

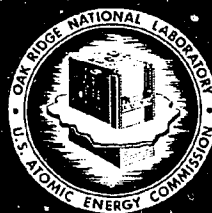
WATER RESEARCH PROGRAM

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FINAL REPORT
MARCH 15, 1970, TO OCTOBER 31, 1972

SEPARATIONS PROCESSES

for the
OFFICE OF SALINE WATER
U.S. Department of the Interior

MASTER



OAK RIDGE NATIONAL LABORATORY
OPERATED BY UNION CARBIDE CORPORATION • FOR THE U.S. ATOMIC ENERGY COMMISSION

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WATER RESEARCH PROGRAM FINAL REPORT

March 15, 1970 to October 31, 1972

SEPARATIONS PROCESSES

Compiled by Robert E. Minturn

James S. Johnson, Jr., Program Director

For the
OFFICE OF SALINE WATER/RESEARCH
Harold E. Podall, Polymer and Biophysics Division
U.S. DEPARTMENT OF THE INTERIOR
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Oak Ridge, Tennessee 37830
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U.S. ATOMIC ENERGY COMMISSION

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Preface

This report completes the account of those activities in the "Separations Processes," Category IV, of the Oak Ridge National Laboratory Water Research Program, supported by the Office of Saline Water, Research Division. The work was carried out under interagency agreements between the Department of the Interior and the Atomic Energy Commission. Since the first agreement in March 1962, results have been reported on a regular basis to the Office of Saline Water, and completed portions, when appropriate, have been published in the open literature. The first biennial report, covering all activities under the program, was issued as a single volume: Office of Saline Water Research and Development Progress Report No. 302 (ORNL-CF-67-8-55), and covered the period March 15, 1962 to March 15, 1964.

For the second biennium, March 15, 1964 to March 15, 1966, work under the program was divided into three categories, "Properties of Solutions," "Reaction and Transport Phenomena at Surfaces and Corrosion Studies," and "Separations Processes." Work for "Separation Processes" was reported in Office of Saline Water Research and Development Progress Report No. 508 (ORNL-CF-69-5-41). Succeeding "Separations Processes" biennial progress reports were also issued as individual reports; that for the biennium 1966 to 1968 as ORNL-TM-4000 in November 1972, and that for 1968 to 1970 as ORNL-TM-4001 in February 1973.

The present report covers the remaining period of the program, from March 15, 1970 through October 31, 1972. Some of the subjects and data discussed in this report have been carried over from experiments begun before March 15, 1970, but are treated here in order to give a complete story.

Work during the biennium that was published in the open literature is also reported here by direct reproduction of the corresponding journal articles. We are grateful to the publishers (Elsevier Publishing Company, Plenum Publishing Corporation, and the American Chemical Society) for permission to reprint the complete texts of these articles. A notation of the source appears at the beginning of each reprinted article. If the work in a particular reprint was cosponsored by some agency other than OSW, the support is acknowledged in the individual article. Similar acknowledgements are made in accounts of unpublished work.

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We have included accounts of some work supported by other agencies where, because of its close relation to the OSW studies, it seemed necessary for a complete picture, and where it seemed likely to be of special interest to potential readers of this report.

Five patents based on work in this program were issued since March 15, 1970, and are assigned to the U. S. Government:

- U. S. Pat. 3,503,789 to J. S. Johnson, Jr. and K. A. Kraus, "Method of Making a Dynamic Solute-Rejecting Membrane," March 31, 1970.
- U. S. Pat. 3,537,988 to A. E. Marcinkowsky, J. S. Johnson, Jr., K. A. Kraus, and J. R. Koppers, "Hyper-filtration Method of Removing Organic Solute from Aqueous Solutions," November 3, 1970.
- U. S. Pat. 3,568,766 to D. G. Thomas, "Corrugated Heat Exchange Member for Evaporation and Condensation," March 9, 1971.
- U. S. Pat. 3,577,339 to J. N. Baird, Jr., J. S. Johnson, Jr., K. A. Kraus, and J. J. Perona, "Filtration Method of Separating Liquids from Extraneous Materials," May 4, 1971.
- U. S. Pat. 3,743,595 to J. S. Johnson, Jr., "Dual-layer Hyper-filtration Membrane and Process for Using Same," July 3, 1973.

One patent was inadvertently omitted from earlier reports, and it is listed here to complete the record:

- U. S. Pat. 3,344,928 to K. A. Kraus, J. S. Johnson, Jr., and A. J. Shor, "Humic Acid as an Additive in a Process of Forming a Salt-Rejecting Membrane," October 3, 1967.

The Office of Saline Water desalination program at the Oak Ridge National Laboratory has had two branches: the Nuclear Desalination Program, directed by R. P. Hammond; the Water Research Program, directed during the first half of this period by K. A. Kraus, and during the rest by J. S. Johnson, Jr. The "Separations Processes" category of the Water Research Program was coordinated during this period by R. E. Minturn.

1. General

1.1 CONTRIBUTORS

The execution of the work has engaged the full or part-time services of many people. Those directly involved in a program that culminated in a publication can be identified from the authors and from the acknowledgements of the publication; contributors to unpublished work are noted below.

The technicians who operated the equipment, and whose contributions to the development of the "art" of dynamic membrane formation were invaluable, were C. G. Westmoreland, whose hand was felt in almost all of the work reported herein, J. Curny, and L. L. Fairchild. Neva Harrison and Donna C. Michelson, along with Westmoreland and Curny, carried out the many chemical analyses that were necessary. W. H. Baldwin and C. E. Higgins with the assistance of Curny and Harrison, synthesized or prepared many of the additives tested, as well as the cast film membranes not otherwise attributed in Section 4.

A. J. Shor, in addition to other activities, supervised the maintenance and modification of equipment and the design of new systems. L. Dresner's theoretical contributions are documented by several reprints. R. B. Bevan carried out a series of hyperfiltration experiments with multicomponent solutions as experimental verifications of Dresner's theories. Bevan also suggested the experiments with boric acid that are reported in Section 3.3.3.5. P. M. Lantz tested alternate inside-outside pressurization of the 7-channel Sela tubes, see Section 3.1.2.1.1.2, and C. G. West contributed technical assistance throughout the period of this report.

Several MIT Practice School teams made major contributions to this work. The team of J. M. Ganzer and A. K. Mehta investigated the performance of a single set of Zr(IV)-PAA membranes under a number of conditions,¹ and their work is included in Section 3.1.3. I. Onal, C. S. Goff, and J. M. Aslam studied, in a series of short-term runs, the effect of various parameters during membrane formation,² included in Section 3.1.2. During this work, R. M. Mayer was director, and M. S. Bautista assistant director, of the Practice School. The team of J. C. Bronfenbrenner and A. J. Heman studied concentration polarization with neutral solutes,³ Section 5.2, and J. B. Cabellon, A. K. Padia, and L. E. Whitesides studied the hyperfiltration of simulated brackish waters by membranes on supports of practical

interest,⁴ i.e., carbon and ceramic tubes with Coalinga water (see Section 3.3.1.1). During the tenure of the last two teams, J. T. Day was the Director and P. H. Wadia the Assistant Director of the Practice School. In addition to his contribution as part of the staff of the School, P. H. Wadia also spent two summers with the Water Research Program. During the first, his work was directed toward understanding those factors that affected dynamic membrane formation (Section 3.1.2), and during the second, he was involved in an economic analysis of cross-flow filtration⁵ and hyperfiltration (see Section 6.1).

Another team from the Practice School, this time with J. T. Day as the Director and S. Amin as the Assistant Director, was S. D. Harms and W. D. Franklin. This team did a study of the extent to which Ca(II) and Mg(II) needed to be removed, by cross-flow pretreatment, from Roswell water in order to achieve satisfactory hyperfiltration results in a second stage⁶ (Section 3.3.1.2.2). They also monitored a 10-day run with pretreated Roswell water, reported in the same section.

G. J. Goetz, L. T. Bauer, and S. V. Demetriou of the Practice School, under J. W. Tester as Director and H. R. Greenberg as Assistant Director, studied the desalination of simulated and natural seawater by multi-stage hyperfiltration, using a commercially available cellulose acetate membrane module and dynamically formed hydrous Zr(IV) oxide-polyacrylate membranes. A description of this work is given in Section 3.3.2.

A paper on the estimation of concentration polarization for ion-exclusion hyperfiltration membranes, reprinted in Section 5.1, is the work of D. G. Thomas, who heads a Reactor Division group of the Water Research Program, located at Y-12, which consists of W. R. Mixon, J. D. Sheppard, P. H. Hayes, R. B. Gallaher, and J. R. Love. The work of this group, which has been closely coordinated with the Separations Processes group, has culminated in the design, construction, and field testing of a 1000 gallon per day (gpd) dynamic membrane desalination pilot plant,⁷ funded by the OSW Membrane Division. Another paper by Thomas, on enhanced heat transfer, is reprinted in Section 8.

1.2 DEFINITIONS

Certain terms which recur throughout this report will be defined here:

Observed rejection, uncorrected for the effect of buildup of rejected solute in the boundary layer, is defined by

$$R_{\text{obs}} \equiv 1 - (c_w/c_t),$$

where c is the concentration, subscript w refers to the effluent or product solution, and subscript t refers to the "cup-mixing" concentration, essentially equivalent here to the concentration in the turbulent core, or the circulating feed, since the volume of product in a single pass is trivial, in all experiments discussed here, compared to that of the pressurized solution.

Intrinsic rejection, defined by

$$R \equiv 1 - (c_w/c_\alpha),$$

where α refers to the feed-membrane interface, may be estimated in some cases by measuring R_{obs} as a function of circulation velocity, u , and extrapolating a plot of $\log (1 - R_{\text{obs}})/R_{\text{obs}}$ vs. $v/u^{0.75}$, where v is the permeation rate through the membrane, to infinite velocity.⁸

It has been observed^{9,10} that the decline in fluxes through hyperfiltration membranes often follows the relationship

$$J(t)/J_1 = (t/t_1)^{-b}$$

where $J(t)$ and J_1 are the fluxes at times t and t_1 , respectively, and b is a constant called the flux decline parameter.

1.3 EQUIPMENT AND METHODS

A brief discussion of the techniques used in these experiments is given in a paper¹¹ which is reprinted as Section 3.1.1, to follow. More detailed descriptions may be found in earlier works^{8,12,13,14} and especially in the biennial report¹⁵ preceding this one. Four different hyperfiltration loops were used for nearly all of the tests described; these loops are sometimes referred to by code numbers. Loop 4^{12,14} is a small capacity titanium loop, pressurized by a 300 cm³/min Milton Roy "Constametric" pump with wetted parts of Hastelloy C. The circulating pump in this loop is a

canned-rotor centrifugal pump capable of 10 liters/min at a differential pressure of about 20 psi. Loop 7 is described in Section 3.1.1, and Loop 8 is similar to Loop 7, except that Loop 8 has a duplex rather than a triplex Milton Roy feed pump and a 30 gpm Roth turbine circulation pump rather than a 100 gpm 100A pump. Loop 10 differs from Loop 7 in that the wetted surfaces are primarily stainless steel and in that it incorporates a low-pressure, high-velocity auxiliary loop. In the auxiliary loop, the pressurizing pump, A Byron-Jackson 3 x 4 x 11 SM chemical process pump, rated at 185 psi head at 100 gpm, also circulates the feed. This allows us to maintain high circulation velocities through the test sections during the initial stages of membrane formation, where, because of the low pressure, our usual circulation pumps would cavitate.

Most of the work reported deals with membranes dynamically formed from materials added to a solution circulated past porous supports under pressure. A more detailed description of the formation of a particular dynamic membrane, the dual-layer hydrous Zr(IV) oxide-polyacrylate [Zr(IV)-PAA] membrane, is given in Section 3.1.1. See also Section 3.1.2.

The experimental test sections were of three types: 1) 5/8" porous stainless steel tubes (~5 micron pores), wrapped with porous films such as Acropor AN or Millipore, and inserted into tubular metal or lucite pressure jackets; 2) carbon or ceramic tubes that could be pressurized on the outside by inserting into similar jackets, or pressurized on the inside by sealing them directly into the brine flow system with epoxy cement; and 3) membrane supports mounted in cells.¹⁶ Membrane areas per support were about 50 cm² in the tubular systems, and about 1.5 cm² in the cells. In the cells, flow patterns and hydrodynamics were too complex for estimates of concentration polarization, and their use was held to a minimum.

Protomodels of potentially practical support materials were tested on occasion; when used they replaced the experimental test sections.

Some porous supports have a surface structure that is too open for the proper formation of dynamic membranes, and need be precreated with a filter aid.¹⁷ The particle size and the concentration of filter aid is usually determined empirically for a given support; we generally added the aids to the feed to make a suspension of about 30-50 ppm. Filter aids commonly used in these experiments are listed in Table 1.1.

TABLE 1.1^a
FILTER AID MATERIALS

Trade Name	Material	Mean Particle Size, Nominal (microns)	Manufacturer or Supplier
<u>FIBERS</u>			
Cellu-Flo O	Cellulose	Coarse ^b	Cellulo Co.
Cellu-Flo 10	Asbestos	Coarse ^b	Cellulo Co.
Solka-Floc, BW-200	Cellulose	50x17	Grefco, Inc. ^c
<u>PARTICLES</u>			
<u>Silica:</u>			
Dicalite 4186	Perlite	16	Grefco, Inc.
Dicalite 436	Perlite	6.5	Grefco, Inc.
Dicalite 416	Perlite	3.9	Grefco, Inc.
Dicalite 215	Diatomite	2.7	Grefco, Inc.
Dicalite Speedex	Diatomite	Medium	Grefco, Inc.
Hyflo Super-Cel	Diatomite	Medium	Johns-Manville
Standard Super-Cel	Diatomite	8	Johns-Manville
Celite 505	Diatomite	Fine	Johns-Manville
Celite 550	Diatomite	Coarse	Johns-Manville
<u>Carbon:</u>			
Vulcan XC-72R	Carbon	0.029 ^d	Cabot Corp.
Medium Regal SRF	Carbon	0.056 ^d	Cabot Corp.
Spheron 9	Carbon	0.029 ^d	Cabot Corp.
Neospectra Mark I	Carbon	0.011 ^d	Columbia Carbon Co.

a. In part, from Ref. 17 in text.

b. Homogenized in blender before use.

c. Dicalite Division

d. Estimated from electron micrographs. We thank K. J. Notz of the ORNL Chemical Technology Division for supplying these materials.

Membrane performance during a run was routinely monitored by measuring the conductivity of the feed and of the product. Chloride concentrations were determined by using a Buchler-Cotlove Chloridometer, Ca(II) and Mg(II) concentrations by titration with EDTA, phosphate by a spectrophotometric method (FWPCA, 1969), turbidity was determined with a Hach 2100 Turbidimeter, carbon by a Beckman Model 915 total carbon analyzer, and color by measuring absorption at 465 nm and comparing to a Pt-Co standard absorption curve. Total cation concentrations were determined by exchanging them on Dowex 50 X12 in the hydrogen form, and titrating the eluted acid with standard base, using a Sargent Model D recording titrator.

The hyperfiltration properties of dynamic membranes were often tested with simulated naturally occurring brackish waters. The compositions used in these tests are given in Table 3.68.

2. Separations by Filtration - A Summary Article

An expansion of a paper presented at the 162nd National ACS Meeting, Washington, D. C., in September 1971 was published,¹⁸ along with other papers from the symposium, in 1972, and is reprinted here. It reviews several of the current interests of the program.

[Reprinted from "Reverse Osmosis Membrane Research," edited by H. K. Lonsdale and H. E. Podall]

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POLYELECTROLYTES IN AQUEOUS SOLUTIONS-- FILTRATION, HYPERFILTRATION, AND DYNAMIC MEMBRANES*

James S. Johnson, Jr.

INTRODUCTION

Filtration is one of the oldest separation techniques, apparently known to the Chinese and Hebrews in ancient times[1]. It remains one of the most important, and new methods of carrying it out, as well as new applications, continue to be devised. In the last century, it expanded beyond the separation of solid particulates from liquids or gases to separations of colloids from fluids, by ultrafiltration. In recent decades, filtration of low-molecular solutes has been found possible, by "reverse osmosis." Thinking of removal of dissolved solids as a filtration process is helpful on occasion, and the alternate name "hyperfiltration" [2] is sometimes used.

Polyelectrolytes enter this discussion in two distinct, though related, ways. First, the hyperfiltration membranes of concern here are of the ion-exchange class, and thus are composed of polyelectrolytes. Second, polyelectrolytes often are added to influence filtration by interaction with the material to be removed, and they are so used in some of this work. We include inorganic polymers and hydrous oxides, which have ion-exchange properties[3], in the polyelectrolyte class.

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HYPERFILTRATION BY DYNAMIC MEMBRANES

Salt filtration by membranes having ion-exchange capacity was observed in the course of ultrafiltration[4] well before neutral membranes such as cellulose acetate were proposed for desalination[5]. The contribution of equilibrium distributions of salt and water between membrane and solution phases was understood qualitatively, and for idealized models, aspects of transport had also been analyzed[6]. Since the activity of a salt depends on the product of ionic activities, the high concentration of mobile ions in an ion exchanger having a charge sign counter to the fixed charge will tend to exclude mobile co-ions from the exchanger phase. In addition to this equilibrium aspect, the concentration of salt in the product of hyperfiltration will depend on the flux of water relative to diffusion of salt in the membrane, and on the coupling of salt and water fluxes[7].

Ion-exchange membranes have received far less attention for hyperfiltration than neutral membranes. Partly, neglect has stemmed from emphasis on seawater desalination; rejections by ion-exchange membranes are expected to decrease with increasing concentration and are not likely to be adequate for producing potable water in a single stage from the ocean. For low-salinity feeds in desalting and for pollution control, however, rejections might be adequate. Further, the fact that rejection depends on a coulombic mechanism might allow use of a membrane having a looser structure and, for a given thickness, higher permeability[8] than one dependent on the short-range forces presumably active with neutral membranes. The problem with ion-exchange membranes has been to prepare them of thickness comparable to the submicron active layers of cellulose acetate, in order to realize potentially high production rates.

In 1965, an observation made in the course of research under the ORNL Water Research Program pointed a way to do this[9]. A sodium chloride solution, containing a Th(IV) salt at about the millimolar level, was circulated under pressure past a porous support, in this case a 0.2 μ Sela Flotronics Co. silver filter. After operation of the order of an hour, analysis of the effluent indicated that an appreciable fraction of the salt was being filtered, at fluxes much higher than those reported at the time for membranes having any significant salt filtration capabilities.

We concluded that a thin layer of hydrous Th(IV) oxide had in some way formed at the interface between pressurized solution and the porous support. On hydrolysis, many metal ions form polymers in solution, and the hydrous oxide precipitates in many respects resemble a solid ion-exchanger formed by cross-linking an organic polyelectrolyte[3]. In equilibrium with acidic media,

they tend to have fewer hydroxides, and the other anions present to maintain charge neutrality frequently are readily exchangeable; in basic solution, the opposite situation holds, and hydrous oxides tend to be cation exchangers.

Attribution of salt filtration to a hydrous oxide film was confirmed in a number of ways. Salts of many other hydrolyzable ions were found to form rejecting membranes dynamically, and membrane formation was easier with colloidal dispersions of hydrous oxides than with solutions of hydrolyzable salts. Some other oxides found to form membranes were Zr(IV), Fe(III), Sn(IV), and U(VI). Hyperfiltration properties as a function of pH are qualitatively as predicted from known ion-exchange properties. With Zr(IV), which has received most attention, results over a wide range of conditions--pH of feed, salt concentration, and valence of ions of feed salt--were successfully correlated[10].

There would appear to be no reason why formation of salt-filtering layers, which we call "dynamic membranes," should be limited to inorganic ion exchangers, and we found that they were indeed formed of such polyelectrolytes as: polyvinyl benzyl trimethyl ammonium chloride, polystyrene sulfonate[11], and dispersions of low crosslinked ion-exchange beads of these polymers; polyvinyl pyridine[12]; polyacrylic acid[13]; polyvinyl sulfonic acid, polymaleic acid, and polyvinyl amine; and humic acid[12], and polyelectrolytes already present in pulp mill wastes[14], sewage[15], and textile dyeing wastes[16]. Membrane formation from particulates has also been observed elsewhere[17].

The promise of high fluxes is frequently realized; values of hundreds of gallons per square foot per day (gpd/ft² or gfd) are sometimes observed. An exceptional example is given in Fig. 1, a hydrous Zr(IV) oxide membrane formed at high circulation velocity past the membrane surface. Use of turbulence promoters has increased flux through membranes[18,19], and high turbulence levels associated with high circulation velocities seem to have a similar effect during membrane formation. The support in the case of interest was porous polyvinyl chloride-acrylonitrile on a nylon fabric, nominal pore size 0.45 μ . This commercial filter material (Acropor AN, from Gelman Co.) was wrapped around a 5/8" O.D. porous stainless steel tube (5 μ), and 0.05 M NaCl containing 10⁻⁴ M hydrous Zr(IV) oxide was circulated in the annulus between the outside of the tube and a pressure jacket[20]. When observed rejection, R_{obs} (percentage of feed salt removed), of over 50% was attained, flux was still over 1400 gfd. At this flux, concentration polarization of filtered salt is high; if the solute concentration at the membrane-feed interface is taken into account [7,21,22], intrinsic rejection, R_i , is estimated to be about 80%.

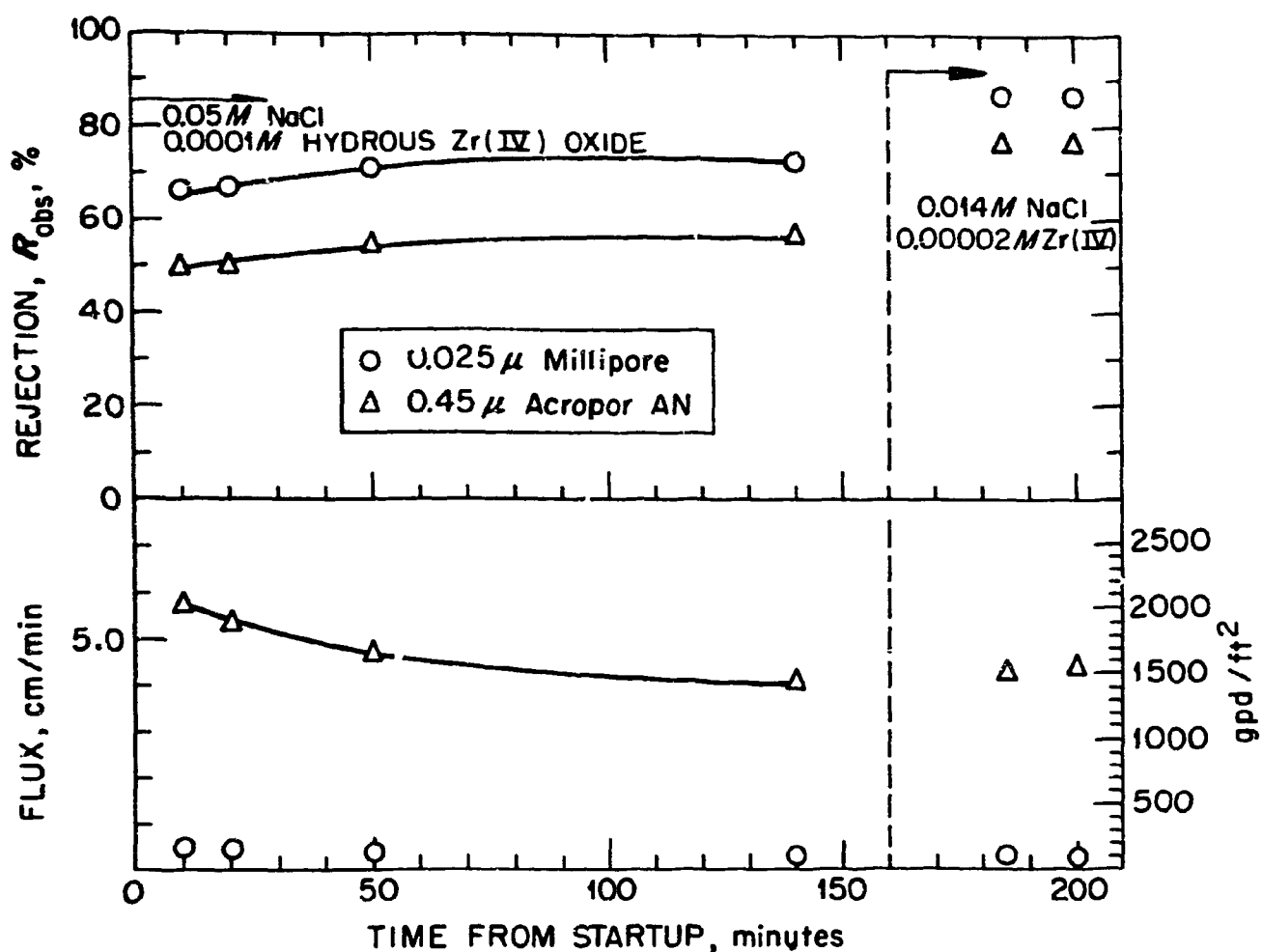


Fig. 1 - Hyperfiltration with Hydrous Zr (IV) Oxide Membrane Formed at High Circulation Velocity (50 ft/sec circulation velocity, pH 4 to 4.5, 1000 psig)

Table 1 lists the zirconium contents of a set of membranes formed in a single run. For a given circulation velocity, there appears to be a rough trend toward higher zirconium content with increasing pore size. For a given pore size, zirconium content is higher at lower circulation velocity, but the correlation of flux with zirconium content and circulation velocity is the opposite of what might be expected in the case of 0.025 μ Millipore. Fluxes through hydrous oxide membranes formed on supports of half-micron pores are usually higher at higher circulation velocities, but, for reasons not understood, are observed to be erratic at the small pore size end of our experimental range.

In another experiment, formation of a polyacrylate layer on a hydrous Zr(IV) oxide membrane, in a manner to be discussed below, did not affect the zirconium content significantly.

TABLE 1
ZIRCONIUM CONTENTS* OF DYNAMIC MEMBRANES
FORMED AT 950 PSIG AND pH 3.8 (25°C)

<u>Support</u>	<u>Velocity (ft/sec)</u>	<u>[Zr] ($\mu\text{g}/\text{cm}^2$)</u>	<u>R_{obs} (%)</u>	<u>Flux (gfd)</u>
0.025 μ Millipore**	35	15	55	171
0.05 μ Millipore	35	31	62	220
0.1 μ Millipore	35	7	64	131
0.45 μ Acropor AN	35	160	64	480
1.2 μ Acropor AN	35	126	62	510
0.025 μ Millipore	14.5	99	57	178
0.45 μ Acropor AN	14.5	232	62	300

*Analyses were by a spectrophotometric method using Arsenazo III as the chromogenic agent. We thank W. R. Laing of the ORNL Analytical Chemistry Division for these results.

**Millipore Corp.

Hydrous oxide membranes exemplify some of the problems, as well as the promise, of dynamic membranes. Hydrous Zr(IV) oxide membranes are easily formed in clean apparatus. In anion-exchange form, their rejection of salt from a NaCl-water solution is good, and from MgCl_2 -water, even better. Unfortunately, the optimum solution acidity is below pH 4, which does not match well most natural saline waters. Further, their rejection is seriously decreased by the presence in feeds of common polyvalent counterions, such as sulfate.

Much of our effort has been directed toward finding a dynamic membrane for which these disadvantages would be minimized. Of organic polyelectrolytes tested, polyacrylic acid formed membranes of relatively good rejection in the neutral pH range[13], but reproducibility was poor, apparently because membrane formation with this additive was sensitive to pore size distribution of the support. In addition, performance was poor with natural water composition, which typically includes calcium and magnesium.

Hydrous Oxide-PAA Membranes

About two years ago, we found that, if a hydrous oxide membrane is exposed to polyacrylic acid at acid pH, these difficulties are ameliorated[23]. Fig. 2 summarizes changes in hyperfiltration properties subsequent to such exposure as NaOH was added to a 0.05 M NaCl feed containing 25 ppm of polyacrylic acid (PAA, Rohm and Haas Co. Acrysol A-3). Rejections of over 90% were attained in the neutral pH range. In experiments in which PAA was introduced at

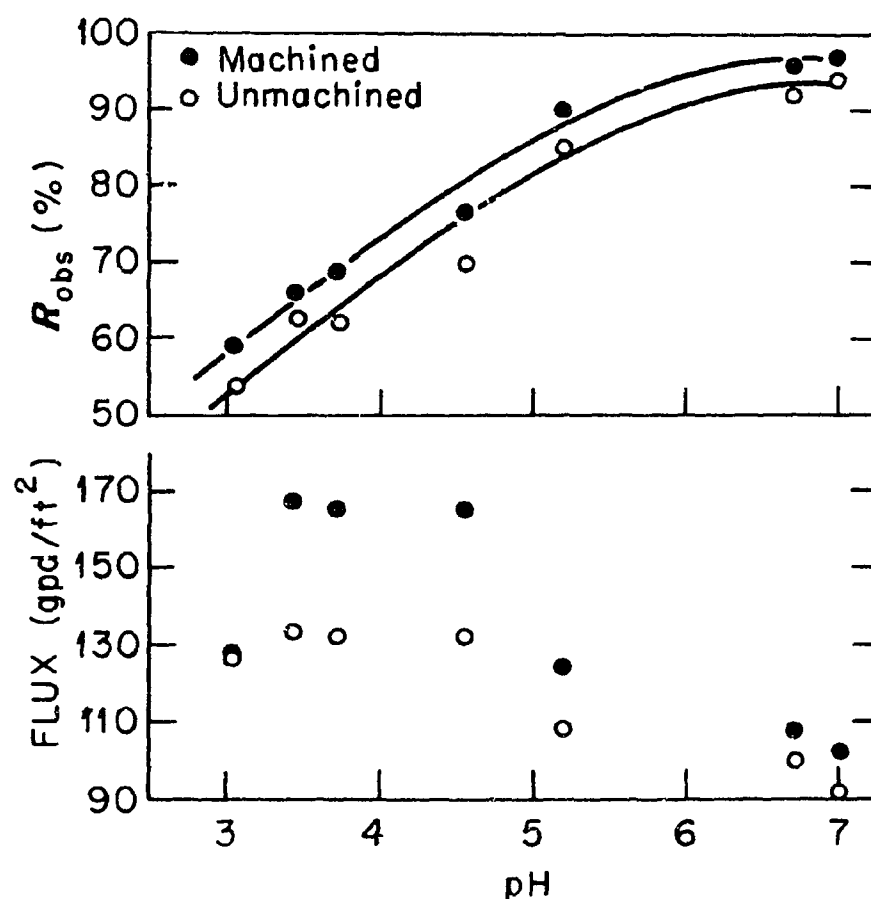


Fig. 2 - Formation Curves for Zr(IV) - PAA Hyperfiltration Membranes on Machined and Unmachined 6C Carbon Tubes. Acrysol A-3 PAA. (0.05 M NaCl, 900 psig, $\sim 60^\circ\text{C}$, 8 ft/sec circulation velocity)

neutral pH, it had little effect until the feed was cycled through acid pH. Apparently the polyacrylic acid becomes attached to the anion-exchange form of the oxide, and remains so, unless the pH is raised to high values, over 10. The rise in rejection reflects the increase in ion-exchange capacity as the carboxyl groups are neutralized.

The supports in the experiment of Fig. 2 were carbon tubes designated 6C by the manufacturer[12]. The extrusion skin had been machined from one of them, a process which improves performance[24]. These tubes seem more likely in the near future to be practical as components of modules for application[25] than wrapped porous metals, even though production rates with the carbon tubes are not usually as high. Many other tubes appear promising for practical application, particularly ceramic tubes[26]. In Fig. 2, fluxes were about 100 gfd at 60°C . Production rates for hydrous Zr(IV) oxide-polyacrylate (Zr(IV)-PAA) membranes depend roughly on the inverse of solution viscosity and would therefore be about half as high at room temperature as at 60°C .

These dual-layer Zr(IV)-PAA membranes have in many respects more favorable properties than single-layer polyacrylate membranes [13]. Advantages include more reproducible properties, less sensitivity to type of porous support (a characteristic presumably contributed by the hydrous oxide sublayer), and better performance with simulated natural waters. Fluxes are also usually higher than with single-layer polyacrylate membranes.

Most effort with hydrous oxide-polycarboxylate membranes has been centered on Zr(IV)-PAA[23,27,28]. Other oxides, such as those of Sn(IV), Fe(III), and Th(IV), can be used as sublayers, and it may well be that one of them would be as good or better than Zr(IV) for this purpose. Examples of results illustrating various properties of Zr(IV)-PAA membranes follow. Not all were obtained with membranes prepared by the most favorable procedures delineated to date. Consequently, there are some differences in rejections and fluxes, even when porous supports and experimental conditions at the time of the tests were similar.

Concentration Dependence of Rejection. Rejections by ion-exchange membranes are expected to decrease with increasing concentration of the feed solution. Fig. 3 illustrates the dependence for NaCl solutions. In these experiments, values of R_{obs} were measured as a function of circulation velocity, and values of R , the fraction of salt present at the pressurized solution-membrane interface not in the effluent, were estimated by an extrapolation to infinite circulation velocity[22]. This procedure is designed to determine the rejection, undistorted by the effect of concentration polarization.

Ideal "Donnan exclusion" theory predicts that a plot of $\log(1 - R)$ vs $\log c_{NaCl}$ should approach a slope of 1 at low concentration, behavior which is observed with hydrous Zr(IV) oxide anion-exchange membranes[10]. In common with other dynamic membranes of organic polyelectrolytes, rejection does not decline with increasing concentration as rapidly as simple theory predicts. A likely explanation is a decrease in membrane water content as the concentration of salt in the contacting solutions increases.

Pressure Dependence. Fig. 4 illustrates the effect of pressure on hyperfiltration properties. At the highest pressure of this series, 65 atm., the flux is not high enough to realize the asymptotic rejection[7], though other measurements indicate that a further increase in pressure will cause only a slight increase in rejection. Fluxes are roughly proportional to pressure.

Effect of Molecular Weight of Polyacrylic Acid Used in Membrane Formation. Two illustrations of the influence of molecular weight of the organic constituent are given. Fig. 5 illustrates the change in properties on raising pH after exposure of the hydrous

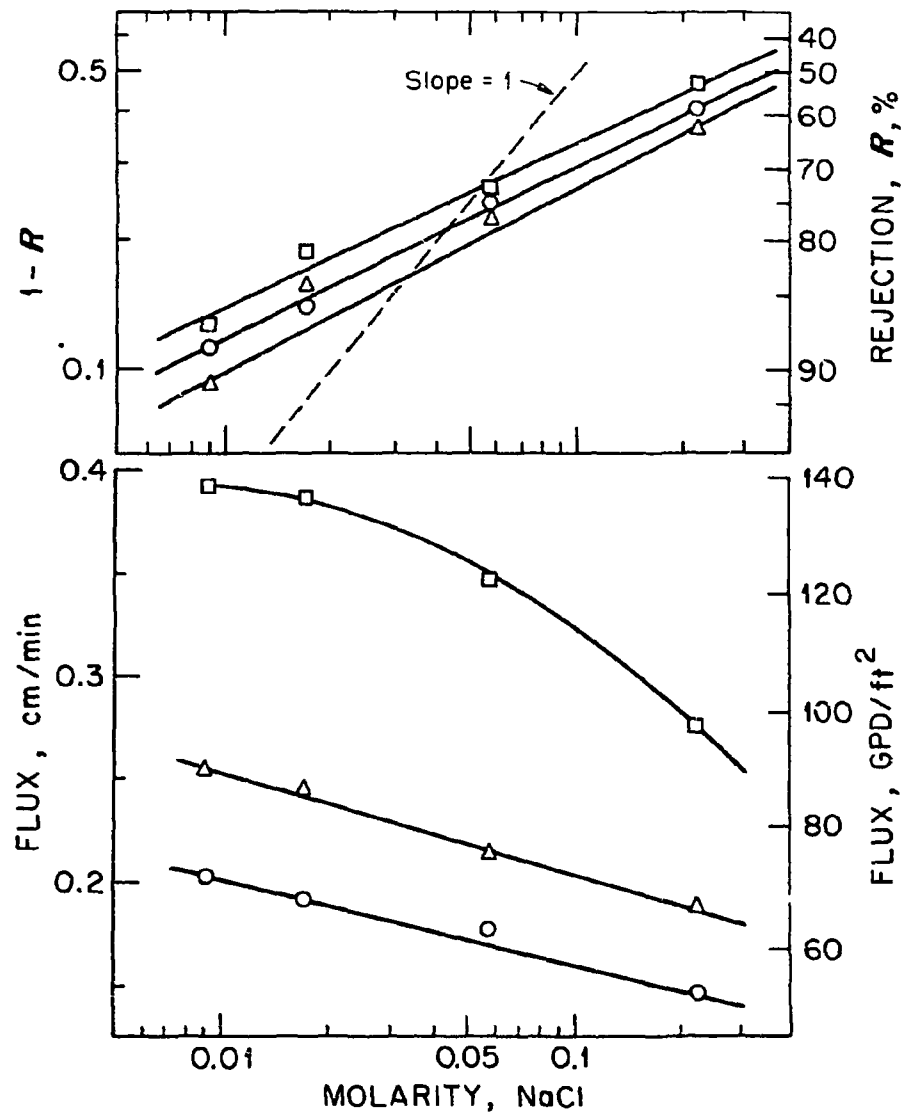


Fig. 3 - Effect of Concentration on Hyperfiltration by
Hydrous Zr(IV) Oxide-PAA Membrane
Pressure 1000 psig
□ 1.2μ Acropor
△ 0.05μ Millipore
○ 0.025μ Millipore

oxide layer to polyacrylic acid (in the case of Nalco Chemical Co. A-1, a high molecular weight polycarboxylate of high charge density) in acid solutions. Results of two series of measurements are given. The reproducibility is fair, except for the highest molecular weight, which gave erratic results. Fig. 6 summarizes results of tests with a simulated natural water. These and other results [23] indicate that best rejections are realized with PAA in the molecular weight range of 50,000 to 150,000.

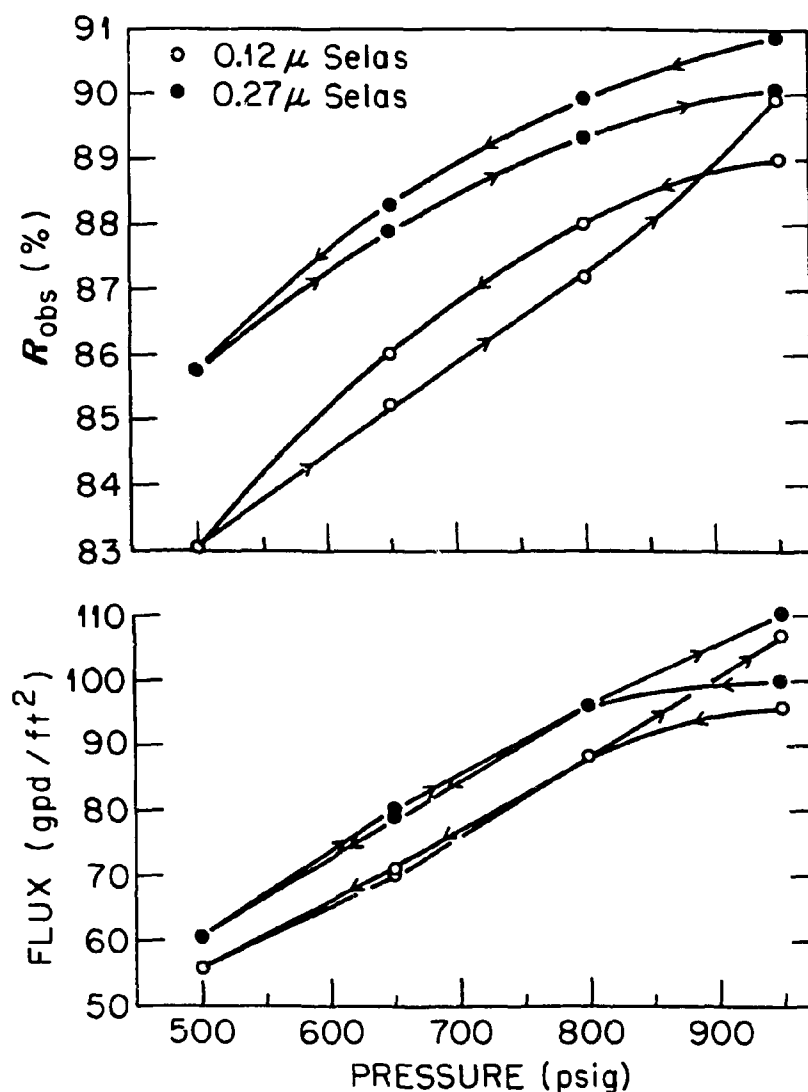


Fig. 4 - Effect of Pressure on Hyperfiltration Properties of Dual-Layer Membranes on Sela Ceramic Tubes. Arrows indicate chronological order of pressure excursion. (0.05 M NaCl, 35 ft/sec circulation velocity, 25°C, pH $\sim$ 7)

Performance with Simulated Natural Waters. For desalination, the usefulness of Zr(IV)-PAA membranes hinges on how well they perform with natural waters. Laboratory experience with compositions typical of waters in the western U. S. have been encouraging. Fig. 7 summarizes tests with several synthetic solutions, approximating natural (1X) compositions[29]; tests were also carried out with twice (2X) or three times (3X) the nominal concentrations, insofar as solubilities of various components permitted, in order to determine the effect of concentration increases incidental to recovery of product water. The best overall measure of rejection performance is probably "total cation," determined by passing

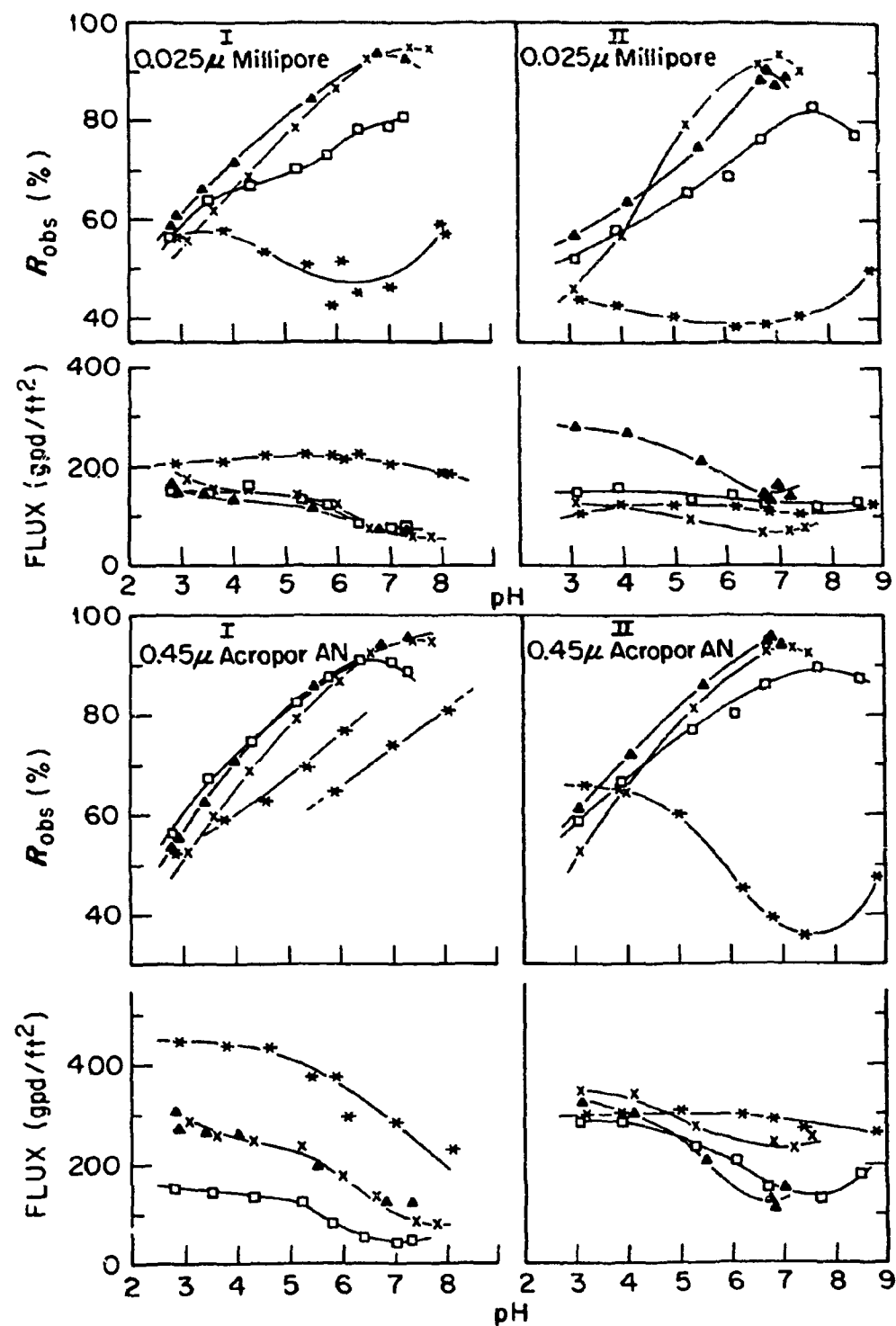


Fig. 5 - Effect of Polycarboxylate Molecular Weight Upon pH Response During Dual-Layer Membrane Formation

I and II are two independent series of experiments.

- $\times$ Acrysol A-1 ($<50 \times 10^3$)
- $\square$ Acrysol A-5 ($<300 \times 10^3$)
- Δ Acrysol A-3 ($\sim 150 \times 10^3$)
- $*$ Nalco A-1 ($6-10 \times 10^6$)

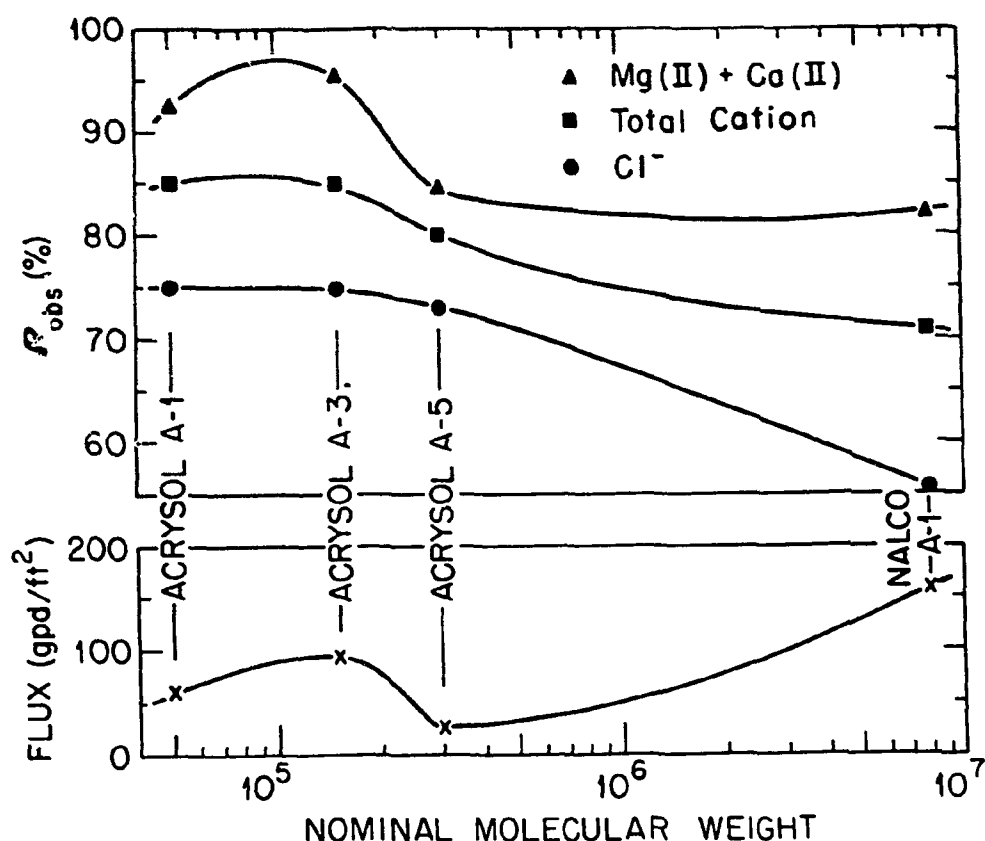


Fig. 6 - Effect of Polycarboxylate Molecular Weight on Hyperfiltration of Coalinga, Calif. Water by Dual Layer Membranes (950 psig; 0.45μ Acropor AN; 35 ft/sec circulation velocity)

samples of feed and product through columns of cation-exchangers in the hydrogen form and titration of displaced acid.

An aspect of the results in Fig. 7 which is not readily explained is the relative insensitivity of rejection to total salinity, in comparison with the dependence for NaCl alone (Fig. 3). Since the rejection of $MgCl_2$ from aqueous $MgCl_2$ solutions is lower than that for NaCl from aqueous NaCl solutions at the same normality, the fact that $Mg(II)$ and $Ca(II)$ are more highly rejected from mixtures than Na^+ is also inexplicable. Similar behavior has been observed with cast PAA membranes[30]. Both rejections and flux were higher for the Zr(IV)-PAA membranes than for dynamic single-layer PAA membranes (half-shaded points of Fig. 7, taken from reference 13), though part of the flux difference may arise from differences in circulation velocity and porous support.

With both the dual-layer and single-layer membranes, presence in the feed of the divalent counterions-- $Ca(II)$ and $Mg(II)$ --generally lowers permeability. However, membrane formation procedures frequently result in higher fluxes than those in Fig. 7.

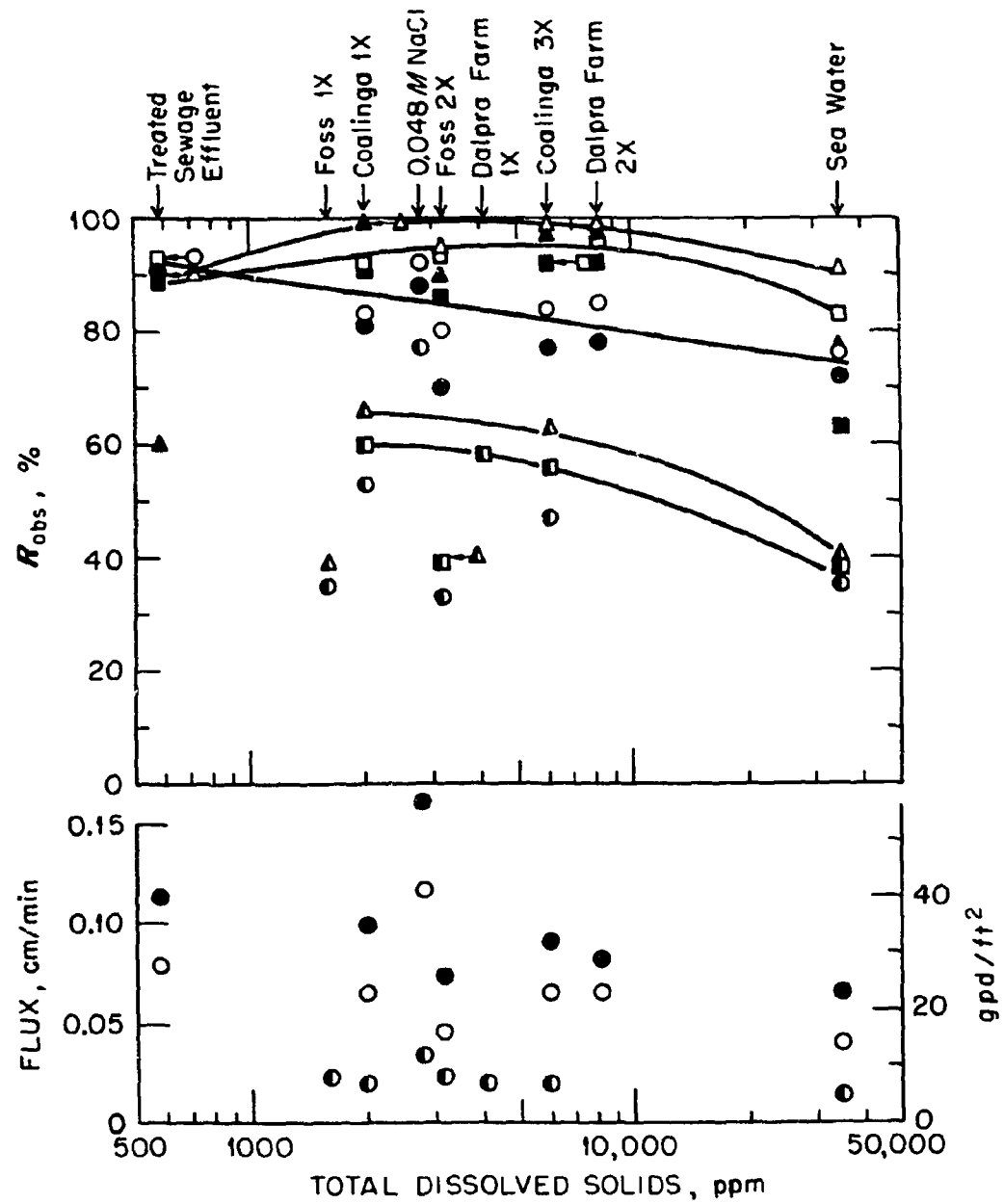


Fig. 7 - Hyperfiltration of Natural Water Compositions With Dynamically Formed Polyacrylate Membranes (1000 psig)

	Chloride	Total Cation	Mg ²⁺ + Ca ²⁺
Dual Layer Hyd. Zr(IV) 0x.-PAA (35 ft/sec) 0.05 μ Millipore	○	□	△
0.45 μ Acropor AN	●	■	▲
Single-Layer PAA (5 ft/sec) 0.3 μ Ceramic Tube	◐	◑	◒

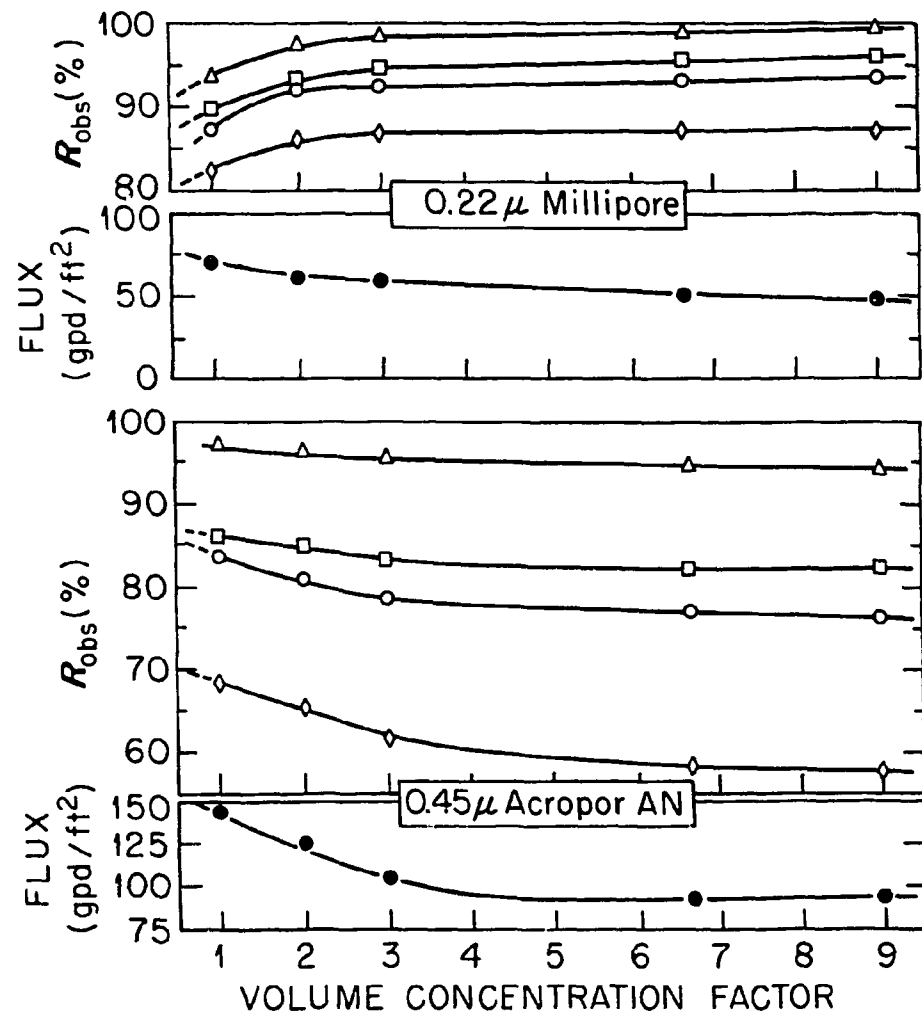


Fig. 8 - Hyperfiltration of Coalinga Water by Dual-Layer Hydrus-Zr(IV) Oxide-Acrysol A-3 Membranes as a Function of Volume Concentration Factor. (950 psig, circ. vel. 35 ft/sec, 25°C)

○ Conductivity △ $Mg(II) + Ca(II)$
 ◇ Cl^- □ Total Cation

Fig. 8 summarizes an experiment with a solution initially similar in composition to that of water at Coalinga, California. Product was discarded, and the feed solution allowed to concentrate to about 1/9 of its original volume. Because of incomplete rejection by these membranes and lower rejections by others present in the same test system (not reported in Fig. 8), concentration of various components was not as great as indicated by the reduction in volume--about a factor of five for chloride, 6 for total cation, and 7 for $Ca(II)$ plus $Mg(II)$. Rejections were comparable to those in Fig. 7 for the membrane on the 0.22 μ support, were somewhat lower for the 0.45 μ, and both were also relatively insensitive to concentration. Fluxes in both cases were higher than those in Fig. 7.

A limited trade-off between rejection and flux is possible by adjusting pH (Fig. 9). The symbol α indicates the first measurement of the series, and ω , the last, after tests both in the presence and absence of added PAA (left and right halves of Fig. 9). The effects of pH seem to be reversible. The open and closed points in the figure represent results for membranes which had been operated at different circulation velocities in experiments carried out prior to those in the figure.

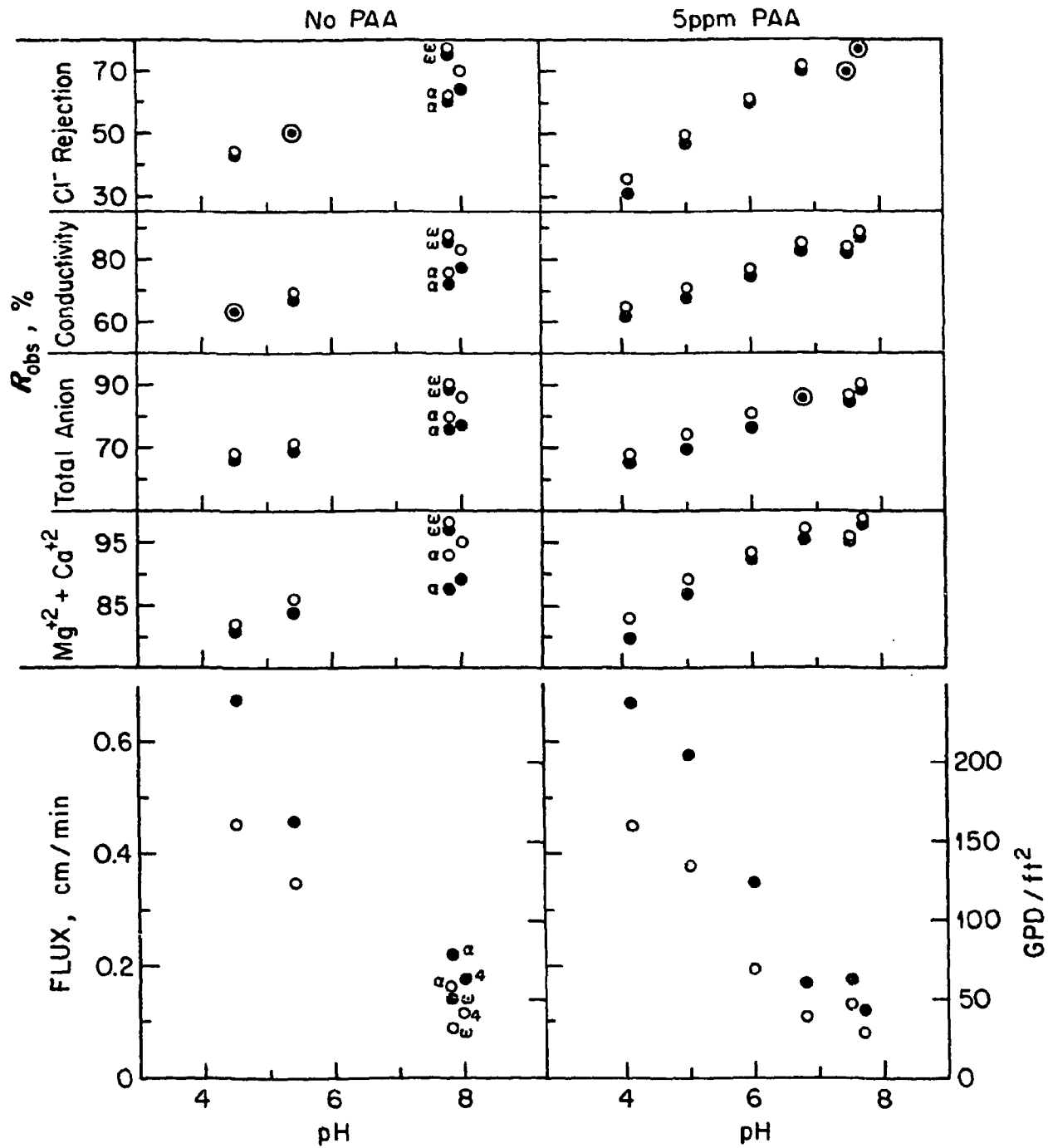


Fig. 9 - Effect of pH on Hyperfiltration of Coalinga Water With Hydrous Zr(IV) Oxide-PAA Membrane. (0.45μ Acropor AN; circ. vel. 35 ft/sec)

Flux Decline. Decrease of production rate with time is a problem with all hyperfiltration membranes. With the dynamic class, there is the possibility of regeneration in situ, without disassembly of equipment. The best way to accomplish this may be by backwashing, which is most readily accomplished if membranes are formed on supports of large pore size, pretreated with filteraids to give a thin layer of fine pore size[31]. While suitable filteraid procedures for Zr(IV)-PAA membranes have not been developed as yet, reasonably good recovery of properties can be attained by chemical washes.

Fig. 10 summarizes fluxes obtained with several membranes in a 13-day run with synthetic Coalinga water, followed by regeneration and further operation for about four days. During most of the run, product was returned to the feed reservoir, and the experimental conditions were those given in the figure legend. From 200 to 317 hours, however, variations in circulation velocities and in concentration were investigated.

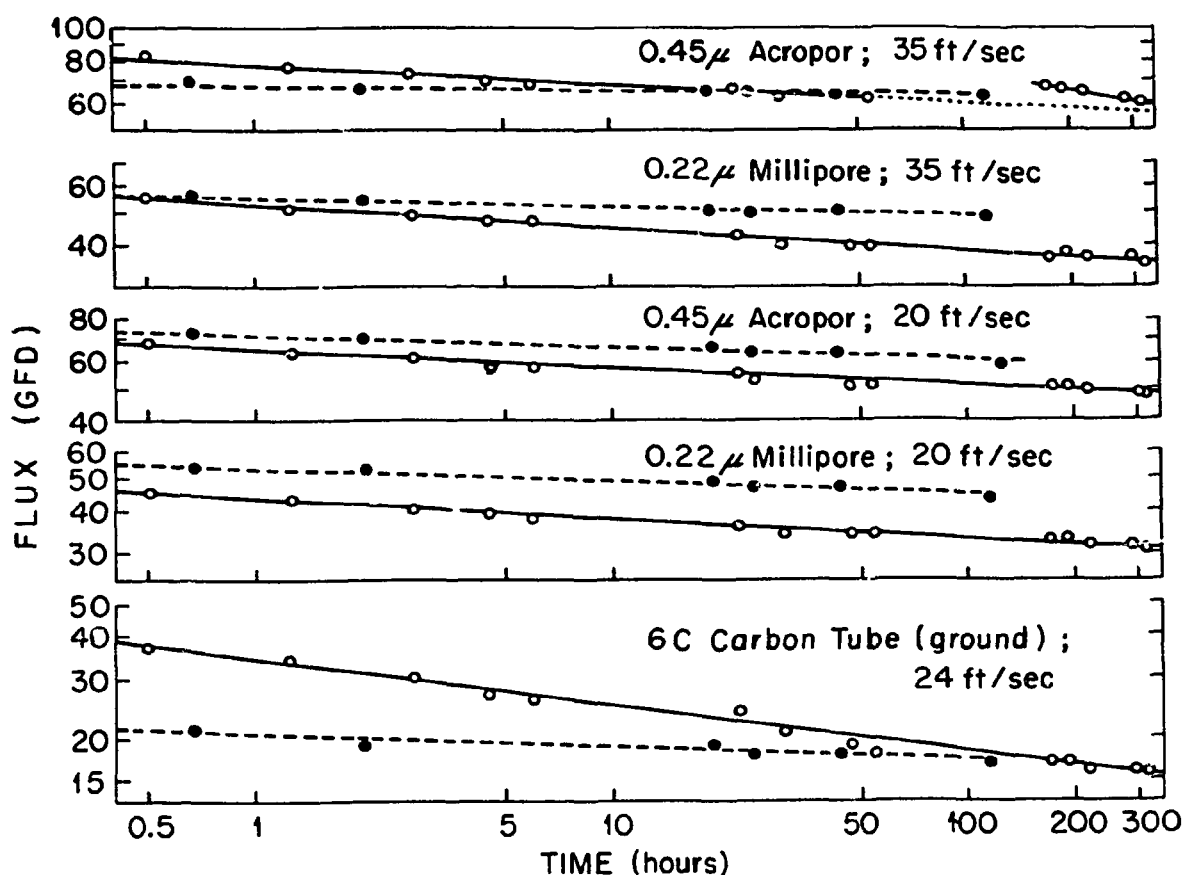


Fig. 10 - Flux Decline Plots for the Hyperfiltration of Coalinga Water by Hydrous Zr(IV) Oxide-PAA Dual-Layer Membranes. (950 psig, 25°C, circulation velocities as shown)
 ○ Initial Run ● After Regeneration

Regeneration was by a five-minute 1 M NaOH wash, followed by circulation of 0.05 M NaCl containing 50 ppm of PAA initially at pH 2.2, with subsequent base additions to neutrality. This amounts to re-forming the polyacrylate layer by the usual procedure. It was not necessary to form the hydrous Zr(IV) oxide layer a second time.

Rejections were similar to others reported here for Coalinga; examples are listed in Table 2. In Fig. 10 the fluxes are plotted according to the common practice, logarithm of flux vs log time. It is an empirical observation that such plots are frequently linear[32], and the negative of the slope, b , is taken as a measure of the rate of flux decline. Slopes are listed in Table 3.

The values of b are in the range usually found for conventional cellulose acetate membranes. In all cases values of b are less after regeneration than before.

TABLE 2

COMPARISON OF HYPERFILTRATION OF COALINGA WATER BY MEMBRANES FORMED AND OPERATED AT DIFFERENT CIRCULATION VELOCITIES. DATA TAKEN AT END OF INITIAL 317 HOUR RUN AND AT END OF POST-REGENERATION SEGMENT OF RUN (115 HOURS) (950 PSIG, 25°C)

<u>Support*</u>	<u>Velocity (ft/sec)</u>	<u>Flux (gfd)</u>	<u>R_{obs} (%)</u>		
			<u>Cl⁻</u>	<u>Mg(II) + Ca(II)</u>	<u>Total Cation</u>
Before regeneration, t = 317 hours					
0.45 μ AP	35	60	71	97	86
	20	48	77	98	90
0.22 μ MP	35	35	92	>99	97
	20	31	92	>99	97
6C Carbon	24	16	70	95	85
After regeneration, t = 115 hours					
0.45 μ AP	35	63	76	98	89
	20	59	67	96	85
0.22 μ MP	35	49	87	>99	95
	20	44	82	99	93
6C Carbon	24	17	74	92	84

*AP = Acropor; MP = Millipore.

TABLE 3
FLUX DECLINE PARAMETERS BEFORE AND AFTER MEMBRANE
REGENERATION FOR THE HYPERFILTRATION OF COALINGA WATER
BY DYNAMIC DUAL-LAYER MEMBRANES (950 PSIG, 25°C).
 J_1 IS FIRST FLUX IN FIG. 10

Support	Circulation Velocity (ft/sec)	Initial Run		After Regeneration	
		J_1 (gfd)	b	J_1 (gfd)	b
0.45 μ Acropor AN	35	83	0.059	69	0.013
0.22 μ Millipore	35	55	0.065	56	0.024
0.45 μ Acropor AN	20	68	0.064	73	0.037
0.22 μ Millipore	20	46	0.056	54	0.040
6C Carbon (ground)	24	37	0.145	21	0.037

Treatment of Waste Streams

Hyperfiltration, both with conventional and dynamic membranes, is also promising for treatment of waste solutions. In many of these problems, a high degree of salt removal is not necessary. The advantages of high flux and the availability of membranes able to operate in a variety of chemical environments may be favorable to the dynamic class relative to conventional membranes.

With some waste streams, the ability of many dynamic membranes to operate at temperatures considerably above 25° may be advantageous, particularly if the product water can be immediately recycled. Present commercial cellulose acetate and polyamide membranes are limited in this regard. Neutral organic solutes frequently are contaminants, and these are filtered to a considerable extent by dynamic membranes[33,34], the rejection being largely dependent on molecular size. Results of considerable promise have been obtained in preliminary tests with sulfite[14] and kraft[35] pulp mill wastes; municipal sewage[15,20]; and textile dyeing wastes [16].

Two examples will be cited here, both taken from a series of tests of a prototype carbon tube module, supplied to us by Union Carbide Corp. The first was with a 50:50 cotton-polyester dye waste, used in other experiments reported elsewhere[16]. The solution contained* about 4000 ppm total dissolved solids, 600 ppm total carbon, 1600 Pt-Co color units, and 2400 ppm chloride, with pH about 12. It was neutralized with HCl before introduction into the loop. Results are summarized in Table 4. The experiment was

*Measured at time of run. Somewhat different from values in Ref. 16.

TABLE 4
HYPERFILTRATION OF 50:50 COTTON-POLYESTER DYE WASTE BY
Zr(IV)-PAA MEMBRANES ON UNION CARBIDE PROTOMODULE
(950 PSIG, 63°C, 12.4 FT/SEC, pH 6.8)

Time (hr)	Flux (gfd)	R_{obs} (% carbon)	R_{obs} (% color)	R_{obs} (% Cl^-)
0.67	76	-	-	-
1.0	72	98	99	84
2.0	59	99	99	87

carried out at a temperature near that of the dyeing process, the objective being to test the possibility of recycle of the hot product water in order to conserve energy. No dyeing tests were carried out with the product of this experiment. In another, however, producing a comparable water, the effluent was reused successfully, and it was further found possible to dye cloth with the concentrated brine [36].

Fig. 11 summarizes another test, on the caustic extract generated in washing kraft pulp between bleaching steps. The solution was neutralized with acidic kraft bleaching waste before use. Temperature of operation was approximately that of the bleaching process, and the feed was concentrated by discarding product. The effects of two regenerations are indicated. In the first, a 1 M NaOH solution, followed by 1 M HNO_3 , was circulated. Both hydrous Zr(IV) oxide and polyacrylate layers were then again formed on the support. The second was by a $NaHCO_3$ - Na_2CO_3 wash, and it was not necessary to re-form the membrane afterwards. As with the experiment of Fig. 10, flux decline was less rapid after regeneration.

CROSS-FLOW FILTRATION

Placing "reverse osmosis" in the category of filtration processes suggests that the use of a flow past the membrane surface might be useful. Circulation is necessary in salt filtration, where rejection is never complete, to combat concentration polarization, and it also inhibits fouling[37,38]. One might expect by analogy that a cross flow in filtration of particulates and colloids would tend to keep the filter cake thin and help maintain flux[39]. The idea has been incorporated in commercial equipment for some time[40], and has been embodied abroad in a tubular configuration[41], similar to our arrangement. Recently, cross flow has been used in "membrane ultrafiltration,"[42] which utilizes an asymmetric preformed detachable membrane.

	REJECTION R_{obs} (%)	CONCENTRATE	PRODUCT
COLOR (Pt-Co Units)	99.9	9000 - 45,000	5 - 35
TOTAL CARBON (ppm)	94 - 97	775 - 3200	25 - 100
CHLORIDE (ppm)	BELOW	1000 - 5000	150 - 1000

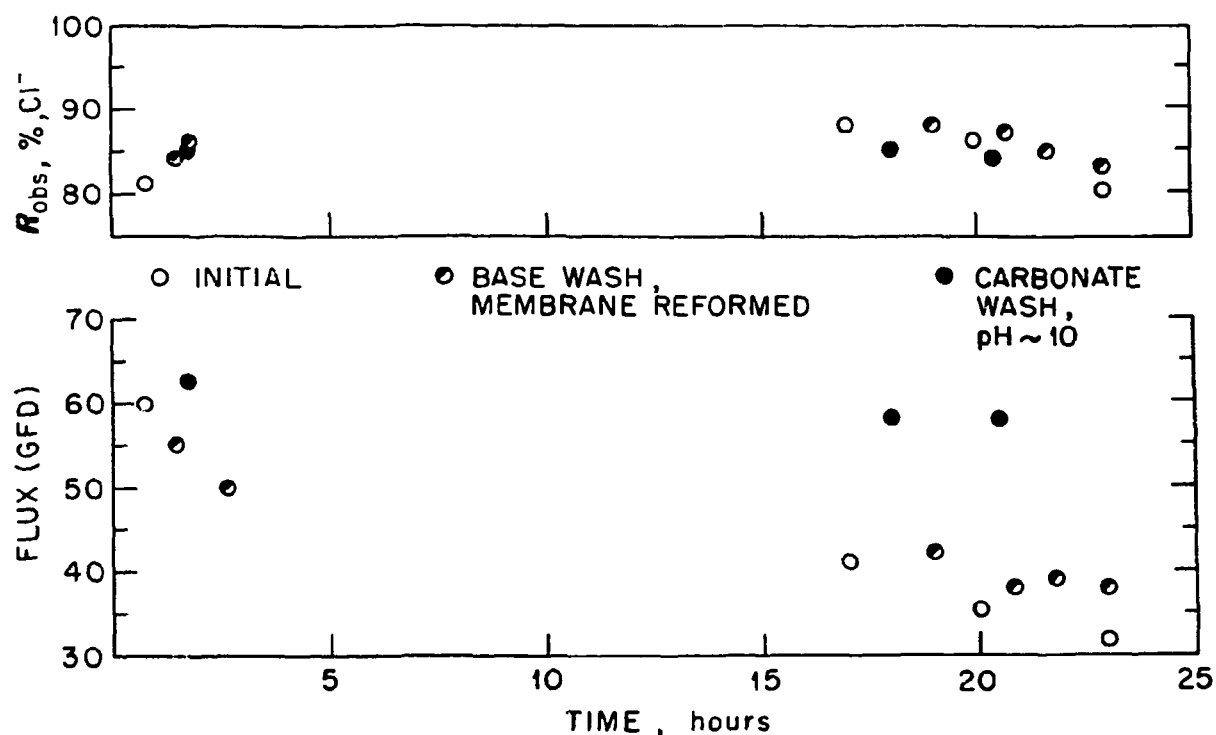


Fig. 11 - Hyperfiltration of Kraft Pulping Wastes with Zr(IV)-PAA Membrane Dynamically Formed in Prototype Module. Feed, caustic extract, acid bleach added to pH 7-7.5. Support, 6C carbon tubes, Union Carbide (950 psig, 12.4 ft/sec circ. vel., 58-67°C)

Most of the effort in this laboratory toward developing cross-flow filtration has been directed toward treatment of municipal sewage, specifically of the effluent from primary treatment [43]. Fig. 12 indicates that use of cross flow indeed slows flux decline. The characteristics of the product indicated in the legend are typical, except that turbidity in this experiment was unusually high; normally it is one JTU or less, about equivalent to local tap water.

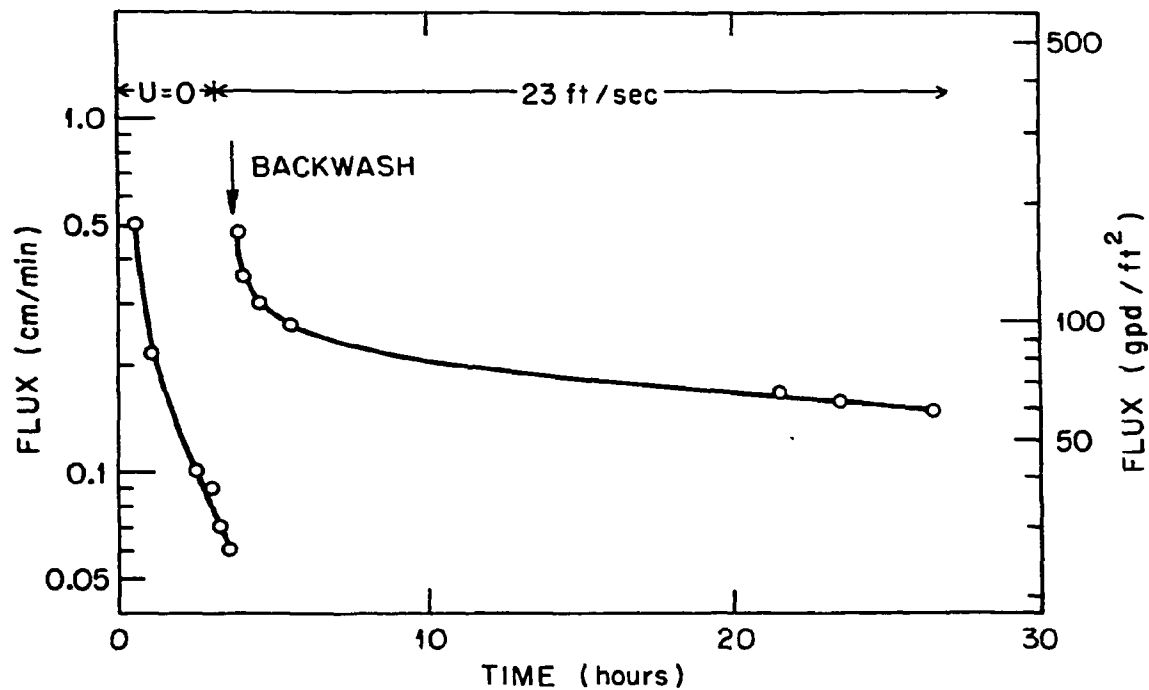


Fig. 12 - Filtration of Sewage With and Without Cross-Flow.
 U is the linear velocity over the membrane surface.
 (15 psi, 325 mesh S.S. screen, PSE with Fe(III) and carbon at 95% water recovery, pH 5.9-6.4)

	Average Removals with Cross-Flow		
	Org C	Phosphate	Turbidity
Product Removal	6 ppm 85%	0.3 ppm 99.3%	3.5 JTU 97.5%

Cross flow alone is, however, not adequate to maintain good performance. Apparently material in sewage which would tend to form dynamic salt-filtering membranes[15] must be hindered from doing so. Since in the first few minutes product is usually cloudy, some sort of dynamic filter cake 'membrane' is necessary for the process, but its characteristics must be controlled. This is accomplished by addition of a hydrolyzable salt, usually of Fe(III) or Al(III), and sometimes powdered carbon. Fig. 13 shows that increasing Fe(III) concentration increases both efficiency of contaminant removal and flux.

The process, as applied to primary sewage effluent, is thus a physical-chemical treatment, with cross-flow filtration used to separate purified water. The product of the treatment is in many respects the equal of that from conventional activated sludge secondary treatment combined with some procedures classed as

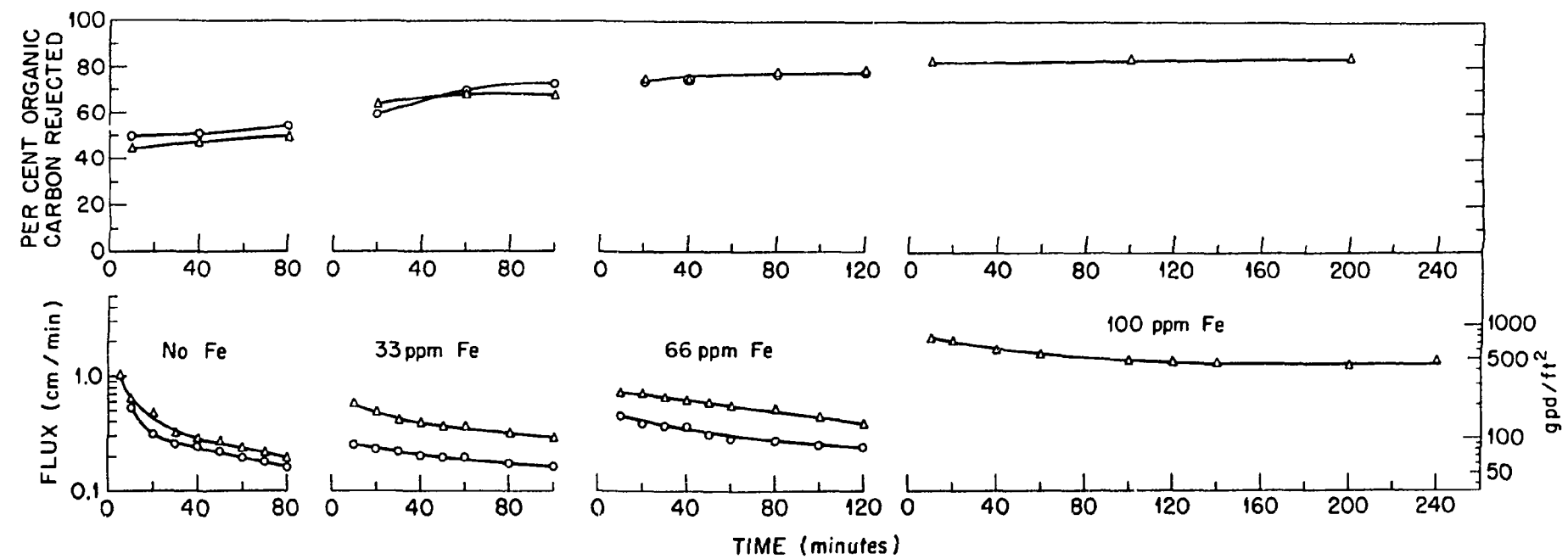


Fig. 13 - Effect of Fe(III) Concentration on Cross-Flow Filtration of Effluent From Primary Treatment of Municipal Sewage. Membrane supports were fire hose jackets: feed inside, o; outside, Δ. (50 psi; 15 ft/sec)

tertiary. A preliminary economic analysis projects that costs will be reasonable, in view of the quality of the product[44].

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R. E. Minturn has directed recent work in hyperfiltration. K. A. Kraus and H. A. Mahlman were in charge of the cross-flow filtration of sewage program; K. A. Kraus and J. A. Dahlheimer were in charge of sewage hyperfiltration[20]. C. G. Westmoreland, W. G. Sisson, L. L. Fairchild, J. Curny, J. W. Myers, and J. R. Love contributed technical assistance. I am also grateful for the advice and support of H. E. Podall, Office of Saline Water.

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3. Dynamic Membranes

Summary

Toward the end of the previous biennium, the dynamically formed dual-layer hydrous Zr(IV) oxide-polyacrylate [Zr(IV)-PAA] membrane was developed. For reasons outlined in Sections 2 and 3.1.1, it appears to be the most promising of the dynamic class with respect to desalination of brackish waters. The greatest effort during the present biennium has been toward improving that membrane and toward testing its performance with a variety of solutions, simulated brackish waters, and industrial effluents.

Section 3.1 is concerned exclusively with the Zr(IV)-PAA membrane. The first subsection, 3.1.1, is a reprint of a paper¹¹ which chronicles the development and many of the properties of the Zr(IV)-PAA membrane. The next subsection, 3.1.2, examines in more detail, and with some overlap, those factors that affect the properties of a membrane during its formation, while those factors that affect membrane performance, once formed, are discussed in 3.1.3.

The Zr(IV)-PAA membrane has properties of the weak polyelectrolyte, polyacrylic acid. The improvement in properties effected by the hydrous oxide sublayer over single-layer PAA membranes¹⁹ suggests that membranes dynamically formed from a variety of other polyelectrolytes, such as for example, strong acids, or basic polyamines with anion-exchange capacities, or from polyelectrolytes with functional groups of both charge signs, might also be better with a sublayer. Many were tried with and without sublayers. The results are reported in Section 3.2.

In agreement with earlier results, poly(maleic acid), in spite of its higher charge density, formed poorer membranes than PAA (Section 3.2.3.1), and the poor performance of single-layer PAA membranes, even when formed from low pH solutions, again emphasized the importance of the hydrous oxide sublayer (Section 3.2.3.2). However, not all hydrous oxides are suitable for sublayers, at least with procedures tested so far, as can be seen from Section 3.2.3.12, which treats experiments with hydrous Al(III) oxide.

Lengthy attempts to form dynamic membranes having negative rejection, i.e., enhancement of the salt concentration in the product, using block copolymers with functional groups of both charge signs, Section 3.2.2, again

met with failure, although the pH dependence of the rejection of salt with some of the membranes was quite interesting.

Section 3.3 outlines tests of possible applications of dynamic membranes. Of primary concern in OSW-supported work is their applicability to the desalination of brackish waters. Section 3.3.1 treats several simulated brackish waters, looking to the effect of membrane composition and formation parameters, of operating conditions while treating the simulated brackish water, and of pretreating the water before hyperfiltration. Considerable effort was devoted to Coalinga water and to Roswell water, lesser effort to Colorado River water, Dalpra farm water, Webster water, Wellton-Mohawk canal water, and one or two others. See Table 3.68, Section 3.3.1, for molar compositions of these brackish waters.

Although the results of Section 3.3.1.1.1, which describe a long-term run with Coalinga water, indicate that with some brackish waters, the Zr(IV)-PAA membrane holds up very well, it is apparent from other work here reported that divalent cations continue to degrade the performance of these dynamic cation-exchange membranes. Experiments with pretreated (either by cross-flow filtration after addition of chemicals or by use of compositions simulating such softening) waters suggest that, in general, optimum performance will require some pretreatment. This was also indicated by work on engineering development of dynamic membranes, leading to a pilot plant for the OSW Roswell, New Mexico, test center. The plant was designed and constructed by a Water Research Program group under D. G. Thomas,⁷ with support from the OSW Membrane Division.

Dynamic membrane hyperfiltration appears to be very promising in the treatment of many industrial and municipal waste effluents. In addition to the tests reported herein, Section 3.3.3, we have also studied paper and pulping wastes,^{20,21} laundry wastes,²² textile dyeing effluent wastes,^{23,24} and several food processing wastes for which the results are, as yet, unpublished. These studies were carried out for the most part under the ORNL-National Science Foundation-Environmental Program, with some help from the Atomic Energy Commission.

Dynamic formation of hydrous Zr(IV) oxide-polyacrylate membranes involves many variables--type of porous support, concentration of additives and of other solutes during formation, pH during formation, pressure, circulation velocity, are by no means a complete list. Our progress toward

identifying factors giving improved membrane performance has been good. With 0.45- μ Acropor supports, the early membranes reported in the previous biennial¹⁵ rejected 80 to 85% of salt from 0.05 M NaCl solutions, for example. Our procedures now rather consistently give membranes of 90 to 95% rejection of 0.05 M NaCl and fluxes upwards of 100 gfd on this support. Rejection with several supports potentially suitable for practical systems are good, though fluxes are frequently not as high.

We summarized the currently favored membrane formation procedure in the paper reprinted in Section 3.1.1, but we have reservations concerning its use in all situations. In spite of vast efforts with cellulose acetate, modifications of casting procedures are still being investigated elsewhere, and, to our knowledge, only our program has, until recently, given serious attention to Zr(IV)-PAA membranes. We can by no means guarantee, therefore, that the procedure outlined is optimum. This is particularly true with potentially practical porous supports of various ceramics and carbons. Most optimization has involved Acropor and Millipore wraps, and there are indications that somewhat different conditions are better for different supports. The same is likely true for application to different feeds.

If the membranes are to be formed in the test loop, the loop must be cleaned thoroughly before the formation process is begun. We generally rinse the system thoroughly with water, then circulate 1 M NaOH at about 400 psig for one hour. Occasionally, when the system has been used with a waste that fouls especially badly, e.g. cottage cheese whey, we raise the temperature of the NaOH to about 60°C. We then rinse out the NaOH, and wash for one hour with 1 M HNO₃ (also occasionally used hot).

After the acid wash, we rinse the system thoroughly with water, then for thirty minutes with distilled water. During this last rinse, we bleed all lines that might have accumulated corrosion products or other contaminants from previous runs. We then proceed with the membrane formation as described in Section 3.1.1.

Several aspects of this procedure have implication for the design and employment of equipment for these membranes. Systems should be constructed so that they may be readily flushed.

Volumes not reached by the circulating solutions should be avoided, or provision made for flushing, and materials of construction should allow

use of appropriate solutions for cleaning, particularly in pollution control applications with highly fouling feeds. With larger membrane areas, fast pumping rates are necessary in initial stages of membrane formation, since permeabilities of the bare supports are high. Further, fast circulation during membrane formation, particularly of the Zr(IV) sublayer, appears desirable, though there is some question regarding optimum velocities with potentially practical supports. These factors may signify that a small auxiliary system for membrane formation, or at least valving arrangements to allow membrane formation on a fraction of the total area of the system, may be advantageous.

Water used in membrane formation needs to be of high quality. Sulfate contamination is particularly deleterious during the formation of the hydrous oxide layer, and perhaps during the low pH exposure to PAA. Divalent cations are particularly bad during the PAA step. A tank to save product water, which likely will need further demineralization, may be needed for rinse and formation procedures. Alternatively, a small still can be incorporated. The experience with the Roswell pilot plant,⁷ while disappointing in the extent of the tests which were possible before the shutdown of the pilot plant, leads us to be optimistic concerning the probability of success in implementing these procedures in the field.

The results presented here were obtained over two and one half years during which our procedures have been undergoing continual evolution. Many of the differences in reported properties of membranes stem from this fact. We have chosen not to omit earlier results, however, because most of them are valid with respect to changes in performance with variables under investigation; and, in some cases, it is not yet clear whether earlier or more recent results will be confirmed by further work.

In most cases, predictions from theory are to some extent possible--increasing the circulation velocity reduces concentration polarization, increase of pH will increase polyacrylate ion-exchange capacity and therefore rejection, increasing salt concentration will usually decrease rejection by any ion-exchange membrane, salts having divalent coions will be more rejected at a given normality than those having monovalent coions, rejection should increase with pressure until a limiting value is reached, etc. Finding the extent

to which observation may be predicted by theory is always one of the goals of experimental work, and hyperfiltration is no exception. Much of the performance of a Zr(IV)-PAA membrane fits expectation, at least qualitatively, but the many puzzling aspects remain. Perhaps the one of greatest practical import yet unresolved is the relationship between properties of porous supports and performance of membranes formed on them. Factors responsible for different characteristics of membranes formed under different conditions and operated in different environments are also obscure.

One experimental condition deserves special mention. We have used circulation velocities in much of this work clearly uneconomic for routine operation. The reason is that we wished to approximate the performance of those membranes undistorted by concentration polarization without taking time to measure rejection as a function of velocity, necessary for obtaining R_c from R_{obs} by extrapolation. Measurements with practical supports indicate that operation at reasonable velocities will give acceptable results, though, as one would expect, fluxes usually decline more slowly at high circulation velocities. We suspect that, as with conventional membrane systems, an important factor in control of flux decline will be appropriate feed pre-treatment. With highly fouling polluted feeds, membrane regeneration by washing with appropriate solutions or by backwashing procedures, followed by membrane re-formation, needs to be developed. Dynamic membranes have, of course, inherent potential advantages in meeting these situations.

3.1 HYDROUS Zr(IV) OXIDE - POLYACRYLATE MEMBRANES

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3.1.1 HYPERFILTRATION XXI. DYNAMICALLY FORMED HYDROUS Zr(IV) OXIDE-POLYACRYLATE MEMBRANES*

J. S. Johnson, Jr., R. E. Minturn, and P. H. Wadia**

INTRODUCTION

Some years ago in this laboratory in the course of desalination research, organic and inorganic polyelectrolytes added to pressurized salt solutions were found to form salt-filtering layers when the solutions were circulated past porous supports^{1,2}. These membranes had hyperfiltration (reverse osmosis) properties qualitatively expected of thin ion-exchange membranes³—high production rates and moderate salt rejection, which decreased with increasing feed concentration.

To distinguish from conventional detachable films, prepared by casting or other procedures, we designated the class "dynamically formed" or "dynamic." A wide assortment of additives have been shown to form membranes in this way: hydrous oxides^{1,4,5}, synthetic organic polyelectrolytes^{2,6}; natural polyelectrolytes, including humic acid and clays⁶; dispersions of low-cross-linked ion-exchange beads⁷; and material in waste streams, such as sewage⁸ or pulp mill wastes⁹. High fluxes, frequently an order of magnitude higher than those through cellulose acetate, aroused interest in the class. For many water treatment problems, the degree of filtration appeared to be adequate.

For practical desalination, most dynamic membranes were less than satisfactory in one respect or another. In some cases salt rejections were not high enough to yield acceptable products from feeds at the total salinity level of most natural brackish waters. In others, the pH range of adequate filtration did not match those of waters to be treated. Most frequently, the presence of polyvalent counterions in feeds deleteriously affected performance to an unacceptable extent. Since most natural waters contain both sulfate and calcium or magnesium, this limitation was severe for both anion and cation exchange membranes.

One polyanion, polyacrylic acid (PAA)¹⁰, formed membranes which, though not immune to effects of divalent cations, had higher rejections in the neutral pH range than most dynamic membranes. However, with the porous supports used, fluxes were low, and there was considerable difficulty in reproducing properties when attempts were made to form membranes on supports which might have been expected to allow higher fluxes.

* Dedicated to Professor J. Th. G. Overbeek on the occasion of the 25th anniversary of his appointment as a Professor of Physical Chemistry.

** ORNL summer employee 1970, 1971. Present address: Department of Chemical Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts.

About two years ago, we found that if a hydrous oxide membrane, previously formed dynamically, were exposed to an acidic solution containing polyacrylic acid, a layer of polyacrylic acid appeared to become attached to the hydrous oxide. On addition of base, the carboxyls were converted to the salt form without displacement of the organic polyelectrolyte from the hydrous oxide. Increase in rejection paralleled the increase in cation-exchange capacity expected from neutralization of the acid, and a polyacrylate membrane superior in many respects to the single layers prepared earlier¹⁰ was formed. This paper reports properties of this membrane.

