9.3							
2,537.0	4.45	370	3.8			180		
2,616.6	2.65	140	5.5					

Notes:

(a) Adjusted to 77°F (25°C).
(b) Flushed for 30 minutes with a solution of Biz in water (7.1 g/l), pH 9.2.
(c) Feed recycled.
(d) Flushed for 30 minutes with a 6M solution of urea adjusted to pH 5.
(e) Returned to one pass flow.

Table CVI

PERFORMANCE OF TUBULAR MEMBRANE SET 3a OPERATED ON PRIMARY AND CONCENTRATED PRIMARY EFFLUENT--CALCULATED VALUES
(Based on properties of product water)

Time (Hr)	gfd[a]	Percent Conductivity Removal	Percent COD Removal	Filtered Percent COD Removal	Percent TS Removal	Percent TDS Removal	Percent NH_3 Removal	Feed Concentration Ratio (TS)
00 Start								
11.0	27.2	87			90			
91.0	11.7	87			90			
163.5	13.1	85			89			
164.5[b]	37.2							
282.0	8.4	84			86			
351.0[c]	5.6	78			86			
424.0	9.9	87			91			
471.0	5.4	88			92			
517.0	3.25	84			89			
614.5[b]	6.0	91			94			
658.6	8.1	89			93			
779.0	2.25	88	95		93			5.1
827.2	2.15	89	95		94			5.1
868.0[b]	5.0	89			92			4.5
1,061.1	4.7	90			94			5.6
1,062.0[b]	3.9							
1,300.9	4.65	90						
1,301.5[b]	3.95							
1,641.4	4.1	90	99		94			7.4
1,642.5[b]	6.85							
1,686.5	5.1		98		95			9.1
1,825.1	3.9	92	96		95	96		7.2
1,826.0[d]	4.45							
1,867.0	3.3	92			96			8.3
1,939.0	3.55	93			95			6.7
1,990.5	3.2	93	99		96		94	5.5
1,991.5[d]	3.45							
2,035.0	3.45	93	96		95			1.6
2,056.0	3.0	91			92			1.7
2,100.0[e]	3.35	92	97		91			1.3
2,101.0[b]	5.45							
2,124.0	5.2	85			89			
2,196.0	2.5	82			80			
2,220.0	2.35	85			91			
2,244.0	2.1	84	96		92			
2,267.0	2.03						83	
2,268.0[b]	6.15							
2,279.0	5.85		94	82	88	88		
2,300.0	6.45							
2,370.0	5.25	86			89		92	
2,469.9[c]	4.00	83			85			2.9
2,470.5[b]	9.3							
2,537.0	4.45	83			89			
2,616.6	2.65	89						

Notes:

(a) Adjusted to 77°F (25°C).
(b) Flushed for 30 minutes with a solution of Biz in water (7.1 g/l), pH 9.2.
(c) Feed recycled.
(d) Flushed for 30 minutes with a 6M solution of urea adjusted to pH 5.
(e) Returned to one-pass flow.

Table CVII

PROPERTIES OF PRIMARY AND CONCENTRATED PRIMARY FEED

Time (Hr)	$\frac{\mu mho}{cm^2}$ Conductivity In[a]	Out[b]	mg/liter COD In[a]	Out[b]	mg/liter TS In[a]	Out[b]	NH_3 - N mg/l In[a]	Out[b]	pH to Membrane
00 Start									
11.0		1,500				792			6.3
91.0		1,500				946			3.1
163.5		1,200				888			5.9
282.0		2,900				1176			3.0
351.0[c]		1,400				841			6.4
424.0		1,750				1199			6.2
471.0		2,500				1825			5.9
517.1		2,900				2116			5.7
614.5		4,400				3258			5.9
658.6		4,400				3682			6.0
779.0	1,400	5,000	280.8	696.7	815.	4184			5.0
827.2	1,380	4,400	304.8	531.6	775.	3922			6.3
868.0	1,350	5,000			837.	3760			6.2
1,061.1	1,280	5,500			763.	4314			5.9
1,300.9	1,300	6,000							
1,461.4	1,350	5,600	151.4 67.7[e]	1,294.8 745.0[e]	737	5479			6.4
1,686.5			107.6	846.6	576.	5267			6.6
1,825.1	1,020	5,500	354.6	1,006.0	771. 610.[f]	5531 5076[f]			5.2
1,867.0	1,150	5,500	111.6 83.7[e]	1,044.0 645.4[e]	609.	5086			6.9
1,939.0	1,150	5,000			678.	4526			
1,990.5	1,320	4,000	60.7	1,224.5	733.	4066	10.7	94.0	6.7
2,035.0	1,100	1,450	117.4	222.6	652.	1039			6.7
2,056.0	900	1,200			575.	954			6.4
2,100.0[d]	1,050	1,300	107.1	178.6	628.	822			5.6
2,124.0		1,000		146.0		759			5.9
2,196.0		850				588			6.5
2,220.0		950				684			5.4
2,244.0		920		175.7		707			5.7
2,267.0								12.7	
2,279.0				175.5 50.1[e]		673 600[f]			
2,370.0		850						13.0	7.6
2,469.9		1,300				805			7.6
2,537.0	900	2,250			572.	1657			3.2
2,616.6		1,300							5.3

(a) Primary effluent from plant into tank (make up for liquid passing through membranes during recycle). Adjusted to 77°F (25°G).
(b) Feed from tank to reverse osmosis system. Concentrated during recycle otherwise identical to feed from plant. Adjusted to 77°F (25°C).
(c) Feed recycled.
(d) Return to one-pass flow.
(e) COD samples filtered through a 0.45μ millipore filter.
(f) TDS samples filtered through a 0.45μ millipore filter.