EXPERIMENTAL

A. Equipment

A typical hyperfiltration loop is shown photographically and schematically in Fig. 1. Feed solution is drawn from feed tank by the Milroyal type C triplex pump (5 g.p.m. at 1500 p.s.i.g. capability) and forced under pressure into the circulation pump, a centrifugal pump of Westinghouse design¹¹ (100-A) which is rated at 100 g.p.m. at 100 p.s.i.g. head. This pump circulates the feed solution through the loop and past the membrane supports, which are placed in test sections at A and A' (only one test section is shown in the photograph). Typical test sections have been described previously⁷; they are designed to direct the feed solution through the annular region between a tubular porous support, upon which the membrane is formed, and the walls of a cylindrical pressure jacket. The jackets may be constructed of lucite, which allows one to observe the support surface while the membrane is being formed or used, or, if pressures higher than 1000 p.s.i.g. or temperatures much above ambient are desired, the jacket may be of stainless steel or other corrosion-resistant materials. Flow velocities past the membrane surfaces, typically 10–35 ft. s⁻¹, are monitored by meters, the temperature of the feed is controlled by the tube-in-tube heat exchanger, and the pressure is regulated by a pneumatically controlled valve in the let-down line which returns the feed to the feed tank at atmospheric pressure. The product which permeates the membranes is monitored as to flux and composition, and is either returned to the feed container, to maintain constant feed composition, or discarded if the feed solution is to be concentrated during the course of the run. All materials used in the loop are corrosion-resistant to minimize interference of corrosion products with the formation of the membranes. The loop is designed to eliminate stagnant side volumes in which materials might collect and contaminate subsequent experiments.

B. Porous supports

Dynamic membranes may be formed on several different porous support materials. In a configuration much used in the work to be reported here, Acropor AN and Millipore films* are wrapped around 5/8 in. porous stainless tubes (pore size ~ 5 μ m). We have also successfully formed dynamic membranes on porous carbon tubes, e.g., Union Carbide Corporation's 563-6C (0.6 cm i.d., 1.025 cm o.d., undetermined pore

* Acropor AN is a copolymer of polyvinyl chloride and polyacrylonitrile on a carbon substrate and is made by the Gelman Instrument Company, Ann Arbor, Michigan; Millipore films are made from modified esters of cellulose by Millipore Filter Company, Bedford, Massachusetts. Both are available in a wide range of nominal pore sizes; those we have used range from 0.025 to 1.2 μ m.

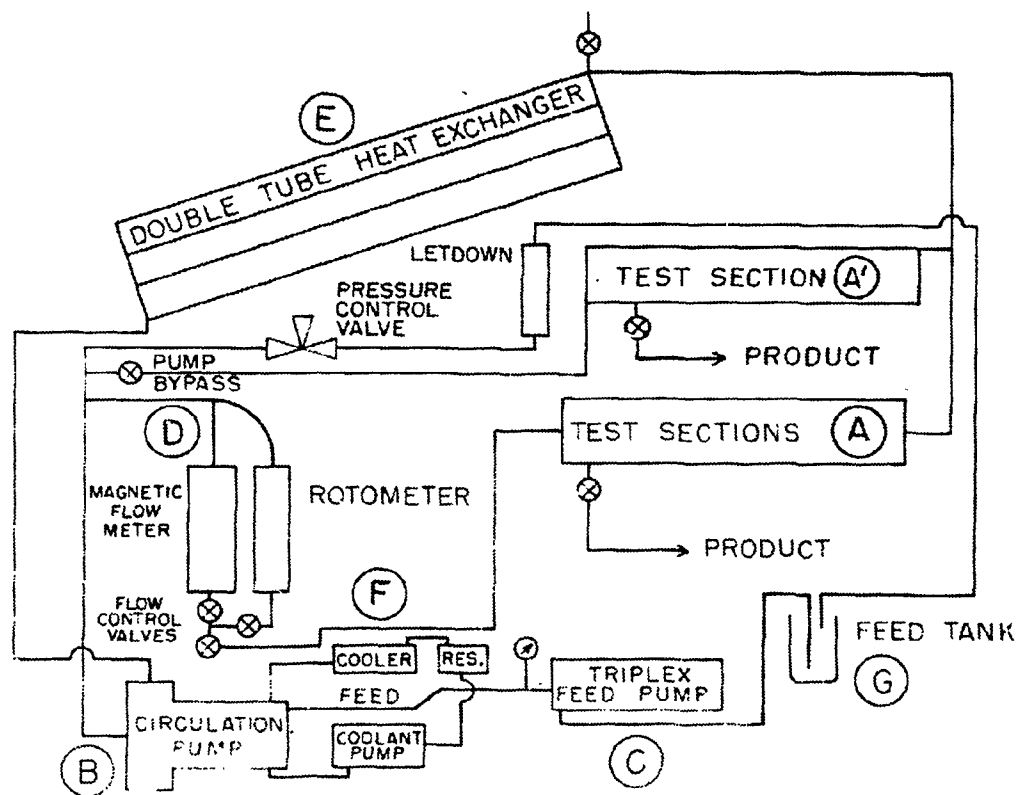
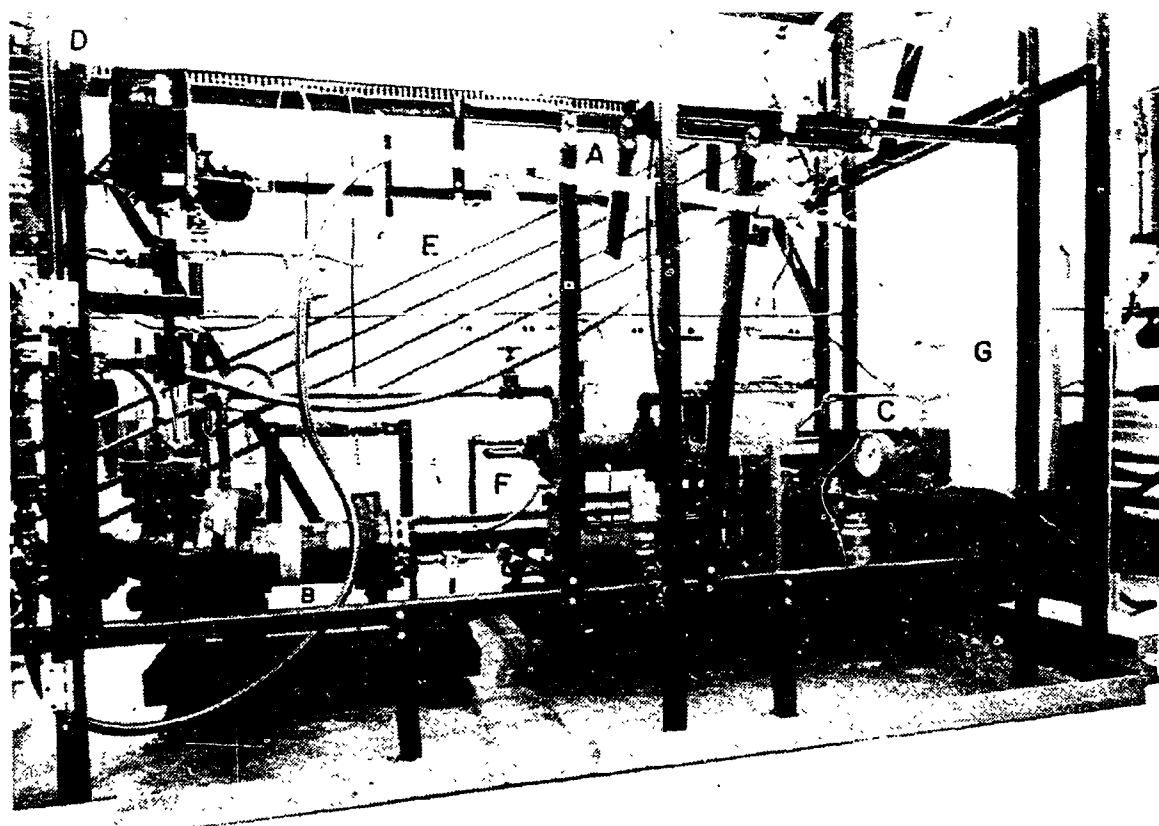


Fig. 1. Hyperfiltration loop.

size), and porous ceramic tubes such as the Sela Ceramic filter element (Sela Flotronics Corporation, Spring House, Pennsylvania). Because of cost, both the carbon and ceramic tubes appear at present to be more promising for practical desalination than do tubes wrapped with the porous films. However, performance of mem-

branes on carbon or ceramic tubes is usually not as good, particularly with respect to flux.

A few experiments were carried out with porous supports mounted in cells¹², which exposed about 1.5 cm² to the pressurized feed.

C. Materials

The membranes were formed in carefully cleaned equipment, to eliminate the interference of contaminants. Even small amounts of impurities appear to affect the hydrous oxide layer during its formation. Between runs, cleaning usually involved a 1 M NaOH wash, followed by 1 M HNO₃, and then water.

Hydrous Zr(IV) oxide was usually used to form the first layer of the dual-layer membranes. This material was taken from a 0.25 M stock solution made up from ZrOCl₂ · 8H₂O (Fisher Scientific Co.). The stock solution had been refluxed at atmospheric pressure for 24 h, to form the hydrous oxide, before being used. Recently we obtained data indicating that membranes made from unboiled solutions of ZrOCl₂ may be as good as those formed from the refluxed material.

TABLE 1

MOLECULAR WEIGHTS OF POLYCARBOXYLIC ACIDS

Source and code no.	Type	Supplier's nominal M. W.	Inherent ^a viscosity
Rohm and Haas Tamol 850	Polymethacrylic	~ 5,000	0.33
Rohm and Haas Acrysol A-1	Polyacrylic	< 50,000	1.03
Borden	Polyacrylic	50,000	2.41
Rohm and Haas Acrysol A-3	Polyacrylic	150,000	2.34
Rohm and Haas Acrysol A-5	Polyacrylic	< 300,000	3.33
Nalco A-1 ^b	Polycarboxylic; high linear charge density	6-10 million	33.

^a Inherent viscosity = $\ln [\text{relative viscosity}/\text{concentration}]$, where the relative viscosity is the time of flow of a dilute solution (0.5 g 100 cm⁻³) of the polymer through the viscometer divided by the time of flow of the solvent (0.1 M NaCl at pH 8.5).

^b We thank Reed S. Robertson of Nalco Chemical Company for supplying this additive.

The several different polycarboxylates we have used are listed in Table 1. We did not consider it worthwhile to carry out the extensive removal of water and other contaminants necessary for an accurate determination of molecular weights by measurements of viscosity in organic solvents. For a crude relative index, however, viscosities of aqueous solutions of the sodium salt in supporting electrolyte were measured. On the basis of these values (Table 1), the Borden material appears a little out of place relative to those from Rohm and Haas.

D. Analytical procedures

Chloride concentrations were determined by the use of a Buchler-Cotlove chloridometer; Mg(II) + Ca(II) concentrations were determined by titration with EDTA at pH 10 using eriochrome black T as indicator; the concentration of total cations was determined by exchanging the cations for hydrogen ions on an ion-exchange resin (Dowex 50X12) and titrating the hydrogen ions against NaOH using a Sargent Model D recording titrator. Routine monitoring of the rejection of electrolytes during a run was accomplished by measuring the conductivity of feed and product. Analyses of the zirconium concentration in dynamic membranes were done by W. R. Laing of the ORNL Analytical Chemistry Division using a spectrophotometric method utilizing arsenazo III as the chromogenic agent.

RESULTS

In discussing the hyperfiltration properties of dynamic dual-layer membranes, we shall first consider the effect of variables in membrane formation on hyperfiltration properties, and then the effect of changes in conditions during operation.

A. Factors that affect membrane formation

1. *Membrane formation.* We stated in the introduction that if a hydrous oxide layer was exposed to an acidic solution containing PAA, a dual-layer membrane could be formed. The sequence of measurements in Table 2 illustrates this point. After the hydrous Zr(IV) oxide membrane was formed, the solution containing the colloidal oxide was replaced by a NaCl solution of pH ~ 6 . The rejection* dropped as a consequence of the decrease in anion-exchange capacity caused by the decrease in acidity^{4,15}. The introduction of polyacrylic acid, partially neutralized to the salt form, caused a decrease in salt rejection, but little change in flux. However, the addition of HCl to an acidic pH (below pH ~ 4 is usually required) caused a substantial increase in

TABLE 2

FORMATION OF HYDROUS Zr(VI) OXIDE-POLYACRYLATE MEMBRANE
(0.05 M NaCl, 1000 p.s.i.g. 35 ft s⁻¹, 0.45 μ m Acropor on tube)

Additive	pH	R_{obs} %	Flux (GFD) ^a
0.001 M hydrous Zr(IV) oxide	3.1	62	630
None	6.0	32	690
20 p.p.m. PAA	5.6	23	700
20 p.p.m. PAA	2.7	53	370
20 p.p.m. PAA	5.6	82	210

^a GFD denotes gallons (U.S.) per square foot per day. 354 GFD is equivalent to 1 cm min⁻¹.

* The rejection, R , of a component is defined by: $R \equiv 1 - (c_w/c_x)$, where c_w is the concentration in the product and c_x is that at the feed-membrane interface. Because of concentration polarization^{3,13,14}, c_x is not equal to c_t , the concentration in the turbulent core of the circulating fluid. In practice, therefore, an "observed rejection," $R_{\text{obs}} \equiv 1 - (c_w/c_t)$, is calculated. R may be determined from a series of R_{obs} values taken at different circulation velocities by an extrapolation to infinite velocity¹⁴. Unless otherwise specified, rejection in this paper refers to R_{obs} .

rejection and decrease in flux. The PAA apparently had become attached in some way to the hydrous oxide layer, and it was not displaced upon subsequent return to the original pH 5.6, through the addition of NaOH. Rejection increased during this addition, presumably because of the increase in ion-exchange capacity upon neutralization of the polyelectrolyte.

The rejection properties are fundamentally those of the polyacrylate layer, as the higher rejections at pH ~ 6 after the acid cycle than those of the simple hydrous Zr(IV) oxide membrane attest. The rejection of salts of ions of different valence is confirmation. In a series of measurements with 0.05 normal salt concentrations, the rejection of NaCl was 82%; of Na₂SO₄, for which the divalent ion is a co-ion to carboxylates, 98%; and of MgCl₂, 64%. The order is that projected for a cation-exchange membrane.

Variations in formation procedure are of interest, though the resulting membranes may have somewhat inferior properties. Additives can be introduced in a single step, if in the premixed hydrous oxide-PAA additive the ratio of equivalents of polyacrylate to moles of Zr(IV) is high, *e.g.*, 10. However, good rejections are attained only if a cycle through acidic pH values is carried out. The only procedure we have found that avoids an acid cycle is to introduce the polyacrylate in a neutral MgCl₂ solution.

There is considerable latitude in the conditions that will result in membranes of fairly good performance, and much of our effort has been devoted to finding the best combination. The following procedure seems most favorable at this time.

A solution 0.05 M in NaCl and 10^{-4} M in Zr(IV) is adjusted to pH ~ 4 with HCl and circulated through the loop until thoroughly mixed. The porous supports are then inserted into the test sections and pressurization and circulation are begun. Initially, the pressure which the pump is able to generate increases only slowly because of the limited flow capacity of the pump and the high permeability of the porous supports. However, as the hydrous oxide is deposited on the supports, the permeability decreases and the pressure increases. Once full pressure (typically 900–1000 p.s.i.g.) is achieved, the rejection is monitored until it is in the range 30–50%, which generally takes from 1 to 3 h. At that time, with the system still under pressure, excess Zr(IV) is rinsed from the loop with distilled water adjusted to pH 4 with HCl. A solution containing 50 p.p.m. PAA and 0.05 M in NaCl, adjusted to pH ~ 2 , is then circulated past the membranes for about 30 min. After this time, the pH is raised to about 3, maintained there for another 30 min and again raised a unit or so. This step-wise increase in pH is repeated until the solution is near neutral. During this process, the rejection of salt by the membrane increases and the flux decreases, as shown in Fig. 2. The excess PAA is then rinsed from the system with distilled water and the membrane is considered formed. Occasionally during the formation procedure, a membrane will show a maximum rejection at about pH 5, with a decreased rejection near neutrality. When this happens, it is usually possible to obtain good rejections by returning the solution, still containing the PAA, to pH 3 or lower, and once again incrementally increasing the pH to neutrality. Once formed, the membranes must not be allowed to dry. They can, however, be stored in water for extended periods although with some sacrifice in their effectiveness in rejecting salts.

The above procedure results in membranes with the most favorable fluxes and rejections, at least on Acropor and Millipore supports. We made five runs, involving a total of 15 different membranes, to test the reproducibility of membrane formation.

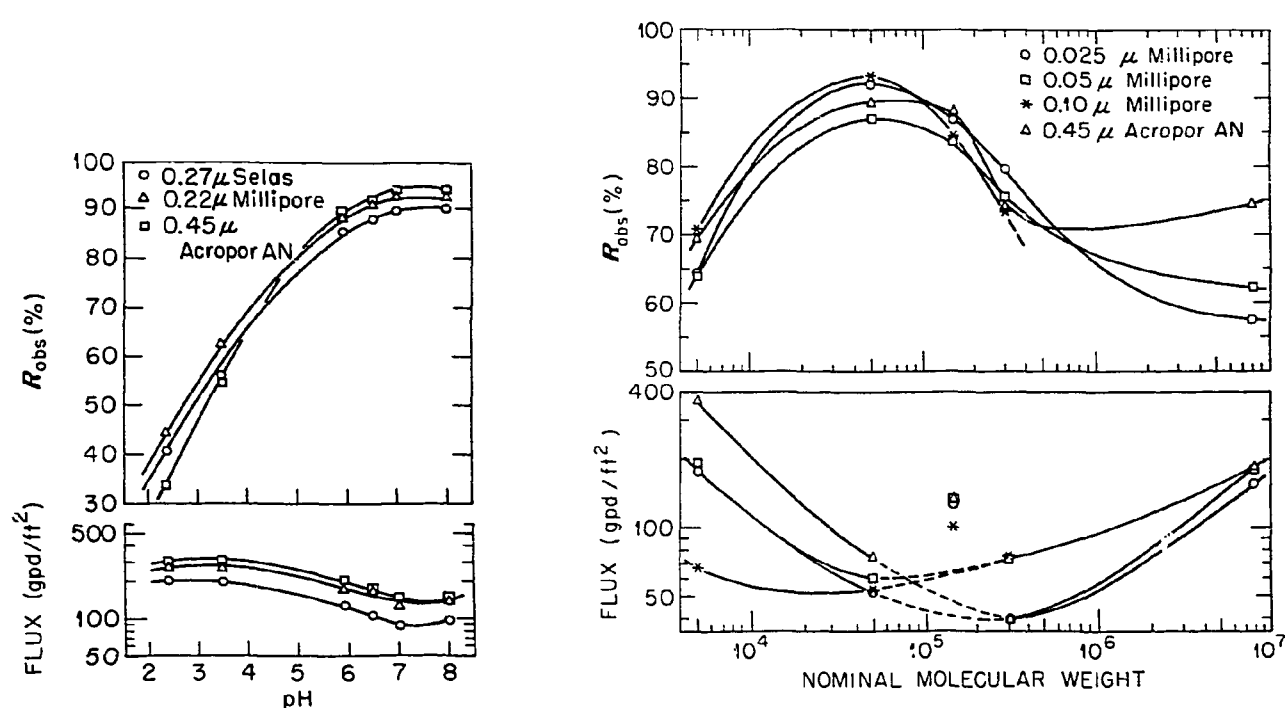


Fig. 2. Effect of increasing pH when hydrous Zr(IV) oxide membrane is exposed to 50 p.p.m. PAA. (0.05 M NaCl, 950 p.s.i.g., 35 ft. s⁻¹, 25°C, Acrysol A-3).

Fig. 3. Hyperfiltration of 0.05 M NaCl by dual-layer membranes with different molecular weight polycarboxylates after exposure to Coalinga water. (1000 p.s.i.g., pH ~ 7, 35 ft. s⁻¹).

The rejections of 0.05 M NaCl ranged between 90 and 95%, while the fluxes, at 950 p.s.i.g., were in the range between 98 and 185 gallons (U.S.) per day per square foot (GFD) in all cases except one, where it was 80 GFD.

The following sections illustrate the types of experiments which led us to the formation procedures outlined above.

2. *Molecular weight of the organic polyelectrolyte.* Figure 3 shows the effect of the molecular weight of the polycarboxylate (Table 1) on hyperfiltration of 0.05 M NaCl by dual-layer membranes formed on supports of several different pore sizes. Before the measurements summarized in Fig. 3 were made, the membranes had had a roughly similar history, including exposure to a solution with a typical natural brackish water composition. The data show that, for the porous supports used, there was a definite maximum in rejection for additives of the intermediate molecular weights, peaking in the region around 50,000–150,000. Fluxes were lower for intermediate weights except for the 150,000 molecular weight additive. For the membranes which gave the best rejections, there is not a large dependence on substrate pore size for either flux or rejection. The polyacrylate of nominal molecular weight 50,000 used in Fig. 3 was Acrysol A-1. Membranes of the Borden additive of similar weight (Table 1) had very similar properties.

3. *Pressure.* Table 3 compares properties of dual-layer membranes which were formed at several different pressures and then tested with 0.05 M NaCl at 950 p.s.i.g. Conditions of flow and temperature were the same for each, and measurements were made at the higher pressure within a few hours after membrane formation. Measurements were also made with 0.025 μ m, 0.05 μ m, and 0.22 μ m Millipore supports and the trend for each pore size was similar to those listed; *i.e.*, the higher the pressure of formation, the better the rejection and the lower the flux.

TABLE 3

THE EFFECT OF PRESSURE DURING MEMBRANE FORMATION ON THE HYPERFILTRATION OF 0.05 M NaCl

Zr(IV)-PAA Membranes on 0.45 μm Acropor (measured at 950 p.s.i.g., 35 ft. s^{-1} , and 25°C)

Formation pressure/p.s.i.g.	Flux/GFD	$R_{\text{obs}}/\%$
95	666	19
350	609	49
600	161	78
950	147	94

4. *Circulation velocity.* For a given porous support, flux through a newly formed hydrous oxide membrane will usually be higher the higher the circulation velocity during formation. It would appear that the membrane is thinner when formed at high velocity, and measurements of the amount of Zr(IV) in membranes supports this. For example, a hydrous oxide membrane formed at 35 ft. s^{-1} on 0.45 μm Acropor contained 126 $\mu\text{g cm}^{-2}$ of zirconium and rejected 62% of salt from a 0.05 M NaCl at a flux of 510 GFD. Another membrane, formed under the same conditions except that the circulation velocity was 14.5 ft. s^{-1} , contained 232 $\mu\text{g cm}^{-2}$ of zirconium, and rejection was 62% at 300 GFD (950 p.s.i.g., pH 3.8, 25°C).

Higher fluxes in the sublayer appear to result in higher fluxes in the dual-layer, although we observe exceptions to this, particularly with membranes on 0.025 μm Millipore. An example of the usual dependence of properties on formation velocity is given in Table 4.

TABLE 4

EFFECT OF CIRCULATION VELOCITY DURING HYDROUS OXIDE LAYER FORMATION ON HYPERFILTRATION PROPERTIES OF BOTH THE SINGLE AND DUAL-LAYER MEMBRANES

(0.05 M NaCl, 1000 p.s.i.g., 0.45 μm Acropor AN)

Hydrous oxide membrane				Zr(IV)-PAA membrane			
Velocity/ft s^{-1}	pH	Flux/GFD	$R_{\text{obs}}/\%$	Velocity/ft. s^{-1}	pH	Flux/GFD	$R_{\text{obs}}/\%$
48	4	1740	50	35	8	340	84
10	4	625	45	35	8	200	71

The circulation velocity during formation of the polyacrylate layer appears to have less effect. In an experiment in which the only difference in formation of two different dual-layer membranes was in the velocity at which the PAA layer was formed, that formed at 45 ft. s^{-1} had an observed rejection of 93% at 140 GFD; that formed at 12 ft. s^{-1} had an observed rejection of 91%, also at 140 GFD. The membranes were formed on 0.45 μm Acropor AN, and tested with 0.05 M NaCl at 1000 p.s.i.g., 35 ft. s^{-1} , and pH 8.2.

5. *Type of hydrous oxide.* In most of our work on dual-layer membranes, Zr(IV) oxide has been used to form the sublayer. However, other oxides may be used,

and, in fact, the initial observations were with hydrous Fe(III) oxide. Rejections as high as 90% with 0.05 M NaCl (55 GFD at 1000 p.s.i.g.) were obtained with Fe(III)-PAA membranes on 0.45 μm Acropor AN supports. Polyacrylate layers on this oxide have appeared to be less stable at high pH than those on Zr(IV), there being a sharp decline in rejection above pH 9.

Tests of Th(IV) and Bi(III) hydrous oxide sublayers were carried out with cells^{1,2}. The best rejection of 0.05 M NaCl was about 72% (17 GFD) with Th(IV) sublayers on 0.025 μm Millipore. For Bi(III), the sublayer was formed from perchlorate solutions, because of the insolubility of BiOCl. Best rejections of 0.05 M NaCl were less than 70%, with fluxes less than 70 GFD. With hydrous Sn(IV) oxide-polyacrylate membranes on 0.45 μm Acropor in tubular configuration, values of R_{obs} for 0.05 M NaCl at pH 7.1 were 80–90% with fluxes of 35–160 GFD.

It is possible that, by optimization, dual-layer membranes of properties as good or better than those on Zr(IV) oxide could be developed. We have concentrated on hydrous Zr(IV) oxide primarily because of the substantial body of information which exists concerning its ion-exchange properties¹⁵ and its properties as a single-layer membrane⁴.

B. Factors that affect membrane performance

We outline below some properties of this membrane system which have been established by hyperfiltration under various experimental conditions.

1. *Concentration polarization.* Observed rejections are lower than intrinsic rejections because of concentration polarization. Concentration polarization would

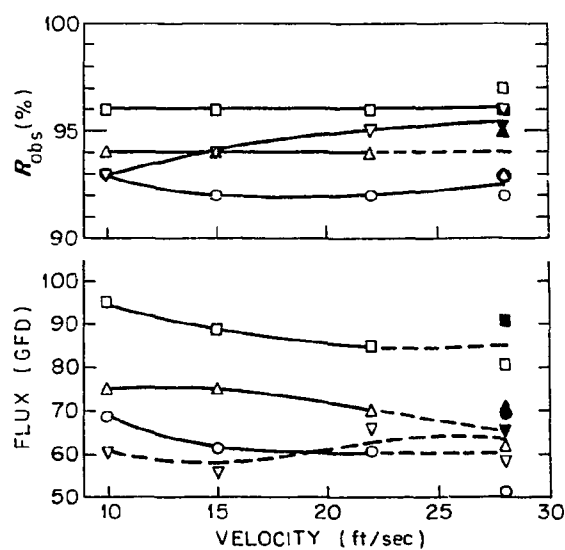


Fig. 4. Effect of velocity on hyperfiltration of NaCl solutions by dual-layer membrane on 0.22 μm Millipore support. (900 p.s.i.g., 50–55°C, pH ~ 7). Open symbols: initial value; solid symbols: final value following velocity excursion. ($\square$) 0.005, ($\triangle$) 0.01, (∇) 0.05, ($\circ$) 0.1 M.

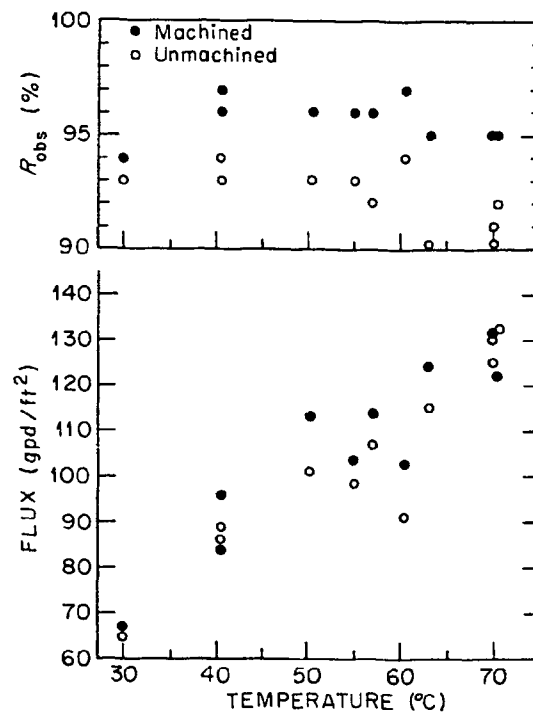


Fig. 5. Effect of temp. on hyperfiltration of 0.05 M NaCl by dual-layer membranes on 6C carbon tubes. (900 p.s.i.g., ~ 8 ft. s⁻¹, pH ~ 7).

increase with decreasing circulation velocities, but for most cases reported here, theory¹³ would indicate that the differences between R and R_{obs} should be small. Figure 4 summarizes measurements made for circulation velocities of 10–28 ft. s⁻¹. The decrease of R_{obs} with decreasing circulation velocity is seen to be small. At room temperature, since salt diffusion coefficients would be smaller, and at higher fluxes, the effect would be somewhat larger.

2. *Temperature.* For a given solution, circulation velocity, and pressure, the flux through a dynamic hyperfiltration membrane increases with the temperature of the solution. This dependence, which reflects the decrease in viscosity with increase in temperature, is demonstrated in Fig. 5. The porous supports in this case were a pair of carbon tubes, one of which had been surface ground to remove the extrusion skin. The membranes were formed on the outside surface of the tubes. Rejections are apparently not affected drastically by changes in temperature, at least in the range we have studied.

3. *Pressure.* Both flux and rejection increase as the pressure drop across the membrane is increased (Fig. 6). The arrows in the Figure show the chronological order in which the points were taken. Rejection theoretically increases with flux to some asymptotic value³, but it is not clear from Fig. 6 that the flux in this particular case is high enough at 900 p.s.i.g. to realize the maximum rejection of this membrane. Judging from other results we have obtained, we would expect little increase in rejection at pressures higher than those in the Figure.

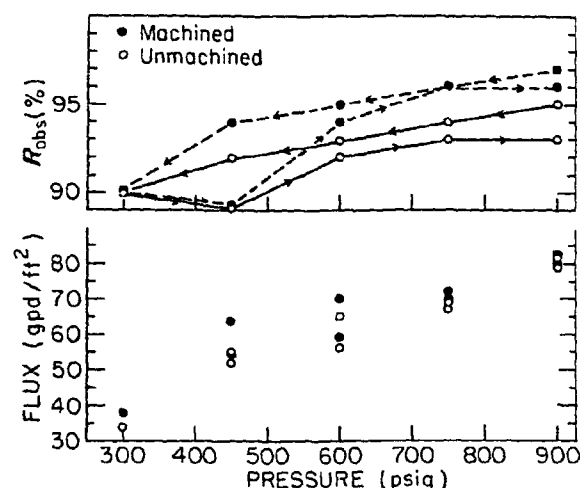


Fig. 6. Effect of pressure on hyperfiltration of 0.05 M NaCl by dual-layer membranes on 6C carbon tubes. (~ 8 ft. s⁻¹, 60°C, pH ~ 7).

4. *Solution composition.* Since the concentration of salt “invading” an ion exchanger (equal to the co-ion concentration) increases with increase in concentration of salt in the solution phase, the intrinsic rejection of an ion-exchange membrane should decrease with increasing salt concentration^{3,16,17}. We have found this to be usually true of dynamically formed membranes. If fluxes are high enough to realize the asymptotic rejection of the membrane, and if the flow of water and invading salt are completely coupled, $(1 - R)$ should equal the distribution coefficient for salt between the membrane and the solution at the α -interface, with concentrations in both phases expressed as moles salt/kg water. Ion-exchange theory would then predict that a plot of $\log(1 - R)$ vs. the logarithm of concentration of a uni-univalent salt should approach unit

slope with decreasing concentration. Hydrous Zr(IV) oxide membranes follow the pattern⁴, though the assumption concerning coupling is questionable¹⁸.

Figure 7 presents typical results for rejection of NaCl as a function of concentration by a Zr(IV)-PAA membrane. The rejections plotted are R_{obs} , but since:

$$\frac{1-R_{obs}}{1-R} = \frac{c_x}{c_t}$$

the slope should not be affected if concentration polarization were the same at all

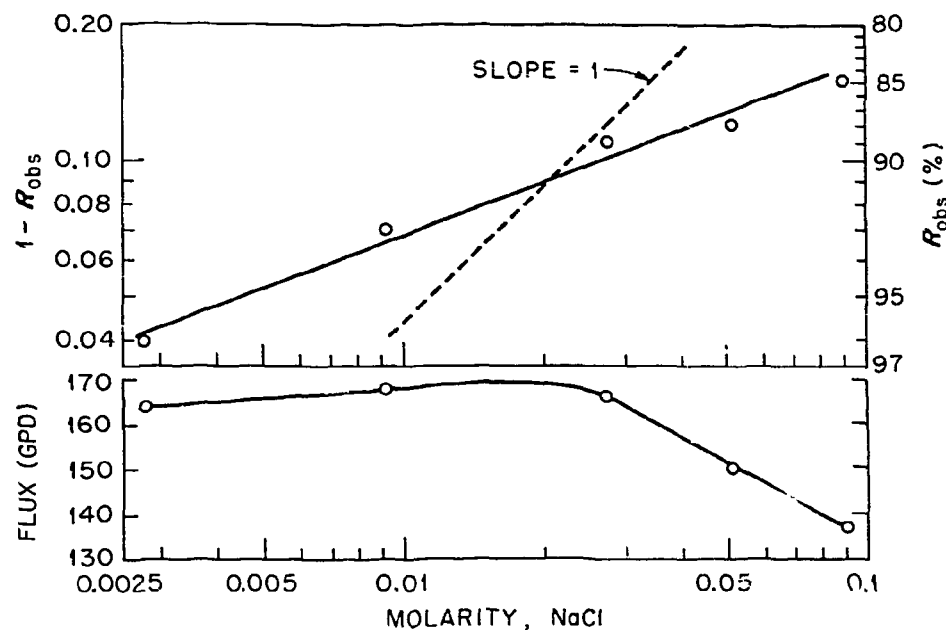


Fig. 7. Effect of concn. on hyperfiltration of NaCl by dual-layer membrane on 0.45 μ m Acropor AN support. (950 p.s.i.g., 35 ft. s⁻¹, 25°C, pH 7).

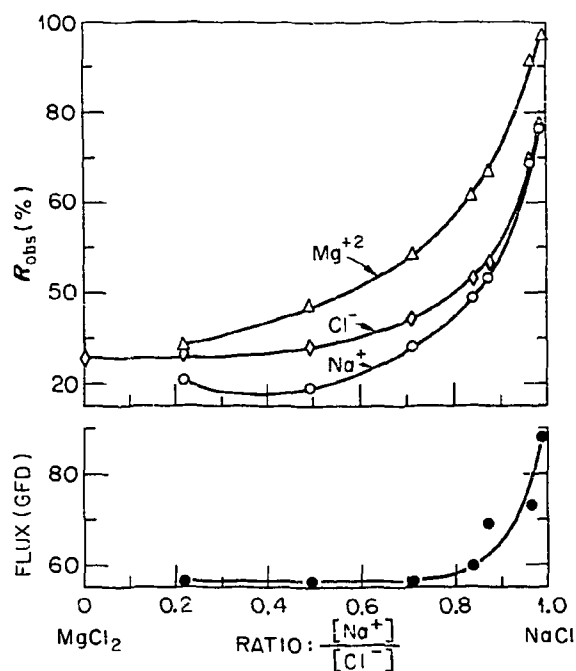


Fig. 8. Hyperfiltration of MgCl₂-NaCl mixtures by dual-layer membrane on inside of 0.27 μ m Sela ceramic tube $[Cl^-] \sim 0.05$ M (450 p.s.i.g., 30 ft. s⁻¹, 55°C, pH $\sim$ 8).

concentrations. Although there will be some variation in polarization because of variations in flux (Fig. 7), the effect should not be enough to obscure the essential aspect of the results, namely that the slope is much less than unity. Rejection does not fall off with increasing concentration as rapidly as predicted. Similar results have been obtained with Zr(IV)-PAA membranes of lower rejection, prepared in earlier procedures, in experiments in which R was evaluated by extrapolation to infinite circulation velocity. Such behavior is, in fact, typical of all dynamic membranes formed of organic polyelectrolytes that we have so far tested.

Performance with mixtures of ions is of both basic and practical interest. Figure 8 presents results for mixtures of MgCl_2 and NaCl , 0.05 M in total chloride. The pressure, 450 p.s.i., is less than in most of the other experiments, and rejections are lower. Fluxes and chloride rejections decrease in the presence of a relatively small fraction of the divalent counterion, Mg(II) .

C. Demineralization of a simulated natural brackish water

We have tested dynamic dual-layer membranes in the demineralization of several solutions which approximate the composition of naturally occurring brackish waters. Figure 9 shows the results of a typical experiment in which a dual-layer membrane on a $0.22\ \mu$ Millipore support was used. The feed solution was made up to simulate a water found near Coalinga, California: 0.0018 M CaCl_2 , 0.0096 M Na_2SO_4 , 0.0028 M NaHCO_3 and 0.002 M MgCl_2 , with total dissolved solids about 2000 p.p.m. The duration of the run was about 430 h, 317 h with the original membrane and the remainder following an *in situ* membrane regeneration. The initial part of the run is indicated by the open symbols in the Figure, the post-regeneration part by the solid points. Regeneration was accomplished by circulating 0.1 M NaOH through the loop under pressure for about 5 min, rinsing the base from the loop, and reforming the PAA layer in the manner described earlier. Before regeneration, the rejection of all of the components measured, chloride, Ca(II) plus Mg(II) , and total cation, was greater

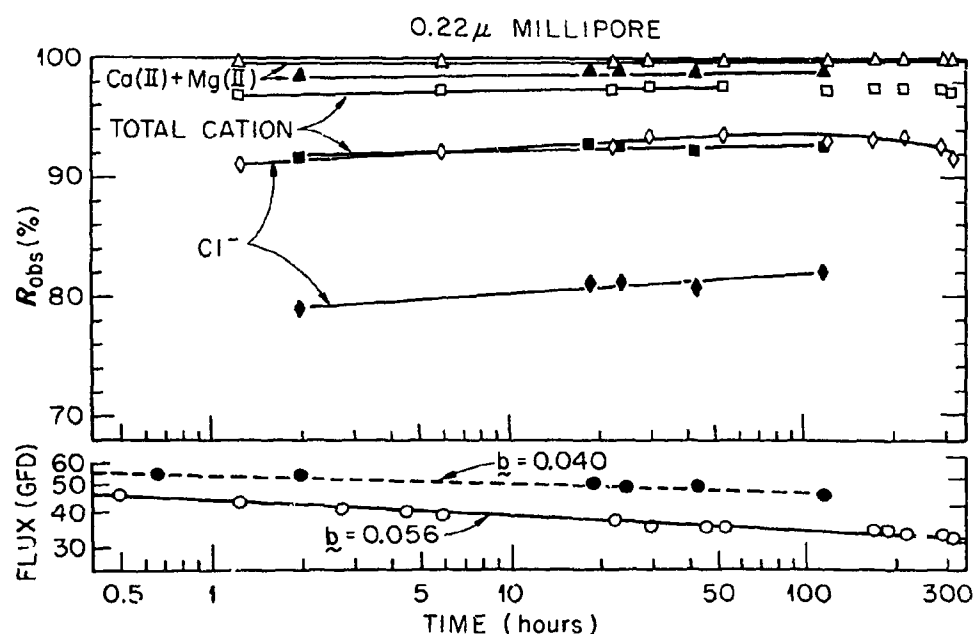


Fig. 9. Hyperfiltration of Coalinga water by dual-layer membrane. Open symbols: initial run; closed symbols: after regeneration (950 p.s.i.g., 20 ft. s^{-1} , 25°C, pH $\sim$ 7).

than 90%. Even though rejections were somewhat lower after regeneration, the product water at this point still contained less than 200 p.p.m. total dissolved solids.

Fluxes declined with time during both phases of the run, but the flux immediately following regeneration was greater than that attained shortly after the run was begun, and the rate of decline in flux after regeneration was lower than that before. The parameter b indicated in the Figure is the flux decline parameter, equal to the negative of the slope of the log flux *vs.* log time plot, and the smaller its value, the lower the rate of flux decline.

During most of this run, feed concentration was kept constant by returning the product to the feed tank. During the last 30 h before regeneration, product was discarded and the concentrations of feed components increased by factors of about 2.5. There was little, if any, rejection decline.

The puzzling lack of dependence of rejection on concentration, much lower than that of NaCl in Fig. 7, has been observed with other simulated brackish waters. In a more striking example with Coalinga, in which the various components were concentrated by factors of five to seven, rejection of total cation by a membrane on a 0.22 μm Millipore support remained greater than 90% during the course of the run. This behavior is clearly of considerable practical significance.

DISCUSSION

The fundamental colloid chemistry underlying the behavior of these membranes appears clear in some cases and doubtful in others. However, since our inferences are based almost entirely on ultrafiltration results, they must be considered as speculations. Rejection properties, at least in the neutral pH range, are determined primarily by the polyacrylate. For solutions of a single salt, rejections are similar to those of dynamic single-layer PAA membranes¹⁰, but the dual-layer membrane has the advantage of higher flux, of less sensitivity to the nature of the porous support, and of better rejections of feeds having typical natural water compositions. Rejection properties also resemble those of thin polyacrylate membranes cast on cellulose acetate-cellulose nitrate¹⁹ or polysulfone supports²⁰, although there are differences in detail; it appears that flux through dual-layer membranes is usually higher than through cast membranes of comparable rejection. Both rejections and fluxes are much higher than with cellophane grafted with polyacrylate¹².

We have already pointed out that the order of rejections of different valence types is that expected for cation-exchange membranes. Presence of polyvalent cations, such as Mg(II), in even a relative small amount appears to have strong effects on the membrane, including a sharp decline in permeability (Fig. 8). Although difficult to predict quantitatively, such effects are not unexpected in view of the strong interaction between polycarboxyls and divalent cations, observed for example with polyacrylate ion-exchange beads. Surprisingly (to us), the effects of exposure to a magnesium salt solution are slow to reverse on return to a NaCl solution, flux remaining depressed for hours in the presence of 0.05 M NaCl. Exposure to higher NaCl concentrations, 1 M for example, hastens flux recovery. It is of interest that, although Mg(II) is more poorly rejected from MgCl_2 -water than NaCl from NaCl-water at the same equivalent concentration, Mg(II) is the better rejected from mixtures of the two (Figs. 8 and 9).

A plausible explanation of the lower-than-expected dependence of rejection

on NaCl concentration (Fig. 7) is that the water content of the polyacrylate layer is lower in contact with solutions of higher concentrations. Large decreases in water content are known to occur with low-cross-linked ion exchangers²¹. An increase in ion-exchange capacity might be expected to offset partially the increase in membrane co-ion concentration expected from an increase in solution phase salt concentration.

The increase in rejection with increasing pH (Fig. 2) is consistent with the neutralization of polyacrylic acid with base. It is probable that many factors contribute to the accompanying decline in flux with increasing pH—changes in thickness of the polyacrylate layer and in the friction of water passing through polyacrylate ionized to varying degrees²², for example. Cast PAA membranes seem better when formed of higher molecular weight material²⁰. We do not understand why PAA of 50,000–150,000 molecular weight seems to form dual-layer membranes of higher rejection than those of higher molecular weight. The reasons for many aspects of the dependence of membrane properties on porous supports are also not obvious. In our opinion, the most important uncertainties, however, are related to the processes involved in the attachment of the polyacrylate to the hydrous oxide layer and the apparent irreversibility of the attachment.

Why polyacrylate appears not to become attached at neutral pH is not clear to us. Possibly the concentration of charges on the polymeric chain relative to the anion-exchange capacity of the hydrous oxide is too high for the adsorption of much polyelectrolyte to occur in neutral solutions. The fact that, once attached during acid excursions, desorption does not occur rapidly on increasing pH is also surprising. In any case, the interaction between the hydrous oxide and PAA layers would appear to be related to that between oppositely charged colloid particles in "complex coacervation"²³. The fact that the polyacrylate layer appears to be displaced at sufficiently high pH values supports the supposition that interaction of ionic groups of opposite charge is involved in its attachment.

However, another effect of lowering pH may also influence formation; the lower charge density should make the polyacrylate more compact. The observation of formation of dual-layer membranes at neutral pH from $MgCl_2$ solutions, where charge density may be low, is consistent with a contribution from compactness, but does not distinguish this possibility from a better balance between charge density on the polyacrylate and the hydrous oxide layer.

In any case, performance of dynamically formed Zr(IV)–PAA membranes justifies consideration of them for practical applications in water treatment. Results with natural brackish waters, typified by Fig. 9, as well as with effluents from the dyeing of textiles²⁴, with kraft pulp mill wastes, and with municipal sewage⁷ are particularly pertinent in this regard.

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SUMMARY

Membranes consisting of a layer of polyacrylic acid on hydrous Zr(IV) oxide appear promising for hyperfiltration (reverse osmosis) of low-salinity waters. These membranes are formed dynamically by exposing a hydrous oxide membrane, also dynamically formed, to an acidic solution containing polyacrylic acid, and then raising the pH. The effects of variables during membrane formation and during subsequent operation on membrane properties are discussed.

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3.1.2 Factors Affecting Membrane Formation

3.1.2.1 Type of Porous Support. In Section 3.1.1, we indicated that dynamic membranes may be formed on a variety of porous support materials. As we have already mentioned, much of our earlier work directed toward maximizing performance was carried out on experimental configurations involving porous stainless steel tubes wrapped with films, e.g. Millipore and Acropor AN, of uniform and controlled porosity and pore size. Such configurations, while convenient, are not likely to be the most useful ones for large scale desalination plants. The present section will describe some experiments in membrane formation on potentially more practical supports. More extended tests of the applicability of dynamic membranes on the various supports to particular feeds will be discussed later in this report in the appropriate sections.

A summary of membrane formation results on the various supports used over the period of this report is given in Section 3.1.2.1.13.

3.1.2.1.1 Selas Flotronics Ceramic Tubes.

3.1.2.1.1.1 Microporous Ceramic Filter Elements. Through the courtesy of Mr. G. V. Jordan and Dr. Emil Blaha of Selas Flotronics, we received a quantity of their microporous ceramic filter elements for test and evaluation. We received elements of four different pore sizes, 0.12- μ , 0.18- μ , 0.27- μ , and 0.8- μ , the pore sizes indicating the maximum particle size retained. All elements were tubes, sealed on one end, 0.21 in. OD, $\sim$ 0.125 in. ID, and 15 in. long. We first did inside-pressurization rupture tests on three types of elements and found that the 0.12- μ element broke when the inside pressure was between 600 and 700 psig; the 0.27- μ element at 550-600 psig, and the 0.8- μ element between 60 and 65 psig. All types easily withstood 800-1000 psig under outside pressurization.

In our first hyperfiltration test of the Selas tubes, we placed three 0.27- μ elements in parallel in a single test jacket with 900 psig outside pressurization and at a velocity of about 14 fps. With this arrangement, flow velocities past the surfaces were not uniform. A dual-layer membrane was formed at 25°C, using Acrysol A-3 (Table I, Section 3.1.1) as the top layer at an initial pH of 2.3. The completed membranes had an average flux of 30 gfd at 95% rejection of 0.05 M NaCl, compared to a control membrane on 0.22- μ Millipore, which at 35 fps, had 48 gfd with 96% rejection.

After 28 hours of operation, the rejection remained at 95%, but the flux had increased slightly to 34 gfd.

The membranes on the Selas tubes were tested against Coalinga water (see Table 3.68), and the results are listed in Table 3.1 along with those of the control membrane. It will be noted that the rejections of the components of Coalinga water are better on the Selas tubes, although the fluxes are somewhat less.

TABLE 3.1
HYPERFILTRATION OF COALINGA WATER BY DUAL-LAYER MEMBRANES
ON SELAS FLOTRONICS CERAMIC SUPPORTS. INITIAL TEST.
(900 psig, ~16 fps, 25°C)

<u>Support</u>	<u>Velocity (fps)</u>	<u>Flux, (gfd)</u>	<u>Cond.</u>	<u>R_{obs} (%)</u>		
				<u>Cl⁻</u>	<u>Ca(II)+ Mg(II)</u>	<u>Total Anion</u>
0.27- μ Selas	14	18	93	89	>99	95
0.22- μ Millipore	35	23	90	86	98	93

Following the test with the Coalinga water, we removed the control membrane and washed, in the loop, the ceramic supports for one hour with 1 M NaOH and then for one hour with 1 M HNO₃. Following a water rinse, we added 50 ppm Acrysol A-3 to the feed tank at pH 2.4. The membrane formed by regeneration of the PAA layer removed, at pH 7.8, 89% of the salt from a 0.05 M NaCl solution at about 60 gfd. After a weekend shutdown, we again reduced the pH to about 3, added another 25 ppm PAA, and raised the pH gradually to 7. After rinsing out the additive and adding 0.05 M NaCl, rejection was 97% at 33 gfd. Within 15 hours, the fluxes had increased to 46 gfd, accompanied by a slight decrease in rejection, to 95%. After another 30 hours of operation, these membranes were still rejecting 95% of the salt, but the fluxes had declined to about 40 gfd.

A new lucite test section jacket was made so that the membranes could be formed on the Selas tubes at higher velocities. The formation curves for a dual-layer membrane on the 0.27- μ Selas, along with two controls, is shown in Fig. 2, Section 3.1.1. The Selas tube gives both rejections and

fluxes only slightly lower than those of the controls, rejection being about 90% at near 100 gfd.

A set of dual-layer hydrous Zr(IV) oxide-Acrysol A-3 membranes were formed on three different types of Selas tubes in a single run for comparison purposes. The formation conditions were 950 psig, 35 fps, and 25°C. With 0.05 M NaCl, all gave reasonably good performance: 0.8- μ , 87% at 136 gfd; 0.27- μ , 90% at 112 gfd; and 0.12- μ , 90% at 114 gfd; but the 0.8- μ and the 0.12- μ proved somewhat fragile to use, and most further tests were done with the 0.27- μ support.

In two runs, we tested the Selas tubes for inside pressurization and flow. At 500 psig and 15 fps, the completed hydrous Zr(IV) oxide-Acrysol A-3 membrane on the inside of a 0.12- μ Selas tube rejected 64% of 0.05 M NaCl at 106 gfd. After running overnight, the flux had increased to 128 gfd, but the rejection was down to 54%. An acid cycle to pH 2.8 and back to 7.6 brought the rejection up to 83% at 92 gfd. The tube fractured soon thereafter, and the run was discontinued. On a Selas 0.27- μ tube, under the same conditions of inside flow, the initial performance values for the dual-layer membrane were 78% rejection at 56 gfd. After about 44 hours of operation; the rejection was 76% at 81 gfd. This tube also ruptured and the run was discontinued. The small loop on which these tests were made is sometimes subject to abrupt pressure spikes, and the rupture of these tubes is attributed to such an occurrence.

With several of these membranes on ceramics, unusual increases in flux with time were observed. Appreciable decreases in rejections occurred in some cases and were absent in others. These cast some doubt on whether or not all changes reported were the result of operating conditions such as pressure or circulation velocity, or the result of time of operation. Membranes on these supports are nevertheless stable enough to be of practical interest.

The 0.18- μ Selas tubes, which were received later than those described above, were tested in a series of independent experiments. In the first, we made three membrane formation runs on the 0.18- μ Selas, all at 55-57°C, with a circulation velocity of 7 fps, unusually low. The results are given in Table 3.2. Run No. 1 gave poor rejections after the first formation procedure, and the acid cycle was repeated. The membranes were

TABLE 3.2
HYPERFILTRATION OF 0.05 M NaCl BY DYNAMIC DUAL-LAYER MEMBRANES
ON 0.18- μ SELAS CERAMIC TUBES
(900 psig, 55-57°C, 7 fps)

Run No.	Hydrous Oxide Layer			Dual Layer		
	pH	Flux (gfd)	R_{obs} (%)	pH	Flux (gfd)	R_{obs} (%)
1 (first PAA cycle)	3.9	440	24	6.2	226	33
1 (second PAA cycle)				7.5	92	84
2	3.8	638	43	8.2	121	89
3	3.8	617	32	6.5	91	92

reasonably good, particularly in view of the low circulation velocities. The membrane of Run No. 1 was not as good as the others, and this probably reflects an inferior hydrous oxide sublayer, which had both a lower flux and a lower rejection than those usually obtained. The membrane of Run No. 3 was tested with Coalinga water (see Table 3.68). The results, for hyperfiltration at 56°C, are listed in Table 3.3. The rejections for this membrane are very good, but the fluxes are unsatisfactory, especially considering that the operating temperature was 56°C. The rate of decline in flux was also high, b , the flux decline parameter, being 0.27.

TABLE 3.3
HYPERFILTRATION OF COALINGA WATER BY DUAL-LAYER MEMBRANE
ON 0.18- μ SELAS TUBE

Time (Hours)	Flux (gfd)	R_{obs} (%)		Total Cation
		Cl ⁻	Ca(II) + Mg(II)	
0.5	40	93	99	98
1.5	24	98	99	99
20	14	98	99	99
90	10	97	99	98

We formed one dual-layer membrane on the inside of a 0.27- μ Sela tube at 450 psig and with a circulation velocity of 30 fps. The temperature during formation was 55°C, and at pH 8 the membrane had an observed rejection of 0.05 M NaCl of 88% at 121 gfd. After an overnight run in the presence of 50 ppm PAA, the rejection had fallen to 77%, and the membrane was once again cycled through acid conditions. When the pH reached 7.2 during this cycle, the rejection was 90% at 103 gfd. Seventy hours later, the flux had risen to 132 gfd at 87% rejection.

This membrane was later tested for 190 hours with Coalinga water (see Section 3.3.1.1.5).

3.1.2.1.1.2 Multi-Channel Ceramic Tubes. The Sela Corporation has also developed ceramic tubes with seven small channels for inside flow at higher pressures. The first samples of these tubes were about 3/8 in. in OD and about 15 in. long. They had a nominal pore size of 0.27- μ , contained seven channels 0.082 in. ID, and had been fired to withstand about 600 psig inside pressurization. We formed dual-layer membranes on the inside of the channels of one of these elements at 500 psig, 28°C, and 17.5 fps. The membranes rejected 90% of the Cl^- from a 0.05 M NaCl solution at a flux of 114 gfd. This was a short-term run, about 20 hours, but the performance was encouraging for this pressure and velocity. This membrane was subsequently tested for 185 hours with Coalinga water, and the results of this test are reported in Section 3.3.1.1.5.

On a second set of samples, which had been designed to withstand 1400 psig internal pressure, we formed dual-layer membranes using a circulation velocity of 15 fps at 1000 psig and 28°C. The newly formed membranes had an average flux of 79 gfd with an observed rejection of 85%, using a 0.05 M NaCl test solution. After 42 hours of operation, the flux had improved to 94 gfd with R_{obs} at 89%. When Coalinga water was added, however, the performance fell drastically, with the observed rejection only 28% and the flux 65 gfd. This performance did not change appreciably during 19 hours of operation with the Coalinga water.

In an attempt to improve performance, we rinsed out the Coalinga water and recycled the membranes to pH 2.3 and back to 6.5 in the presence of 25 ppm PAA in 0.05 M NaCl. Rejection of 0.05 M NaCl improved to 94%, with flux at 49 gfd. Performance with a simulated Coalinga water feed, however, was

once again unsatisfactory, 53 gfd at 24%. No improvement resulted during an additional 22 hours of operation.

In a second test on these Selas tubes, we attempted to capitalize on the high strength of the tubes which allows them to be pressurized from either the inside or the outside. Our plan was to form dynamic membranes in the channels of the tube, test them against brackish waters until fluxes fell to unacceptable levels, and then to reverse the pressurization in order to form a membrane on the outside surface of the tube. In the process, we would, by the backwash, remove the previously formed membranes from the inside surfaces. In principle, the operation could be repeated indefinitely. The results of a series of tests and operations are given in Table 3.4.

In each run, a dual-layer membrane was formed from 0.05 M NaCl, and its performance with this solution recorded. Coalinga water was then added to the loop, and the results from this test observed. Membranes were alternately formed on the inside and the outside of the tube, with various pretreatments interspersed. Water rinses, pressurized in a direction so as to remove the previous membrane, did not suffice to restore previous fluxes (runs 1 through 5), and we resorted to base and acid washes. There was no appreciable difference in either flux or rejection between membranes formed in the channels or on the outside of the tubes when tested against 0.05 M NaCl. Appreciable benefits seemed to accrue from a pretreatment with a filter aid before the dual-layer membrane was formed, presumably by preventing plugging of the pores in the ceramic by components of the membrane or of the feed solutions.

3.1.2.1.1.3 Protomodules with Selas Tubes. To obtain results with membrane support areas somewhat larger than those of our typical test sections, we have tested several small protomodules. Selas Flotronics has kindly supplied several of these, and we have constructed a few of our own, using tubes supplied by Selas. These modules all have areas considerably smaller than those envisioned for eventual application, but they were kept small to be compatible with our pumping capabilities.

The first small module we received from Selas contained 46 0.21 in. OD ceramic tubes of 0.12- μ pore size, and had about 3.2 ft² of surface area.

TABLE 3.4
RESULTS OF REVERSE-FLOW TESTS ON 7-CHANNEL SELAS CERAMIC FILTER ELEMENTS
(Zr(IV)-PAA membranes, 1000 psig, 30-34 fps, 25°C)

Run ^a	Pretreatment ^b	0.05 M NaCl Solution		Time ^c	Simulated Coalinga Water				
		Flux (gfd)	R _{obs} (%)		Flux (gfd)	Observed Rejection (%)			
						Cond.	Cl ⁻	Ca(II) + Mg(II)	Total Cation
1-I	None	92	92	26	56	77	71	88	78
2-0	Water rinse	47	95	2	18	92	99	99	93
3-I	Water rinse	60	93	18	23	71	66	85	75
4-0	Water rinse	41	94	15	12	92	89	90	95
5-I	Water rinse	31	87	66	10	52	50	60	57
6-0	Base-acid wash	156	86	18	86	76	69	93	81
7-I	Water rinse	115	92	16	33	83	80	89	81
8-0	Base-acid wash	118	88	2	86	72	64	91	77
9-I	Base-acid wash	127	90	20	46	80	77	89	83
10-0	Base-acid wash	149	88	18	51	81	74	96	85
11-I	Base-acid wash, Filter-aid added	145	93	19	56	84	79	92	85
12-0	Base-acid wash, Filter-aid added	97	92	2	53	80	75	97	85
13-I	Base-acid wash Filter-aid added	117	88	17	28	75	72	87	79
14-I	Base-acid wash, Filter-aid added	87	88	42	21	73	71	86	78

(a) In chronological order. I indicates inside, 0 indicates outside, pressurization.

(b) Water rinse in direction to remove membrane. Base-acid wash: one-hour wash with each 1 M NaOH and 1 M HNO₃.

(c) Time in hours after addition of Coalinga water.

Flow was directed around the outside of the tubes, which were supported by a perforated silicone rubber adaptor at the bottom of the module. Flow patterns in the module were far from ideal, and the maximum circulation velocity, on the average, that we could obtain was about 3.5 fps. Pressures were limited to 400 psig or less by the type of seal used in the module. With room temperature operation, we were able to achieve with this module only about 40% rejection of 0.05 M NaCl at 65 gfd, using Zr(IV)-PAA dynamic membranes.

We next constructed a small module for inside pressurization and flow by sealing the ends of fifty 0.27- μ Sela tubes with epoxy resin into a two-inch diameter pipe about 14 inches long. The inside surface area was about 1.6 ft². The feed was directed straight through the module, and the product was collected on the inside of the pipe and drained by a side-arm into a reservoir. Dual-layer membranes in this module, at 400 psig, 20 fps, and 25°C, gave us 62% rejection of 0.05 M NaCl at 61 gfd. After an overnight run, the temperature was raised to 55°C, at which point the flux had risen to 154 gfd, but the rejection had decreased to 37%. Soon after this measurement was taken, the seal between the epoxy and stainless pipe gave way, and the test was abandoned.

The third Sela module tested was supplied by the Corporation, and was designed for 1000 psig pressurized flow on the outside of 31 removable 0.27- μ tubes, with a total area of about 2 ft². With our pumps, the maximum velocity, on the average, that we could reach was about 9.5 fps, but at 25°C we achieved, with Zr(IV)-PAA membranes, 83% rejection of 0.05 M NaCl at 62 gfd. After the membranes were put through an acid cycle in the presence of PAA at 60°C, rejection was 80% at 90 gfd.

We made one more attempt to epoxy tubes to a pipe, sealing thirty-one 0.27- μ Sela tubes into a two-inch stainless steel pipe, and forming Zr(IV)-PAA membranes on the insides of the tubes at 450 psig and 28 fps. The performance of the hydrous Zr(IV) oxide membrane was similar to that which we expect from Millipore and Acropor supports, with 39% rejection of 0.05 M NaCl at 560 gfd at pH 3.9. However, we were able to realize only 70% rejection (100 gfd) for the dual-layer membrane at pH 6.8. An acid cycle increased the rejection only slightly to 74%, but caused a large decrease in flux to 18 gfd, also at pH 6.8.

A base wash to remove the PAA layer, and reformation of that layer, did little to improve performance. At pH 7.1, rejection was 74% at 23 gfd. We attempted to increase flux by increasing the temperature, but the strain caused by the difference in coefficient of expansion between the ceramic tubes and the steel envelope caused several of the tubes to break and the experiment was discontinued. It became obvious from this experiment that if ceramic tubes are to be used in steel jackets at least one header end of the tube bundle must be free to float to allow for expansion.

The first protomodule incorporating the new Selas 7-channel ceramic tube was supplied to us by the Corporation and contained seven of the tubes with a total surface area for membrane formation of about 1.2 ft². The module itself was about 3 1/2 in. OD by 16 in. long, and the tubes were individually removable for replacement if necessary. Membrane formations on this module were carried out at 950 psig, 35 fps, and about 25°C, and with 0.05 M NaCl, the rejection was 91% at 48 gfd. After 62 hours of operation with NaCl, the flux had increased to 67 gfd, but the rejection had fallen to 88%. This module was later tested with low-level ORNL process waste (Section 3.3.3.6), with Dalpra Farm water (3.3.1.5), and with a pretreated cooling tower blowdown (3.3.3.2.2).

We also tested a protomodule made up of 31 of the 7-channel Selas tubes, and supplied to us for testing by Selas. The tubes were mounted in parallel, "O"-ringed into machined steel bulkheads at each end, and oriented for inside flow and pressurization. Total membrane area of this small module was about 4.5 ft². A series of tests of this module is described below.

We placed the module in a test loop (loop 10) which contained a high-capacity (100 gpm) low pressure (0-185 psig) circulation loop in parallel with the standard high pressure loop. This feature allows us to circulate feed at high velocities at low pressures, which is an advantage when forming membranes dynamically on larger surface areas. During the formation of the hydrous oxide sublayer, one of the ceramic tubes burst at about 750 psig. The loop was shut down and the tube replaced. A second tube ruptured at about 950 psig; it was replaced and thereafter the module was

operated at pressures no greater than about 850 psig.* The dual-layer membrane was completed at 850 psig, 25°C, and 17 fps circulation velocity, the highest attainable with our pumping capacity for a 31-tube configuration. During the formation procedure, we twice more had to shut down to fix leaks through "O" rings that were improperly seated.

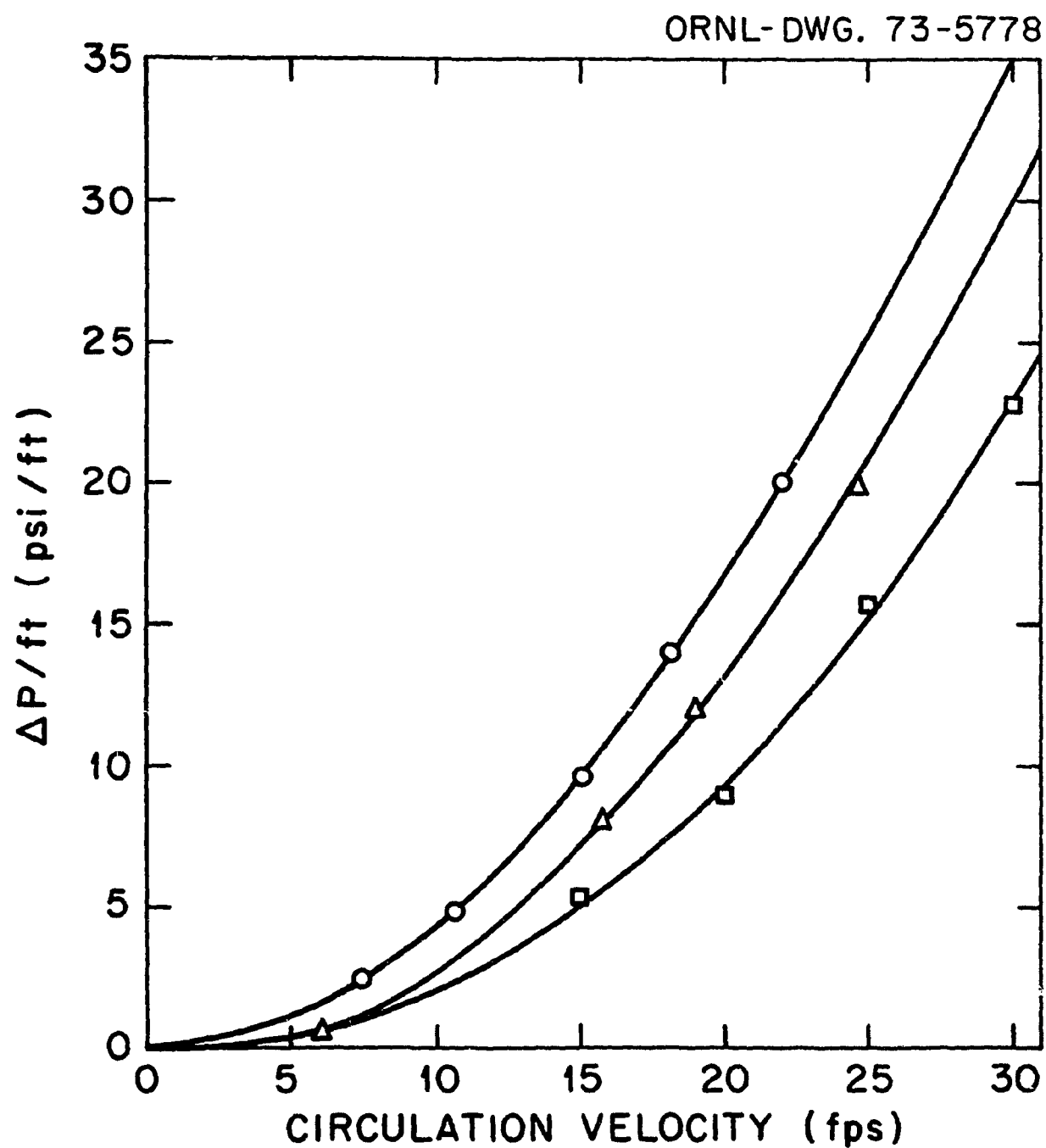
Perhaps because of the excessive number of shutdowns during the membrane formation procedure, the properties of the final membranes were not as good as those we had previously obtained with these ceramic tubes. With 0.05 M NaCl, observed rejection was about 85% at 36 gfd. After 19 hours of operation, flux had increased to 53 gfd, while rejection remained constant.

The module was subsequently tested with the product from a cross-flow treatment of municipal sewage (Section 3.3.3.7.2) and with Colorado River water (Section 3.3.1.3) and with soybean whey. All the tests demonstrated promise for the tubes as a practical membrane support in large-scale systems.

The largest protomodule with Sela tubes that we tested was provided by the Corporation, and consisted of thirty-nine 7-channel tubes in series, with inside pressurization. The module incorporated about 7 ft² of support area in a volume of roughly 0.1 ft³, but there was considerable pressure drop across the module under our usual flow conditions. We made some measurements of pressure drop versus velocity with a single 7-channel tube, see Fig. 3.0, with and without a membrane in place. We also calculated what the pressure drop would be at 65°C, and these data are also included in the figure. Based upon these measurements, the pressure drop across the 39 tube module would be about 470 psi at 15 fps for the module before membrane formation, and about 350 psig after membrane formation, both at 21°C. At 65°C, with a membrane in place, the pressure drop at 15 fps would be reduced to about 245 psi.

The pressure head developed by our normal circulation pump is somewhat less than 100 psi, and, in order to handle these large pressure drops, we removed the circulation pump from the system and directed all of the output of the Milton-Roy pressurizing pump through the module. We changed flow rates, when desired, by adjusting the output of the Milton-Roy pump.

*These difficulties with rupture led the manufacturers to increase the wall thickness of subsequent tubes, which should easily withstand pressures greater than 1000 psig.



PRESSURE DROP VERSUS VELOCITY FOR
7-CHANNEL SELAS TUBE, TAP WATER FLUID

	TEMP	MEMBRANE	DETERMINED
○	21°C	None	Measured
△	21°C	Zr(IV)-PAA	Measured
□	65°C	Zr(IV)-PAA	Estimated

Fig. 3.0

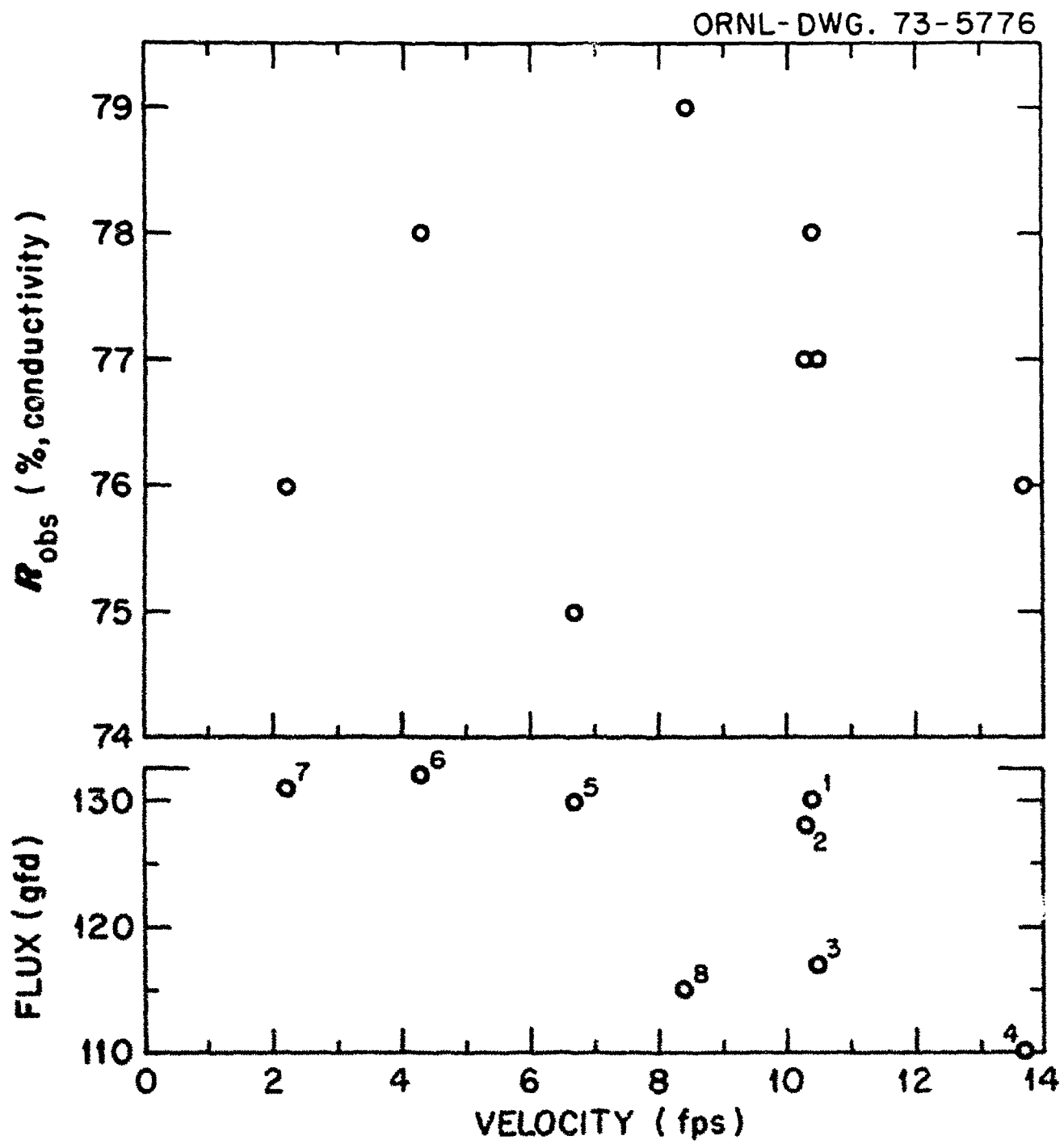
In the module, the thirty-nine tubes were sealed with O-rings into stainless steel headers, and we had some trouble in the initial stages with leaks at these seals. However, we were able eventually to form membranes at about 20 fps, 25°C, and 900 psig inlet pressure. Under these conditions, the completed membrane rejected about 86% with 0.05 M NaCl, with a flux of about 20 gfd. Both flux and rejection increased somewhat, to 29 gfd at 88%, when the circulation velocity was decreased to 10 fps, the increases presumably resulting from a higher average pressure in the module.

When, after 24 hours of operation, the feed temperature was increased to 54°C, the rejection decreased to 83%, but the flux increased to about 100 gfd. At 80°C, we achieved 72% rejection at 218 gfd. We returned to 65°C, and ran the velocity excursion illustrated in Fig. 3.1. The numbers in the lower part of the figure refer to the order in which the points were taken. At about 10.5 fps, the first velocity tested at 65°C, the average flux decreased from about 130 gfd to 117 gfd in about four hours. When the velocity was increased to about 14 fps, the flux dropped still further, to about 110 gfd. However, at lower velocities, fluxes exceeded 130 gfd, presumably because the average pressure in the module was higher than it was at the higher circulation velocities. Circulation velocity in this limited range appeared to have little effect on membrane rejection.

Although the rejection and flux characteristics of the membranes formed with this module were not very good, the experiment itself was encouraging, since some degree of success had been attained under conditions far from ideal. At 25°C, 900 psig, and 10 fps, we achieved water production rates over 2000 gallons per day per cubic foot. At 54°C, flux densities of 7000 gallons per day per cubic foot were attained.

3.1.2.1.2 Ferro Ceramic Tubes. Ferro types 600 and 202 ceramic tubes* have rather large pore structures, and may thus be backwashable, a distinct advantage in membrane regeneration. We have tested both types before (Ref. 15, Section 4.3.8), but were able to get encouraging results only on the 202's. Further tests on both of these supports are reported below.

*Available from the Electro Refractories and Abrasives Division of Ferro Corporation, Huntington Beach, California.



VELOCITY TEST WITH SELAS MODULE WITH
39 7-CHANNEL CERAMIC TUBES IN SERIES
(0.05M NaCl, 900 psig inlet, 65°C, pH 7)

Fig. 3.1

3.1.2.1.2.1 Ferro 202. Supports of Ferro 202, porous ($\sim 5\text{-}\mu$) stainless steel, $0.22\text{-}\mu$ Millipore and $0.45\text{-}\mu$ Acropor were inserted into test sections to give a flow velocity during membrane formation of 35 fps. Another finger with $0.22\text{-}\mu$ Millipore and $0.45\text{-}\mu$ Acropor supports was inserted in a bypass test section to operate concurrently at 14.5 fps. With the pressurizing pump operating, 25 ppm Hyflo Super-Cel and then 25 ppm Celite 505 (both Johns-Manville filter aids, see Table 1.1) were injected into the feed (0.05 M NaCl with 10^{-4} M Zr(IV) at pH 4) upstream from the test section containing the Ferro and the porous stainless steel supports. As soon as plugging occurred and pressurization was achieved, the circulation pump was started. The Zr(IV) and the filter aids were rinsed from the system when the rejections reached 40–50%, and Acrysol A-3 was added (50 ppm in 0.05 M NaCl) at pH 2.3. The final results are listed in Table 3.5. In this test, membranes on filter aid treated Ferro and stainless steel tubes were much inferior to our standard wraps. The standard wraps even at 14.5 fps gave much better rejections than did the Ferro and steel supports at 35 fps. After overnight operation, fluxes and rejections had not changed much from the values given in Table 3.5.

TABLE 3.5
HYPERFILTRATION OF 0.05 M NaCl BY DYNAMIC DUAL-LAYER MEMBRANES ON
SEVERAL POROUS SUPPORTS. FILTER AIDS ADDED DURING SUBLAYER FORMATION
(950 psig, 25°C , pH 7.1)

<u>Support</u>	<u>Velocity (fps)</u>	<u>Flux (gfd)</u>	<u>R_{obs} (%)</u>
Ferro 202	35	155	36
Porous stainless steel	35	69	63
$0.22\text{-}\mu$ Millipore	35	127	92
$0.45\text{-}\mu$ Acropor AN	35	128	94
$0.22\text{-}\mu$ Millipore	14.5	55	84
$0.45\text{-}\mu$ Acropor AN	14.5	53	84

In our earlier tests of the Ferro 202, rejection was unstable on the addition of base after the initial exposure to PAA. Only after a second acid excursion were reasonably high rejections maintained. The inferior results presented here are therefore not necessarily in conflict with the earlier tests, although it is also possible that our earlier formation procedures may have been more favorable for the particular support. In addition, in some cases with filter aid pretreated supports, we have found that circulation velocities greater than 30 fps lead to poorer results, and such might be the case here.

3.1.2.1.2.2 Ferro 600 and 600p. We made two attempts to form membranes on some Ferro 600 ceramic tubes, 0.55 in. OD, using the techniques which had contributed to good membranes on the Selas and on the carbon tubes. Formation and operation were carried out at 950 psig, 25°C, and 35 fps. In the first trial, we deposited the dual-layer membrane directly on the Ferro tube, adding the Acrysol A-3 at pH 2.3 after the hydrous Zr(IV) oxide layer had been completed. At pH 6.7, the rejection (0.05 M NaCl) was only 43% at 25 gfd. In the second attempt, we first added a filter aid, Celite 505, to the feed and then formed the sublayer. After the dual-layer was formed, the rejection at pH 7.2 was 50%, the flux 22 gfd. Under these conditions, the Ferro 600's did not give nearly as good results as did the Selas ceramics.

We next obtained some Ferro 600p tubes that had been pretreated by Thomas'⁷ group in the manner they had developed in preparing supports for dynamic membranes for their prototype desalination unit, recently tested at OSW's Roswell, New Mexico, test facility. Since these tubes had been precoated with ZrO₂ and fired, they did not require filter aid pretreatment. We tested several of the 7-tube bundles developed for the Roswell loop, as well as some individual tubes similarly prepared.

We formed membranes on individual Ferro tubes in twelve separate runs, but in only three of these did we use standard formation techniques. In the other runs, we varied formation parameters, and results are described in later sections. The membranes formed by standard techniques averaged 93% rejection of 0.05 M NaCl (range 85-97%) and 70 gfd flux (range 61-80 gfd).

In our first attempt to form membranes on the 7-tube bundle, which had a surface area of about 2.5 ft², we got good membranes (90 to 95% rejection at 50 to 59 gfd) on four of the tubes, but inferior membranes on the others (950 psig, 25°C, 17 fps). One of the objects of this particular experiment was to check the operation of the module and bundle at higher temperatures, but some end fittings failed because of improperly sized O-rings after only a short operation at 65°C, and the run was terminated.

A new tube bundle was inserted into the module and new Zr(IV)-PAA membranes formed. Once again a seal gave way when the temperature was raised to 65°C, but this was replaced and no further trouble was encountered in this respect. After overnight operation with 0.05 M NaCl at 25°C, 950 psig, and 17 fps, the average rejection was 89% at 71 gfd for all seven tubes. These membranes were then used on a food waste which reduced the flux to 13 gfd at 25°C. The membranes were stripped from the Ferro supports by a one-hour wash with 1 M NaOH followed by a one-hour wash with 1 M HNO₃. Both layers were then reformed in the standard way, resulting in membranes that rejected 66% of 0.05 M NaCl at 58 gfd. An acid cycle in the presence of 10 ppm PAA brought the rejection to 70%, but the flux had dropped to 41 gfd. Three more times the membranes were stripped and reformed; each time the rejection improved slightly, but the flux decreased. The final values were 83% at 20 gfd. Despite the low fluxes, these membranes were used in an unpublished test with a dilute textile dye waste with satisfactory results at the higher temperatures used.

Following the dye waste test, the module was once again subjected to a base and acid wash, then set aside for three weeks while other experiments were carried on. Following these, the Ferro tube module was again inserted into the loop, and new membranes formed. With 0.05 M NaCl, these rejected 75% at 41 gfd, and they were subsequently used in a laundry waste test, at elevated temperatures, also with satisfactory results.²²

Following a two week period during which the module lay idle, membranes were reformed that gave 74% rejection at 45 gfd; these were used with a potato grinding waste.

Our inability to form membranes on these tubes satisfactory for desalination, although adequate for other purposes, after the acid and base washes is indicative of fouling material being present in the loop during

membrane formation. The base washes turned quite dark, even after repeated washes, and we subsequently tried a wash with 0.5 M NaOH at 45°C. The ensuing membranes were still not good, 68% at 35 gfd, and another base and acid wash and reformation of membranes was carried out. The resulting membranes, 52% at 48 gfd with 0.05 M NaCl, while still not good, were used with some success in another test with potato grinding waste.

We removed the test section from the loop, and washed the loop several times with hot (65°C) 1 M base and hot 1 M acid before we got the wash waters to run clean. In the module, we found extensive residues of previous wastes trapped in several places between the tubes and the pressure vessel. These evidently make cleanup very difficult, if not impossible, without removing the tube bundles.

We inserted a new bundle of Ferro tubes, and replaced the module in the test loop. Now, with the clean loop and tube bundle, the membranes we formed at 950 psig, 15 fps, and 25°C rejected 0.05 M NaCl at 91% with a flux of 76 gfd. These membranes were used to treat a modified starch filtrate food waste. Following this, we were, once again, unable to clean up the loop and tube bundle and to reform satisfactory membranes with the tube bundles in place. The best membrane we got had 55% rejection at 51 gfd. However, when we removed the tube bundle, cleaned up the loop with hot washes, and put in a new tube bundle, we were able to form quite satisfactory membranes (96% at 54 gfd). These were used in a simulated seawater study described in Section 3.3.2.

Visual inspection of a fouled tube bundle and module suggests that the fouling occurs excessively at those points where the tubes lay very close to the wall of the pressure vessel. Perhaps a little more clearance between vessel and tubes would allow one to clean up the tube bundle in situ, even after operation with such difficult feeds. The 7-tube bundles have performed very well in the Roswell test pilot plant,⁷ with a rejection of dissolved solids of 90-91%, sulfate rejection 93-95%, and Cl⁻ rejection of 83-94% at fluxes greater than 100 gfd over a two week period of continued operation (inlet pressure, 1000 psig; 13.5 fps).

3.1.2.1.3 Union Carbide Carbon Tubes. Because of their cheapness and strength, porous carbon tubes have long held our interest as possible practical supports for dynamic membranes. We reported results of dual-layer membrane formation on carbon tubes in the 1968-70 Biennial

(Ref. 15, Section 4.3.4), and the results we got there, e.g., 85% rejection of .05 M NaCl at 950 psig at 85 gfd, were sufficiently encouraging to cause us to restudy them from time to time as new techniques were developed.

Our studies on carbon tubes were confined to three types: one designated 4A-3, which had a nominal median pore size about 0.4- μ , and was 0.26 cm ID and 1.09 OD; one designated 563-6A, which is reportedly similar to the 4A-3, except that it is 0.6 cm ID, and 1.025 cm OD; and the third designated as 563-6C, which is described as more coarse than the 6A, but otherwise similar.* Previous experiments with carbon tubes are described in references 13 and 25.

We tested the carbon tubes with both inside and outside pressurization. In the case of the 6C tubes, we tested them in an "as received" condition as well as with 0.04 inches removed from the OD by either machining or centerless grinding, in an effort to remove any extrusion "skin" that might impede product flow through the walls of the tube.**

3.1.2.1.3.1 4A-3 Carbon Tubes. Table 3.6 summarizes a series of runs where pressure, velocity, and pH were the variables in studying the formation of dual-layer hydrous Zr(IV) oxide-Acrysol A-3 membranes on 4A-3 carbon tubes. The data points were taken after the membranes had been in use for the periods indicated in the "time" column. Performance values for reference membranes, on 0.45- μ Acropor AN supports, which were formed in the same loops at the same times as were those on the carbon tubes, are listed in the table as "controls".

Inside and Outside Pressurization Effects: In Runs 1 and 2, where the membranes were formed at 600 psig, both the fluxes and the rejections were higher for carbon tubes pressurized on the inside than for those pressurized on the outside. In Run 2, this advantage was maintained when the pressure was raised to 1000 psig, and again when it was changed back to 600. However, when formation was carried out at 1000 psig, see Runs 3 and 4, neither mode of operation had a clear-cut advantage.

*We are indebted to L. M. Litz of Union Carbide Corporation for supplying these tubes.

**This effect had been discovered several years ago by D. G. Thomas' group for hydrous oxides, and is mentioned in: W. R. Mixon, "Application of Detached Turbulence Promoters to a Tubular Hyperfiltration System with Dynamically Formed Membranes," ORNL-TM-2150, March 1969.

TABLE 3.6
HYPERFILTRATION BY DUAL-LAYER HYDROUS Zr(IV) OXIDE-ACRYSOL A-3
MEMBRANES ON 4A-3 CARBON TUBES

(0.05 M NaCl, 950 psig, pH 7-9, 25°C)

Run	Pressure (psig)	Time (hours)	pH*	Porous Support**	Velocity (fps)	Flux (gfd)	R _{obs} (%)
1	600	>16	3.3	4A-3 (I)	33	41	65
			3.3	4A-3 (O)	39	41	54
			3.3	Control	36	225	65
2	600	~4	3.1	4A-3 (I)	34	77	79
			3.1	4A-3 (O)	39	61	63
			3.1	Control	36	81	85
	1000	>16	3.1	4A-3 (I)	34	129	82
			3.1	4A-3 (O)	39	105	71
			3.1	Control	36	147	84
	600	>16	3.1	4A-3 (I)	34	86	80
			3.1	4A-3 (O)	39	68	66
			3.1	Control	36	89	80
3	1000	>16	3.1	4A-3 (I)	34	31	56
			3.1	4A-3 (O)	39	50	59
			3.1	Control	36	188	90
4	1000	>16	3.1	4A-3 (I)	25	52	70
			3.1	4A-3 (O)	25	38	79
			3.1	4A-3 (O)	40	41	73
5	1000	~6	2.2	4A-3 (O)	35	23	83
			2.2	Control	35	98	94

*pH at which PAA additive added to feed.

** (I) = inside pressurization and flow; (O) outside pressurization and flow; Control = 0.45-μ Acropor AN.

Effect of pressure during formation: Membranes formed and operated under 1000 psig did not perform appreciably better than did those at 600 psig. However, those membranes formed at 600 psig and operated at 1000 psig, see Run 2, were better than any others in this series of tests.

Velocity effects: The two membranes formed with outside pressurization in Run 4, one at 25 fps and the other at 40 fps, did not demonstrate any great effect of formation velocity.

Effect of pH at time of PAA addition: Although the rejection of the membrane on the 4A-3 tube of Run 5 is somewhat better than that experienced in the earlier runs, the lower flux does not suggest advantages from using low pH at time of addition of PAA when forming dual-layer membranes on 4A-3 carbon tubes.

Comparison with control: Although the control membranes formed on the Acropor supports in this series of runs were not especially good, except for perhaps Runs 3 and 5, they were usually appreciably better than those formed on the 4A-3 carbon tubes. The marked improvement in membrane performance upon going to 1000 psig from 600 psig in Run 2 suggests an avenue for further research on these and other carbon tubes.

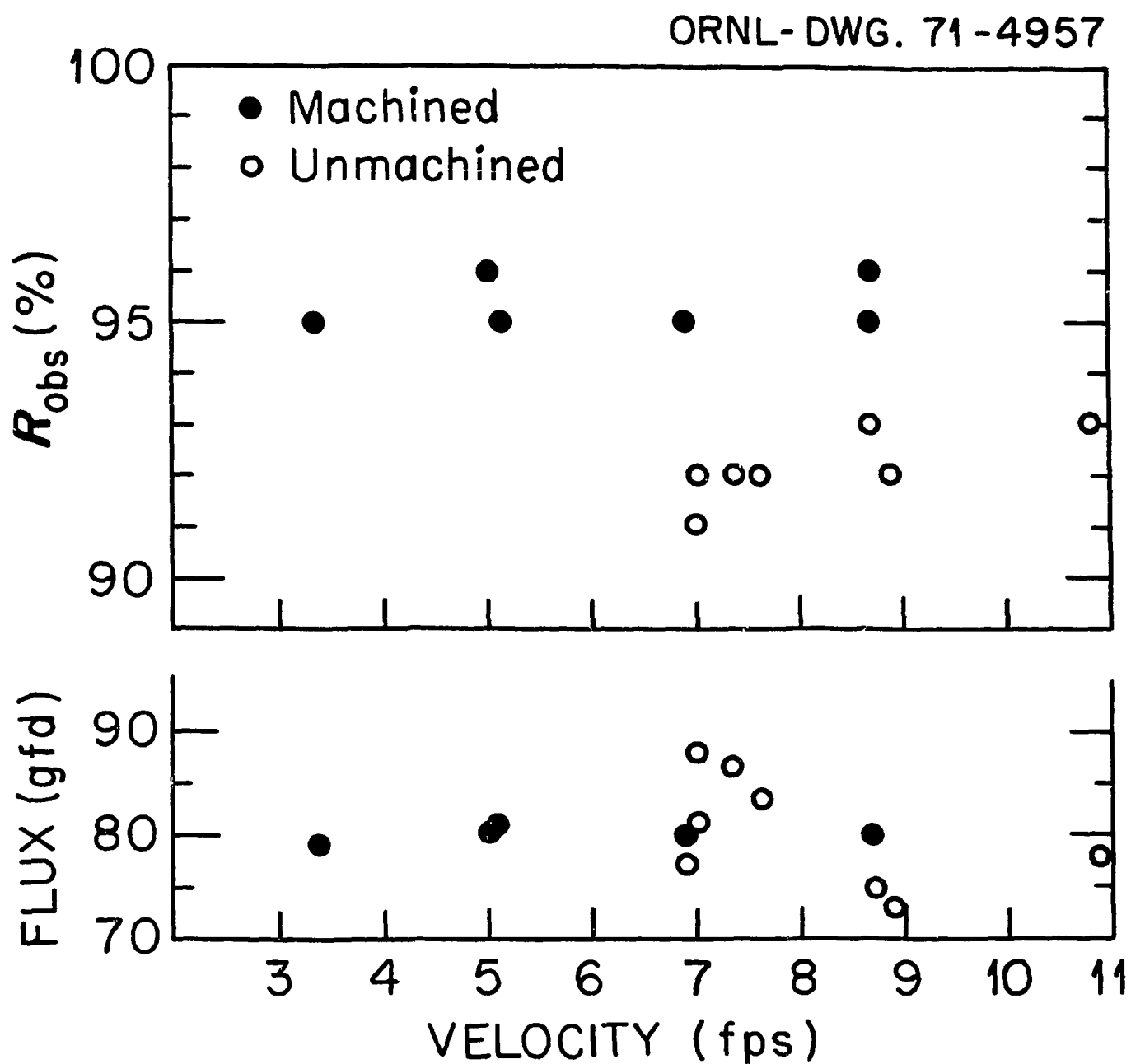
Rejection of Coalinga water: The membranes of Run 1 and Run 5 were tested with Coalinga water, and found wanting. By conductivity, rejections for the carbon tube membranes of Run 1 averaged about 50% at about 30 gfd compared with the control's 55% rejection at 147 gfd, both at 600 psig. In Run 5, at 950 psig, the values were 72% at 18 gfd with the control at 85% at 68 gfd.

3.1.2.1.3.2 563-6A and 563-6C Carbon Tubes. The 563-6C tubes, hereinafter referred to as 6C, were tested both with and without removal of the extrusion skin. The first such run was made at 20°C, 14.5 fps, and 900 psig, and demonstrated a very large machining effect. At the end of 20 hours of operation, following the formation of the membrane, the machined tube rejected 88% of 0.05 M NaCl at 64 gfd, while the unmachined tube showed only 45% rejection at 29 gfd. It was at this time that we decided to try to form and test membranes at higher temperatures, both to see what results might be obtained in this way, and also to test performance at the temperatures typical of many industrial waste streams.

In the second run, using one machined and one unmachined 6C carbon tube, both layers of the membrane were formed at about 60°C. The hydrous oxide layer was formed at pH 3.7, while Acrysol A-3 was added to the feed solution at pH 1.9. As the pH was raised, the rejections of both supports reached a maximum at about pH 5.2 and then decreased as the pH was raised further. When the pH was returned to 5, the fluxes were much higher than those originally seen at that pH, but the rejections had fallen off considerably; part of the membrane had apparently left the surface. The pH was lowered to 2.6, 25 ppm of PAA were added, and this time, with very gradual addition of base, rejections rose to greater than 90%. Properties of the membranes at neutral pH, with rejections from 94 to 97%, verified by Cl^- analysis as well as by conductivity, and fluxes near 100 gfd, were very encouraging, especially considering the formation velocities, which were about 8 fps. The effect of temperature on the hyperfiltration performances of these membranes was shown as Fig. 5 in Section 3.1.1. Rejections were not appreciably affected by temperature changes, but the fluxes varied roughly as the inverse of the viscosity.

After an overnight shutdown, the membranes described above were tested with Coalinga water. The results are listed in Table 3.7. The fluxes dropped rapidly during the first hour or so of operation, but fell more slowly thereafter. Rejections remained relatively constant, and were quite high for all of the components of the Coalinga water. The same temperature dependences that were observed with NaCl solutions were again observed with Coalinga water.

Following the Coalinga studies, the same membranes, now somewhat reduced in permeability, were tested for the effect of pressure (Fig. 6, Section 3.1.1), and of velocity (Fig. 3.2) on their performance with 0.05 M NaCl solutions. Both rejections and fluxes declined as the pressure was decreased from the 900 psig at which the membranes were formed, and there was a certain amount of hysteresis as the pressure was once again raised to the original value. Very little effect was noted in either flux or rejection with variations in the flow velocities, but all of the velocities used here were low, and velocity effects might very well be hidden by scatter in the data.



Effect of velocity on hyperfiltration
of 0.05 *M* NaCl by dual-layer
hydrous Zr(IV) oxide-Acrysol A-3
membranes on 6C carbon tubes.
(900 psig, 60°C, pH 7)

Fig. 3.2

TABLE 3.7
HYPERFILTRATION OF COALINGA WATER^a BY
DUAL-LAYER MEMBRANES ON 6C CARBON TUBES
(900 psig, 8 fps)

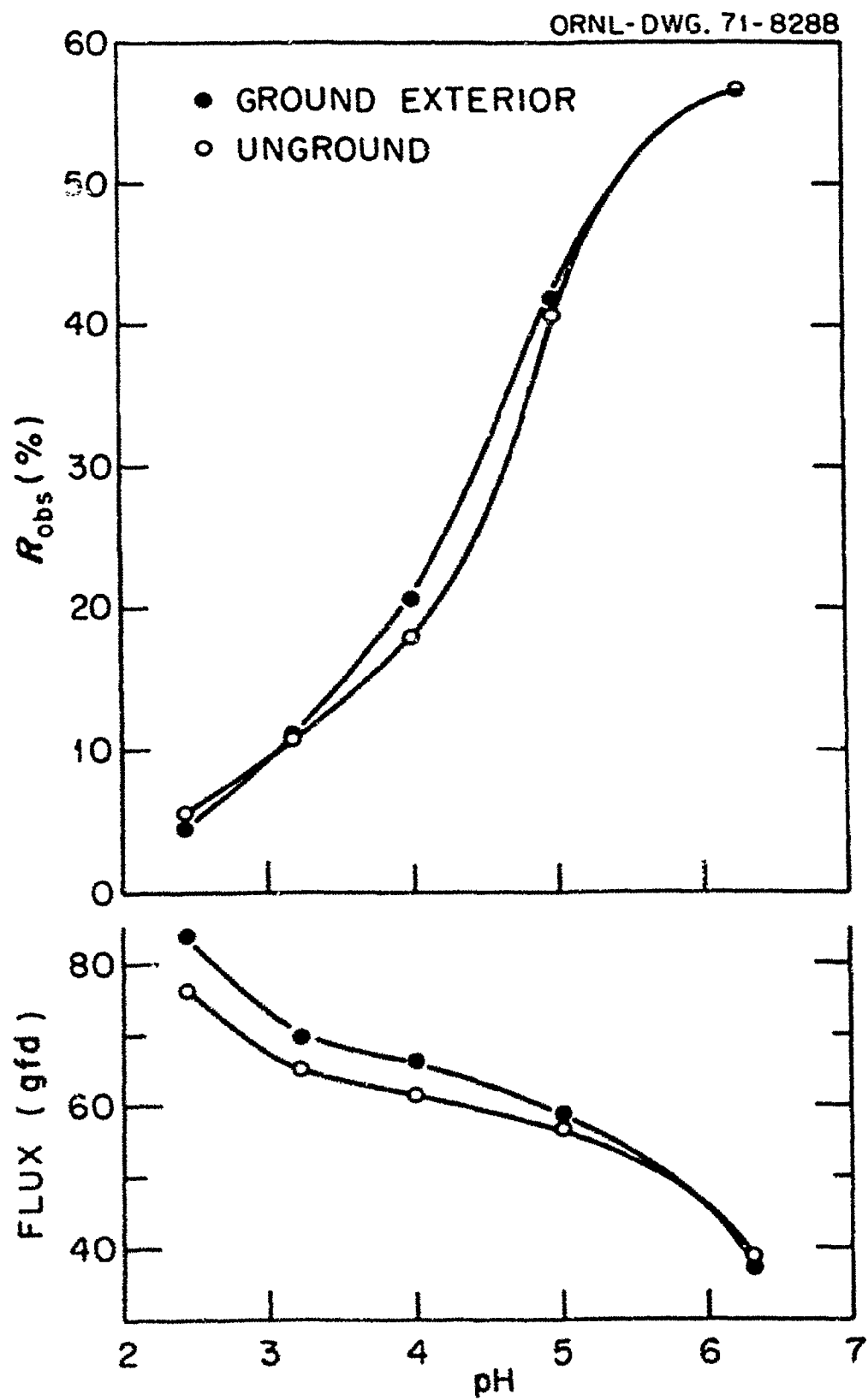
Time ^b	Temp. (°C)	Support ^c	Flux (gfd)	Rejections (%)			
				Conduc- tivity	Cl ⁻	Ca(II) + Mg(II)	Total Cation
0.5	62	U	75	91	83	98	91
		M	96	95	89	99	95
1.0	59	U	55	91	--	--	--
		M	62	95	--	--	--
2.0	72	U	65	92	--	--	--
		M	67	95	--	--	--
2.5	39	U	35	92	--	--	--
		M	33	93	--	--	--
3.0	41	U	35	93	--	--	--
		M	35	94	--	--	--
3.5	60	U	50	93	86	98	93
		M	56	96	91	99	96
4.0	60	U	50	93	--	--	--
		M	56	96	--	--	--

a. Refer to Table 3.68, Section 3.3.1.

b. Time in hours from addition of Coalinga water.

c. U = Unmachined 6C carbon tube; M = machined 6C carbon tube.

The improvements noted above when the extrusion skin was removed may have resulted from the increased permeability of the tubes with the skin removed, or the grinding may have altered the surface in such a way as to make it more amenable to membrane formation and retention, or both. We attempted to determine which by simultaneously forming membranes on the inside of two tubes, one with the exterior surface ground while the other, under otherwise identical conditions, was left unground. The results are given in Fig. 3.3. Although neither tube formed good membranes, a result not uncommon at 300 psig, there is negligible difference between them, either in flow or in rejection. This would indicate that the



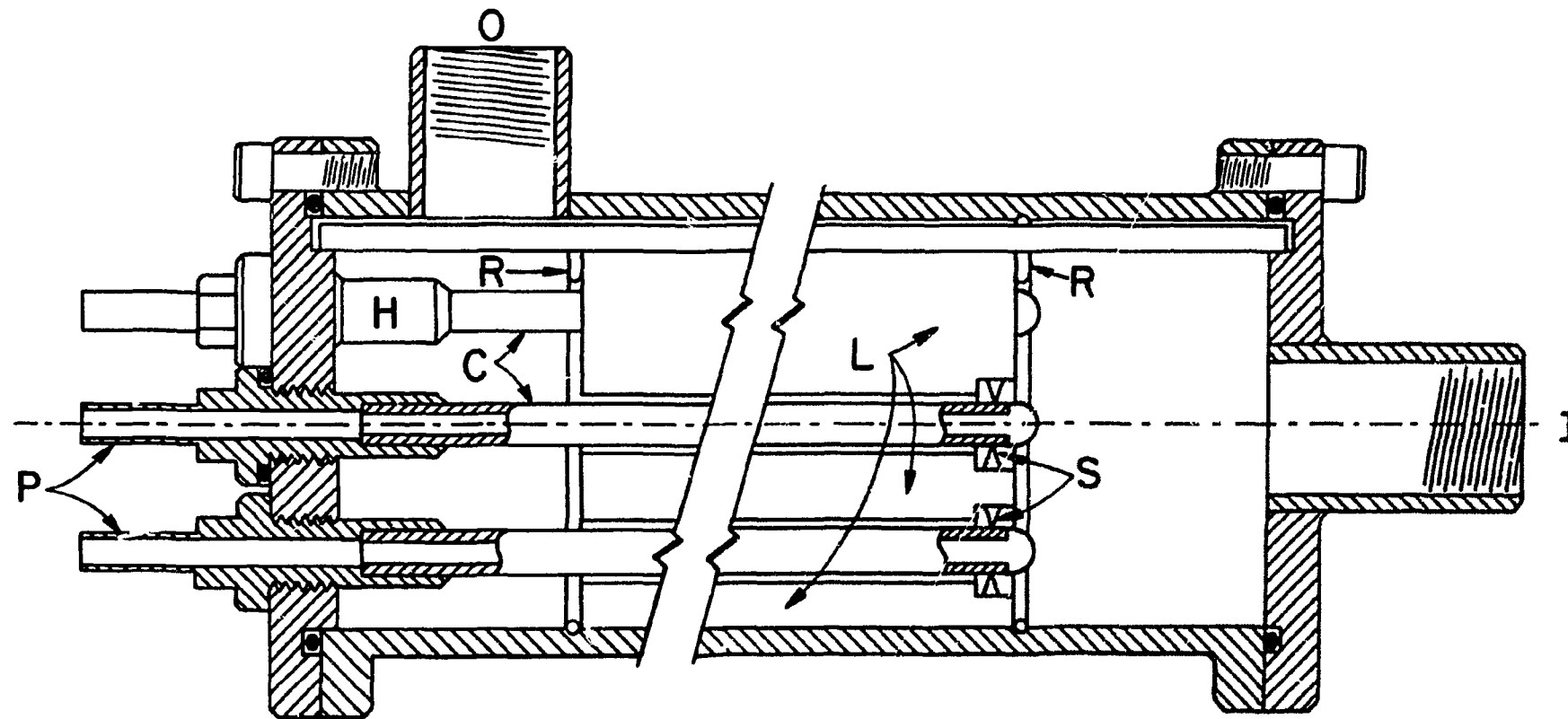
PAA MEMBRANE FORMATION, HYDROUS $Zr(IV)$
OXIDE SUBLAYER, ON 6C CARBON TUBES.
INSIDE FLOW AND PRESSURIZATION.
(0.05M NaCl, 300 psig, 55°C, 30 fps)

Fig. 3.3

differences reported previously for ground and unground tubes are due more to changes in surface conditions than they are to changes in porosity. Scanning electron micrographs of the two surfaces indicated that the ground surface is much rougher than that of the tube with the extrusion skin intact.

3.1.2.1.3.3 Carbon Tube Protomodules. Performances of membranes on the 563-6A (6A) carbon tubes were compared to those on 6C tubes by experiments carried out using a small module for experiments with tubular supports designed by A. J. Shor. A half-sectional schematic diagram of the module is shown in Fig. 3.4. The pressurized feed solution enters the module at inlet I, is channeled by machined lucite blocks (L) to flow through an annulus around each of the seven carbon tubes (C), and leaves the module at the outlet (O). The product is recovered from the tubes P. The tubes are fastened with epoxy resin to the holders H, which may be individually removed from the module should a carbon tube need to be replaced. The tubes are positioned in their respective channels by spiders (S), which are designed to offer little impedance to flow. The lucite blocks are held in place by snap rings R. The upstream ends of the tubes are plugged with steel inserts which are sealed with epoxy cement. Each of the seven tubes can be up to about 128 cm (~50 inches) long, and the total surface area available for hyperfiltration, with 0.4 in. o.d. tubes, is about 3 ft². Tubes of other sizes can be used by substituting lucite blocks with channels of other diameters.

In the first test, performed on loop 7, we formed dual-layer hydrous Zr(IV) oxide-Acrysol A-3 membranes on three 6A and four 6C carbon tubes, all unground. The hydrous oxide sublayer was slow to form, presumably because the Zr(IV) was depleted from the feed by deposition on the relatively large area of the membrane support. However, by adding three times the usual amount, to a nominal concentration of 3×10^{-4} , we were able to form a satisfactory sublayer. It was not necessary to add additional PAA beyond the 50 ppm we normally use to form the polycarboxylate layer. The PAA was added at pH 2.3. The results of this first test are summarized in Table 3.8. The data tabulated were taken after an overnight run (~16 hours) and indicate disappointingly low rejections and fluxes.



Carbon tube module for hyperfiltration studies.
 I, feed inlet ; O, feed outlet ; P, product outlet ; C, carbon tubes ;
 H, tube holders (7 each) ; L, lucite block with machined channels ;
 S, tube-positioning spiders ; R, snap rings to position lucite block .

Fig. 3.4

TABLE 3.8
COMPARISON OF 6A AND 6C CARBON TUBES IN A SEVEN-TUBE
EXPERIMENTAL HYPERFILTRATION MODULE
(24 fps, 950 psig, 25°C, pH ~ 7.6)

<u>Feed</u>	<u>6A Tubes^a</u>		<u>6C Tubes^b</u>	
	<u>Flux (gfd)</u>	<u>R_{obs} (%)</u>	<u>Flux (gfd)</u>	<u>R_{obs} (%)</u>
0.05 M NaCl	7	77	29	83
Coalinga ^c Water:	6		24	
Conductivity		57		68
Cl ⁻		53		62
Ca(II) + Mg(II)		70		84
Total Anion		62		72

^aAverage of three.

^bAverage of four.

^cRefer to Table 3.68, Section 3.3.1.

A thirty-minute wash with 1 M NaOH brought the fluxes up to about 27 gfd for the 6A's and about 150 gfd for the 6C's, but the rejections of 0.05 M NaCl dropped to less than 25% for both types.

Following a weekend shutdown, we tried to improve the performance of the carbon tubes by adding, at pH 2.9, 50 ppm of the low-molecular-weight (~5000) Tamol 850 polymethacrylic acid. After raising the pH to 7.6 in a series of steps, rejections were about 78% at 40 gfd for the 6C's and 72% at 8 gfd for the 6A's. The loop was shut down and the module removed to storage.

During the three to four weeks following the storage of the module, we continued to experiment with carbon tubes in our usual single-finger configurations. A series of experiments testing the effect of temperature on rejections and fluxes, described in the previous section, led to favorable performances by membranes on carbon supports. This prompted us to reactivate the module, and it, with the original tubes still in place, was placed into loop 8 for operation. At pH 2.2, 50 ppm Acrysol A-3

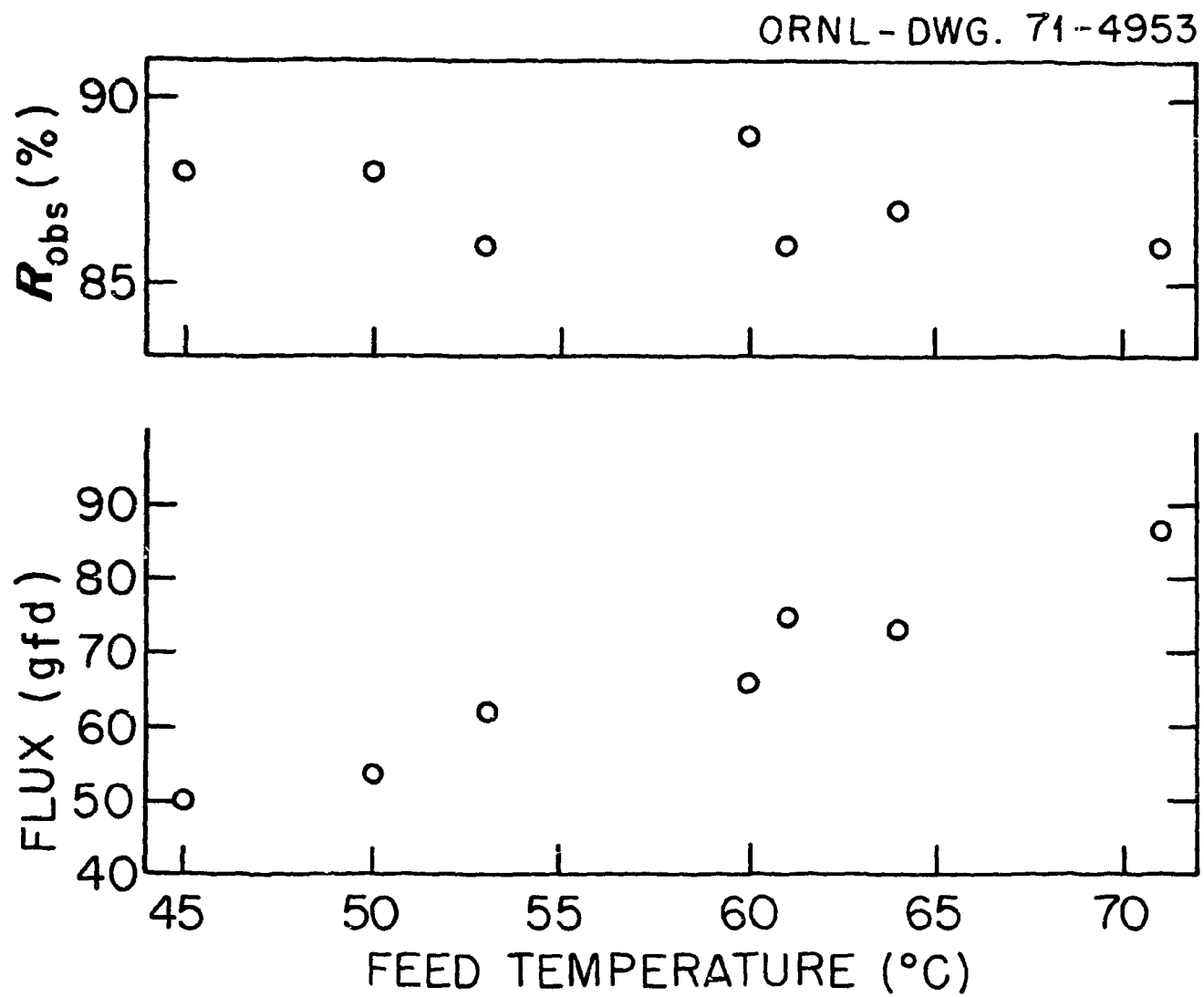
were added to the feed, the temperature of the feed was raised to $\sim 60^{\circ}\text{C}$, and the pH slowly raised to 7.0. At that point, the rejections of 0.05 M NaCl were about 89% for both types of tube, and the fluxes, while still low, had improved by 30 to 40% over the first-run results of Table 3.8.

Encouraged by this improved performance, we removed the original batch of carbon tubes and replaced them with seven fresh 6C tubes. We eliminated the 6A's because of their poor fluxes. With the more porous tubes in place, it was necessary to add seven times the usual amount of Zr(IV) before a satisfactory sublayer would form. We did this at pH 4, with the pressure at 900 psig, the temperature at 60°C ., and the velocity at 14 fps, the maximum we could generate in loop 8 in which the module was now placed. The PAA was added at pH 2.3, and the pH gradually raised to 7.1. At that point the average rejection was 81% with an average flux of 85 gfd. The pH was once again reduced to 2.3, 25 ppm Acrysol A-3 were added, and the pH again gradually raised to 7. At this point, the average rejection was 91% but the flux had dropped to 54 gfd.

After an overnight shutdown, the effect of temperature on rejections and fluxes was determined. The results are shown in Fig. 3.5. Temperature apparently has little effect on rejections, but does have a pronounced effect on the flux. The latter effect results from the decrease in viscosity as the feed temperature is increased, and has been seen often before.²⁵

Through the courtesy of Drs. O. C. Trulson and L. M. Litz of Union Carbide Corporation, we received two hyperfiltration protomodels for test and evaluation. Each module, designed for outside flow and pressurization, contained seven porous 6C carbon tubes which were fastened in parallel inside a two-inch diameter stainless steel tube. The area in each module was $\sim 2.25\text{ ft}^2$. The two modules differed only in the way in which the tubes were fastened at the ends; in the one case they were fixed firmly at the ends with epoxy resin and in the other they were allowed to float through "O-ring" seals at steel bulkheads flanged onto the tubing. The exterior surface of the 6C tubes had been ground to remove the extrusion skin.

We first tried to form membranes in the protomodel in which the tubes had been fastened with epoxy, but this failed when several of the tubes ruptured, probably due to strain induced by temperature changes.



Effect of temperature on the hyperfiltration performance of 6C carbon-tube module. Points average of 7 tubes. (0.05 *M* NaCl, 900 psig, 14 fps, pH 6.9, dual layer hydrous Zr(IV) oxide-Acrysol A-3 membranes).

Fig. 3.5

The module with the "O-ring" seals was then inserted into the test loop and used over a four-week period to carry out a set of experiments described below.

Membrane formation: We formed membranes on the carbon tubes of the protomodule by using, at 25°C, the standard formation techniques described earlier in Section 3.1.1. The flow velocity was about 12.5 fps and during the course of the sublayer formation we twice added additional increments of Zr(IV), to a total concentration of 1.7×10^{-4} . It took about three hours for the rejection of 0.05 M NaCl to reach 32% (588 gfd), and at that point we rinsed excess Zr(IV) from the system and added 50 ppm of Acrysol A-3 to the feed at pH 2.2. The pH was increased in steps to 6.4, at which point the rejection of 0.05 M NaCl was 88% at 86 gfd. We rinsed the excess PAA from the solution, adjusted the pH to 6.7, and began to increase the temperature of the feed. The changes in flux and rejection with temperature are shown in Table 3.9.

TABLE 3.9
TEMPERATURE DEPENDENCE OF HYPERFILTRATION OF 0.05 M NaCl BY DUAL-LAYER
MEMBRANES IN A UNION CARBIDE CARBON TUBE PROTOMODULE

(950 psig, 12.4 fps, pH 6.7)

Temperature (°C)	Flux (gfd)	Product Rate (gpd)	R_{obs} (%)
25	83	188	87
40	126	286	86
50	185	420	80
57	235	533	80
63	302	686	76
64	320	726	71
67	336	762	69

In an attempt to improve rejection, 25 ppm PAA were added to the feed, and the pH cycled to 2.5 and back, in steps, to 6.7. At this point, the rejection at 64°C was 90% with a flux of 98 gfd.

These membranes were used in a dye waste test, and then in the Coalinga test described in Section 3.3.1.1.7. After the Coalinga water test, the loop was rinsed with distilled water and washed for one hour at

25°C and two hours at 60°C with 1 M NaOH. The hydrous oxide sublayer was reformed using 5×10^{-5} M Zr(IV), which is less than the 10^{-4} M usually used for membrane formation on fresh supports, and the PAA layer was reformed using 25 ppm PAA, both formations at 25°C. For 0.05 M NaCl, the flux at 25°C was 37 gfd with 90% rejection, while at 62°C the flux was 111 gfd at 86%. The module was then used in some kraft process waste tests described in reference 20.

Following the runs with the kraft waste the membranes were once again regenerated with a half-hour wash with 0.1 M Na₂CO₃ at pH 10. Although the flux increased to 96 gfd, the rejection of 0.05 M NaCl was only 68%. An acid cycle in the presence of PAA increased rejection to 84%, but the flux dropped to 35 gfd. At this point, we gave the system a complete cleaning, with the carbon tubes in place, by washing first one hour with 1 M NaOH, then one hour with 1 M HNO₃, rinsing with 0.5 M NaOH, and finally rinsing for one hour with distilled water. Both layers of the membrane were then reformed on the carbon tubes by the standard procedure, and rejection of 0.05 M NaCl was 80% at 91 gfd.

Membrane regeneration trials: We next did a series of experiments in which we tested the module and membranes with Coalinga water and NaCl while trying various things to maintain or restore fluxes while maintaining rejections. The results are listed in chronological order in Table 3.10. The one-half hour Na₂CO₃ wash (between runs 1 and 2) was as effective as any in restoring flux, and it is by far the simplest to do. The rejections, however, were not as good after the wash as before it. The wash with 1 M NaCl was not effective in this case. The performance characteristics of the membranes given in Table 3.10 are not as good as those achieved earlier in the history of these supports (see Table 3.9) and none of the cleanup procedures tried improved them very much. The carbon tubes used here are capable of withstanding a few hundred pounds inside pressure, and it is possible that with minor modifications of the module, backwashing, perhaps coupled with chemical treatment, would be effective in restoring the supports to their original condition.

TABLE 3.10
CHRONOLOGICAL RECORD OF REGENERATION TESTS OF MEMBRANES FORMED
ON CARBON TUBES IN UNION CARBIDE PROTOMODULE
(950 psig, 25°C (unless noted), 12.5 fps)

Run	Feed Solution	Time ^a	Flux (gfd)	Conduc-tivity	R _{obs} (%)	
					Cl ⁻	Ca(II) + Mg(II)
1	Coalinga ^c	0.5	34	73	--	--
		18.0	24	77	70	92
		22.0	25	81	70	92
Wash: one-half hour with Na ₂ CO ₃ , pH 10.						
2	Coalinga ^c	0.5	43	59	--	--
		1.5	39	62	56	82
		18.0	32	67	61	86
Wash: Complete cleanup. ^b Acid cycle with 25 ppm PAA.						
3	0.05 <u>M</u> NaCl	0.5	43	84	--	--
		18.0	44	84	--	--
	Coalinga ^c	0.5	21	75	--	--
		2.0	14	79	73	93
Wash: Fifty minutes with 1 <u>M</u> NaCl, 950 psig.						
4	Coalinga ^c	0.5	16	76	--	--
		64.0	12	78	75	91
Wash: Complete cleanup. ^b Both layers reformed.						
5	0.05 <u>M</u> NaCl	0.5	82	78	--	--
		18.0	87	74	--	--
Wash: Complete cleanup. ^b Temperature raised to 60°C; both layers reformed at 60°C.						
6	0.05 <u>M</u> NaCl @ 60°C	0.5	133	79	--	--
		18.0	109	84	--	--

^aTime in hours from the time the feed solution was added.

^bComplete cleanup: One hour wash with 1 M NaOH, one hour with 1 M HNO₃, rinse with 0.5 M NaOH, and one-hour rinse with water.

^cRefer to Table 3.68, Section 3.3.1.

3.1.2.1.4 Woven Fabric Hoses. Results with fire hose jackets have indicated that such jackets pretreated with filteraids have promise as supports.²⁶ With the feed on the inside, the hose provides both a pressure support and a surface for membrane formation. A difficulty, particularly at pressures above 500 psig, has been the frequency of membrane defects, evidenced by sprays. Hoses of smaller diameter might ameliorate this situation. It is difficult to obtain weaves equivalent to fire hose jackets in diameters less than one inch, but we have briefly tested tubes of several other fabrics (Table 3.11). Some of these tests were carried out in a preliminary survey of the treatment of textile dye waste solutions, supported by the National Science Foundation-RANN.

The first test utilized the two 1/4" hoses listed in Table 3.11, one of cotton and one of nylon. Seven-inch sections were sealed with epoxy to metal tubes, and pressurized feeds were circulated inside. After a coat of filteraid (Hyflo Supercel) had been laid, a solution generated in the dyeing of a cotton-polyester fabric was introduced. Small jets indicated that a membrane which adequately covered the surface did not form. Introduction of hydrous Zr(IV) oxide and more filteraid gave some indication of plugging of the cotton hose, but the nylon did not improve, and the system was shut down to remove it. One half-hour after resuming operation, a difference between the appearance of feed and product indicated that some filtration was occurring. At this time, the flux was about 100 gfd at 200 psig (6 fps circulation velocity); both conductivity and organic carbon rejection were about 45%. Raising the pressure to 250 psig resulted in obvious leaks, which quickly plugged. At 700 psig, more leaks occurred, particularly near the tube-hose connections, and when they did not cease, the experiment was terminated. The 1/4" cotton hose may merit further testing.

The Buffalo 5/8" nylon hose was tested unsupported with pressure on the inside. A hydrous Zr(IV) oxide membrane, formed after treatment with Celite 505 and 535 filteraid, rejected 12% of salt from 0.05 M NaCl at about 100 gfd (200 psig). At 300 psig, the fabric failed near the end fitting.

TABLE 3.11
FABRIC HOSES TESTED AS DYNAMIC MEMBRANE SUPPORTS

<u>Diameter</u>	<u>Material</u>	<u>Manufacturer's Identification</u>	<u>Source^a</u>
1/4"	Cotton	2-20-48 T72/B72	A
1/4"	Nylon	T68/B72	A
3/8"	Cotton	2-20-48 T68/B72	A
3/8"	Dacron	3-ply polyester, 3x 35/50 on 48 collier	A
5/8"	Nylon		B

(a) A - Waverly Braid Mills, Gastonia, N. C.
B - Buffalo Weaving and Belting

We made one attempt to form a hyperfiltration membrane on a woven hose, Black Nylon Hose #8926, manufactured by Buffalo Weaving and Belting Co. The hose, which was one-half inch in diameter, was attached to the test loop with special pressure fittings so as to achieve inside flow and pressurization. We plugged the hose first with 50 ppm of an equal-weight mixture of three filter aids, Celite 550, Celite 505, and Hyflo Supercel, and then added hydrous Zr(IV) oxide to the feed to a concentration of 5×10^{-4} M. The film which formed on the inside of the hose was very unstable, even after more filter aid was added. We reached 350 psig at 12 fps where the rejection was 18% at 337 gfd (0.05 M NaCl), but then more sprays appeared, and rejection decreased drastically.

3.1.2.1.5 Impregnated Glass Fiber Tubes. Through the courtesy of Dr. Malcolm Morrison, we received several samples of a resin-impregnated glass fiber tube which Calgon-Havens Systems, now Universal Oil Products, uses as a support for their reverse osmosis membranes. On the inside of one tube, we formed a dual-layer membrane by our standard techniques using 33 fps and 950 psig, but were able to realize only 2% rejection of 0.05 M

NaCl, at 65 gfd. In a second attempt, we precoated a tube with a filter aid, using 10 ppm Dicalite Speedex in water, before applying the dual-layer membrane. Results were only slightly better: 4% at 80 gfd. We suspect that concentration polarization may have been very high; that the salt-rejecting membrane may have been embedded deeply into the porous wall where the lack of axial flow would permit excessive salt buildup.

3.1.2.1.6 Celanese Micro-Porous Polypropylene. Through the courtesy of V. Lampariello of Celanese Plastics Co., we received two samples of micro-porous polypropylene films made by his company. A dual-layer membrane on a sample labeled 2400W showed a rejection of 88% at 38 gfd flux (950 psig, 35 fps, pH $\sim$ 7). With Coalinga water, this same membrane rejected 59% of the Cl^- and 88% of the $\text{Ca(II)} + \text{Mg(II)}$ at a flux of 27 gfd. A membrane on the Celanese 2400, however, rejected only 50% of 0.05 M NaCl at 10 gfd.

3.1.2.1.7 Films from DeBell & Richardson. We received press mouldings of two DeBell and Richardson formulations from Mr. R. A. White. A hydrous oxide sublayer on formulation 96858-1, which had a nominal porosity of 44 volume percent void space and approximately 0.1 micron hole size, rejected 60% of 0.05 M NaCl at 99 gfd (950 psig, 35 fps, 25°C, pH 3.9). The dual-layer membrane on this formulation had an R_{obs} of 81% at 26 gfd. After twenty-four hours of operation under the same conditions, the flux had risen to 32 gfd, but the rejection had dropped to 77%. When tested with Coalinga water, the membrane showed a rejection, by conductivity, of 74% at 19 gfd.

The second DeBell & Richardson formulation, 82653, with 17 volume percent void space and approximately 0.3 micron pore size, did not do as well. For 0.05 M NaCl, rejection was 20% and the flux at 950 psig was 2.5 gfd.

3.1.2.1.8 Aqua-Chem Tubes. Through the courtesy of Mr. James Kavanaugh of Aqua-Chem, we received an aluminum tube with axial product-collecting grooves, similar in configuration to those they use in their commercially available cellulose acetate modules. The impregnated paper tube membrane supports we received as liners for the aluminum tube had about 0.25 ft² of surface area, and were similar to their production tubes

except that the cellulose acetate membrane had not been applied to the inside of the tubes. We were unable to form hydrous Zr(IV) oxide membranes on the inside of any of the first batch of tubes supplied, presumably because they were too porous to plug properly with the hydrous oxide.

One attempt to line one of the tubes with 0.45 μ Acropor AN failed when the lining tore as soon as the circulation pump was activated.

A second batch of tubes with a less-permeable coating was then tested with somewhat better results. In the first run on these supports, dual-layer membranes were formed at 900 psig, 35 fps, and 25°C. At pH 7.1, the rejection of 0.05 M NaCl was 78% at 204 gfd. After an acid cycle in the presence of 50 ppm PAA, the rejection increased to 84% but the flux dropped to 167 gfd. After 16 hours of operation, the flux had decreased to 149 gfd, with the rejection unchanged. A drop in circulation velocity to 5 fps resulted in a rejection decline to 73% without a change in flux, but this effect was reversible when the velocity was returned to 35 fps. This membrane removed about 60% of the chloride from Coalinga water at about 90 gfd after 20 hours of exposure to it.

In a second run using the Aqua-Chem protomodule, we simultaneously formed a membrane on a standard 0.22- μ Millipore-wrapped porous stainless steel tube for comparison purposes. The membranes were formed at 30 fps, 950 psig, and around 25°C, and the results are listed in Table 3.12. A membrane was obviously formed on the Aqua-Chem tube, but the higher fluxes and lower rejections than those of the control suggest the possibility of leakage around the fittings at the end of the tubes. Small leaks at these points would allow some feed solution to mix with the product.

In a third run, we mixed 25 ppm Hyflo SuperCel and 25 ppm Celite 505 filteraids to the feed during the formation of the hydrous Zr(IV) oxide sub-layer. Conditions were otherwise similar, as were the results. The final rejection for the dual layer was 68% at 105 gfd. Upon raising the temperature to 60°, we encountered a drastic loss in flux, perhaps due to compaction of either the paper tube or the coating upon it. In any event, the run was terminated.

TABLE 3.12

TEST OF DYNAMIC DUAL-LAYER MEMBRANE IN AQUA-CHEM PROTOMODULE
(950 psig, 30 fps, 25-27°C, pH ~ 7)

Test Solution	Aqua-Chem Protomodule				0.22- μ Millipore Control			
	Flux (gfd)	R_{obs} (%)			Flux (gfd)	R_{obs} (%)		
		Cond.	Cl ⁻	Ca(II) + Mg(II)		Cond.	Cl ⁻	Ca(II) + Mg(II)
0.05 M NaCl	107	69			83	94		
Coalinga* water:								
1 hour:	104	64	44	86	40	90	83	98
18 hours:	100	65	42	85	37	91	85	98

*Refer to Table 3.68, Section 3.3.1.

The fourth and final test we made with the Aqua-Chem protomodule differed from the others in that we used a hydrous oxide feed stock that had been refluxed for 48 hours rather than the usual 24. This material is considerably more turbid than that usually used, an indication of higher aggregation. However, after formation of the PAA layer, rejection of 0.05 M NaCl was similar, 83% at 128 gfd. After two hours of exposure to Coalinga water, the membrane rejected 47% of the chloride and 71% of the Ca(II) + Mg(II) at 98 gfd.

3.1.2.1.9 North Star Polysulfone-Lined Tube. At 800 psig, 25°C, and only 5 fps, we were able to form a Zr(IV)-PAA membrane on a polysulfone-lined American Standard (now Abcor) tube, provided through the courtesy of Dr. L. T. Rozelle of North Star Research and Development Institute, which uses the lined tubes to support thin film cellulose acetate membranes.²⁷ With 0.05 M NaCl, the membrane showed good rejection (96%), but, at 35 gfd, the flux was lower than those we normally attain with dynamic membranes. The low velocity and the relatively low pressure, however, undoubtedly contribute to the low flux. An earlier attempt to form a membrane at 35 fps on a polysulfone-lined tube resulted in a rupture of the polysulfone support.

After 48 hours of operation with 0.05 M NaCl, the membrane formed at 5 fps showed an increase in flux to about 42 gfd, while the rejection had dropped to 93%. The loop was shut down for a weekend, and when it was restarted, the membrane had a rejection of 91% at 50 gfd. The NaCl was rinsed out and the membrane tested against Coalinga water. Over a 24-hour period, the flux remained constant at 20 gfd while the rejection was 92-93% by conductivity.

Following the Coalinga water test, the test section containing the membrane was removed and stored in water for four days. At the end of this time, the loop was cleaned up and the test section reinstalled. Over a 48-hour period with 0.05 M NaCl at 800 psig, 5 fps, and pH about 8, fluxes varied from 47-61 gfd while rejections varied from 84 to 88%. A one-day test with Coalinga water gave 83% rejection at about 36 gfd; a one-day test with Roswell water gave 70% rejection at about 37 gfd.

The membrane was subsequently tested with simulated pretreated Colorado River water in which the Ca(II) and Mg(II) had been replaced by sodium. In a 19-hour test, flux remained constant at 42 gfd with 91% rejection. When Ca(II) was added to the extent normally found in Colorado River water, rejection fell to 72% while the flux decreased to about 40 gfd.

3.1.2.1.10. General Electric Nuclepore Films. General Electric markets films in which pores of a narrow range of sizes are produced by irradiation, followed by etching. We received samples of several pore sizes through the courtesy of Mr. H. J. Schneider of General Electric Co. We have made preliminary tests on two pore sizes, 0.4 micron and 0.6 micron. With the former, the support compared favorably with others used in the same run. (Table 3.13). In this run, rejections were, with one exception, high, but fluxes were uniformly lower than those we expect for fresh dynamic membranes.

In the first test with 0.6-micron Nuclepore, the membrane, of 78% rejection and 43 gfd flux (0.05 M NaCl), was inferior to that formed on 0.45-micron Acropor at the same time (90% at 90 gfd). In a second test, the Nuclepore gave the same results as a 0.05-micron Millipore support, namely 88% at about 36 gfd.

TABLE 3.13
COMPARISON OF HYPERFILTRATION PROPERTIES OF Zr(IV)-PAA MEMBRANES
ON 0.4-MICRON NUCLEPORE WITH OTHER SUPPORTS
(950 psig, 25°C, 35 fps, 0.05 M NaCl)

<u>Support</u>	<u>Flux (gfd)</u>	<u>R_{obs} (%)</u>
0.4-μ Nuclepore	47	97
0.025-μ Millipore	49	98
0.22-μ Millipore	47	98
0.45-μ Acropor	52	86
0.27-μ Sela tube	50	95

With the limited evidence to date, the Nuclepore supports seem comparable to the Millipore and Acropor supports we have used extensively in the past, when used as supports for Zr(IV)-PAA membranes. Earlier experiments with dynamic membranes of low cross-linked poly(styrene sulfonate), (homogenized Dowex 50X0.25), on Nuclepore supports have been described in reference 15, pp. 218f and 242f.

3.1.2.1.11. Wolverine Porous Stainless Steel Tubes. A porous stainless steel tube under development by the Wolverine Tube Division of Universal Oil Products Company was suggested to us as a possible dynamic membrane support by Dr. Fred Witmer of OSW, and samples were kindly provided to us by Mr. T. J. Allen of Wolverine. The tubes were of type 316L stainless steel, 0.5 in. ID x 0.64 OD, and had a nominal pore size, outside surface, of about 1.5 microns interconnecting. Inside surface pore size was estimated at about 8 microns.

We fabricated two 60 cm² sections of the tube into two configurations such that in one pressure and flow could be applied to the outside of the tube, while in the other pressure and flow were on the inside. We then ran the following experiments on this one set of supports, cleaning and backwashing the supports thoroughly between runs. In the first run, we formed membranes on the tube in the usual way, without pretreatment with filter aids. Flow velocities were 34 fps inside, 30 fps outside. We were not able to get satisfactory Zr(IV) layers--the support plugged to less

than 100 gfd at rejections below about 20%. Twenty-one hours after the formation of the dual-layer with PAA, flux was less than 2 gfd with inside flow with ~40% rejection, and less than 20 gfd at 70% rejection, outside flow (0.05 M NaCl, 950 psig). We next tried to improve performance by circulating 10 ppm Celite 505 and 10 ppm Hyflo Supercel filter aids past the membrane to precoat them, prior to forming the Zr(IV)-PAA membranes in the regular manner. However, rejection and flux were unsatisfactory on the Zr(IV) sublayer and the experiment was discontinued. Insufficient cleanup of the tubes prior to starting was suspected. In the next attempt, 20 ppm Celite 505 were circulated under pressure until the flux through the tubes dropped to about 400 gfd. At that time, 10^{-4} M Zr(IV) was added at pH 4. At 950 psig, rejections of about 40% with fluxes 200-300 gfd were attained. The PAA (Acrysol A-3) was added at pH 2.3, and cycled to pH 6.3. At that time, the rejection of 0.05 M NaCl was 81% at 50 gfd, inside flow, and 79% at 41 gfd, outside flow. A recycle to acid conditions and back in the presence of 10^{-5} M Zr(IV) and 25 ppm PAA failed to improve rejections or fluxes. These membranes were tested briefly at 65°C with simulated brown stock wash, prepared by diluting, to 1% solids, "weak black liquor," the effluent from the digestion of pulp in the kraft process. Fluxes ran from 60 to 70 gfd, rejections by conductivity were about 80%, and appreciable color was apparent in the product streams.

In the fourth membrane formation trial, we precoated the supports with 20 ppm Celite 505 by circulating it under pressure, then added 10 ppm of Cabot Regal SR carbon black, and circulated this mixture for another 10 minutes. Circulation velocities during the pretreatment operation with again 34 and 30 fps, as before. The filter aid was rinsed out, and the dual-layer membranes formed in the regular way. Rejections of 0.05 M NaCl with inside flow were 79% at 37 gfd, with outside flow 70% at 37 gfd.

We reduced the circulation velocities to 16 and 14 fps, and repeated an acid cycle with the additives still in solution. There was a slight improvement in rejections, but none in flux.

We repeated the preceding experiment with the circulation velocities reduced to 16 and 14 fps, inside and outside flow, respectively, during the pretreatment phase as well as during the membrane formation process. Rejections of 0.05 M NaCl were considerably improved over that of the previous experiments, the completed membranes showing 90% rejection. Flux with inside flow was 48 gfd; with outside flow, it was 59 gfd. After overnight operation, fluxes and rejections remained essentially unchanged. This last set of membranes performed favorably with simulated brown stock wash in an experiment described in reference 21.

The experience here provides an example supporting the caution in the Summary of Section 3, that the conditions for formation of the best membranes may not be the same for all supports (also see Section 3.1.2.9). It is not clear, in retrospect, that some of the earlier attempts, without the layer of extremely fine carbon particles, might not have given better results if circulation velocities had been lower during formation. With Acropor and Millipore supports, in contrast, circulation velocities at the high end of those used here have appeared advantageous, at least during formation of the hydrous oxide layer.

3.1.2.1.12 Glasrock Porous Epoxy Rods. Mr. Edward R. Carter of Glasrock Products, Inc., of Atlanta, Ga., sent us two porous epoxy rods, each about 1/2" in diameter and about 6 inches long. One rod was made entirely of porous epoxy; the other was a composite tube of porous epoxy filled inside with bonded beads for structural back-up. The porosities were estimated at about 22%, the average pore diameter at about 4 microns. The two samples were precoated by circulating 20 ppm of Celite 505 filter-aid past them under pressure, and then membranes were formed on the coated epoxy rods and two control supports at 950 psig, 25°C, and 10 fps. The results of tests with these membranes are given in Table 3.14. The homogeneous epoxy rod is referred to as "coarse," the composite rod as "fine" in the table.

3.1.2.1.13 Summary. During the period of this report, we have formed many Zr(IV)-PAA membranes, on a variety of porous supports, under more or less standard formation conditions. The results of these formations are summarized in Table 3.15. The data listed with regard to flux

TABLE 3.14
Zr(IV)-PAA MEMBRANE FORMATION ON POROUS EPOXY RODS
(GLASROCK) AND TWO CONTROLS
(0.05 M NaCl, 950 psig, 25°C)

Time (hr:min)	pH	Support	Velocity (fps)	Flux (gfd)	R_{obs} (%)	
0	4.1	0.05 μ Millipore	10	182	46	Hydrous oxide sublayer
		0.6 μ Nuclepore	10	215	45	
		Coarse Glasrock	20	800	17	
		Fine Glasrock	22	61	34	
0 PAA added at pH 2.3						
0:45	2.3	0.05 μ Millipore	10	48	38	Beginning of formation of PAA layer
		0.6 μ Nuclepore	10	47	47	
		Coarse Glasrock	20	45	26	
		Fine Glasrock	22	11	24	
14:55	3.1	0.05 μ Millipore	10	28	55	
		0.6 μ Nuclepore	10	27	55	
		Coarse Glasrock	20	25	46	
		Fine Glasrock	22	5	40	
16:00	5.5	0.05 μ Millipore	10	30	82	
		0.6 μ Nuclepore	10	29	83	
		Coarse Glasrock	20	26	80	
		Fine Glasrock	22	5	53	
17:00	7.0	0.05 μ Millipore	10	34	89	
		0.6 μ Nuclepore	10	31	89	
		Coarse Glasrock	20	40	53	
		Fine Glasrock	22	4	40	
17:30	Rinsed additives additives from system; replaced the 0.05 <u>M</u> NaCl.					
20:45	6.8	0.05 μ Millipore	10	39	88	
		0.6 μ Nuclepore	10	36	88	
		Coarse Glasrock	20	24	82	
		Fine Glasrock	22	5	12	

and rejection were taken at the end of the membrane formation step, before the membranes were tested with other feeds, and are averages for performance of membranes on a particular support with a 0.05 M NaCl solution. Membranes were typically formed at 950 psig and at 25°C; the greatest variation in formation parameters for the results listed was in velocity of formation, which may have varied from a low of about 10 fps to a high of about 50 fps. Most membranes were formed between 15 and 35 fps.

TABLE 3.15
DEPENDENCE OF FLUX AND OBSERVED REJECTION ON POROUS SUPPORT.
Zr(IV)-PAA MEMBRANES FORMED UNDER SIMILAR CONDITIONS.

(0.05 M NaCl, 950 psig, 25°C, 10-50 fps)

Porous Support	Approx. Pore Size (μ)	Approx. Void Fraction	Number of Samples	Avg. Flux (gfd)	Avg. R_{obs} (%)
WRAPPED FILMS					
Millipore	0.025	0.70	47	83	90
	0.05	0.72	32	81	91
	0.10	0.74	9	82	88
	0.22	0.75	40	114	93
	0.45	0.79	5	71	93
Acropor AN (Gelman)	0.45	0.57	92	118	91
	1.20	0.57	14	126	88
Nuclepore (General Electric)	0.4	0.13 ^a	1	82	92
	0.6	0.08 ^a	2	40	83
Celgard 2400W (Celanese)	0.1	0.35	1	23	89
CARBON TUBES (Union Carbide Corp.)					
563-6A	0.5	0.22	3	11	67
563-6B--as received	?	?	1	12	77
	--drilled out	-	2	80	90
563-6C--as received	0.4	0.33	4	45	76
	--surface ground	-	31	57	83
4A-3	0.4	0.27	6	33	51
CERAMIC TUBES					
Selas - ceramic filter element	0.27	0.57 ^b	19	65	91
	- 7-channel ceramic tube	0.27	0.57 ^b	26	52
Ferro - precoated 600p ceramic	7-tube module (Thomas)	?	5	63	91
	Single tube	?	7	69	90
	202 ceramic tube	?	0.16	1	121
POROUS STAINLESS STEEL TUBES					
Wolverine (filteraid pretreated)					
Inside surface	8 ^c	0.15	3	45	83
Outside surface	1.5 ^c	0.15	3	46	80

^aCalculated from maximum pore diameter and pore density supplied by G.E.

^bEstimated from data in Selas' Bulletin 80003.

^cManufacturer's estimate before filteraid treatment.

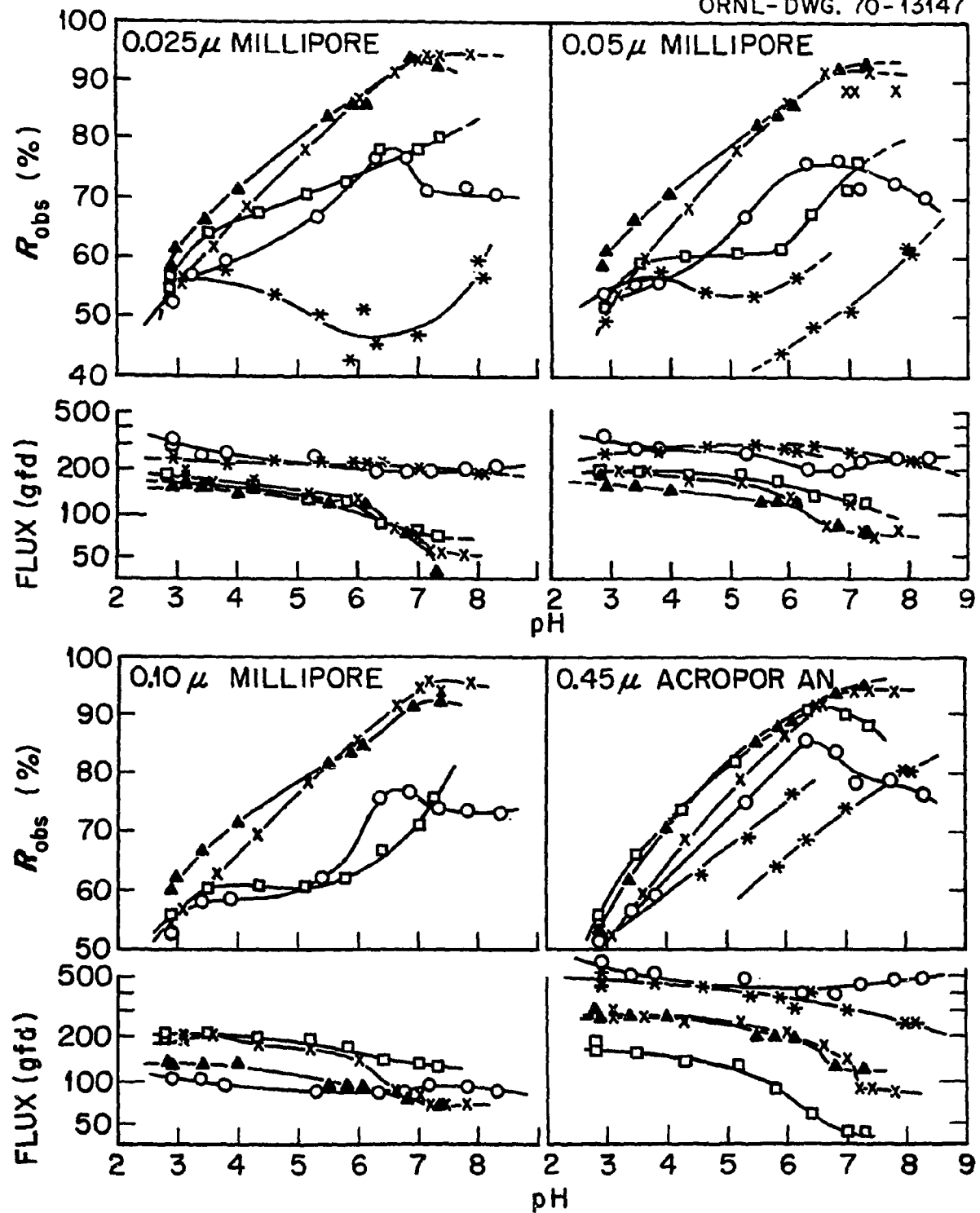
Because of this velocity difference, the averages listed are probably not for the optimum velocity for the support in question (see Section 3.1.2.9). However, although the reliability of the listing is compromised by this fact, it perhaps gives some indication of the relative performances of membranes on different supports. The differences in these averages seems to correspond with our subjective evaluations of these supports for dynamic membranes.

The results with the 0.22-micron Millipore and the 0.45-micron Acropor were superior to those on any other support; however, this may reflect the fact that we used these supports more than any other while developing the optimum membrane formation procedure.

3.1.2.2 Molecular Weight and Support Pore Size. Additional data on the effect of polyacrylate molecular weight and of support pore size, not completely included in the papers of Sections 2 and 3.1.1, are given below. The effect on hyperfiltration properties upon increasing pH after the addition of PAA upon completion of the hydrous Zr(IV) oxide sublayer is shown for a number of molecular weight polyacrylates and a number of supports in Fig. 3.6 (See Table I, Section 3.1.1, for list of additives). Formation and testing procedures were so far as possible identical except for the polycarboxylate used. Nominal molecular weights varied from 5000 (a polymethylacrylate) to several million. The lower molecular weight Acrysols, A-1 and A-3, appeared to respond smoothly to increasing pH. The observed rejections uniformly increased and the fluxes gradually decreased. On the other hand, rejection by membranes of Tamol 850 reached a maximum between pH 6 and 7, then declined. The results for the Nalco additive are not good; there is an obvious discontinuity in the R_{obs} versus pH curves, but it appears that, except for the 0.45- μ support, a distinct minimum in rejection occurs at about pH 5. Nalco was not tested on the 0.1- μ support. Rejections by Nalco membranes were usually lower than with other additives on all of the supports. Rejection by membranes of Acrysol A-5 was not good on any but the largest pore-size support, where it peaked at about 92% at pH 6.5. Flux was poor, however, under these conditions.

Salt rejection during membrane formation was apparently independent of the nature of the porous support for all additives tried except the two

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EFFECT OF CARBOXYLATE MOLECULAR WEIGHT UPON
pH RESPONSE DURING DUAL-LAYER MEMBRANE
FORMATION (0.05 *M* NaCl AT 950 psi)

○ TAMOL ($\sim 5 \times 10^3$); x A-1 ($< 50 \times 10^3$); ▲ A-3 ($\sim 150 \times 10^3$);
□ A-5 ($< 300 \times 10^3$); * NALCO A-1 ($6-10 \times 10^6$)

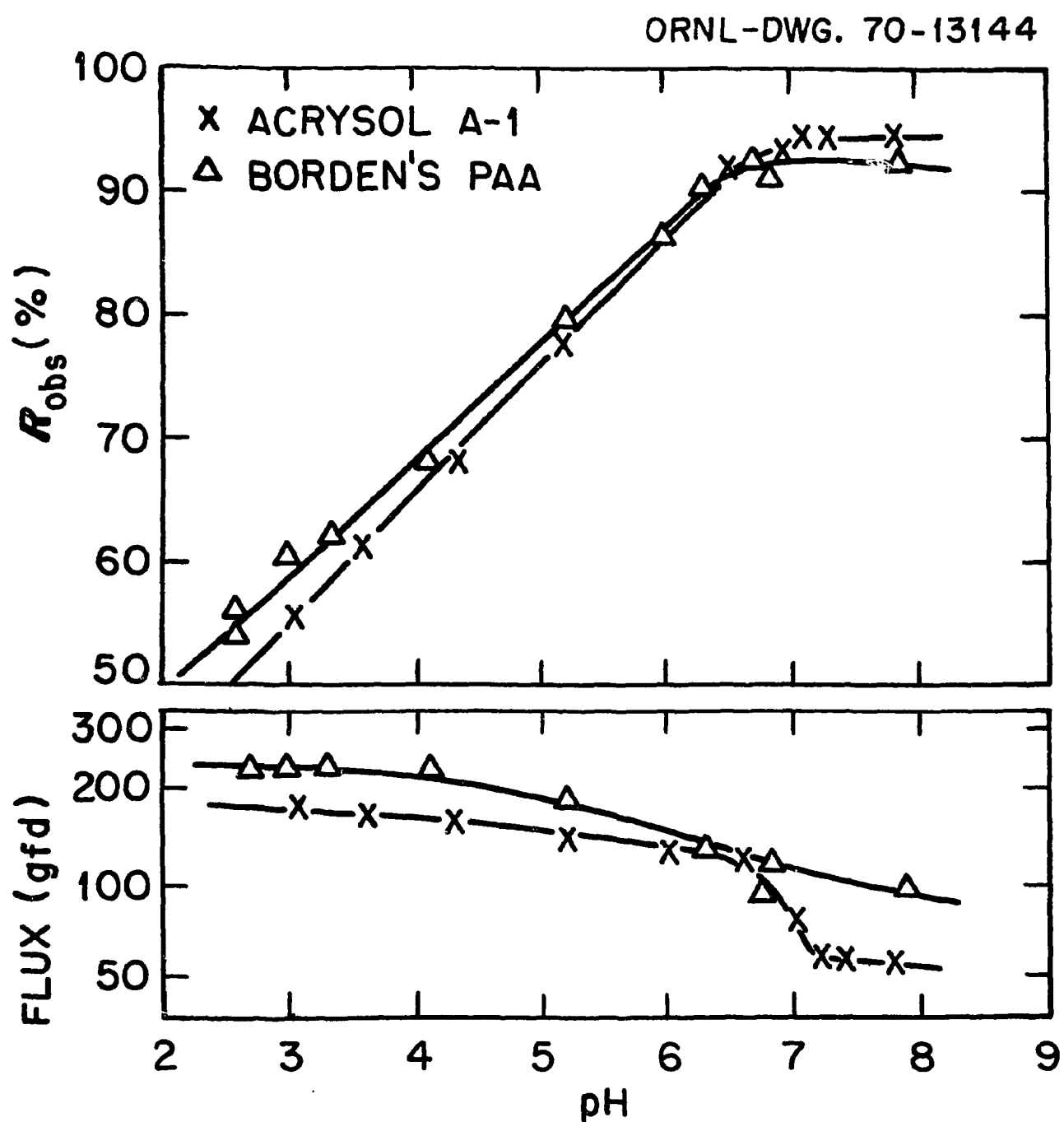
Fig. 3.6

with highest molecular weight, Acrysol A-5 and Nalco, while, except for 0.1- μ Millipore, the fluxes increased with increasing pore size. The best combination encountered during membrane formation was an Acrysol A-3-hydrox zirconium oxide membrane on a 0.45- μ Acropor AN support at pH about 7.5, where R_{obs} for 0.05 M NaCl was 95% and the flux was about 125 gfd.

Figure 3.7 shows the properties during membrane formation for two different PAA's, Acrysol A-1 and Borden's PAA, of the same reported molecular weight, approximately 50,000. The rejection curves are very similar, although the flux at neutral pH is appreciably higher for the Borden additive. Viscosity measurements, see Table 1, Section 3.1.1, cast some doubt about the similarity of the molecular weights of these two additives, but in any event, their hyperfiltration properties as part of a dual-layer membrane are apparently similar.

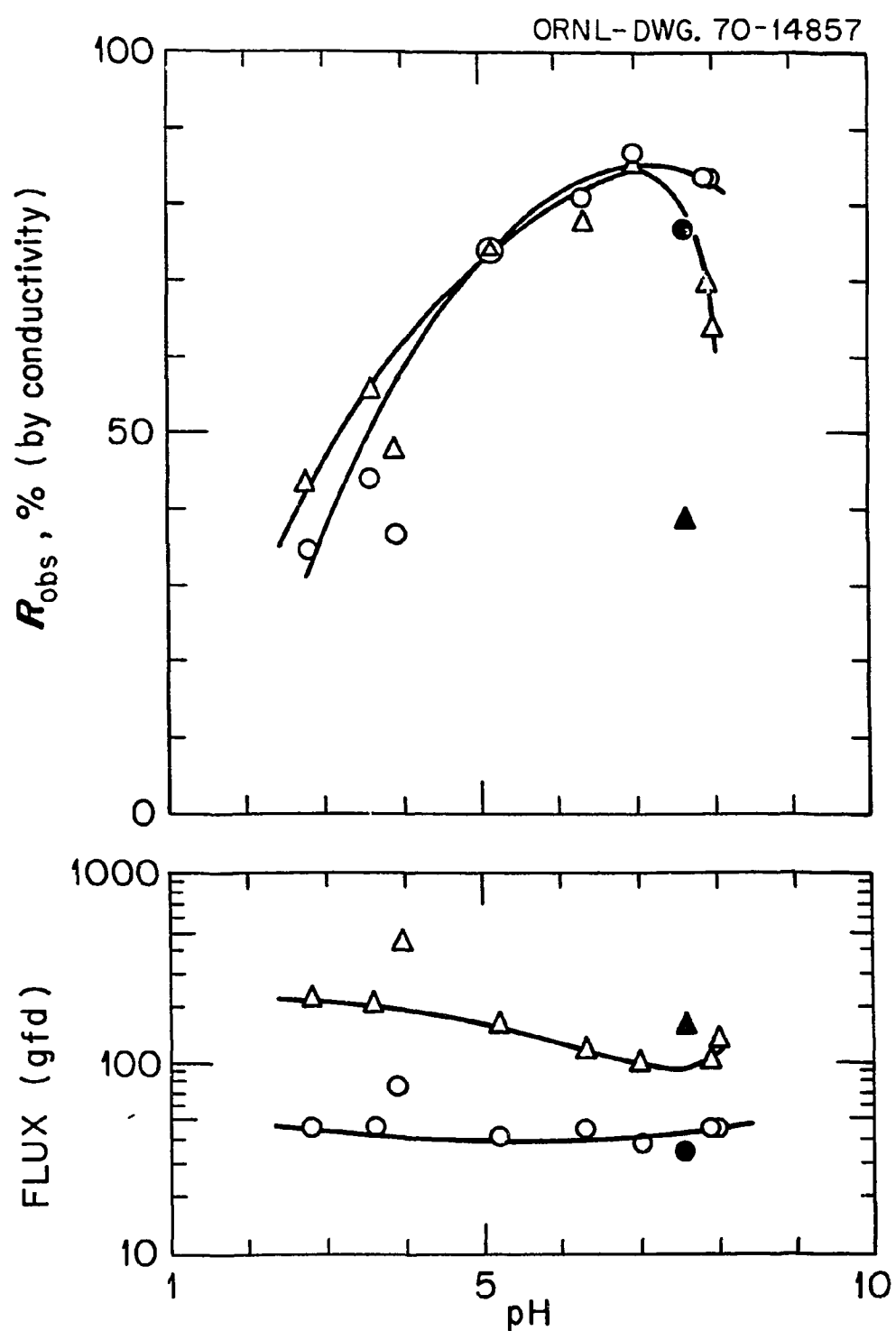
The Millipore and Acropor substrates that have been used as membrane supports have a distribution in pore size around the nominal average. Because of this distribution, one may presume that a given molecular weight additive may not be the optimum one for all pores in a given support. Consequently, we ran one experiment in which four different polycarboxylate additives were mixed in equal parts by weight and the mixture, at a total polyelectrolyte concentration of 50 ppm, used to form the second layer of a dual-layer membrane on a 0.025- μ Millipore support and on a 0.45- μ Acropor AN support. The results are shown in Fig. 3.8. The open symbols are the points for the flux and observed rejection of a solution 0.05 M in NaCl during the formation process. The solid symbols indicate flux and observed rejection for synthetic Coalinga water, using product conductivity to measure R_{obs} . Table 3.16 indicates the rejection of specific ions. Perusal of Fig. 3.8 and Table 3.16 indicates that the mixture of polyacrylates forms membranes which are in general inferior in flux and rejection to ones formed by individual PAA additives such as the Acrysols A-1 and A-3.

Nalco A-1, reported upon above, is a polycarboxylate of high linear charge density and a molecular weight in the range 6 to 10 million. A polymer of similar charge density, but with a molecular weight reported to be about three times as high, was supplied to us by Nalco Chemical Co.,



PERFORMANCE ν s pH DURING FORMATION
OF DUAL-LAYER MEMBRANES USING PAA'S OF
EQUAL MOLECULAR WEIGHT (Nominal 50×10^3)
FROM DIFFERENT SOURCES
(1000 psig , 0.025μ Millipore)

Fig. 3.7



PROPERTIES OF HYDROUS Zr(IV) OXIDE-
POLYCARBOXYLATE MEMBRANES FORMED
FROM A MIXTURE OF ADDITIVES OF
DIFFERENT MOLECULAR WEIGHTS
(1000 psig , 35 fps)

	0.05M NaCl	Coalinga
0.025 μ Millipore	○	●
0.45 μ Acropor	△	▲

Fig. 3.8

TABLE 3.16
REJECTION AND FLUX FOR COALINGA^a WATER BY
Zr(IV)-MIXED PAA^b DUAL-LAYER MEMBRANE
(1000 psig, 35 fps, pH 7.6)

Support	Flux (gfd)	From Conductivity	R _{obs} (%)		
			Cl ⁻	Ca(II) + Mg(II)	Total Anion
0.025-μ Millipore	35	77	59	95	80
0.45-μ Acropor	160	39	33	54	43

^aSee Table 3.68, Section 3.3.1.

^bMixed PAA: 12.5 mg/liter each of Acrysol A-1, Acrysol A-3, Acrysol A-5, and Nalco A-1.

and we carried out some preliminary tests with this additive (AlX3). These tests were conducted in hyperfiltration cells on a hydrous Zr(IV) oxide sublayer on a 0.45-μ Millipore support and on a bare 0.45-μ Millipore support.

Rejection of 0.05 M NaCl by the hydrous Zr(IV) oxide membrane, before exposure to polyacrylic acid, was 50%, flux 140 gfd at 1000 psig. After the system had been rinsed with distilled water and an unused support mounted in a second cell, 50 ppm of AlX3, dissolved in water at pH 7.8, was circulated for 30 minutes; NaCl was then added to 0.05 M. Some results taken at various pH values are summarized below.

pH	Polycarboxylate Membrane		Polycarboxylate Membrane on Hydrous Oxide	
	R _{obs} (%)	Flux (gfd)	R _{obs} (%)	Flux (gfd)
5.5	43	200	33	120
3.3	41	80	57	50
6.6	50	130	42	90

After an overnight shutdown, the rejection of the dual-layer membrane at pH 6.2 had deteriorated substantially, to 35%, and the single-layer slightly, to 47%; fluxes were 10-20% higher. Rejections were sensitive to changes in pH, ranging from about 40% at pH 3.4 to 55% at pH 9 for the single layer, and from 54% to 30% over the same pH range for the double

layer. Fluxes through the single layer, from 100 to 150 gfd at different pH values, were consistently higher than those through the dual layer.

In this test, performance with a simple polycarboxylate membrane exceeded that of a dual-layer, contrary to our usual experience. Neither was equal to what we have come to expect of well-formed dual-layer membranes, nor with Nalco A1 in a single layer.

Somewhat better rejections were obtained with Nalco A1X3 (25 ppm) on Gulf General Atomic cellulose acetate-cellulose nitrate supports (see Ref. 15, p. 232f) in cells. For 0.05 M NaCl, the following sequence was observed:

pH	GGA 3000		GGA 300	
	$\bar{R}_{obs}$ (%)	Flux (gfd)	$\bar{R}_{obs}$ (%)	Flux (gfd)
5.8	54	145	52	40
3.0	47	53	46	11
7.0	90	31	86	10

The effect of carboxylate molecular weight on membranes formed on several Sela ceramic supports is given in Table 3.17. The low-molecular-weight Tamol 850 gave the lowest rejections, but produced the highest

TABLE 3.17

EFFECT OF CARBOXYLATE MOLECULAR WEIGHT ON HYPERFILTRATION PROPERTIES OF DUAL-LAYER MEMBRANES ON SELAS CERAMIC SUPPORTS

(0.05 M NaCl, 950 psig, 35 fps, 25°C, pH ~7)

Additive*	Nominal Molecular Weight	Support	Flux (gfd)	$\bar{R}_{obs}$ (%)
Tamol 850	~5,000	0.27- μ Selas	216	76
		0.12- μ Selas	200	79
Acrysol A-1	<50,000	0.27- μ Selas	80	94
Acrysol A-3	~150,000	0.8- μ Selas	136	87
		0.27- μ Selas	112	90
		0.12- μ Selas	114	90
Acrysol A-5	<300,000	0.27- μ Selas	38	91
		0.12- μ Selas	30	88

*All additives manufactured by Rohm and Haas.

fluxes. The high-molecular-weight Acrysol A-5 gave reasonable rejections coupled with low fluxes, while the two intermediate Acrysols gave good rejections and good fluxes.

An analysis of the results of experiments with several polycarboxylates of different molecular weights on a variety of porous supports has led us to the following conclusions:

1) Nalco A-1 on hydrous Zr(IV) oxide sublayers yields membranes distinctly inferior in the rejection of 0.05 M NaCl to those of the Acrysols on all supports tested. The fluxes through Nalco membranes are distinctly higher for the larger pore size supports than those through the Acrysols, but no better for pore sizes 0.1 μ or smaller.

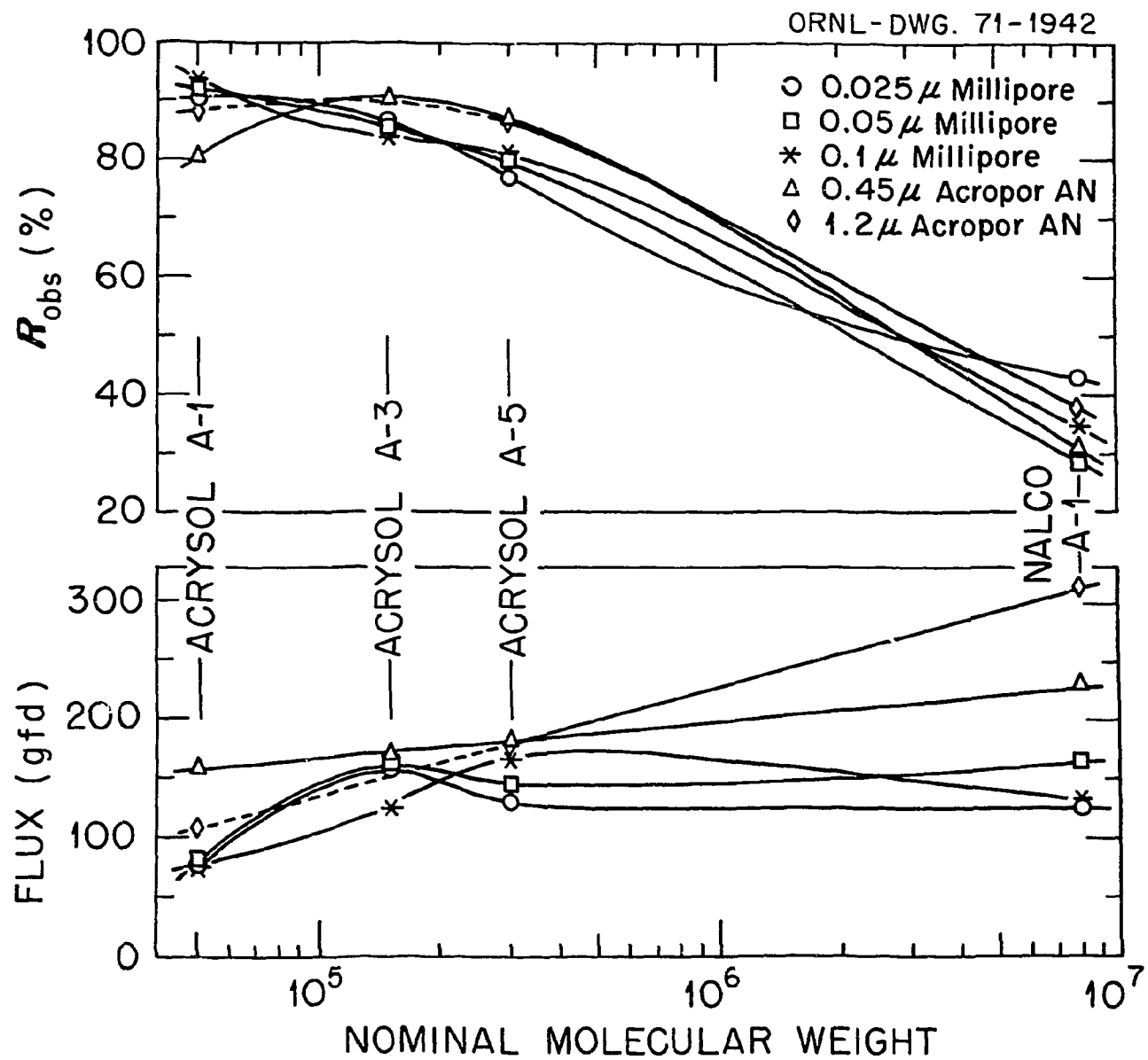
2) Tamol 850 yields membranes inferior to the Acrysols on all supports tried except possibly the 0.45- μ Acropor AN. There the maximum rejection of 0.05 M NaCl was only about 85% (pH 6.3) but the high flux ($\sim$ 400 gfd) at this rejection makes the Tamol 850-0.45- μ Acropor combination an interesting one.

3) With the exception of the very light Tamol 850, the observed rejection decreases as the molecular weight of the polycarboxylate increases for all porous supports tested except the 0.45- μ Acropor AN, where the rejection was greatest for Acrysol A-3 (Fig. 3.9). For the 0.025- μ and 0.05- μ pore size supports, fluxes also appear to be greatest for A-3, but for the other supports fluxes increased as the additive molecular weight increased (Fig. 3.9). Differences in rejections between additives of molecular weight 50,000 to 300,000 are not as great as between these and the ones outside this range.

4) To date, the best membranes we have formed for the hyperfiltration of synthetic Coalinga water are the hydrous Zr(IV) oxide-Acrysol A-3 dual-layer membranes on 0.45- μ Acropor AN porous supports. Comparative data for the A-3 and other carboxylate additives are shown in Fig. 6, Section 2.

5) The rejection of 0.05 M NaCl after exposure of the membrane to Coalinga water decreases with increasing molecular weight for molecular weights of 150,000 or more (Fig. 3, Section 3.1.1).

6) Dual-layer membranes of Zr(IV) oxide and Acrysol A-3 on 0.45- μ Acropor AN supports consistently give better than average performance in both rejection and flux than do other combinations so far tried.



EFFECT OF POLYCARBOXYLATE MOLECULAR WEIGHT
ON HYPERFILTRATION PROPERTIES
OF DUAL-LAYER MEMBRANES

(Membranes Aged by Operation ~16 Hours Before Tests;
950 psig; 35 fps ; pH ~7)

Fig. 3.9

3.1.2.3 The Effect of Zr(IV) Concentration During Sublayer Formation.

Table 3.18 compares membranes formed at different Zr(IV) concentrations during sublayer formation. In general, lower Zr(IV) concentrations resulted in sublayers of greater fluxes, but a lower practical limit appeared to result from the incapability of the feed pump to reach high pressures at high permeation rates; at 1×10^{-5} M Zr(IV), 1000 psig was not reached for several hours, and final membrane performance evidently suffered therefrom. Sublayers were formed more readily at 2×10^{-5} M Zr(IV), but the performances never matched those of membranes formed from more concentrated feeds. At least with Acropor supports, high circulation velocities usually give rise to better membranes, and it is possible that part of the differences found in Table 3.18 is due to this fact. Differences between the molecular weights of the PAA additives also influence results (see previous section). With these important reservations, however, there is some evidence that a Zr(IV) concentration in the range between 5×10^{-5} M and 5×10^{-4} M is optimum. Experience with the Roswell pilot unit⁷ supports this concentration range, though successive additions of additive were sometimes necessary to provide enough hydrous oxide.

TABLE 3.18
EFFECT OF Zr(IV) FEED CONCENTRATION ON MEMBRANE PERFORMANCE
(0.45 μ Acropor AN, 950 psig, 0.05 M NaCl)

[Zr(IV)] (M)	Velocity (fps)	PAA [†]	Zr(IV) Layer		Dual Layer	
			Flux (gfd)	R_{obs} (%)	Flux (gfd)	R_{obs} (%)
5×10^{-4}	48	A-5	580	59	235	80
1×10^{-4}	35	A-3	1200	54	164	92
5×10^{-5}	48	A-5	1740	50	340	84
2×10^{-5}	35	A-3	2920	26	258	81
1×10^{-5}	35	A-3	>3000	3	176	60

[†] Rohm and Haas Acrysols A-3 and A-5.

3.1.2.4 State of Aggregation of the Hydrous Oxide. In early work, it had been our practice to form the sublayer of dual-layer membrane systems from colloidal dispersions of hydrous oxides, prepared by refluxing solutions of the hydrolyzable salts for several hours at atmospheric pressure. The sublayer membrane can also be formed from unboiled solutions of hydrolyzable salts, however, and the first dynamic formations were from salt solutions.²⁸ We ran a set of experiments designed to determine if there is an optimum state of aggregation of the oxide. A solution 0.25 M in $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ (Fisher Scientific Co.) was refluxed and aliquot samples were extracted at 1, 6, 12, 24, and 48 hours. The solutions ranged in appearance from having a barely visible turbidity at 1 hour to having a dense milky appearance at 48 hours. Five sets of Zr(IV)-PAA membranes were formed, using portions of the different aliquots to form the hydrous oxide sublayers. In addition, two other sets of membranes were formed, one by using an unboiled solution of $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ in preparing the hydrous oxide sublayer, and the second by using a solution of A. D. Mackay, Inc. zirconyl chloride, boiled for 48 hours. Each set of membranes was tested with 0.05 M NaCl at 950 psig, 25°C, and pH $\sim$ 7. The results of these tests are summarized in Table 3.19.

TABLE 3.19

EFFECT OF TIME OF REFLUX OF HYDROUS OXIDE SOLUTIONS ON HYPER-FILTRATION PROPERTIES OF HYDROUS Zr(IV) OXIDE-PAA MEMBRANES

(0.05 M NaCl, 950 psig, 25°C, 35 fps, pH $\sim$ 7)

Run No.	Hours Refluxed	No. Membranes*	Average Flux (gfd)	Average R_{obs} (%)
1	0	5	145	95
2	1	5	114	92
3	6	8	112	91
4	12	3	142	92
5	24	3	134	92
6	48	5	119	91
7	48**	2	104	77

*Substrates used: 0.025- μ , 0.05- μ , and 0.22- μ Millipore; 0.45- μ and 1.2- μ Acropor.

**Zirconyl chloride from A. D. Mackay, Inc., all others from Fisher Scientific Co.

The unboiled material appears to give somewhat better results than that refluxed for various times. For those membranes incorporating hydrous oxides aggregated by boiling, there appears to be little dependence on the time of refluxing. Since we had had trouble before in forming good membranes from the zirconyl chloride obtained from Mackay, we suspect that the inferior results shown here stem more from the nature of the material than from the length of time it had been refluxed.

The results of the experiments described above differ from many that we have collected in the past with respect to the effect that support pore size has on the hyperfiltration properties of dual-layer membranes. For example, 0.025 μ Millipore has often given membranes of relatively high rejection, but the fluxes were usually considerably lower than those on, say, a 0.45 μ Acropor of comparable rejection. In the present set of experiments, however, all of the supports gave quite similar values of flux and rejection for the dual layer. This is illustrated by the membranes of Run 1, Table 3.19, where the rejection of 0.05 M NaCl was as follows:

Support	Hydrous Oxide Sublayer		Zr(IV)-PAA Dual Layer	
	Flux (gfd)	R_{obs} (%)	Flux (gfd)	R_{obs} (%)
0.025- μ Millipore	821	45	136	96
0.05- μ Millipore	878	42	141	96
0.22- μ Millipore	637	36	139	96
0.45- μ Acropor	1870	31	141	96
1.2- μ Acropor	1557	42	168	91

This consistency in performance, which was evident in the other runs of Table 3.19 as well, is less puzzling than our usual experience in that it is what one would intuitively expect to find if defect-free membranes of similar thickness were formed on these supports. This expectation arises from the fact that each of the supports is at least an order of magnitude more permeable than the completed dual-layer membrane, and, consequently, almost all of the resistance to solvent flow must arise in the membrane itself. Analyses of the amount of zirconium in the membranes formed from 24-hour boiled hydrous oxide (see Table I, Section 2.1) indicate that, for a given circulation velocity during formation, the smaller the pore size,

the less the amount of zirconium in the membrane. This should mean thinner membranes on the smaller pore size supports, but, as indicated, we have almost always gotten lower fluxes through these.

We tested the membranes of Run 1, Table 3.19, with Coalinga water to determine whether or not a lower state of aggregation of the hydrous oxide would have a deleterious effect on the performance of membranes with simulated natural waters. The results are given in Table 3.20. A rupture occurred in the pressurizing pump diaphragm during operation and the brackish water was contaminated with oil during the latter stages of the run. The oil had little effect, apparently, on the membrane, and was itself rejected very strongly. Both fluxes and rejections for these membranes fell within the range of our better results by Zr(IV)-PAA membranes with Coalinga water feed.

TABLE 3.20
HYPERFILTRATION OF COALINGA^a WATER BY DUAL-LAYER MEMBRANES IN WHICH
THE Zr(IV) LAYER UTILIZED UNBOILED ZrOCl₂ SOLUTION
(950 psig, 35 fps, 25°C)

Time ^b	Support	Flux (gfd)	R _{obs} (%)				
			Cond.	Cl ⁻	Ca(II)+ Mg(II)	Total Cation	Org. Carbon ^c
1	0.025-μ Millipore	56	93	90	99	95	---
	0.05-μ Millipore	58	93	90	99	94	---
	0.22-μ Millipore	56	93	90	98	95	---
	0.45-μ Acropor	95	76	70	90	77	---
	1.2-μ Acropor	93	84	78	96	87	---
70	0.025-μ Millipore	56	95	92	99	95	98
	0.05-μ Millipore	58	94	90	99	95	97
	0.22-μ Millipore	56	95	92	99	96	99
	0.45-μ Acropor	99	80	72	94	81	98
	1.2-μ Acropor	93	86	80	97	86	97

^a See Table 3.68, Section 3.3.1.

^b Time in hours from addition of Coalinga Water.

^c After contamination of feed by oil from leaking pressurizing pump (88 ppm organic carbon).

Our data indicated that membranes from unboiled solutions were at least as good as those made from more highly aggregated stocks, but one

question which remained was whether or not membranes from unboiled solutions maintained hyperfiltration properties as well as the others. We ran one experiment designed to shed light on this question.

Hydrous Zr(IV) oxide membranes were formed on 0.22-micron Millipore and 0.45-micron Acropor supports on a double finger at 1000 psig and 35 fps, using unboiled stock. This finger was removed from the loop and stored overnight in distilled water, with a total storage time at about 18 hours. An identical finger was inserted into the loop, and, under similar conditions, membranes were formed from 24-hour boiled stock. This finger was also removed and stored overnight in distilled water, with a total storage time of about 17 hours. This procedure probably resulted in poorer membranes than it is possible to make, but it did give both membranes a similar history. The next morning, both fingers were returned to the loop, and the PAA layer deposited. The performance of both sets of membranes is tabulated in Table 3.21.

TABLE 3.21

COMPARISON OF HYPERFILTRATION PROPERTIES OF DUAL-LAYER MEMBRANES
IN WHICH THE SUBLAYERS WERE MADE FROM EITHER BOILED (24-HOUR)
OR UNBOILED ZrOCl_2 SOLUTIONS
(1000 psig, 35 fps, 25°C)

Time*	Solution	Support	Unboiled		Boiled	
			Flux (gfd)	R_{obs} (%)	Flux (gfd)	R_{obs} (%)
1	0.05 M NaCl	0.22- μ Millipore	87	85	93	94
		0.45- μ Acropor	110	93	100	90
66	0.05 M NaCl	0.22- μ Millipore	80	91	100	93
		0.45- μ Acropor	130	90	100	91
70	Coalinga	0.22- μ Millipore	50	80	58	84
		0.45- μ Acropor	103	74	85	75

*Time in hours from completion of dual-layer membranes.

There does not appear to be much difference between the results when using boiled and unboiled hydrous oxide solutions. The membrane on the Millipore support utilizing boiled stock seemed to be somewhat better than

its unboiled counterpart, while the opposite was true of membranes on the Acropor support. There seems, at present, to be no advantage to boiling the ZrOCl_2 stock solution.

Perusal of subsequent results indicates that while the use of boiled material leads to membranes of somewhat higher flux, it may lead to lower rejections. Averages for a number of directly comparable cases are given in Table 3.22. Although the number of examples is small, in each case

TABLE 3.22

AVERAGE VALUES FOR FLUX AND REJECTION FOR A LIMITED NUMBER OF
DUAL-LAYER Zr(IV)-PAA MEMBRANES MADE UNDER CONDITIONS
SIMILAR EXCEPT FOR LENGTH OF REFLUX TIME
IN PREPARATION OF STOCK HYDROUS OXIDE

(0.05 M NaCl, 950 psig, 25°C, 30-35 fps, pH ~ 6.5)

Reflux time:	0 hours			12 hours			24 hours		
Support	No.*	Flux (gpd)	R_{obs} (%)	No.*	Flux (gpd)	R_{obs} (%)	No.*	Flux (gpd)	R_{obs} (%)
6C carbon	2	32.5	90.5	1	40	84	0	--	--
0.45- μ Acropor	4	80	88	2	94	84	1	101	83
0.45- μ Millipore	1	60	89	1	78	84	0	--	--
0.22- μ Millipore	1	47	98	0	--	--	1	85	90
0.27- μ Sela	1	50	95	0	--	--	1	56	86

*The number of membranes formed with the given support under the given conditions.

which can be compared, the flux increased and the rejection decreased as more highly aggregated hydrous oxide stock was used.

3.1.2.5 Amount of Zr(IV) in Membranes. We know little about the amounts of material in dynamically formed membranes. One measurement of the amount of zirconium in a hydrous Zr(IV) oxide membrane on a ceramic tube¹² indicated about 50 $\mu\text{g}/\text{cm}^2$. We have determined the amounts of zirconium in membranes formed on supports of different pore sizes and at different circulation velocities, in search for correlations with differences in hyperfiltration properties which correspond to these variables. We briefly mentioned the results in Section 2, and give them in more detail here.

Two sets of membranes were formed from 10^{-4} M hydrous Zr(IV) oxide suspensions. The first set, designated Run Zr-1, utilized five different porous supports, two of them at two different velocities, and contained the zirconium layer only. A second set of membranes, Run Zr-2, was made with which to test the effect that a PAA top layer would have on the retention and/or analysis of the zirconium in the sublayer.

The results of the analyses are given in Table 3.23. During Run Zr-1, feed samples were also taken to determine zirconium concentrations in an effort to get a material balance. From an analysis of the stock Zr(IV) solution the concentration put into the feed was about 9 mg zirconium per liter of feed (10^{-4} M). However, the first feed sample, which was taken before the main circulation pump was turned on, contained only about 2.4 mg per liter. It is possible that some of the additive immediately deposited out on the walls of the system. During the 230 minutes it took to form the zirconium sublayers, the zirconium concentration in the feed dropped to about 1.2 mg per liter. Of the 60 mg that disappeared from the feed after circulation began, less than 30% (16.5 mg) actually was found in the membranes themselves. We do not know what happened to the remainder, but its disappearance did not preclude our determination of the relative amounts on the supports under different experimental conditions.

An examination of the analytical results from these experiments leads us to the following conclusions:

Of all the porous supports used in this study, the highest zirconium concentrations were found in membranes on the 0.45- μ Acropor AN supports. The amount of zirconium on the 0.1- μ Millipore support was anomalously low, but our supply of this particular support has very often given us results inconsistent with pore-size-dependent trends we have otherwise established. We suspect it is either mislabeled or a bad lot. Aside from the 0.1- μ support, the lowest concentrations were found in the supports with smallest pores. There is no obvious correlation between the amount of zirconium in a membrane and its rejection, and there is at most only a slight indication that, for membranes formed on a given support under similar conditions, fluxes fall off as zirconium concentration increases.

TABLE 3.23
ZIRCONIUM CONCENTRATIONS¹ IN DYNAMIC MEMBRANES
FORMED AT 950 psig AND pH 3.8 (25°C)

Run	Support	Velocity (fps)	PAA	[Zr] ₂ μg/cm ²	R _{obs} (%)	Flux (gfd)
Zr-1	0.025-μ Millipore	35	No	15	55	171
	0.05-μ Millipore	35	No	31	62	220
	0.1-μ Millipore	35	No	7	64	131
	0.45-μ Acropor AN	35	No	160	64	480
	1.2-μ Acropor AN	35	No	126	62	510
	0.025-μ Millipore	14.5	No	99	57	178
	0.45-μ Acropor AN	14.5	No	232	62	300
Zr-2	0.025-μ Millipore	35	No	12	42	312
	0.45-μ Acropor AN	35	No	155	49	975
	0.025-μ Millipore	35	Yes ²	5	48	425
	0.45-μ Acropor AN	35	Yes ²	176	44	1180

¹Analyses were by a spectrophotometric method using Arsenazo III as the chromogenic agent. We thank W. R. Laing of the ORNL Analytical Chemistry Division for these results.

²Acrysol A-3, added at ~ pH 3.

Membranes formed at 14.5 fps contained more zirconium than those formed at 35 fps. This effect was especially pronounced in the case of the 0.025-μ Millipore support. With 0.45-μ Acropor, higher Zr(IV) content corresponded to lower flux, but there was no correlation with 0.025-μ Millipore.

A top layer of PAA apparently had little effect on either the concentration of zirconium or the ease with which it could be determined analytically.

The porous supports are mounted on the stainless fingers in such a way that there are two layers of support through which the product water must pass. For four membranes, we analyzed for zirconium in each of the layers separately, and the results are given in Table 3.24. These results indicate substantial amounts of additive penetrate to the second layer. It also appears that the larger the pore size the greater is the fraction of the total zirconium that is retained in the outer layer. This conclusion

TABLE 3.24
 RATIO OF Zr CONCENTRATION IN OUTER LAYER
 TO THAT IN INNER LAYER OF SUPPORT
 (950 psig, 35 fps)

<u>Run</u>	<u>Support</u>	<u>PAA</u>	<u>Ratio</u>
Zr-1	0.45- μ Acropor AN	No	4.8
	1.2- μ Acropor AN	No	11.5
Zr-2	0.025- μ Millipore	Yes	2.4
	0.45- μ Acropor AN	Yes	4.7

seems contrary to what one would intuitively suspect, i.e., that the more open a support structure, the more likely the additive is to penetrate to the second layer. Analytical uncertainties at low levels may have affected determination of this ratio with 0.025- μ supports.

Past experience has shown that as the hydrous zirconium oxide membranes are formed, the supports assumed a grayish hue, which may become quite dark on some occasions. Invariably, those membranes which have the greatest flux, i.e., the large-pore membranes, assume the darkest color. One of the membranes formed in the present set had an obvious gradation in grayness along the length of the support, being quite light at one end and relatively dark at the other. This membrane, formed on 0.025- μ Millipore at 14.5 fps, was cut in two and the darker end was analyzed separately from the lighter. The darker end had an average zirconium concentration of 67.2 $\mu\text{g}/\text{cm}^2$, more than twice that of the lighter end, 32 $\mu\text{g}/\text{cm}^2$. Samples of all the membranes analyzed were kept for color comparison with the zirconium concentrations found. There were exceptions, but in general, the darker the membrane, the higher the zirconium concentration. The darkest membrane, however, was the 1.2- μ Acropor AN membrane of Run Zr-1, for which the analysis indicated a lower zirconium concentration than for any of the 0.45- μ Acropors.

A practical implication of these results is that the cost of the zirconium additive in a membrane is small. From Table 3.23, the membrane with the highest Zr(IV) content contained less than 250 micrograms of Zr(IV) per cm^2 . Assuming that reagent grade ZrOCl_2 , at \$17/lb, rather than the technical grade at 52¢/lb, is used, the cost for the Zr(IV) in a membrane

would be about $0.5\text{¢}/\text{ft}^2$. Of course, in practice, not all of the Zr(IV) added to the feed during the membrane formation step ends up in the membrane, and some is wasted. Experience with a dynamic membrane desalination pilot plant built for testing at OSW's Roswell test station⁷ indicates that Zr(IV) costs, estimated from total chemicals added during membrane formation, may run as high as $5\text{¢}/\text{ft}^2$ if reagent grade additive is used and if no attempt is made to conserve unused feed solution. This figure is probably high, since, in the pilot plant, the feed volume to membrane surface ratio is surely much higher than it would be in a full-scale plant, and the ratio of other surface areas where additive might be adsorbed to membrane surface area is much greater in the pilot plant.

One aspect of the results is particularly puzzling. At 950 psig, flux through all the supports before the membranes are deposited should be at least an order of magnitude higher than those reported in Table 3.23, for supports with membranes. It follows that most of the resistance to flow arises from the materials laid on the supports during operation. If the lesser amounts of zirconium of the small pore sizes implies thinner membranes, fluxes should be much higher through, for example, membranes on 0.025- μ Millipore than through those on 0.45- μ Acropor AN. The trend of the results is, however, in the opposite direction.

During a later experiment, we again kept samples of the feed before, during, and after sublayer formation. No analysis was made of the Zr(IV) content in the membrane, but the results were somewhat perplexing. The Zr(IV) was added to the feed tank and circulated through the loop before the porous supports were placed into the test sections. The loop was shut down, the porous supports inserted into the loop, and a sample of the feed taken. At this point, the Zr(IV) concentration was 3.35 mg/l, down from the nominal 9 mg/l originally added. However, after 30 minutes of operation at pressure with the circulation pump on, the Zr(IV) concentration in the feed had risen to about 8.7 mg/l. At the end of membrane formation, the Zr(IV) concentration had dropped to about 8.5 mg/l. This loss is only slightly greater than what one could reasonably expect to be incorporated into the membranes themselves. The hydrous oxide membranes formed in this experiment were reasonably good.

In practical applications, where areas will be orders of magnitude larger than those we presently use, it may be necessary to supplement the hydrous oxide supply during membrane formation.

3.1.2.6 Effect of Presence of PAA on Formation of Hydrous Oxide Layer. Polyanionic electrolytes are well known to be coagulants for hydrous oxides in the anion-exchange form. Presence of PAA, even in small amounts, during the formation of the hydrous oxide layer might be expected to affect membrane properties. Table 3.25 indicates that the flux through the sublayer is decreased slightly by the presence of 0.5 ppm (10^{-5} N) of PAA, but perhaps not significantly. Fluxes through the dual-layer membranes, however, are much lower if PAA was present during formation of the hydrous oxide layer.

TABLE 3.25
EFFECT OF PRESENCE OF PAA DURING HYDROUS Zr(IV) OXIDE SUBLAYER
(0.05 M NaCl, 1000 psig, 35 fps, 25°C)

<u>Support</u>	<u>PAA Concentration During Sublayer Formation (ppm)</u>	<u>After Sublayer Formation</u>		<u>Zr(IV)-PAA Membrane</u>	
		<u>Flux (gfd)</u>	<u>R_{obs}(%)</u>	<u>Flux (gfd)</u>	<u>R_{obs}(%)</u>
0.45- μ Acropor	0	1740	50	340	84
	0.5	1590	40	180	87
0.025- μ Millipore	0	725	45	270	78
	0.5	660	38	140	83

3.1.2.7 Effect of Presence of Hydrous Zr(IV) Oxide on Formation of PAA Layer. In our attempts to optimize membrane formation procedures, we investigated the effect of rinsing and not rinsing the hydrous Zr(IV) oxide from the solution following the completion of the sublayer and before the addition of the PAA under acid conditions. The results from an initial run in which the Zr(IV) sublayer was formed as in standard runs, but the excess Zr(IV) not removed from the feed before the PAA was added, are given in Table 3.26. This procedure resulted in several good membranes in Run 2, which differed from Run 1, with its mediocre results, chiefly in the

TABLE 3.26
 PROPERTIES OF DUAL-LAYER MEMBRANES FORMED WITHOUT
 RINSING OUT EXCESS Zr(IV) BEFORE PAA ADDITION
 (950 psig, .05 M NaCl, Acrysol A-5)

Run	[Zr(IV)] Molarity	Support*	Velocity (fps)	Flux (gfd)	R_{obs} (%)
1	10^{-4}	0.025- μ M	35	87	83
		0.05- μ M	35	89	84
		0.1- μ M	35	95	84
		0.45- μ A	35	130	80
		1.2- μ A	35	201	76
		0.025- μ M	14.5	78	74
		0.45- μ A	14.5	97	74
2	5×10^{-5}	0.025- μ M	35	71	95
		0.05- μ M	35	74	94
		0.45- μ A	35	117	94
		0.45- μ A	35	117	91
		0.025- μ M	18	71	95
		0.45- μ A	18	103	91
		0.45- μ A	44	124	92

*M = Millipore; A = Acropor AN.

concentration of the Zr(IV). The membranes of Run 2 were tested with synthetic Coalinga water and rejections were good, although the fluxes were disappointing (Table 3.27). When later again tested against 0.05 M NaCl,

TABLE 3.27
 HYPERFILTRATION OF COALINGA WATER BY MEMBRANES OF RUN 2, TABLE 3.26
 (950 psig)

Support*	Velocity (fps)	Flux (gfd)	Conduc- tivity	R_{obs} (%)		
				Cl ⁻	Mg(II)+Ca(II)	Total Cation
0.025- μ M	35	38	91	84	98	92
0.05- μ M	35	33	90	82	-	-
0.45- μ A	35	57	86	78	97	88
0.45- μ A	35	57	77	72	-	-
0.025- μ M	18	29	91	85	-	-
0.45- μ A	18	50	80	70	-	-
0.45- μ A	44	73	80	71	-	-

*M = Millipore; A = Acropor AN.

these same membranes showed a loss of 2 to 5% in rejection at substantially the same fluxes they had before exposure to Coalinga water.