Table CVIII

PERFORMANCE OF MEMBRANE SET 6 (REGENERABLE UNIT 6) OPERATED ON PRIMARY AND CONCENTRATED PRIMARY EFFLUENT

Time (Hr)	GFD[a]	Conductivity[a] $\left(\frac{\mu mho}{cm^2}\right)$	TS (mg/l)	Percent Removal Conductivity	Percent Removal TS	pH
00 Start						
11	7.9	420	188.	72	76	5.7
91	3.1	370	204.	75	79	5.7
163.5	2.5	460	238.	62	73	6.4
164.5[b]	8.7					
282	3.2	330		89		
351[c]	2.4	620	187.	56	78	6.0
424	1.6	650	338.	63	72	6.1
471	1.2	1,100	603.	56	67	6.2
517[b]	0.9	1,100	671.	62	68	6.5
545	1.4	1,000		67		
615	0.8	1,500	840.	66	74	6.5

(a) Adjusted to 77°F (25°C).

(b) Flushed for 30 minutes with a solution of Biz in water (7.1 g/l), pH 9.2.

(c) Recycle.

Appendix D

SPECTROGRAPHIC CONSTITUENT ANALYSES OF DEPOSITS ON MEMBRANE SURFACES

Element	Sponge Ball Solids Removal After Two Weeks on Primary Effluent Feed (% Constituent)	Scrapping of Deposits from Membrane Surface After Two Weeks on Concentrated Primary Effluent Feed (% Constituent)
Chromium	0.15	0.42
Nickel	0.052	0.056
Titanium	0.090	0.24
Molybdenum	Trace	Trace
Silver	0.002	0.0066
Zinc	Nil	0.32
Strontium	0.04	0.11
Sodium	9.0	6.6
Calcium	5.6	1.9
Potassium	3.6	Nil
Silicon	2.0	3.2
Magnesium	1.6	0.32
Iron	0.32	7.8
Phosphorous	2.4	7.4
Barium	0.11	1.1
Aluminum	0.11	0.52
Lead	0.91	3.8
Manganese	0.36	0.0048
Tin	0.034	0.074
Copper	0.44	0.56
Other Elements	Nil	Nil

1 Accession Number	2 Subject Field & Group	SELECTED WATER RESOURCES ABSTRACTS INPUT TRANSACTION FORM
W		

5 Organization

McDonnell Douglas Corporation
Astropower Laboratory
Newport Beach, California 92660

6 Title

Use of Improved Membranes in Tertiary Treatment by Reverse Osmosis

10 Author(s)

Bishop, H. K.

16 Project Designation

WQO Program 17020 DHR Contract No. 14-12-417

21 Note

22 Citation

23 Descriptors (Starred First)

Water Pollution, membranes, reverse osmosis, sewage treatment, waste water treatment, cellulose acetate, carbon treated secondary effluent, primary effluent, solid removal, organic removal, inorganic removal

25 Identifiers (Starred First)

27 Abstract

The purpose of this reverse osmosis study was threefold: (1) to compare tubular membranes prepared from transesterified (modified) cellulose acetate with commercially available cellulose acetate (control), (2) to evaluate the in-situ regenerable membrane reverse osmosis design on waste water and (3) to evaluate the membranes on carbon-treated secondary effluents, primary effluents and concentrated primary effluents.

The test results were: (1) tubular membranes prepared from transesterified cellulose acetate produced water fluxes slightly greater than those of membranes prepared from commercially available cellulose acetate, (2) the in-situ regenerable membranes produced fluxes below that of tubular units but showed suficient promise for further development, (3) product water flux from operations on carbon-treated secondary effluents gradually declined from initial levels of between 15 and 25 gfd. However, product water flux could be maintained near these initial levels by periodic cleaning with enzyme-active laundry presoak solution, (4) product water flux on primary and concentrated primary effluents declined gradually from initial levels of between 15 and 25 gfd and stabilized between 4 to 5 gfd on concentrated primary effluent even with the use of enzyme-active laundry presoak solution, (5) removal of most waste water constituents was between 90 to 100% and was generally unaffected by the type of feed water or time of test. Chloride and nitrate reductions averaged approximately 70 percent.

The test results indicate that it is technically feasible to treat primary effluents with tubular reverse osmosis process. However, further development is needed to determine economic feasibility.

Abstractor	Institution
H.K. Bishop	McDonnell Douglas Corporation

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McDonnell Douglas Corporation, Use of Improved Membranes in Tertiary Treatment by Reverse Osmosis, Final Report WQO Program No. 17020 DHR, December 1970.

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Reverse osmosis
Sewage treatment
Waste water treatment
Cellulose acetate
Carbon-treated secondary effluent
Primary effluent
Solid removal
Organic removal
Inorganic removal

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