Table 3.28 gives the results of two more runs, this time with Acrysol A-3 as the PAA, in which the excess Zr(IV) was not removed from the feed solution. Again the better membranes occurred in the run with the lower Zr(IV) concentration.

TABLE 3.28
PROPERTIES OF DUAL-LAYER MEMBRANES FORMED WITHOUT RINSING
EXCESS Zr(IV) BEFORE PAA ADDITION
(900 psig, 0.05 M NaCl, Acrysol A-3, pH 7-7.5)

Run	[Zr(IV)] Molarity	Acropor AN Support	Velocity (fps)	Flux (gfd)	R_{obs} (%)
1	3×10^{-4} *	0.45- μ	35	99	74
		0.45- μ	35	105	72
		1.2- μ	35	115	73
		1.2- μ	35	115	61
2	10^{-4}	0.45- μ	33	120	84
		0.45- μ	33	146	82

*Added in three steps.

The results of a no-Zr(IV)-rinse run with a 7-channel Sela tube and two control supports, 0.22-micron Millipore and 0.45-micron Acropor, are given in Table 3.29. The membranes formed without the intermediate rinse gave appreciably better results, especially in the case of the Sela support, where both rejections and fluxes were better. Earlier experience in Thomas' group with ceramic tubes had also favored adding PAA without removing residual hydrous Zr(IV) oxide.

In a subsequent series of membrane formations, we compared performances of membranes formed with and without rinsing the Zr(IV) from the loop and feed tank before adding the PAA. At 950 psig, six membranes on 0.45-micron Acropor which were formed with the rinse averaged 86% rejection and 110 gfd; the four formed on this support without the rinse averaged 80% rejection and 120 gfd. On 0.27-micron Sela tubes, outside flow, three membranes with the rinse averaged 90% at 71 gfd while four without were not as good,

TABLE 3.29

EFFECT OF RINSING HYDROUS Zr(IV) OXIDE FROM THE SYSTEM BEFORE
ADDING PAA DURING FORMATION OF DUAL-LAYER MEMBRANES

(950 psig, 35 fps, 25°C)

Run	Time ^a	Feed ^b	Selas		0.22-μ Millipore		0.45-μ Acropor	
			Flux (gfd)	R _{obs} (%)	Flux (gfd)	R _{obs} (%)	Flux (gfd)	R _{obs} (%)
1	Zr(IV) rinsed out after formation of sublayer:							
	0:20	0.05 M NaCl	60	59	87	97	90	96
	2:05	SPRW	54	60	80	99	80	97
2	Zr(IV) not rinsed out after formation of sublayer:							
		0.05 M NaCl	74	92	95	93	124	96
	1:10 ^c	SPRW	60	98	85	97	100	98
	4:50	SPRW	60	98	81	97	98	98
	67:35	SPRW	66	98	83	97	124	97
	71:50	SPRW	66	98	81	97	124	97

^aTime (hours:minutes) from addition of simulated natural water.

^bSPRW: simulated pretreated Roswell water (see Table 3.68, Section 3.31), without divalent cations.

^cVelocity of Selas section reduced to 15 fps, others to 18 fps.

81% at 55 gfd. The seven-channel Selas tube performed slightly better in both flux and rejection in one case with rinse than in one case without. These data, although not conclusive, seem to favor rinsing between poly-electrolyte additions, contrary to the observation described in the preceding paragraph.

A final test of the effect of Zr(IV) concentration when it is not rinsed out prior to PAA addition is summarized in Table 3.30. At 10^{-3} M Zr(IV), the fluxes for the dual-layer membrane were relatively high, but the rejections were unsatisfactory. However, better overall results were obtained with a concentration of 3×10^{-4} than with the 1×10^{-4} M usually used. Whether or not the presence of residual hydrous Zr(IV) oxide when the PAA layer is formed is beneficial has not been established conclusively for all supports.

3.1.2.8. Effect of Time. Our usual procedure in forming the hydrous Zr(IV) oxide layer is to circulate a 0.05 M NaCl feed solution, containing 10^{-4} M Zr(IV), past the support while increasing the pressure to 950-1000

TABLE 3.30

EFFECT OF Zr(IV) CONCENTRATION ON PROPERTIES OF COMPLETED Zr(IV)-PAA
MEMBRANE WHEN Zr(IV) IS NOT RINSED OUT PRIOR TO PAA ADDITION

(0.05 M NaCl, 950 psig, 25°C, 30 fps)

Zr(IV) Conc. (M)	Support	Flux (gfd)	R_{obs} (%)
1×10^{-3}	6C carbon tube	93	70
	Ferro 600p (coated)	62	50
	0.05- μ Millipore	150	61
	0.45- μ Acropor	220	59
3×10^{-4}	6C carbon tube	65	92
	Ferro 600p (coated)	90	85
	0.05- μ Millipore	78	94
	0.45- μ Acropor	120	92
1×10^{-4}	6C carbon tube	58	92
	Ferro 600p (coated)	70	96
	0.05- μ Millipore	70	89
	0.45- μ Acropor	80	97

psig as rapidly as possible. The solution is then circulated at pressure until the observed rejection of the salt is in the order of 30-40%. In efforts to optimize membrane performance, we investigated the effect of variations in the length of time during which the Zr(IV) was circulated before the PAA layer was formed.

We performed two variations on the usual procedure: in one, we rinsed out the Zr(IV) as soon as we reached full pressurization, and in the second, we allowed the Zr(IV) solution to circulate until there was no longer any change in the observed rejection. The results obtained for these runs on a 0.45- μ Acropor support at 35 fps are listed as Runs 1 and 7 in Table 3.31 which also contains comparable results from several other membrane formations. The length of time taken for the PAA layer formation is also listed. Data were taken also on several other support materials and at other circulation velocities, but the trends with time, or lack thereof, were similar for all.

Short formation times for the Zr(IV) layer apparently result in somewhat better fluxes on the average than do longer times. The average flux for the first four runs is about 168 gfd; that for the last four is 136 gfd, although this average reflects the low (93 gfd) flux of the very tight

TABLE 3.31

PERFORMANCE OF DYNAMIC Zr(IV)-PAA MEMBRANES
FORMED ON DIFFERENT TIME SCHEDULES

(0.05 M NaCl, 0.45- μ Acropor, 950 psig, 35 fps, 25°C, pH 6.2 - 7.4)

Run	T_{Zr}^a	Zr(IV) layer ^b		T_{PAA}^c	Dual-layer ^d	
		Flux (gfd)	R_{obs} (%)		Flux (gfd)	R_{obs} (%)
1	0:30	No data		5:10	170	93
2	0:45	1870	31	5:00	145	91
3	1:40	1303	52	22:15 ^e	181	90
4	1:45	1250	52	3:00	175	90
5	2:00	2500	29	2:35	163	92
6	2:10	920	33	22:00 ^e	93	97
7	2:15	850	47	21:30 ^e	141	92
8	3:20	1450	51	2:30	147	92

^aTime in hours and minutes from startup to rinsing out Zr(IV) from loop.

^bFormed at pH $\sim$ 4.

^cTime in hours and minutes from addition of PAA at pH $\sim$ 2 to rinsing at pH $\sim$ 6.5.

^dData taken after overnight operation ($\sim$ 18-22 hours following rinsing out of PAA).

^eIncludes overnight operation in presence of 50 ppm PAA at pH $\sim$ 3.

membrane of Run 6. Why membranes of similar Zr(IV) layer performance, e.g., Runs 4 and 8 or Runs 6 and 7, should give such different dual-layer performance is not known. The length of time the PAA is circulated, at low pH, apparently affects final performance very little (see Runs 3 and 4).

The ordinary procedure in forming the top layer of the dual-layer dynamic membrane is to add the PAA to the feed at pH 2 and then to increase slowly the pH stepwise to 7 or 8. It had never been clearly established whether or not the membrane is "formed" at pH 2, and that the increase in pH simply leads to better rejection as the ion-exchange capacity of the membrane is increased through neutralization of the functional groups. In one run on five different supports, we attempted to shed light on this matter by maintaining the membrane at pH 2 for about the two to three hours

we normally take to neutralize the solution, and then rapidly (10 minutes) bringing the pH up to 7.5. This process resulted in fair fluxes, 92-325 gfd at 950 psig, but poor rejections, 67-18%. It appears as if the membrane is somehow "fixed" during the slow rise in pH.

3.1.2.9. Effect of Circulation Velocity. In Section 3.1.1, we indicated that, for a given porous support, both rejection and flux with a newly-formed hydrous oxide membrane will usually be higher, the higher the circulation velocity during formation. The better properties of the sub-layer are usually reflected in better properties for a subsequently completed dual-layer membrane. However, the correlation seems better established with some supports than with others. Table 3.32 is a summary of those membrane formations during this biennium in which given supports were exposed to different velocities during the same membrane formation; i.e., all conditions were identical except velocity.

TABLE 3.32

EFFECT OF VELOCITY ON Zr(IV)-PAA MEMBRANE PERFORMANCE. BOTH LAYERS FORMED, AND PERFORMANCE MEASURED, AT THE SAME VELOCITY.

(0.05 M NaCl, 950 psig, 25°C)

<u>Support</u>	<u>Number of Comparisons</u>	<u>Velocity^a</u>	<u>Average Flux (gfd)</u>	<u>Average R_{obs} (%)</u>
0.45- μ Acropor	14	Fast	140	92
		Slow	103	86
0.22- μ Millipore	4	Fast	142	92
		Slow	90	87
0.025- μ Millipore	7	Fast	81	90
		Slow	84	90
6C carbon tube	4	Fast	40	77
		Slow	39	85
7-channel Sela tube	4	Fast	56	84
		Slow	48	83

^aFast is taken as greater than 34 fps, slow as less than 26 fps.

For the cases of the Acropor and Millipore supports in the half-micron range, higher velocities are clearly desirable during membrane formation.

With the 0.025-micron Millipore, however, little if any advantage accrues, and this is true also for the carbon and Sela cases we were able to compare. Apparently, the pronounced dependence on velocity found in the first two cases of Table 3.32 does not result from pore size alone, since the Sela tubes compared were of nominal 0.27 micron pore size.

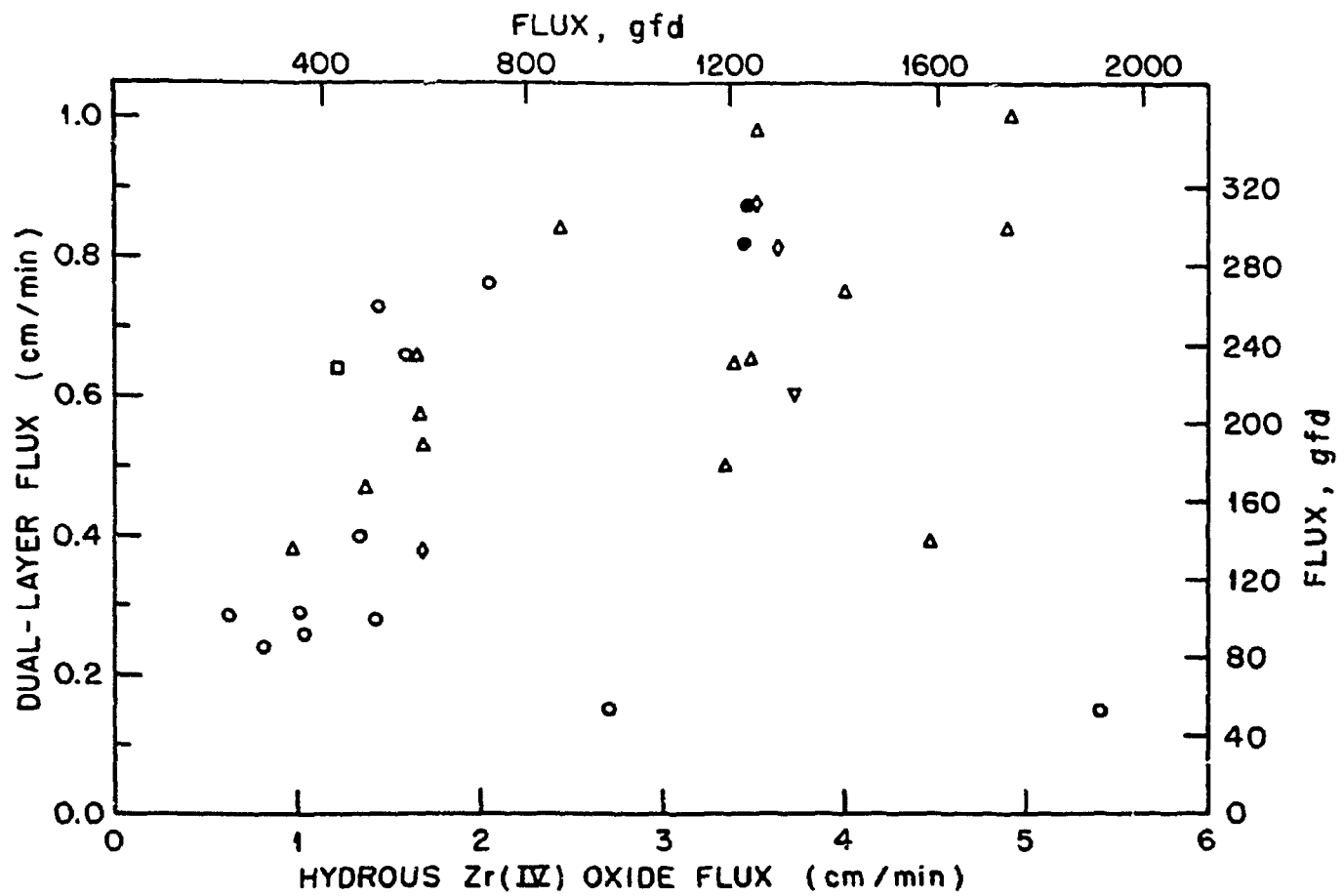
Correlations of performance with velocity, or lack thereof, are not quite so easily made if membranes from different runs are compared, as in Fig. 3.10. Membranes represented in this figure, some of which are included in the averaging of Table 3.32, were prepared under a variety of conditions, and cases in which flux through the sublayer was very high because of defects would obscure a correlation. We suspect this happened in some runs, and have arbitrarily excluded a few points from Fig. 3.10, for which R_{obs} of the hydrous Zr(IV) oxide membrane was less than 40%. There appears to be a trend, particularly, again, with supports of large pore size, but scatter obscures the correlation.

More details on some of the studies summarized in Table 3.32 are given below.

Table 3.33 summarizes the effect that velocity had on the flux and rejection of 0.05 M NaCl by dual-layer membranes of different additives on two different porous supports. The data were taken after 18-20 hours of operation. For a given additive on a given support, the observed rejection was apparently independent of the formation velocity, with the possible exception of membranes from the additive Nalco A-1, where rejection was much lower than the others. One must remember that concentration polarization would tend to decrease observed rejection more for the 14.5 fps case than for the 35 fps one. For the 0.025- μ Millipore support, there was no appreciable velocity effect on the flux through the Acrysol A-1 and A-5 membranes (A-3 was not tried). On the 0.45- μ Acropor, higher formation velocities invariably resulted in higher fluxes.

In Table 3.33, performances were measured at the same velocities at which the membranes were formed. In Tables 3.34 and 3.35, we report results on the performances of dual-layer membranes which had the hydrous zirconium oxide layers formed simultaneously but at different velocities, while the PAA layers were later formed at the same velocities. The fluxes and

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RELATION BETWEEN FLUX THROUGH HYDROUS OXIDE SUBLAYER
AND DUAL-LAYER PAA MEMBRANE (1000 psig)

MILLIPORE, μ	ACROPOR AN, μ
○ 0.025	△ 0.45
□ 0.05	▽ 1.2
● 0.1	
◇ 0.2	

Fig. 3.10

TABLE 3.33

EFFECT OF FORMATION VELOCITY ON DUAL-LAYER MEMBRANE PERFORMANCES

(950 psig; pH 7-8; hydrous Zr(IV) oxide sublayer)

Additive	Support ^b	Formation Velocity ^a			
		14.5 fps		35 fps	
		Flux (gfd)	R_{obs} (%)	Flux (gfd)	R_{obs} (%)
Acrysol A-1	1	75	91	79	90
	2	84	91	159	92
Acrysol A-3	2	126	88	158	94
Acrysol A-5	1	135	80	132	77
	2	135	88	183	88
Nalco A-1	1	84	29	128	43
	2	128	28	230	31

(a) Both layers formed at the same velocity, and the measurements taken at that velocity.

(b) Support 1 is 0.025- μ Millipore, Support 2 is 0.45- μ Acropor AN.

rejections were measured for the hydrous oxide sublayers at 22 fps (Table 3.34) and for four of the dual-layer membranes at 35 fps (Table 3.35). The

TABLE 3.34

EFFECT OF CIRCULATION VELOCITY DURING FORMATION OF
HYDROUS ZIRCONIUM OXIDE DYNAMIC MEMBRANES
UPON HYDROUS OXIDE MEMBRANE PERFORMANCE

(0.05 M NaCl, 950 psig, pH 4)

Membrane Support	Velocity* (fps)	Flux (gfd)	R_{obs} (%)
0.025- μ Millipore	18	495	37
	30	190	28
	42.5	173	49
0.45- μ Acropor AN	18	1050	36
	30	1100	28
	42.5	1200	40

*Formation velocity; reported rejections and fluxes were measured at 22 fps.

data are confusing in that, for the sublayer membranes, fluxes decrease with increasing velocity for the 0.025- μ Millipore support, but increase for the 0.45- μ Acropor AN. Rejections, on the other hand, were minimum at the intermediate velocity. For the dual-layer membranes, behavior in both rejections and fluxes is opposite for the two different supports.

TABLE 3.35
EFFECT OF SUBLAYER FORMATION VELOCITY ON PROPERTIES
OF DUAL-LAYER MEMBRANES

(0.05 M NaCl, 950 psig, pH 7.5)				
	V* (fps)	V** (fps)	Flux	R _{obs}
	1	2	(gfd)	(%)
0.025- μ Millipore	30	35	64	73
	42.5	35	47	82
0.45- μ Acropor AN	30	35	147	88
	42.5	35	190	84

*Velocity at which hydrous Zr(IV) oxide sublayer formed.

**Velocity at which PAA layer formed and measurements of flux and R_{obs} taken.

In an experiment to determine whether or not high velocities are necessary during the formation of the PAA layer as well as the Zr(IV) layer, we ran the experiment summarized in Table 3.36. Here we formed the sublayer on four supports at 30 fps, then dropped the velocity to 15 fps during the formation of the PAA layer. Rejections in the final membrane appear to be reasonably good, although fluxes are lower than one would like. This single experiment is not, however, sufficient to decide the point in question.

The membranes of Table 3.36 were tested with Roswell water. The results are given in Section 3.3.1.2.8.

We have one experiment that points to superior results, at least with some supports, from formation velocities even higher than the 35-40 fps usually used. During the early stages of forming hydrous oxide sublayers on 0.22-micron Millipore and 0.45-micron Acropor supports, we inadvertently set the circulation velocity at 60 fps, nearly double the 35 fps we usually use. We caught the mistake after 45 minutes of operation, but by that time the sublayer was essentially formed. For the Acropor support we had

TABLE 3.36

PROPERTIES OF MEMBRANES FOR WHICH THE SUBLAYER WAS FORMED AT 30 fps AND THE PAA LAYER AT 15 fps. PROPERTIES WERE MEASURED AT THE VELOCITY OF FORMATION
(0.05 M NaCl, 950 psig, 25°C)

Support	Hydrous Oxide Layer (Formed at 30 fps)		Final Dual-Layer (Formed at 15 fps)	
	Flux (gfd)	R_{obs} (%)	Flux (gfd)	R_{obs} (%)
0.45- μ Acropor	940	56	73	95
0.05- μ Millipore	310	59	60	93
Ferro 600p (coated)	510	27	64	87
Celanese 2400W	240	50	23	89

a flux of 1750 gfd with rejection of 0.05 M NaCl at 61%; for the Millipore, 1300 gfd at 52%. We completed the dual-layer formation at 35 fps, and the final values for the membranes were: Acropor, 155 gfd at 95%; Millipore, 130 gfd at 92%. The values realized with the Acropor support are among the best we have achieved to date.

We have also tested the effect of different circulation velocities during formation of the polyacrylate layer on hydrous Zr(IV) oxide membranes formed at the same velocity. Supports of 0.025- μ Millipore, 0.45- μ Acropor AN, Dupont Tyvek 1043, and Gulf General Atomic 3000 cellulose nitrate/cellulose acetate were used. Tyvek is a spunbonded polyolefin cloth, which we had tried earlier in cells (See Table 4.2, Ref. 15). GGA-3000 is the more permeable of two experimental CN/CA supports, supplied us by H. K. Lonsdale, which we have used in experiments previously reported (p. 232, Ref. 15).

Results are summarized in Table 3.37. Hydrous Zr(IV) oxide layers were formed from 0.05 M NaCl, 10^{-4} M colloidal Zr(IV) oxide, pH 4, at circulation velocities of 35 fps for all test sections. Agreement between membrane properties on duplicate porous supports was good. The circulation velocities for test sections A-D were increased to 46 fps, and for E and F, decreased to 12 fps. The feed was changed to 0.05 M NaCl with 50 ppm PAA, pH 3. Over four hours, the pH was gradually raised, until, at the neutral range, the PAA concentration was dropped to ~ 2 ppm. It is clear (Table 3.37)

TABLE 3.37
EFFECT OF CIRCULATION VELOCITY DURING FORMATION OF PAA LAYER
(0.05 M NaCl, 1,000 psig)

pH	Circ. Vel. of Measurement, (fps)	Tyvek (A)		GGA 3000 (B)		0.025-μ Millipore (C)		0.45-μ Acropor AN (D)		0.025-μ Millipore (E)		0.45-μ Acropor AN (F)	
		R _{obs} ,%	Flux (gfd)	R _{obs} ,%	Flux (gfd)	R _{obs} ,%	Flux (gfd)	R _{obs} ,%	Flux (gfd)	R _{obs} ,%	Flux (gfd)	R _{obs} ,%	Flux (gfd)
Hydrous Zr(IV) Oxide Layer													
4.0	35	30	205	59	250	52	280	44	970	51	270	44	960
PAA Layer, Formed at													
46 fps													
8.2	Formation Velocity	57	42	77	62	81	75	94	100	73	120	92	100
8.2	35	59	40	78	65	78	85	93	140	76	125	91	140
Over Weekend at													
12 fps													
8.5*	35	73	16	79	53	83	65	88	85	71	125	89	125
Overnight at													
35 fps													
8.3	35	70	18	78	65	82	65	88	100	72	120	90	140

*After acid cycle at weekend velocities.

from measurements, both before adjusting all velocities to 35 fps and after, that high circulation velocities during the formation of the PAA layer did not tend to give membranes of much higher fluxes, as they frequently do when used during formation of the hydrous oxide layer.

The circulation velocities were then reversed over a weekend from the values used during formation of the PAA layer i.e., those formed at 46 fps were run at 12, and those formed at 12 were run at 46. All rejections deteriorated, the values Monday morning ranging between 55 and 80% (fluxes with 0.45- μ were over 200 gfd with R_{obs} 70 to 80%). An acid cycle brought rejections back to near the earlier level. Comparison of values after the cycle indicated that flux loss was less for the membranes exposed over the weekend to the higher velocity (Table 3.37). A second overnight velocity reversal did not affect properties drastically.

For some reason, not clear, from the time of the initial formation of the PAA layer at 12 fps, rejections by the membrane on 0.025- μ Millipore E were lower, and fluxes frequently higher than the other "standard" supports, C, D, and F. Properties of the GGA 3000 were similar to those of the 0.025- μ Millipore operated at the same velocity. Both rejections and fluxes of the membrane on Tyvek were poorer than for the others.

In Table 3.38, we report results of two runs in which all of the membranes were formed at high velocities, but, since some velocities were higher than others, some information about the effect of velocity can be obtained. Although the two types of Sela tubes may not be directly comparable, higher circulation velocities led to higher sublayer fluxes in five out of five cases, and three of these led also to higher dual-layer fluxes. Higher sublayer rejections at the higher velocity also resulted in five out of five cases, but the rejections by the dual-layer membranes were mixed and showed no definite correlation with velocity.

One series of formations of dual-layer membranes on 0.27 micron Sela ceramic supports seemed to indicate that performance improved as the formation velocity was lowered. In this series, for two membranes formed at 44.5 fps, the fluxes were 34 and 38 gfd with R_{obs} 91 and 86% for 0.05 M NaCl at 950 psig. For two membranes formed at about 35 fps, the values were 50 and 87 gfd at 95 and 84%, and for one membrane formed at 8 fps, the flux was 77 gfd while R_{obs} was 90%.

TABLE 3.38

THE EFFECT OF CIRCULATION VELOCITY DURING FORMATION ON
PROPERTIES OF Zr(IV)-PAA MEMBRANES. FLUXES AND REJEC-
TIONS WITH 0.05 M NaCl MEASURED AT FORMATION VELOCITIES.

(950 psig, 25°C, pH 6-8)

Run	Support	Velocity (fps)	Sublayer		Dual Layer	
			Flux (gfd)	R_{obs} (%)	Flux (gfd)	R_{obs} (%)
1	0.05- μ Millipore	28	310	48	95	80
		50	420	67	53	91
		50	525	49	88	90
	0.45- μ Acropor	28	450	42	95	84
		50	1350	52	130	93
		50	1000	44	120	74
2	0.22- μ Millipore	35	740	35	91	91
		45	800	40	100	91
	0.45- μ Acropor	35	1200	43	126	91
		45	1450	46	140	89
	0.27- μ Selas ^(a)	8	425	28	77	90
	Selas-7 ^(b)	35	750	40	69	85

(a) Ceramic filter element, outside pressurization.

(b) 7-Channel ceramic hyperfiltration tube, inside pressurization.

In a series of tests of the hyperfiltration of food and paper wastes, we simultaneously gathered information of the effect of velocity during formation for membranes formed on 7-channel Selas tubes. For these tests, we constructed a small module containing three sections in series. The first section contained a single tube, the second contained two tubes in parallel, and the third contained three tubes in parallel. With this configuration, results could be obtained at three velocities in a single run, with all other conditions essentially equal. After each run with a food or a paper waste, the tubes in the module were washed with 1 M base and 1 M acid under pressure, and rinsed with water, and a new membrane formation was carried out. In some cases, the clean-up procedure was apparently inadequate, due, we believe, to the presence in the loop of a Ferro-tube module which had a tendency to trap organic materials in inaccessible places. In these cases, subsequent membranes were inferior. Thus, out of eleven formations in which the series-parallel Selas-tube module was used, four resulted in membranes which averaged less

than 80% rejection, and results from them are not used in the following comparisons. Of the other seven, we compared formation velocities of 10, 15, and 30 fps. At 10 fps, the R_{obs} for 0.05 M NaCl at 950 psig and 25°C, after membrane formation and before exposure to food or paper wastes, averaged about 87% (range 82 to 91%) at about 38 gfd (range 27 to 64 gfd). At 15 fps, the values were 87% (83 to 93) at 49 gfd (22 to 94), and at 30 fps, 85% (81 to 91) at 53 gfd (26 to 86). Rejections at all velocities were comparable, but the fluxes were appreciably better at 15 and 30 fps than at 10 fps. The small difference in average flux between 15 and 30 fps, even if verified, would point to no advantage for membrane formation at the higher, less economical, velocity. These supports appear to differ from, for example, 0.45-micron Acropor in response to this variable.

When loop 10 was constructed (see Section 1.3), we were able to test high circulation velocities during the early stages of membrane formation, where, because of low pressure, our usual circulation pumps would cavitate. In the first experiment in which we utilized the Byron-Jackson pump (100 gpm at 185 psig) we formed dual-layer membranes on 0.025-micron Millipore and 0.45-micron Acropor supports at 35 fps from the beginning. When the system pressure increased to 185 psig, the test sections were switched to the high pressure loop and the 100-A circulation pump put into use. At pH 6.6 and 950 psig, rejection of 0.05 M NaCl was 97% at 108 gfd on the Acropor and 93% at 25 gfd on the Millipore. The fluxes were lower than anticipated and may have been the result of several shutdowns which occurred during adjustments to the equipment in this initial run.

The next run with loop 10 was a repeat of the run just described, except that 0.22-micron Millipore was used instead of the 0.025-micron Millipore used before. The changeover to the high pressure loop was made at 170 psig, and the resulting membranes were no better than those we had come to expect on other loops. After 18 hours of operation, the membrane on the Acropor rejected 92% of 0.05 M NaCl at 128 gfd, while that on the Millipore rejected 94% at 113 gfd (950 psig).

The third test of the new equipment involved formation of dual-layer membranes on a 31-tube Sela protomodule (0.27-micron pore size, 2 ft² area) that had been tested before on another loop (see Section 3.1.2.1.1.3). We

achieved 88% observed rejection at 41 gfd (950 psig, 10 fps, 28°C, pH 6.5), a performance roughly equivalent to that which we got before.

Results from experiments with this equipment indicate that it is probably not of prime importance to have high circulation velocities at the onset of membrane formation.

It is difficult to summarize the effect of circulation velocity during the various steps of membrane formation, because it appears to be different with different supports. Further, the tests reported here have been done at various times in the evolution of membrane-forming procedures. Consequent differences in methods, as well as inadvertent variations in conditions, such as loop cleanliness, result in considerable scatter in properties. Conclusions are necessarily tentative, and most confidence can probably be placed in comparisons between membranes formed and tested in the same run at different circulation velocities and on different supports.

It appears, however, that, with membranes formed on Millipore and Acropor filters of, say, greater than 0.1-micron pore size, fluxes through the hydrous oxide sublayer are usually higher when formation is at higher circulation velocities, and the advantage is maintained when the polyacrylate layer is added. Circulation velocity during the formation of the polyacrylate layer seems less important. With pore sizes less than 0.1 micron, and with carbon and ceramic supports, correlation of fluxes with circulation velocity is less clear.

We have no explanation for differences in membrane properties on different supports of comparable pore size. Further, when comparisons of permeabilities of bare supports with those of membranes on the same supports are considered, it is clear that most of the pressure drop is through the membrane layer. Thus, differences in permeability between membranes on supports of different pore sizes are puzzling.

These questions have obvious practical importance. It is in one sense encouraging that, with supports which seem more amenable for practical application, e.g. carbon or ceramic, high velocities during membrane formation do not seem to result in greatly improved performance. However, membranes formed on these practical supports are comparable to those formed on 0.45-micron Acropor and 0.22-micron Millipore at lower velocities, and it is

perhaps more accurate to say that increasing velocity does not improve the properties of membranes on the ceramic and carbon supports to the extent that it does with the filter sheets.

3.1.2.10 Effect of Pressure. Because the cost of hyperfiltration processes are higher for high-pressure operation than they are for low-pressure operation, we made a series of studies on the hyperfiltration properties of membranes formed at pressures lower than the 950 to 1000 psig we normally use. Even if the process hyperfiltration were to be carried out at higher pressures, it might prove to be less costly to form the membranes at low pressures and then move them to the high-pressure process loop when needed. However, the results reported below do not encourage us concerning the value of this procedure.

3.1.2.10.1 Formation at 95 psig. We preformed two dual-layer membranes at about 95 psig on 0.025- μ Millipore and 0.45- μ Acropor substrates in a low-pressure stainless steel loop. We then transferred these membranes to the high-pressure loop and measured their characteristics at 950 psig. At the higher pressure, fluxes were high but rejections less than 40%. The addition of 5 ppm PAA (Acrysol A-5) at constant pH (~ 7.2), caused a sharp decrease in flux (to 25 and 51 gfd) and an increase in observed rejection to about 80%. Cycling the feed to pH ~ 4 caused little change in membrane performance when the pH was returned to 7.3.

3.1.2.10.2 Formation at 350 psig. In four separate runs, which included the formation of twenty different dual-layer hydrous Zr(IV) oxide-PAA (Rohm and Haas Acrysol A-3) membranes at 350 psig, we consistently found poorer performance than we have come to expect from similar membranes made at 950-1000 psig. At 350 psig, R_{obs} for 0.05 M NaCl never exceeded 80% and usually was much lower, while the fluxes were usually well below 100 gfd. There were no significant differences noted between 350 psig membranes formed at 35 fps circulation velocity and those formed at 12 fps.

When the membranes formed at 350 psig were exposed to 0.05 M NaCl solution at higher pressures (950-1000 psig), the rejections did not change significantly, although the fluxes improved approximately proportional to the change in pressure (see Table 3.39). Upon returning to 350 psig, membrane performance reverted to that shown originally at that pressure.

TABLE 3.39
HYPERFILTRATION PERFORMANCE BY DUAL-LAYER MEMBRANES FORMED AT 350 PSIG
(0.05 M NaCl, 35 fps)

Run	Pressure	0.025- μ Millipore		0.05- μ Millipore		0.45- μ Acropor	
		Flux (gfd)	R_{obs} (%)	Flux (gfd)	R_{obs} (%)	Flux (gfd)	R_{obs} (%)
1	350	57	67	60	75	81	76
	950	126	78	198	79	609*	49*
	350	62	57	80	61	226*	42*
2	350	115	44	76	49	50	53
	950	226	65	170	70	204	54
3	350	71	56	57	70	78	48
	950	108	71	138	76	229	47
4	350	68	58	64	61	98	54
	950	110	66	154	67	237	58

*The high fluxes and especially low rejections here probably indicate a membrane rupture upon going to the higher pressure.

The best rejections of synthetic Coalinga water by these membranes, as measured by conductivity, were 45% at 143 gfd at 350 psig and 66% at 143 gfd at 950 psig. At both pressures, rejection was somewhat lower than that we would expect from membranes formed at 950 psig, typically about 80% at fluxes near 100 gfd in short-term runs.

3.1.2.10.3. Formation at 600 psig. Three different runs were made (Table 3.40), and each of them gave evidence that membranes formed at 600 psig have properties better than those formed at lower pressures, but not as good as those formed at the normal 950 psig. The best of the membranes rejected about 90% of the salt from 0.05 M NaCl solution with a flux of about 50 gfd. Fluxes increased, with some sacrifice in R_{obs} , upon raising the pressure to 950 psig. Upon returning to 600 psig, fluxes declined somewhat without a commensurate rise in rejection. There was no discernible difference in 600 psig membranes formed at different velocities.

The intermediate pressure membranes were also poorer in the rejection of the constituents of synthetic Coalinga water, R_{obs} being some 10 to 15% lower than those we expect from a typical 950 psig membrane. Fluxes were appreciably lower also (see Table 3.41).

TABLE 3.40
HYPERFILTRATION BY DUAL-LAYER MEMBRANES FORMED AT 600 psig
(0.05 M NaCl, 35 fps, 10^{-4} M Zr(IV); 50 ppm Acrysol A-3)

Run	pH	Pressure (psig)	Support *	Flux (gfd)	R_{obs} (%)
1	8.0	600	0.025- μ M	46	90
			0.45- μ A	64	89
	7.1	1000	0.025- μ M	90	89
			0.45- μ A	161	78
	8.8	600	0.025- μ M	64	83
			0.45- μ A	89	80
2	8.0	600	0.025- μ M	81	68
			0.45- μ A	147	77
3	9.0	600	0.025- μ M	82	76
			0.05- μ M	95	82
			0.1- μ M	73	79
			0.45- μ A	172	78
			1.2- μ A	147	79

* M = Millipore
A = Acropor AN

TABLE 3.41
HYPERFILTRATION OF SYNTHETIC COALINGA WATER BY DUAL-LAYER MEMBRANES
FORMED AT 600 PSIG IN RUN 3 OF TABLE 3.40
(35 fps; 600 psig)

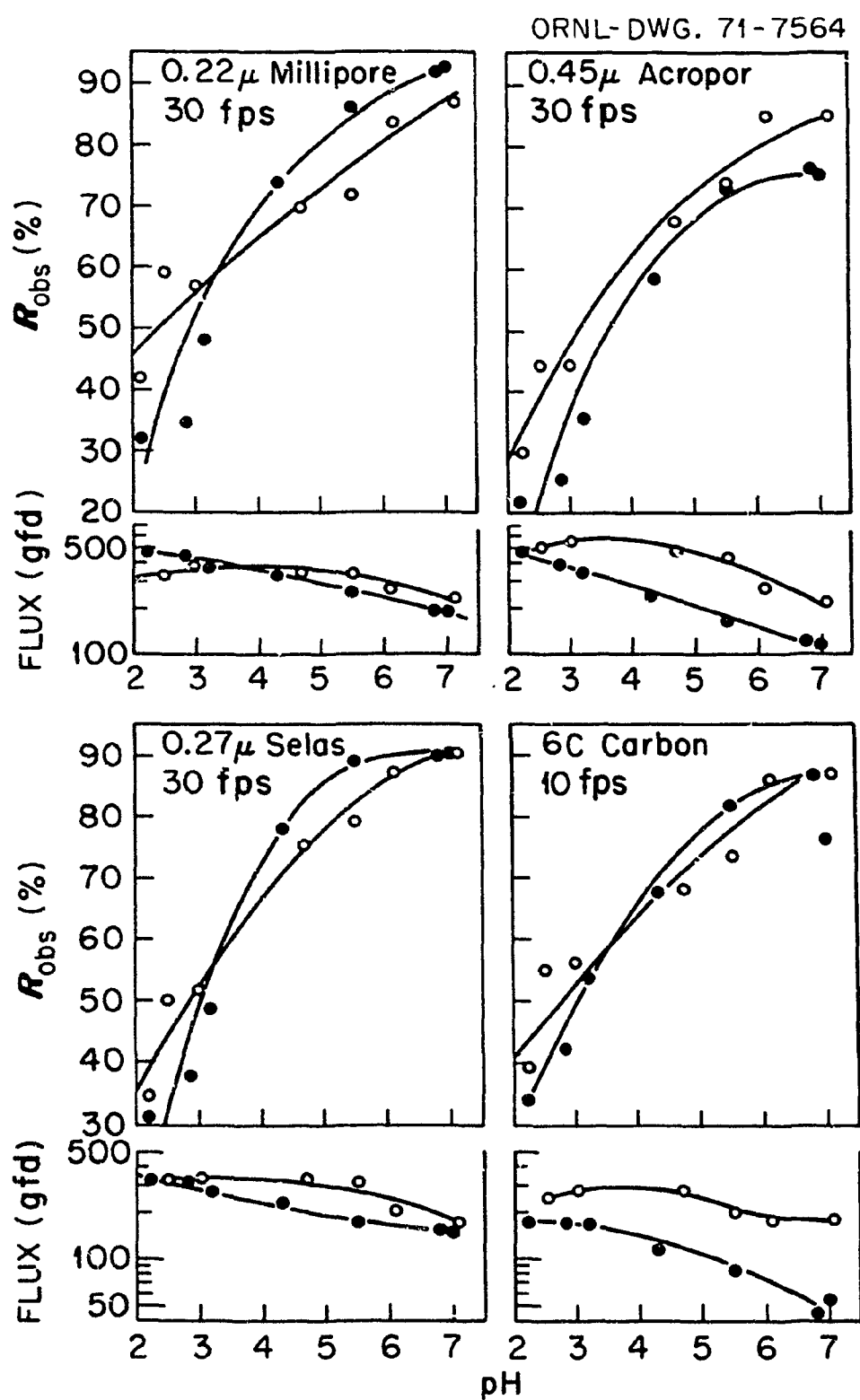
Support *	Flux (gfd)	Conductivity	Cl ⁻	Mg ⁺² + Ca ⁺²	Total Cation
.025- μ M	47	67	48	91	75
.05- μ M	42	71	59	93	79
.1- μ M	38	69	51	92	75
.45- μ A	82	66	47	89	72
1.2- μ A	68	62	45	82	65

* M = Millipore
A = Acropor AN

3.1.2.11. Effect of Temperature. We have had some indication that formation at 55-60°C tended to produce more stable dual-layer membranes, especially on carbon and ceramic supports, than did formation at 25°C. We consequently ran a set of experiments to determine if it were advantageous or not to maintain the higher temperatures during the formation of the sublayer as well as during the formation of the PAA layer. Fig. 3.11 presents the changes in properties during an increase in pH after PAA addition for four different supports already carrying the hydrous oxide sublayer. The open circles indicate the results when both the sublayer and the PAA layer are formed at the higher temperature. The solid circles are the results of a run in which the sublayer was formed at 25°C, the PAA layer at 55-60°C. Although there is no definite trend of rejections at pH 7, fluxes are invariably better for the case in which both layers were formed at the higher temperatures. The advantage is particularly apparent for the Sela and the carbon supports, where final rejections are comparable for the two techniques.

The two sets of membranes described above were tested on Coalinga water at 25°C. The results of these short-term runs are listed in Table 3.42. The rejections were measured by conductivity. Once again, the fluxes are better for the case in which both layers were formed at the higher temperatures, except for the Acropor support, where the very low rejection, 22%, indicates serious membrane deterioration. The performance of the two-temperature membrane of the Sela tube has apparently also been impaired. Except for the high rejection on the two-temperature membrane of the Millipore support, the rejections for the two cases appear to be comparable. Since these results come from a single pair of runs, conclusions derived from them must be considered tentative.

3.1.2.12. Effect of pH. In early studies, polyacrylate was usually introduced at pH values in the range of 3 to 4. Subsequently, in work in engineering development⁷ and in this program, we found that carrying out this step at lower pH substantially improved performance. By reducing the pH to about 2 at the time the PAA was added, we could usually form membranes that reject 90-95% of the salt from 0.05 M NaCl solution at fluxes between 100 and 160 gfd. Data for five different runs made in this way are



PAA MEMBRANE FORMATION, HYDROUS
Zr(IV) OXIDE SUBLAYER.
(900 psig, 55-60°C)

- BOTH LAYERS FORMED AT 55-60°C
- Zr(IV) LAYER FORMED AT 25°C
PAA LAYER FORMED AT 55-60°C

Fig. 3.11

TABLE 3.42

HYPERFILTRATION OF COALINGA WATER BY DUAL-LAYER HYDROUS Zr(IV)
OXIDE--PAA MEMBRANES WITH THE TWO LAYERS FORMED AT THE SAME
TEMPERATURE (55-60°C) AND AT DIFFERENT TEMPERATURES (SUBLAYER
AT 25°C, PAA LAYER AT 55-60°C)

(900 psig, 25°C)

	Velocity (fps)	Same Temperature		Different Temperature	
		Flux (gfd)	R_{obs} (%)	Flux (gfd)	R_{obs}
0.22- μ Millipore	30	85	66	37	92
0.45- μ Acropor AN	30	115	55	130	22
0.27- μ Selas	30	62	68	15	21
6C Carbon	10	63	62	11	69

presented in Table 3.43. Run 4 was a repeat of Run 3, but for some reason, the fluxes obtained were appreciably lower than those obtained in Run 3. By standards at that time, however, even the Run 4 results would have been considered good. Run 5 differs from 3 and 4 only in the molecular weight of the Acrysol used. The values given in Table 3.43 are for fresh (< 4 hours) membranes, except for Run 1, where the data were taken after 17 hours operation.

We also made one run to test whether or not a pH near 1.0 at the time of PAA addition would give even better membranes than the ones described above. In this run, hydrous Zr(IV) oxide sublayers were deposited on two double-fingers, each wrapped with one 0.025- μ Millipore and one 0.45- μ Acropor AN support, under nearly identical conditions of flow and pressure. One finger was then removed while PAA was added to a 0.05 M NaCl solution at pH 1.3. This feed was circulated under pressure past the remaining finger for thirty minutes. At that time, the loop was shut down, the pH was raised to 2.9, and the removed finger reinserted. The loop operation was resumed, and the usual procedure of "forming" the double-layer membrane by incremental increases in pH was carried out. The results of this experiment are tabulated as Run 6 in Table 3.44.

These results indicate no clear advantage is to be gained by going to such acid conditions (pH 1) at the time the PAA is added, although the membrane on 0.45- μ Acropor AN, with a flux of 207 gfd at 87% rejection, is an interesting one. Concentration polarization at 207 gfd is appreciable, even at 35 fps, and the intrinsic rejection of this membrane is certainly in the 90% range.

TABLE 3.43
HYPERFILTRATION RESULTS OF DUAL-LAYER
HYDROUS Zr(IV) OXIDE--PAA MEMBRANES
(0.05 M NaCl, 35 fps, 950 psig)

Run No.	pH*	Porous** Support	PAA	Flux (gfd)	R _{obs} (%)
1	2.2	.22-μ M	A-3	132	95
		.45-μ A		185	90
2	2.3	.45-μ A	A-3	132	92
	3.6	.45-μ A		255	80
3	2.2	.22-μ M	A-3	162	95
		.22-μ M		147	94
		.45-μ A		141	94
		.45-μ A		147	94
4	2.2	.22-μ M	A-3	100	94
		.22-μ M		99	94
		.45-μ A		80	94
		.45-μ A		98	94
5	2.3	.22-μ M	A-5	160	95
		.22-μ M		163	95
		.45-μ A		167	92
		.45-μ A		164	91

*pH at which PAA was added; rejections and fluxes measured at pH 7-8.

**M = Millipore; A = Acropor AN.

TABLE 3.44
EFFECT OF INITIAL pH VALUES ON PERFORMANCE OF DUAL-LAYER
HYPERFILTRATION MEMBRANES. FLUXES AND REJECTION OBTAINED AT pH 7.2
(0.05 M NaCl, 35 fps, 950 psig)

Run	Support	pH at Zr(IV) Addition	pH at PAA Addition	Flux (gfd)	R _{obs} (%)
6	0.025-μ Millipore	3.7	1.3	64	86
	0.45-μ Acropor AN	3.7	1.3	207	87
	0.025-μ Millipore	3.7	2.9	85	82
	0.45-μ Acropor AN	3.7	2.9	255	78
7	0.025-μ Millipore	2.1	2.1	79	87
	0.05-μ Millipore	2.1	2.1	86	86
	0.22-μ Millipore	2.1	2.1	105	93
	0.45-μ Acropor AN	2.1	2.1	122	91
	1.2-μ Acropor AN	2.1	2.1	75	86

We tried also, see Run 7, Table 3.44, to form both the hydrous zirconium oxide and the PAA layers at a pH near 2. In practice, it was difficult to form hydrous zirconium oxide sublayers at this pH; for some reason, it does not seem to deposit properly on the porous support. To form the sublayers of Run 7, we had to resort to injecting the hydrous oxide just upstream of the test sections so that the porous supports were exposed to zirconium concentrations appreciably higher than the 10^{-4} M solution we usually use. Because of the extra time and effort required to form the sublayer and because the results do not indicate any advantage, we conclude that forming the hydrous oxide layer at pH 2 is not desirable.

3.1.2.13. Effect of Feed Composition During Membrane Formation.

3.1.2.13.1. Effect of NaCl Concentration. Since, in the formation of a Zr(IV)-PAA membrane, the PAA is introduced from an acid solution (pH $\sim$ 2), where the polyelectrolyte should be predominantly in the uncharged hydrogen form, it might appear unlikely that the salt concentration in the solution should have a major effect on the conformation of the polymer*. However, in a series of tests, results of which are given in Table 3.45, we have shown that the salt concentration during membrane formation does have an appreciable effect of the properties of the completed membrane.

In comparing runs 1 and 2, it can be seen that final fluxes were higher for the membranes formed at 0.05 M NaCl, but that the rejections were somewhat higher for those formed at 0.01 M. Runs 3 and 4 show mixed results; better membranes were made on the Millipore support from the lower concentration (0.05 M) than from the higher (0.1-0.25), but the opposite held true for the 0.45-micron Acropor. The last four runs were made to determine if membranes made from more concentrated salt solutions might not be affected as much by the divalent ions in naturally occurring brackish waters. The results of those experiments are described later (Section 3.3.1.2.7), but as far as hyperfiltration of 0.05 M NaCl is concerned, high NaCl concentration during formation appears to result in lower flux. This is especially true if the NaCl concentration is high during the formation of the PAA layer,

*The coiling phenomena in the presence of salt is well documented by the many studies of the viscosity of polymer solutions as a function of ionic strength.²⁹

TABLE 3.45
EFFECT OF NaCl CONCENTRATION DURING THE FORMATION OF
Zr(IV)-PAA MEMBRANES
(900-1000 psig, ~25°C)

Run	<u>M (NaCl)</u> during formation		Support	Velocity (fps)	Zr(IV) Layer ^a		PAA Layer ^b	
	Zr(IV) Layer	PAA Layer			Flux (gfd)	R _{obs} (%)	Flux (gfd)	R _{obs} (%)
1	0.01	0.01	0.025-μ Millipore	45	480	58	82 ^c	88 ^c
			0.45-μ Acropor	45	2120	37	150 ^c	90 ^c
2	0.05	0.05	0.025-μ Millipore	45	725	45	270 ^c	78 ^c
			0.45-μ Acropor	45	1740	50	340 ^c	84 ^c
3	0.05	0.05	0.22-μ Millipore	35	765	48	174	94
			0.45-μ Acropor	35	1480	45	102	86
4	0.10	0.25	0.22-μ Millipore	35	480	38	150	79
			0.45-μ Acropor	35	1135	40	185	89
5	1.0	1.0	6C carbon tube	33	865	3	27	94
			Coated Ferro 600p	32	780	3	30	95
			0.05-μ Millipore	32	822	3	27	98
			0.45-μ Acropor	32	822	3	42	78
6	0.05	1.0	6C carbon tube	31	555	52	33	94
			Coated Ferro 600p	30	440	46	30	82
			0.05-μ Millipore	32	800	66	23	96
			0.45-μ Acropor	32	735	58	32	96
7	1.0	0.05	6C carbon tube	31	557	6	68	91
			Coated Ferro 600p	30	380	4	62	90
			0.05-μ Millipore	32	235	13	58	94
			0.45-μ Acropor	32	425	15	105	93
8	0.3	0.3	6C carbon tube	31	595	4	70	84
			Coated Ferro 600p	30	637	3	56	86
			0.05-μ Millipore	32	403	12	44	89
			0.45-μ Acropor	32	935	8	106	84

(a) Measurements made at salt concentration at which hydrous Zr(IV) oxide layer was formed.

(b) Measurements made with 0.05 M NaCl.

(c) Measurements made at 35 fps.

as in runs 5 and 6. Here the fluxes are relatively low, but the rejections, with the exception of one support in each run, are high. In run 7, where 1 M NaCl was used during the Zr(IV) layer formation, rejections are satisfactory, but fluxes seem somewhat low. In run 8, where both layers were formed from intermediate concentrations, neither fluxes nor rejections were outstanding.

3.1.2.13.2. Effect of Presence of Na_2SO_4 . We formed one set of dual-layer membranes by depositing the hydrous oxide layer in the normal fashion from 0.05 M NaCl and the PAA layer from a 0.025 M Na_2SO_4 solution. The resulting membranes were satisfactory with respect to the hyperfiltration of 0.025 M Na_2SO_4 , but only fair with respect to 0.05 M NaCl. The results are given in Table 3.46.

TABLE 3.46

HYPERFILTRATION BY DUAL-LAYER MEMBRANES IN WHICH THE HYDROUS
OXIDE SUBLAYER WAS FORMED FROM 0.05 M NaCl AND THE PAA LAYER
FROM 0.025 M Na_2SO_4

(900 psig, 27°C)

Solution	Support	Velocity (fps)	Zr-Layer (pH 4)		Dual-Layer (pH 7.2)	
			Flux (gfd)	R_{obs} (%)	Flux (gfd)	R_{obs} (%)
0.05 <u>M</u> NaCl	0.22- μ Millipore	35	1110	46	--	--
	0.45- μ Acropor	35	1470	47	--	--
	0.27- μ Sela	32	867	52	--	--
	6C carbon	10	496	31	--	--
0.025 <u>M</u> Na_2SO_4	0.22- μ Millipore	35	--	--	130	98
	0.45- μ Acropor	35	--	--	126	96
	0.27- μ Sela	32	--	--	91	95
	6C carbon	10	--	--	44	88
0.05 <u>M</u> NaCl	0.22- μ Millipore	35	--	--	122	88
	0.45- μ Acropor	35	--	--	124	85
	0.27- μ Sela	32	--	--	88	84
	6C carbon	10	--	--	46	76

We then formed a set of dual-layer membranes where both layers were deposited from 0.025 M Na_2SO_4 , (see Table 3.47). Although the hydrous oxide layers at pH 4 exhibited reasonable fluxes (i.e., ~ 900 gfd), the

TABLE 3.47

HYPERFILTRATION BY DUAL-LAYER MEMBRANES IN WHICH BOTH LAYERS WERE
FORMED FROM 0.025 M Na₂SO₄ SOLUTION

(1000 psig, 28°C)

Solution	Support	Velocity (fps)	Zr-Layer (pH 4)		Dual-Layer (pH 7)	
			Flux (gfd)	R _{obs} (%)	Flux (gfd)	R _{obs} (%)
0.025 <u>M</u> Na ₂ SO ₄	0.025-μ M*	35	905	2	6	89
	0.22-μ M*	35	870	2	6	91
	6C carbon tube	12	870	2	6	94
0.05 <u>M</u> NaCl	0.025-μ M*	35	--	--	6	68
	0.22-μ M*	35	--	--	5	82
	6C carbon tube	12	--	--	4	84

*M = Millipore

fluxes dropped drastically when the PAA was added to the feed solution in the presence of sulfate. Permeabilities of the completed membranes were low with both chloride and sulfate solutions. It is not obvious to us what caused the low fluxes, but the reason must involve the hydrous oxide layer. A loose hydrous oxide layer could conceivably permit penetration of excessive polyacrylic acid, but there is no indication from the fluxes that the hydrous oxide layers formed from sulfate are in fact more open than those formed from chloride.

3.1.2.13.3. Effect of Presence of MgCl₂. We formed a set of dual-layer membranes in which 0.025 M MgCl₂ was used instead of 0.05 M NaCl during the formation of both layers. The results of a series of tests on these membranes are shown in Table 3.48. In tests 1 and 2, the results indicate that fluxes through hydrous oxide layers formed from the MgCl₂ differ little from those for membranes formed from 0.05 M NaCl solutions. For the 0.22-μ Millipore and 0.45-μ Acropor supports at 35 fps, the fluxes for the MgCl₂ case may be compared with the results of run 3 in Table 3.45. The higher rejections of MgCl₂, a salt with a divalent coion, are expected for an anion-exchange membrane.

TABLE 3.48
HYPERFILTRATION TESTS OF DYNAMIC MEMBRANES FORMED
FROM 0.025 M MgCl_2 SOLUTIONS

(1000 psig, 25°C)

Test No.	Test Solution	pH	PAA (ppm)	Support	Velocity (fps)	Flux (gfd)	R _{obs} (%)	Comments
1	0.025 <u>M</u> MgCl ₂	3.8	0	0.22-μ MP	20	480	53	Zr(IV) layer only
				0.45-μ AP	20	695	57	
				6C carbon	24	355	52	
				0.22-μ MP	35	810	62	
				0.45-μ AP	35	1350	66	
2	0.025 <u>M</u> MgCl ₂	7.0	0	0.22-μ MP	20	410	9	Zr(IV) layer
				0.45-μ AP	20	680	6	
				6C carbon	24	325	14	
				0.22-μ MP	35	765	12	
				0.45-μ AP	35	1300	8	
PAA circulated for 45 minutes, 0.025 <u>M</u> MgCl ₂ , pH 6.4:								
3	0.025 <u>M</u> MgCl ₂	6.4	50	0.22-μ MP	20	120	12	Dual-layer
				0.45-μ AP	20	100	11	
				6C carbon	24	85	7	
				0.22-μ MP	35	34	50	
				0.45-μ AP	35	39	41	
4	0.05 <u>M</u> NaCl	7.0	0	0.22-μ MP	20	61	80	Dual-layer
				0.45-μ AP	20	64	74	
				6C carbon	24	37	56	
				0.22-μ MP	35	68	87	
				0.45-μ AP	35	89	84	
5	0.025 <u>M</u> MgCl ₂	2.2	50	0.22-μ MP	20	79	38	Dual-layer
				0.45-μ AP	20	89	35	
				6C carbon	24	50	24	
				0.22-μ MP	35	122	41	
				0.45-μ AP	35	143	37	
Through acid cycle, 0.05 <u>M</u> NaCl, no additives:								
6	0.05 <u>M</u> NaCl	7.8	0	0.22-μ MP	20	20	95	Dual-layer
				0.45-μ AP	20	26	86	
				6C carbon	24	19	55	
				0.22-μ MP	35	20	96	
				0.45-μ AP	35	26	94	
Through acid cycle, 0.025 <u>M</u> MgCl ₂ , 50 ppm PAA:								
7	0.025 <u>M</u> MgCl ₂	7.8	50	0.22-μ MP	20	4	93	Dual-layer
				0.45-μ AP	20	10	82	
				6C carbon	24	15	70	
				0.22-μ MP	35	5	67	
				0.45-μ AP	35	10	66	

(Continued on next page)

TABLE 3.48 (Continued)

Test No.	Test Solution	pH	PAA (ppm)	Support	Velocity (fps)	Flux (gfd)	R_{obs} (%)	Comments
Loop rinsed 1 hour with water; 0.05 <u>M</u> NaCl circulated 1 hour:								
8	0.05 <u>M</u> NaCl	7.2	0	0.22- μ MP	20	14	95	Dual-layer
				0.45- μ AP	20	20	83	
				6C carbon	24	20	79	
				0.22- μ MP	35	18	96	
				0.45- μ AP	35	25	94	
Washed with 1 <u>M</u> NaCl for 2.5 hours:								
9	0.05 <u>M</u> NaCl	7.6	0	0.22- μ MP	20	44	92	Dual-layer
				0.45- μ AP	20	70	82	
				6C carbon	24	26	74	
				0.22- μ MP	35	67	97	
				0.45- μ AP	35	79	93	

After we had formed the hydrous oxide layer in the presence of MgCl_2 at pH 3.8, we raised the pH to 7 and again measured fluxes and rejections (test 2). Fluxes decreased by only 8% or so, but rejections of the MgCl_2 , as expected from the change in ion-exchange capacity,¹³ decreased drastically. Polyacrylic acid was added to the solution at neutral pH and circulated, with no acid cycle, past the membranes for about 45 minutes. Test 3 shows that the MgCl_2 was rejected by 50% or less, but test 4 demonstrated that the rejection of 0.05 M NaCl, after the MgCl_2 was rinsed out, was reasonably high. It appears that effective ion-exchange membranes had been formed; these rejections are the best we have achieved for dynamic PAA membranes formed without exposing the sublayer to PAA at low pH*. Lowering the pH to 2.2 in the presence of 0.025 M MgCl_2 and 50 ppm PAA (test 5) caused an increase in flux, but reduced the rejections, as measured by conductivity, to less than half those found in Test 4.

*We tried once again, following this test, to form an effective dual-layer membrane by adding the PAA to 0.05 M NaCl from neutral solution, using four different porous supports already carrying the hydrous oxide layer. After 30 minutes of circulation at 950 psig, all rejections were lower than 45%. Since an acid cycle in the presence of PAA at least doubled all values of R_{obs} , the hydrous oxide layer must have been satisfactory. Exposure of a hydrous Zr(IV) oxide sublayer to a Mg(II)-containing solution at neutral pH appears to have a very different effect than exposure to a Na^+ -containing solution. Since the most obvious property that solutions of PAA in 0.05 M NaCl at acidic pH have in common with solutions of PAA in 0.025 M MgCl_2 at neutral pH is coiling of the polymer, these observations suggest that this may be the critical factor in formation of the second layer.

Except for the membrane on the carbon tube, rejections were increased substantially by an acid cycle in the presence of 0.05 M NaCl, but without excess PAA in solution (test 6). Fluxes, however, dropped to about a third of their previous value. Tests 7 and 8 indicated that the addition of PAA to a 0.025 M solution of MgCl_2 causes, upon going through an acid cycle, a very strong reduction in fluxes, with erratic effects on rejection. A two and one-half hour wash with 1 M NaCl improved fluxes appreciably in test 9; perhaps some of the Mg(II) was displaced.

3.1.2.13.4. Effect of Using Tap Water. To determine the possibility of forming dynamic membranes under conditions in which a convenient supply of distilled water might not be available, we ran experiments in which we attempted to form dual-layer membranes from typical city tap waters. The first of these was based on the composition of Roswell, New Mexico city water. The formulation chosen had 204 ppm Ca(II) , 53 ppm Mg(II) , 99 ppm Na^+ , 500 ppm $\text{SO}_4^{=}$, 167 ppm Cl^- , 223 ppm HCO_3^- , and 0.33 ppm iron, with a TDS of 1,250 ppm.

In the first experiment, we substituted Roswell city water for distilled water in our normal membrane formation procedure, i.e., we used 0.05 M NaCl made up with Roswell city water. In the second, we did the same, but excluded 0.05 M NaCl from the membrane formation feed solutions. Five membranes were formed in each run, and the best flux for a completed membrane was 35 gfd for a membrane formed on 0.45-micron Acropor at 35 fps in the absence of additional NaCl. The rejection for this membrane was less than 40%, and none of the rejections in either run exceeded 42%.

These experiments indicated that Roswell tap water is not suitable for formation of dynamic Zr-PAA membranes.

In a third experiment we formed membranes from 0.05 M NaCl in ORNL process water using a 6C carbon tube, a coated Ferro 600p tube, and 0.05- μ Millipore and 0.45- μ Acropor supports. With 0.05 M NaCl in distilled water, the completed membranes all showed rejections less than 65% at less than 40 gfd. Evidently the impurities in tap water interfere with proper membrane formation.

3.1.2.13.5. Effect of Using Nitrate Instead of Chloride. We normally use 0.05 M NaCl solutions to carry the polyelectrolytes used in forming dynamic membranes. However, some hardware systems may suffer corrosive attack from chloride solutions at low pH, and we ran one experiment, early in this biennium, to test the efficacy of 0.05 M nitrate as a solution from which to form membranes. In loop 8, which contained only stainless steel and titanium fittings, we formed sublayers on 0.025-micron Millipore and 0.45-micron Acropor supports at pH 3.7, using 10^{-4} M zirconyl chloride in 0.05 M NaNO_3 solution. The chloride concentration resulting from the zirconium salt, 2×10^{-4} M, probably did not affect the membrane formation in this case, but could conceivably be deleterious to hyperfiltration equipment made from less resistant materials. After about 3 hours of operation at 950 psig and 31 fps (25°C), the flux through the sublayer was 481 gfd ($R_{\text{obs}} = 18\%$) and 1133 gfd ($R_{\text{obs}} = 16\%$) on the Millipore and Acropor, respectively. The solution was rinsed from the loop with distilled water for about 30 minutes, 50 ppm of PAA (Acrysol A-5) in 0.05 M NaNO_3 was added, and the pH adjusted to 2.9 with concentrated nitric acid. After the pH was incrementally raised to 6.3, the additives were rinsed out, 0.05 M KNO_3 was added at pH 6.7, and the fluxes and rejections by conductivity were measured. For the Millipore support, rejection was 90% at 32 gfd; for the Acropor support, rejection was 85% at 89 gfd. These results were comparable to those we obtained with NaCl solutions during this early period. It seems quite probable that results equivalent to those we now obtain with NaCl solutions could be realized with nitrate solutions as well by using modifications in membrane formation techniques we have developed since these early tests. Tentatively, nitrate media appear to be acceptable alternatives to chloride when containment problems are lessened by their use.

3.1.2.14. Effect of Premixing Hydrous Oxide and Polyacrylate. If a membrane of favorable properties could be formed by depositing both hydrous oxide and polyacrylic acid on porous supports simultaneously, membrane preparation would be simplified. We attempted this with mixed Zr(IV)-PAA additives. In an initial experiment, additive stocks were prepared by adding about 0.005 moles of Zr(IV) in 500 cc to 500 cc of a PAA solution containing about 0.07 equivalents. Two stocks were used, one with the zirconium-containing solution prepared by dissolving ZrOCl_2 , and the other with a similar Zr(IV)

solution boiled about a day. Precipitates appeared in both mixings, but the aggregates produced by the unboiled Zr(IV) solution settled out noticeably faster than those in the other stock.

Membranes were formed on the inside of carbon 4A-3 tubes of 0.26 cm i.d. from 0.05 M NaCl containing mixed additive of 50 ppm PAA content. Pressures were 1000 psig, and circulation velocity 25 fps. With the unboiled additive, rejection reached 17% at 360 gfd in thirty minutes (pH 3.3). After an overnight shutdown, the additive-containing solution was replaced with fresh 0.05 M NaCl, and NaOH added. When the pH reached 7.6, rejection was 86% at 60 gfd.

With additive from boiled Zr(IV), performance was similar, though flux was higher. At pH 8.5, R_{obs} was 78% at 155 gfd. After an overnight shutdown, a pH scan produced the following results:

pH	$R_{obs}, \%$	Flux, gfd
2.9	33	175
4.5	47	165
6.7	83	115
8.5	83	115

Feed was changed to 0.01 M NaCl, pH 7.0; R_{obs} was 88% at 140 gfd.

These results were promising enough to lead us to do a series of experiments in the one-step formation of Zr(IV)-PAA membranes. In each run, the Zr(IV) and 50 ppm PAA were mixed together in the feed tank and the pH adjusted to a pre-selected value before the feed was circulated to the test sections. Several different membranes and circulation velocities were tested simultaneously. The results are presented in Table 3.49.

One may conclude from these results that, at least under the conditions tried, premixing the zirconium hydrous oxide and the PAA does not produce as good membranes as introducing them in separate steps. Except for Run 2, where the mixture was introduced into the loop at neutral pH, this procedure results in lower fluxes for the 0.45- μ Acropor support than for the 0.025- μ Millipore support, a result opposite from that usually found. Reducing the zirconium concentration to 3.5×10^{-5} M (Run 3) appeared to result in reduced flux and slightly higher rejections, but a further reduction (Run 4) reversed this apparent trend.

TABLE 3.49

PROPERTIES OF HYPERFILTRATION MEMBRANES FORMED FROM PREMIXED Zr(IV) AND PAA
(950 psig, 0.05 M NaCl, Acrysol A-5)

Run	[Zr(IV)] Molarity	pH(1)*	pH(2)*	Support***	Velocity (fps)	Flux (gfd)	R _{obs} (%)
1	10 ⁻⁴	3.7	7.8	0.025-μ M	35	85	75
				0.05-μ M	35	105	80
				0.1-μ M	35	78	72
				0.45-μ A	35	78	76
				0.025-μ M	12	92	74
				0.45-μ A	12	103	72
2	10 ⁻⁴	6.7**	8.0	0.025-μ M	35	103	78
				0.025-μ M	35	74	80
				0.22-μ M	35	110	81
				0.45-μ A	35	124	72
				0.025-μ M	21	73	76
				0.45-μ A	21	119	72
				0.45-μ A	50	143	69
3	3.5 x 10 ⁻⁵	3.3	8.5	0.025-μ M	35	74	87
				0.05-μ M	35	71	88
				0.22-μ M	35	94	76
				0.45-μ M	35	52	46
				0.025-μ M	18	51	89
				0.45-μ A	18	32	52
				0.45-μ A	44	32	51
4	2.0 x 10 ⁻⁵	3.4	7.0	0.025-μ M	35	147	72
				0.05-μ M	35	169	71
				0.45-μ A	35	81	52
				0.025-μ M	18	122	76
				0.45-μ A	18	73	57
				0.45-μ A	44	68	51

*pH(1) = pH at which the premixed additives were introduced to loop; 50 ppm PAA (~0.0007N). pH(2) = pH at which flux and R_{obs} were measured, after PAA reduced to 1-2 ppm.

**Subsequently taken through an acid cycle to pH 3 and back to pH 8 before reported measurements were made.

***M indicates Millipore, A indicates Acropor AN.

The hyperfiltration of synthetic Coalinga water by the membranes of Run 2 was also inferior to what we expect from dual-layer membranes. In Run 1, membrane rejection was improved somewhat by cycling the feed solution through acidic pH's with 50 ppm additional PAA. However, all rejections were still less than 90% and fluxes were low (40-80 gfd).

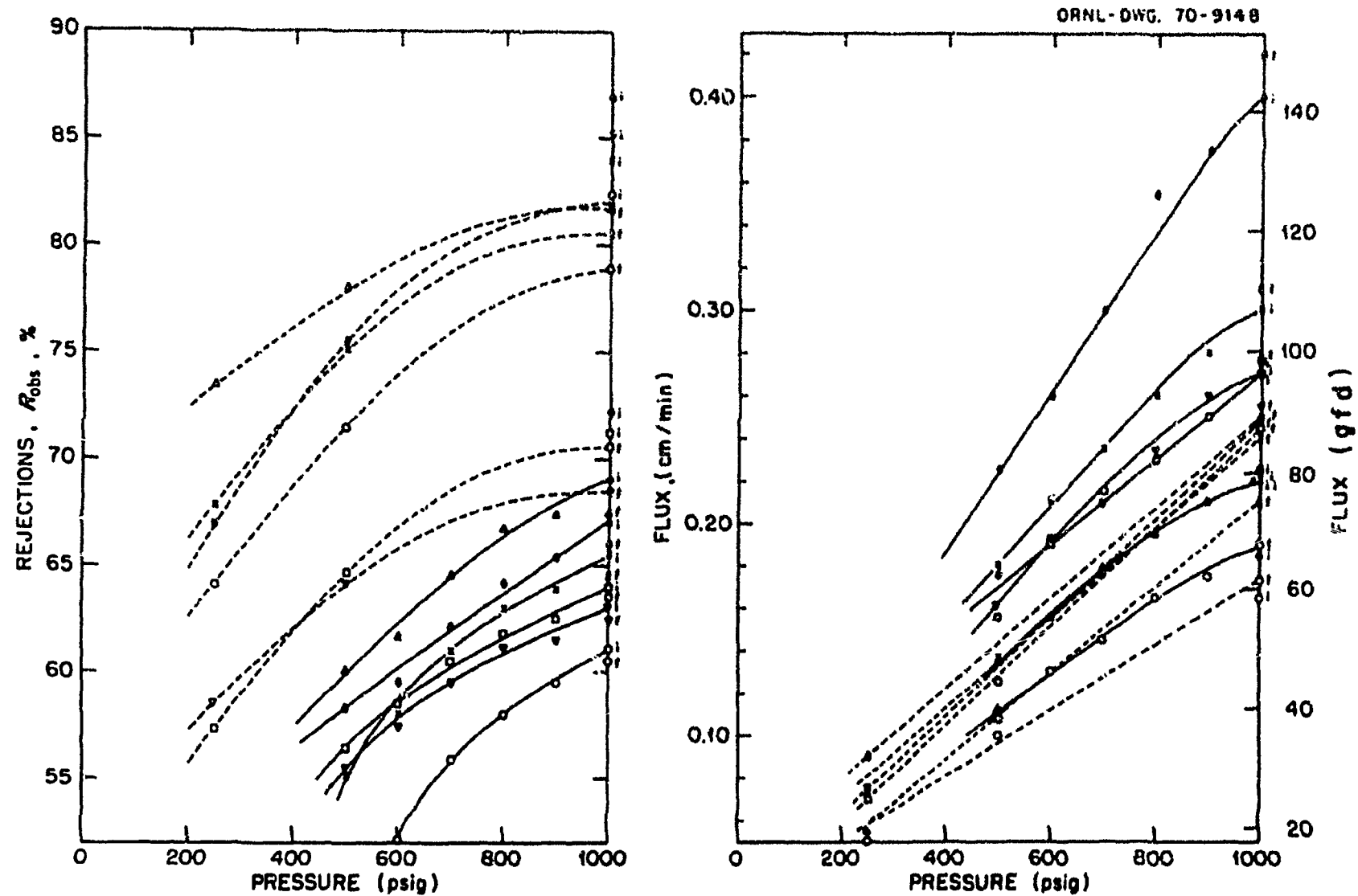
We also investigated the possibility of forming Zr-PAA membranes in a one-step process using additives which were premixed at pH 1.8 and then slowly neutralized with NaOH before being added to the loop to duplicate out-of-loop the usual pH adjustment during membrane formation. The membranes which resulted when the mixture was deposited on three different supports, 0.025- μ Millipore and 0.45 and 1.2- μ Acropor, however, fell far short of the capabilities of our usual dual-layer membranes, the best having an R_{obs} for 0.05 M NaCl of 63% at 75 gfd after 18 hours of operation. This one-step process appears inferior to that reported above, in which adjustment of pH from acidic to neutral values occurs after deposition of the membrane additive on the porous support.

3.1.3. Factors Affecting Membrane Performance

3.1.3.1. Pressure. The effect of pressure on the hyperfiltration properties of completed Zr(IV)-PAA membranes was discussed in Sections 2 and 3.1.1. Additional data on this effect are given below.

Fig. 3.12 summarizes a run in which pressures were twice cycled below the normal 950-1000 psig; first to about 500 psig after five days of operation, and secondly, to 250 psig after ten days. In the first excursion, carried out with 5 ppm PAA in the feed, pressures were lowered in steps from the initial value; in the second, with 1 ppm PAA, the lowest pressure was measured first, and the pressure was raised in steps back to 1000 psig. The curves drawn to connect points in the figure reflect this sequence by connecting to the initial (i) or final (f) 1000 psig points, whichever was closest in time to the point at the next lower pressure.

Rejections increased with pressure, and it does not appear that maximum rejections were obtained with these membranes at the highest pressure of operation (1000 psig) permissible with transparent pressure jackets. Fluxes generally increased, though not quite linearly, with pressure; fluxes per



EFFECT OF PRESSURE ON HYPERFILTRATION WITH $Zr(IV)$ OXIDE - PAA MEMBRANE
(0.05M NaCl ; 35 fps)

AFTER OPERATION FOR : — 5 days, pH-6 ; ---- 10 days, pH-7
 SUPPORTS, MILLIPORE : $\circ$ 0.025 μ , $\blacktriangle$ 0.05 μ , $\square$ 0.1 μ , $\blacklozenge$ 0.22 μ
 ACROPOR AN : $\bullet$ 0.45 μ , $\times$ 1.2 μ
 i, BEGINNING PRESSURE EXCURSION ; f, END

Fig. 3.12

unit pressure were greater after operation at lower pressures (f points usually were of higher flux than i points). Rejections were generally higher, and fluxes lower, after longer operation. There is no clear correspondence between orders of rejections or fluxes and order of pore size, even if the 0.1 and 0.22- μ points are ignored.

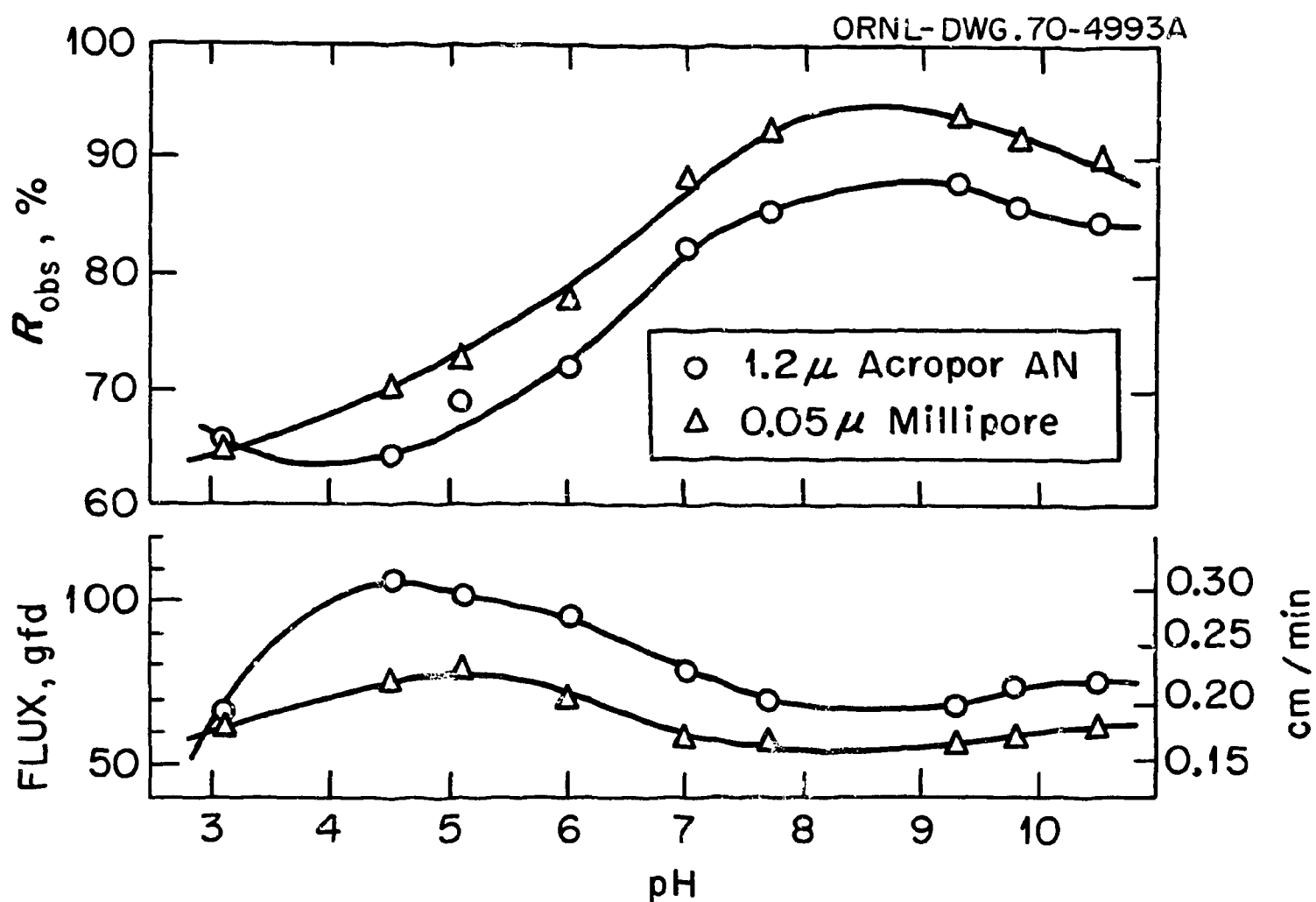
Between the two pressure cycles, the loop was operated at lower PAA levels. There was also some operation at circulation velocities between 20 and 35 fps. Results in these experiments were somewhat inconclusive, but there appeared to be no great effect on membrane properties of operations in this range of velocities, outside of expected differences in concentration polarization.

3.1.3.2. Effect of pH. There are numerous illustrations throughout this report of the effect of raising solution pH on the performance of Zr(IV)-PAA membranes during formation (e.g., Sections 2 and 3.1.1, Figs. 3.3, 3.6, 3.7, 3.8, and 3.11). In general, as one expects, rejection rises as the carboxylate groups are neutralized to the salt form and the ion-exchange capacity increases. Fig. 3.13 illustrates that the increase in rejection with increasing pH is reversible. The membranes in this case had been formed earlier, and used in other experiments before the pH scan in the figure. The feed contained 5 ppm of PAA. Rejections of 0.05 M NaCl reached a maximum of 85 to 95% at pH 8.5. It is of interest that in titration of Rohm & Haas A-5 PAA with NaOH, pH values in this range had to be reached before neutralization was complete. The slight drop in rejection at higher pH may indicate a loosening or displacement of organic polymer from the hydrous oxide sublayer.

In general, the dependence of pH appears similar to that observed with single-layer membranes,¹⁹ but rejections and fluxes are generally lower for single-layer membranes.

The results of a test of the effect of pH on the hyperfiltration of $MgCl_2$ solutions are given in Section 3.1.3.3.2 and Table 3.52.

3.1.3.3. Solution Composition. Brackish water compositions vary considerably depending upon their source, and ion-exchange membranes have different hyperfiltration properties with the different compositions (see Ref. 30, Section 2.4, p. 62ff). We have investigated further the effects of feed composition, and the results are summarized below.



EFFECT OF pH ON HYPERFILTRATION PROPERTIES OF
POLYACRYLATE MEMBRANE DYNAMICALLY FORMED ON
A HYDROUS $Zr(IV)$ OXIDE SUBLAYER

(0.05 M NaCl ; 1000 psig ; 35 fps)

Fig. 3.13

3.1.3.3.1. NaCl. In Section 2 (Fig. 3) and Section 3.1.1 (Fig. 7), we reported on a study of the concentration dependence of the hyperfiltration of NaCl solutions by dual-layer membranes. Rejections increased with decreasing salt concentration, but the dependence was less strong than that one would expect for ideal ion-exchange membranes. Our interpretation of this lower dependence was that it arose from a decrease in the ion-exchange capacity caused by the increase in the water content. Increases in water content are known to occur in low-cross-linked ion exchangers as the salt content of the contacting solution is decreased.

The interaction between NaCl and PAA, when present together in the feed solution, is illustrated by the data in Table 3.50. This Table compares results obtained at 50 ppm additive with results at 1 ppm. At the lowest NaCl concentration, 0.009 M, rejection was, if anything, slightly higher at low additive level. One might expect a small effect in this direction at low salt concentration, since the polyacrylate could contribute several percent to the sodium ion concentration, and therefore to feed activity. At 0.2 M NaCl, R_{obs} dropped substantially on decrease of additive concentration. The decrease in rejection might imply that PAA was displaced from the membrane by high salt concentration. However, the results in Table 3.50 were obtained in early studies of Zr(IV)-PAA membranes and we have not observed similar effects of additive concentration in other runs with membranes formed by current procedures. We tentatively attribute this to the fact that only about two days operation had taken place with

TABLE 3.50
EFFECT OF NaCl AND PAA CONCENTRATION
(1.2- μ Acropor, 1000 psig, 35 fps, 25°C, pH 6)

PAA (ppm)	0.009 M NaCl		0.22 M NaCl	
	R_{obs} , (%)	Flux (gfd)	R_{obs} (%)	Flux (gfd)
1	87	144	43	108
50	85	136	50	87.5

this membrane, and it may not have stabilized.

In another set of experiments, some aged membranes that had been tested with Coalinga water were also used to study the effect of concentration on the hyperfiltration of NaCl. The results are given in Table 3.51. Fluxes remained high (> 135 gfd) over the concentration range studied, but the observed rejections decreased from about 96% for 0.0028 $\underline{M}$ NaCl to 85–90% for 0.09 $\underline{M}$ NaCl.

Since rejections were not measured as a function of circulation velocity, intrinsic rejection $\mathcal{R}$ cannot be evaluated by extrapolation. Quantitative correlation of changes in $1 - \mathcal{R}$ with feed concentration in terms of concentration dependence of ion-exchange distribution coefficients is therefore not possible. However, in agreement with earlier results with PAA membranes,¹⁹ the slope of $\log (1 - \mathcal{R})$ vs $\log c_{\text{NaCl}}$ appears to approach 0.5 at low concentration, rather than the theoretical value, 1.

TABLE 3.51
HYPERFILTRATION OF NaCl SOLUTIONS BY Zr(IV)–PAA MEMBRANES
(950 psig, 35 fps, 25°C, pH ~ 7)

NaCl (M)	Concen- tration (ppm)	0.22- μ Millipore		0.22- μ Millipore		0.45- μ Acropor AN		0.45- μ Acropor AN	
		Flux (gfd)	$\mathcal{R}_{\text{obs}}$ (%)	Flux (gfd)	$\mathcal{R}_{\text{obs}}$ (%)	Flux (gfd)	$\mathcal{R}_{\text{obs}}$ (%)	Flux (gfd)	$\mathcal{R}_{\text{obs}}$ (%)
0.0028	166	162	97	160	97	166	96	164	96
0.0092	538	150	95	164	95	168	93	168	93
0.0277	1620	149	93	166	93	168	89	166	89
0.0512	2990	137	93	149	93	152	89	150	88
0.0901	5266	135	91	135	91	137	85	137	85

3.1.3.3.2. MgCl_2 . The results of an early experiment on the effect of pH on the hyperfiltration of MgCl_2 solutions are given in Table 3.52. The membranes had been used previously in several other experiments, but were rinsed thoroughly with distilled water before beginning the present tests. The acidity of the solution was varied by adding MgO or HCl.

TABLE 3.52
HYPERFILTRATION OF MgCl_2 BY Zr(IV) -PAA MEMBRANES AS A FUNCTION OF pH

(All measurements at 1000 psig and 35 fps)

Feed	pH	0.025- μ Millipore		C.45- μ Acropor AN		0.025- μ Millipore		0.45- μ Acropor AN	
		R_{obs} , %	Flux (gfd)	R_{obs} , %	Flux (gfd)	R_{obs} , %	Flux (gfd)	R_{obs} , %	Flux (gfd)
0.05 M NaCl	7.8	81	75	88	125	71	125	89	135
0.025 M MgCl_2	5.5	44	70	53	140	68	140	57	195
	7.3	38	40	39	65	-	-	38	90
	5.4	43	50	57	90	70	125	60	140
	4.3	54	85	62	175	74	140	65	250
Overnight at		46 fps				12 fps			
	4.4	54	70	62	140	76	135	65	215
	3.5	65	85	64	190	78	140	67	270
	4.6	54	70	63	140	76	135	66	215
	5.5	50	55	59	90	72	125	61	160
	7.3	39	34	41	45	37	75	39	70
	8.7	41	28	56	32	37	60	52	45
	9.3	41	28	59	28	39	55	55	40
Weekend Shutdown									
	8.2	32	40	49	40	34	60	38	55
	4.7	79	65	48	65	64	110	49	195
0.05 M NaCl	8.0	75	45	82	55	72	75	79	75

Although results were somewhat erratic, and the history of the various membranes apparently influenced properties, certain trends stood out. Both rejections and fluxes, measured at 35 fps, were higher from feeds of acidic pH. Operation of the two test sections at different velocities overnight did not drastically change properties measured at 35 fps, but a weekend shutdown brought about a decrease in rejection. Whether because of the shutdown, of aging, or of exposure to a divalent counterion, a deterioration in membrane properties was noted on return to NaCl feed. Deleterious effects of exposure to Mg(II) have been noted in other experiments when PAA was present. From these results, it appears that the deterioration results primarily from Mg(II) , though some influence of the simultaneous presence

of additive cannot be ruled out.

This conclusion was confirmed in an experiment in which a dual-layer membrane using Acrysol A-5 PAA was formed on a carbon tube. At the end of formation, the rejection of 0.05 M NaCl at pH 8 was 83% at a flux of 30 gfd (1000 psig, 3 ppm PAA). On changing to 0.025 M MgCl₂ without PAA, rejection varied from 55% at pH 6, 37 gfd, to 11% at pH 9, 5 gfd. Addition of HCl to pH 5.5 brought rejection back to 54% at 65 gfd. Ten ppm of PAA were then added and the pH increased again with MgO to 9. At this point, rejection became negative, $R_{obs} = -10\%$, and flux very low, 0.7 gfd.

In one experiment, we tested a membrane that had been washed for 30 minutes with 1 M NaOH, a procedure that we think essentially removes the PAA layer, with 50 ppm PAA in the presence of 0.025 M MgCl₂. Without recourse to an acid cycle, we got rather mixed results. At 1000 psig, 26°C, 30 fps, and pH 7.2, R_{obs} was 71% at 39 gfd on a 0.22- μ Millipore support and 82% at 31 gfd on a 0.27- μ Sela tube, but, under the same conditions, only 9.5% at 170 gfd on a 0.45- μ Acropor support. When the solution was once again made 0.05 M in NaCl, the rejections by the membranes on the Millipore and the Sela tube were within 3% of the values with MgCl₂, but that on the Acropor increased to 66%. Fluxes were up a factor of three for the first two supports, but down to 125 gfd for the Acropor. Perhaps a rupture or hole in the membrane on the Acropor support, most noticeable at the time the MgCl₂ was in the loop, was partially repaired when the final tests were made.

Experiments with different mixtures of NaCl and MgCl₂ with 0.05 M total chloride, were described in Section 3.1.1 (Fig. 8).

We also tested with 0.025 M MgCl₂ a set of membranes formed with an Al(III) sublayer and a quaternized polyvinylpyridine top layer, in the hope that on this anion-exchange membrane divalent cations would not have the usual deleterious effect they have on Zr(IV)-PAA membranes. Membranes formed on 0.45-micron Acropor were inferior to ones formed on 0.025-micron Millipore, which showed maximum rejection (80-87%) of MgCl₂ at the lowest pH, 4.1, where the fluxes ranged from about 80 to 115 gfd. Maximum fluxes were reached at about pH 6, 90 to 140 gfd, but the rejections there had dropped to 61-68%. Rejections did not change much at higher pH values, but

fluxes dropped, reaching about 60–90 gfd at pH 10. These particular membranes showed no advantage over the Zr(IV)–PAA membrane for the hyperfiltration of MgCl_2 solutions at neutral pH.

3.1.3.3.3. CuCl_2 or NiCl_2 . We have noticed on occasion some poor performance of Zr(IV)–PAA membranes in hyperfiltration of sewage that had been treated by low-pressure cross-flow filtration after pretreatment by coagulation (see Section 3.3.3.7). It seemed possible that deterioration of membrane properties had resulted from copper or nickel ions introduced by corrosion of the cross-flow filtration apparatus, rather than from the small concentration of organic matter left after the pretreatment. Since these ions might be expected to turn up in other feeds, we tested their effect on membrane properties by preparing a dual-layer membrane on a carbon tube and intentionally added these contaminants to the 0.05 M NaCl feed solution. The results for Cu(II) are given in Table 3.53.

TABLE 3.53
EFFECT OF Cu(II) ON HYPERFILTRATION BY Zr(IV)–PAA MEMBRANES
4A-3 CARBON TUBE

(0.05 M NaCl, 1000 psig, 25 fps, pH adjusted with NaOH)

Acrysol A-5 (ppm)	Contaminant	pH	$R_{\text{obs}},\%$	Flux (gfd)
50	Just before CuCl_2 addition	8.0	88	48
50	10^{-5} <u>M</u> CuCl_2	7.7	87	50
50	10^{-4} <u>M</u> CuCl_2	6.3	88	65
50	10^{-4} <u>M</u> CuCl_2	8.8	87	31
5	10^{-4} <u>M</u> CuCl_2	6.5	53	60
5	10^{-4} <u>M</u> CuCl_2	7.6	73	44
5	10^{-4} <u>M</u> CuCl_2	8.9	81	38

The feed solution was blue when the last point of Table 3.53 was taken. It turned brown during a weekend shutdown; membrane properties were only slightly affected. Addition of HCl to pH 6.5 clarified the solution, but decreased R_{obs} to 50% (67 gfd). Changing the feed to 0.05 M NaCl, 3×10^{-5}

$\underline{\text{M}}$ CuCl_2 , 1×10^{-5} $\underline{\text{M}}$ NiCl_2 , and 2 ppm PAA, pH 6, brought rejection to 59%, with the same flux. Increasing Ni(II) to 10^{-4} $\underline{\text{M}}$ had only slight effect at pH 5.4 but adjustment of pH to 9 brought rejection to 85% and flux to 31 gfd.

The effect on membrane properties of these ions cannot be clearly separated from a pH effect by means of the above results. In addition to the effect of pH increase on the membranes, hydrolysis of the Cu(II) would occur, and the consequent decrease in Cu(II) concentration may contribute to the increase in rejection at pH ~ 9 .

3.1.3.3.4. Comparison of NaCl , Na_2SO_4 , and MgCl_2 . Table 3.54 compares the performance of a Zr(IV) -PAA membrane on a 0.05-micron Millipore support with 0.05 N solutions of NaCl , with univalent ions; of Na_2SO_4 , with a divalent coion; and with MgCl_2 , with its divalent counterion. As expected with a cation-exchange membrane, rejection of Na_2SO_4 was higher, and of MgCl_2 , lower, than of NaCl . Exposure to a magnesium salt clearly had a profound effect on the membrane, since flux decreased almost an order of magnitude, and did not return to the previous value immediately on return to NaCl feed. It is possible that the effect was accentuated by the high PAA concentration (50 ppm) maintained during these tests (see, however, Sections 3.1.3.3.2 and 3.1.2.13.3). There was a gradual increase of flux with time of subsequent operation with NaCl feed.

TABLE 3.54
HYPERFILTRATION OF NaCl , Na_2SO_4 , AND MgCl_2 SOLUTIONS
WITH Zr(IV) -PAA MEMBRANE ON 0.05- μ MILLIPORE
(1000 psig, 35 fps, pH 7)

<u>Feed</u>	<u>$R_{\text{obs}}, \%$</u>	<u>Flux (gfd)</u>
0.05 $\underline{\text{M}}$ NaCl	82	74
0.025 $\underline{\text{M}}$ Na_2SO_4	98	72
0.025 $\underline{\text{M}}$ MgCl_2	64	9
0.05 $\underline{\text{M}}$ NaCl	90	28

Table 3.55 summarizes some results from an experiment in which another set of Zr(IV)-PAA membranes was exposed sequentially to a series of different brines. Trends are similar to those found in Table 3.54, but here the fluxes are higher and the values of R_{obs} are lower, due partly to greater concentration polarization, because of higher fluxes, in the present case. Some deterioration in membrane properties occurred during the course of these runs, either from the effects of time or from exposure to these feeds.

TABLE 3.55
HYPERFILTRATION OF 0.05 N SOLUTIONS BY
Zr(IV)-PAA MEMBRANES.
RESULTS ARE AVERAGES OF TWO MEMBRANES
(1000 psig, 35 fps, pH 8)

Added Salt	PAA (ppm)	Molarity	0.45- μ Acropor		0.025- μ Millipore	
			Flux (gfd)	$R_{obs},\%$	Flux (gfd)	$R_{obs},\%$
NaCl	1	0.05	290	86	225	77
NaCl	1	0.20	290	74	240	63
Na ₂ SO ₄	1	0.025	300	92	225	91
MgCl ₂	1	0.025	115	40	90	39
NaCl	1	0.05	145	78	120	74
Acid cycle with no PAA in feed						
NaCl	0	0.05	200	66	140	73
Acid cycle with 10 ppm PAA in feed						
NaCl	10	0.05	120	83	95	79

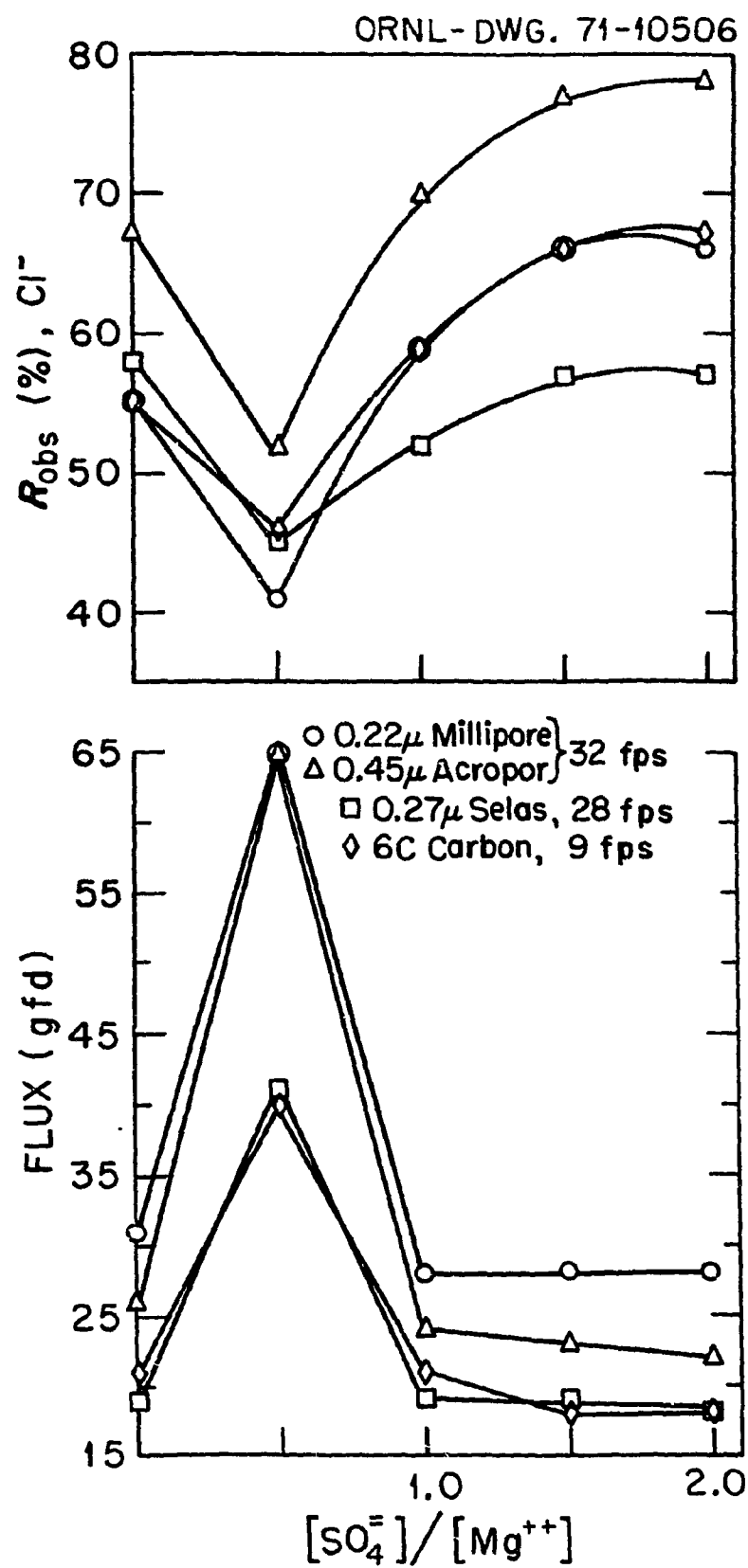
A question of interest is whether deterioration of membrane properties stems from displacement of PAA from the hydrous oxide layer, or from a loosening of the polyacrylate by binding at fewer points on the Zr(IV) layer. If the former, presence of PAA during an acid cycle to restore performance is necessary; if the latter, no PAA should be necessary. We attempted to distinguish between these two possibilities by rinsing the system with water and cycling to acidic pH with no PAA. No improvement of membrane properties occurred. An acid cycle (interrupted by a shutdown)

in presence of 10 ppm PAA restored rejections to almost the values at the beginning of the series, although fluxes were lower.

3.1.3.3.5. MgCl_2 - Na_2SO_4 Mixtures. We have studied the hyperfiltration of simulated brackish waters of compositions approximating those of both Coalinga and Roswell water, and details will be discussed later in this report (Section 3.3.1). These two waters have similar TDS (2000-2100 ppm), but hyperfiltration by dynamic Zr(IV)-PAA membranes has usually been more successful with Coalinga water than with the Roswell. A major way in which these waters differ is in the ratio of sulfate concentration to $\text{Mg(II)} + \text{Ca(II)}$ concentrations. The ratio is about 2.5 for the Coalinga, but only about 0.9 for the Roswell. To investigate the possibility that the sulfate in some way ameliorates the effect of divalent cations, we measured the rejection of Cl^- as a function of the $\text{SO}_4^{=}/\text{Mg(II)}$ ratio. In one test, sodium sulfate was added to a 0.05 M MgCl_2 solution. The results we obtained in this experiment are shown in Fig. 3.14. The fluxes doubled and the rejection dropped when one-half the equivalent amount of sulfate was added to the MgCl_2 solution, but both fluxes and rejections returned to about their original values when the number of equivalents were equal. At higher ratios, the fluxes remained about constant, but the rejections increased.

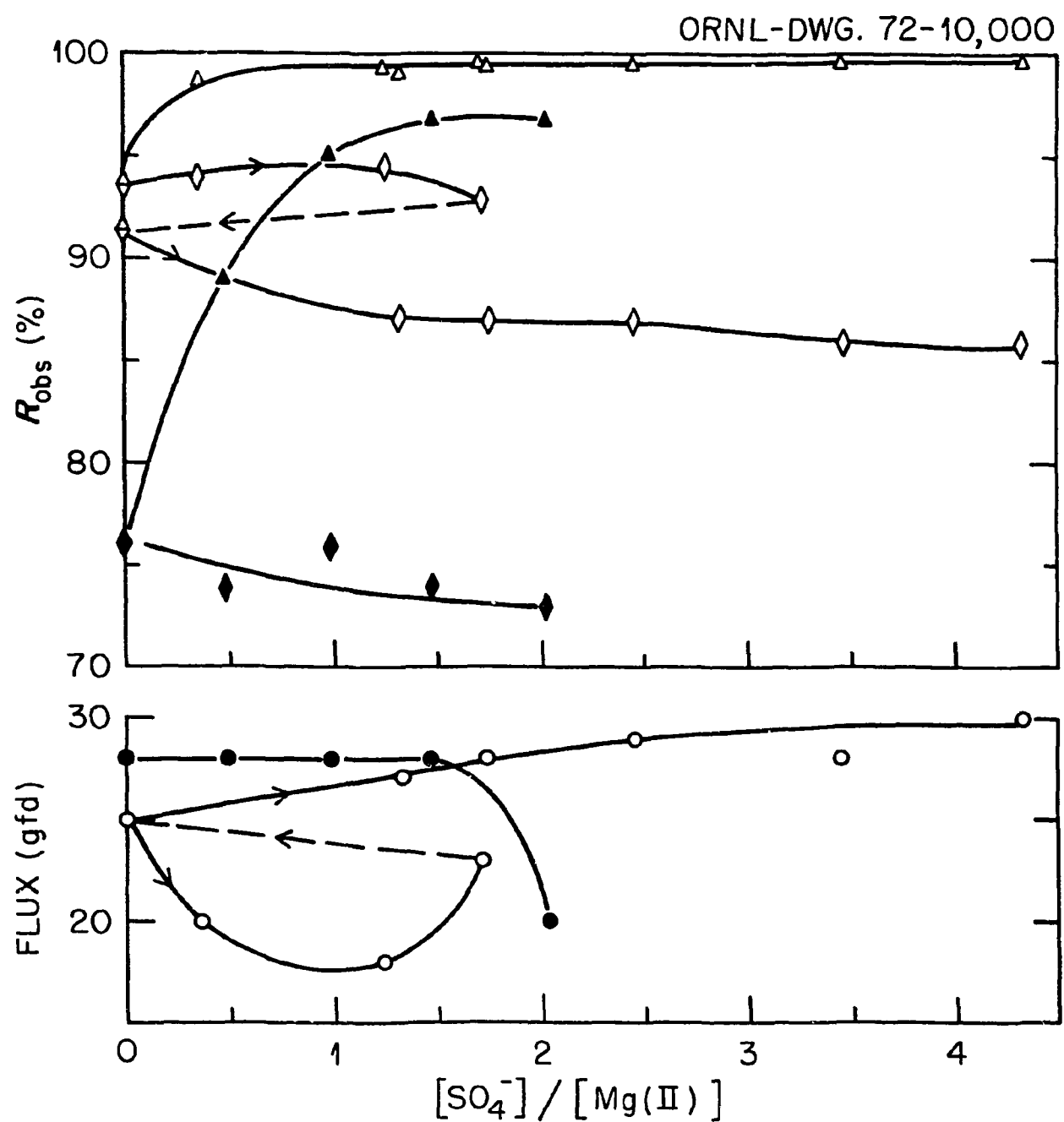
The maximum at $\text{SO}_4^{=}/\text{Mg(II)} = 0.5$ is unexpected, and the experiment was repeated, using membranes which had shown high rejection of NaCl shortly after formation. The experiment was run at two different Cl^- concentrations, and the results for the 0.025-micron Millipore support are shown in Fig. 3.15. Membranes on other supports used, 0.22-micron Millipore, 0.4-micron Nuclepore, 0.45-micron Acropor, and 0.27-micron Sela, gave similar results.

These results are not compatible with those of Fig. 3.14, and the earlier ones are likely in error. Here we found no marked maximum in flux and minimum in rejection at $[\text{SO}_4^{=}]/\text{Mg(II)} = 0.5$, and the chloride rejections here decreased, rather than increased, at higher sulfate concentrations. Magnesium rejections, on the other hand, increased with increasing values of the sulfate-magnesium ratio. This effect was most dramatic in solutions of higher total salt concentration.



EFFECT OF SULFATE/MAGNESIUM RATIO ON
HYPERFILTRATION OF Na_2SO_4 - $MgCl_2$ MIXTURES.
Total $[Cl^-] \sim 0.05M$. (900 psig, $25^\circ C$, pH 7)

Fig. 3.14



EFFECT OF SULFATE / MAGNESIUM RATIO ON
HYPERFILTRATION OF Na_2SO_4 - MgCl_2 MIXTURES
(0.025μ Millipore, 950 psig, 25°C , 35 fps, $\text{pH} \sim 8$)

	$\sim 0.05 \text{ M Cl}^-$		$\sim 0.18 \text{ M Cl}^-$	
Cl^-	$\diamond$		$\blacklozenge$	
Mg(II)	Δ		$\blacktriangle$	

Fig. 3.15

Two runs were made at the lower chloride concentration; the dotted lines in Fig. 3.15 indicate a return to zero sulfate concentration after the first run. The rejection results for magnesium were similar in the two runs, those for chloride and for flux were not.

Addition of sulfate appears to have a beneficial effect at lower sulfate-magnesium ratios, but it does not appear that the differences in performance between Coalinga and Roswell compositions are explainable from this factor alone.

3.1.3.4. Circulation Velocity. The set of membranes used in the pressure excursion test of Fig. 4, Section 2.1, was also tested for the effect of circulation velocity on performance. The results are shown in Fig. 3.16, where the lines with arrows were drawn to indicate the chronological sequence of points. Except for some initial increases in flux as the velocity was decreased, which may have been due partly to time of operation, velocity seems to have had little effect on flux. The effects of the velocity excursion were not completely reversible.

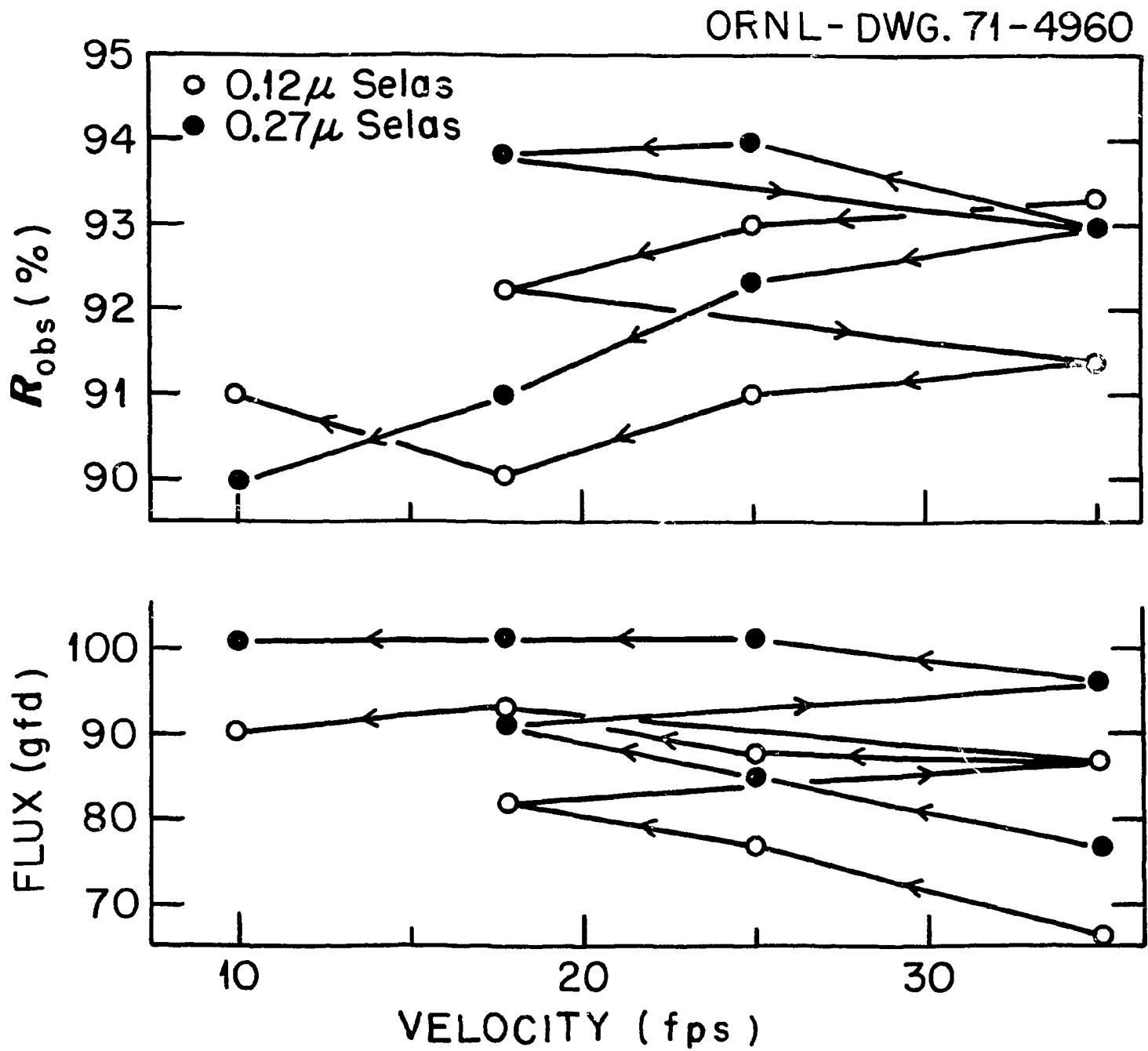
The velocity dependence of performance by a Zr(IV)-PAA membrane made from Acrysol A-1 is given in Table 3.56. Fluxes through the membrane, formed on a 0.27-micron Sela tube, drifted upward with time. Values of R_{obs} decreased slightly as the velocity was lowered, but returned at 35 fps. After an overnight operation (~16 hours), this same membrane was rejecting 92% of 0.05 M NaCl with a flux of 97 gfd.

TABLE 3.56

EFFECT OF VELOCITY ON PROPERTIES OF Zr(IV)-PAA MEMBRANES

(0.27- μ Sela tube, 0.05 M NaCl, 950 psig, 25°C, pH ~7 Acrysol A-1 PAA)

<u>Velocity (fps)</u>	<u>Flux (gfd)</u>	<u>R_{obs}, %</u>
35	80	94
25	81	94
18	88	92
10	94	90
45	92	93
35	94	93



Effect of circulation velocity on hyperfiltration properties of dual-layer membranes formed on SelaS ceramic tubes. Arrows indicate chronological order of velocity excursion. (0.05M NaCl, 950 psig, 25°C, pH 7)

Fig. 3.16

3.1.3.5. Membrane Age. Although no very long tests of dynamic membrane life times have been made, a few intermediate term tests have indicated reasonable longevity. Later, in Section 3.3.1, we describe some of these intermediate term tests (18-24 days) with simulated brackish waters; here we outline some observations on aging made in a 30-day series of tests with NaCl, Na₂SO₄, and MgCl₂ solutions, and a number of brackish waters. The membranes were prepared on a set of supports early in our investigation of Zr(IV)-PAA membranes. Results for feeds other than NaCl are discussed in appropriate sections of this report; periodic measurements with NaCl feeds over the first fifteen days of the run are summarized in Fig. 3.17. For the Zr(IV)-PAA membrane on a 0.45-micron Acropor support, rejection increased from 70% to 90% while fluxes dropped from about 150 gfd to somewhat less than 50 gfd in the fifteen days. The membrane was tested again with 0.05 M NaCl at the end of the run (30 days), and the performance at that time is compared for all supports to the initial performance in Fig. 3.18. There were some differences in experimental conditions for the two sets of points; the higher rejections and lower fluxes of the month-old membrane probably stem partially from the higher pH used in the tests of the aged membrane (see Fig. 3.13). Further, the various feeds and experimental conditions to which the membrane had been exposed during the course of the run undoubtedly affected subsequent results.

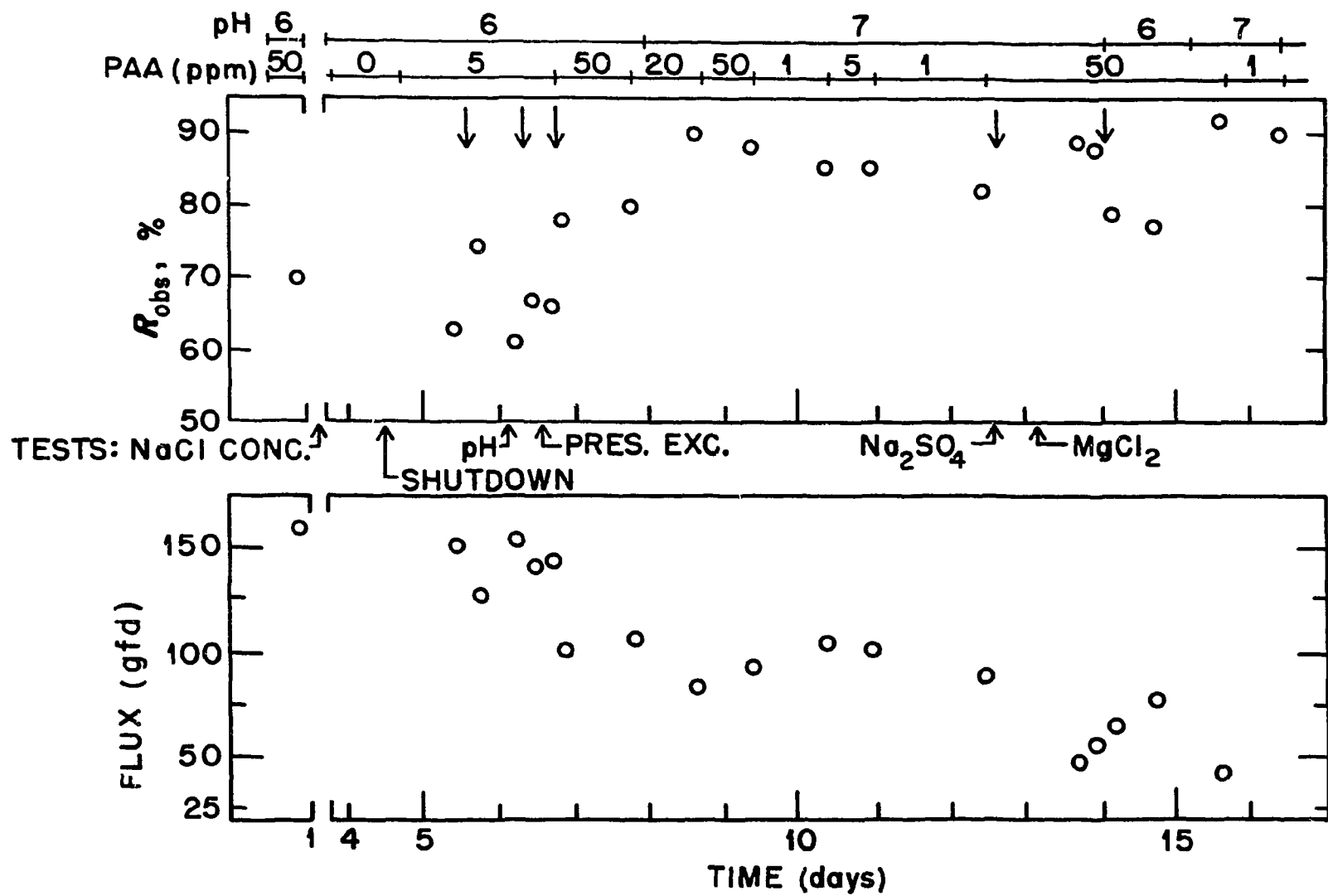
3.2 DYNAMIC MEMBRANES OTHER THAN Zr(IV)-PAA

3.2.1 Dual-Layer Membranes From Polyelectrolytes of Opposite Charge Sign

If the advantages of hydrous oxide-polyacrylate membranes arise from the opposite signs of the fixed charges on the sublayer and on the polyacrylate, one might expect two layers of oppositely charged organic polyelectrolytes to also show some advantages, such as, for example, ease of formation. We have, therefore, formed membranes from several combinations of polyelectrolytes of opposite charge sign. The results indicate less than universal benefits from this concept.

3.2.1.1. Nalco D - Poly(styrene sulfonate) Membranes. We attempted to prepare a polystyrene sulfonate membrane, from an additive of molecular weight about five million, on top of a sublayer of Nalco D polycationic additive (this is the additive of lower molecular weight and higher charge

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HYPERFILTRATION OF HYDROUS $Zr(V)$ OXIDE-PAA MEMBRANE

PRESSURE: 1000 psig

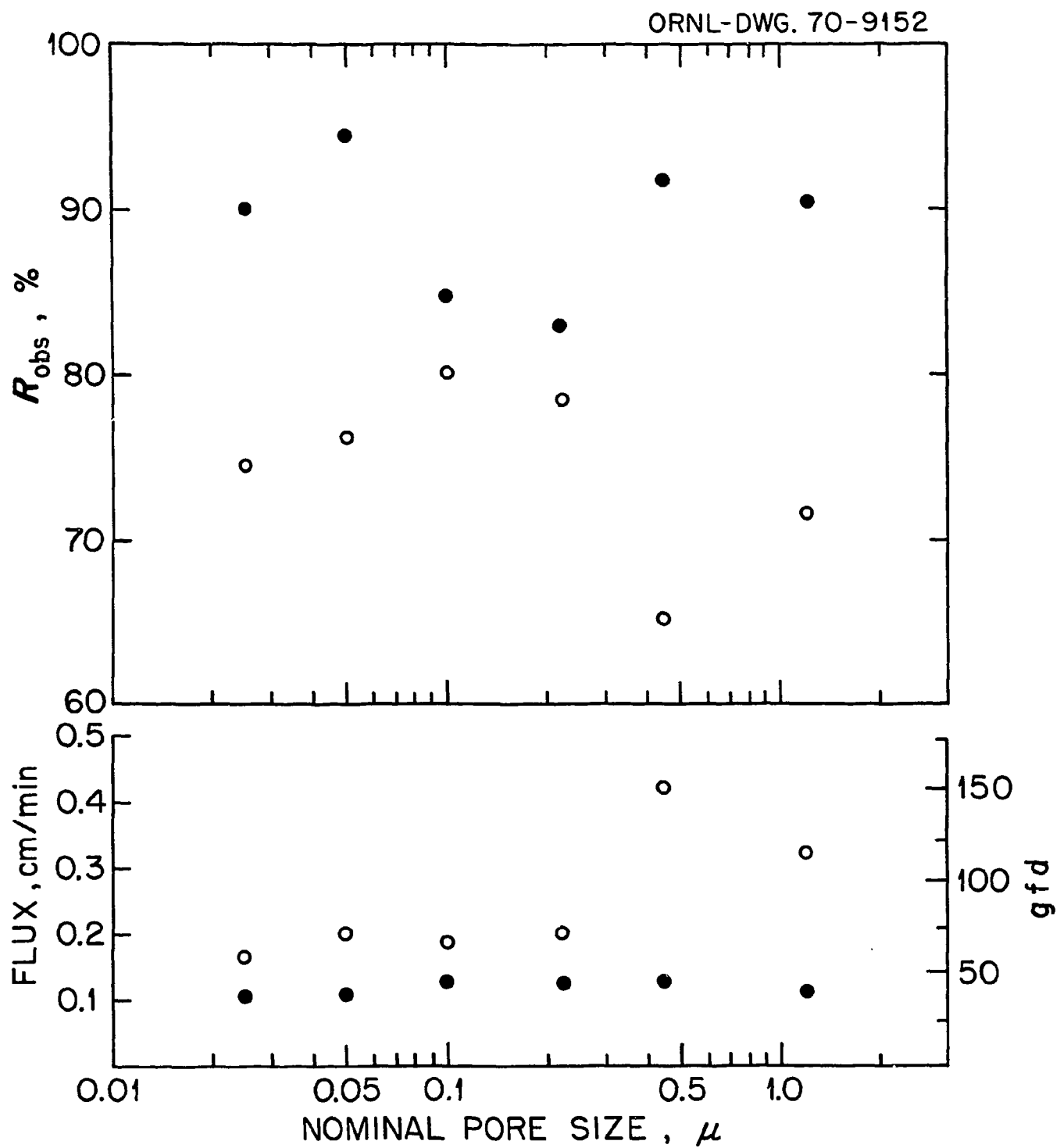
NaCl CONC.: 0.05 M

VELOCITY: 35 fps

SUPPORT: 0.45 μ Acropor

↓ CYCLES OF FEED TO ACIDIC pH

Fig. 3.17



CHANGE IN PROPERTIES OF HYDROUS $Zr(IV)$
OXIDE-PAA MEMBRANE WITH TIME ($0.05M$ NaCl)

	pH	Circ.Vel., fps	PAA, ppm
○ 1 DAY OLD	6.1	20 to 40	50
● 1 MONTH OLD	7.5	35	1

Fig. 3.18

density reported on in Section 3.3.7 of Ref. 15). For comparison purposes, we also formed a polystyrene sulfonate membrane, without the sublayer of Nalco D, in the same experiment. The supports were 0.45-micron Acropor, mounted in cells.

We first formed a sublayer on one support, using 25 ppm Nalco D in 0.05 M NaCl; rejection was below 23% for pH 3 to 9, with fluxes from 160 to 180 gfd at 1000 psig. We then rised the system with water, mounted another Acropor support in the second cell, and introduced 25 ppm polystyrene sulfonate in 0.05 M NaCl. Rejections were poor, 26% or less on the fresh support, and less than 25% on the support with the polycationic sublayer. Fluxes were 140-240 through the single layer, and 140-170 gfd through the dual layer. The effect of pH on rejection and flux was not great in the range investigated, pH 3 to 9.

Although these results are not as promising as those with dual-layer configurations with these additives, the poor performance by the single layers suggests extraneous influences in these tests.

3.2.1.2. Acropor (Treated) - Poly(styrene sulfonate) Membranes. We attempted to treat Acropor supports to give them an ion exchange capacity that might be utilized in the formation of membranes from two entities of opposite charge sign. When Acropor (0.45-micron) was exposed to triethylamine on a steam bath for one hour, it gained an anion-exchange capacity of 0.009 meq/cm². Similar treatment with pyridine resulted in a capacity of 0.003 meq/cm². In separate runs with cells, each of these was compared with untreated Acropor in the formation of membranes of the polystyrene sulfonate class.

The triethylamine treated Acropor was first tried with 0.05 M NaCl containing homogenized 0.25% cross-linked Dowex-50. In three hours, rejection by the membrane on the untreated support was 57%, flux 280 gfd and on the treated, 64% at 360 gfd (1000 psig, pH 9.7). With fresh supports, membranes were formed from feeds containing 10 ppm of 40,000 MW polystyrene sulfonate (see Ref. 15, p. 96), to which 10 ppm of 2 to 4 million MW of the same polyelectrolyte were subsequently added. At pH 8.3, rejection by the membrane on the untreated support was higher in this case, 50%, 360 gfd vs. 41% at 500 gfd for the treated.

The pyridine-treated support and a new untreated Acropor were then installed without changing feed. For some reason, membrane formation on both was poor. In five hours operation at pH values between 3 and 8, highest rejection attained by the untreated was 31%, and by the other, 11%.

The triethylamine-treated Acropor was also tested with polyacrylic acid. After formation from 0.05 M NaCl containing 25 ppm PAA, pH 3, and adjustment to pH 7, R_{obs} for the untreated was 79%, flux, 250 gfd, and of the treated, 30%, at 80 gfd.

A small anion-exchange capacity (< 0.1 meq/gm) of quaternized amine was placed on Acropor AN 450 by treatment with triethylene tetramine at 70° for 50 minutes, followed by exposure to aqueous NaOH and dimethyl sulfate. A test of this material with PAA was inconclusive; R_{obs} values (0.05 M NaCl) were $< 15\%$ for it and for an untreated Acropor AN 450 control.

In these tests, ion-exchange capacity on the support did not appear helpful in forming good membranes by binding polyelectrolytes to the porous support.

3.2.1.3. Clay-Poly(vinylbenzyl trimethyl ammonium chloride). Since natural clays are ion exchangers of positive charge, they seem a logical choice as sublayers for anion-exchange membranes.³¹ We have used bentonite, a montmorillonite-type clay, before on several occasions, for example, once as a sublayer for a humic acid membrane,³⁰ and once mixed with humic acid.¹² Since humic acid, like the clays, carries a negative charge, one would not expect to be helped by opposite charge signs between the two layers. However, with a positively charged polyelectrolyte, the clays could possibly form a superior sublayer, and the following experiments were carried out to test the hypothesis.

Two sets of membranes were formed with natural clay sublayers, the first with bentonite, and the second with vermiculite, a clay with high ion-exchange capacity. Supports were 0.025-micron Millipore and 0.45-micron Acropor, and membranes were formed on each type at two velocities, 35 and 50 fps. Fines from a suspension of the bentonite clay formed sublayers with fluxes which averaged about 370 gfd at about 22% rejection (0.05 M NaCl, 950 psig). Membranes from vermiculite fines resulted in high-flux (average 2300 gfd) membranes of unsatisfactory rejection ($\sim 4\%$). After the dual layers were formed, pH scans with both membrane sets failed to reveal any regions of promising performance.

3.2.2 MEMBRANES FROM ADDITIVES WITH FUNCTIONAL GROUPS OF BOTH CHARGE SIGNS

3.2.2.1. Block Copolymers Synthesized by Stille. We have carried out some tests on the hyperfiltration properties of membranes formed on porous supports by a series of block copolymers and terpolymers synthesized by Dr. J. K. Stille and co-workers at the University of Iowa and provided to us on the initiative of Dr. H. E. Podall. Stille's data on the polymers are summarized in Table 3.57. All of the block polymers tested were ampholytic; the basic block was always of poly(2-vinylpyridine) while the acid block was of either polyacrylate or polymethylacrylate. The terpolymers tested contained blocks of either polystyrene or poly (α -methyl-styrene), the latter in very small amounts only.

Dynamic membrane formation with these membranes has interesting possibilities. Perhaps the most intriguing is a mosaic-type membrane, the effluent from which might be enriched in salt relative to feed ("piezodialysis"), rather than depleted. We have in the past formed membranes of several additives having ion-exchange groups of both charge signs, without observing negative rejection.¹⁵ However, in these additives, oppositely charged groups were close to one another, and behavior might be different with the charges of a given sign segregated in blocks, as here. The Stille copolymers, particularly those with high pyridine-carboxylate ratios, also offer a possible device for stabilizing a dynamic neutral poly(vinylpyridine) membrane, an objective which has eluded us for several years, by attachment of carboxylate segments to a hydrous oxide sublayer.

The experiments were run in two different test loops, in loop 4, using cells of about 1.5 cm² area, and in loop 8, using test sections, each with two 50 cm² tubular supports (see Section 1.3). Comparison of data from the two loops, using the same additive, indicates that the results obtained are independent of the loop used.

Fig. 3.19 shows the pH dependence of R_{obs} (measured by conductivity) and flux for hyperfiltration of 0.05 M NaCl by membranes formed from block copolymers 1, 3, and 4 of Table 3.57, which all have the structure A-B, and which differ only in the ratios of their acidic to their basic segments.

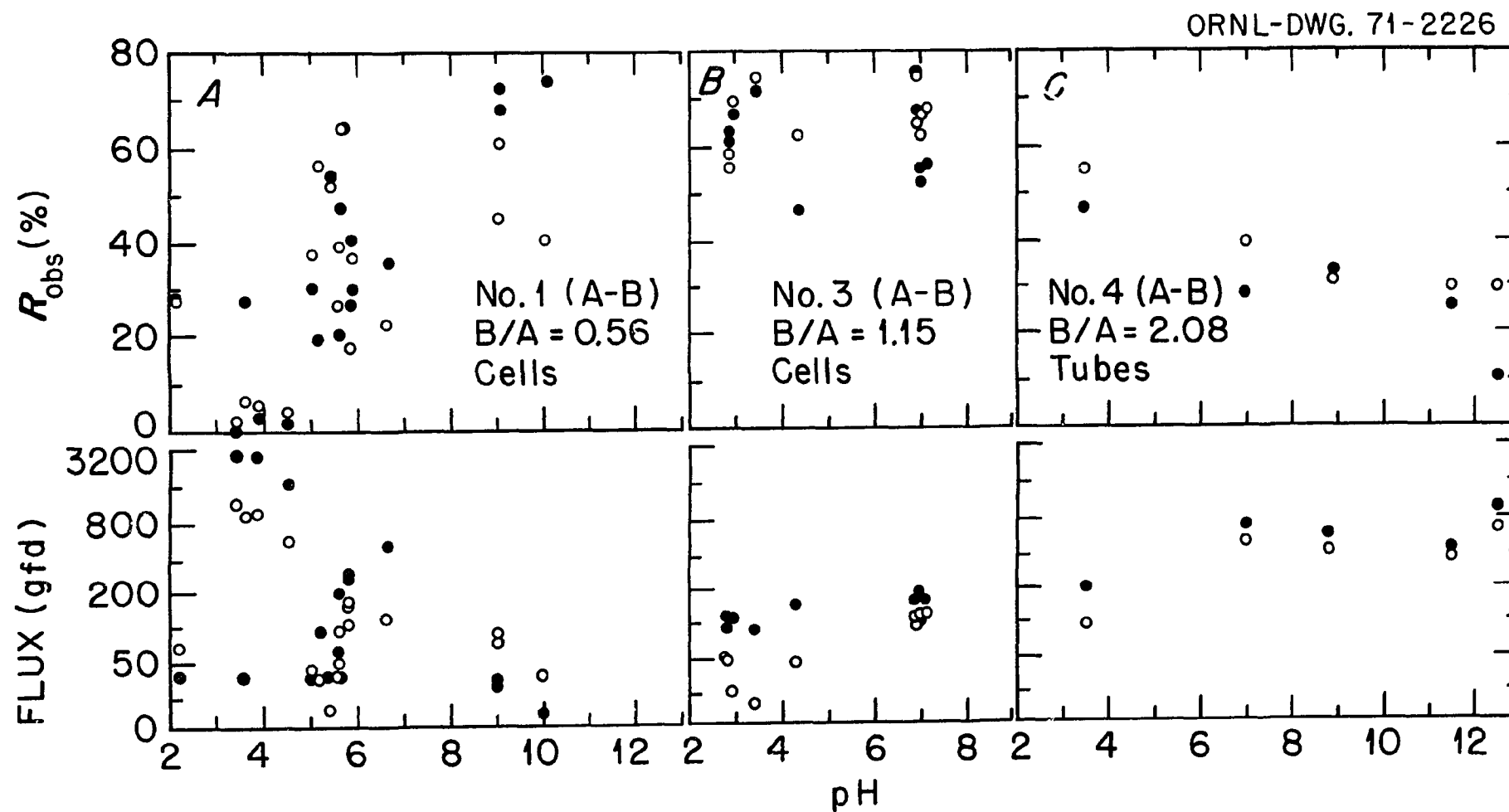
TABLE 3.57
PROPERTIES OF STILLE BLOCK COPOLYMERS

Polymer No.	Stille Code ^a	Structure ^b	% Hydrolyzed	B/A Ratio ^c	pH of Maximum Turbidity	Remnant Ester
1	M-13-1-AC	A-B	100	0.56	?	-
2	M-11-1-AC	A'-B	100	0.90	6.1	-
3	M-15-1-AC	A-B	100	1.15	5.3	-
4	M-16-1-AC	A-B	100	2.08	?	-
5	M-15-A1	A-B	18	6.39	<12	tert-butylacrylate
6	M-14-1-AC	A-B-I-B-A	100	1.05	5.3	-
7	M-8-2-A1	A-B-I'-B-A	76	21.7	?	methyl acrylate
8	M-8-1-A1	A-B-I'-B-A	48	34.5	?	methyl acrylate
9	M-6-1-AC	A'-B-I'-B-A'	?	?	>2	methyl methacrylate
10	K-10-5 ^d	A'-B	100	1.0	?	-
11	K-20-4-Q-DH ^d	A'-Quat. B	100	1.0	?	-
12	K-21-4-Q-DH ^d	A'-Quat. B	100	0.81	?	-

- (a) Stille, J. K., *et al.*, Quarterly Progress Report to OSW for Period Ending May 31, 1970, Department of Chemistry, University of Iowa. See also OSW R & D Progress Report No. 792 (1972).
- (b) A = Polyacrylate; A' = Polymethacrylate; B = Poly(2-vinylpyridine); I = Poly(α -methylstyrene) (present in very small amount); I' = Polystyrene.
- (c) Ratio of amine functional groups to exchangeable acid functional groups after hydrolysis.
- (d) J. K. Stille, private communication.

Although the data scatter badly*, it does appear that that polymer which is most acidic (No. 1) rejects best in basic solution, that polymer of nearly equal acidity and basicity (No. 3) rejects equally well in basic and neutral (and presumably acid) solution, while the most basic polymer (No. 4) has superior rejection in acid solution. The fluxes through the various membranes

*Membranes of these block copolymers seem to change properties considerably during aging. Consequently, there is a large scatter in results.



Membrane performance versus pH for dynamic membranes of block copolymers No. 1 (A), No. 3 (B), and No. 4 (C) (Table 3.57). ○ 0.025 μ Millipore, ● 0.45 μ Acropor AN (0.05M NaCl, 950-1000 psig)

Fig. 3.19

have a relationship inverse to that shown by the observed rejections.

Additive No. 2, Fig. 3.20A, differs from No. 3 in that the acidic segment of the former is a polymethacrylate rather than a polyacrylate, and No. 2 has a slightly smaller base-to-acid ratio. The pH dependence of the rejection and flux of 0.05 M NaCl solution for an aged membrane of No. 2 (the solid points of Fig. 3.20A resemble, as far as it is possible to determine from the data in hand, those of No. 3, but the points for the fresh membrane (open circles) do not. Points for 0.025 M Na₂SO₄ and 0.025 M MgCl₂ solutions are also shown in the figure.

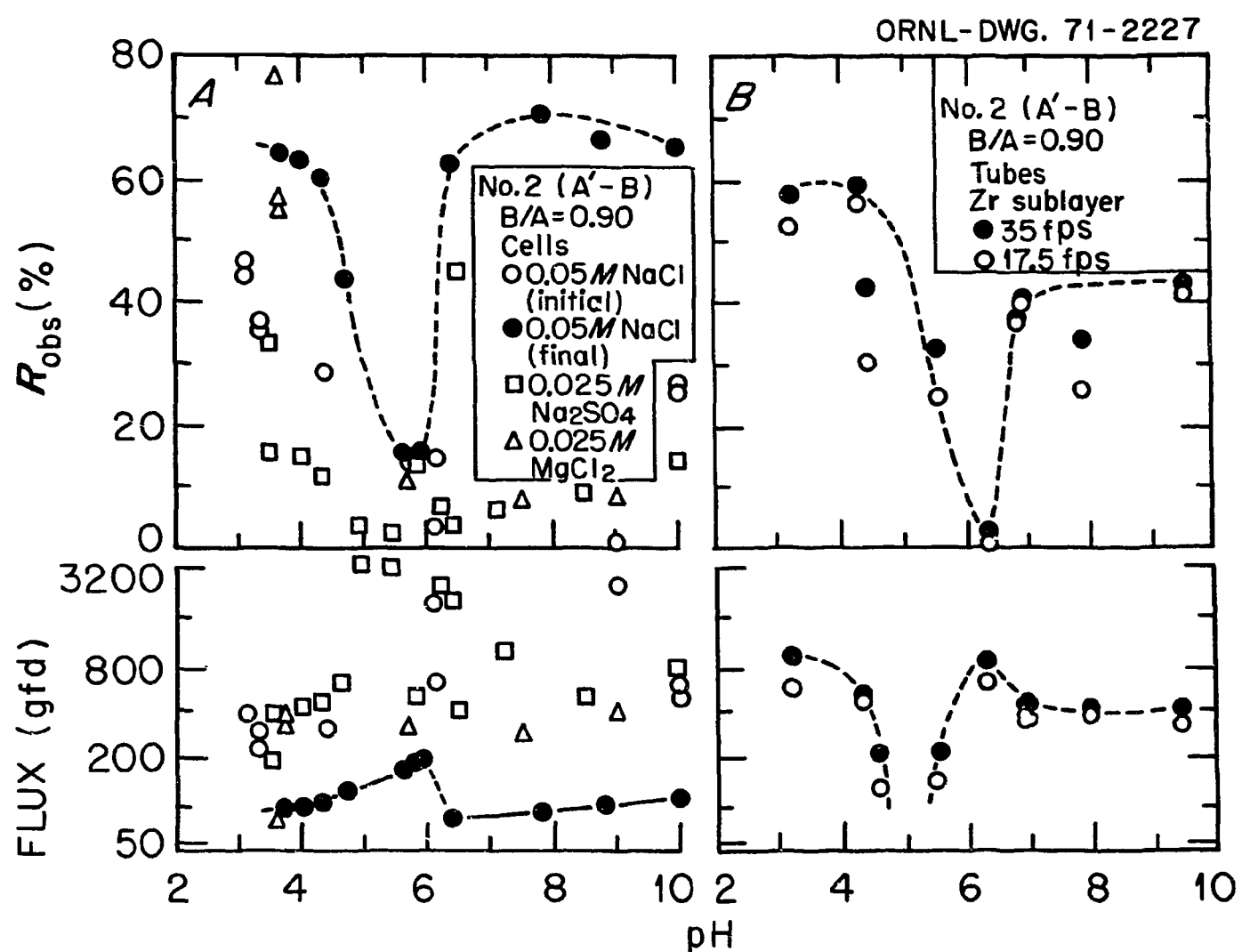
Additive No. 2 was also deposited as the top layer of a dual-layer dynamic membrane, hydrous zirconium oxide sublayer, in an experiment run in Loop 8. The data are shown for two formation velocities in Fig. 3.20B. Except for somewhat lower observed rejections overall, the effect of pH is the same as experienced in the earlier run. Both polymers Nos. 2 and 3 show a drastic reduction in R_{obs} at their pH of maximum turbidity, i.e., at that point at which they are least soluble. Similar data were obtained on 0.025- μ Millipore supports.

Block polymers Nos. 7 and 8, which have the highest base-to-acid ratios of any here tested, were run separately in Loop 4 (Fig. 3.21) and, with a hydrous Zr(IV) oxide sublayer, mixed together in equal amounts in Loop 8 (Fig. 3.22). Again there is considerable scatter and hysteresis in the Loop 4 experiments, and the Loop 8 results are probably more representative of the behavior of these polymers in hyperfiltration.

Polymer No. 5, Fig. 3.23A, is identical to No. 3, Fig. 3.19B except that, because of a low degree of hydrolysis, it has a high B/A ratio. It behaves more nearly like No. 8, Fig. 3.21B which also has a high B/A ratio. No. 3, on the other hand, appears to behave much like No. 6, Fig. 3.23B, which has a different structure, but nearly the same composition and degree of hydrolysis.

The composition and degree of hydrolysis of terpolymer No. 9 is not known. Its performance at a few pH values is shown in Fig. 3.23C.

Additive No. 10, is similar to No. 2, except that it has an equal number of 2-vinyl-pyridine and methacrylic acid units. The acid units were 100% hydrolyzed. The effect of pH on the properties of dual-layer

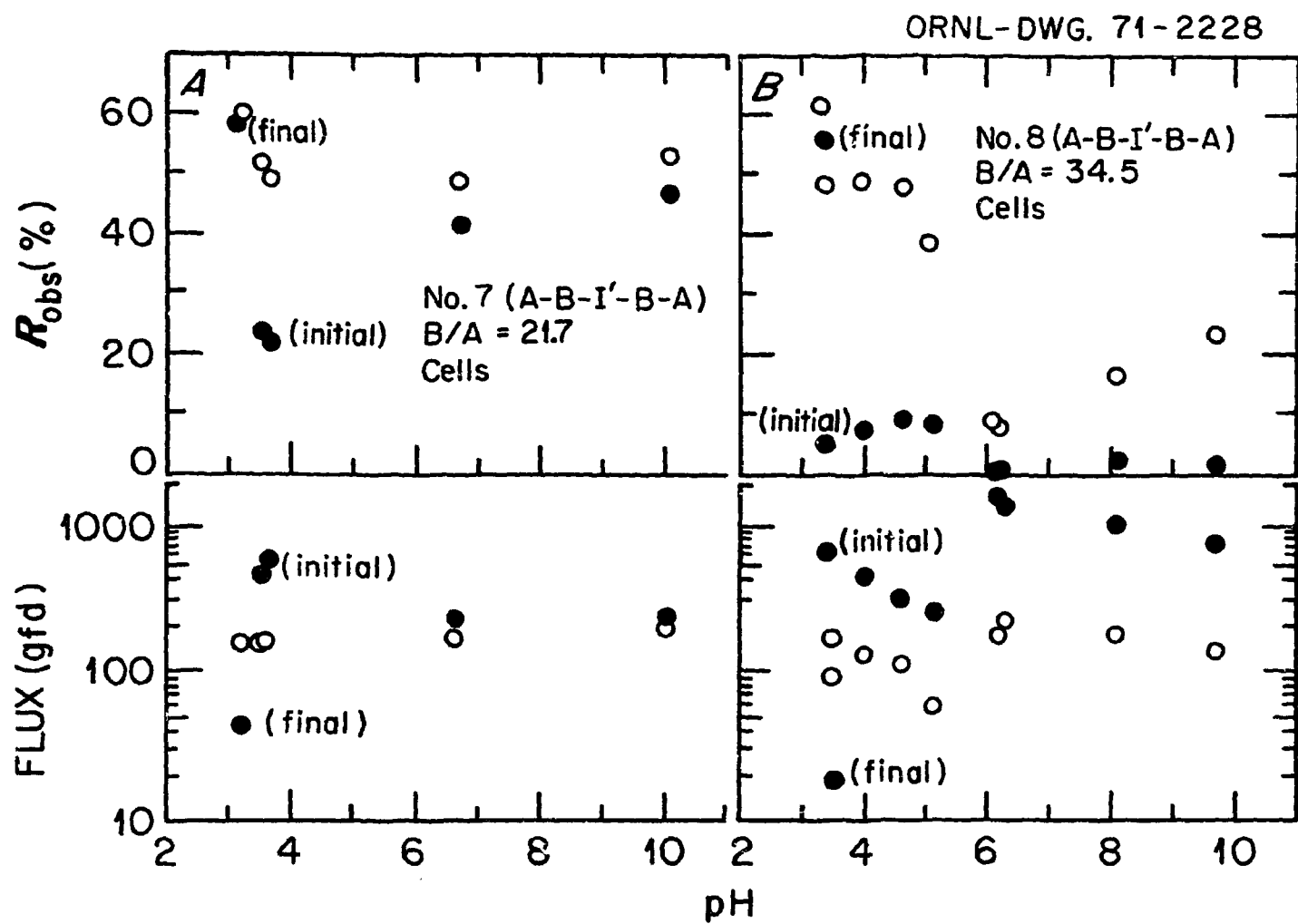


Membrane performance versus pH for dynamic membranes of block copolymer No.2 (Table 3.57)

A: Single layer membrane, loop 4.

B: Dual-layer membrane, loop 8, at two velocities, 0.05M NaCl. (950-1000 psig)

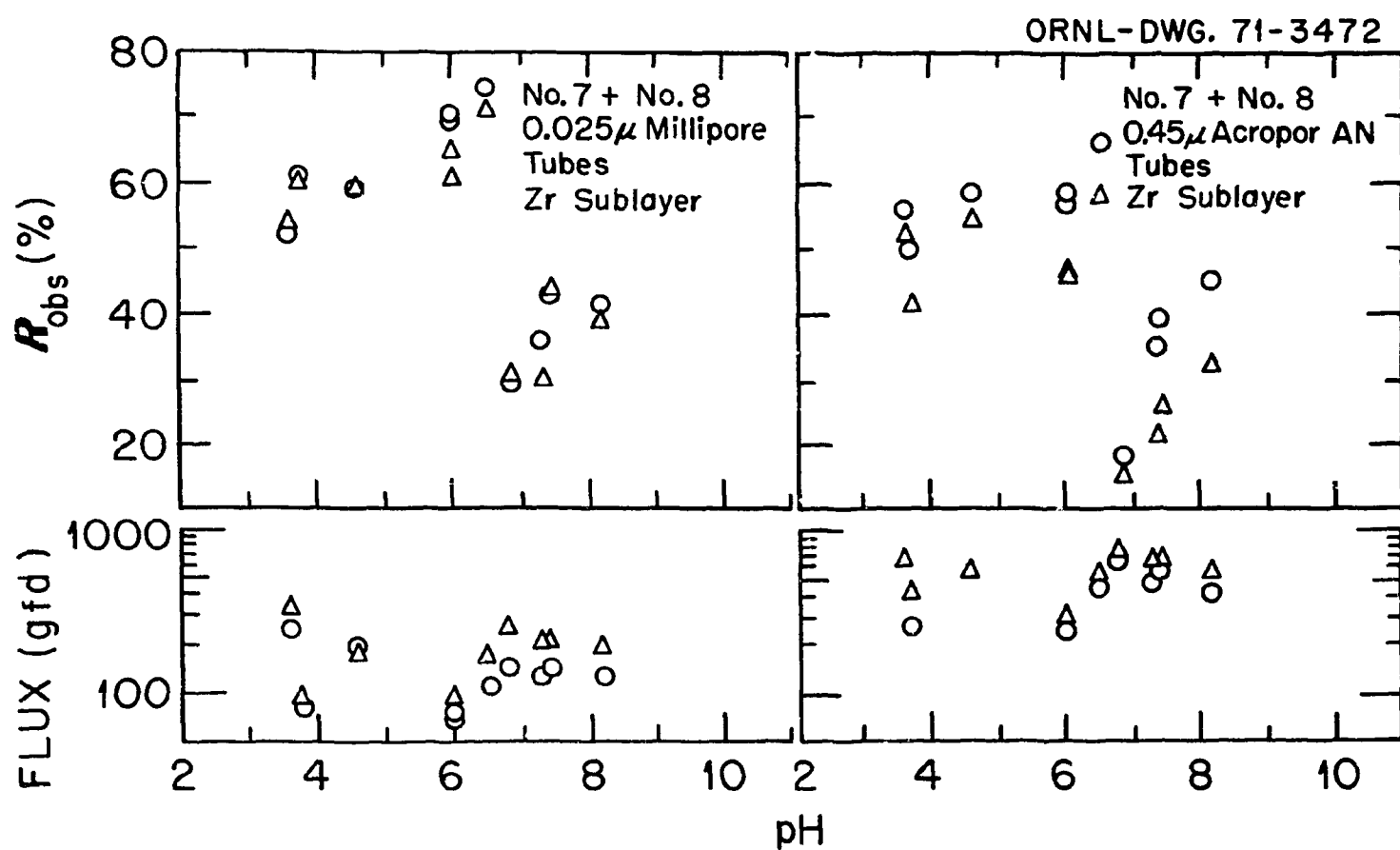
Fig. 3.20



Membrane performance versus pH for dynamic membranes of block copolymers 7 and 8 (Table 3.57)

○ 0.025 μ Millipore ; ● 0.45 μ Acropor AN (0.05M NaCl, 1000 psig)

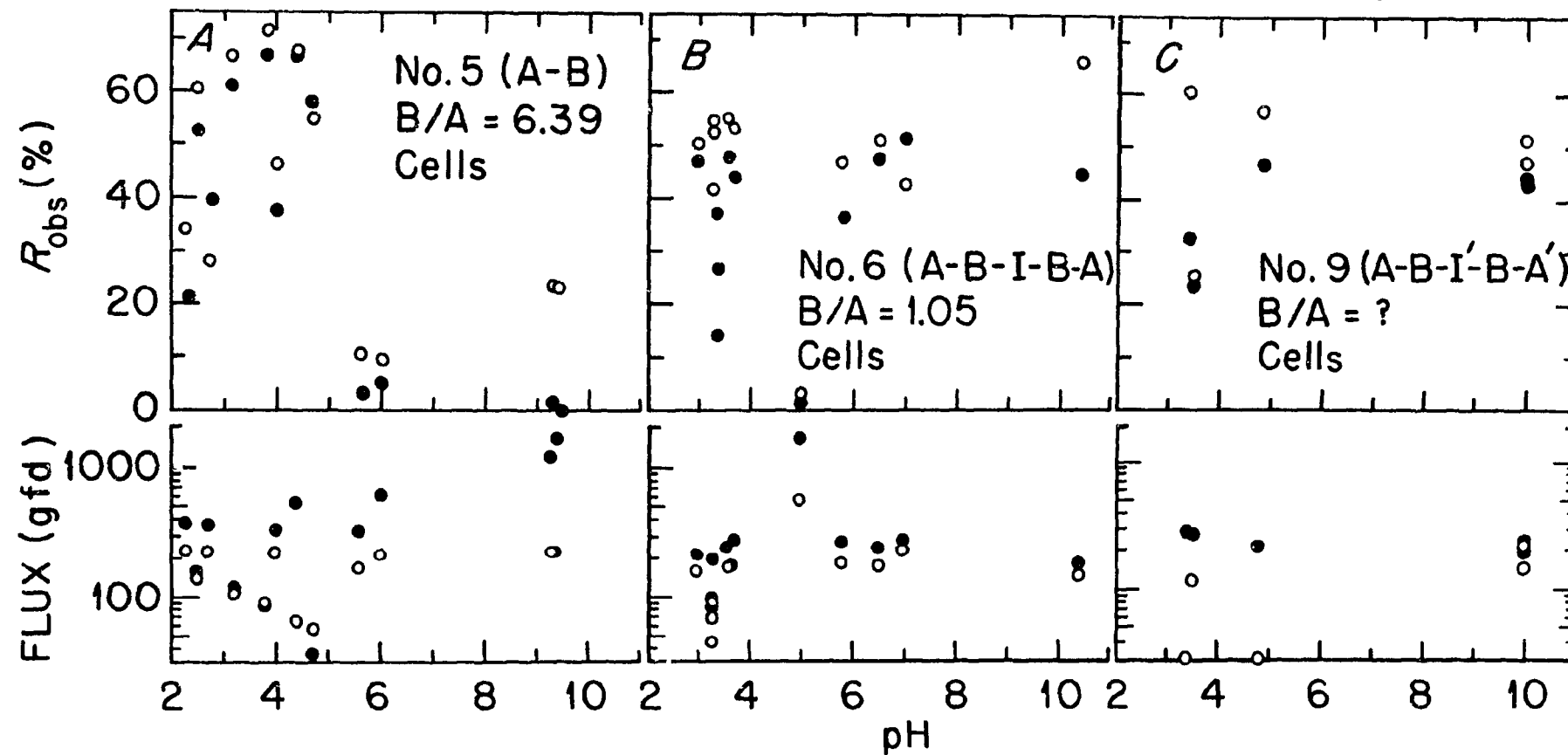
Fig. 3.21



Membrane performance versus pH for dynamic membranes of a 50-50 mixture of block copolymers No. 7 and No. 8 on hydrous-Zr-oxide sublayer.

○ 35 fps , △ 17.5 fps (0.05 *M* NaCl , 900 psig)

Fig. 3.22



Membrane performance versus pH for dynamic membranes of block polymers No.5 (A), No.6 (B), and No. 9 (C) (Table 3.57):
 ○ 0.025 μ Millipore , ● 0.45 μ Acropor AN (0.05M NaCl, 1000 psig)

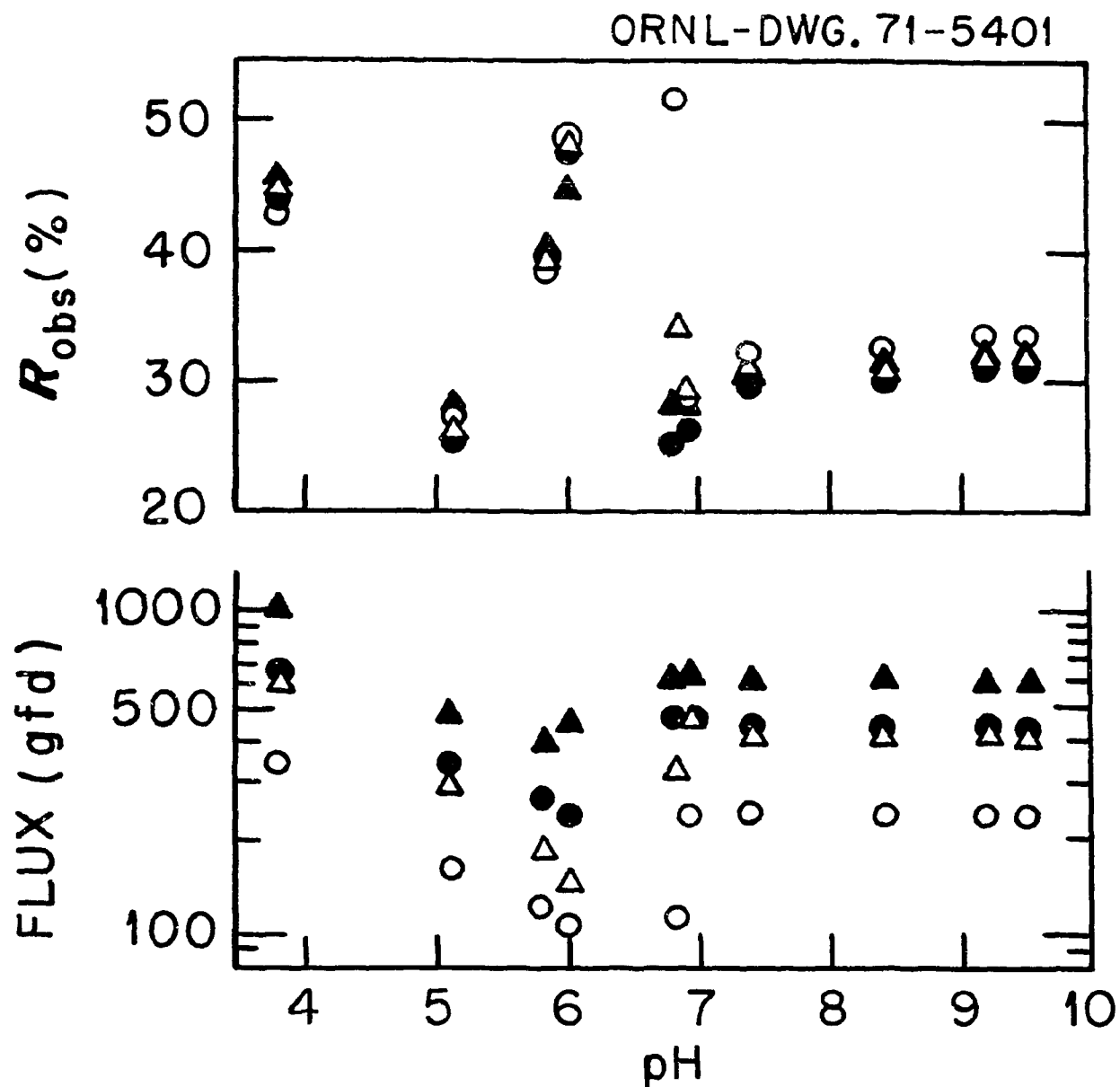
Fig. 3.23

membranes, made in Loop 8, utilizing this additive is shown in Fig. 3.24 using a 0.05 M NaCl feed solution at 900 psig and at two different velocities. Although the fluxes through the membranes were high, the rejections were poor, generally less than 50%. The peculiar response of the observed rejections to changes in pH is hard to explain, and it differs even qualitatively from that shown by the similar block copolymer, No. 2, in Fig. 3.20.

None of the additives discussed above formed membranes with which we were able to achieve product enriched relative to the feed. This so-called "negative rejection" can occur to an appreciable extent only if blocks of a given charge sign penetrate the complete thickness of a membrane, and are small enough so that electrical resistance in the external solution is not high enough to cause the blocks to act as individual salt-rejecting ion-exchange membranes (see Section 7.1). It is difficult to check whether these two conditions are being met by dynamic membranes of these polymers, although one would expect the domains to be sufficiently small. A third possible difficulty would arise from the fact that both segments are weak electrolytes. For the additives through No. 10, it may possibly be that there is no pH at which both are sufficiently in the salt form for salt enrichment, even at the pH of maximum turbidity.

Professor Stille provided several samples of additives with quaternized pyridine groups, which should be present as pyridinium ions at pH values at which carboxylates are sodium salts. Fig. 3.25 shows the results for hyperfiltration of 0.05 M NaCl as a function of pH for four membranes made from a block copolymer (Additive No. 11) consisting of an equal number of quaternized 2-vinylpyridine and methacrylic acid units (Polymer No. 11). Two of the membranes (dark points) were made with hydrous Zr(IV) oxide sublayers, the others (open points) were made only from the block copolymer. The results shown in Fig. 3.25 for the dual-layer membranes do not appear to be significantly different from those obtained with sample No. 10 (Fig. 3.24), which differed only in that the pyridine groups were not quaternized.

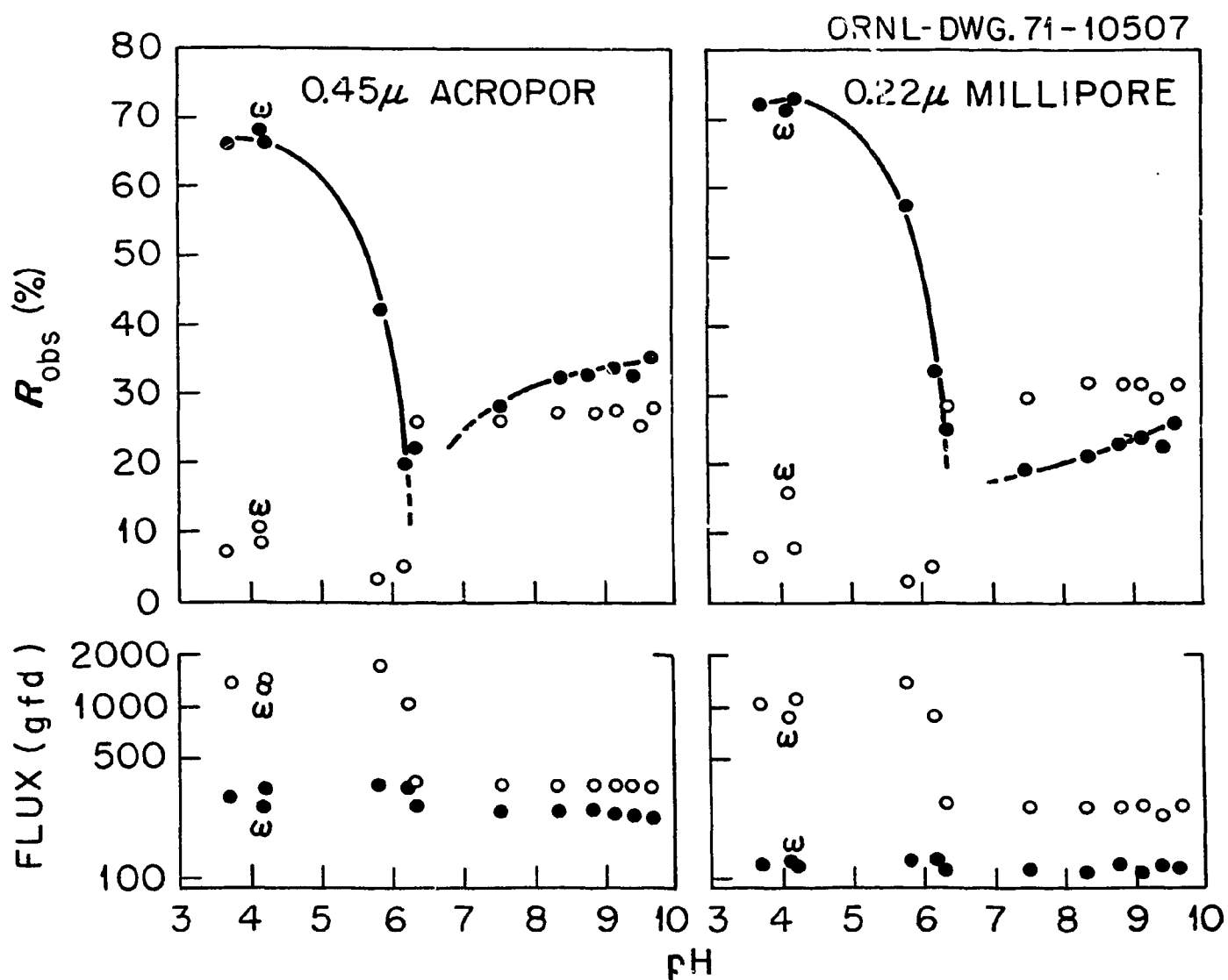
The pH dependence of the rejection by the dual-layer membranes, shown in Fig. 3.25, is so similar to that observed¹³ for hydrous oxide membranes alone as to suggest that no dual-layer membrane had been formed. However,



Membrane performance versus pH for dynamic hydrous $Zr(IV)$ oxide - poly (2-vinylpyridine - block-methacrylic acid) dual-layer membranes. (Additive 10) ($0.05M$ NaCl, 900 psig, $25^{\circ}C$)

Support	Velocity	
	17.5 fps	35 fps
0.05 μ Millipore	○	●
0.45 μ Acropor AN	△	▲

Fig. 3.24



HYPERFILTRATION BY DYNAMIC MEMBRANES INCORPORATING POLY(2-VINYLPYRIDINE-BLOCK-METHACRYLIC ACID) WITH THE PYRIDINE GROUPS QUATERNIZED.

(0.05M NaCl, 900 psig, 25 fps, 25°C)

- Hydrous Zr(IV) Oxide-Block Copolymer Dual Layer Membrane
- Block Copolymer Single Layer Membrane

ADDITIVE No. 11

Fig. 3.25

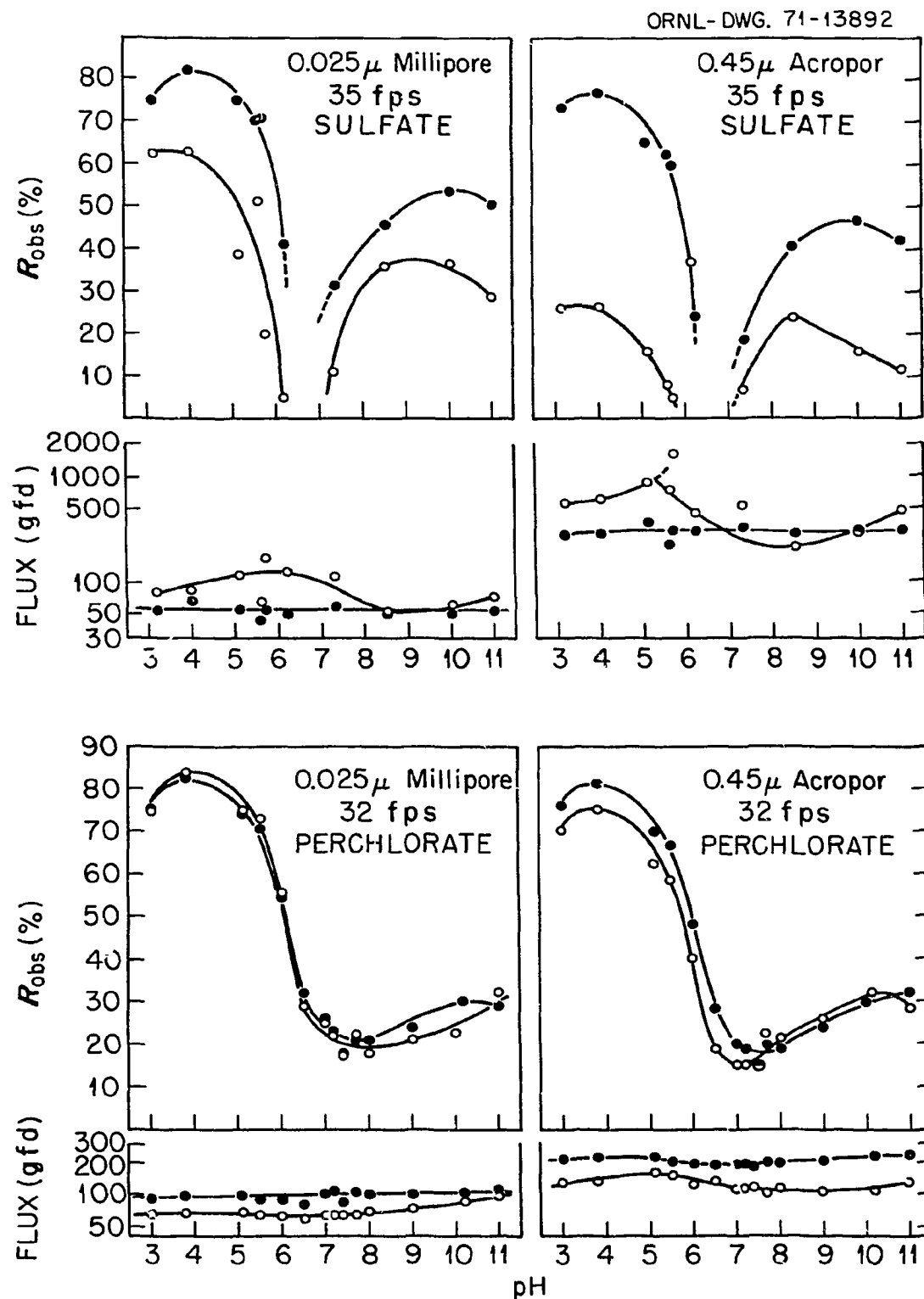
experiments described below for polymer No. 12 show that this is not the case. For the single-layer membranes of polymer No. 11, we found high fluxes at low rejections in acid solution, with an abrupt change, near neutral pH, to lower fluxes and higher rejections in basic solution. This effect was reasonably reversible, the points marked ω were taken at the end of the run after a pH excursion from 3.7 to 9.7.

Polymer No. 12 differed from 11 only in the relative size of the blocks. Membranes of this additive were formed from sulfate and from perchlorate solutions instead of from NaCl solutions. These solutions were chosen to determine the effect of the water content in the polymer on the properties of the membranes made thereof. If quaternized pyridine polymers are similar to quaternized benzyl amine polymers, the pyridine part of the membranes made from perchlorate should have somewhat lower water contents, and those from sulfate somewhat higher contents, than those formed from chloride solutions³². Since formation is from acidic solution, the charge density of the polyacrylate blocks should be low. The results are presented in Fig. 3.26.

The pH dependence of the rejection by both the single and dual-layer membranes formed from the sulfate solution is very like that reported for the similar, but unquaternized, No. 2 in Fig. 3.20B. The membranes formed from perchlorate solution, on the other hand, very closely resemble the dual-layer membranes reported in Fig. 3.25. Since both the single and dual-layer membranes show the same pH dependence, it seems likely the pH dependence of the dual-layer membrane of polymer No. 11 (Fig. 3.25) is not due to the hydrous oxide layer alone.

The membranes formed from sulfate solutions were more permeable than those formed from perchlorate. Most of the single-layer membranes had higher fluxes than their dual-layer counterparts, but on the 0.025-micron Millipore support, fluxes through the single-layer membrane formed from perchlorate were lower than through the dual layer.

In none of the tests with the Stille additives was there any indication of a poly(vinyl pyridine) membrane in neutral form, stabilized by attachment of carboxyls to a hydrous Zr(IV) oxide sublayer. In addition, although production rates were frequently high, none of the block polymers tested in this series looks promising as an additive to form hyperfiltration membranes



pH DEPENDENCE OF HYPERFILTRATION OF 0.05M NaCl BY
DYNAMIC MEMBRANES FORMED OF STILLE BLOCK COPOLYMER
FROM 0.025M Na₂SO₄ AND 0.05M NaClO₄ SOLUTIONS
(1000 psig, 25°C, Polymer No. 12)

- Without Sublayer
- With Hydrous Zr(IV) Oxide Sublayer
Formed From 0.05M NaCl

Fig. 3.26

on porous supports. Maximum rejections were usually less than 80%, and usually were very low in the neutral pH region. The shape of the curves of the R_{obs} dependence on pH depended more on the relative amounts of acid and base in the polymer than they did on the actual structure of the polymer. Of possible reasons for failure to attain piezodialysis, the most likely appears to us to be lack of complete penetration through the thickness of the dynamically formed membrane of regions having a given charge sign.

3.2.2.2. Poly(maleic acid-co-montrek-12). By treating Dow poly-ethylenimine Montrek-12 with a large excess of maleic anhydride in dimethyl formamide, we formed amides of the 25% primary amines and the 50% secondary amines in the polymer. The other 25% nitrogens, present as tertiary amines, did not react. The product thus had three carboxyl groups per tertiary amine group.

We tested this additive with 0.45- μ Millipore supports in formation of a single-layer membrane and in formation of a membrane on top of a hydrous Zr(IV) oxide sublayer, using cells. The sublayer, at the end of formation from a 0.05 M NaCl-0.0005 M hydrous Zr(IV) oxide solution, pH $\sim$ 3, rejected 60% of solute at 310 gfd (1000 psig). A fresh 0.45- μ Millipore was installed in a second cell, and operation was resumed with 0.05 M NaCl and 20 ppm of the sodium form of the additive (pH $\sim$ 6). Flux through the Zr(IV) treated support was initially about 600 gfd, but this gradually dropped to about 300 gfd as the pH was cycled to 9 and back to 3. Little flux change occurred during a later pH change to 9.6. Rejection was highest, about 50%, at pH 3 and dropped to 25% at pH 9.6.

A good single-layer membrane did not form. On the bare Millipore, flux, which was initially about ten thousand gfd, declined with time while pH was varied. At the end, pH 9.6, flux was about 1000 gfd and R_{obs} , about 5%.

The additive does not form useful membranes under the conditions tried in this test.

3.2.2.3. Poly(maleic acid-co-methylvinylamine) Synthesized by Amdur. Another copolymer that we have used as an additive in the formation of dynamic membranes is one synthesized by Dr. S. Amdur of SUNY-Buffalo and

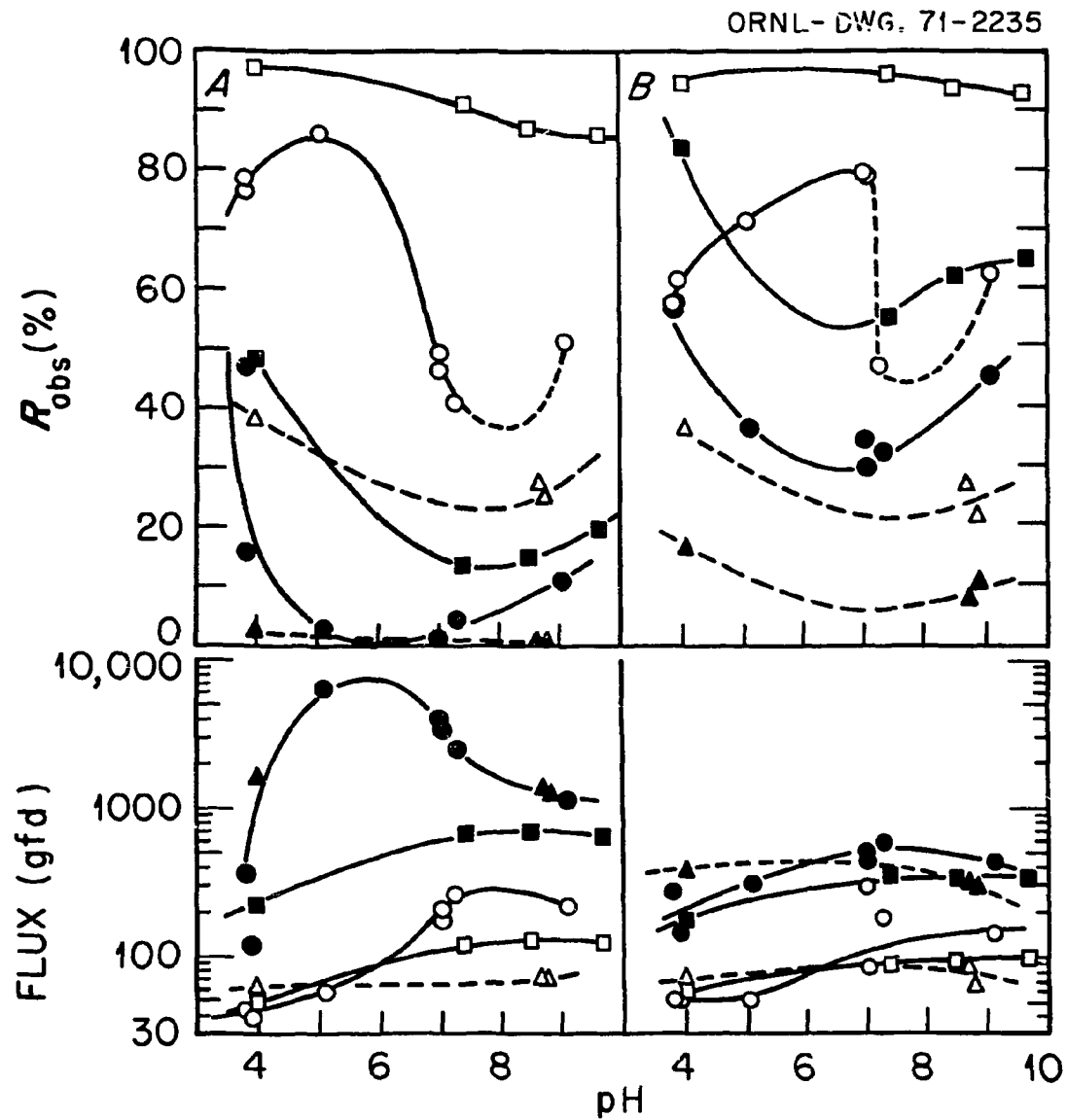
sent to us by Dr. L. M. Kindley of OSW. The pH dependence of flux and R_{obs} for the copolymer, poly(maleic acid-co-methylvinylamine), is shown in Fig. 3.27* for three different salt solutions and two different porous supports. Part A shows the results for a single-layer membrane formed by the copolymer on porous supports, while Part B is for a dual-layer membrane, the first layer of which is hydrous zirconium(IV) oxide. In both cases, it appears as if the pH dependence of R_{obs} for the hyperfiltration of 0.05 M NaCl by membranes on the 0.025- μ Millipore support was qualitatively different from that by membranes on the 0.45- μ Acropor support. This is especially true for the dual-layer case. There appeared to be minimum rejection of all solutes tested in the pH range 7-8. Both the single-layer and dual-layer membranes on 0.025- μ Millipore supports gave good performance in the hyperfiltration of Na_2SO_4 at all pH's tested. Rejection of $MgCl_2$ was very poor.

3.2.3. Membranes From Other Additives

3.2.3.1. Poly(maleic acid). Because it has a higher linear charge density, poly(maleic acid) might be expected to form a better dual-layer membrane than polyacrylic acid. Earlier tests (see Ref. 15, p. 85) did not justify this expectation, nor do the experiments reported below, in which we used more recent techniques of membrane formation. For these experiments, we used a poly(maleic anhydride) of molecular weight about 1000, manufactured by the Drew Chemical Corp.** The results are shown in Table 3.58. The initial rejections were somewhat better than those we found before, but these decreased during the course of an overnight run. Fluxes were considerably better than those found previously, but this may be due in part to the fact that the present membranes were formed at rather high circulation velocities while the earlier studies were carried out in cells. The decrease in rejections and increase in fluxes following overnight operation may indicate that the membrane was somewhat unstable and that some of the polymer had been leached from the support surface.

*The lines are drawn as an aid in visualizing results rather than to interpolate behavior between points.

**We thank Dr. Harold E. Podall for bringing the availability of this material to our attention, and Dr. D. R. Sexsmith of Drew Chemical Corp. for providing us with a sample.



Membrane performance versus pH for dynamic membranes formed from poly(maleic acid-co-methyl vinyl amine).
A: single layer membrane. *B*: dual-layer membrane with hydrous Zr oxide sublayer (35 fps , 900 psig).

Solute	Support	
	0.025μ Millipore	0.45μ Acropor-AN
0.05 <i>M</i> NaCl	○	●
0.025 <i>M</i> Na ₂ SO ₄	□	■
0.025 <i>M</i> MgCl ₂	△	▲

Fig. 3.27

TABLE 3.58
HYPERFILTRATION OF 0.05 M NaCl BY DYNAMIC DUAL-LAYER HYDROUS
Zr(IV) OXIDE-POLY(MALEIC ACID) MEMBRANES
(950 psig, 25°C)

<u>Time*</u>	<u>pH</u>	<u>Support</u>	<u>Velocity (fps)</u>	<u>Flux (gfd)</u>	<u>R_{obs} (%)</u>
0.5	6.3	6C carbon tube	35	88	83
		0.025- μ Millipore	35	77	88
		0.45- μ Acropor	35	217	68
		0.27- μ Sela ceramic	32.5	60	81
17.0	6.9	6C carbon tube	35	121	74
		0.025- μ Millipore	35	101	76
		0.45- μ Acropor	35	240	68
		0.27- μ Sela ceramic	32.5	90	76

*Time in hours following completion of membrane.

3.2.3.2. Single-Layer PAA. We had found in the past¹⁹ that single-layer polyacrylate membranes did not show as good hyperfiltration properties as the Zr(IV)-PAA dual-layer combination. Techniques of formation, however, have changed with time, and it seemed advisable to check to see if the hydrous oxide sublayer does, indeed, contribute to the properties of the finished membrane. For this reason, we formed single layers of PAA on several supports, using present techniques, which differ from those used formerly in tests of single-layer PAA membranes chiefly in adding the PAA at low pH (~ 2).

Table 3.59 gives the results for five different polyacrylic acid (Acrysol A-3) membranes formed by introducing the PAA at pH 2, and gradually increasing the pH to 6.8. Very little plugging of the substrates occurred with 50 ppm PAA, and the concentration was increased to 75 ppm before the pH was increased. The membranes of best rejection for 0.05 M NaCl were formed on the supports of smallest pore size, and fluxes with these were low, in comparison with membranes formed where a hydrous oxide layer had been previously deposited.

TABLE 3.59
HYPERFILTRATION OF 0.05 M NaCl BY
DYNAMICALLY FORMED POLYACRYLATE MEMBRANES
(950 psig, 35 fps, 25°C, pH 6.8)

<u>Support</u>	<u>Flux (fps)</u>	<u>R_{obs} (%)</u>
0.025- μ Millipore	28	74
0.05- μ Millipore	30	75
0.22- μ Millipore	121	21
0.45- μ Acropor	65	15
1.2- μ Acropor	1415	0

We made two attempts to form dynamic single-layer PAA membranes on 0.27- μ Sela ceramic tubes. In the first, we circulated 50 ppm PAA in 0.05 M NaCl at pH 2.0 past the support at 8.3 fps, 1000 psig, and 28°C, and then raised the pH in steps to 7.1. At that point, the rejection was only 53% and the flux 22 gfd. The largest drop in flux, from 1250 gfd to 37 gfd, occurred during the first base addition, which raised the pH from 2.0 to 2.9. We therefore made a second attempt in which we monitored flux closely during very slow increases in pH at the lower values, and rinsed the PAA from the loop when the flux had dropped to about 500 gfd, which occurred near pH 2.25. We then incrementally increased pH to neutrality. The rejection was somewhat higher in this case, 83%, but the flux was again very low, 13 gfd. The hydrous oxide sublayer clearly appears to be beneficial.

In some early experiments, we compared properties of single-layer polyacrylate membranes formed from 0.05 M NaCl solutions to those formed from 0.05 M NH₄Cl solutions. In each case, the membranes were formed on both a 0.025- μ and a 0.45- μ Millipore support mounted in cells. The feed, neutralized to pH 7.5 to 8, contained 50 ppm PAA. With both NaCl and NH₄Cl, we found it necessary to cycle through acidic pH values to attain rejections greater than 50%, in spite of the fact that there was no intentional hydrous oxide sublayer. We list on the following page hyperfiltration properties after returning to pH values greater than 6.5, and values obtained subsequently in testing the membrane formed from the NH₄Cl medium with 0.05 NaCl feed (containing 5 ppm additive), and vice versa. An acid cycle was carried out in each case before the second test.

<u>Feed</u>	<u>pH</u>	<u>R_{obs}, %</u>	<u>Flux (gfd)</u>	<u>Feed</u>	<u>pH</u>	<u>R_{obs}, %</u>	<u>Flux (gfd)</u>
<u>0.025-μ</u>							
NH ₄ Cl*	6.7	82	39	NaCl*	8.6	65	115
NaCl	7.4	88	22	NH ₄ Cl	7.5	84	37
<u>0.45-μ</u>							
NH ₄ Cl*	6.7	79	100	NaCl*	8.6	81	120
NaCl	7.4	79	75	NH ₄ Cl	7.5	79	105

*Membrane formed in presence of this salt.

When minor variations in conditions (and pH variations are probably more than minor) are taken into account, rejections by membranes formed from NH₄Cl feeds are not clearly different from those formed from NaCl feeds. The membrane formed on a 0.025-μ Millipore support from NaCl appears to be an exception, but its rejection is so low that one suspects the presence of defects. There are significant differences in fluxes, but these may arise from time of operation.

3.2.3.3. Calgon Copolymers. Dr. Lee M. Kindley provided us with several anionic and cationic copolymers from the Calgon Corporation. These additives had a range of ion-exchange capacities, and the information we have is summarized in Table 3.60.

TABLE 3.60
CHARGE TYPE AND ION-EXCHANGE CAPACITY
FOR SOME CALGON CORPORATION COPOLYMERS

<u>Sample No.</u>	<u>Charge Type</u>	<u>Ion-Exchange Capacity (meq/g)</u>
CP #2*	Cationic	-
CP #3	Cationic	1.2
CP #4	Anionic	0.69
CP #5	Anionic	2.1
CP #6	Anionic	4.8
CP #7	Anionic	3.5
CP #8	Cationic	3.1
CP #9	Cationic	3.7

*Condensation polyamine of the PEI type.

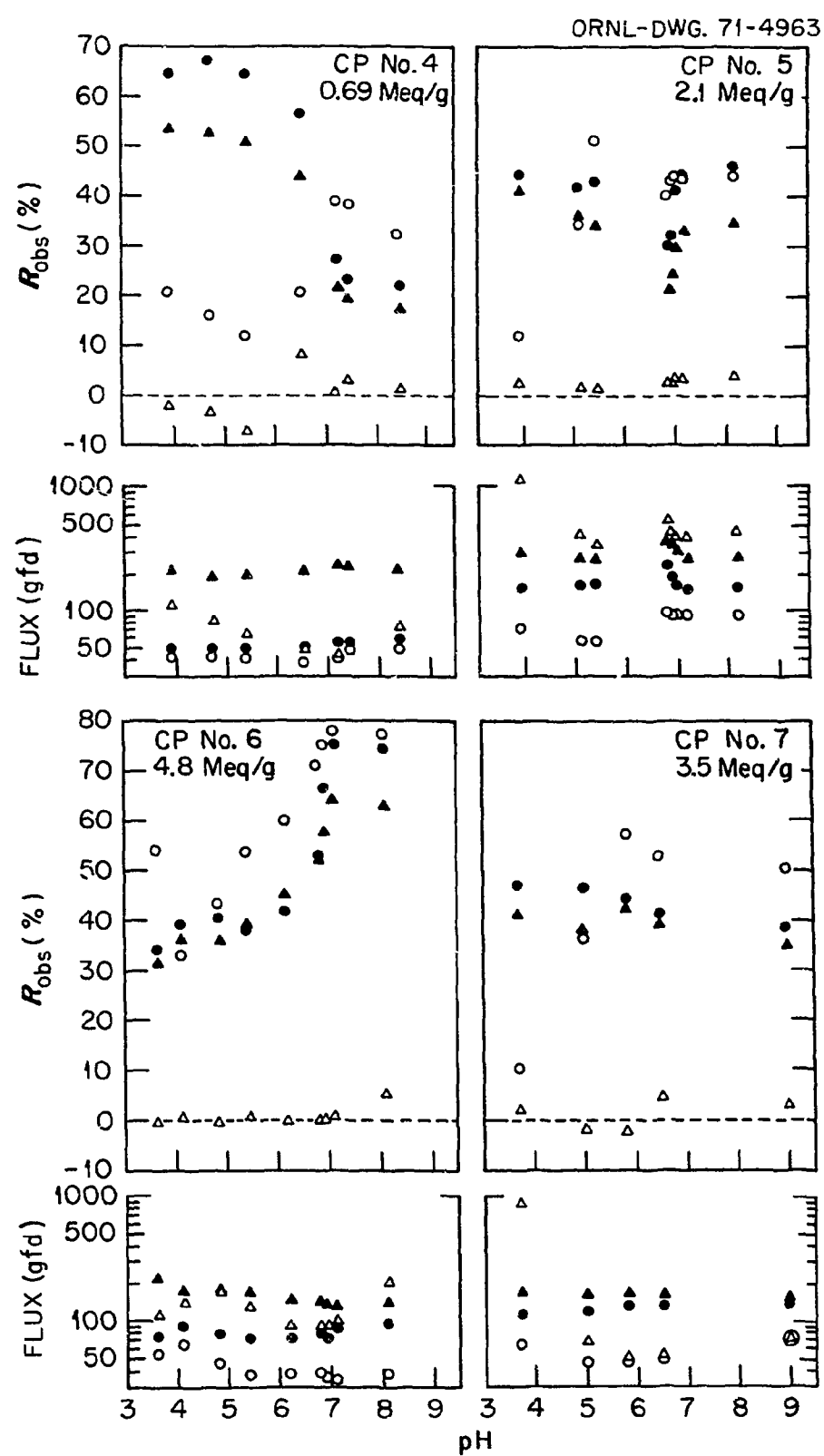
We formed membranes of these additives both on hydrous oxide sublayers and directly on porous supports. A hydrous Zr(IV) oxide membrane was formed by our usual procedures on 0.025- μ Millipore and 0.45- μ Acropor AN, wrapped around tubes. The loop was rinsed, shut down, and test sections with fresh wraps were introduced. The Calgon additive was then introduced at 50 ppm in 0.05 M NaCl, pH < 4, and hyperfiltration properties determined as NaOH was added. The results are summarized in Fig. 3.28 and 3.29.

Although fluxes were high, rejections were not high enough for great practical interest. There were curious aspects, however. The polyanionic additive of highest capacity, CP-6, both with and without hydrous oxide sublayers on 0.025- μ Millipore, and with sublayer, on 0.45- μ Acropor, formed a membrane of pH response typical of a polycarboxylate, rejections being up to 75% at neutral pH values (Fig. 3.28). Without sublayer on the 0.45- μ support, however, fluxes were virtually the same as with sublayer, but rejections were essentially zero.

With the polyanion of lowest capacity, rejection as a function of pH appeared typical of the hydrous oxide sublayer. Without sublayer, rejections for the 0.025- μ support were scattered, and small negative rejections were observed for the large pore size. Enrichments were confirmed in a separate experiment. Rejections by the polymers of intermediate capacity were of indeterminate character, though not typical of hydrous oxides. In both cases, with the 0.45- μ support without sublayer, rejections were low, without abnormally high fluxes.

Anion-exchange membranes formed from the polycationic additives might be expected to have properties resembling hydrous Zr(IV) oxide in the pH range studied, and the membranes without sublayers are therefore of greater interest. With 0.025- μ supports, rejections, as expected, increased with increasing capacity. Rejections on 0.45- μ supports were low, as they were with the other charge sign, but in this case, high fluxes were consistent with faulty membrane formation.

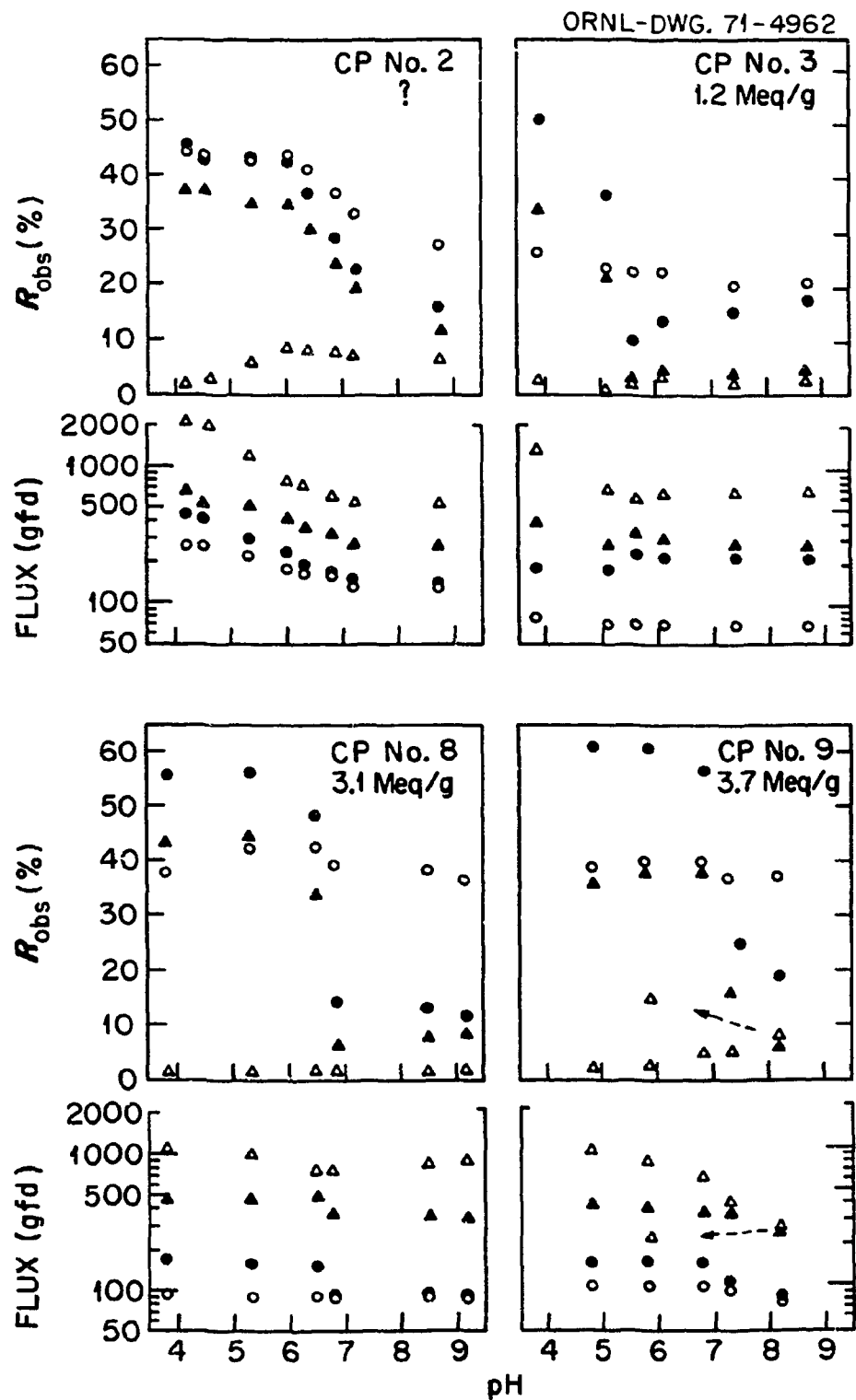
3.2.3.4. Polyphosphates. We have from time to time tried various procedures to form membranes dynamically with phosphate ion-exchange groups, but have had little success. Although the formulation of commercial products may vary considerably, the household presoak, Biz, was listed in the



Membrane performance versus pH for dynamic membranes of Calgon copolymers of anionic charge type. (0.05M NaCl, 900 psig, 25°C)

Support	Single-layer membrane	Dual-layer membrane with hydrous oxide sublayer
0.025 μ Millipore	○	●
0.45 μ Acropor AN	△	▲

Fig. 3.28



Membrane performance versus pH for dynamic membranes of Calgon copolymers of cationic charge type. (0.05 M NaCl, 900 psig, 25°C)

Support	Single-layer Membrane	Dual-layer membrane with hydrous oxide sublayer
0.025 μ Millipore	○	●
0.45 μ Acropor AN	△	▲

Fig. 3.29

September 14, 1970, Chemical and Engineering News, page 17, as containing about 74% sodium tripolyphosphate. It seemed of interest to try Biz as an additive. Tests were carried out in cells with 0.025- μ and 0.45- μ Millipore supports. Membranes were formed from 0.05 M NaCl feed containing 1 g/l of Biz, pH 9.5. After two hours, R_{obs} for the 0.025- μ was 45%, flux 80 gfd, and for the 0.45- μ , 46%, flux 170 gfd (1000 psig). At that time, NaCl concentration was reduced to 0.01 M and Biz to 40 ppm, and the effect of feed acidity determined (Fig. 3.30). Differences between the initial (α) and final (ω) 0.01 M NaCl points indicated changes in the membrane during the pH scan. Effect of acidity with Na_2SO_4 and MgCl_2 feeds is also shown in the figure.

After MgCl_2 , NaCl concentrations of 0.05 M and 0.01 M in water were tested, then 0.01 M NaCl in primary sewage effluent. The results are listed below.

<u>M</u> NaCl	<u>0.025-μ Millipore</u>		<u>0.45-μ Millipore</u>	
	<u>R_{obs}, %</u>	<u>Flux, (gfd)</u>	<u>R_{obs}, %</u>	<u>Flux, (gfd)</u>
0.05	74	43	72	140
0.01	90	55	90	160
0.01 (in sewage)	63	25	58	90

Biz membranes appear to be of the cation-exchange class, as one would expect if the active ingredient were phosphate.

We also tried, at the suggestion of Dr. H. E. Podall, to form both single and dual-layer membranes from a sodium metaphosphate additive. Hydrous Zr(IV) oxide sublayers were formed on 0.45- μ Acropor and 0.22- μ Millipore supports at 30 fps and on 0.45- μ Acropor and 0.025- μ Millipore substrates at about 12 fps. The Zr(IV) was rinsed from the loop and a third double finger, wrapped with 0.45- μ Acropor and 0.22- μ Millipore, was inserted into the remaining test section, also run at 35 fps. Fifty ppm of Baker and Adamson reagent grade sodium metaphosphate were added to the 0.05 M NaCl feed at pH 5.8, and the pH lowered to 3.3. The pH was then increased to increments to 9.8. At that point, the fluxes and rejections were as listed in Table 3.61, under Cycle 1. An additional 25 ppm of sodium metaphosphate, dissolved in dilute acid, was added to the

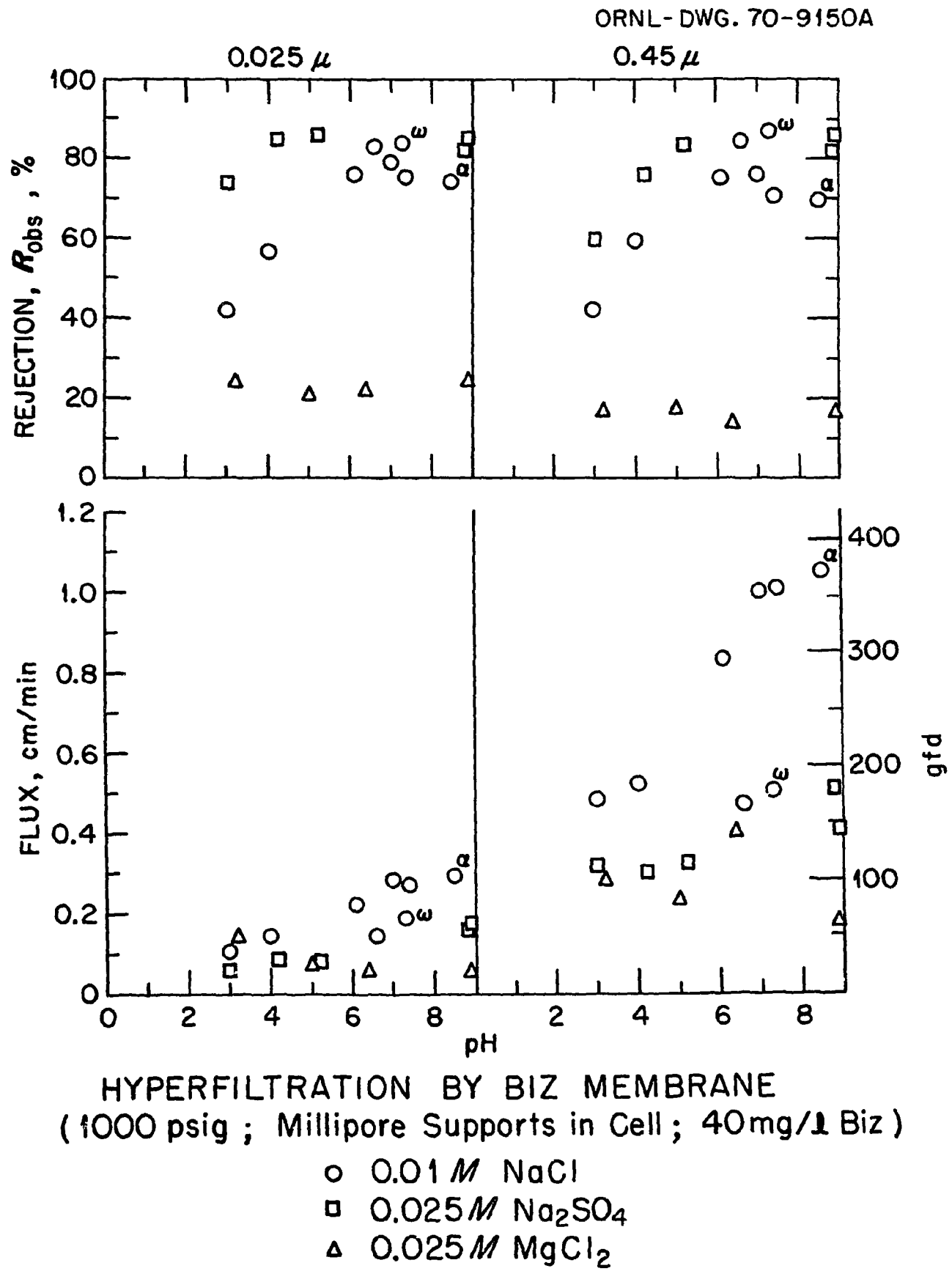


Fig. 3.30

TABLE 3.61
HYPERFILTRATION BY POLYPHOSPHATE MEMBRANES WITH AND WITHOUT
HYDROUS Zr(IV) OXIDE SUBLAYERS
(950 psig, 25°C)

<u>Cycle</u>	<u>Support*</u>	<u>Velocity (fps)</u>	<u>Sclution</u>	<u>Zirconium Sublayer</u>	<u>pH</u>	<u>Flux (gfd)</u>	<u>R_{obs} (%)</u>		
1	0.22-μ MP	30	0.05 <u>M</u> NaCl	yes	9.8	445	52		
		30		no		600	28		
	0.45-μ AP	30		yes		700	51		
		30		no		1100	24		
		12		yes		285	46		
	0.025-μ MP	12		yes		34	62		
	2	0.22-μ MP		30		yes		360	55
				30		no		355	45
		0.45-μ AP		30		yes		550	52
30				no		470	45		
12				yes		173	48		
0.025-μ MP		12	yes		51	60			
0.22-μ MP		30	0.025 <u>M</u> Na ₂ SO ₄	yes	7.7	350	86		
		30		no		300	73		
0.45-μ AP		30		yes		560	83		
	30		no		440	74			
	12		yes		179	74			
0.025-μ MP	12	yes		30	92				
0.22-μ MP	30	0.025 <u>M</u> MgCl ₂	yes	6.3	350	2			
	30		no		405	2			
0.45-μ AP	30		yes		565	4			
	30		no		690	3			
	12		yes		184	4			
0.025-μ MP	12	yes		29	17				

*MP is Millipore, AP is Acropor AN.

feed at pH 7.8, and another acid cycle carried out. The results of this second cycle are also shown in the table, Cycle 2. The loop was rinsed thoroughly and the polyphosphate membranes were tested first with 0.025 M Na_2SO_4 and then with 0.025 M MgCl_2 . These results are listed in Table 3.61 under the appropriate solution headings.

It is readily apparent from the table that the dual-layer membranes consistently give better rejections than do those made from a polyphosphate layer alone. None of the rejections are very good, although the higher values for rejection during the run with Na_2SO_4 demonstrate the cation exchange properties of the phosphate membrane. The values for rejection of MgCl_2 are anomalously low, indicating perhaps a detrimental complexing of the ion-exchange sites. Except for the 0.025- μ Millipore support, fluxes were good for all of the membranes. Especially interesting are the high fluxes at reasonable rejections for the hyperfiltration of sulfate solutions by the dual-layer membranes on the 30 fps membranes on 0.22- μ Millipore and 0.45- μ Acropor supports. At fluxes of 350 and 560 gfd, concentration polarization is undoubtedly appreciable.

3.2.3.5. Sulfonated Poly(phenylene oxide). The promising results obtained by a research group from General Electric Company (Ref. 33 and 34) who used cast sulfonated polyphenylene oxide (SPP0) films for the reverse osmosis desalination of brackish waters prompted us to prepare such a polymer for use in the formation of dynamic membranes. Our sample, which was prepared by the sulfonation of polyphenylene oxide by chlorosulfonic acid in chloroform at -40°C , had a capacity of 5.7 meg/g. Unfortunately, so much cross-linkage by sulfone groups occurred that the SPP0 was quite insoluble and the solid was not easily dispersed by grinding and blending. However, the slightly turbid supernatant liquid which resulted from the attempts at solution and dispersion was decanted and added to a 0.05 M NaCl feed solution for deposit on two different substrates, 0.025- μ Millipore and 0.45- μ Acropor, at two different circulation velocities (18.7 and 35 fps). No good membranes were formed (e.g., maximum R_{obs} = 12% at 708 gfd), but the poor results are most likely due to having much too low a concentration of additive in the feed solution.

3.2.3.6. Poly(sodium ethene sulfonate). We have prepared dynamic membranes with hydrous Zr(IV) oxide sublayers and top layers of the strong polyelectrolyte, poly(sodium ethene sulfonate), or polyvinyl sulfonate. We used polymers of two molecular weights, $\sim 30,000$ and $\sim 60,000$, and the results for the lighter polymer are listed in Table 3.62.

TABLE 3.62

HYPERFILTRATION RESULTS OF DUAL-LAYER HYDROUS Zr(IV)
OXIDE-POLY(SODIUM ETHENE SULFONATE) MEMBRANES

(0.05 M NaCl, 900 psig, 25°C, Polymer Molecular Wt. $\sim 30,000$)

pH	17.5 fps				35 fps			
	0.025- μ Millipore		0.45- μ Acropor		0.025- μ Millipore		0.45- μ Acropor	
	Flux(gfd)	R_{obs}	Flux(gfd)	R_{obs}	Flux(gfd)	R_{obs}	Flux(gfd)	R_{obs}
4.0	226	47	470	51	370	34	720	43
5.5	220	28	425	37	370	26	595	34
8.2	130	39	385	45	246	37	555	41
8.25	126	42	310	46	236	39	535	41
8.25	118	44	289	47	225	40	495	42
7.3	115	45	278	47	213	40	495	44

The heavier polymer was prepared by polymerizing sodium ethene sulfonate with potassium persulfate and sodium bisulfite. The molecular weight was estimated from viscosity measurements. Dual-layer membranes were formed on two sets of tubular supports (0.025- μ Millipore and 0.45- μ Acropor AN) at 35 and 17.5 fps. A pH scan was run and rejections were unsatisfactory, varying from about 30% to 60%. Fluxes were 400 to 500 gfd at neutral pH, and we could detect no appreciable difference between membranes formed at different velocities.

3.2.3.7. Poly(styrene sulfonate). One of the earliest additives tested at this laboratory in the formation of dynamic membranes was a polystyrene sulfonate (PSS) of molecular weight roughly 300,000, obtained from Dow Chemical Company (Ref. 35). More recently, we have tested as additives in forming dynamic membranes several locally prepared PSS additives as well as some commercially available ones (Ref. 15, p. 96 ff). All were tested

as single-layer membranes and rejections have been lower than with polyacrylate membranes. During this biennium, we prepared a new sample by adding a dilute solution of chlorosulfonic acid in chloroform to a dilute solution of Borden's polystyrene, molecular weight 2.3×10^5 , in chloroform at -40°C . This procedure differs from former ones in that the acid was diluted before it was added to the polystyrene solution. The resulting PSS had an exceptionally high capacity of 6.5 meq/g of solid, and it was used to form single-layer dynamic membranes on tubular supports wrapped with 0.025- μ Millipore and 0.45- μ Acropor AN. The membranes were formed at 950 psig and 35 fps. Observed rejections of 0.05 M NaCl were high for PSS, $\sim 70\%$ for both supports. Fluxes were quite high, 390 gfd through the 0.025- μ support and 570 gfd through the others. At these fluxes, concentration polarization is appreciable, and intrinsic rejection by these membranes probably approaches 80%.

3.2.3.8. Chitosan (Polyaminoglucose). Chitosan is deacetylated chitin, a natural polymer, N-acetyl polyaminoglucose, derived from the shells of marine animals. We tested the membrane properties of chitosan by dissolving it in 0.05 M NaCl at pH 4, and depositing it from acid solutions on two porous supports, 0.025- μ Millipore and 0.45- μ Acropor, mounted in cells in a small test loop. The rejection and flux of 0.05 M NaCl was measured at 1500 psig at three different pH's, and the results are given in Table 3.63. The chitosan did not form good membranes, and they were especially poor on the 0.45- μ support. The rejections appeared best in acid to neutral solutions, and became worse in basic solution, as one would expect with amine functional groups.

3.2.3.9. Cobalt Complexes of Poly(ethylene imine). In an attempt to form a better anion-exchange membrane, we complexed Montrek 600, a Dow Chemical Company poly(ethylene imine) of about 60,000 molecular weight, with Co(III). The Co(III) forms a chelate with two nitrogens in the PEI chain, and the Co(III) itself acts as the fixed charge site in the membrane. We added 50 ppm of the complex to 0.05 M NaCl at pH 6.5, and formed single-layer membranes at 1500 psig and 27°C on two supports, 0.025- μ Millipore and 0.45- μ Acropor AN, both in cells with an additional 0.025- μ Millipore backing. We got 83% rejection at 57 gfd on the Millipore support, but only 9% rejection at 36 gfd on the Acropor support. After an acid cycle to

TABLE 3.63

HYPERFILTRATION RESULTS WITH DUAL-LAYER
HYDROUS Zr(IV) OXIDE-CHITOSAN MEMBRANES

pH	0.025- μ Millipore		0.45- μ Acropor	
	Flux(gfd)	R_{obs} (%)	Flux(gfd)	R_{obs} (%)
4.4	210	40	230	2
4.4	183	41	216	5
4.4	170	40	182	6
6.5	160	46	160	6
6.0	180	40	174	6
8.8	107	15	285	0.3
8.8	89	20	254	0

pH 3.1 and back to 6.5, the flux through the Millipore support had fallen to about 20 gfd, still at 83% rejection. The final flux through the Acropor support was but 17 gfd at 30% rejection. Both flux and rejection seemed essentially independent of pH for these membranes.

3.2.3.10. Casein. A quarterly report to OSW from the Environgenics Company of Aerojet-General, (Ref. 36) which describes the use of casein in the formation of dynamic hyperfiltration membranes prompted us to try casein as the top layer in a dual-layer membrane, as well as a single-layer membrane. Shuey and Saltonstall deposited the casein on a composite polysulfone-Dacron support in a braided, resin-impregnated glass fiber tube and got, at 15 gfd, 93% rejection of the salt from a solution 3000 ppm in Na_2SO_4 . We formed a hydrous Zr(IV) oxide sublayer on two supports, 0.025- μ Millipore and 0.45- μ Acropor AN, at 950 psig and 35 fps circulation velocity. After rinsing excess Zr(IV) from the system, we inserted other Millipore and Acropor-wrapped fingers into the test loop and added 0.05 M NaCl and 50 ppm casein to the feed solution at pH 8.5. The rejections and fluxes of the resulting membranes at two different pH values are given in Table 3.64. For given conditions and support, the dual-layer membranes out-performed those made from casein alone. In general, rejections were better from acid solution (pH 4) than from solutions at higher pH's.

3.2.3.11. Molybdenum(VI). We have in the past attempted to form membranes from certain mixed hydrous oxides, analogous to the ion exchangers "zirconium tungstate" and "zirconium molybdate" (Ref. 37). More recently,

TABLE 3.64
HYPERFILTRATION OF 0.05 M NaCl BY DYNAMIC MEMBRANES OF CASEIN,
WITH AND WITHOUT SUBLAYERS OF HYDROUS Zr(IV) OXIDE
(950 psig, 25°C)

<u>pH</u>	<u>Support*</u>	<u>Velocity (fps)</u>	<u>Sublayer</u>	<u>Flux (gfc)</u>	<u>R_{obs} (%)</u>
8.3	0.025- μ MP	35	no	49	62
	0.45- μ AP	35	no	325	10
	0.05- μ MP	35	no	71	57
	0.22- μ MP	35	no	141	44
	1.20- μ AP	14.5	no	130	22
	0.025- μ MP	35	yes	26	72
	0.45- μ AP	35	yes	133	42
4.0	0.025- μ MP	35	no	22	74
	0.45- μ AP	35	no	470	7
	0.05- μ MP	35	no	35	70
	0.22- μ MP	35	no	91	33
	1.20- μ AP	14.5	no	80	28
	0.025- μ MP	35	yes	21	87
	0.45- μ AP	35	yes	89	69

*MP is Millipore, AP is Acropor AN.

we attempted to form dynamically a single-layer membrane of hydrous Mo(VI) oxide. We mounted supports of 0.025- μ Millipore and 0.45- μ Acropor AN, backed by a 0.025- μ Millipore cushion, in cells, and added 0.001 M Mo(VI) in a solution 0.008 M in NaCl at pH 3.6. We obtained a maximum rejection of about 5%. We removed the solution from the loop ($\sim$ 2 liters) and boiled it for 30 minutes to increase the degree of polymerization, but the performance was not improved.

3.2.3.12. Hydrous Al(III) Oxide. In our early work, we formed hydrous oxide layers from a variety of hydrous oxides, but have, more recently, concentrated on hydrous Zr(IV) oxide primarily because of its favorable ion-exchange characteristics, low solubility, and our familiarity with its chemistry. Our membrane formation techniques have changed over the years, however, and it is possible that other oxides might give superior performances as sublayers if formed by the present techniques. In addition, certain

hydrous oxides as sublayers might contribute to a dual-layer membrane that is more effective at either high or low pH values than are those we now use. With this in mind, we ran tests with hydrous Al(III) oxide as the sublayers, and with PAA and poly(vinyl pyridine) as top layers.

3.2.3.12.1. Al(III)-PAA Membranes. One Al(III)-PAA dual-layer membrane was formed at 35 fps and another at 59 fps, on double fingers wrapped with 0.025- μ Millipore and 0.45- μ Acropor. Results were not encouraging. Before the PAA was added, maximum rejection by the sublayer was less than 40% and it occurred at pH 10 to 12. There appeared to be a minimum around 7 or 8, while the rejection at pH 4.4 was about 8-11%. The PAA was added at pH 2.1, and the pH increased stepwise to 8.0. At pH 8, rejections ranged from 60 to 67%, the highest values we reached with this membrane.

At a given pH, rejections on the various supports were roughly similar, but the membranes formed at the high velocity had appreciably higher fluxes. This was especially true of the two 0.45-micron Acropor supports; the membrane formed at 59 fps was from 2 to 3 times more permeable than was that formed at 35 fps. At pH 6.8, the membrane formed at the higher velocity rejected 59% of 0.05 M NaCl at 170 gfd.

3.2.3.12.2. Al(III)-PVP Membranes. We have tried many times in the past to form good dual-layer membranes using polyelectrolytes other than polyacrylates. We have given special attention to forming membranes from anion exchangers (amines), but have not been very successful. During the term of this report, we formed some dual-layer anion-exchange membranes with hydrous Al(III) oxide sublayers.

The membranes were dual-layer dynamic membranes with sublayers formed from solutions 10^{-4} M AlCl₃ in 0.05 M NaCl, and top layers of poly(2-vinyl pyridine), (PVP), using 50 ppm of the organic polyelectrolyte in 0.05 M NaCl. In the first case, the Al(III) was introduced at pH 4.0, but full pressurization could not be achieved until the pH was raised to 4.6. Some reasonably good sublayer membranes were formed (e.g., 2160 gfd at 48% and 550 gfd at 71%), but when PVP was added at pH 3.7, and the pH slowly raised to 7.0, membranes of poor rejection resulted. In the second case, the sublayer was deposited at pH 11.0 and the PVP was also added in basic solution and then cycled step-wise to acid and back to

neutral. Maximum rejection, less than 70%, occurred at about pH 4.4, and at no pH were the membranes as good as those we have formed with Zr(IV)-PAA.

In a third try, we hoped to form better membranes by increasing the basicity of the ion-exchange groups by utilizing quaternized pyridines. Again the sublayer was deposited from basic solution. Following this, the Al(III) additive was rinsed from the system, and the quaternized (80%) poly(4-vinyl pyridine) was introduced at 50 ppm in a 0.05 M NaCl solution at pH 11. A cycle to pH 4 and back to 10 failed to reveal any pH value at which this membrane showed properties justifying further work.

3.2.3.13. Cross-Linked Poly(vinyl pyridinium bromide). Dr. Alan Rembaum of the Polymer Research Section of the Jet Propulsion Laboratory of the California Institute of Technology kindly sent us several samples of cross-linked polyvinyl pyridinium bromide resins which were prepared from 4-vinyl pyridine and α, ω dihalides. The charge density of a particular resin is determined by the chain length of the dihalide used as the cross-linking agent. We formed dynamic membranes, with and without hydrous Zr(IV) oxide sublayers, with two of these resins. The results of a pH scan of membranes formed from the resin in which the cross-linking agent had been dibromo ethane are given in Table 3.65. The scan was made with 50 ppm of the polymer in the feed solution.

TABLE 3.65

pH SCAN OF PROPERTIES OF MEMBRANES FORMED FROM 4-VINYL PYRIDINE
CROSS-LINKED BY DIBROMO ETHANE (REMBaum)

(0.05 M NaCl, 50 ppm Additive, 950 psig, 25°C, 35 fps)

pH	Without Sublayer				With Hydrous Zr(IV) Oxide Sublayer			
	0.22- μ Millipore		0.45- μ Acropor		0.22- μ Millipore		0.45- μ Acropor	
	Flux(gfd)	R_{obs} (%)	Flux(gfd)	R_{obs} (%)	Flux(gfd)	R_{obs} (%)	Flux(gfd)	R_{obs} (%)
3.8	510	63	602	57	553	63	644	59
4.4	517	58	608	54	538	57	652	55
5.0	510	47	617	48	546	44	681	47
5.8	525	29	623	26	574	25	695	19
6.3	560	17	638	14	595	15	708	11
6.7	540	14	645	10	574	12	710	8
7.5	517	4	595	4	560	8	681	6
8.1	524	4	580	4	552	11	658	8
9.4	453	6	496	5	467	22	588	13
10.0	439	7	468	6	446	26	538	16
10.7	390	9	410	7	439	30	502	18

After an overnight run at pH 10.7, the fluxes had decreased to about half, or less, of their value in the table above, but the rejections were essentially unchanged. When the pH was lowered to 4, rejections increased to 70 to 75%; fluxes remained unchanged. Membranes with the sublayer had slightly better fluxes throughout the pH range, approximately equal rejections from acid solutions, and somewhat better rejections in basic solution.

We formed a second set of membranes with a resin made from 4-vinyl pyridine cross-linked with 2 dibromobutane. Although this polymer should be very similar to the one described above, differing chiefly in having a lower charge density, the membranes formed from it were quite different. At low pH's, fluxes for the membranes without sublayer were greater than 1000 gfd, but the rejections were less than 10%. At high pH, fluxes were about 200 gfd, and the rejections about 18%. For the membranes with the Zr(IV) sublayer, fluxes changed less with pH, dropping from about 450 gfd at pH 4 to 330 gfd at pH 11; rejections were 30-45% at pH 4 and 20-35% at pH 11. These membranes also lost permeability rapidly with time, especially those without the hydrous oxide sublayer.

3.2.3.14. Polyethyleneimine Cross-Linked In Situ. In Section 3.2.3.9 above, we describe attempts to form membranes from cobalt complexes of polyethyleneimine (PEI), and in our preceding biennial (Ref. 15, p. 130 ff) we reported on experiments with quaternized polyethyleneimines. Membranes in both cases were disappointing. During this biennium, we attempted to form a more stable polyamine membrane by depositing a layer of PEI on porous supports under pressure, and then cross-linking the polymer in situ with methyl acrylate.

50 ppm of PEI, molecular weight 50,000 - 1,000,000, were circulated past the supports for 2-1/2 hours at 950 psig, 65°C, and pH 7. Then 50 ppm of methyl acrylate were added to the pressurized feed. After 1-1/2 hours, another 50 ppm of the cross-linking agent were added, and the solution recirculated past the support surfaces for another 16 hours. At that time, the excess additives were rinsed from the system, and the dependence of hyperfiltration properties on pH, with 0.05 M NaCl solutions, was determined. The results of this test and subsequent operations are given in Table 3.66.

TABLE 3.66

PROPERTIES OF MEMBRANES FORMED FROM DYNAMICALLY DEPOSITED
POLYETHYLENEIMINE CROSS-LINKED IN SITU WITH METHYL ACRYLATE

(0.05 M NaCl, 950 psig, 25°C, 33-35 fps)

pH	0.27- μ Selas Tube		6C Carbon Tube		0.05- μ Millipore		0.45- μ Acropor	
	Flux(gfd)	R_{obs} (%)	Flux(gfd)	R_{obs} (%)	Flux(gfd)	R_{obs} (%)	Flux(gfd)	R_{obs} (%)
7.0	108	18	122	21	100	29	194	22
4.1	68	45	100	46	93	51	125	49
5.0	70	45	102	44	91	46	128	48
6.0	71	39	101	38	91	44	132	41
6.9	74	23	97	22	85	31	152	28
8.1	76	8	90	13	85	12	163	8
9.3	66	16	85	26	85	18	141	9
Overnight operation at pH 6:								
6.0	61	35	87	37	75	41	118	42
Added 50 ppm PEI:								
7.0	58	34	77	34	75	36	105	41
3.5	41	60	73	58	73	57	87	60
4.4	45	60	77	58	77	58	91	61
5.7	52	48	81	47	77	50	100	53
6.8	54	37	79	36	78	39	103	45
7.5	54	33	73	34	75	35	98	42
8.2	48	32	64	31	71	31	85	37
9.2	32	20	50	21	59	22	63	24
10.0	22	21	41	23	52	20	49	14
Over-weekend operation at pH 7; added HCl to pH 4.3:								
4.3	22	76	53	70	57	70	58	71
Rinsed out PEI, added 0.05 M NaCl plus HCl:								
3.4	28	80	54	69	62	70	61	70
Increased temperature to 65°C:								
3.4	132	36	128	65	148	63	110	65
Neutralized, then added 100 ppm methyl acrylate:								
7.0	86	61	147	51	167	51	135	54
Overnight operation:								
6.5	96	51	154	31	185	30	148	34
4.2	80	68	141	58	184	55	116	58
7.2	92	36	156	28	178	28	175	26
9.2	80	29	139	27	170	17	168	12

The results for these PEI membranes appear very similar to some we obtained during the 1966-1968 biennium (see Ref. 30, Fig. 2.15, p. 61), where rejections decreased with increasing pH and fluxes appeared more dependent on the passage of time than on the pH of the solution. The maximum rejections in the present case, about 60 to 70% at pH 3 or 4, were lower than the 80% attained with the quaternized PEI mentioned above.

3.2.3.15. Hydrous Zr(IV) Oxide-Sodium Heparinate. In some experiments on the hyperfiltration of shower bath water (Ref. 38), done in collaboration with Clemson University, we found that some dynamic membranes, while relatively impermeable to most impurities in the solution, were quite permeable to urea. Because of this property, Dr. Charles Hester, Chairman of the Department of Mechanical Engineering at Clemson, suggested the possibility of utilizing dynamic membranes in artificial kidney machines for the purification of human blood. We subsequently considered the possibility of using sodium heparinate (heparin sodium), which is used as an anti-coagulant, as the membrane forming additive. Membranes were formed on a series of supports upon which a hydrous Zr(IV) oxide sublayer had been formed, using 50 ppm of sodium heparinate in 0.05 M NaCl at 950 psig and 25°C. The results are given in Table 3.67.

TABLE 3.67

HYPERFILTRATION BY DYNAMIC Zr(IV)-SODIUM HEPARINATE MEMBRANES

(0.05 M NaCl, 950 psig, 25°C)

pH	0.05-μ MP*(35)**		0.45-μ AP* (35)**		0.05-μ MP* (15)**		0.45-μ AP* (15)**	
	Flux(gfd)	R _{obs} (%)	Flux(gfd)	R _{obs} (%)	Flux(gfd)	R _{obs} (%)	Flux(gfd)	R _{obs} (%)
6.5	104	21	210	16	95	17	145	15
9.0	105	37	192	33	95	32	133	30
10.0	108	40	186	36	95	35	130	34
11.1	111	36	173	33	85	32	124	32
6.9	90	24	180	13	81	18	122	14
Added 25 ppm sodium heparinate:								
7.0	90	26	173	15	79	20	120	16
6.0	85	18	170	14	73	19	118	14
7.0	84	30	167	18	73	23	114	19
4.9	79	21	165	29	68	30	110	27
7.0	92	28	162	20	77	25	112	21
3.9	79	25	163	34	68	36	106	34
7.2	91	38	160	28	73	30	105	24

*MP is Millipore, AP is Acropor.

** () indicates velocity in fps.

3.3 TESTS OF APPLICATIONS OF DYNAMIC MEMBRANES

3.3.1 Desalination of Brackish Waters

The motivation for the research described in this report was the development of dynamic membranes that would provide high-flux systems for the desalination of naturally occurring brackish waters. We have tested various dynamic membrane systems against a variety of simulated brackish waters of various compositions, which are, in this report, named after the location to which they are attributed. The compositions used in these tests are given in Table 3.68.

Earlier sections in this report have already treated some of the experiments we have done with brackish waters. For example, in Section 2, some tests are described with several synthetic solutions at 1, 2, and 3 times the nominal concentrations, see Fig. 7, and a number of tests of dynamic membranes with synthetic Coalinga water are also summarized. Fig. 9 of Section 3.1.1 also describes a typical experiment with Coalinga water. In the present section, we shall discuss in more detail these, as well as other experiments with the waters listed in Table 3.68.

3.3.1.1. Coalinga Water.

3.3.1.1.1. Long-Term Run. In a practical system, dynamic membranes would need to retain good rejections and reasonably high fluxes for long periods of time. To test the stability of the dynamic membrane, we prepared a set of five dual-layer membranes with which to test Coalinga water in a relatively long-term run. The characteristics of the membranes with respect to the hyperfiltration of 0.05 M NaCl before being exposed to Coalinga water are listed in Table 3.69. With the exception of the membrane on the carbon tube, all of the membranes showed good rejection of 0.05 M NaCl at reasonable fluxes. They were apparently typical dynamic membranes, neither the best nor the worst seen in normal operation.

For the first 220 hours of the run with Coalinga water, no deliberate changes were made in the process variables. The pressure was maintained at 950 psig, and, except for an inadvertent rise due to a failure in the temperature control system from about 100 to 140 hours, the temperature was maintained at 25°C. The circulation velocities were kept at those values used during the membrane formation indicated in Table 3.69.

TABLE 3.68

MOLARITIES OF SIMULATED BRACKISH WATERS

Ion	Coalinga ^a	Colorado ^b	Dalpra ^c	Roswell ^d	Webster ^c	Wellton- ^e
	Water	River	Farm	Water	Water	Mohawk Canal
Ca(II)	0.0018	0.0024	0.00294	0.004	0.00539	0.00609
Mg(II)	0.0020	0.0014	0.003	0.00209	0.00325	0.00362
Na(I)	0.0220	0.0017	0.0385	0.02022	0.00352	0.0411
K(I)	--	0.005	0.0004	--	--	0.00041
Cl ⁻	0.0076	0.0026	0.0037	0.02	0.00056	0.0341
SO ₄ ⁼	0.0096	0.0045	0.0202	0.00408	0.00747	0.0102
HCO ₃ ⁻	0.0028	0.0027	0.0078	0.00375	0.00582	0.00582
NO ₃ ⁻	--	--	0.0001	--	--	0.00013
SiO ₂	--	--	--	--	0.00033	0.00047
B	--	--	--	--	--	0.00016
TDS (ppm)	1,990	1,059	3,648	2,010	1,490	2,883
TEC ^f	0.0296	0.0143	0.0514	0.0322	0.0214	0.0613
[divalent cations] ^g	0.128	0.266	0.116	0.189	0.404	0.158
TEC						
[SO ₄ ⁼] ^g	0.324	0.315	0.393	0.127	0.349	0.166
TEC						

(a) OSW Res. & Dev. Rpt. No. 134 (1966).

(b) J. F. Smith, "Imperial Valley Salt Balance," Imperial Irrigation District, 1966.

(c) OSW Res. & Dev. Prog. Rpt. No. 684 (1971).

(d) Roswell Test Facility Laboratory Report, Sample No. 284-71-1, 10/12/71.

(e) Dr. F. E. Witmer, OSW, private communication.

(f) Total equivalent concentration.

(g) Concentrations in equivalents.

TABLE 3.69

INITIAL PERFORMANCE BY MEMBRANES USED IN LONG-TERM RUN ON COALINGA WATER

(0.05 M NaCl, 950 psig, 25°C, pH 7.2)

Support	Velocity (fps)	Flux (gfd)	R _{obs} (%)
0.45-μ Acropor AN	35	120	94
0.22-μ Millipore	35	100	98
0.45-μ Acropor AN	20	108	95
0.22-μ Millipore	20	94	96
6C Carbon (ground)	24	41	76

The product streams were returned to the feed tank in order to keep feed composition constant. At 220 hours, the Coalinga water in the feed tank was replaced with fresh Coalinga water to check whether or not specific fouling agents had been depleted from the original feed.

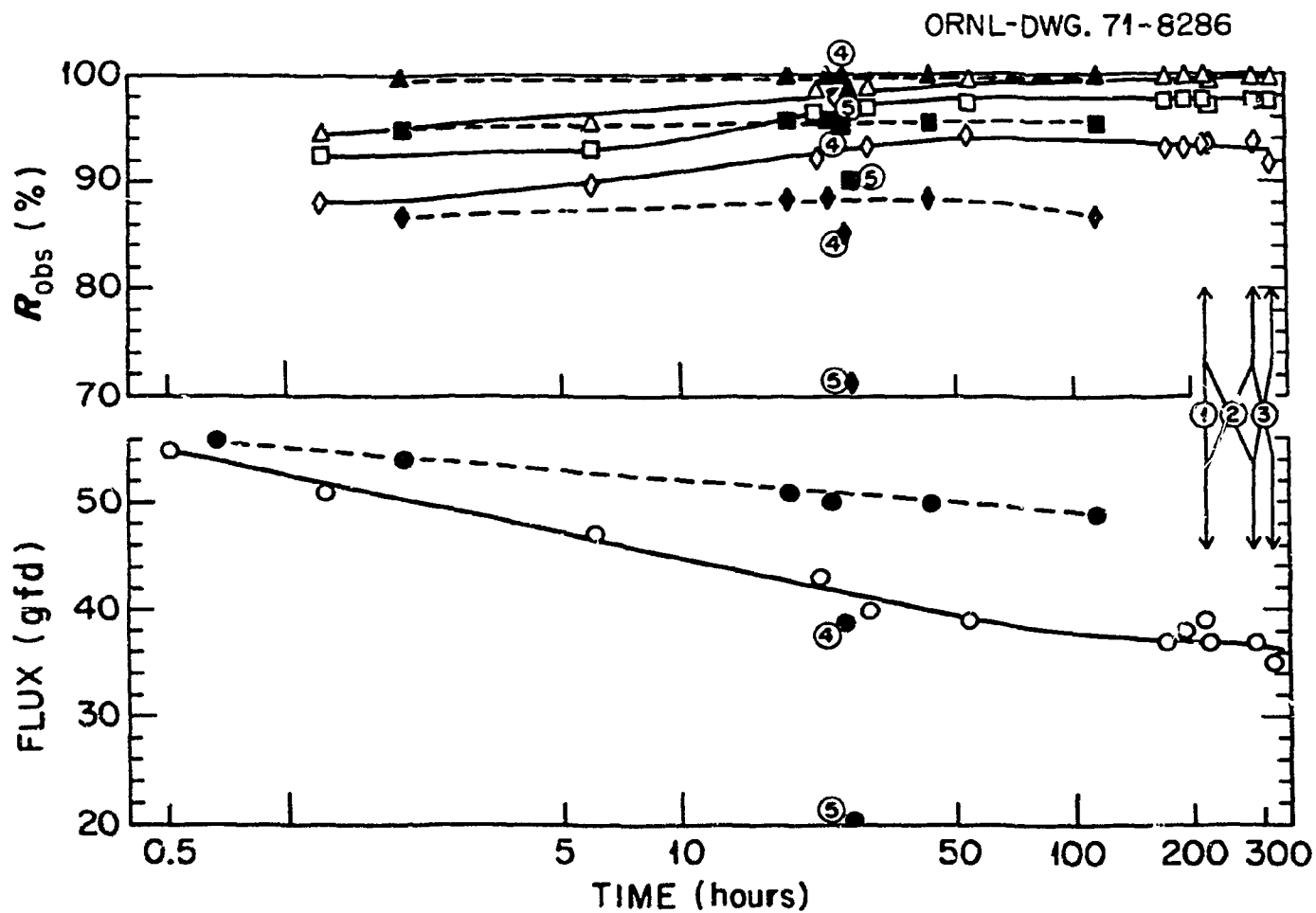
During the second portion of the run, which lasted from the 220th to the 317th hour, the effect of a change in circulation velocities on performance was investigated. Toward the end of this portion of the run, we concentrated the feed to one-third volume (i.e., 67% water recovery) by discarding the product streams.

Finally, after 317 hours of operation, the membranes were regenerated by first circulating 1 M NaOH through the loop past the membranes for about five minutes at 350 psig and then reforming the PAA layers by adding 50 ppm PAA to a 0.05 M feed at pH 2.2 and 950 psig, and slowly bringing the solution up in pH to neutrality. Following this regeneration procedure, fresh Coalinga water was introduced into the feed tank and the run was continued for another 115 hours. During this portion of the run, the effect of operating for short periods at reduced pressures, 700 and 300 psig, was determined.

After a total of 432 hours, or 18 days, of operation, the Coalinga water run was terminated only because it appeared that further operation would not result in any significantly new information.

Complete results for the run on two of the membranes, those formed and operated at 35 fps, are given in Figs. 3.31 and 3.32. The circled numbers 1, 2, and 3 in the region from 200 to 300 hours mark times and intervals at which and during which the indicated changes were made, namely, 1, fresh Coalinga water was used to replace that in the feed tank; 2, the circulation velocity past the membranes was reduced from 35 fps to 15 fps from about 220 hours to 287 hours; and 3, the product streams were discarded and the feed allowed to concentrate to about one-third volume from 287 hours until the membranes were regenerated at 317 hours.

In order that performance after regeneration could be directly compared with that before, the t_1 for the post-regeneration part of the run was taken as the time at which Coalinga water was added following regeneration. Thus, the two parts of the run are plotted on the same time

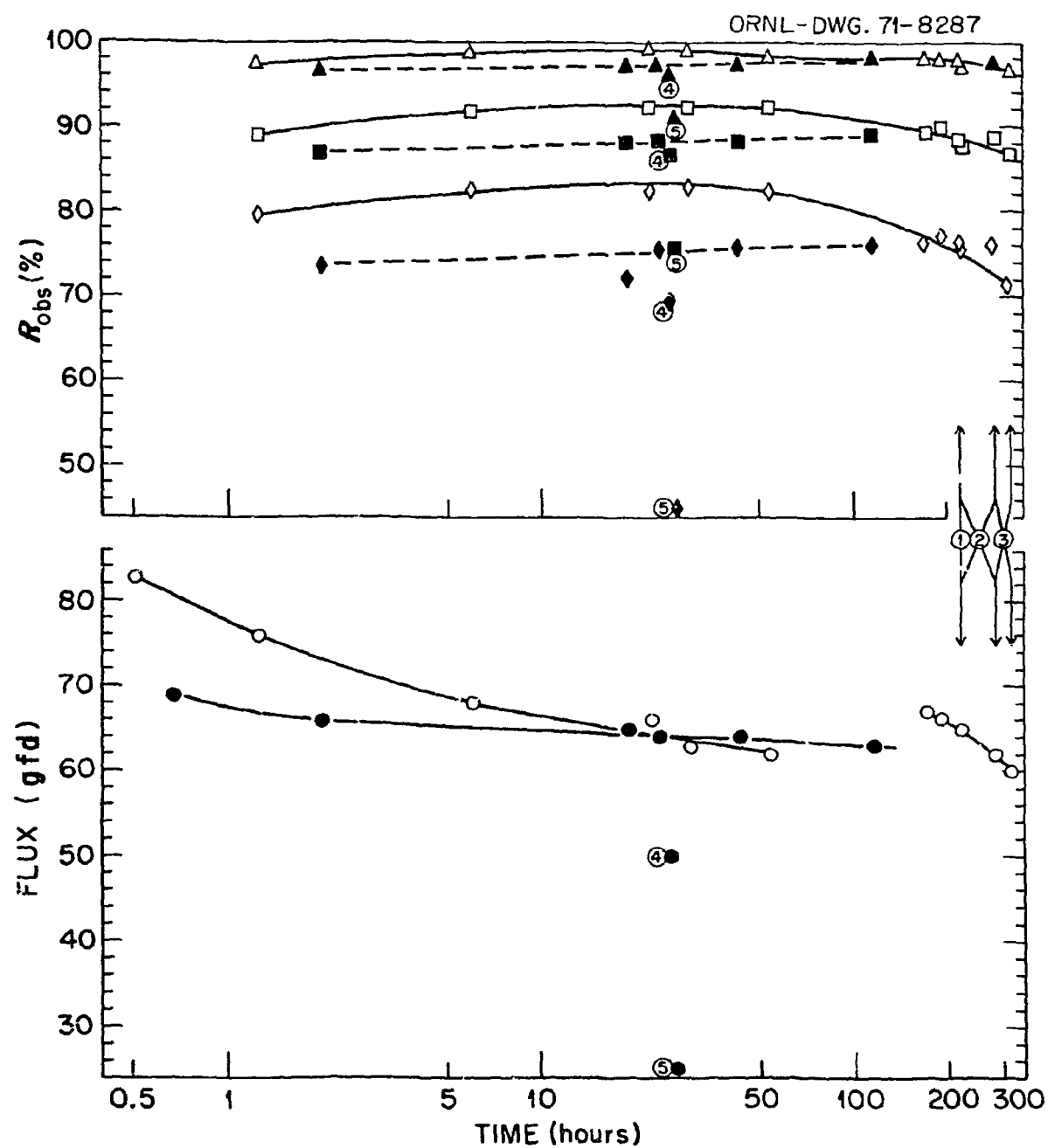


HYPERFILTRATION OF COALINGA WATER BY DYNAMIC
Zr(IV) OXIDE-PAA MEMBRANE ON 0.22μ MILLIPORE SUPPORT.
(950 psig, 35 fps, 25°C)

OPEN SYMBOLS : INITIAL RUN ; CLOSED SYMBOLS : AFTER REGENERATION
 $\Delta\Delta$ Mg(II) + Ca(II) ; $\diamond\diamond$ Cl^- ; $\square\square$ TOTAL CATION

- ① FRESH COALINGA WATER ADDED
- ② VELOCITY: 15 fps
- ③ CONCENTRATION OF FEED TO 1/3 VOLUME
- ④ 700 psig
- ⑤ 300 psig

Fig. 3.31



HYPERFILTRATION OF COALINGA WATER BY DYNAMIC
Zr(IV) OXIDE-PAA MEMBRANE ON 0.45μ ACROPOR AN SUPPORT.
(950 psig, 35 fps, $25^\circ C$)

OPEN SYMBOLS: INITIAL RUN ; CLOSED SYMBOLS: AFTER REGENERATION

Δ $Mg(II) + Ca(II)$; $\diamond$ Cl^- ; $\square$ TOTAL CATION

① FRESH COALINGA WATER ADDED

② VELOCITY: 15 fps

③ CONCENTRATION OF FEED TO 1/3 VOLUME

④ 700 psig

⑤ 300 psig

Fig. 3.32

base; open symbols are used for the pre-regeneration data, closed symbols are used for the post-regeneration data. The circled numbers 4 and 5 attached to the solid points at about 26 hours after regeneration indicate pressure excursions to 700 and 300 psig, respectively.

On the 0.22- μ Millipore support, Fig. 3.31, the rejection of the components of Coalinga water was good for a Zr(IV)-PAA membrane over the entire course of the run, both before and after regeneration. Chloride, normally the most poorly rejected component, was more than 90% rejected during most of the initial part of the run, and more than 85% following the regeneration procedure. Within one day of operation, the rejection of Ca(II) + Mg(II) had risen to 98% and exceeded that thereafter, while about 95% of total cations were rejected.

Rejections by the membrane on the 0.45- μ Acropor AN supports, Fig. 3.32, were not as good as those described above for the Millipore support, but the fluxes were appreciably higher. Part of the explanation for the lower observed rejection is, of course, increased concentration polarization because of the higher fluxes, but this is probably not the only cause. Since little change in rejection was seen when the circulation velocity was changed from 35 to 15 fps, concentration polarization was probably small.

The rejections by membranes formed and operated at 20 fps on the Millipore and Acropor supports were very similar to those of their 30 fps counterparts, although the fluxes were somewhat lower. Table 3.70 shows the rejections and fluxes of all of the membranes at the end of both the initial segment and at the end of the post-regeneration segment of the run. The values given are typical of those recorded throughout the run. The membrane formed on the 6C carbon tube was inferior to all of the others.

The decline in product fluxes for all of the membranes was linear on a log flux vs. log time plot (see Fig. 10, Section 2). Flux decline parameters before and after membrane regeneration are given in Table 3.71, together with the t_1 values for the fluxes, J_1 . Except for the pre-regeneration segment of the results with the carbon tube, none of the flux decline parameters were very large. Oddly, values of b were less after regeneration than before.

TABLE 3.70

COMPARISON OF HYPERFILTRATION OF COALINGA WATER BY MEMBRANES
FORMED AND OPERATED AT DIFFERENT CIRCULATION VELOCITIES.
DATA TAKEN AT END OF INITIAL 317 HOUR RUN AND AT END OF POST-
REGENERATION SEGMENT OF RUN (115 HOURS)
(950 psig, 25°C)

<u>Support*</u>	<u>Velocity (fps)</u>	<u>Flux (gfd)</u>	<u>R_{obs}(%)</u>		<u>Total Cation</u>
			<u>Cl⁻</u>	<u>Mg(II) + Ca(II)</u>	
Before regeneration, <u>t</u> = 317 hours					
0.45-μ AP	35	60	71	97	86
	20	48	77	98	90
0.22-μ MP	35	35	92	> 99	97
	20	31	92	> 99	97
6C Carbon	24	16	70	95	85
After regeneration, <u>t</u> = 115 hours					
0.45-μ AP	35	63	76	98	89
	20	59	67	96	85
0.22-μ MP	35	49	87	> 99	95
	20	44	82	99	93
6C Carbon	24	17	74	92	84

*AP = Acropor; MP = Millipore.

TABLE 3.71

FLUX DECLINE PARAMETERS, b, BEFORE AND AFTER MEMBRANE REGENERATION
FOR THE HYPERFILTRATION OF COALINGA WATER BY DYNAMIC DUAL-LAYER MEMBRANES
(950 psig, 25°C)

<u>Support</u>	<u>Velocity (fps)</u>	<u>Initial Run</u>		<u>After Regeneration</u>	
		<u>J₁ (gfd)</u>	<u>b</u>	<u>J₁ (gfd)</u>	<u>b</u>
0.45-μ Acropor AN	35	83	0.059	69	0.013
0.22-μ Millipore	35	55	0.065	56	0.024
0.45-μ Acropor AN	20	68	0.064	73	0.037
0.22-μ Millipore	20	46	0.056	54	0.040
6C Carbon (ground)	24	37	0.145	21	0.037

The flux through the 35 fps membrane on the 0.22- μ Millipore support, originally about 100 gfd with the 0.05 M NaCl feed (Table 3.69), dropped to 55 gfd by the time the first reading was made on Coalinga water, about 30 minutes after the brackish water had been added to the loop. At the end of 317 hours of continuous operation, the flux had decreased to about 35 gfd. Regeneration restored the flux to about 55 gfd and this dropped in the ensuing 115-hour run to about 44 gfd. Although the regeneration of the 35 fps membrane on the Acropor support did not return the flux to its original value, the regenerated membrane had better long-term properties than had the original, because of the lower rate of decline.

The rejection of inorganic carbon by the 20 fps membrane on the 0.22- μ Millipore support was monitored throughout the course of the run. The inorganic carbon concentration in the Coalinga water averaged about 32 ppm, and the rejection stayed constant at about 84%. The concentration in the feed after regeneration was about 34 ppm; the rejection was about 75%.

There were small decreases in both flux and rejections of all components when the concentration to one-third volume was carried out at the end of the first stage of the long-term run (see Table 3.72). Because of some salt loss in the product stream, the decrease to one-third volume resulted in a lesser increase in salt concentrations: Cl^- , 2.25; $\text{Mg(II)} + \text{Ca(II)}$, 2.58; and total cation, 2.34. The small decreases in fluxes and rejections should not, however, preclude the use of similar membranes in processes requiring reasonable water recovery levels.

Table 3.73 indicates the changes in both rejections and fluxes that resulted when the pressure was changed to lower values at the 26th and 27th hours of the run with regenerated membranes. Except for the carbon tube, fluxes declined somewhat less than proportionately with pressure, and values of $1 - R_{\text{obs}}$ were roughly twice as high at 300 psig as at 950. The decreases were reversible and the rejections and fluxes returned to previous levels when the pressure was again raised to 950 psig.

3.3.1.1.2. Effect of Molecular Weight of Polyacrylate. In Fig. 3.33 are collected results from the hyperfiltration of Coalinga water by dual-layer membranes utilizing three different molecular weight polyacrylates. For both supports, rejections decreased with increasing molecular

TABLE 3.72

THE EFFECT OF CONCENTRATING COALINGA WATER TO ONE-THIRD VOLUME
ON THE HYPERFILTRATION PERFORMANCE OF AGED (290 HOUR) DUAL-
LAYER MEMBRANES. THIRTY HOURS OPERATION BETWEEN 1 AND 3.

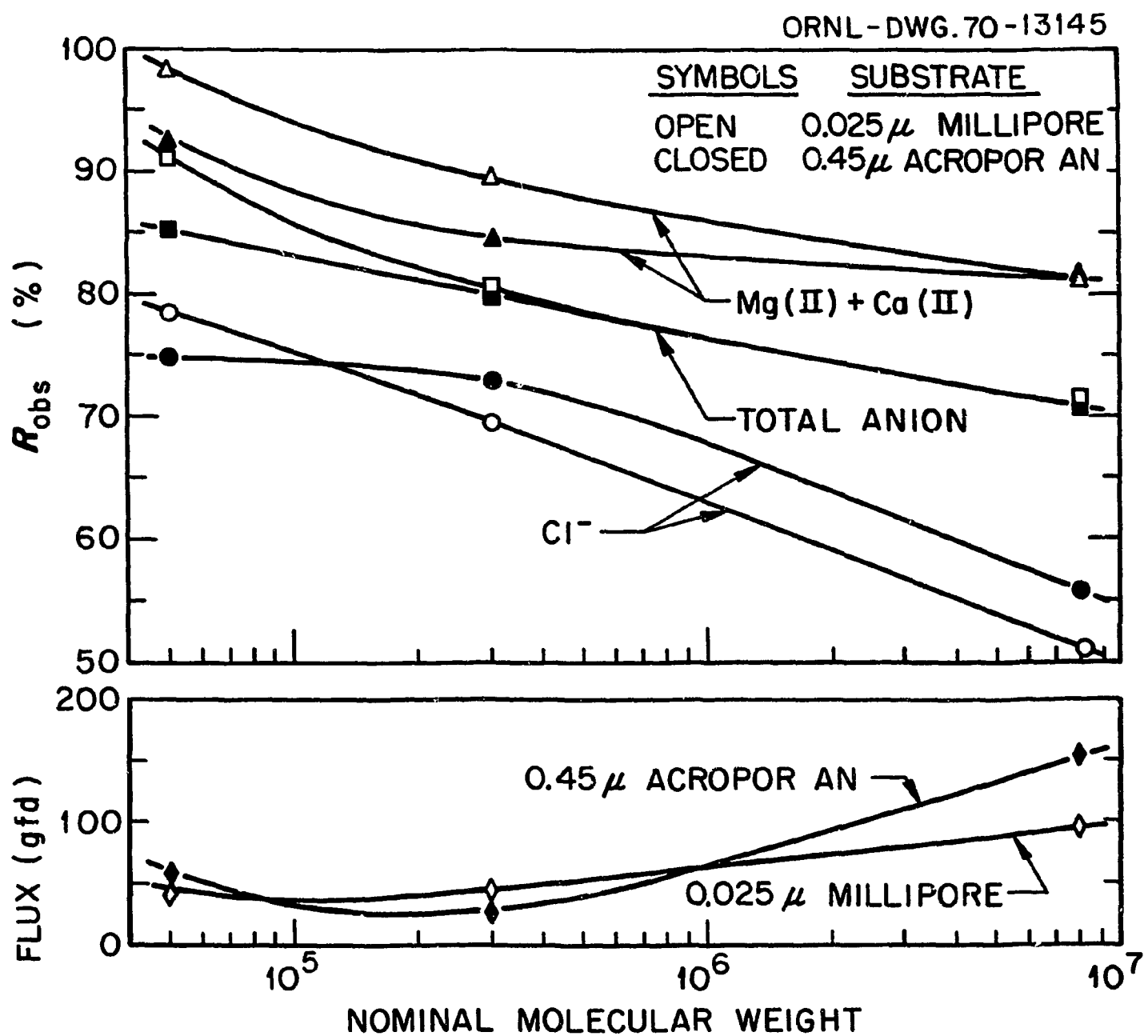
(950 psig, 25°C)

<u>Support</u>	<u>Velocity (fps)</u>	<u>Concen- tration Factor</u>	<u>Flux (gfd)</u>	<u>R_{obs} (%)</u>		
				<u>Cl⁻</u>	<u>Ca(II) + Mg(II)</u>	<u>Total Cation</u>
0.45-μ Acropor	35	1	62	77	98	90
		3	60	71	97	86
0.22-μ Millipore	35	1	37	93	> 99	98
		3	35	92	> 99	97
0.45-μ Acropor	20	1	50	81	98	92
		3	48	77	98	90
0.22-μ Millipore	20	1	32	93	> 99	97
		3	31	92	> 99	97
6C Carbon (ground)	24	1	16	75	96	88
		3	16	70	95	85

TABLE 3.73

THE EFFECT OF PRESSURE ON THE HYPERFILTRATION OF COALINGA
WATER BY DYNAMIC HYDROUS Zr(IV) OXIDE-PAA MEMBRANES

<u>Support</u>	<u>Velocity (fps)</u>	<u>(25°C)</u>		<u>R_{obs} (%)</u>		
		<u>Pressure (psig)</u>	<u>Flux (gfd)</u>	<u>Cl⁻</u>	<u>Ca(II) + Mg(II)</u>	<u>Total Cation</u>
0.45-μ Acropor	35	950	64	76	97	88
		700	50	69	96	87
		300	25	45	91	75
		950	64	75	97	88
0.22-μ Millipore	35	950	50	88	> 99	96
		700	39	85	> 99	95
		300	20	71	99	90
		950	50	89	> 99	96
0.45-μ Acropor	20	950	64	64	94	82
		700	50	58	93	80
		300	24	36	87	71
		950	64	64	94	81
0.22-μ Millipore	20	950	47	81	99	93
		700	37	78	98	92
		300	19	60	96	86
		950	47	81	99	92
6C Carbon (ground)	24	950	18	71	89	81
		700	13	66	86	78
		300	10	27	47	40
		950	18	70	87	79



EFFECT OF POLYCARBOXYLATE MOLECULAR WEIGHT
 ON HYPERFILTRATION OF COALINGA WATER BY
 DUAL LAYER MEMBRANES (1000 psig)

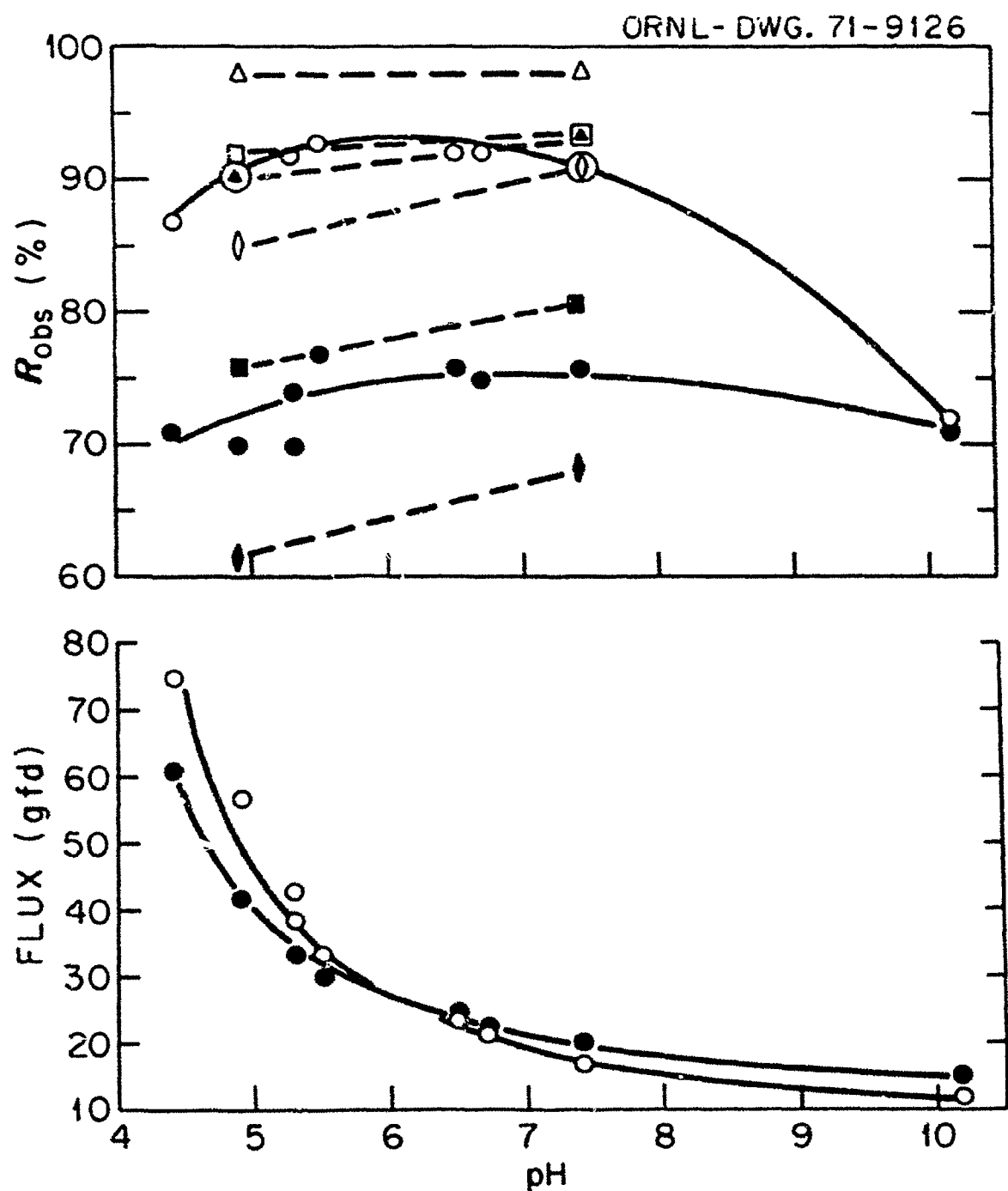
Fig. 3.33

weight while fluxes were highest for highest molecular weight additive Nalco A-1 (see Table 1, Section 3.1.1). Of the three additives tested in this experiment, Acrysol A-1, with a molecular weight of about 50,000, appears most satisfactory for the desalination of Coalinga water. Acrysol A-3, molecular weight about 150,000, was not tested at this time.

3.3.1.1.3. Effect of pH. One test of the effect of pH on the hyperfiltration of Coalinga water was discussed in Section 2 (see Fig. 9). The results of another test with dual-layer membranes on Millipore and Acropor supports is shown in Fig. 3.34. In both cases, the rejections appear to reach a maximum around neutral pH values, but the fluxes increase very rapidly as one goes to more acidic conditions. This flux behavior is in contrast to that observed (see Section 3.1.2.13.3) with simple MgCl_2 solutions, where the rejections decreased with increasing acidity. From a practical point of view, it appears that some trade-off between rejection and flux may be possible by adjustment of acidity.

3.3.1.1.4. Effect of Circulation Velocity. Dual-layer membranes on two kinds of Sela tubes, the 0.27-micron filter element and the 7-channel ceramic tube, were tested with Coalinga water so as to determine their relative performance at several circulation velocities, including those that might be encountered in practical use. The results are given in Fig. 3.35. There appears to be a fall-off in rejection with both tubes at velocities below about 10 fps. For the filter element, fluxes held up to very low velocities in this short-term run, but with the 7-channel tube, fluxes apparently decreased below about 15 fps. As we have seen several times before, the filter element gave both better fluxes and better rejections than the 7-channel tube. Fluxes were not particularly good on either support in these runs.

3.3.1.1.5. Effect of Pressure. We made two tests of Coalinga water in which the dual-layer membranes were formed and operated at medium pressure. In the first of these, the membrane was formed at 450 psig and 55°C on the inside of a 0.27-micron Sela filter element. The results of the 190-hour run, taken at 450 psig, 30 fps, and 25°C, are shown in Fig. 3.36.



pH EFFECT ON HYPERFILTRATION OF COALINGA
WATER BY DUAL-LAYER MEMBRANES.

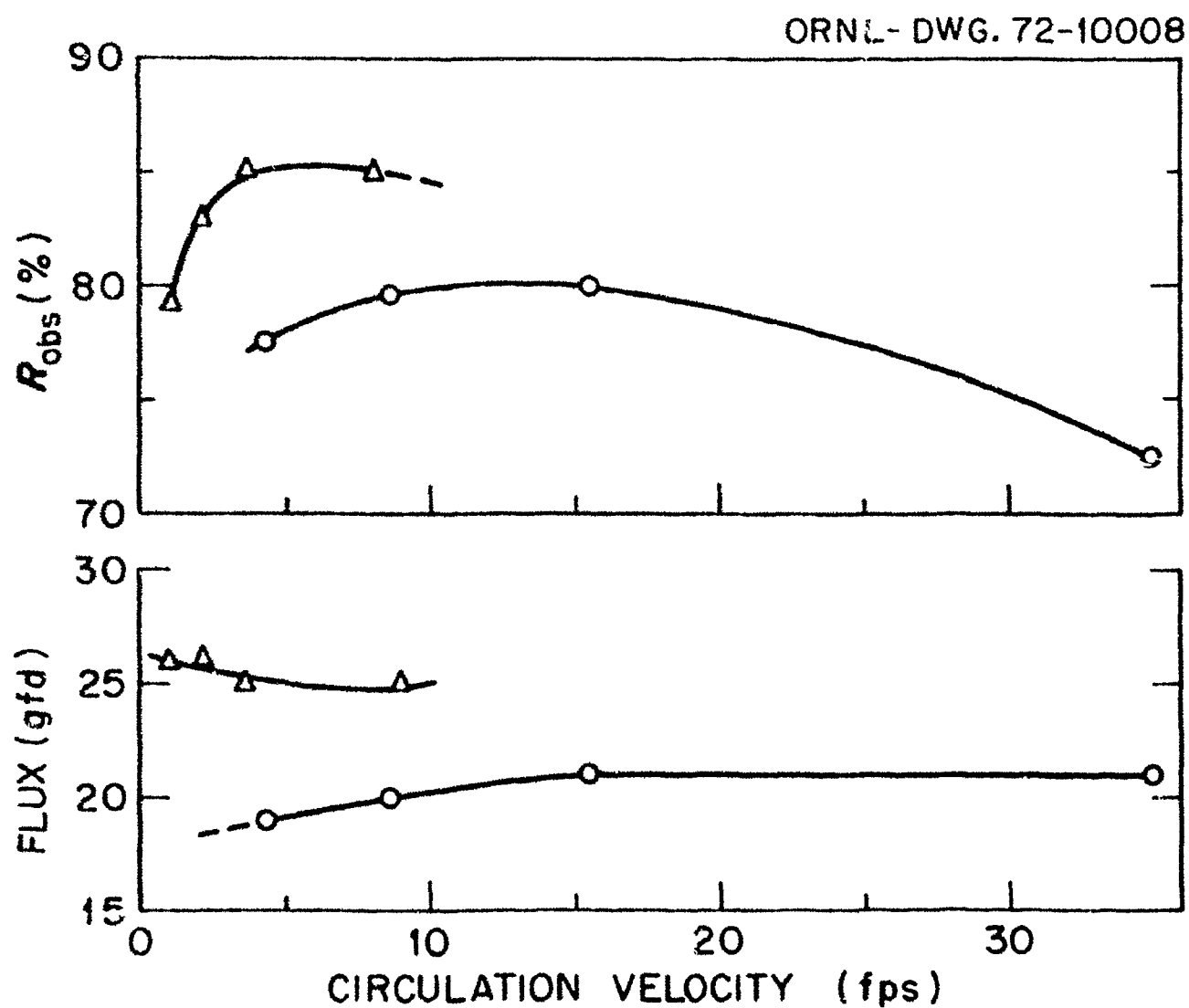
(900 psig, 25°C, 28 fps)

Open Symbols : 0.22 μ Millipore

Solid Symbols : 0.45 μ Acropor AN

$\circ \bullet$ Conductivity , $\blacklozenge$ Cl^- , $\Delta \blacktriangle$ $Mg(II) + Ca(II)$,
 $\square \blacksquare$ Total Cation

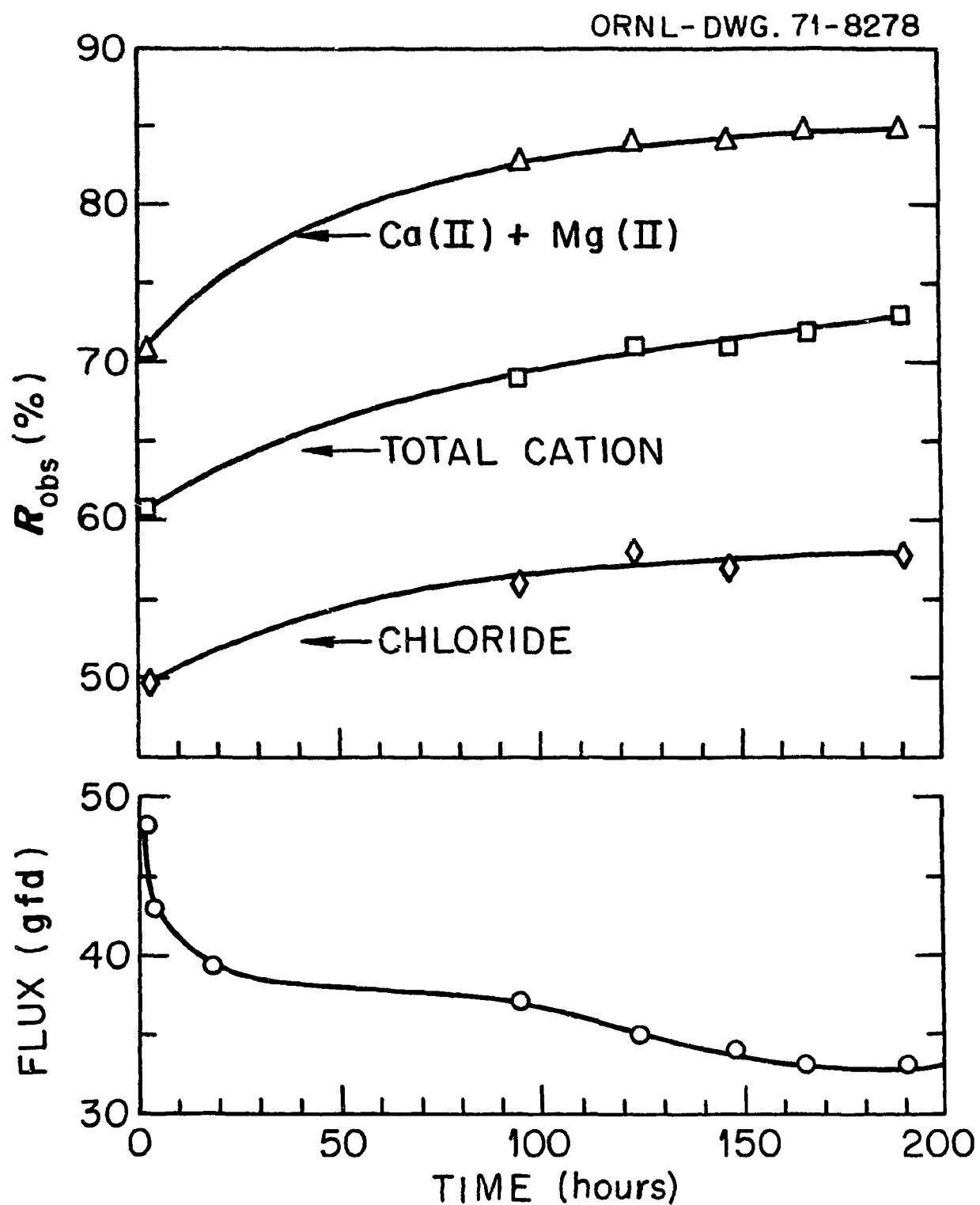
Fig. 3.34



VELOCITY DEPENDENCE OF HYPERFILTRATION OF
COALINGA WATER BY Zr(IV)-PAA MEMBRANES
(950 psig, 25°C, pH~8)

Δ 0.27 μ FILTER ELEMENT, OUTSIDE PRESSURE
 O 7-CHANNEL CERAMIC, INSIDE PRESSURE

Fig. 3.35



HYPERFILTRATION OF COALINGA WATER BY
HYDROUS $Zr(IV)$ OXIDE-PAA MEMBRANE
ON INSIDE OF 0.27μ SELAS CERAMIC TUBE.
MEMBRANE FORMED AT $55^{\circ}C$.
(450 psig, 30 fps , $25^{\circ}C$)

Fig. 3.36

Neither the rejections nor the fluxes were as good as at higher pressures: Cl^- rejection averaged about 56%; total cation about 70%; and Ca(II) plus Mg(II) about 83%. The flux fell from an early (1.5 hour) value of 45 gfd to 33 gfd after 190 hours. The flux decline parameter was about 0.08.

In the second run, a dual-layer membrane was formed and operated at 500 psig, 28°C, and 17.5 fps on the inside of a 7-channel Sela ceramic tube. With 0.05 M NaCl, this membrane rejected 90% of the Cl^- at a flux of 114 gfd. The results of a 185-hour run with Coalinga water are given in Table 3.74. During the course of this run, the feed was concentrated by discarding product, and the value in the "Nominal Concentration" column indicates the feed concentration relative to the nominal concentration (IX) of Coalinga water. Since the solubility of some of the components was exceeded at high concentration levels, the nominal concentration and the actual concentration during the run were not necessarily the same.

Fluxes remained reasonably high until the pressure was reduced to about 200 psig late in the run.

3.3.1.1.6. Effect of Simulated Pretreatment. The vitiating effect of divalent cations on dynamically formed Zr(IV)-PAA membranes has been well documented. All natural brackish waters of interest contain appreciable concentrations of divalent cations (see, for example, Table 3.68), which cause loss of flux and rejection when used with Zr(IV)-PAA membranes. The possibility exists of using cross-flow filtration (Ref. 5) following chemical treatment to effect removal of divalent cations as well as suspended solids. We made a run to determine the differences in hyperfilterability between Coalinga water with and without divalent cations. We simulated a pretreated Coalinga water by replacing Ca(II) and Mg(II) by equivalent amounts of sodium ion, and tested it, as well as the normal simulated water, with some membranes formed on Acropor and Millipore supports. The results are given in Table 3.75. Both fluxes and rejections are appreciably higher when divalent cations are absent, and the rate of flux decline is considerably lower with the simulated pretreated water.

TABLE 3.74
HYPERFILTRATION OF COALINGA WATER BY DUAL-LAYER MEMBRANES FORMED ON INSIDE OF 7-CHANNEL SELAS TUBE
(17.5 fps, 28°C)

<u>Time (hrs)</u>	<u>Nominal Conc.</u>	<u>Pressure (psig)</u>	<u>Flux (gfd)</u>	<u>R_{obs} (%)</u>			
				<u>Cond.</u>	<u>Cl⁻</u>	<u>Ca(II) + Mg(II)</u>	<u>Total Cation</u>
1	1X	500	51	72	65	91	74
2	2X	500	49	62	62	90	73
3	3X	500	46	59	62	78	72
4	4X	500	46	60	61	78	71
5	5X	500	46	61	59	78	70
70	5X	500	46	--	56	79	--
99	5X	500	47	66	56	79	--
135	5X	500	46	70	61	82	80
139	5X	200	17	61	39	81	69
160	5X	200	19	66	46	84	75
185	5X	200	19	66	45	84	70

TABLE 3.75
HYPERFILTRATION OF COALINGA WATER, WITH AND
WITHOUT DIVALENT CATIONS, BY Zr(IV)-PAA MEMBRANES
(950 psig, 25°C, pH ~8)

Divalent Cations	Support	Velocity (fps)	Flux (gfd)	Observed Rejection (%)			
				Cond.	Total Cation	Ca(II)+Mg(II)	Cl ⁻
Yes	0.22-μ Millipore	35	20-17*	96	--	--	--
	0.45-μ Acropor	35	30-25*	92	--	--	--
	0.45-μ Acropor	45	40-33*	92	--	--	--
No	0.22-μ Millipore	35	48-47*	98	--	--	--
	0.45-μ Acropor	35	52-54*	98	98	--	96
	0.45-μ Acropor	45	73-75*	98	--	--	--
Yes**	0.22-μ Millipore	35	19	94	--	--	--
	0.45-μ Acropor	35	27	88	90	97	84
	0.45-μ Acropor	45	39	89	--	--	--

*Initial flux and flux after 15 hours of operation.

**Normal concentrations of Ca(II) and Mg(II) added to solution of preceding run.

3.3.1.1.7. Hyperfiltration With Union Carbide Protomodule. The desalination of simulated Coalinga water with Zr(IV)-PAA membranes formed on 6C carbon tubes in a Union Carbide protomodule (see Section 3.1.2.1.3.3) was somewhat discouraging. Perhaps because the membranes had been used previously for several different tests, the fluxes with Coalinga water were quite low. In the first measurement, taken after 40 minutes operation with the simulated water, the flux was only 13 gfd with a rejection (conductivity) of 77% (950 psig, 25°C). When, within three hours, the flux had fallen to 8 gfd, at 83% rejection, we rinsed out the Coalinga water and washed the system for 70 minutes with 1 M NaOH. After treatment, followed by an acid cycle in the presence of 50 ppm PAA, the flux for a 0.05 M NaCl solution was only 30 gfd with 91% rejection. A subsequent 2-hour base wash followed by another acid cycle resulted in no improvement in hyperfiltration properties.

Coalinga water was again added to the feed tank and the flux remained relatively steady at about 10 gfd at 85-87% rejection over a period of about 18 hours.

3.3.1.1.8. Two-Stage Hyperfiltration. Dual-layer membranes were formed on two 0.22-micron Millipore supports and two 0.45-micron Acropor supports. Simulated Coalinga water was treated by these membranes at 950 psig, 25°C, and 35 fps to about 67% water recovery. The average flux was about 67 gfd and 77 gfd for the Millipore and Acropor supports, respectively, and the composite product, which was saved for a second-stage desalination, was $2.1 \times 10^{-3} \text{ M Cl}^-$, $2.6 \times 10^{-4} \text{ M Mg(II)}$ plus Ca(II), and $5.7 \times 10^{-3} \text{ M}$ total cation.

Another set of dual-layer membranes, this time with Acrysol A-5, rather than A-3, as the PAA, were formed on one 0.22-micron Millipore and one 0.45-micron Acropor support, and the composite product from the run immediately above was tested at 950 psig, 35 fps, and 25°C. Comparative results for the two runs are given in Table 3.76. Fluxes were appreciably higher in the second stage, and rejections were somewhat better. Total dissolved solids were reduced from about 2000 ppm in the original simulated Coalinga water feed to less than 25 ppm in the second stage product. The second stage recovery was not carried beyond zero percent in this experiment, but with the good rejections obtained, operation to high recovery levels would have been feasible. Two-stage hyperfiltration clearly can produce water of adequate quality; whether it would be economical or not at these fluxes would require economic analysis.

3.3.1.1.9. Other Tests. Other experiments on simulated Coalinga water have been discussed previously in this report. Hyperfiltration by Zr(IV)-PAA membranes on machined and as-received 6C carbon tubes is reported in Table 3.7; by membranes formed from unboiled Zr(IV) and PAA in Table 3.20; by membranes formed from more dilute Zr(IV) solutions and PAA in Table 3.27; by dual-layer membranes formed at 600 psig in Table 3.41; by dual-layer membranes formed at 55-60°C in Table 3.42; and as a function of circulation velocity in Table 2, Section 2.

3.3.1.2. Roswell Water. The first opportunity to field test dynamic membranes in the desalination of brackish waters came through an OSW Membrane Division program, under D. G. Thomas of the ORNL Reactor Division. A 1000 gpd demonstration plant was designed and built at ORNL and tested at the OSW Roswell, New Mexico, test facility (see Ref. 7). In support of this

TABLE 3.76
TWO-STAGE HYPERFILTRATION OF SYNTHETIC COALINGA WATER BY Zr(IV)-PAA MEMBRANES
(950 psig, 35 fps, 25°C)

Support	Average Flux ^a Stage 1	Flux ^a Stage 2	R _{obs} ^b (%)	R _{obs} (%) Cl ⁻		R _{obs} (%) Mg(II)+Ca(II)		R _{obs} (%) Total Cation	
				Stage 1 ^c	Stage 2	Stage 1 ^c	Stage 2	Stage 1 ^c	Stage 2
0.22-μ Millipore	67	98	95	94	98	>99	>99	95	99
" "		101	94	90	97	99	>99	95	99
0.45-μ Acropor AN	77	127	93	88	97	>99	>99	94	98
" "		125	92	87	96	99	>99	93	98

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(a) Fluxes in gfd.

(b) By conductivity.

(c) The consolidated product from Stage 1, which was the feed for Stage 2, was 2.1×10^{-3} M Cl⁻, 2.6×10^{-4} M Mg(II) + Ca(II), and 5.7×10^{-3} M total cation.

effort, we tested compositions similar to the feed water at the Roswell station in a number of experiments during this biennium. The total dissolved solids in ppm for Roswell water are about the same as with Coalinga water, but the molarity of $\text{Ca(II)} + \text{Mg(II)}$ is about 1.5 times higher in Roswell, and sulfate is about half as high. Roswell water has, therefore, a less favorable composition for Zr(IV) -PAA membranes than does Coalinga.

3.3.1.2.1. Initial Test. Zr(IV) -PAA membranes were formed at 950 psig and 25°C on 0.22- μ Millipore, 0.45- μ Acropor AN, and 6C carbon tube supports at 35 fps and on a 6C carbon tube at 20 fps for testing with Roswell water. Two membrane regenerations were carried out during the course of the test. Results with 0.05 M NaCl before exposure to Roswell water indicated that the membranes on the Millipore and Acropor supports were satisfactory, with rejections of 97 and 94%, respectively. The membrane on the Millipore support gave the best rejections with Roswell water, though the fluxes were disappointing. The results for the run are given in Table 3.77.

The results for the 20 fps 6C carbon tube were similar to those for the one with the faster circulation velocity, and they are not included in the table. Regeneration by a one-hour wash with 1 M solution of NaOH , followed by an acid cycle in the presence of 25 ppm PAA caused a large increase in flux with no sacrifice in rejection, except for the carbon tubes. Increasing the temperature to 55°C caused a further increase in flux, but some loss in rejection. The membrane on the Acropor support was apparently damaged during this excursion to higher temperatures and its performance deteriorated considerably. A second regeneration with 1 M NaOH , this time followed by a re-formation of both layers of the dual-layer membrane, resulted in quite low fluxes, and after a brief evaluation at 57°C , the run was discontinued.

3.3.1.2.2. Hyperfiltration After Pre-Treatment. Deleterious effects of divalent cations on performance of Zr(IV) -PAA membranes in hyperfiltration has been amply documented in this report. Although sensitivity to polyvalent counterions is not as great as with many ion-exchange membranes, benefits from the removal of Ca(II) and Mg(II) , the most ubiquitous in natural waters, is of obvious interest.

TABLE 3.77
HYPERFILTRATION OF ROSWELL WATER BY DYNAMIC DUAL-LAYER MEMBRANES
(950 psig, 35 fps, pH 7.2)

Time*	Temp. (°C)	Support**	Flux (gfd)	R _{obs} (%)		
				Cl ⁻	Ca(II) + Mg(II)	Total Cation
0.5	25	0.22-μ MP	48	87	95	89
		0.45-μ AP	70	65	82	70
		6C carbon	32	56	72	60
14.5	25	0.22-μ MP	36	91	98	89
		0.45-μ AP	54	70	89	76
		6C carbon	20	63	77	65
Regeneration (1 hour 1 <u>M</u> NaOH) with new PAA layer formation.						
1.5	25	0.22-μ MP	73	86	97	89
		0.45-μ AP	79	74	91	81
		6C carbon	47	52	62	58
6.3	55	0.22-μ MP	120	78	93	83
		0.45-μ AP	485	--	--	--
		6C carbon	79	45	59	49
Regeneration (1.3 hours 1 <u>M</u> NaOH) with new dual-layer formation.						
2.0	25	0.22-μ MP	38	78	93	83
		0.45-μ AP	56	--	--	75
		6C carbon	28	65	82	71
5.5	57	0.22-μ AP	71	72	90	78
		0.45-μ AP	128	--	--	70
		6C carbon	48	60	78	66

*Time in hours from each addition of Roswell water.

**MP = Millipore; AP = Acropor AN; carbon = ground carbon tube.

With this in mind, we studied the hyperfiltration of Roswell water with pretreatment to remove varying amounts of Ca(II) and Mg(II), and compared the results with those from untreated water. K. A. Kraus and F. Nelson of the ORNL Chemistry Division and an MIT Practice School team consisting of S. D. Harms and W. D. Franklin cooperated in this study. J. T. Day was the Director and S. Amin the Assistant Director of the Practice School during this period.

3.3.1.2.2.1. Initial Test. Simulated Roswell water was treated with carbonate, and NaOH was added to bring the pH to about 11.5. About 10% excess carbonate was used, and, at this pH, both CaCO_3 and $\text{Mg}(\text{OH})_2$ are essentially insoluble. The resulting slurry was then clarified by using a cross-flow filter cell designed by Nelson and Kraus. This cell employed a 120-mesh stainless steel screen on a rotating drum as the filter element, and an asbestos filter aid was used to provide a tighter filter. The filtrate from the cross-flow process contained about $5.4 \times 10^{-5} \text{ M}$ Ca(II) plus Mg(II), corresponding to about 99% removal. Concentrations of other components remained essentially unchanged.

The product from the filter cell was treated by hyperfiltration through Zr(IV)-PAA membranes on three different supports. Untreated Roswell water was also run to provide a comparison. The results, including a preliminary 97-hour run with an NaCl feed, are listed in Table 3.78. Chloride rejections were very close to the rejections determined by conductivity measurements, listed in the table, while rejections of total cations ran from one to four percent higher.

When the pretreated Roswell water was introduced to the loop at about 97 hours, fluxes decreased on the average about 10%, while rejections changed by up to a few percent in each direction. Changes in the velocity of flow past the membranes, made at about 100 and again at about 121 hours had little systematic effect on the hyperfiltration results. However, changing from pretreated to untreated Roswell water resulted in drastically lowering both fluxes and rejections. This effect is at least partially reversible, as indicated by the improvement when 0.05 M NaCl replaced the Roswell water in the test loop at 147 hours.

TABLE 3.78
INITIAL TEST OF HYPERFILTRATION OF ROSWELL WATER WITH AND WITHOUT PRETREATMENT^a
(1000 psig, 25°C, pH 7.5)

Time ^b	Feed	0.22-μ Millipore				0.45-μ Acropor				6C carbon	
		15 fps		35 fps		15 fps		35 fps		33 fps	
		Flux (gfd)	R _{obs} (%)	Flux (gfd)	R _{obs} (%)	Flux (gfd)	R _{obs} (%)	Flux (gfd)	R _{obs} (%)	Flux (gfd)	R _{obs} (%)
0.5	0.05 M NaCl	101	87	128	91	108	83	150	93	20	82
24.0	0.05 <u>M</u> NaCl	105	88	135	91	114	84	163	92	21	82
96.0	0.05 <u>M</u> NaCl	96	87	126	91	100	83	147	92	23	81
98.0	Pretr. Roswell	105	84	105	93	93	83	118	94	20	88
Velocities changed to:		<u>35 fps</u>		<u>15 fps</u>		<u>35 fps</u>		<u>15 fps</u>		<u>14 fps</u>	
103	Pretr. Roswell	113	87	113	92	91	86	124	94	16	85
120	Pretr. Roswell	116	86	114	93	91	86	125	94	22	86
Velocities changed to:		<u>15 fps</u>		<u>35 fps</u>		<u>15 fps</u>		<u>35 fps</u>		<u>33 fps</u>	
121	Pretr. Roswell	120	83	115	94	93	83	122	94	20	86
122	Roswell	61	61	80	63	75	55	116	69	37	32
144	Roswell	47	70	58	71	55	67	75	75	24	42
147	0.05 <u>M</u> NaCl	93	82	93	92	85	82	120	91	16	73

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(a) Removal of 99.1% of the Ca(II) + Mg(II) by precipitation and cross-flow filtration.

(b) Time in hours from completion of membrane formation.

Performance did not deteriorate during an overnight run with pretreated Roswell water (98 hours through 121 hours), but the fluxes decreased markedly during an overnight run with the untreated water (122 hours through 144 hours).

Performance on the carbon tube support was greatly inferior to that of the other supports tested and under all conditions.

3.3.1.2.2.2. Effect of Extent of Removal of Divalent Cations.⁶

The MIT Practice School team did a systematic study of the extent to which Ca(II) and Mg(II) needed to be removed in order to achieve satisfactory hyperfiltration results in a second stage. After adding enough carbonate, in addition to that normally in the water, to precipitate a given fraction of the Ca(II), they increased the pH of the solution to the point at which CaCO_3 precipitated, and then filtered the resulting slurry by cross-flow filtration (see Refs. 7 and 26). If Mg(II) was to be removed also, the pH was raised above 11 by addition of NaOH, and the Mg(OH)_2 floc was removed along with the precipitated CaCO_3 by cross-flow filtration.

Firehose jackets (1 in. dia.) were used as cross-flow filtering surfaces, with both inside and outside flow configurations. Little difference was noted in the performance of the different configurations, and most of the product collected in the course of the experiments was obtained using flow inside the pressure jacket. Typical axial velocities were about 8 fps, and the pressures ranged from 26-30 psig. No filter aids were used.

For most cross-flow runs, fluxes decreased with time, but the smallest fluxes were in excess of 100 gfd. The results of the cross-flow filtration tests are listed in Table 3.79. The products from these tests were used in the hyperfiltration tests described in the next sections.

Zr(IV)-PAA membranes were formed in the standard way on 0.22-micron Millipore and 0.27-micron Sela ceramic tube supports at 1000 psig, 25°C, and about 35 fps. With a 0.05 M NaCl feed, the Millipore support had a R_{obs} of 93% at 103 gfd, and the Sela rejected 92% at 130 gfd. These two membranes were subsequently used for all of the tests to be described in this section. The products from the cross-flow runs described above were neutralized to pH 7.5 to 8 before each in turn was added to the hyperfiltration loop. The results of the tests, including one in which

TABLE 3.79
CROSS-FLOW FILTRATION OF ROSWELL WATER CHEMICALLY TREATED
TO REDUCE CONCENTRATIONS OF DIVALENT CATIONS
(25°C, 8 fps, fire hose jackets)

<u>Pressure (psig)</u>	<u>pH</u>	<u>Chemical^a Addition</u>	<u>Flux (gfd)</u>	<u>Ca(II) + Mg(II) Removal (%)</u>
26	11.5 - ~10 ^b	110	210 - 215	99
28	11.2	110	135 - 110	98
28	10.5	90	250 - 140	91
30	10.4 - 10.0	88	460 - 320	84
28	9.5 - 9.2	66	~700	68

^aPercent of stoichiometric amount needed to precipitate all Ca(II) and Mg(II).

^bNo pH control during this cross-flow run.

the feed consisted of untreated Roswell water and another in which it consisted of Roswell water with equivalent amounts of sodium ion replacing all Ca(II) and Mg(II) (corresponding to 100% pretreatment), are summarized in Table 3.80. The run number indicates the chronological order of the experiments. All hyperfiltrations were carried out at 15 fps and 25°C. Between different pretreated waters, the rejection and flux with 0.05 M NaCl were determined. In each subsequent run with the pretreated Roswell water, the "initial" flux was determined by extrapolating the log flux versus log time plot back to 0.1 hour. Normalized fluxes were calculated by multiplying the "initial" flux by a factor: $100/J_{\text{NaCl}}$, where J_{NaCl} was the water flux for the 0.05 M NaCl test just preceding the run of interest. Thus, the "normalized" flux is the flux which would be realized for a given pretreated water through a membrane capable of 100 gfd for 0.05 M NaCl. This allows a more meaningful determination of the effects of the pretreatments, because it tends to minimize factors due to membrane aging.

Most of the runs of Table 3.80 were followed for only 20 hours or so, and there was considerable scatter in the data. Consequently, the flux decline parameters, b , must be considered to be very rough values. It is apparent from the table that both fluxes and rejections improve as the degree of pretreatment increases. There is an appreciable increase

TABLE 3.80
HYPERFILTRATION OF ROSWELL WATER PRETREATED^a TO REDUCE Mg(II) AND Ca(II) CONCENTRATIONS
(950 psig, 15 fps, 25°C, pH 7.5-8)

Run	Pretreatment		Flux (gfd)		<u>b^d</u>	<u>R_{obs} (%)</u>		
	% Removal	<u>M</u> (Ca(II) + Mg(II))	<u>Initial^b</u>	<u>Normalized^c</u>		<u>Cond.</u>	<u>Cl⁻</u>	<u>Tot. Cation</u>
0.27-micron Selas support:								
2 ^e	100	0.0	92	110	-----	93-95	-----	----
1	99	0.81 x 10 ⁻⁴	134	103	0.094	93-96	95	96-97
5	98	1.41 "	86	86	0.044	93	91	95-96
4	91	5.5 "	80	93	0.037	90-91	89-90	91-92
3	84	9.95 "	72	86	0.070	89-91	88-89	91-93
6	68	19.7 "	80	92	0.123	84-86	77-85	85-89
7	0	60.9 "	78	98	0.053	71-76	76	77
0.22-micron Millipore support:								
2 ^e	100	0.0	92	114	-----	92-96	-----	-----
1	99	0.81 x 10 ⁻⁴	125	121	0.115	94-96	95-97	92-97
5	98	1.41 "	90	95	0.081	94	92-93	93-94
4	91	5.4 "	77	93	0.065	90-92	90-92	91-93
3	84	9.95 "	58	73	0.047	91-92	91	93-94
6	68	19.7 "	65	79	0.093	86	84-85	89
7	0	60.9 "	61	85	0.041	75	88	76

(a) Pretreatment consisted of chemical precipitation followed by cross-flow filtration.

(b) Extrapolated to 0.1 hours after addition of Roswell water in each run.

(c) Adjusted to compensate for changes in flux due to membrane aging, see text.

(d) Flux decline parameter, b, is the negative of the slope of the log flux versus log time plot.

(e) No cross-flow pretreatment. Simulated Roswell water with equivalent amounts of Na⁺ replacing both Ca(II) and Mg(II) was used as feed. This run, of less than one hour duration, was made at 35 fps rather than 15 fps.

in flux between the 98 and the 99% pretreated samples. Rejections are less sensitive to small increases in divalent cation concentrations at the more dilute end of the range studied.

A final series of tests was made with the same membranes which gave the results recorded in Table 3.80. The loop was rinsed thoroughly with distilled water and a synthetic Roswell water was added in which, like the "100% pretreated" water of Table 3.80, all Ca(II) and Mg(II) had been replaced by equivalent amounts of Na(I). Fluxes and rejections were measured and then just 0.1% of the nominal Ca(II) concentration of Roswell water was added. Fluxes and rejections were again measured and another small increment of Ca(II) was added. This process was repeated up to 5% of the normal amount, and the data are tabulated in Table 3.81. Rejections seem to be insensitive to small concentrations of divalent cations, but fluxes appear to decrease when concentrations were as low as 10^{-5} M.

An overnight run (~14 hours) at a Ca(II) concentration of about 3×10^{-4} M resulted in further decreases in flux, but with a slight increase in rejection. A one-hour rinse with distilled water resulted, when Roswell water without Ca(II) and Mg(II) was again tested, in regained fluxes and good rejections. When the membranes were cycled through acidic pH's with 25 ppm PAA in 0.05 M NaCl, rejections were increased and fluxes lowered.

3.3.1.2.2.3. Effects of pH and Velocity Changes. Because of the caustic added during the cross-flow treatment, the product water was quite basic and had to be neutralized before the hyperfiltration membranes were exposed to it. Since the carbonate is essentially all removed, the amount of acid required for neutralization is small. To determine the optimum pH for operation with treated water, the MIT team did a pH scan while running the hyperfiltration tests on the 99%-treated water of Table 3.80. They found that rejections were maximum around pH 8, somewhat lower at pH 9, the highest pH they tested, and considerably lower at pH 6. Fluxes tended to increase as pH was lowered, the increase becoming very rapid at the lower pH values. Both rejection and pH effects are consistent with results we have obtained previously.

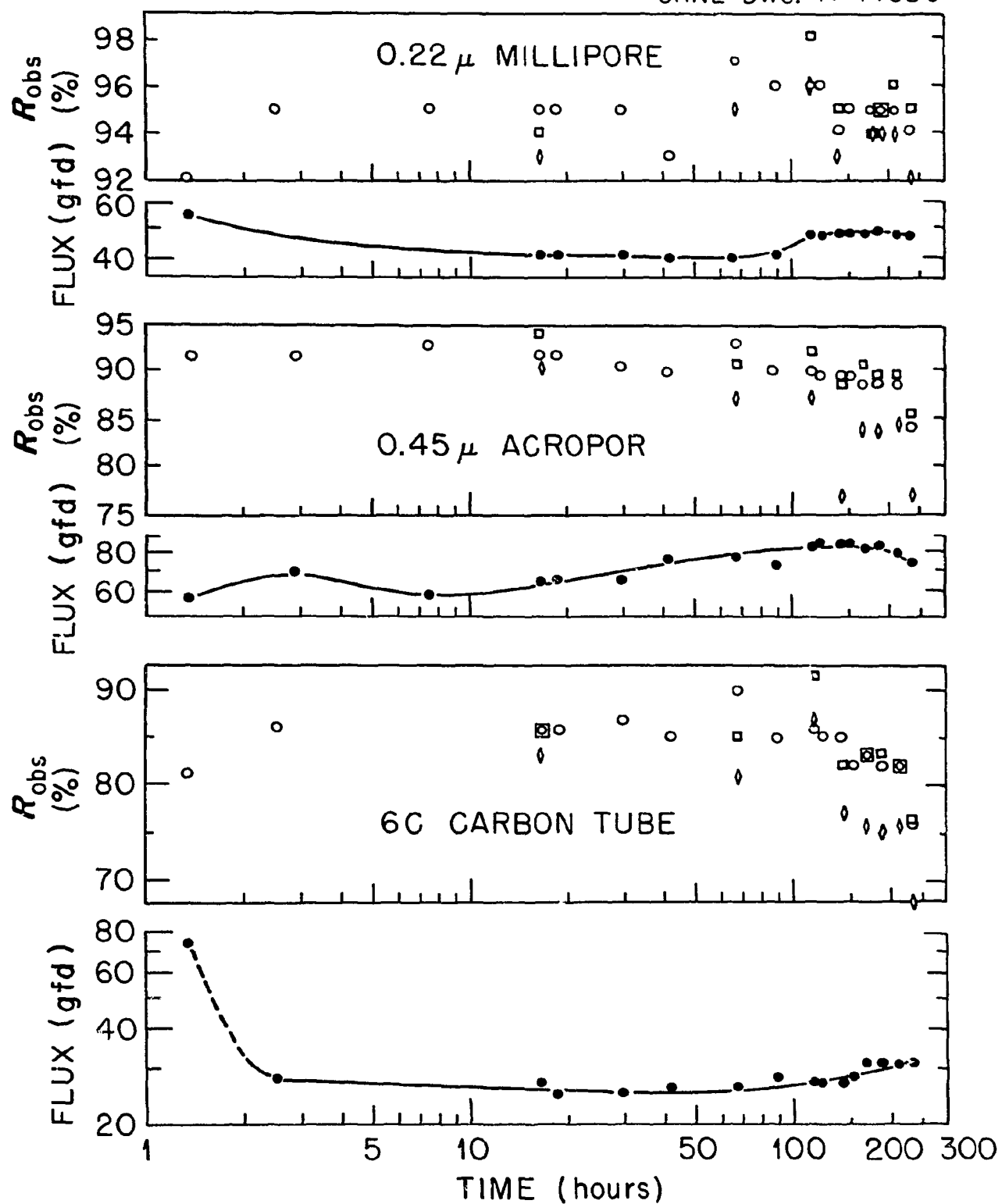
TABLE 3.81
HYPERFILTRATION OF A SYNTHETIC ROSWELL WATER MADE UP WITH LESS
THAN THE USUAL CONCENTRATIONS OF Ca(II) AND Mg(II)
(1000 psig, 15 fps, 25°C, pH 7.5)

[Ca(II) + Mg(II)]		0.22-micron Millipore		0.27-micron SelaS	
% Nominal	M	Flux (gfd)	R _{obs} (%)	Flux (gfd)	R _{obs} (%)
0.0	0.0	98	93	100	93
0.1	6.09×10^{-6}	96	93	99	93
0.2	1.2×10^{-5}	93	93	95	93
0.5	3.05×10^{-5}	85	93	92	93
1.0	6.09×10^{-5}	79	93	86	92
2.0	1.2×10^{-4}	73	93	80	92
5.0	3.05×10^{-4}	61	92	72	90
Overnight run (~14 hours):					
5.0	3.05×10^{-4}	55	93	69	91
One-hour water rinse:					
0.0	0.0	100	92	102	93
Water rinse, then acid cycle with PAA (25 ppm) in 0.05 M NaCl at 35 fps:					
0.0	0.0	61	97	77	96

3.3.1.2.2.4. Ten-Day Run. The MIT team monitored an extended run on the 99% pretreated water from the cross-flow filtration experiments. They used dual-layer membranes that had been formed at 35 fps on a 0.22-micron Millipore and 0.45-micron Acropor, and a surface-ground 6C carbon tube. The experiment was run at about 980 psig, 28°C, and 15 fps circulation velocity. The cross-flow product was neutralized to pH 8 before the hyperfiltration stage. Rejections were monitored routinely by conductivity measurements, and selected samples were analyzed for chloride and total cation concentrations. The results for the 235-hour run are shown in Fig. 3.37.

The fluxes, for some reason, did not appear to follow the linear log-log decline normally observed for similar runs, and were lower initially than those in most of the runs described in the previous sections.

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HYPERFILTRATION OF PRE-TREATED ROSWELL
WATER (98.7% REMOVAL OF $\text{Ca}(\text{II}) + \text{Mg}(\text{II})$)
BY DUAL-LAYER MEMBRANES
(980 psig, 28°C, 15 fps, pH ~8)

◦ Conductivity ◊ Chloride ◻ Total Cation

Fig. 3.37

The increase in fluxes after 100 hours operation may have been due to a slight deterioration in the membranes, for they were accompanied by slight decreases in rejection. The final points (~235 hours) were taken after some product had been discarded to 60% water recovery, and a corresponding increase in feed concentration.

At about 120 hours, the volume of the feed was increased by about 40% through the addition of more of the cross-flow product. This was done to determine whether or not any fouling component of the feed may have been depleted from the original charge. The lack of any significant changes in either rejections or flux led us to believe that the behavior observed is probably representative of what would happen if the feed were to be continually replenished.

The membrane on the 0.22-micron Millipore support gave satisfactory results throughout the run. Fluxes varied from a low of about 40 gfd to about 47 at the end of the run. All rejections measured were 92% or better, with most clustered around 95%. Fluxes through the Acropor membrane were higher (58 to 85 gfd) but rejections were somewhat lower. Performance by the membrane on the carbon tube was inferior to the others in both fluxes and rejections.

3.3.1.2.3. Pre-Treatment with Dynamic Membranes at Low Pressure.

Dynamic membranes might conceivably prove valuable as low pressure pretreatment membranes to remove constituents that foul commercially available RO systems. Example of such constituents are suspended solids, organics, and multi-valent cations that form insoluble carbonates, sulfates, or oxides, e.g., Ca(II), Mg(II), and Fe(III). We report a test in which Zr(IV)-PAA membranes were formed on 6C carbon tube, on 0.45-micron Acropor, and on 0.45-micron Millipore at 35 fps, and on a 0.27-micron Sela ceramic filter element, outside pressurization, at 44.5 fps. Formation pressure was 200 psig and the temperature was 25°C. These membranes were tested with simulated Roswell water, and the results are given in Table 3.82. The large increases in fluxes and decreases in rejections for the membranes on the carbon and ceramic tubes when the pressure was increased indicated that stable membranes had not been formed upon them at 200 psig. The rejection of Ca(II) plus Mg(II) at 200 psig just before the pressure was increased was 20% by the

TABLE 3.82
TEST OF Zr(IV)-PAA MEMBRANES FORMED AT 200 PSIG AS PRETREATMENT
MEMBRANES FOR THE SOFTENING OF ROSWELL WATER
(25°C, pH 8.2, R_{obs} by conductivity)

Time (hr:min)	6C Carbon (15 fps)		0.45- μ Millipore (17 fps)		0.45- μ Acropor (17 fps)		0.27- μ Selas (22 fps)	
	Flux (gfd)	R_{obs} (%)	Flux (gfd)	R_{obs} (%)	Flux (gfd)	R_{obs} (%)	Flux (gfd)	R_{obs} (%)
Pressure 200 psig:								
1:00	30	16	43	23	56	22	30	23
2:30	27	15	37	24	51	23	27	20
20:45	19	17	33	26	47	24	35	16
21:00 Pressure changed to 950 psig:								
22:00	950	2	98	53	350	24	280	8
23:30	710	4	83	56	300	27	270	12

carbon tube, 34% by the Millipore, 29% by the Acropor, and 25% by the Selas tube. The results of this preliminary test are not encouraging with regard to pretreatment by low-pressure operation with Zr(IV)-PAA membranes.

3.3.1.2.4. Effect of Divalent Cations. In Section 3.3.1.1.6, we discussed the hyperfiltration of simulated pretreated Coalinga water by Zr(IV)-PAA membranes on some film-wrapped supports. We used the same membranes to test a simulated Roswell water, also with and without divalent cations. The results are given in Table 3.83. As with the Coalinga study mentioned above, both fluxes and rejections decreased appreciably when the divalent cations were added.

3.3.1.2.5. Effect of $SO_4^{=}$. We mentioned in Section 3.1.3.3.5 that hyperfiltration by Zr(IV)-PAA membranes is usually more successful for Coalinga water than it is for Roswell, and that these waters differ mainly in the ratio of sulfate ion to divalent cations. We consequently looked at Roswell water with and without sulfate ions to see if their presence or absence made a detectable difference in the filterability properties. The results are given in Table 3.84. Before the modified Roswell water was added, the membrane on the carbon tube, with 0.05 M

TABLE 3.83
HYPERFILTRATION OF ROSWELL WATER, WITH AND WITHOUT
Divalent CATIONS, BY Zr(IV)-PAA MEMBRANES
(950 psig, 25°C, pH 8-8.1)

Divalent Cations	Support	Velocity (fps)	Flux (gfd)	Cond.	Observed Rejection (%)		
					Total Cation	Ca(II)+ Mg(II)	Cl ⁻
NO	0.22-MP*	35	50	97	--	--	--
	0.45-AP*	35	54	96	97	--	96
	0.45-AP	45	76	96	--	--	--
YES	0.22-MP	35	18	89	--	--	--
	0.45-AP	35	28	81	84	94	79
	0.45-AP	45	39	81	--	--	--

*MP is Millipore, AP is Acropor

NaCl, gave 90% rejection at 67 gfd; that on the Ferro, 82% at 92 gfd; that on the Millipore, 94% at 78 gfd; and that on the Acropor, 90% at 120 gfd.

The results indicate appreciable flux and rejection losses occur when Roswell water replaces 0.05 M NaCl, and that the presence or absence of 0.004 M sulfate has little effect on the hyperfiltration properties.

At the end of the run of Table 3.84, we rinsed the membranes for 30 minutes with water, one hour with 1 M NaCl, and about two more hours with water. With 0.05 M NaCl, fluxes were restored to the 60 to 80 gfd level, while rejections exceeded 90% on all membranes except that on the Ferro tube, which had 80%.

3.3.1.2.6. Effect of Carbonate. During the operation of the Roswell test loop,⁷ some difficulties arose that were tentatively attributed to a temporary inadvertent increase in carbonate levels in the feed. We checked the effect of higher carbonate levels in a laboratory run which is summarized in Table 3.85. When the carbonate level was increased from 0.004 to 0.14 M at 21:12, there was little change in the hyperfiltration properties of the membranes. A 30-minute wash with 0.1 M bicarbonate, adjusted to pH 10, caused an increase in permeability in all membranes, but resulted in lower rejections with all membranes but the Acropor.

TABLE 3.84
HYPERFILTRATION OF SIMULATED ROSWELL WATER, WITH AND WITHOUT
 $\text{SO}_4^{=}$, BY Zr(IV)-PAA MEMBRANES
(950 psig, 15 fps, 25°C, pH 7.5-8)

<u>Time (hr:min)</u>	<u>Support</u>	<u>Flux (gfd)</u>	<u>R_{obs} (%) Cond.</u>
0:00	Added Roswell water without sulfate ion:		
1:00	6C carbon tube	13	77
	Coated Ferro 600p ^a	15	83
	0.05-μ Millipore	15	83
	0.45-μ Acropor	39	75
3:00	6C carbon tube	11	79
	Coated Ferro 600p	13	87
	0.05-μ Millipore	14	86
	0.45-μ Acropor	33	77
18:30	6C carbon tube	10	81
	Coated Ferro 600p	12	85
	0.05-μ Millipore	12	88
	0.45-μ Acropor	24	79
18:40	Added 0.0041 M Na_2SO_4 :		
20:00	6C carbon tube	10	83
	Coated Ferro 600p	13	80
	0.05-μ Millipore	12	89
	0.45-μ Acropor	23	81
Rinsed with water, then one hour with 1 M NaCl, then 1/2 hour with water.			
0:00	Added Roswell water with sulfate included:		
1:00	6C carbon tube	13	80
	Coated Ferro 600p	14	66
	0.05-μ Millipore	15	85
	0.45-μ Acropor	33	76
2:30	6C carbon tube	13	82
	Coated Ferro 600p	14	76
	0.05-μ Millipore	13	87
	0.45-μ Acropor	32	78
18:00	6C carbon tube	8	86
	Coated Ferro 600p	12	92
	0.05-μ Millipore	12	91
	0.45-μ Acropor	27	80

(a) See reference 7 in text.

TABLE 3.85

TEST OF THE EFFECT OF HIGH CARBONATE CONCENTRATIONS ON THE
HYPERFILTRATION OF SIMULATED ROSWELL WATER BY Zr(IV)-PAA MEMBRANES

(950 psig, 25°C, 15 fps, pH 7.6-8.2)

Time (hr:min)	6C carbon		Ferro 600p*		0.05-μ Millipore		0.45-μ Acropor	
	Flux (gfd)	R_{obs} (%)	Flux (gfd)	R_{obs} (%)	Flux (gfd)	R_{obs} (%)	Flux (gfd)	R_{obs} (%)
0:30	42	81	40	67	34	89	51	89
2:00	32	85	30	75	30	92	45	92
4:00	30	86	30	78	28	93	43	92
20:30	23	89	22	84	22	95	35	93
21:15	Increased NaHCO_3 concentration from 0.004 to 0.014 M:							
21:50	22	89	21	85	21	94	32	92
22:30	21	89	21	84	20	95	30	92
24:00	21	90	20	86	20	95	30	92
24:30	Rinsed 30 minutes with water, 30 minutes with 0.1 M Na_2CO_3 adjusted to pH 10, and 30 minutes with water.							
26:00	Added fresh Roswell water:							
27:30	32	80	27	70	34	81	37	92
42:30	27	84	21	77	28	84	35	92
49:30	27	85	21	79	27	85	35	91
65:00	27	85	20	79	27	85	34	90

*Modified with ZrO_2 coating.

3.3.1.2.7. Effect of NaCl Concentration During Membrane Formation On The Hyperfiltration of Roswell Water. In Section 3.1.2.13.1, we described the formation of a set of membranes from stronger NaCl solutions than the 0.05 M solution we normally use. We thought it possible that higher salt concentrations during formation might result in membranes less susceptible to degradation by divalent cations. The results of tests of these membrane sets with simulated Roswell water, as well as some others in one case, are given below.

Table 3.86 gives the results for the hyperfiltration of NaCl, simulated Colorado River Water, and simulated Roswell water by a set of membranes in which both the hydrous Zr(IV) oxide sublayer and the PAA top layer were formed from 1 M NaCl (Run No. 5, Table 3.45). Rejections, for

TABLE 3.86

HYPERFILTRATION OF SIMULATED NATURAL WATERS AND NaCl SOLUTIONS
BY Zr(IV)-PAA MEMBRANES FORMED FROM 1 M NaCl

(Run No. 5 from Table 3.45, 950 psig, 25°C, ~15 fps, pH 7-8)

Time (hr:min)	Feed Solution	Support	Flux (gfd)	Observed Rejection (%)			
				Cond.	Total Cation	Ca(II)+ Mg(II)	Cl ⁻
1:00	0.05 M NaCl	6C carbon tube	30	95	--	--	--
		Coated Ferro 600p	30	96	--	--	--
		0.05-μ Millipore	30	98	--	--	--
		0.45-μ Acropor	44	80	--	--	--
2:00	Colorado River	6C carbon tube	20	88	--	--	--
		Coated Ferro 600p	17	94	--	--	--
		0.05-μ Millipore	17	94	--	--	--
		0.45-μ Acropor	35	58	--	--	--
16:00	Colorado River	6C carbon tube	17	88	88	94	83
		Coated Ferro 600p	13	96	96	99	92
		0.05-μ Millipore	13	96	--	--	--
		0.45-μ Acropor	49	36	--	--	--
17:30	Roswell Water	6C carbon tube	15	84	--	--	--
		Coated Ferro 600p	13	94	--	--	--
		0.05-μ Millipore	13	93	--	--	--
		0.45-μ Acropor	46	44	--	--	--
19:30	Roswell Water	6C carbon tube	14	84	86	90	85
		Coated Ferro 600p	12	94	95	98	94
		0.05-μ Millipore	13	94	--	--	--
		0.45-μ Acropor	46	41	--	--	--
20:15	0.05 M NaCl	6C carbon tube	20	96	--	--	--
		Coated Ferro 600p	16	97	--	--	--
		0.05-μ Millipore	20	98	--	--	--
		0.45-μ Acropor	46	53	--	--	--
34:15	0.05 M NaCl	6C carbon tube	21	95	--	--	--
		Coated Ferro 600p	17	98	--	--	--
		0.05-μ Millipore	20	96	--	--	--
		0.45-μ Acropor	44	53	--	--	--
34:30	Washed membranes for one hour with 1 M NaCl.						
37:00	0.05 M NaCl	6C carbon tube	50	90	--	--	--
		Coated Ferro 600p	38	95	--	--	--
		0.05-μ Millipore	34	96	--	--	--
		0.45-μ Acropor	60	58	--	--	--
38:00	Roswell Water	6C carbon tube	19	77	--	--	--
		Coated Ferro 600p	15	93	--	--	--
		0.05-μ Millipore	16	93	--	--	--
		0.45-μ Acropor	44	35	--	--	--

(continued next page)

TABLE 3.86 (Continued)

Time (hr:min)	Feed Solution	Support	Flux (gfd)	Observed Rejection (%)			
				Cond.	Total Cation	Ca(II)+ Mg(II)	Cl ⁻
54:15	Roswell Water	6C carbon tube	14	79	--	--	--
		Coated Ferro 600p	11	96	--	--	--
		0.05- μ Millipore	13	92	--	--	--
		0.45- μ Acropor	46	29	--	--	--
61:00	Roswell Water	6C carbon tube	13	80	--	--	--
		Coated Ferro 600p	10	96	--	--	--
		0.05- μ Millipore	12	93	--	--	--
		0.45- μ Acropor	47	25	--	--	--

0.05 M NaCl, are high for membranes on all of the supports except the 0.45-micron Acropor, but fluxes are low for all. When Colorado River water was added at 2:00, both fluxes and rejections decreased, although the rejections on the Ferro tube and on the Millipore support remained relatively high. An overnight run with simulated Colorado River water resulted in a further decrease in flux, except with the Acropor-supported membrane, which did not show good properties throughout this run. Rejections changed little during this overnight run.

When Roswell water was exchanged for Colorado River water at 17:30, both rejections and fluxes dropped slightly. When the Roswell water was flushed out and replaced with 0.05 M NaCl at 20:15, the rejections returned to the values originally obtained with NaCl, but fluxes recovered only slightly, even after 14 hours of exposure to the dilute salt solution. However, a one-hour wash with 1 M NaCl restored the fluxes to values higher than those at the beginning of the run. A second exposure to Roswell water (38:00) decreased fluxes by better than a factor of two for the better membranes, and they continued to drop for the remainder of the run.

Rejections by membranes on the Ferro tube and the 0.05-micron Millipore film were high throughout for hyperfiltration by Zr(IV)-PAA membranes of brackish water compositions high in divalent cations, but the fluxes were low. The membrane on the 0.45-micron Acropor deteriorated early in the test. Rejections of divalent cations, of total cations, and of Cl⁻, in those few cases in which analyses were made, were good on the Ferro tube, and perhaps adequate on the carbon tube.

In Tables 3.87 and 3.88, results are given for the hyperfiltration of simulated Roswell water for membranes in which one of the layers was formed from 1 M NaCl, while the other layer was formed from the usual 0.05 M NaCl. Neither were satisfactory: when the PAA layer was formed from 1 M NaCl (Table 3.87), a membrane having very low fluxes was formed; when the sublayer was formed from the more concentrated solution, fluxes were higher, and rejections were poor.

The final run in this series was made from membranes both layers of which had been formed from an intermediate concentration of NaCl, 0.3 M. As indicated by the results in Table 3.89, rejections were poor, and fluxes not favorable.

In all of these cases in which higher NaCl concentrations were used during formation, membranes formed on the Ferro tube and the Millipore wrap were superior to those on the carbon tube and the Acropor wrap, a situation generally not observed, especially insofar as the Acropor wrap is concerned.

TABLE 3.87

HYPERFILTRATION OF ROSWELL WATER WITH Zr(IV)-PAA MEMBRANES
IN WHICH THE SUBLAYER WAS FORMED FROM 0.05 M NaCl AND THE PAA
LAYER WAS FORMED FROM 1 M NaCl

(Run No. 6 of Table 3.45, 950 psig, 25°C, 15 fps)

Time (hr:min)	Support	Flux (gfd)	Observed Rejection (%)			
			Cond.	Total Cation	Ca(II)+ Mg(II)	Cl ⁻
1:30	6C carbon tube	8	85	--	--	--
	Coated Ferro 600p	9	92	--	--	--
	0.05- μ Millipore	7	91	--	--	--
	0.45- μ Acropor	9	86	--	--	--
3:00	6C carbon tube	7	86	88	97	87
	Coated Ferro 600p	7	95	96	99	95
	0.05- μ Millipore	7	92	--	--	--
	0.45- μ Acropor	8	87	--	--	--

TABLE 3.88

HYPERFILTRATION OF ROSWELL WATER WITH Zr(IV)-PAA MEMBRANES
IN WHICH THE SUBLAYER WAS FORMED FROM 1 M NaCl AND THE PAA
LAYER WAS FORMED FROM 0.05 M NaCl

(Run No. 7 of Table 3.45, 950 psig, 25°C, ~15 fps)

Time (hr:min)	Support	Flux (gfd)	R_{obs} (%) Cond.
0:45	6C carbon tube	27	69
	Coated Ferro 600p	27	78
	0.05- μ Millipore	22	88
	0.45- μ Acropor	40	80
2:15	6C carbon tube	24	74
	Coated Ferro 600p	21	86
	0.05- μ Millipore	20	89
	0.45- μ Acropor	35	83
6:00	6C carbon tube	21	77
	Coated Ferro 600p	19	89
	0.05- μ Millipore	17	91
	0.45- μ Acropor	32	84

TABLE 3.89

HYPERFILTRATION OF ROSWELL WATER WITH Zr(IV)-PAA MEMBRANES
FORMED FROM 0.3 M NaCl

(Run No. 8 of Table 3.45, 950 psig, 25°C, ~15 fps)

Time (hr:min)	Support	Flux (gfd)	R_{obs} (%) Cond.
1:15	6C carbon tube	37	56
	Coated Ferro 600p	21	71
	0.05- μ Millipore	21	66
	0.45- μ Acropor	64	50
2:45	6C carbon tube	34	61
	Coated Ferro 600p	20	77
	0.05- μ Millipore	20	69
	0.45- μ Acropor	59	53
18:45	6C carbon tube	23	72
	Coated Ferro 600p	16	85
	0.05- μ Millipore	16	78
	0.45- μ Acropor	42	64

3.3.1.2.8. Other Tests. In Section 3.1.2.9 and Table 3.36, we discussed the hyperfiltration properties with NaCl solutions of a set of membranes in which the sublayer was formed at 30 fps and the PAA layer at 15 fps. Results of a test of these membranes with Roswell water are given in Table 3.90.

Fluxes with these membranes were relatively low even with NaCl after formation, (see Table 3.36) and they became even lower when the Roswell water was added. Rejections, with the exception of that for the membrane on the Celgard film, were relatively good for Roswell water, especially by the membranes on the Ferro tube.

3.3.1.3. Colorado River Water. We discuss several experiments with both nominal and pre-treated Colorado River water in section 3.3.1.8, to follow, and reported some results in Table 3.86 in the preceding section. Here we discuss a preliminary experiment to determine whether or not a pre-treatment step could be avoided by precipitating Ca(II) and Mg(II) in the hyperfiltration feed rather than in a separate step. To a simulated Colorado River water feed, being treated by dual-layer membranes on 7-channel Selas tubes (950 psig, 15 fps), we added an amount of CaO equivalent to the excess of bicarbonate over Ca(II), and raised the pH to 9.6 with NaOH to precipitate the Ca(II) as the carbonate. At this pH, little of the Mg(II) would be precipitated as the hydroxide, but we were prevented from going to higher pH values because of the detrimental effect of high pH on the membranes.

The chemical additions did not prevent flux loss; it decreased rapidly to 23 gfd at 30 minutes, from 94 gfd with 0.05 M NaCl before starting, and was 19 gfd at the end of 22 hours of operation. Rejections were good: 91% by conductivity; 95% for total cation; 97% for Ca(II) and Mg(II), final concentration 8×10^{-5} M; and 90% for chloride. We then added enough EDTA to complex the Mg(II), and fluxes increased slightly to 23 gfd while the rejections remained essentially unchanged. At the end of another 120 hours of operation, the flux was 17 gfd, and the conductivity rejection was 93%.

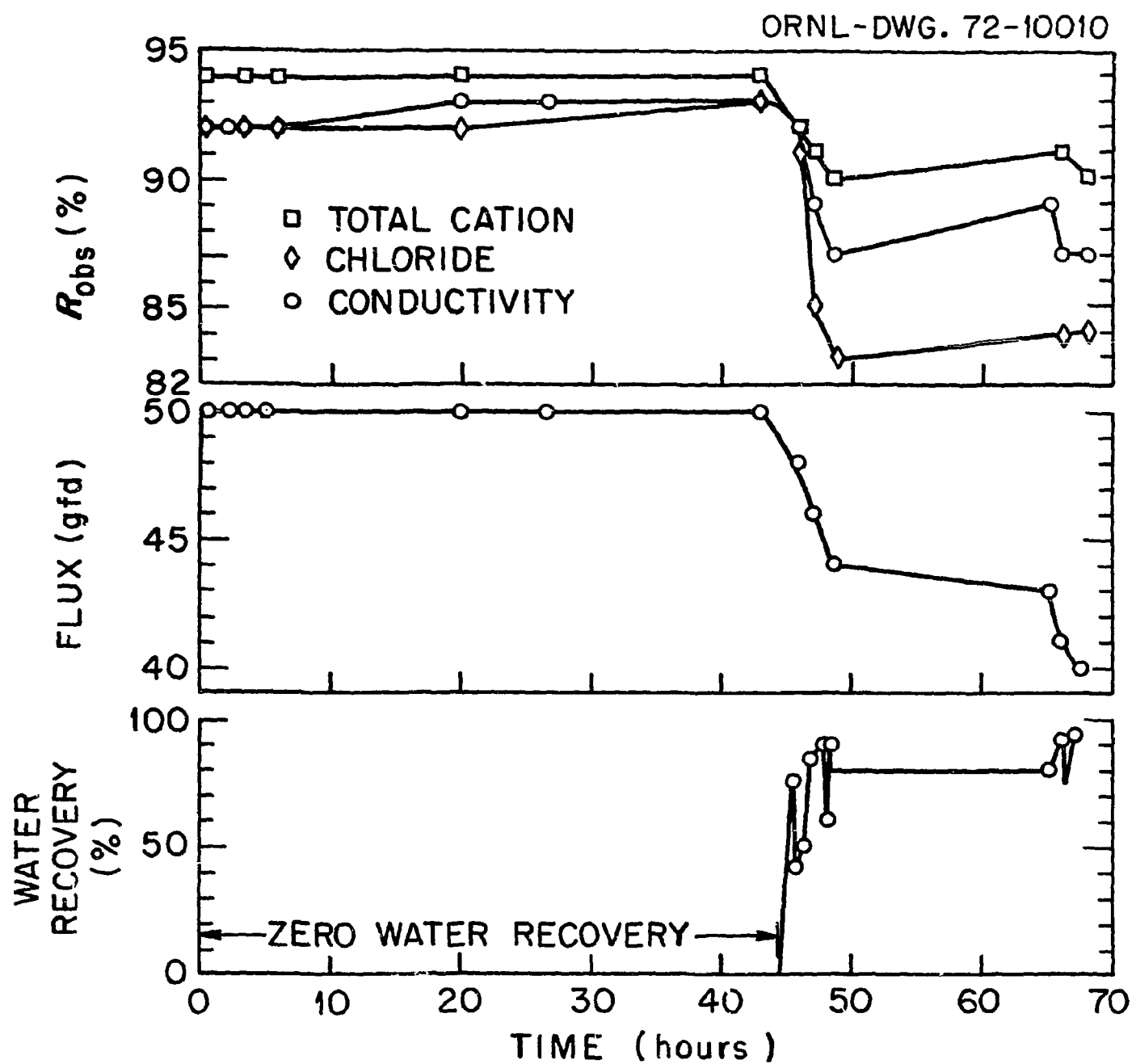
In another experiment, we simulated pretreatment by making up a quantity of Colorado River water, substituting sodium for the divalent cations, and tested this brine with a module, described in Section 3.1.2.1.1.3, containing 31 7-channel Selas tubes. The results, for operation at 850 psig, 17 fps, and 25°C, are shown in Fig. 3.38. The run extended nearly 70 hours,

TABLE 3.90

HYPERFILTRATION OF ROSWELL WATER BY Zr(IV)-PAA MEMBRANES IN
WHICH THE SUBLAYER WAS FORMED AT 30 fps AND THE PAA LAYER AT 15 fps

(Tests run at 950 psig, 15 fps, 25°C, pH 7.6-8)

Time (hr:min)	% Water Recovery	Support	Flux (gfd)	Observed Rejection (%)				
				Cond.	Total Cation	Ca(II)+ Mg(II)	Cl ⁻	SO ₄ ⁼
1:00	0	Celgard 2400W	11	78	--	--	--	--
		0.05-μ Millipore	16	90	--	--	--	--
		0.45-μ Acropor	20	90	--	--	--	--
		Coated Ferro 600p	14	91	--	--	--	--
3:00	0	Celgard 2400W	10	78	--	--	--	--
		0.05-μ Millipore	16	89	--	--	--	--
		0.45-μ Acropor	20	90	--	--	--	--
		Coated Ferro 600p	14	95	97	99.7	96	--
19:00	0	Celgard 2400W	10	72	--	--	--	--
		0.05-μ Millipore	15	91	--	--	--	--
		0.45-μ Acropor	16	90	--	--	--	--
		Coated Ferro 600p	11	97	--	--	--	--
19:10	Rinsed system with distilled water, added fresh simulated Roswell water:							
21:40	0	Celgard 2400W	11	72	--	--	--	--
		0.05-μ Millipore	15	90	--	--	--	--
		0.45-μ Acropor	16	90	--	--	--	--
		Coated Ferro 600p	11	98	--	--	--	--
40:30	0	Celgard 2400W	13	74	--	--	--	--
		0.05-μ Millipore	15	90	--	--	--	--
		0.45-μ Acropor	16	89	--	--	--	--
		Coated Ferro 600p	11	98	--	99.8	98	97
134:00	0	Celgard 2400W	15	59	--	--	--	--
		0.05-μ Millipore	15	92	--	--	--	--
		0.45-μ Acropor	16	89	--	--	--	--
		Coated Ferro 600p	11	98	--	--	--	--
139:10	12	Celgard 2400W	15	81	--	--	--	--
		0.05-μ Millipore	15	93	--	--	--	--
		0.45-μ Acropor	16	85	--	--	--	--
		Coated Ferro 600p	11	98	--	--	--	--
155:40	64	Celgard 2400W	15	71	--	--	--	--
		0.05-μ Millipore	14	91	--	--	--	--
		0.45-μ Acropor	16	84	--	--	--	--
		Coated Ferro 600p	8	98	99	99.9	99	--



HYPERFILTRATION OF SIMULATED PRETREATED
COLORADO RIVER WATER BY Zr(IV)-PAA
MEMBRANES ON 7-CHANNEL SELAS
TUBES IN 31-TUBE MODULE
(850psig, 17 fps, 25°C, pH 8.4)

Fig. 3.38

and was carried to 94% water recovery. At zero water recovery, rejections remained constant at over 92% and the flux constant at 50 gfd. Both rejections and fluxes decreased as the feed was concentrated by discarding product. At 94% water recovery, Cl^- rejection was 84%, while that of total cation was 90%, and the flux was 40 gfd.

Following this test, the module was rinsed with distilled water and once again tested with 0.05 M NaCl. Performance had returned to that obtained before the Colorado River water was placed in the loop, i.e., 52 gfd at 85% rejection.

The 31-tube module was then used with a second-stage sewage (see Section 3.3.3.7.2), and the membranes were regenerated by rinsing with a solution containing 50 ppm EDTA. At the end of the rinse, the rejection of 0.05 M NaCl was 84% at 57 gfd. Simulated pretreated (no divalent cations) Colorado River water was again added, and the results of a series of tests are given in Table 3.91. Dropping the pressure to 300 psig resulted in a drop of flux from 54 to 15 gfd, and rejections also decreased slightly.

TABLE 3.91

HYPERFILTRATION OF SIMULATED COLORADO RIVER WATER, WITH AND WITHOUT
DIVALENT CATIONS INCLUDED, BY Zr(IV)-PAA MEMBRANES ON A 31-TUBE
SELAS MODULE

(25°C, 17 fps, pH ~8.3)

Time (hr:min)	Pressure (psig)	% Water Recovery	Flux (gfd)	Cond.	Observed Rejection (%)		
					Cl^-	Total Cations	Ca(II) + Mg(II)
0:15	850	0	56	98	-	-	-
0:45	850	0	54	97	96	98	-
1:45	300	0	15	95	90	97	-
1:55	MgSO ₄ added to make solution 0.0014 M:						
2:30	300	0	7	88	71	92	-
16:15	300	0	6	83	60	88	94
16:30	Added salts to make solution 0.0011 M in CaSO ₄ and 0.0024 M in CaCl ₂ :						
18:00	300	0	7	60	45	68	81
19:30	Began to concentrate feed by discarding product:						
21:30	300	50	6.5	56	34	70	76
47:20	300	83	5.3	44	34	57	70

Adding MgSO_4 to the Mg(II) concentration indicated for Colorado River water in Table 3.68 caused an immediate decrease in both flux and rejection, and rejection dropped even further when the Ca(II) was added. When we began to concentrate the feed by discarding product, the deterioration in performance continued.

From these results, pretreatment to remove divalent cations from feeds of similar composition can tentatively be concluded to be beneficial with membranes formed by present procedures on Sela tubes. Chemical costs for removal of Ca(II) alone would run about 4 cents/kgal; for removal of both Ca(II) and Mg(II) , the cost would be about 19 cents/kgal.

3.3.1.4. Webster Water . Dual-layer membranes on 0.025-micron Millipore and 0.45-micron Acropor supports were tested with Webster water at 1X and 3X concentrations, and the performance compared to that with 0.05 M NaCl. The results for these tests, run in early 1970, are given in Table 3.92. Results were not significantly different for the 1X and 3X concentrations. Fluxes were lower with the Webster water feed than with the NaCl, and, with Webster water, 1 ppm of PAA in the feed during operation seemed to result in a slight improvement in observed rejections.

TABLE 3.92
HYPERFILTRATION OF WEBSTER WATER WITH HYDROUS Zr(IV) -PAA MEMBRANE
(1000 psig, 35 fps, 25°C)

Feed	Total Cation Analysis, M	Support	PAA, ppm	Flux (gfd)	Conduc- tivity	$R_{\text{obs}}, \%$	
						Total Cation	$\text{Mg(II)} + \text{Ca(II)}$
Webster, 1X	0.0164	0.025- μ MP*	0	42	74	83	85
		0.45- μ AP*	0	52	67	76	78
Webster, 3X	0.0460	0.025- μ MP	0	40	72	80	84
		0.45- μ AP	0	47	65	73	76
0.05 M NaCl		0.025- μ MP	0	64	76		
		0.45- μ AP	0	73	78		
Webster, 1X	0.020**	0.025- μ MP	1	31	83	89	92
		0.45- μ AP	1	38	73	80	83

*MP is Millipore, AP is Acropor

**This was prepared by shaking and diluting 3X, and we may have picked up too much solid.

3.3.1.5. Dalpra Farm Water. Zr(IV)-PAA membranes were formed in a module containing seven 7-channel Sela tubes, and an experiment, described in Section 3.3.3.6, involving low-level radioactive waste was carried out. Following this test, the membranes were operated for about 40 hours with 0.05 M NaCl (~50 gfd at 85% rejection) before simulated Dalpra Farm water was introduced into the feed tank. Rejections (conductivity) remained about 85%, but the fluxes fell to about 15 gfd over a 15-hour run. Dalpra is a high-sulfate water, with appreciable amounts of divalent cations. A 2-hour water wash and a 22-hour 0.05 M NaCl run brought fluxes only to about 25 gfd, indicating that restoration of membrane performance following Dalpra water was not complete.

3.3.1.6. ORNL Process Water. As a preliminary step toward testing the formation of dual-layer membranes from tap rather than distilled water, we tested a set of membranes with a solution of 0.05 M NaCl in ORNL Process water. The membranes had been formed in the usual manner with the solutions made up from distilled water. The results are tabulated in Table 3.93, along with tests on 0.05 M NaCl in distilled water for comparison purposes. Both fluxes and rejections dropped sharply when the tap water was added, and were lower still after operation overnight. Return to a distilled water solution restored rejections but only partially restored flux, although from experience we predict that further operation would probably have resulted in additional flux gains. ORNL process water contains about 0.001 M Ca(II) + Mg(II), and these divalent cations are most likely responsible for the decreases noted.

3.3.1.7. Wellton-Mohawk Canal Water. This brackish water, which is derived from irrigation runoff in Arizona, is harder than Webster water, and has almost double the TDS (Table 3.68). In our first test of this water with dynamic membranes, we formed Zr(IV)-PAA membranes on a set of supports at 950 psig, 33-35 fps, and 25°C. Comparison of the hyperfiltration properties of these membranes with 0.05 M NaCl and with Wellton-Mohawk water is given in Table 3.94.

The second test with Wellton-Mohawk Canal water was made on a set of membranes which had been used to test the effect of sulfate on the hyperfiltration properties of Roswell water (see Table 3.84). Before exposure to the Canal water, these membranes were tested with 0.05 M NaCl. At

TABLE 3.93
HYPERFILTRATION OF SOLUTIONS MADE FROM ORNL PROCESS WATER
BY Zr(IV)-PAA MEMBRANES

(1000 psig, 33.5 fps, 26°C, pH ~7.3)

Feed	Time ^a	Porous Support ^b							
		0.025- μ MP		0.05- μ MP		0.45- μ AP		1.2- μ AP	
		Flux (gfd)	R _{obs} (%)	Flux (gfd)	R _{obs} (%)	Flux (gfd)	R _{obs} (%)	Flux (gfd)	R _{obs} (%)
0.05 M NaCl in distilled water	0:30	92	71	107	93	175	90	165	86
0.05 M in process water	3:00	44	58	59	82	95	77	90	74
0.05 M NaCl in process water	16:30	38	60	53	84	89	75	79	76
0.05 M NaCl in distilled water	18:40	53	72	87	93	140	89	131	87

^aTime in hours and minutes following formation of the membrane.

^bMP is Millipore; AP is Acropor.

950 psig and 25°C, fluxes were from 60 to 80 gfd, and rejections exceeded 90% for all membranes except that on a Ferro tube support, where it was 80%. The results with these membranes with simulated pretreated (i.e., without Ca(II) but with Mg(II)) Wellton-Mohawk Canal water are given in Table 3.95.

Rejections are considerably improved over those found when Ca(II) was present (see previous table), even though the Mg(II) was still present. Ca(II) is relatively easy to remove especially in high carbonate waters, but the fluxes obtained in this experiment are unfavorable.

3.3.1.8. Long-Term Run With Simulated Natural Waters. This set of experiments was designed to provide information on the durability of the Zr(IV)-PAA membrane in the hyperfiltration of brackish feeds, and, in particular, to test the integrity of the Sclas ceramic support under many hours of operation. The membrane was tested with several different natural brackish water compositions, with and without pretreatment. In several cases, we simulated pretreatment by adding compositions in which the nominal

TABLE 3.94

HYPERFILTRATION OF WELLTON-MOHAWK CANAL WATER AND NaCl SOLUTIONS
WITH Zr(IV)-PAA MEMBRANES FORMED AT 950 PSIG, 33-35 FPS, AND 25°C

(Tests run at 950 psig, 15 fps, 25°C, and pH 7-8)

Time (hr:min)	Solution	Support	Flux (gfd)	Cond.	Observed Rejection(%)		
					Total Cation	Ca(II)+ Mg(II)	Cl ⁻
0:0	0.05 M NaCl	0.27-μ Selas tube	80	90	--	--	--
		6C carbon tube	70	85	--	--	--
		0.05-μ Millipore	58	81	--	--	--
		0.45-μ Acropor	100	83	--	--	--
0:35	Wellton-Mohawk	0.27-μ Selas tube	14	82	--	--	--
		6C carbon tube	15	80	--	--	--
		0.05-μ Millipore	12	80	--	--	--
		0.45-μ Acropor	26	72	--	--	--
4:05		0.27-μ Selas tube	13	83	87	96	82
		6C carbon tube	13	80	85	96	80
		0.05-μ Millipore	11	80	--	--	--
		0.45-μ Acropor	25	72	--	--	--
19:35		0.27-μ Selas tube	12	85	--	--	--
		6C carbon tube	12	83	--	--	--
		0.05-μ Millipore	10	80	--	--	--
		0.45-μ Acropor	25	62	--	--	--
20:00	Washed one hour with 1 M NaCl, two hours with distilled water:						
24:35	0.05 M NaCl	0.27-μ Selas tube	60	89	--	--	--
		6C carbon tube	68	83	--	--	--
		0.05-μ Millipore	61	73	--	--	--
		0.45-μ Acropor	80	71	--	--	--

concentrations of Ca(II) and Mg(II) were replaced by equivalent amounts of sodium ion. We will refer to such waters as simulated pretreated.

3.3.1.8.1. Initial Tests. A Zr(IV)-PAA membrane was formed, with inside flow and pressurization, on a 7-channel Selas ceramic filter element at 950 psig, 25°C, and with a circulation velocity of 35 fps. The resulting membrane was relatively poor, rejecting only 80% of the salt from 0.05 M NaCl at 57 gfd. Performance was somewhat better with simulated pretreated Colorado River water, but deteriorated when increments of Ca(II) and Mg(II) were added, see Table 3.96. The 45-minute water wash at 102 hours was not sufficient to eradicate the deleterious effects of the Ca(II) and Mg(II) additions.

TABLE 3.95

HYPERFILTRATION OF SIMULATED PRETREATED WELLTON-MOHAWK CANAL WATER
(WITHOUT Ca(II)) BY USED Zr(IV)-PAA MEMBRANES

(950 psig, 15 fps, 25°C, pH ~8)

Time (hr:min)	Support	Flux (gfd)	Observed Rejection (%)			
			Cond.	Total Cation	Ca(II)+ Mg(II)	Cl ⁻
15:15	6C carbon tube	12	93	--	--	--
	Treated Ferro 600p	16	94	--	--	--
	0.05-μ Millipore	15	96	--	--	--
	0.45-μ Acropor	22	92	--	--	--
18:45	6C carbon tube	12	93	94	99	93
	Treated Ferro 600p	16	95	96	99.5	95
	0.05-μ Millipore	15	96	--	--	--
	0.45-μ Acropor	22	92	--	--	--
39:45	6C carbon tube	13	90	--	--	--
	Treated Ferro 600p	16	94	--	--	--
	0.05-μ Millipore	15	96	--	--	--
	0.45-μ Acropor	22	92	--	--	--
45:45	6C carbon tube	13	92	--	--	--
	Treated Ferro 600p	16	94	--	--	--
	0.05-μ Millipore	15	96	--	--	--
	0.45-μ Acropor	22	92	--	--	--
63:15	6C carbon tube	13	93	--	--	--
	Treated Ferro 600p	16	94	--	--	--
	0.05-μ Millipore	15	96	--	--	--
	0.45-μ Acropor	22	92	--	--	--
158:15	6C carbon tube	13	90	--	--	--
	Treated Ferro 600p	16	93	--	--	--
	0.05-μ Millipore	16	96	--	--	--
	0.45-μ Acropor	23	92	--	--	--
159:45	Began concentrating to 30% water recovery:					
183:15	6C carbon tube	13	91	--	--	--
	Treated Ferro 600p	16	93	--	--	--
	0.05-μ Millipore	15	96	--	--	--
	0.45-μ Acropor	23	91	--	--	--

TABLE 3.96

TEST OF FIRST Zr(IV)-PAA MEMBRANE ON 7-CHANNEL SELAS TUBE IN EXTENDED RUN.
 FEED IS SIMULATED PRETREATED COLORADO RIVER WATER,
 WITH APPROPRIATE AMOUNTS OF Ca(II) AND Mg(II) ADDED LATER
 (950 psig, 35 fps, 25°C, pH ~8.5)

Time ^a	Feed Concentration		Flux (gfd)	Observed Rejection (%)			
	Ca(II)	Mg(II)		Cond.	Cl ⁻	Ca(II)+ Mg(II)	Total Cation
0:20	0.0	0.0	76	93	89	---	97
6:50	0.0	0.0	55	92	90	---	94
9:10	0.0007 M MgSO ₄ added:						
11:05	0.0	0.0007	34	73	76	92	84
76:50	0.0	0.0007	27	81	68	83	77
78:38	0.0007 M MgSO ₄ plus 0.0024 M CaSO ₄ added:						
80:35	0.0024 ^b	0.0014 ^b	38	52	48	68	58
97:05	0.0024 ^b	0.0014 ^b	32	59	52	63	62
102:00	45-minute water wash:						
102:45	Simulated pretreated Colorado River water added:						
103:40	0.0	0.0	40	81	--	---	--
121:10	0.0	0.0	38	85	79	---	88

(a) Time (hours:minutes) from first addition of pseudo-pretreated Colorado River water.

(b) Nominal concentration of Ca(II) and Mg(II) in Colorado River water.

3.3.1.8.2. Second Membrane. After the system and the support had been thoroughly cleaned by a one-hour wash with 1 M NaOH, followed by a one-hour wash with 1 M HNO₃ and a thorough rinse with distilled water, a new dual-layer membrane was formed on the Selas tube. This membrane had a somewhat higher rejection of 0.05 M NaCl, 90%, but lower flux, 46 gfd, than did the first, but its performance with simulated pretreated Colorado River water was appreciably better, as can be seen from Table 3.97. Both Table 3.97 and Fig. 3.39 give a chronological record of the experiments carried out with the second membrane. At the top of Fig. 3.39 is the name of the simulated water tested during the periods indicated by the arrows; immediately

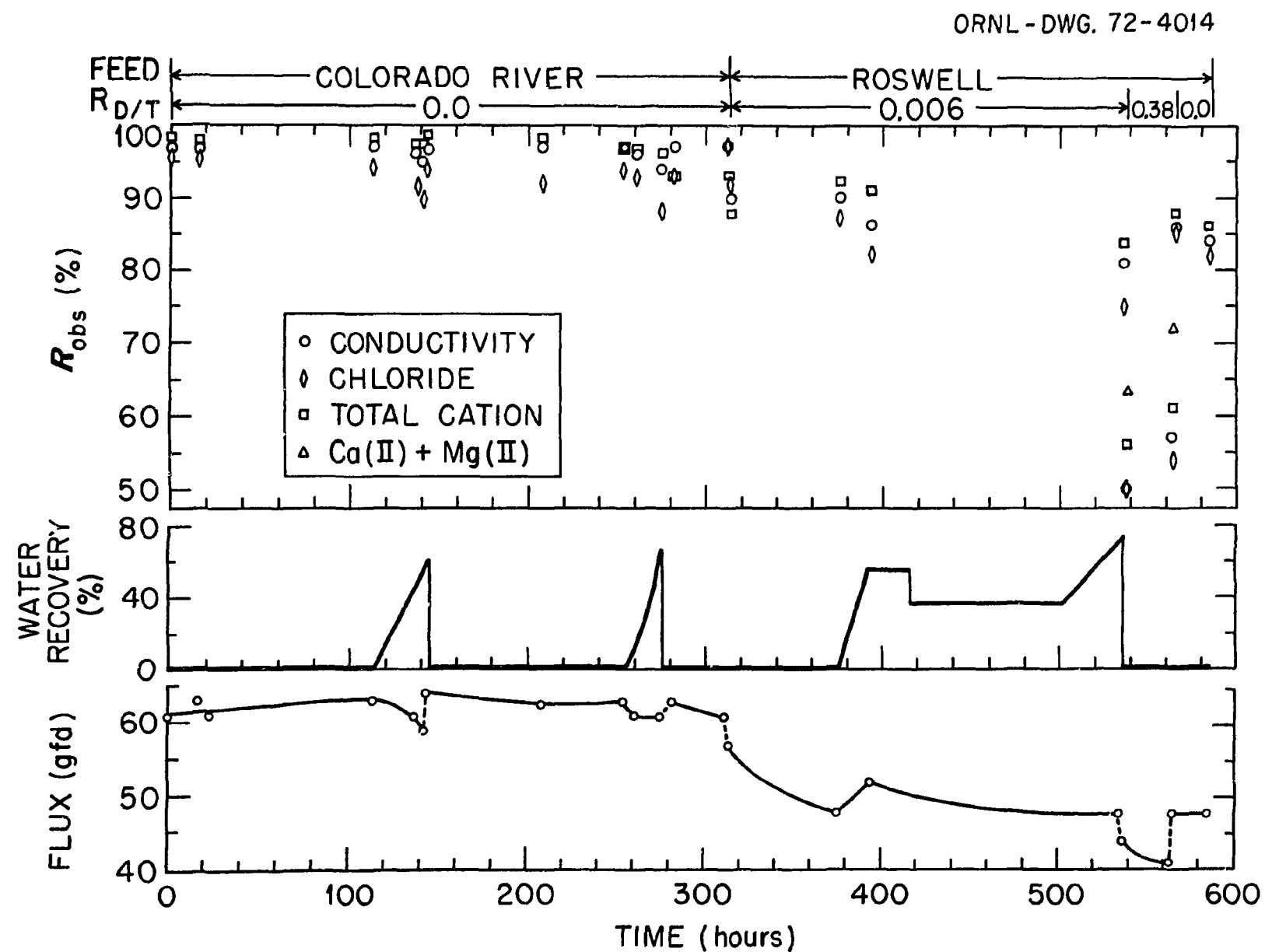
TABLE 3.97
HYPERFILTRATION ON BRACKISH WATERS BY SECOND MEMBRANE ON
7-CHANNEL SELAS TUBE IN EXTENDED RUN
(950 psig, 15 fps,^a 25°C, pH 7.5-8)

Time ^b	Feed ^c	% Water Recovery	Flux (gfd)	Observed Rejection (%)			
				Cond.	Cl ⁻	Ca(II)+ Mg(II)	Total Cation
0:30	SPCRW	0.0	61	97	96	--	98
16:50	"	"	63	97	96	--	98
23:20	"	"	61	97	96	--	98
113:35	"	"	63	97	94	--	98
113:45	Began to concentrate feed by discarding product:						
136:45	SPCRW	45	61	96	92	--	97
141:05	"	61	59	95	90	--	97
141:30	Rinsed system with water, added fresh brine:						
143:05	SPCRW	0.0	64	97	94	--	98
208:10	"	"	65	97	92	--	98
253:40	"	"	63	97	94	--	97
255:20	Began to concentrate feed by discarding product:						
260:50	SPCRW	17	61	96	93	--	97
275:20	"	67	61	94	88	--	96
275:50	Rinsed system with water, added fresh brine:						
282:50	SPCRW	0.0	63	97	93	--	93
312:50	"	"	61	97	97	--	93
313:20	Rinsed with water, added pretreated Roswell water:						
314:15	PRW	0.0	57	90	92	--	88
375:15	"	"	48	90	87	--	92
377:45	Began to concentrate feed by discarding product:						
393:15	PRW	55	52	86	82	--	91
535:15	"	73	48	81	75	--	84
535:30	Rinsed with water, added simulated Roswell water:						
537:15	RW	0.0	44	50	50	63	56
563:30	"	"	41	57	54	72	61
563:40	Rinsed with water, added simulated pretreated Roswell water:						
565:00	SPRW	0.0	48	86	85	--	88
584:20	"	"	48	84	82	--	86

(a) First two points taken with a circulation velocity of 35 fps, all others at 15 fps.

(b) Time (hours:minutes) from beginning of run.

(c) SP: simulated pretreated; P: pretreated by cross-flow filtration after chemical treatment; CRW: Colorado River water; RW: Roswell water.



HYPERFILTRATION OF SIMULATED PRETREATED BRACKISH WATERS
 $R_{D/T}$ is the ratio of divalent cation equivalents to total ion equivalents in feed.
 (950 psig, 15 fps, 25°C, pH 7.5-8)

Fig. 3.39

below the names is a number, $R_{D/T}$, which is the ratio of the equivalent concentration of divalent cations to the equivalent concentration of all ions in the feed. A value of 0.0 indicates simulated pretreatment resulting in a water without divalent cations. The nominal composition for Colorado River water has a $R_{D/T}$ value of 0.466, for Roswell water, 0.38. A typical cross-flow filtration of chemically treated brackish water compositions would result in about 98% removal of Ca(II) and Mg(II). For Colorado River water, this would result in a $R_{D/T}$ of 0.0093; for Roswell, 0.0075.

The first two points in the run were taken with a circulation velocity of 35 fps, but dropping the velocity to 15 fps at 23:20 had negligible effect on the hyperfiltration properties. During the remainder of the 584-hour run, the velocity was maintained at 15 fps. At about 114 hours, we began to concentrate the feed by discarding the product. At 61% water recovery, fluxes had dropped to 59 gfd with the drop in rejections that one might expect from treating brines of higher salt concentrations. Following the concentration phase, the loop was rinsed with distilled water, and fresh simulated pretreated brine was added. Both fluxes and rejections recovered the losses incurred during the preceding concentration run. At about 255 hours, another concentration was carried out, and the results were very similar to those observed earlier.

At 313:30, we rinsed the system and added a simulated Roswell water that had been pretreated by the addition of Na_2CO_3 and NaOH, to pH ~ 11 , to precipitate the Ca(II) as the carbonate and the Mg(II) as the hydroxide. After the chemical treatment, the resulting slurry was cross-flow filtered at 10 psig and 1 fps, the fluxes ranging from 220 to 102 gfd over the course of the run. About 98% of the Ca(II) plus Mg(II) was removed by the process, and the cross-flow permeate was neutralized with H_2SO_4 before being added to the feed tank of the hyperfiltration loop. Even the small amount of the divalent cation still remaining in the water, $9 \times 10^{-5} \text{ M}$, caused appreciable decreases in fluxes and rejections. After discarding product to a water recovery level of 73%, at about 535 hours, the flux was 48 gfd with 75% rejection of the chloride and 84% rejection of total cations.

The partial pretreatment of Roswell water, described in the preceding paragraph, is of considerable benefit even though it does not remove

all of the Ca(II) and Mg(II). This is demonstrated by the drastic decrease in performance caused by the addition of untreated Roswell water at 535:30. This decrease is mostly reversible, however, as can be seen from the recoveries in flux and rejections with a feed not containing Ca and Mg during the last twenty hours of the run.

The 584-hour run (Table 3.97 and Fig. 3.39) with various brackish waters resulted in about a 25% reduction in flux and a 10-15% reduction in observed rejections from those obtained at the start of the run. We attempted to improve rejections by adding a few ppm of PAA to the feed brine, but this was not effective. We then rinsed out the brine, added 0.05 M NaCl and 25 ppm PAA, and went through an acid cycle to reform the PAA part of the dual-layer membrane. Rejections improved appreciably, with simulated pretreated Roswell water they were 92-94%, but the fluxes had decreased to about 30 gfd. At this point, we stripped the old membrane from the Selas support with a base-acid wash cycle, and reformed the dual-layer membrane completely.

3.3.1.8.3. Third Membrane. The third hydrous Zr(IV) oxide-PAA membrane on the same Selas 7-channel tube was appreciably better in flux, 90 gfd, at about the same rejection, 89%, with 0.05 M NaCl than was the second. The improved performance was reflected by better hyperfiltration of simulated brackish waters throughout a 523-hour run that is described chronologically in Table 3.98 and Fig. 3.40.

After testing the membrane with 0.05 M NaCl, we added simulated pretreated Roswell water. Both fluxes and rejections improved. At 18 hours and 15 minutes into the run, we began to concentrate the feed by discarding the product instead of returning it to the feed container. At 24% water recovery, both fluxes and rejections remained high, but they had begun to decrease at the 75% water recovery level. A simple rinse with water, however, and a return to the unconcentrated simulated pretreated brine, brought flux levels to higher values than those observed initially, and brought rejection levels back to within a few percent of the initial values. After an additional 360 hours of operation with this same feed, fluxes were still about 95 gfd and rejections had decreased by only 3 or 4 percent. The overall flux decline parameter, b, which is the negative of the slope of the log flux vs. log time plot, was about 0.013 for this segment (365-hour) run

TABLE 3.98
HYPERFILTRATION OF SIMULATED BRACKISH WATERS
BY A THIRD SUCCESSIVE MEMBRANE ON A SELAS 7-CHANNEL CERAMIC TUBE
(950 psig, 15 fps, 25°C, pH ~8)

Time ^a	Feed ^b	% Water Recovery	Flux (gfd)	Observed Rejection (%)			
				Cond.	Cl ⁻	Ca(II)+ Mg(II)	Total Cation
0:50	NaCl	0.0	90	89	--	--	--
1:15	Rinsed system with water, added simulated pretreated Roswell water:						
2:00	SPRW	0.0	97	93	92	--	94
17:15	"	"	95	92	--	--	--
18:15	Began to concentrate by discarding product:						
24:00	SPRW	24	94	91	89	--	91
38:30	"	75	91	81	78	--	83
38:55	Rinsed with water, added fresh simulated pretreated Roswell water:						
40:15	SPRW	0.0	101	89	--	--	--
45:45	"	"	105	89	88	--	91
157:00	"	"	106	88	86	--	90
233:15	"	"	98	88	86	--	90
349:00	"	"	98	86	85	--	88
403:45	"	"	95	86	84	--	88
404:00	Rinsed with water, added cross-flow pretreated Colorado River water:						
404:25	PCRW	0.0	114	92	80	--	94
418:30	"	"	95	94	85	--	95
423:30	Began to concentrate by discarding product:						
426:10	PCRW	8	100	92	--	--	--
440:50	"	63	90	90	--	--	--
446:45	"	69	86	89	76	--	93
447:00	Rinsed with water, added Colorado River water, pretreated to remove most of the Ca(II) only:						
447:50	PCRW	0.0	87	77	65	93	80
462:35	"	"	60	83	73	96	86
464:00	Added polyphosphate equivalent to concentration of Ca(II) + Mg(II) in feed:						
465:35	PCRW	0.0	42	89	81	98	91

(Table continued next page)

TABLE 3.98 (continued)

Time ^a	Feed ^b	% Water Recovery	Flux (gfd)	Observed Rejection (%)			
				Cond.	Cl ⁻	Ca(II)+ Mg(II)	Total Cation
465:50	Began to concentrate by discarding product:						
469:35	PCRW	9	41	89	80	98	90
485:20	"	47	37	89	78	98	90
490:20	"	58	35	87	77	97	89
490:30	Operated with 0.05 <u>M</u> NaCl for 15 hours, then for one hour with 1 <u>M</u> NaCl; added 0.05 <u>M</u> NaCl:						
506:30	NaCl	0.0	80	87	--	--	--
506:40	Rinsed with water, added simulated pretreated Colorado River water with only the Ca(II) replaced by Na. Added 20 ppm polyphosphate:						
507:10	SPCRW	0.0	53	84	--	--	--
507:40	"	"	49	86	78	98	88
509:25	"	"	46	86	78	97	88
523:55	"	"	38	88	81	97	90

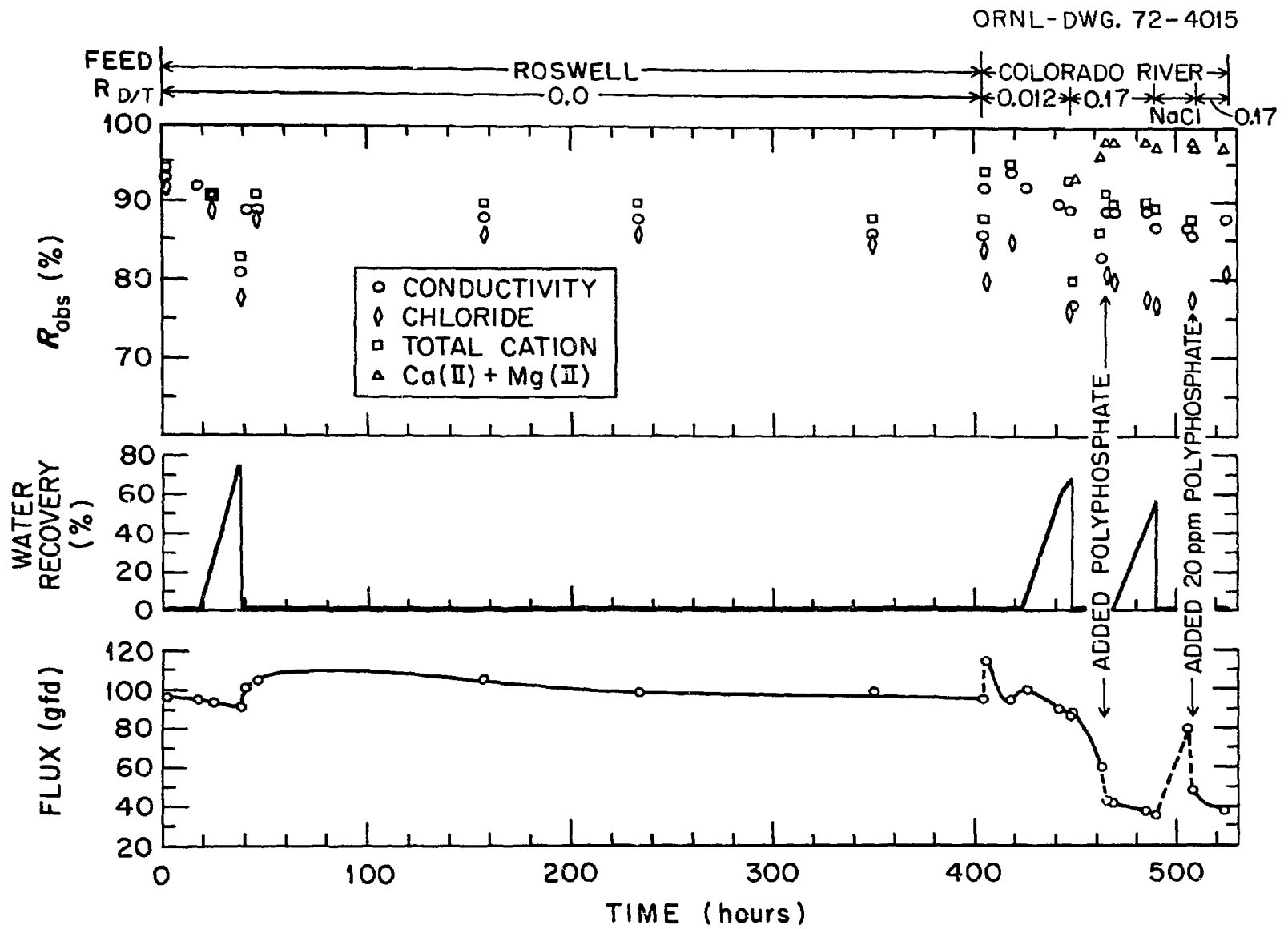
(a) Time (hours: minutes) from beginning of run.

(b) NaCl: 0.05 M; RW: Roswell water; CRW: Colorado River water; P: pretreated; SP: simulated pretreated, see text for explanation.

with a single feed. During the first 120 hours, the fluxes actually increased slightly; during the final 250 hours, they declined with $\bar{b} = 0.082$.

At 404 hours, we rinsed the system with distilled water, and added some simulated Colorado River water that had been pretreated by cross-flow filtration after chemical additions to precipitate the Ca(II) and Mg(II). The divalent cation concentration after pretreatment was about 0.0001 M. Initial fluxes were high (114 gfd) and rejections fair at 80% for the chloride and 94% for the total cations. At 69% water recovery, the flux had dropped to 86 gfd, and the chloride rejection was 76%, the total cation, 93%.

In the next phase of the run, we rinsed with water and added a cross-flow pretreated Colorado River water from which we had tried to remove only the bulk of the Ca(II). By leaving the Mg(II) in the feed, one



HYPERFILTRATION OF SIMULATED PRETREATED BRACKISH WATERS

$R_{D/T}$ is the ratio of divalent cation equivalents to total ion equivalents in feed.
(950 psig, 15 fps, 25°C, pH 8)

Fig. 3.40

can make a substantial savings in the chemical cost of pretreatment, since the base needed to increase the pH to about 11, and thus ensure the precipitation of $\text{Mg}(\text{OH})_2$, contributes the major portion of the chemical cost. In addition, if the pH is kept near neutral, no acid need be added to neutralize the solution after the pretreatment, and further savings are thus effected.

The partially pretreated Colorado River water added at 447 hours contained about 0.0014 M $\text{Ca}(\text{II})$ plus $\text{Mg}(\text{II})$, most of it $\text{Mg}(\text{II})$. Rejections were immediately lower, and the flux dropped to about 60 gfd within 15 hours. This drop in flux was accompanied by rise in all of the rejections measured, but they never reached the values we had attained just previously with the fully pretreated brine.

At 464 hours, we added enough polymetaphosphate (Calgon) to be equivalent to the divalent cation concentration remaining in the feed, in the hopes that the phosphate would complex the $\text{Mg}(\text{II})$ and prevent it from affecting the performance of the membrane. Rejections improved appreciably, but the flux suffered a 33% loss. During the ensuing concentration excursion, to 58% water recovery, flux declined further to 35 gfd, but rejections were little affected. That declining most, chloride, fell from 81 to 77% in the 25-hour run.

Flux through the membrane was regained by operating first with dilute NaCl , and then with 1 M NaCl . The dilute solution increased the flux to about 68 gfd, and the short rinse with the more concentrated solution brought it up to 80 gfd.

During the last phase of the run, we again tested the possibility of adding polyphosphate to prevent the deleterious effect of divalent cations. This time, we added the Calgon to a simulated pretreated Colorado River water which contained the normal amount of $\text{Mg}(\text{II})$, but no $\text{Ca}(\text{II})$, before the membrane was exposed to the brine. The effect was similar to that in the previous test, fluxes declined to 38 gfd in 17 hours, and rejections remained substantially unaffected.

3.3.1.8.4. Summary. Following completion of the tests just described, we transferred the Selas tube and the third membrane it carried to a small loop for further lifetime tests. Fifty-five days had elapsed since

the first membrane had been formed on the support, and tests had been carried out on simulated brackish waters for fifty-three of those days. We had twice stripped the old membrane, by chemical means, from the support and formed new ones in situ. These regenerations were carried out when the fluxes fell to levels we felt were below the capabilities of dynamic membranes, e.g., 40 gfd, and when fluxes and rejections could not be restored to higher levels through simple washes with water or NaCl solutions. The decreases in performance for each membrane can be associated with our deliberately exposing the membrane to feed constituents we know are deleterious, e.g., divalent cations. If feeds are pretreated to remove Ca(II) and Mg(II), both high fluxes and high rejections will likely be maintained for much longer times than those we report here. The Selas support itself, in the above tests and in another month or more of intermittent operation, showed no signs of weakening or deterioration, and no lessening of its suitability as a support for dynamic membranes.

From the results presented in this section, it appears that one can expect good performance with pretreated brackish waters with present dynamic membranes on practical supports. It seems likely that more specific attention to a particular brackish water should result in even better membrane performance, for previous experience has indicated that some support structures yield better results than others. The present results demonstrate once again that divalent cations in the feed lead to appreciably poorer performance, as with the untreated Roswell water in Table 3.97 and Fig. 3.39, and that removal of only the Ca(II) leads to some improvement in performance. Addition of polyphosphate to tie up the divalent cations in the feed did not appear helpful from the present experiments.

3.3.2. Hydrous Zr(IV) Oxide-PAA Membranes as a Second Stage in Hyperfiltration of Sea Water

During the last year of this biennium, the Office of Saline Water has shifted emphasis from brackish water to sea-water desalination. Since it is characteristic of ion-exchange membranes that salt rejection decreases as salt concentration increases, Zr(IV)-PAA dynamic membranes are not promising for single-pass sea water desalting. However, there remains the possibility that a two-stage process, utilizing a neutral membrane of moderate rejection and flux as the first stage, and a high-flux, medium-rejection

dynamic membrane as the second stage, might lead to more economical desalination of seawater than attainable with low-flux, high-rejection, single-pass reverse osmosis membranes.

The use of two stages does not result in great reductions in pressure necessary in the first stage from those usually projected for single-stage operation (typically 100 atm). Sea-water osmotic pressure is about 25 atm, and if, for example, one wished to attain 50% recovery, the reject stream osmotic pressure would be 50 atm. If 20% increase in osmotic pressure at the membrane-brine interface is allowed for concentration polarization, and one wishes to maintain about 20 atm pressure in excess of osmotic to maintain flux and rejection, about 80 atm, or 1200 psi, would be required, plus an increment to compensate for brine pressure drop from flow through the system. The advantages of less stringent requirements of membrane rejection (probably greater than 99% for single-pass operation) and the higher fluxes which might be attained by this relaxation would have to be sufficient to compensate for the costs of the second stage. With conventional membranes in both stages, the question is still open³⁹; as we suggested above, a high-flux dynamic membrane in the second stage might increase the attractiveness of a two-stage system.

The filtrate from a properly selected cellulose acetate system would seem accessible to a Zr(IV)-PAA membrane. For example, a membrane giving 96% overall rejection would reduce an average 50,000 ppm brine to 2000 ppm, and the fact that rejection of the troublesome divalent counterions, Ca(II) and Mg(II), is higher is also favorable. If, for example, rejection of these was 99%, the filtrate would contain about 0.001 M Ca(II) plus Mg(II), higher than desirable for best performance of Zr(IV)-PAA membranes, but probably still tolerable.

We have carried out some preliminary tests in cooperation with a team from the Oak Ridge Station of the M.I.T. School of Chemical Engineering Practice.* The equipment available was not well suited for our purposes. For the first stage we utilized a unit with three GESCO model 4100 "ROGA" spiral-wound brackish water modules, of nominal 3000 gpd total production

*Members of the team were G. J. Goetz, L. T. Bauer, and S. V. Demetriou. J. W. Tester was Director, and H. R. Greenberg, Assistant Director, of the Station. Further details can be found in Report ORNL-MIT-165, (Feb. 1973).

rate, for which the maximum allowable operating pressure was only 600 psi. Even with as low water recovery as practical, effective pressure (over osmotic) with sea-water feed was small. In addition, the unit had been used for nearly a year in investigations of CaSO_4 fouling, and its properties had considerably deteriorated from initial values. In a test with 0.05 M NaCl at the time of the sea-water experiments, rejection was from 85 to 89%, in comparison with approximately 94% obtained with brackish waters when the module was new.

A pretreatment procedure, which we feel has possibilities with real sea water, perhaps also for methods other than reverse osmosis, was incorporated for experience. Sodium hydroxide equivalent to bicarbonate present was added, and the resulting CaCO_3 precipitate removed by low-pressure (suction) filtration through a fire-hose jacket. Approximately 20% of Ca(II) and 10% of Mg(II) were removed. The objective was, however, to remove fouling constituents, rather than to lower hardness, by using the precipitate as a filter-cake for removal of particulates and at least some of the colloidal matter. In actual practice, instead of NaOH , one would probably add half a mole of CaO per mole of HCO_3^- present, so that bicarbonate would be essentially completely removed. The acid required to adjust the pH to values suitable for cellulose acetate membranes should be greatly reduced, and overall chemical costs thus probably lowered. A cross-flow would be used in filtration. In such operation with the pretreatment unit of the Roswell dynamic membrane pilot plant,⁷ fluxes of 500 gfd were attained with inlet pressures of less than 50 psi and 16 fps inlet velocity; filtration costs with this performance⁵ may not be excessive.

In the first-stage hyperfiltration with the GESCO unit of a pretreated solution having the composition of sea water, overall rejection of solutes in two runs was about 75% and of $\text{Ca(II)} + \text{Mg(II)}$, about 97%. Although recovery was carried only to between 20 and 25%, the product contained about 9000 ppm TDS and about 0.017 M $\text{Ca(II)} + \text{Mg(II)}$. The low effective pressure was indicated by the flux, only ~ 7 gfd at 600 psig. This composition is not ideal for Zr(IV) -PAA membranes; in second-stage operation utilizing a Ferro seven-tube bundle of the Roswell design⁷, R_{obs} varied from 94% at 0% recovery to 91% at 33% water recovery, and flux from 27 to 25 gfd (950 psig, 17 fps). The composite product contained about 900 ppm TDS.

In another run, to determine what performance might be expected if the first stage were adequate, product from the GESCO module was put through it a second time, to yield 1100 ppm TDS of less than 10^{-5} M divalent cations (20 gfd). With this product used as feed for Zr(IV)-PAA membranes, rejections at 50% water recovery, were about 92%, and TDS of overall product was less than 100 ppm (53 gfd at 950 psig, 15 fps).

These results are not conclusive concerning the viability of sea-water desalination by a two-stage approach involving a dynamic membrane second-stage, but they indicate promise. For evaluation, a suitable conventional membrane first stage is necessary. We attempted to gain some information on this by utilizing at high pressure porous stainless steel tubes wrapped with cellulose acetate, but the films on hand had deteriorated. After further tests to determine technical feasibility, an economic optimization of the overall system will be required.

3.3.3. Applications Not Primarily Involving Desalination

3.3.3.1. Introduction. In addition to testing the applicability of dynamic membranes to the desalination of brackish waters, we have, from time to time, carried out tests to determine their applicability to problems of pollution control. Most of these tests have been supported by agencies other than OSW, and some of the results are, or will shortly be, available elsewhere (see below). Results not available elsewhere will be summarized in this section because of their presumed general interest to those involved in treatment of waters with membrane technology. Work supported by the Atomic Energy Commission is identified in the title of the section by the initials AEC, and that by the National Science Foundation, under the Oak Ridge National Laboratory National Science Foundation environmental program, by the initials ORNL-NSF-EP.

We have tested dynamic membrane hyperfiltration and cross-flow filtration in the clarification of waste streams from pulp and paper mills. The earlier work has been published as an ORNL report.²⁰ Later work was presented at the May, 1973, TAPPI Conference in San Francisco. A paper based on that presentation has been submitted for publication; the abstract for the paper presented at the meeting reads as follows:

HYPERFILTRATION (REVERSE OSMOSIS) OF KRAFT PULP MILL AND BLEACH PLANT WASTES

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Chemistry Division, Oak Ridge National Laboratory
Oak Ridge, Tennessee

ABSTRACT

Over the past two years, the Water Research Program of the Oak Ridge National Laboratory, in collaboration with the International Paper Company, has carried out laboratory tests of certain filtration techniques for the processing of various kraft pulping streams. The techniques of interest here are high-pressure hyperfiltration (reverse osmosis) utilizing dynamic membranes rather than films of cellulose acetate, for example, moderate-pressure low-salt-rejection ultrafiltration, and filtration of chemically treated effluents at low pressures. In all three, the feed solutions are circulated parallel to the filtering surface; cross flow tends to reduce concentration polarization and inhibit fouling.

Among the effluents tested were brown-stock wash, decker and screen-room effluent and bleach-plant effluent from the kraft process. Dewatering of weak black liquor was also attempted. For hyperfiltration, polyacrylate membranes formed on a sublayer of hydrous Zr(IV) oxide were used. In ultrafiltration, the membranes were single-layers of hydrous Zr(IV) oxide or of neutral organic polymers. Decontamination appeared adequate for reuse of filtrates in many cases, and fluxes were considerably higher than usual with conventional detachable membranes. Further, filtration could be carried out at the temperature of the process, and in-situ regeneration, or removal and re-formation of the membranes, was possible.

In addition to pulp and paper wastes, we have looked at waste streams from commercial laundries,²² and food processing wastes such as cottage cheese whey, soy bean whey, potato peeling and grinding wastes, wheat and corn starch process wastes, and olive storage brine wastes. The food waste results are to be reported in a forthcoming report to the National Science Foundation. In cooperation with Drs. Craig Brandon and Jeff Porter of Clemson University, and with C. Aurich and K. Turner of Gaston County (N. C.) Dyeing Machine Company, we have applied dynamic membrane technology to samples of textile dye house waste streams.^{23, 24}

3.3.3.2. Cooling Tower Blowdown. (Joint OSW-AEC) The blowdown from a typical cooling tower may contain significant quantities of $\text{SO}_4^{=}$, Ca(II), Mg(II), Cr(III), Cr(VI), Zn(II), and phenol. All of these are pollutants,

and the chromate, added to reduce corrosion of pumps and related equipment, and the phenol, usually added as pentachlorophenol to prevent the growth of fungi, are relatively toxic. It is thus desirable to remove these constituents from the effluent of cooling towers before release to the environment. We have completed a short-term preliminary study of the possibility of utilizing hyperfiltration techniques and cross-flow filtration techniques to treat cooling tower blowdown, using as a feed some water drawn from the cooling tower in the 6000 area of ORNL.

3.3.3.2.1. Hyperfiltration. The results from dual-layer membranes on five supports are given in Table 3.99. The starting concentrations in the feed were Cr(III) plus Cr(VI), 0.000643 M, Ca(II) plus Mg(II), 0.00259 M, total cation, 0.00745 M, and organic carbon, about 9 ppm. The concentration of the di- and trivalent cations was evidently great enough to cause a sharp decrease in fluxes when the blow-down feed was introduced into the loop, although the rejections held up well. After the blowdown water was added, the flux decline parameters ranged from about 0.055 for the Acropor support at 35 fps to 0.087 for the same support at 15 fps. The rejections of organic carbon listed in the table are approximate only, since the analytical techniques we used are not sensitive at the low levels found. The organic carbon concentrations in all products of this study were less than 6 ppm.

Rejections increased slightly and fluxes fell somewhat when the pH was adjusted at about 47 hours. The volume concentration factor of 2.5 corresponded to an increase of somewhat less than a factor of two in the concentrations of the components for which we ran analyses.

3.3.3.2.2. Hyperfiltration Following Cross-Flow Pretreatment. Rejections were satisfactory in the above hyperfiltration run, but fluxes less so. It seemed probable that a pretreatment of the blow-down before hyperfiltration, to remove di- and trivalent cations, would result in improved performance, and a second test was run to check this. In this test, we tried a partial pretreatment, wherein we reduced the Cr(VI) to Cr(III) with FeSO_4 at pH 3.6, and then cross-flow filtered after raising the pH to 6.7 with NaOH. This reduced the total chromium concentration from about 11 to about 4 ppm and reduced the Ca(II) plus Mg(II) concentration about 25% to 0.0015 M. This pretreatment was not sufficient to prevent flux

TABLE 3.99
HYPERFILTRATION OF COOLING TOWER BLOWDOWN BY Zr(IV)-PAA MEMBRANES

Time ^a	Feed	Nom. Conc. ^b	pH	Support ^c	Flux (gfd)	Observed Rejection (%)				
						Cond.	Ca(II)+ Mg(II)	Cr(III) +Cr(VI)	Organic Carbon	Tot. Cation
0:15	NaCl	0.05 M	6.6	A	98	90	--	--	--	--
				B	147	95	--	--	--	--
				C	81	84	--	--	--	--
				D	147	92	--	--	--	--
				E	46	84	--	--	--	--
2:50	Blow-down	1X	5.8	A	27	91	96	86	67	93
				B	68	94	91	92	78	95
				C	33	92	96	85	44	94
				D	81	87	94	80	67	90
				E	30	82	90	72	67	83
20:20	Blow-down	1.2X	5.9	A	22	93	98	91	--	95
				B	61	95	95	93	--	95
				C	27	91	98	86	--	83
				D	70	89	98	80	--	90
				E	25	83	91	72	--	85
46:00	Blow-down	2.3X	5.9	A	21	94	98	94	75	95
				B	57	94	98	94	83	96
				C	26	91	97	89	75	93
				D	68	86	94	86	67	89
				E	25	82	89	80	67	84
48:30	Blow-down	2.4X	7.2	A	17	95	99	97	--	96
				B	46	96	99	98	--	97
				C	21	93	98	94	--	94
				D	55	88	96	92	--	90
				E	20	83	91	87	--	84
66:30	Blow-down	2.5X	7.0	A	17	95	--	--	--	--
				B	46	96	--	--	--	--
				C	21	93	--	--	--	--
				D	55	88	--	--	--	--
				E	20	82	--	--	--	--

(a) Time in hours and minutes from formation of membrane.

(b) For blow-down, concentration in terms of original volume: 1X equals original volume, 2X equals 1/2 original volume, etc.

(c) Porous supports: A: 0.025- μ Millipore @ 15 fps; B: 0.025- μ Millipore @ 35 fps; C: 0.45- μ Acropor @ 15 fps; D: 0.45- μ Acropor @ 35 fps; and E: 6C carbon tube @ 21 fps.

loss, however, when the cross-flow product was hyperfiltered with membranes formed on a Selas module (seven 7-channel tubes) described in Section 3.1.2.1.1.3. Within 30 minutes, the flux had dropped from about 80 gfd to 31 gfd with 89% rejection. After 22 hours, the flux was only 19 gfd, although the rejection had risen to 96% (conductivity). Chromium in the product was below our limits for detection. We attribute the flux decline to the appreciable concentration of divalent cations still remaining in the cross-flow product. Most of this could be removed, of course, by more extensive pretreatment.

3.3.3.2.3. Cross-Flow Filtration. In these tests, we attempted to attain adequate treatment with cross-flow filtration alone. The limiting factor in the recirculation of cooling water seems usually to be CaSO_4 scaling. Instead of trying to remove the chromium compounds from the water blowdown and to add makeup to stay below CaSO_4 solubility, we attempted to remove the hardness, so that the water and chromate could be recycled to the tower. We had noted in earlier experiments that most Cr(III) appeared to be filtered, along with CaCO_3 and Mg(OH)_2 , while most chromate seemed to pass through the filter. Hexavalent chromium is adsorbed very little, if at all, on the CaCO_3 - Mg(OH)_2 precipitate. We therefore oxidized the Cr(III) to Cr(VI) with peroxide, a procedure earlier utilized by Phillips and Kraus, before the cross-flow filtration.

Results of analysis of the cooling water blowdown (from the ORNL cyclotron tower) used in this test were as follows:

$\text{Ca(II)} + \text{Mg(II)}$	0.00292 <u>M</u>
Ca(II)	0.00203 <u>M</u>
Bicarbonate	0.00065 <u>M</u>
$\text{Cr(VI)} + \text{Cr(III)}$	29.4 ppm, about 10% Cr(III)

Sodium carbonate was added to 150 liters of blowdown to bring the concentration to 0.003 M Na_2CO_3 , and 35 g of NaOH brought pH to about 11. Five ppm of H_2O_2 were added to oxidize Cr(III) . In cross-flow filtration, we utilized 1-inch fire-hose jackets, pressurized solution inside. Initial removal of Ca(II) and Mg(II) was unsatisfactory (71%), and CaO , NaHCO_3 , and NaOH were added to increase slurry concentration by 0.003 M CaCO_3^* ,

*In practical operation, these additions should not be necessary, since a sufficient CaCO_3 filter cake would be built up in the early stages of continuous operation.

pH 11; two additional ppm of H_2O_2 were also added. Removal of Ca(II) + Mg(II) was then 92%, with 450 gfd at 20 psi. Circulation velocity was not measured directly because of instrument failure, but we estimated it to be less than 2 fps. Product collection was started and the subsequent fluxes were as follows:

<u>Hours</u>	<u>% Water Recovery</u>	<u>Flux, (gfd)</u>
1	21	360
2	41	310
2.5	51	285

Water recovery was limited by the volume of the system relative to the feed tank, but from removal of $\text{CaCO}_3\text{-Mg(OH)}_2$ by cross-flow filtration in other tests, we would expect that most of the water could be removed. At termination, the concentration of chromium was essentially the same in the filtrate (28 ppm) and in the supernate of the concentrate (29.5 ppm), a confirmation that little appears to be adsorbed on the precipitate. We found that the chromate remaining in the unfiltered solution could be reduced by stoichiometric amounts of Fe(II) ; the residual could therefore be precipitated as Cr(III) hydroxide for removal or recovery.

Of the approaches we have described with cooling tower blowdown, this appears to us to be the most attractive for further development. The filtration step should also aid in keeping down the level of biological contaminants in the water. Several questions remain to be answered. Attainment of the expected high water recovery should be demonstrated. The fate and subsequent effects of excess peroxide should be traced. Whether or not the filtrate, pH 11, needs to be neutralized in a separate step is not clear (0.009 moles of acid per liter were required to bring the pH to 7 in this test). If so, CO_2 is about the only agent which will not introduce objectionable constituents, or constituents which would build up in the system. However, the treated stream is presumably small in comparison with the total volume in the tower, and it may be sufficient to merge it with the circulating stream, and to allow neutralization to take place by subsequent equilibration with the atmosphere. In any case, other salts in the intake water will build up, and another sidestream will have to be withdrawn and processed in some way to keep the next limiting solute at a tolerable concentration. For this approach to be useful, the volume

of the second stream will have to be small relative to present blowdown; that is, a high concentration of the second limiting solute will have to be allowable. Possible gains from softening of intake water, perhaps after mixing with blowdown, should be evaluated. What happens to other contaminants and additives needs to be determined.

3.3.3.3. Simulated Mercury-Containing Wastes. We carried out a few tests on removal of mercury at low concentrations from concentrated NaCl solutions, a composition we understand is typical of certain streams in chlor-alkali plants. In one test, hydrous Zr(IV) oxide-PAA membranes formed for another purpose were tested with a 1 M NaCl solution containing initially 50 ppm of HgCl₂. Results, along with membrane properties with 0.05 M NaCl feed before and after exposure to the Hg-containing solution, are summarized in Table 3.100. Mercury rejections of 75 to 90% were observed.

TABLE 3.100
MERCURY REMOVAL BY HYDROUS Zr(IV) OXIDE-PAA MEMBRANE
(1000 psig; 35 fps; tubes)

Feed			0.025- μ Millipore				0.45- μ Acropor			
NaCl, moles/l	pH	Hg(II) ppm	Product Hg, ppm	$R_{obs}, \%$		Flux, (gfd)	Product Hg, ppm	$R_{obs}, \%$		Flux, (gfd)
				Cond.	Hg			Cond.	Hg	
0.05	6.7	-	-	81	-	81	-	88	-	135
1.0	8.5	-	-	40	-	57	-	29	-	135
1.0	7.8	46	3.8	37	92	70	11	31	76	130
1.0	8.0	45	3.5	35	92	70	5.4	33	88	125
1.0	8.1	37	2.8	29	90	80	2.8	31	92	135
0.05	8.0	-	-	86	-	105	-	87	-	180

However, the Hg(II) content of the feed declined over the two hours of the test, which may indicate the removal of mercury on loop surfaces. This possibility raises questions about the validity of these results. In addition, measurements by F. Nelson at ORNL on the adsorption of Hg(II) on various surfaces indicates that mercury may also have been removed from the product, downstream from the membrane, by the porous stainless steel support.

Another procedure, suggested by H. Podall of OSW, was tested in another loop, which contained a good many stainless steel components. Here we used a leonardite membrane and a high feed concentration of this cheap natural additive in hope that it would bind the mercury and thus make its filtration more complete. In this case, the disappearance of Hg(II) from the feed was so rapid (for example, from 25 ppm to < 0.2 ppm in 2-1/2 hours) that we do not attempt to draw any conclusions.

3.3.3.4. Simulated Space Station Shower Wastewater. (AEC) The requirements of long-duration flights in the space effort include the reclamation of water used by crew personnel. The NASA Langley Research Center indicated an interest, through Dr. Craig Brandon of Clemson University, in the possibility of the purification of shower water by hyperfiltration methods. Because of the possibility of the production of toxins by bacteria colonies which might accumulate in filters, the purification procedure must also destroy all bacteria which might produce such toxins. Hyperfiltration by dynamic membranes seemed a feasible method for such purifications because such membranes have been shown to operate very well at high temperatures (see, for example, Fig. 3.5).

Several liters of shower bath water were collected under conditions which, according to NASA, simulated those in flight. This water was subjected to hyperfiltration by a dual-layer membrane on a 6C carbon tube, the experiments being carried out by Dr. Brandon and the ORNL Water Research group on ORNL equipment. The loop used was not designed for high-temperature experiments, but by turning off the cooling water and putting an auxiliary heater in the feed tank, we were able to operate as high as 83°C. Under the conditions at hand, 97% of the organic carbon, originally 1500 ppm, was rejected and R_{obs} by conductivity was about 92%. Fluxes at 1000 psig

fell from 19 gfd soon after starting to about 12 gfd at the end of 18 hours of operation. Bacteria concentrations, which were too numerous to count in the original shower water, were reduced to zero in the product, according to analyses carried out by N. Bolton of the ORNL Industrial Hygiene Department of the Health Division.

Samples were sent to the Langley Research Center, and the report of their analysis is given in Table 3.101.

TABLE 3.101
HYPERFILTRATION OF SHOWER WATER^a

<u>Contaminant</u>	<u>Cold Shower Water</u>	<u>Product Accumulate</u>	<u>Percent Reduction</u>
Total Carbon, ppm	1190	55	95.4
Total Solids, ppm	1600	115	92.8
Chloride, ppm	69	7	89.9
Ammonia, ppm	34	2.4	92.9
Nitrate, ppm	9.3	< 0.5	> 94.6
Urea, ppm	<50	<50	----
Fluoride	-	< 0.1	
Sodium, ppm	93	9.3	90.0
Potassium, ppm	40	1.7	95.8

(a) Analyses by Langley Research Center.

The results of these experiments must be considered preliminary, since the amount of feed available was small and no modification of the hyperfiltration equipment was made. The results, however, strongly suggest the applicability of dynamic membranes to problems associated with resource reclamation in isolated systems.

A summary of additional work in this field, done in cooperation with us, has been published as a NASA report.³⁸

3.3.3.5. Boric Acid Solutions. (Joint OSW-AEC) Rejection of B(III) from brackish waters is of considerable interest in the desalination field because of the adverse effect boron compounds have on plant life. Experience has shown that B(III) is difficult to remove effectively by conventional membrane techniques,⁴⁰ and we looked into the possibility of treating borate-containing waters with dynamically formed membranes.

In addition to removing borate from irrigation waters, another application of interest is in treating borate-containing solutions used in the control of certain atomic reactors. Our initial experiments were designed with the latter use in mind. Borate levels in reactor control solutions could be conveniently controlled if a process existed by which a side stream of the circulating solution could be divided into two streams, one relatively concentrated in boron, the other relatively dilute. These two streams could subsequently be re-mixed in such proportion as to achieve the proper boron balance in the reactor.

To test the possibility of controlling the boron concentration, we treated a solution containing about 2000 ppm B(III) and about 0.1 M Li(I) (from LiOH and H_3BO_3) with dynamically formed Zr(IV)-PAA membranes on four different porous supports. The results for one of the supports, a Selas Flotronics micro-porous filter element with nominal pore size of 0.27 microns, is given in Table 3.102. Results for the other supports gave roughly comparable results, with somewhat higher fluxes, but lower rejections. In all cases, pressurization was on the outside of the support. Not surprisingly, the rejection of borate by this membrane depends quite strongly on the pH of the solution. At pH 9.2, about three quarters of the borate is rejected, while at pH 6.3 only about one-fourth is retained by the filter. This pH

TABLE 3.102

HYPERFILTRATION OF BORATE SOLUTIONS CONTAINING LITHIUM SALTS AT VARIOUS pH VALUES. HYDROUS Zr(IV) OXIDE-POLYACRYLIC ACID MEMBRANE ON A 0.27-MICRON SELAS FILTER ELEMENT
(950 psig, 35 fps, 25°C)

Feed Concentration		pH	Flux (gfd)	Observed Rejection (%)		
Boron (ppm)	Lithium (M)			Cond.	Total Cation	Boron
1816	0.096	9.2	32	85	92	76
2021	0.096	8.9	64	79	83	64
2548	0.091	8.3	70	78	81	55
2164	0.088	7.7	76	73	79	34
2202	0.087	7.1	88	68	74	22
2202	0.086	6.3	80	78	84	25
System rinsed with distilled water, and fresh boric acid solution added:						
1664	0.00	6.0	114	86	80	16
Circulation velocity reduced to 15 fps from 35 fps; pH increased:						
1660	0.068	9.2	60	94	--	~ 63

behavior is to be expected for an ion-exchange membrane, for boric acid is a very weak acid; even at pH 9.2 only about one-half of the boric acid is in the ionic form. In addition, it should be pointed out that the pH of the solution was lowered by adding HCl. Consequently, the salt concentration in the solution increased as the pH was lowered from 9.2 to 6.3. Before the point at pH 6.0 was taken, the salt was rinsed from the loop and fresh boric acid solution was added. There was an immediate rise in flux, indicating the properties of the membrane may have been changed somewhat by the presence of the salt. The difference in the properties between the first point and the last, both at pH 9.2, is more likely due to this change in membrane characteristics than it is to the change in circulation velocity, which usually has little effect in the range used here. Fluxes tended to increase as the pH was decreased, and, of course, would be higher at temperatures higher than 25°C.

The membrane used in this test was not a particularly good one, since prior to the addition of the borate solution, it had a flux of only 38 gfd for 0.05 M NaCl solution at 91% rejection. Usually, flux through such a membrane would be over 80 gfd with similar rejection.

3.3.3.6. Low-Level Radioactive Wastes (AEC). Hyperfiltration with dynamic membranes seemed a reasonable approach to removing radioactive contaminants, present at a low level, from ORNL process wastes. Two approaches were used, one a two-stage process with cross-flow filtration followed by hyperfiltration, and the second a cross-flow filtration after adsorption of particular nuclides on filterable additives.*

3.3.3.6.1. Two-Stage Process. We pretreated about 50 gallons of low-level waste so as to precipitate CaCO_3 and $\text{Mg}(\text{OH})_2$. The resulting slurry was cross-flow filtered, using fire-hose jacket as the filter support. Before pretreatment, this waste was about 0.0024 M in HCO_3^- , 0.0011 M in Ca(II), and 0.0004 M in Mg(II), and contained about 150 disintegrations per minute per milliliter (dpm/ml) of Sr^{90} , 230 dpm/ml of gross beta activity, and about 9 counts per minute per milliliter (cpm/ml) gross gamma activity.

*All analyses of radioactivity were done by E. I. Wyatt's group, Analytical Chemistry Division, ORNL.

The cross-flow filtration removed about 82% of the Sr^{90} , and 78% of the gross beta activity. Gamma activity had been reduced to levels below background (~ 4 cpm/ml).

The product from the cross-flow filtration was then hyperfiltered with membranes formed on the Sela tubes of a 7-tube protomodule (Section 3.1.2.1.1.3). At 950 psig, 15 fps, and 25°C , the rejection of 0.05 M NaCl, before the process waste was added, was 88% at 67 gfd. After hyperfiltration of the first-stage product to about 50% water recovery, 99.96% of the Sr^{90} and 99.8% of the gross beta activity present in the original feed had been removed. During the run, which was carried to 90% water recovery, fluxes fell from 75 to 41 gfd over 36 hours, but rejections remained high.

3.3.3.6.2. Cross-Flow Filtration With Additives.* It would be advantageous if adequate removal could be attained by low-pressure filtration alone. One way to do this might be addition of a cheap adsorbent for Sr^{90} which would also be removed in filtration. We tried addition of a ferric salt, and here compare results with the above first-stage cross-flow filtration in which no ferric salt had been added.

In the two cases, feed analyses of the process water influent to the treatment plant were as follows:

	<u>Earlier**</u>	<u>This Test</u>
HCO_3^-	0.00235 M	0.00242 M
Ca(II)	0.00105	0.00112
Ca(II) + Mg(II)	0.0014	0.0013

Hardness was precipitated by addition of 2 to 2.5 lbs. NaOH/kgal (CaO could replace most of this base and would be cheaper). In this test FeCl_3 was also added to 10 ppm Fe(III). Filtration was with fire-hose jackets.

*In cooperation with K. A. Kraus, F. Nelson, and H. O. Phillips.

**Test described in Section 3.3.3.6.1.

The results of the two tests were as follows (dpm):

	Earlier Test				This Test			
	Water Recovery (%)	Feed (dpm)	Product (dpm)	Removal (%)	Water Recovery (%)	Feed (dpm)	Product (dpm)	Removal (%)
Sr ⁹⁰	0	150	-	-	0	84	0.79	99
	50	-	27	82	50	-	0.81	99
Gross β	0	228	-	-	0	195	44	78
	50	-	50	78	50	-	43	78

Fluxes in the earlier test were 450 to 200 gfd (10 to 30 psi) and in this test 500 to 350 (10 psi). In this test, rejection of Ca(II) + Mg(II) was 94% and of Fe(III), 99.9%.

We tried a third cross-flow filtration of low-level process waste, this time adding a clay, Grundite Bond, presently used in the ORNL process waste treatment plant, as well as the 10 ppm of Fe(III). Before treatment, the waste water contained 0.00085 M Ca(II), 0.00025 M Mg(II), 18 ppm carbon, and showed the following activity: Sr⁹⁰, 574 dpm/ml; gross beta, ~280 cpm/ml; and gross gamma, 82 cpm/ml. The radioactivity analyses were done by E. Wyatt's group in the ORNL Analytical Chemistry Division. Gross gamma counts done through the courtesy of F. Nelson, ORNL Chemistry Division, gave somewhat higher levels, namely about 130 cpm/ml.

In addition to the iron and the clay, we added 0.0005 M CaO and increased the pH to about 10, and then to 11.5, to precipitate the Ca(II) as the carbonate and the Mg(II) as the hydroxide. The results of the run are given in chronological order in Table 3.103.

If the decontamination achieved in these cross-flow runs is adequate, costs for treatment by this method should be much lower than by schemes involving hyperfiltration.

3.3.3.7. Hyperfiltration of Municipal Sewage. (AEC)

3.3.3.7.1. Two-Stage Hyperfiltration. On an Environmental Protection Agency program, we have investigated treatment, by hyperfiltration with dynamically formed membranes, of the effluent from primary treatment of municipal sewage. Several membranes have looked promising in our preliminary survey, and the results have given us valuable experience with feeds which tend to foul membranes badly. It seemed worthwhile to test performance in a second hyperfiltration of the product, both to evaluate

TABLE 3.103

CROSS-FLOW FILTRATION OF ORNL PROCESS WASTE USING
FIRE HOSE JACKETS, WITH INSIDE AND OUTSIDE PRESSURIZATION, AS FILTER SUPPORTS
(8-10 psig, 7 fps, 21°C)

Time (hr:min)	pH	Clay (ppm)	% Water Recovery	Flow	Flux (gfd)	Sr ⁹⁰		Gross β		Gross γ	
						dpm/ml	R _{obs}	cpm/ml	R _{obs}	cpm/ml	R _{obs}
0:50	10.6	50	0	OUT	613	--	--	--	--	--	--
				IN	668	--	--	--	--	--	--
1:30	10.1	50	0	OUT	467	--	--	--	--	--	--
				IN	445	--	--	--	--	33	76
3:30	11.5	50	0	OUT	361	--	--	--	--	--	--
				IN	337	--	--	--	--	36	74
4:35	11.5	100	0	OUT	379	--	--	--	--	--	--
				IN	314	--	--	--	--	21	84
5:05	11.5	100	0	IN	--	--	--	--	32	76	
6:15	11.5	150	0	OUT	326	--	--	--	--	--	--
				IN	259	--	--	--	--	24	81
Shut down overnight.											
7:00	11.3	200	0	OUT	258	--	--	46*	84	--	--
				IN	214	--	--			13	90
12:00	11.3	400#	50	OUT	177	--	--	40*	93	--	--
				IN	150	--	--			15	94#
Added more pretreated feed.											
13:00	10	280#	28	OUT	208	--	--	72*	82#	--	--
				IN	182	--	--			22	88#
Shut down for long weekend; added new feed with additives.											
15:00	11.5	368#	46	OUT	258	--	--	--	--	13	95#
				IN	118	--	--	--	--	14	94#
20:30	11.5	738#	73	OUT	195	--	--	--	--	--	--
				IN	100	--	--	--	--	--	--
Shut down overnight.											
21:40	11.5	786#	75	OUT	290	--	--	--	--	--	--
				IN	99	--	--	--	--	--	--
24:00	11.5	1800#	90	OUT	248	33	99.4#	18	99.2#	10	98.6#
				IN	98	37	99.3#	20	99.2#	--	--

*Samples analysed were composite products from both test sections.

#Calculated from original composition and known concentration factor.

the possibilities of further purification and to find to what extent components that interfere with membrane performance were removed in the first step. Hyperfiltration will generally remove more than 80% of 500 ppm NaCl from water feeds, but in primary sewage effluents, salt at this concentration will be removed by only 50-60%. In addition, with membranes formed on 0.45- μ Acropor AN supports, rather high circulation velocities of sewage feeds are required to maintain product fluxes above 50 gfd for a few weeks.

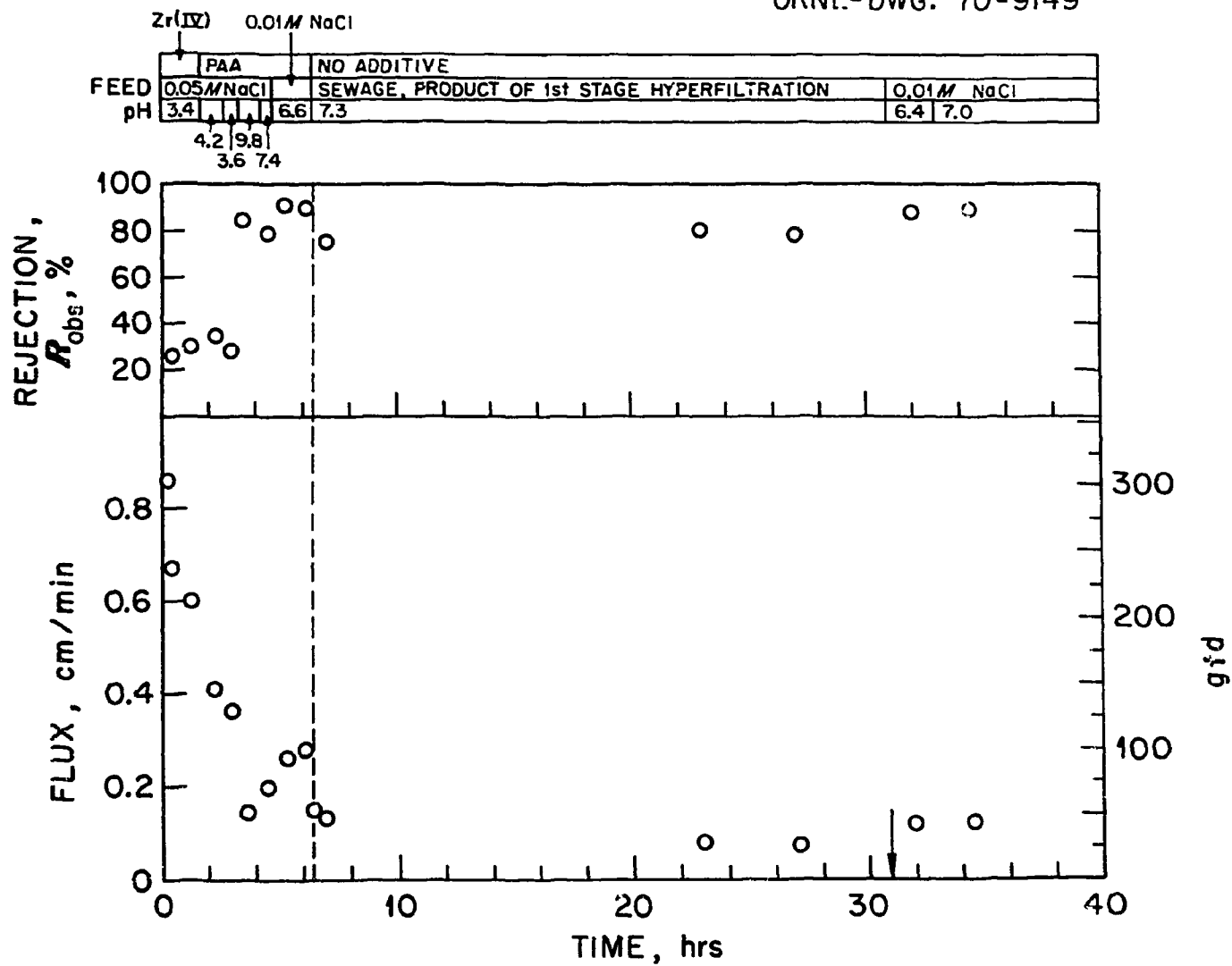
Fig. 3.41 summarizes formation of a dual-layer Zr(IV)-Acrysol A-5 membrane on the inside of a carbon tube, and subsequent tests with product from sewage hyperfiltration. The first stage, carried out at the Oak Ridge Sewage Plant, was with Sephadex CM-C-25 membranes. Chloride rejection in the first stage ranged between 47 and 66%; organic carbon, 85-95%; and fluxes 9 to 100 gfd (1000 psig).

With the above treated sewage as feed, after we added NaCl to 0.01 M to allow comparisons under similar conditions, R_{obs} dropped quickly from 90%, for 0.01 M NaCl in water, to 75%, and flux from 100 gfd to 45. There was a further decline in flux to 25-30 gfd overnight, with some increase in rejection. After a shutdown, and change back to 0.01 M NaCl in water, rejection was back up to near 90%, but flux was only about half what it was before exposure to sewage.

Although the organic carbon in the product from the first hyperfiltration was only 5 to 10 ppm, constituents which deleteriously affected membrane performance were nevertheless present. These results are reminiscent of observations with sewage feeds pretreated by coagulation and cross-flow filtration. (See Ref. 15, p. 296 ff)

3.3.3.7.2. Hyperfiltration of Cross-Flow Product. In EPA supported work, cross-flow filtration of municipal sewage after chemical additions, for example Fe(III), alum, or powdered carbon, to primary sewage effluent has appeared a promising alternative to settling or to standard filtration methods. Woven fire hose jackets are frequently used as filters. Although the cross-flow treatment is effective in removing most of the organic materials, and nearly all of the phosphates when Fe(III) or Al(III) salts are used, it does not remove the inorganic salts in the sewage or added in chemical treatment. We therefore tried a 3l-tube Sela module (Section 3.1.2.1.1.3) with Zr(IV)-PAA membranes as a possible second-stage treatment

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SECOND STAGE HYPERFILTRATION TREATMENT
OF PRIMARY EFFLUENT
(Hydrous Zr(IV) Oxide-PAA Membrane on Carbon
tube; 1000 psig; 25 fps)

Fig. 3.41

of municipal sewage.

The first batch of cross-flow product that we tested had a pH about 5.4 and a slight blue color, evidently copper from some cooling coils used in the cross-flow apparatus. Fifteen minutes after the feed was introduced, the rejection was only 50% (conductivity) at 49 gfd. Chloride and total cations were each about 0.012 M, and rejection of both was about 48%. Base was added to bring the pH to 6.7, which resulted in the feed becoming turbid. Within one hour the flux had fallen to 30 gfd, the rejection to 44%. Further operation led to further deterioration in performance.

The cross-flow effluent was washed from the loop, and the module was rinsed for one hour with a 0.1 M bicarbonate solution, pH 10, and then for one hour with distilled water. When tested with 0.05 M NaCl, the flux improved to 54 gfd, the rejection to 65%. We added 50 ppm EDTA to the 0.05 M NaCl feed to try to complex any multivalent cations (Cu?) that might be held on the ion-exchange sites on the membranes, and rinsed overnight with this solution. After a further one-hour water rinse, flux with 0.05 M NaCl was 55 gfd and the rejection was 81%. We repeated the EDTA rinse, and this brought the flux to 61 gfd and the rejection to 84%.

The second batch of cross-flow product from primary sewage effluent had been obtained by running at somewhat higher pH and did not become cloudy when we neutralized it with NaOH. It also was not as blue as the first sample; and the concentrations of chloride and total cations were less, about 0.003 M. Initially, the rejections were about 65% at 48 gfd. After 22 hours of operation and 83% water recovery, the flux had fallen to 34 gfd and the rejection of Cl^- to 59%, while that for total cation was 64%.

These experiments indicated again that substances remained in the cross-flow filtrate which affect deleteriously the performance of Zr(IV)-PAA membranes. Whether the copper impurities, introduced from experimental equipment and not typically present in projected feeds, or other materials are responsible is not clear at this point. (See Section 3.1.3.3.3. for tests with Cu(II)).

4. Cast Film Membranes

4.1 DETACHABLE ION-EXCHANGE MEMBRANES

Detachable ion-exchange membranes have potential advantages over those dynamically formed for testing transport equations. Independent measurements of distribution coefficients, diffusion coefficients, water content, and other properties which enter into hyperfiltration are possible with conventional films. On the other hand, the commercial ion-exchange membranes, made for electrodialysis, are frequently not homogeneous and are developed to have low water permeability, and this is undesirable in hyperfiltration studies.

4.1.1 Sulfonic Cation-Exchange Membranes

We have tested several commercial sulfonic cation-exchange membranes (Table 4.1), in unsuccessful attempts to find films suitable for fundamental studies. Nalfilm 1B was tested in a tubular configuration and in a cell. The others were tested only in cells. Conditions were 0.05 M NaCl feed, pH $\sim$ 5, and 1000 psig. Flux through the Nalco film fell from 50 gfd just after startup to 6 after three hours; rejections were negligible, 1 to 2%. Flux through MC-3470XL dropped in a few hours from 27 to 2 gfd, while rejection was essentially zero. No appreciable flux was obtained through any of the others.

Since membranes having the stated ion-exchange capacities should filter fairly high fractions of salt, it appears that most of the observed flux arose from imperfections in the membranes.

TABLE 4.1

DETACHABLE ION-EXCHANGE MEMBRANES

<u>Membrane</u>	<u>Manufacturer</u>	<u>Thickness</u> <u>mm</u>	<u>Capacity</u> <u>meq/dry gram</u>	<u>Ref.</u>
Nalfilm 1B	Nalco Chemical	0.1	--	a
C-103	American Machine & Foundry	0.16	1.2	a
MC-3142	Ionac (Sybron)	0.15	1.06	b
MC-3470XL	Ionac (Sybron)	0.3	1.05	b

(a) F. Helferrich, Ion Exchange, McGraw-Hill (1962), information for Nalfilm 1 and Ionac C-103C.

(b) Manufacturers' literature (these membranes are heterogeneous).

4.1.2 CANN DEA Anion-Exchange Membranes

Preliminary attempts were made to prepare a cellulose acetate support carrying anion exchange capacity (tertiary amine) by casting films from cellulose acetate NN diethyl amino acetate (CANN DEA) (Eastman Catalog No. 8324). The aminoacetic acid esterifies free hydroxyls on cellulose acetate. Solutions of 1 gm. of this material in 6 grams of formamide (F) or 6 grams of acetic acid (AA) were used in casting.

In the first test, one sample of the AA-cast and one of the F-cast films, each backed by 5- μ Millipore, were tested in cells. When the pressure was raised above 500 psig, a sharp increase in flux from both cells indicated the membranes had ruptured. We next tried samples cushioned from the porous metal pressure support by 0.45- μ Millipore disks. With 0.05 M NaCl feed, no additive, flux, after 2 hours at 1000 psig, was 18 gfd through F, with $R_{obs} = 15\%$; through AA, 20 gfd, $R_{obs} = 52\%$, the latter value representing a rise from 17% after 30 minutes operation, at approximately twice the flux.

After an overnight shutdown, which had only small effects on properties, 25 ppm Nalco D (See Ref. 15, p. 140 ff) polycationic additive was added. This material has the same charge sign as that on the membrane and no special interaction would be expected. However, rejection on F increased to 67%, with flux 6 gfd, and on AA to 74%, flux 10 gfd.

Possible anisotropy of the AA films was checked by running simultaneously samples with the opposite sides of the sheet up. After two hours operation, differences in properties were not significant, with R_{obs} for both between 61 and 64%, and fluxes between 17 and 20 gfd. Addition of 25 ppm of polystyrene sulfonate (MW 5,000,000, see Ref. 15, p. 96 ff), which has a charge sign opposite that of the membrane, affected rejections by only a few percent, but cut fluxes in half.

It is not clear what aspects of these results arise from the cellulose acetate character of these films, and what from the ion-exchange groups attached. Additives may have functioned only to plug defects. There is no indication of a special effect of charge sign on the polymer relative to that of the membranes.

4.2 DETACHABLE NEUTRAL MEMBRANES: CHITIN

We prepared some cast films of n-acetyl polyaminoglucose (chitin) and tested their value as hyperfiltration membranes by backing them with 0.025- μ Millipore supports and placing them in cells of about 1.2 cm² area in a small test loop. At 1500 psig, the rejection of 0.05 M NaCl was less than 35% at 5 to 6 gfd in neutral solutions and about 39% at 6 gfd in basic (pH 10) solutions. The membranes were soluble in acid. Dynamic membranes of chitosan (deacetylated chitin)(see Section 3.2.3.8) have also been found to be unsatisfactory for desalination.

5. Concentration Polarization

Summary

We have continued our study of boundary layer effects, although not as intensively as in the last two biennia (see Ref. 30, p. 85 ff and Ref. 15, p. 253 ff). In Section 5.1, we reprint a paper by D. G. Thomas, originally published in I&EC Fundamentals⁴¹, that confirms the validity of the linear extrapolation of a plot of $\ln[(1-R_{\text{obs}})/R_{\text{obs}}]$ vs. $v/u^{0.75}$ to obtain the intrinsic rejection, R^8 , where v is the flux in cm/sec and u is the axial velocity in cm/sec.

Section 5.2 reports some further work with concentration polarization with neutral solutes.

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5.1 ESTIMATION OF CONCENTRATION POLARIZATION FOR ION-EXCLUSION HYPERFILTRATION MEMBRANES WITH TURBULENT FLOW

D. G. Thomas

Concentration dependence of intrinsic rejection of ion-exclusion membranes was included in turbulent flow concentration polarization equations assuming low flux and high rejection. Comparison with experimental data indicated that the approximate equations retained usefulness for rejections as small as $\sim 75\%$ and fluxes as large as 0.45 cm/min (~ 160 gal/ft²·day). Within the limitations of the approximate equations, the concentration dependence of intrinsic rejections affects only the slope of the curve on a plot of $\ln [(1 - R_{\text{obsd}})/R_{\text{obsd}}]$ vs. $v/u^{1/2}$. This confirms the validity of linear extrapolation on such a plot to obtain intrinsic rejection as originally proposed by Sher, *et al.* (1968a).

Knowledge of the value of concentration polarization in hyperfiltration of salts is important in fundamental studies of transport of salts within membranes, in evaluation of permeability and intrinsic rejection of membranes, and in predicting when precipitation of slightly soluble salts might occur. Because the concentration boundary layer is so thin at the Schmidt numbers of interest ($500 < N_{\text{Sc}} < 1000$), direct measurement of concentration polarization appears to be restricted to Reynolds numbers less than ~ 1400 with presently available techniques (Hendricks and Williams, 1971). Consequently, resort must be made to indirect means for evaluating concentration polarization.

Semitheoretical equations for concentration polarization in hyperfiltration under turbulent flow conditions have been developed by Sherwood, *et al.* (1965), Johnson, *et al.* (1966), and Brian (1965), assuming, among other things, a fully developed concentration profile, that the eddy diffusivity and radial variation of the axial velocity are the same as in turbulent flow in an impermeable tube, and neglecting axial convection. The result of the analysis is

$$\frac{c_a}{c_t} = \frac{\exp[25(v/u)N_{\text{Re}}^{1/2}N_{\text{Sc}}^{2/3}]}{R + (1 - R) \exp[25(v/u)N_{\text{Re}}^{1/2}N_{\text{Sc}}^{2/3}]} \quad (1)$$

In deriving this equation, use was made of the Colburn "j-factor" to obtain the relation between the mass-transfer coefficient and the friction factor; for turbulent flow in tubes this approach yields the numerical coefficient of 25 in eq 1. For evaluating system performance, eq 1 is frequently rewritten as

$$\ln \frac{1 - R_{\text{obsd}}}{R_{\text{obsd}}} = 25 \frac{v}{u} N_{\text{Re}}^{1/2} N_{\text{Sc}}^{2/3} + \ln \frac{1 - R}{R} \quad (2)$$

where the observed rejection, R_{obsd} , is given by

$$R_{\text{obsd}} = 1 - \frac{c_w}{c_t} \quad (3)$$

and the intrinsic rejection, R , is given by

$$R = 1 - \frac{c_w}{c_a} \quad (4)$$

According to eq 2, a plot of $\ln [(1 - R_{obsd})/R_{obsd}]$ vs. $v/u^{1/2}$ should give a straight line in turbulent flow; extrapolation to $v/u^{1/2} = 0$ is a convenient method for determining the intrinsic rejection (Shor, *et al.*, 1968a).

The assumption inherent in the development of eq 1 and 2 is quite good for small ratios of flux to axial velocities and results consistent with these equations have been obtained: by Sherwood, *et al.* (1967), using a rotating cylinder apparatus, salt solutions with Schmidt numbers of 608 and 750 at fluxes from 0.025 to 0.038 cm/min; by Rosenfeld and Loeb (1967) in tubular geometry with a Schmidt number of 585 at fluxes of 0.055 to 0.16 cm/min; and by Shor, *et al.* (1968a), with tubular geometry, Schmidt numbers of 600 and 815 and fluxes of 0.2 and 0.3 cm/min. Based on these experimental results there seems to be little doubt of the general applicability of eq 1 and 2 in correlating hyperfiltration results within the constraints of the assumptions used in their derivation.

Other procedures [besides the slope-intercept method proposed by Shor, *et al.* (1968a)] may be used for calculating the concentration polarization or the intrinsic rejection. For instance, the intrinsic rejection can be calculated directly from eq 2, or eq 3 and 4 can be substituted into eq 2 and the interface salt concentration, c_a , calculated from results of measurement of c_w and c_r . However, as pointed out by McAdams (1954), in heat transfer studies the j -factor (and other semitheoretical correlations) correlates the data with a maximum deviation of $\pm 40\%$. It would seem imprudent, until proven otherwise, not to expect similar variability in hyperfiltration studies and hence considerable error might occur in calculating concentration polarization from eq 1 or 2, assuming a numerical coefficient of 25. Of course, the slope-intercept method does not require knowledge of the value of the numerical coefficient in eq 1 and 2.

In practice, hyperfiltration membranes may be either neutral or charged. With both types of membrane the intrinsic rejection increases to an asymptotic value as the flux increases, and in addition the intrinsic rejection of charged membranes decreases with increased salt concentration (Johnson, *et al.*, 1966; Shor, *et al.*, 1968a,b). Consequently some care must be used in reduction of data to obtain the values of the concentration polarization, *i.e.*, according to eq 1 as the axial velocity is decreased, concentration polarization increases; this always decreases the effective pressure difference across the membrane (because of increased osmotic pressure difference), hence decreasing both the flux and the intrinsic rejection. With charged membranes, increased concentration polarization causes an additional reduction in intrinsic rejection due to the concentration-dependent rejection of these membranes. Both these effects must be accounted for in applying eq 1 and 2 to experimental results.

Sheppard and Thomas (1970a) showed that asymptotic rejection of cellulose acetate membranes is not achieved, even at the unexpectedly large flux of 50 gal/ft²-day, and that the theoretical predictions of Johnson, *et al.* (1966) that

$$\frac{1 - R}{R} \propto \frac{1}{J} \quad (5)$$

are followed quite closely. In turbulent flow the flux decreases slightly as axial velocity decreases (due to increased osmotic pressure difference as concentration polarization increases). In one test with a cellulose acetate membrane, Sheppard and Thomas (1970b) reported a decrease in flux from 29 to 26 gal/ft²-day as the axial velocity decreased from 24 to 4 ft/sec. The correction to intrinsic rejection at infinite circu-

lation velocity required to calculate accurate values of concentration polarization is small and is easily made (Sheppard and Thomas, 1970b).

With ion-exchange type membranes, the intrinsic rejection is not only a function of flux (Shor, *et al.*, 1968b) but also is a function of the concentration at the membrane-solution interface, c_a (Shor, *et al.*, 1968a). Shor, *et al.* (1968a), developed an iteration procedure using eq 4, the concentration dependence of R determined to fit experimental results, and the experimental value of c_a to calculate values of R for each different circulation velocity and feed concentration. The calculated values of R were then used, together with eq 2, to calculate R_{obsd} . The computation is repeated until the difference between R_{obsd} and $(R_{obsd})_{calcd}$ is minimized and a single expression obtained which fits the experimental dependence of R on c_a . With this procedure the calculated points were always within $\pm 2\%$ and most were within $\pm 1\%$ in rejection for a constant value of the numerical coefficient in eq 1 and 2. (The value of the numerical coefficient of eq 1 was determined in the iteration procedure.) The value of numerical coefficient determined in the computer calculation was $1/2$ to $1/3$ the value determined from the slope of the experimental results on a plot of $\ln [(1 - R_{obsd})/R_{obsd}]$ vs. $v/u^{1/2}$, indicating the importance of considering concentration dependence of rejection. The fact that the results of Shor, *et al.* (1968a), for salt concentrations from 0.007 to 0.26 *M*, and with circulation velocities from 110 to 670 cm/sec, could be correlated with a simple expression for R as a function of concentration indicates the self-consistency of the approach. The convergence of the computation on essentially the same value of the numerical coefficient in eq 1 for both salts for such a wide range of conditions indicates that other possible dependencies, *e.g.*, the exponent on the Reynolds number, are not primarily involved.

In the following sections concentration polarization equations will be developed which account for the dependence of intrinsic rejection on c_a for the limiting case of low flux and low concentration; then the range of applicability of the limiting equations will be evaluated by comparison with experimental results obtained with ion-exchange type membranes.

Concentration Polarization Equations

Shor, *et al.* (1968b), have shown that

$$D_a^*(C^*/m_a + zD_a^*)^2 \Gamma_a^{z+1} - z^2 = 0 \quad (6)$$

When the coefficient relating coupling between solvent flow and solute flow is unity, then

$$R = 1 - D_a^* \quad (6a)$$

Equations 6 and 6a describe the concentration dependence of intrinsic rejection for ion-exchange type membranes for rejections from less than 10% to greater than 99%. To simplify the analysis, the concentration dependence of rejection will be assumed to be

$$\frac{d \ln (1 - R)}{d \ln (c_a)} = n \quad (7)$$

Examination of available experimental data (Shor, *et al.*, 1968b; Sachs, *et al.*, 1969) indicates that n usually has non-integer values and that at low concentrations (for which $R \geq 60\%$) n is substantially a constant for any given salt and membrane material.

Because of this dependence of intrinsic rejection on concentration it is necessary to distinguish between the intrinsic

rejection extrapolated to infinite axial velocity, R_∞ , and the intrinsic rejection at finite velocity, R_u , when concentration polarization has a finite value. With this distinction eq 1 becomes, for small values of the exponent in eq 1

$$\frac{c_p}{c_t} - 1 \approx R_u \left(K \frac{v}{u} N_{Re}^{1/2} N_{Sc}^{1/3} \right) \times \left\{ 1 - (1 - R_u) \left(K \frac{v}{u} N_{Re}^{1/2} N_{Sc}^{1/3} \right) \right\} \quad (8)$$

and for high rejections

$$\frac{c_p}{c_t} - 1 \approx R_u \left(K \frac{v}{u} N_{Re}^{1/2} N_{Sc}^{1/3} \right) \quad (9)$$

A relation between R_u and R_∞ can be obtained from eq 7

$$(1 - R)_u = (1 - R)_\infty (c_p/c_t)^n \quad (10)$$

Combining eq 9 and 10 gives

$$(1 - R)_u \approx (1 - R)_\infty \left[1 + R_u \left(K \frac{v}{u} N_{Re}^{1/2} N_{Sc}^{1/3} \right) \right]^n \quad (11)$$

and for small values of the term on the right in the brackets, series expansion gives

$$R_u \approx R_\infty \left[(1 - n(1 - R_u) \left(K \frac{v}{u} N_{Re}^{1/2} N_{Sc}^{1/3} \right)) \right] \quad (12)$$

For high rejections the group of terms in the right of the brackets is much less than 1 and within the limits of the present approximation $R_u \approx R_\infty$. Equations 9 and 12 then give

$$\frac{c_p}{c_t} - 1 = R_\infty \left(K \frac{v}{u} N_{Re}^{1/2} N_{Sc}^{1/3} \right) \quad (13)$$

from which concentration polarization can be estimated for ion-exchange type membranes under turbulent flow conditions by a linear extrapolation using eq 2 (to obtain R_∞) provided the flux, v , is not large and the rejection is near unity.

Equation 2 can be modified to account for the concentration dependence of the intrinsic rejection by dividing eq 11 by eq 12

$$\left(\frac{1 - R}{R} \right)_u \approx \left(\frac{1 - R}{R} \right)_\infty \left[1 + nR_u \left(K \frac{v}{u} N_{Re}^{1/2} N_{Sc}^{1/3} \right) \right] \quad (14)$$

Substitution of eq 14 into eq 2 and rearranging gives

$$\ln \left[\left(\frac{1 - R_{obsd}}{R_{obsd}} \right) / \left(\frac{1 - R}{R} \right)_\infty \right] \approx K \frac{v}{u} N_{Re}^{1/2} N_{Sc}^{1/3} + \ln \left[1 + nR_u \left(K \frac{v}{u} N_{Re}^{1/2} N_{Sc}^{1/3} \right) \right] \quad (15)$$

and for small values of the last term in the brackets on the right

$$\ln \left[\left(\frac{1 - R_{obsd}}{R_{obsd}} \right) / \left(\frac{1 - R}{R} \right)_\infty \right] \approx (1 + nR_u) K \frac{v}{u} N_{Re}^{1/2} N_{Sc}^{1/3} \quad (16)$$

or in hyperfiltration j -factor from

$$j = \frac{v N_{Sc}^{2/3}}{u \ln \left[\left(\frac{1 - R_{obsd}}{R_{obsd}} \right) / \left(\frac{1 - R}{R} \right)_\infty \right]} \approx \frac{1}{K_{app} N_{Re}^{1/2}} \quad (17)$$

where

$$K_{app} = (1 + nR_u)K \quad (18)$$

Equation 16 differs from eq 2 only by the factor $(1 + nR_u)$ multiplying the term on the right. Thus, at low fluxes and high rejections, a linear extrapolation on a plot of $\ln [(1 - R_{obsd})/R_{obsd}]$ vs. $v/u^{1/2}$ is a satisfactory procedure for determining the value of the intrinsic rejection at infinite circulation velocity, R_∞ . Note that for membrane whose rejection is independent of concentration (e.g., neutral membranes such as cellulose acetate), $n = 0$, and eq 16 reduces to eq 2.

The relation between the apparent concentration polarization assuming constant intrinsic rejection, R_∞ , and the true concentration polarization where the intrinsic rejection is a function of velocity may be obtained by combining eq 13 and 18

$$\frac{c_p}{c_t} - 1 = \frac{(c_p/c_t) - 1}{1 + nR_\infty} \quad (19)$$

Equipment and Procedure

Hyperfiltration tests were carried out in a stainless steel recirculation loop. The loop consisted of a 50 gal per min canned rotor pump, a heat exchanger to maintain the circulating stream at a steady temperature, air-operated control valves, and a line bypassing the test section. High flow rates were measured with a calibrated Venturi and low flow rates were measured with a high-pressure rotameter. Feed was introduced with a Hydropulse pump rated at 3 1/2 gal per min. This capacity was sufficient to permit a large portion of the circulation stream to be let down to atmospheric pressure, mixed with product water, and returned to the loop, thus minimizing concentration changes during a run.

Porous carbon tubes were used as support for the dynamic membranes; they were 20 in. long, 0.39 in. o.d., 0.24 in. i.d., and were capable of withstanding a pressure of 1000 lb/in. when pressurized internally.

For most of the tests, the membrane was formed by circulating a solution of 0.0001 *M* hydrous zirconium oxide, 0.015 to 0.04 *M* $MgCl_2$, and sufficient HCl to give a pH of 3 through the carbon tube at a linear velocity of 5.8 ft per sec (a Reynolds number of about 13,000) under a pressure of 600 psig. After a membrane formation period of 16 to 18 hr, the membrane was sufficiently stable to give reproducible results for circulation velocities from 1/2 to 18 ft per sec using the same feed composition as during the membrane-forming portion of the run. Rejections were computed from chloride analysis of samples taken from the feed solution and the effluent from the carbon tube.

Results

Observed rejections for hydrous zirconium oxide dynamic membranes were determined for axial velocities from 100 to 1000 cm/sec ($6000 \leq N_{Re} \leq 60,000$) for membranes with intrinsic rejections, (R_∞), from 80 to 99% and fluxes from 0.09 to 0.34 cm³/min (32 to 120 gal/ft²-day).

The membranes used in the present studies were formed following the procedure described by Shor, *et al.* (1968a,b). The concentration dependence of rejection was determined by extrapolating to infinite circulation velocity on a plot of $\ln [(1 - R_{obsd})/R_{obsd}]$ vs. $v/u^{1/2}$. (At infinite circulation velocity, concentration polarization is by definition 0 and $c_p = c_t$.) Results in the present study (Figure 1) were parallel to and about 20% above the curve for $MgCl_2$ obtained by

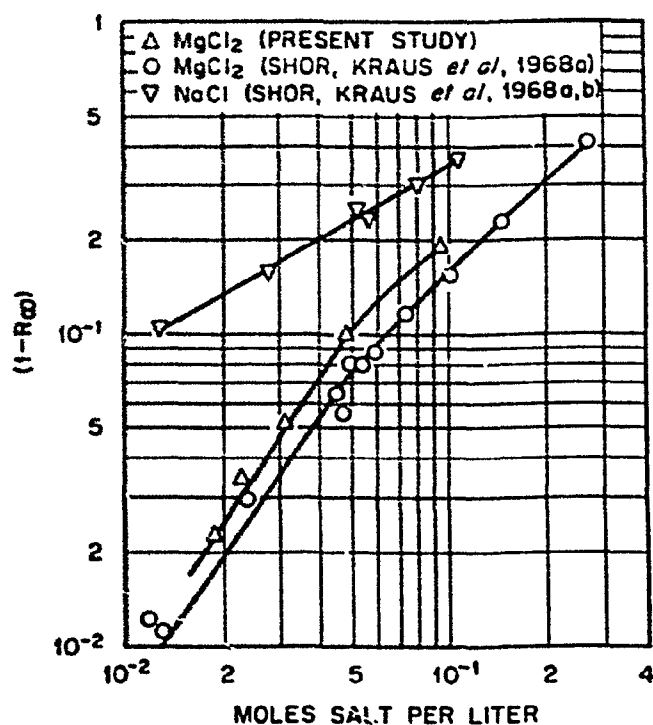


Figure 1. Concentration dependence of intrinsic rejection of Zr(IV) dynamic membranes

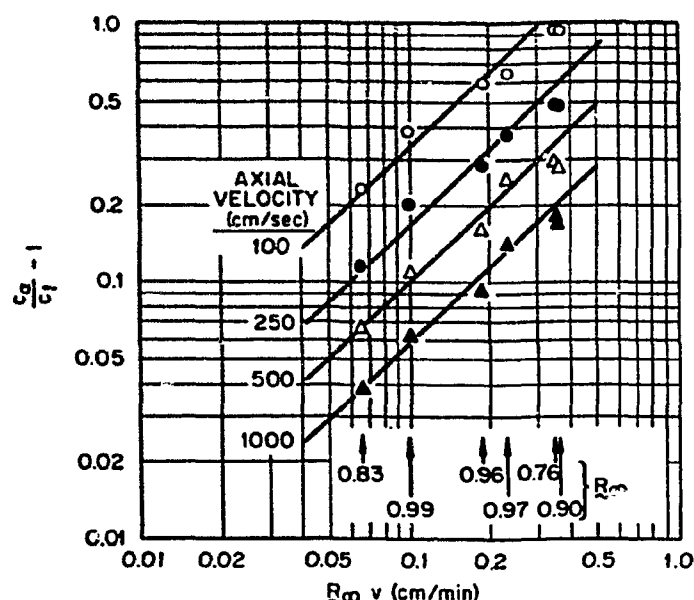


Figure 2. Effect of axial velocity, flux, and rejection on concentration polarization. (Tube diam, 0.60 cm; $N_{sc} = 800$, solid lines from eq 13)

Shor, *et al.* (1968a,b). For the range of concentrations of interest in the present study, the value of n in eq 7 was 1.57.

Values of the ratio c_a/c_t were calculated for each velocity by iteration using the observed rejection, the experimentally determined concentration dependence of the intrinsic rejection, and the identity

$$\frac{c_a}{c_t} = \frac{1 - R_{obsd}}{1 - R_u} \quad (20)$$

The results of the calculation are shown in Figure 2 plotted as $[(c_a/c_t) - 1]$ vs. $R_0 v$ with axial velocity, u , as a parameter, coordinates suggested by eq 13. The solid lines were calculated from eq 13 using a value of $K = 25$ (Shor, *et al.*, 1968a). The agreement between the approximate curve, eq 13, and the experimental concentration polarization is quite good for the range of velocities 100 to 1000 cm/sec.

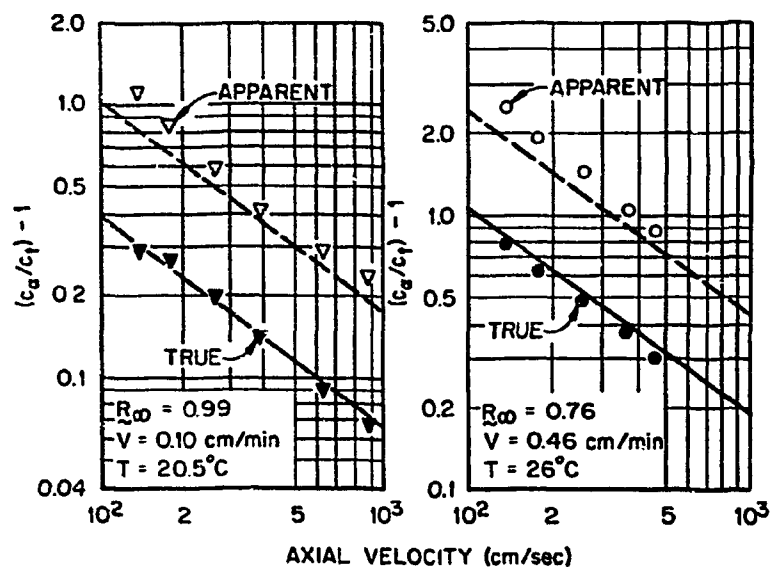


Figure 3. Comparison of true and apparent concentration polarization for hyperfiltration with ion-exchange type membranes. (Solid line from eq 13; dashed line from eq 19)

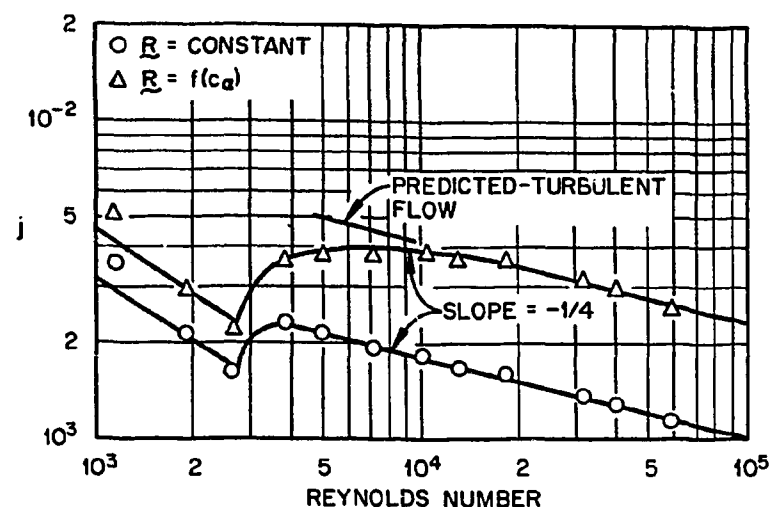


Figure 4. Comparison of hyperfiltration j -factor for ion-exchange type membrane assuming constant and variable intrinsic rejection. ($R_0 = 0.90$; $v = 0.34$ cm/min; $T = 30^\circ\text{C}$)

The magnitude of the error of not taking into account the dependence of intrinsic rejection on concentration at the membrane-solution interface is illustrated in Figure 3. The open points are the apparent concentration polarization calculated assuming $R = R_0$, while the solid points are the true concentration polarization calculated using the iteration procedure described above. The solid lines (true concentration polarization) on this figure were calculated from eq 13, while the dashed lines (apparent concentration polarization assuming $R = \text{constant}$) were calculated from eq 13 and 19. The agreement of eq 13 with the results for the true concentration polarization is quite good, even for the results on the right, which had flux of 0.46 cm/min and a rejection of only 76%, extreme conditions considering the approximations involved in eq 13. The agreement of the curve for the apparent concentration polarization with the calculated results is not as good as is desirable.

The calculation of c_a/c_t also gave values of the intrinsic rejection at finite velocity, R_u , which permitted a test of eq 16, the approximate equation for the effect of axial velocity on observed rejection for ion-exchange type membranes. Figure 4 is a plot of the hyperfiltration j -factor vs. Reynolds

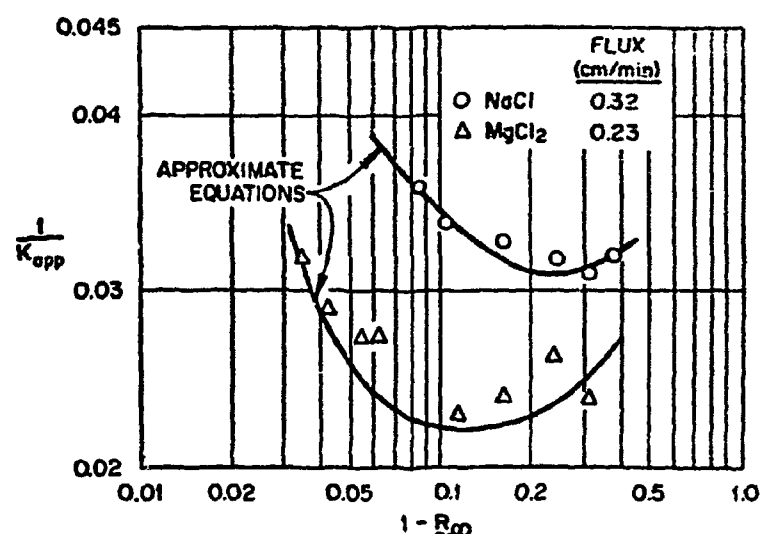


Figure 5. Estimation of apparent coefficient in ion-exchange type membranes. (Data of Shor, *et al.*, 1968a; solid curve calculated from eq 18; points calculated assuming $R_{\infty} = \text{constant}$)

Table I. Experimental Values of Coefficients in Concentration Polarization Equations

	v , cm/min	N_{Sc}	R , %	K^a
Sherwood, <i>et al.</i> (1967)	0.03–0.04	600–750	60–99	21, 36
Rosenfeld and Loeb (1967)	0.10–0.15	585	85–97	42, 45
Richardson, <i>et al.</i> (1968)	0.06–0.09	600	95–97	22, 30
Shor, <i>et al.</i> (1968a)	0.2–0.3	600–820	60–96	21, 23
Hamer (1969)	0.06	730	95	42
Richardson, <i>et al.</i> (1970)	0.06	610	97	38
Sheppard and Thomas (1970b)	0.08	580	92	44
Present study	0.09–0.46	650–1000	80–99	20–29
Average and maximum deviation				32 +40% –38%

^a K = experimental value of coefficient in eq 1 and 2.

number for an ion-exchange type dynamic membrane having intrinsic rejection, $R_{\infty} = 0.90$, and a flux of 0.34 cm/min. Two sets of points are shown on Figure 4, one calculated assuming that the intrinsic rejection was a constant independent of velocity, and the other calculated from the true value of the intrinsic rejection, R_u . Both sets of points follow a $-1/4$ slope for Reynolds numbers greater than 10^4 , as expected from eq 17. The ratio of the results for Reynolds numbers greater than 10^4 , using the two assumptions for the intrinsic rejection, is, within experimental error, the value calculated from eq 18. The $-1/4$ slope for both curves substantiates the linear extrapolation of results on a plot of $\ln [(1 - R_{obsd})/R_{obsd}]$ vs. $v/u^{3/4}$ to obtain the intrinsic rejection at infinite circulation velocity as was originally proposed by Shor, *et al.* (1968a).

A further test of the approximate relations of the present paper is afforded by the extensive results of Shor, *et al.* (1968a), which were obtained with two different salts (hence different values of n in eq 7), each at substantially constant flux but with a wide range of feed concentrations so that the intrinsic rejection covered a range $0.59 < R_{\infty} < 0.97$. Shor,

et al. (1968a), data were recalculated in the j -factor form (eq 17) assuming a constant intrinsic rejection, R_{∞} . Values of K_{app} (eq 18) determined from the best line through the j -factor points are shown in Figure 5 plotted vs. $1 - R_{\infty}$. Shor, *et al.* (1968a), calculated a single value for K (eq 2) which fitted all their data for a given salt; $K = 21.4$ for NaCl and $K = 23.2$ for MgCl₂. Using these values together with the experimental values for R_{∞} and values for n determined from Figure 5 of the paper by Shor, *et al.* (1968a), the curves shown in Figure 5 were calculated from eq 18. The agreement of the calculated curves and the experimental values for K_{app} appears to be within the precision of the experimental values.

Although there is considerable evidence (Sherwood, *et al.*, 1967; Rosenfeld and Loeb, 1967; Shor, *et al.*, 1968a; Richardson, *et al.*, 1968; Sheppard and Thomas, 1970b) that experimental hyperfiltration results are in satisfactory agreement with the Reynolds number dependence predicted by eq 1 and 2, only Shor, *et al.* (1968a), have attempted to verify the value of the numerical coefficient in these equations. Values of the coefficient can be determined in at least two ways. Since, for the time being, the coefficient is assumed to be unknown, simultaneous solution of eq 2 with data for two different velocities in fully developed turbulent flow will yield the desired result; or alternatively the slope-intercept method proposed by Shor, *et al.* (1968a), may be used to evaluate the intrinsic rejection independent of the value of the numerical coefficient. The coefficient can then be evaluated by substitution of the intrinsic rejection in eq 2 or the j -factor may be calculated from eq 17 and the coefficient evaluated from the results that are clearly in fully developed turbulent flow using a plot such as that shown in Figure 4. Data from the literature and the present results have been evaluated using the slope-intercept procedure and the j -factor plot to obtain the coefficients given in Table I. The present results for the coefficient in eq 1 and 2 have a mean of 24.5 with a maximum deviation of $\pm 20\%$ which supports the use of 25 as a coefficient in eq 13 to calculate the solid lines in Figures 2 and 3. However, when the aggregate results given in Table I are combined with the present ones, they give a mean value of 32 for the coefficient in eq 1 and 2 with a maximum deviation of $\pm 40\%$ and -38% . The extent of the deviation is not surprising since, as pointed out in the introduction, McAdams (1954) recommended equations for turbulent-forced convection heat transfer correlate the data with a maximum deviation of $\pm 40\%$.

Discussion

Approximate equations were developed for estimation of concentration polarization of ion-exchange type membranes, with turbulent flow for the limiting conditions of high rejection and low flux. Comparison of the approximate equations with experimental results, corrected for the concentration dependence of intrinsic rejection, showed satisfactory agreement for rejections as small as 76% and fluxes as large as 0.46 cm/min (~ 160 gal/(ft²-day)). As expected from the nature of the approximations, the best agreement was obtained for rejections greater than 90% and fluxes less than 0.20 cm/min, although the error for maximum flux and minimum rejection in the present study was less than 20%.

Because of the not unexpected $\pm 40\%$ range in experimental values for the coefficient in eq 1 and 2, the recommended procedure for evaluating the concentration polarization is to first determine the intrinsic rejection at infinite circulation velocity on a plot of $\log [(1 - R_{obsd})/R_{obsd}]$ vs. $v/u^{3/4}$ and then determine the value of intrinsic rejection

at finite velocity using the procedures of the present paper [or the more precise ones suggested by Shor, *et al.* (1968a)] when the membrane is the ion-exchange type or the procedure suggested by Sheppard and Thomas (1970b) when the membrane is neutral; finally calculate c_m/c_i from eq 20.

The present results confirm the previous analysis of Shor, *et al.* (1968a), in which linear extrapolation on a plot of $\ln [(1 - R_{obs,d})/R_{obs,d}]$ vs. $r/u^{1/2}$ was used to obtain the value of the intrinsic rejection at infinite circulation velocity for ion-exchange type membranes. As shown by the approximate equations, the effect of the concentration dependence of intrinsic rejection is reflected primarily in the value of coefficient K of eq 16 and 18, and does not affect the value of the exponent on flux or velocity and hence the extrapolation to infinite circulation velocity on a plot of $\log [(1 - R_{obs,d})/R_{obs,d}]$ vs. $r/u^{1/2}$.

Nomenclature

- C^* = membrane capacity, equiv/kg of H_2O in exchanger
 c_m = concentration at membrane-solution interface, mole/kg of H_2O
 c_i = concentration in turbulent core, mole/kg of H_2O
 c_p = concentration of product, mole/kg of H_2O
 D_m^* = equilibrium distribution coefficient, dimensionless
 j = hyperfiltration j -factor, dimensionless
 J = flux, gal./ft²-day
 K = coefficient in eq 1
 K_{app} = coefficient in eq 18
 m_s = moles of solute/kg of H_2O
 n = eq 7
 N_{Re} = Reynolds number, dimensionless
 N_{Sc} = Schmidt number, dimensionless
 $R_{obs,d}$ = observed rejection, dimensionless
 R = intrinsic rejection, dimensionless
 R_u = intrinsic rejection at velocity, u , dimensionless
 R_∞ = intrinsic rejection at infinite circulation velocity, dimensionless

- u = axial velocity, cm/sec
 v = flux, cm/sec
 z = charge of ion with same sign as membrane fixed charge

GREEK LETTERS

- Γ_m = γ_m^*/γ_s
 γ_m^* = mean ionic activity coefficient of salt in membrane
 γ_s = mean ionic activity coefficient of salt in solution

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5.2 CONCENTRATION POLARIZATION WITH NEUTRAL SOLUTES

In our last biennial, (see Ref. 15, p. 266 ff), we reported some results from a study of the effect that concentration polarization had on hyperfiltration of a neutral solute, sucrose. We attempted to establish an experimental value for the "Colburn parameter"⁴² by measuring rejection and flux as a function of circulation velocity for hydrous Zr(IV) oxide single-layer membranes. Rejections of neutral solutes have appeared to be less dependent on feed concentrations than rejections of salts, and it was hoped that use of sucrose would diminish the complications in our earlier studies of concentration polarization with salt solutions,⁸ without sacrificing the advantages of high fluxes in testing theory. The data at that time had considerable scatter, and there appeared to be, contrary to expectations,⁴³ some dependence of rejection on sugar concentration. The dependence, if real, was in the opposite direction from that of electrolytes, sucrose rejection increasing with increasing feed concentration. Such a dependence has been reported for cellulose acetate.⁴⁴

We were fortunate during this investigation to have help from an MIT Practice School Team,* and this team investigated concentration polarization with neutral solutes. Heman and Bronfenbrenner modified the equations of Shor et al.⁸ to accommodate concentration polarization in annular flow systems, arriving at:

$$\ln \left\{ \frac{1 - R_{\text{obs}}}{R_{\text{obs}}} \right\} = K \left\{ \frac{d_2 - d_1}{\eta_K} \right\}^{1/4} \left\{ \frac{\eta_K}{D} \right\}^{2/3} \left\{ \frac{v}{\bar{u}^{0.75}} \right\} + \ln \left\{ \frac{1 - R}{R} \right\} \quad (1)$$

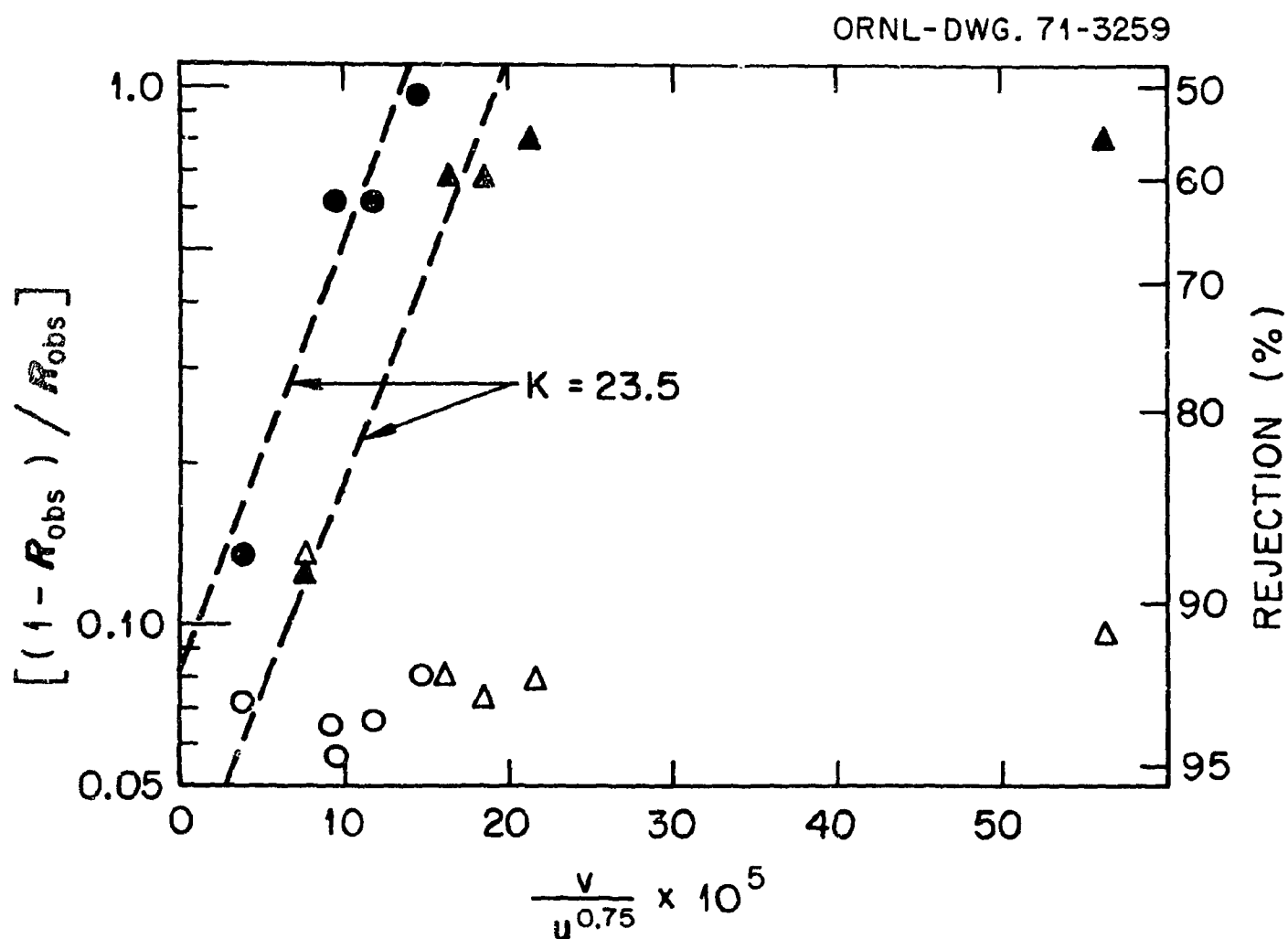
where R_{obs} is the observed rejection, K is the "Colburn parameter," d_1 and d_2 are the inside and outside diameters of the annulus, respectively, in cm, η_K is the kinematic viscosity, D is the solute diffusion coefficient in the solution phase, v is the permeation rate in cm/min, $\bar{u}$ is the circulation velocity in cm/min, and R is the intrinsic rejection. R can, in principle, be extracted from the data by extrapolating a plot of $\ln (1 - R_{\text{obs}})/R_{\text{obs}}$ vs $v/\bar{u}^{0.75}$. The intercept at $v/\bar{u}^{0.75} = 0$ is equal to $\ln(1 - R)/R$ and the Colburn parameter, K , can be evaluated by measuring the slope.

*The team members were A. J. Heman and J. C. Bronfenbrenner. The Oak Ridge Station of the MIT School was directed by John Day with the assistance of P. H. Wadga.

In common with the earlier work, (see Ref. 15, p. 266 ff), the MIT group found wide scatter in their data as well as some evidence for a dependence of rejection on sucrose concentration. They tried both single-layer hydrous Zr(IV) oxide membranes and dual-layer hydrous oxide-PAA membranes on a variety of Millipore and Acropor porous supports. They did not achieve reproducible results with the Zr(IV) membranes.

Once a hydrous oxide membrane had been exposed to sucrose solution, it became impossible to form a good dual-layer hydrous oxide-PAA membrane, especially if the sucrose was still in the feed solution when PAA was added. However, when good dual-layer membranes were formed in the absence of sucrose, they behaved as expected toward 0.05 $\underline{\text{M}}$ NaCl even after sucrose was added to the feed. On these membranes, the rejection of sucrose, as determined by organic carbon analysis, declined with time from about 90% to 50%, while the concurrent rejection of 0.005 $\underline{\text{M}}$ NaCl, measured by conductivity, remained relatively steady at about 93%. A plot of the data for two of the seven membranes formed in this run is shown in Fig. 5.1. The dotted lines have a slope corresponding to a Colburn parameter of 23.5, an empirical estimate from heat transfer. These lines extrapolate to an intrinsic rejection of 92% for the 0.05- μ Millipore support and about 97% for the 0.45- μ Acropor AN support, but the scatter is such that little reliance should be placed on these numbers. The reason for a lack of self-consistency in the data is not known, but it is probable that the membranes under the conditions of these runs were constantly changing and did not have a characteristic intrinsic rejection.

In another experiment, we formed Zr(IV)-PAA membranes with Acrysol A-5 PAA, and tested them with sucrose solutions. We added 5000 ppm of sucrose to a 0.005 $\underline{\text{M}}$ NaCl solution and measured rejection and flux at several different circulation velocities. Pressure was maintained constant at 950 psig. Results for four of the membranes are shown in Fig. 5.2. The solid lines have a slope corresponding to a Colburn parameter equal to the theoretical value 23.5, the dotted lines are approximate best fits of the points and all indicate a Colburn parameter much lower than 23.5. The dotted lines extrapolate to the intrinsic rejections listed in Table 5.1.

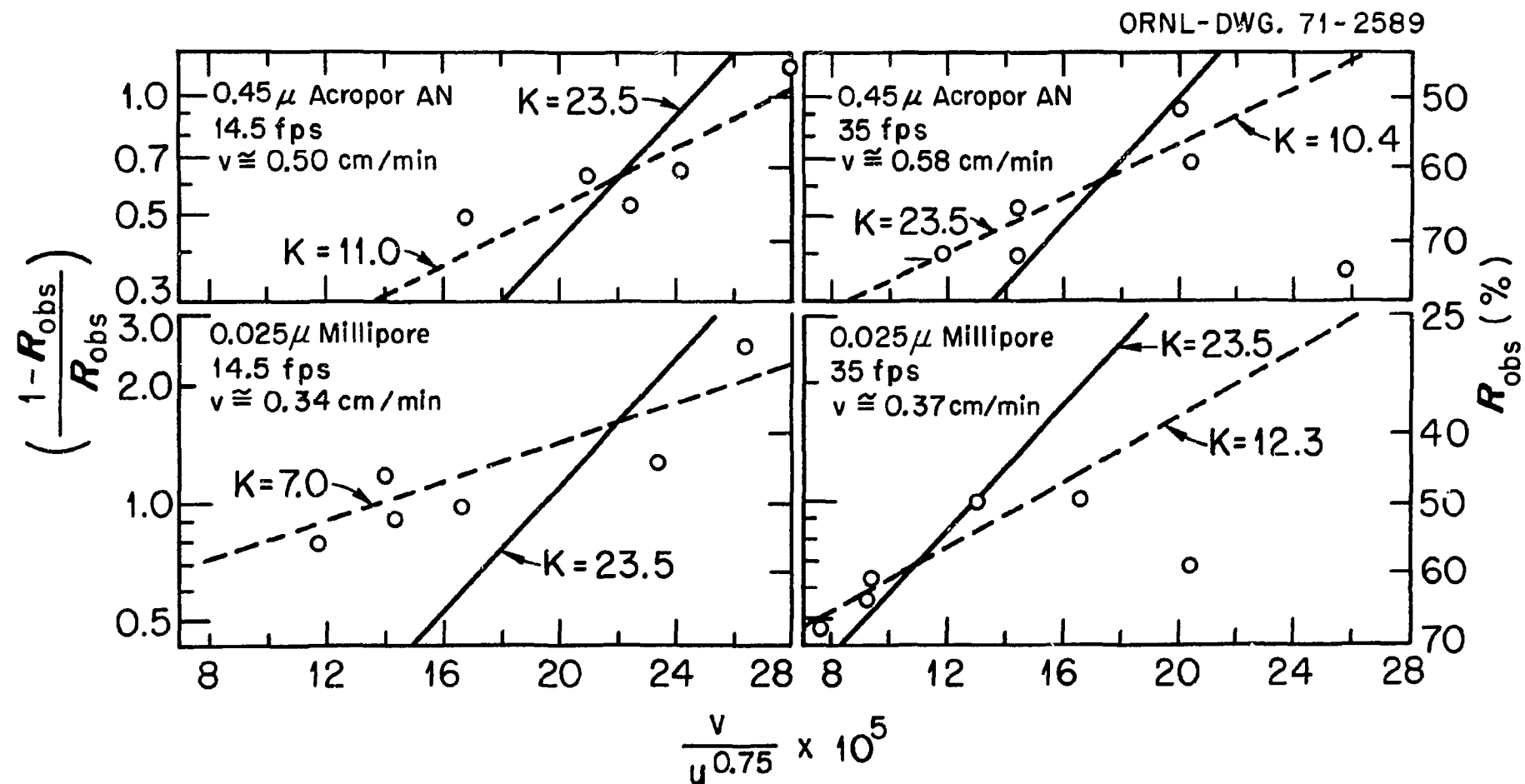


$[(1 - R_{\text{obs}}) / R_{\text{obs}}]$ versus $v/u^{0.75}$ for
1000 ppm sucrose in 0.005M NaCl.

(Zr(IV) hydrous oxide - Acrysol A-3
membranes, 950 psig, pH ~ 7)

R_{obs} By	0.05 μ Millipore ($v \cong 0.48$ cm/min)	0.45 μ Acropor AN ($v \cong 0.62$ cm/min)
Conductivity	○	△
Organic Carbon	●	▲

Fig. 5.1



$(1-R_{obs})/R_{obs}$ versus $v/u^{0.75}$ for 5000 ppm sucrose
in 0.005 *M* NaCl.

(Hydrous Zr(IV) oxide-Acrysol A-5 membranes,
950 psig, pH ~ 7.5)

Porous support and formation velocity indicated.

Fig. 5.2

These data also have much scatter, and again suggest that there is appreciable time-dependence in the behavior of these membranes toward sucrose solutions.

Drift in membrane properties precludes inferences concerning the value of the Colburn parameter and its possible dependence on membrane flux (see preceding Section 5.1).

TABLE 5.1
INTRINSIC REJECTIONS OF SUCROSE BY DUAL-LAYER HYDROUS ZR(IV) OXIDE-ACRYSOL
A-5 DYNAMIC MEMBRANES
(5000 ppm sucrose in 0.005 M NaCl, 950 psig, pH $\sim$ 7).

Formation Velocity	<u>0.025-μ Millipore</u>	<u>0.45-μ Acropor AN</u>
14.5 fps	68	92
35 fps	81	87

6. Economic Analyses

Summary

We have previously assessed hyperfiltration by membranes having assumed properties typical of available dynamic membranes. These analyses have been parametric and have been aimed primarily at finding conditions under which use of high-flux membranes of moderate rejections might be advantageous.⁴⁵ Other studies, including Section 6.2 to follow, were aimed at defining when use of more than one stage was feasible.⁴⁶ For these purposes most capital amortization costs and operating expenses (the major exception being energy) were combined in a single variable $\underline{C}_A$, a daily cost per square foot of membrane surface, and numbers which seemed reasonable were assumed for this figure. With our increasing concentration on Zr(IV)-PAA membranes, it becomes possible to visualize more clearly possible configurations of practical installations and to define better the various components of $\underline{C}_A$. Analysis also becomes more needed for location of major cost centers and for guidance of development effort.

A reprint of a paper on the economic analysis of Donnan softening by L.Dresner is given in Section 6.3.

6.1 PRELIMINARY ECONOMIC ANALYSIS

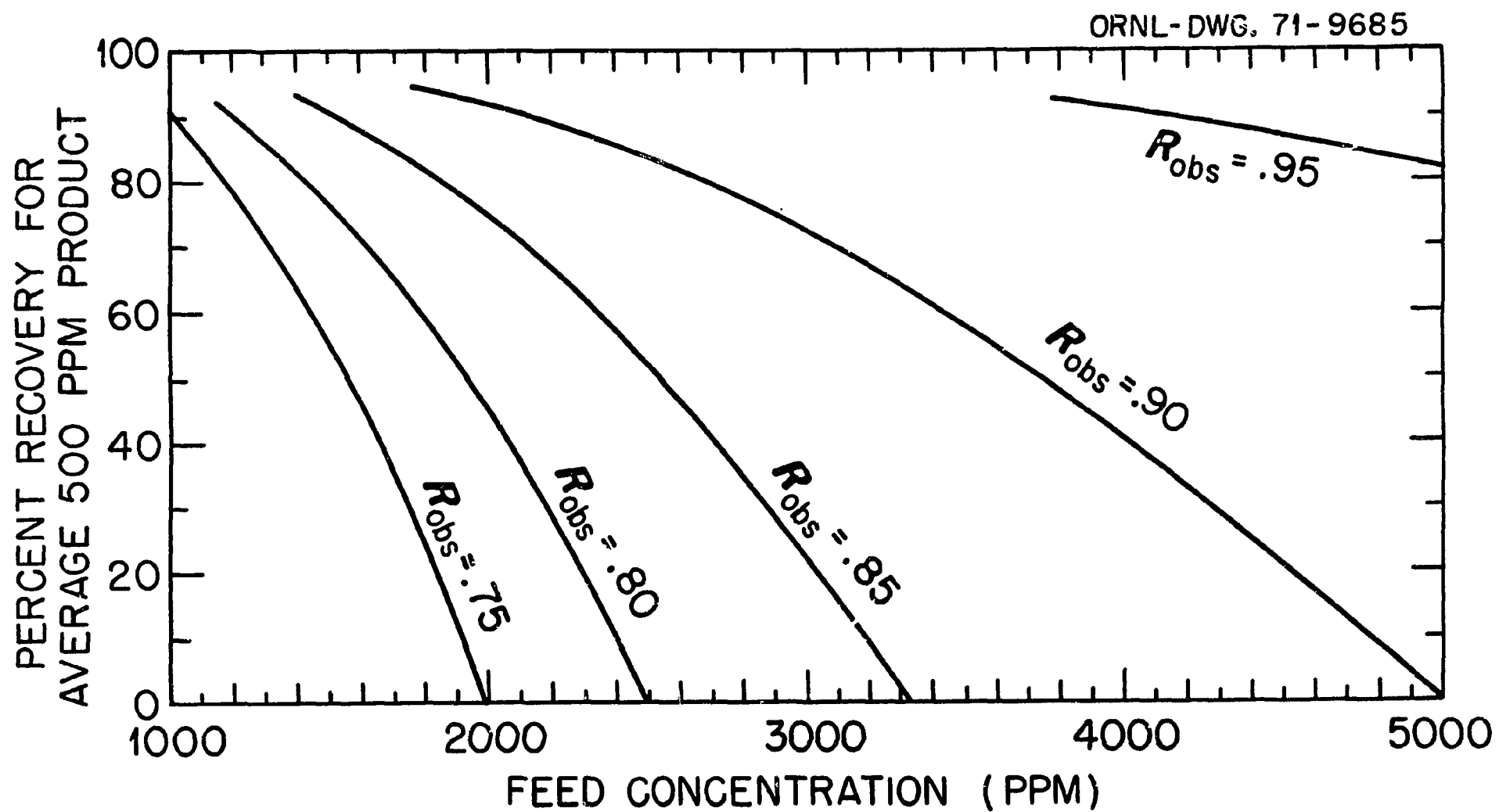
We outline here the results of a preliminary analysis* in which the characteristics of the plant and assumptions concerning membrane performance were selected in view of experience with Zr(IV)-PAA membranes in laboratory experiments utilizing potentially practical porous supports and simulated natural brackish water feeds. A more detailed analysis, which is based on experience with Roswell pilot plant⁷, and which utilized more up-to-date cost parameters, is underway. The results presented here are tentative, but the variations of water cost with membrane flux, plant size, and circulation velocity, may be of interest. The computations were referenced to a million-gallon-per-day plant, utilizing membranes producing an average of 50 gfd in operation at an average pressure of 850 psig

*This analysis was done by P. H. Wadia, at that time (1971) with the MIT Practice School, during summer employment by the Water Research Program.

(minimum 550, maximum 1100 at various points in the system) and an average circulation velocity of 14 fps (minimum 11, maximum 17), product being 70% of feed water. Interest rate of 4.6% and plant life of 30 years were assumed. In the plant layout, the most uncertain equipment cost was that of the membrane modules; these were estimated from analogy with a tube-in-shell heat exchanger, as we did in an analysis of cross-flow filtration.⁵ Pressurized feed is on the outside of the tubes supporting the membranes. Variations of product water cost with plant size, circulation velocity, and cost of electricity were investigated. No pretreatment or brine disposal costs are included.

With typical brackish water compositions, rejections by Zr(IV)-PAA membranes have been insensitive enough to concentration to justify neglect of variations for present purposes. Further, the primary consideration in selection of circulation velocities was what our experience has indicated may be necessary for maintenance of flux. Under the conditions assumed, the effect of concentration polarization on rejection is not great. For a membrane of 90% intrinsic rejection (R_i), the largest effect in the cases treated would be for flux of 200 gfd and 10 fps average circulation velocity; observed rejection would be about 85%. The computations do not take explicit account of concentration polarization. Neglect of effect on rejection of salt concentration and concentration polarization greatly simplifies computations in comparison with the earlier parametric analyses.^{45, 46}

The primary significance of rejection here is to limit the feeds accessible to treatment for given specifications of product concentration and product recovery. Figure 6.1 summarizes the recoveries attainable in single-stage operation with product averaging 500 ppm as a function of feed concentration, for different values of R_{obs} . Rejections of Zr(IV)-PAA membranes are affected by relative amounts of various ions in feeds, as well as by other variables, but overall rejections of 90% are not rare. Rejection of 90% would imply that 70% recovery should be feasible for feeds at least up to 3000 ppm.

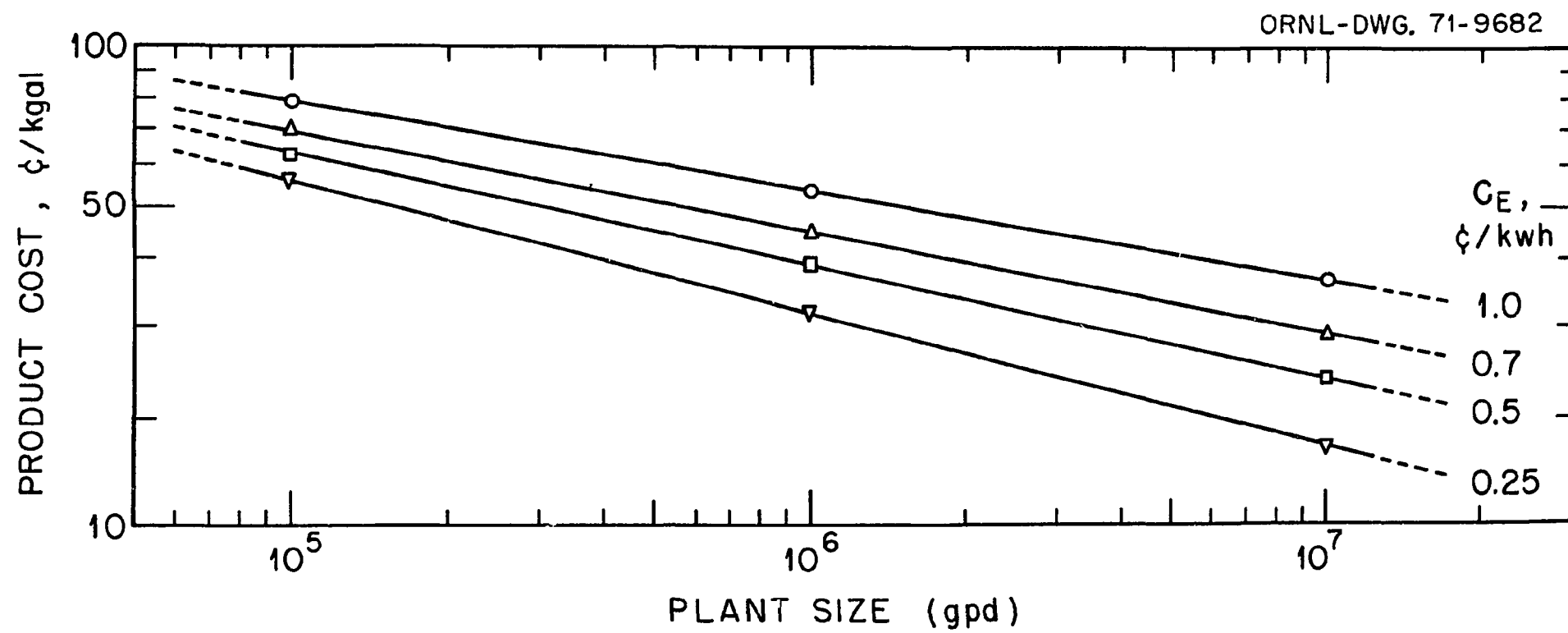


RECOVERY AS FUNCTION OF FEED CONCENTRATION
AND REJECTION

Fig. 6.1

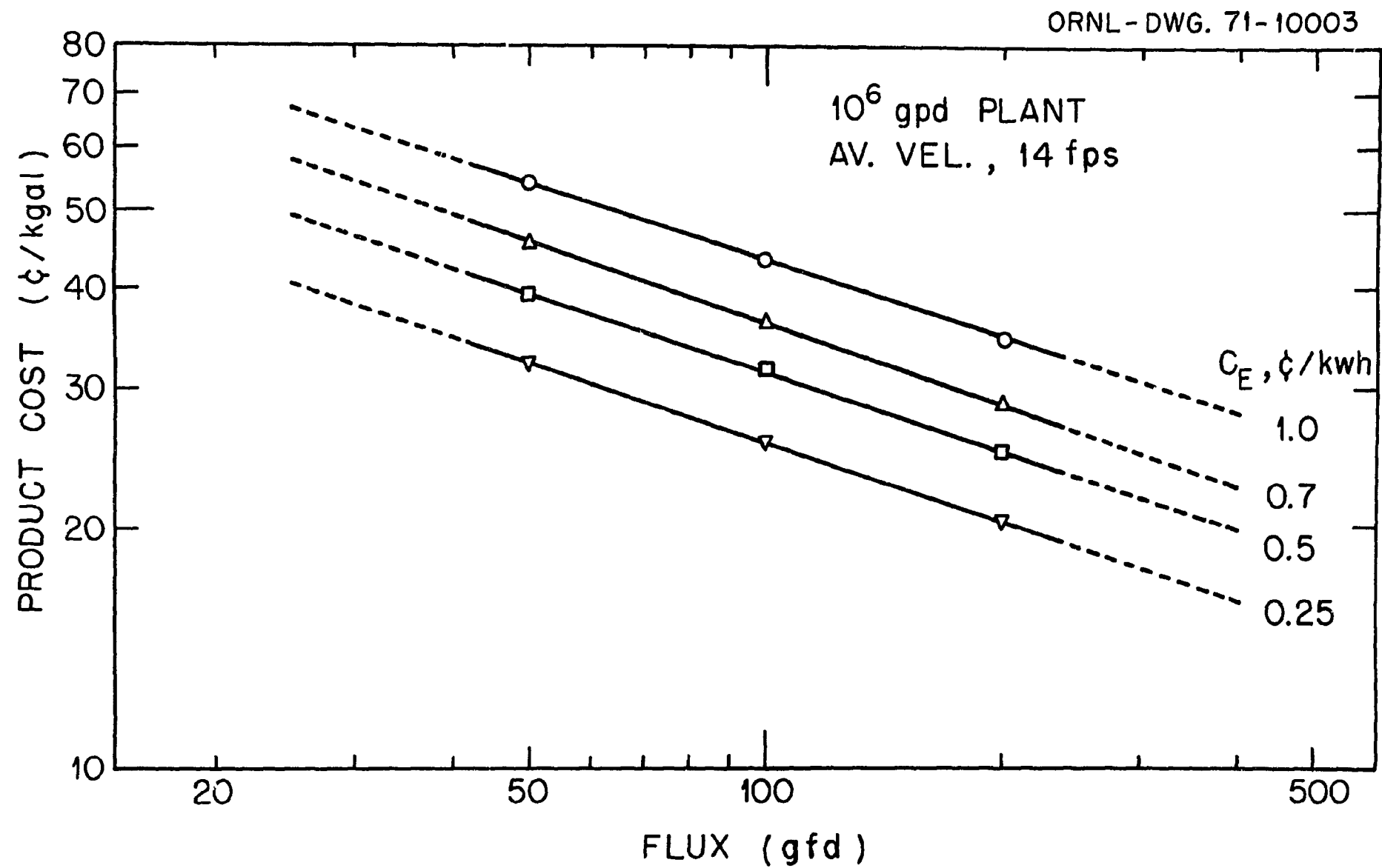
A more detailed analysis based on experience with the Roswell pilot plant is underway⁷, and the results presented here are tentative. We summarize the dependence of product cost on plant size (Fig. 6.2), on average flux (Fig. 6.3), and on circulation velocity (Fig. 6.4). As expected, costs decrease with increasing plant size, and the decrease indicated by Fig. 6.2 seems reasonable. For a given plant size, developments that increase flux would greatly decrease water cost (Fig. 6.3). Substantial advantages would also be realized if membrane flux can be maintained at lower circulation velocities, particularly down to 10 fps (Fig. 6.4). Membrane modules contribute from a third (100,000 gpd level) to half (10,000,000 gpd) the cost of desalting equipment (capital exclusive of building and land). Development of cheap supports would be helpful, but, since capital costs appear to contribute only about a third of total water costs, decreases in product costs attainable by decrease of module costs are somewhat limited.

Because of many uncertainties in this analysis, which could affect costs either way, comparison with other hyperfiltration concepts cannot be very reliable. With this reservation, it would appear in Fig. 6.5 that even though this analysis did not attempt to develop an optimized plant and even though far less effort has gone toward development of the dynamic membrane concept, comparison with recent projected costs for cellulose acetate are not unfavorable.



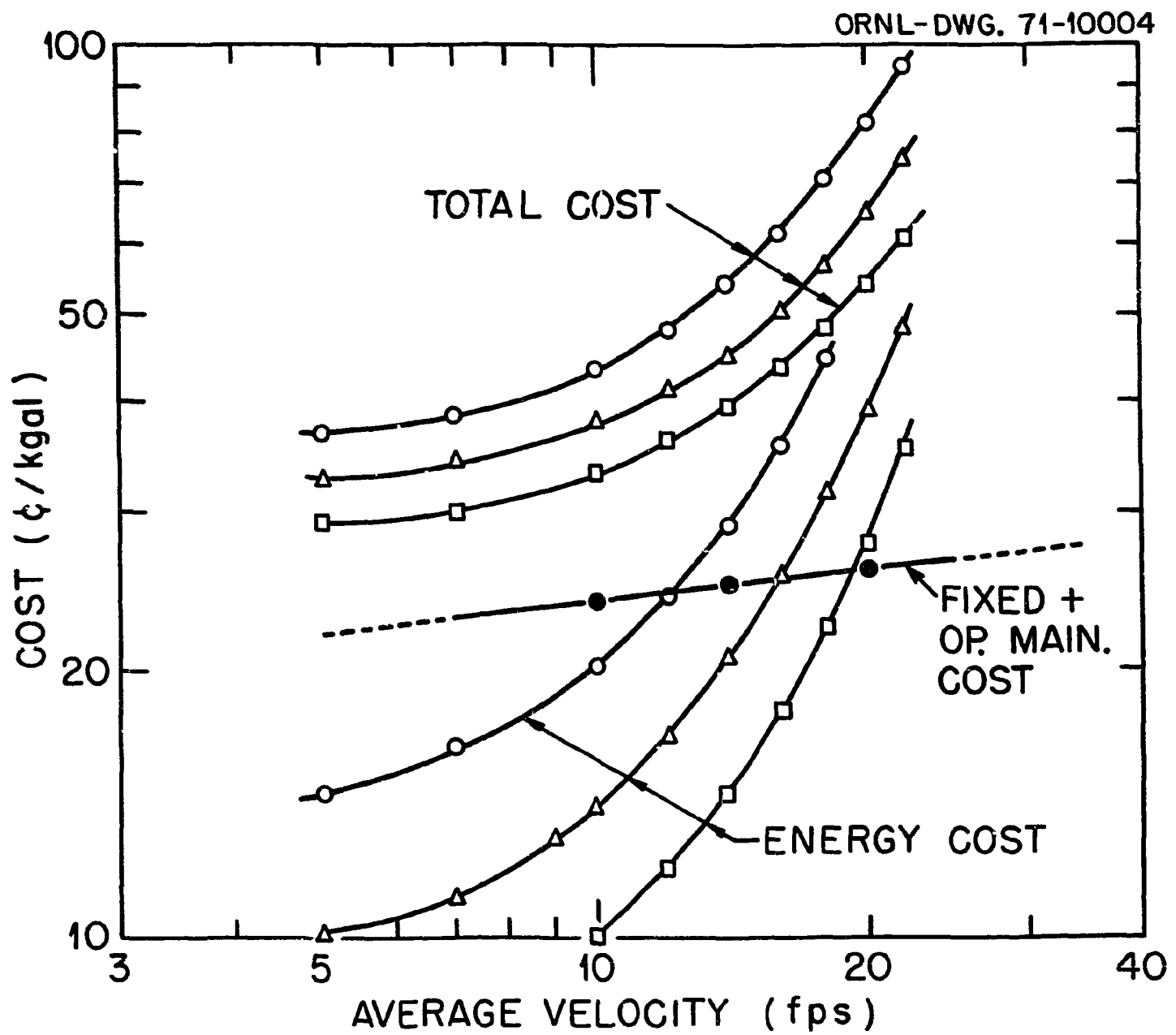
EFFECT OF PLANT SIZE AND ENERGY COST ON WATER COST
 (Flux, 50 gfd ; Circ. Vel., 14 fps ; Pressure, 825 psig)

Fig. 6.2



WATER COST AS A FUNCTION OF AVERAGE
FLUX AND UNIT COST OF ENERGY

Fig. 6.3

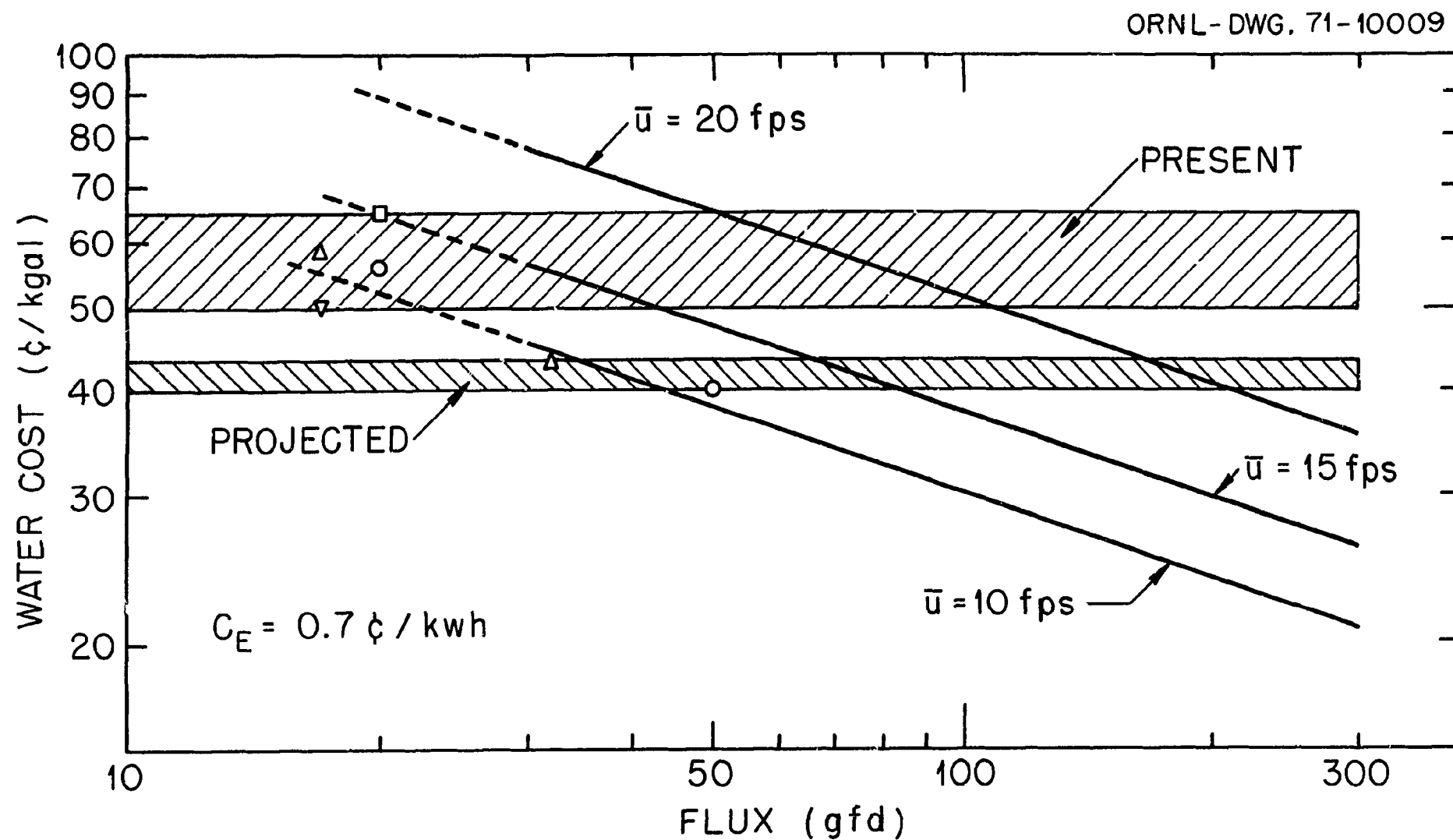


VARIATION OF WATER COST WITH AVERAGE CIRCULATION VELOCITY

C_E , ¢/kwh : $\circ$ 1.0, Δ 0.7, $\square$ 0.5

FLUX, 50 gfd ; PLANT SIZE, 10^6 gpd

Fig. 6.4



COMPARISON OF THIS STUDY WITH PRESENT AND
PROJECTED CELLULOSE ACETATE TECHNOLOGY

○ HARRIS⁴⁶, ◻ ALCALAY⁴⁷, △ HITTMAN⁴⁸, ▽ CLARK⁴⁹

Fig. 6.5

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6.2 MULTISTAGE HYPERFILTRATION PLANTS FOR THE DESALINATION OF BRACKISH WATERS*

Joseph J. Perona and Richard S. Dillon

SUMMARY

A computer program was developed which finds optimum inlet flow velocities and inlet pressures for hyperfiltration plants having as many enriching stages as necessary to produce water meeting product specifications. Stripping stages are used if high water recoveries are specified. Membranes with intrinsic rejections of 40 to 95% were studied with feed concentrations of 1000 to 5000 ppm. Optimum membrane permeabilities and water recoveries were found.

The optimum permeability for a 95% rejecting membrane with 5000 ppm feed is 18 gal/day · ft² · atm, which requires a two-stage plant. For a 75% membrane with 5000 ppm feed, and for 50 and 75% membranes with 1000 ppm feed, optimum permeabilities were ~ 5 gal/day · ft² · atm. As permeabilities up to 15 were studied, plants required up to 6 enriching stages. In comparison with plants using cellulose acetate-type membrane characteristics ($R = 0.95$, $\mathcal{P} = 0.5$, pressure limited to ~ 600 psig), costs range from slightly higher to much less with the moderately rejecting, high flux membranes in multistage plants.

Flow velocities, pressures and water recoveries which result in a minimum cost for a given membrane often do not minimize the number of stages required. Optimum permeabilities did not coincide with minimum stages. Therefore, a reduction in stage requirements is not in itself a valid means of cost reduction.

INTRODUCTION

A large number of researchers throughout the world are currently engaged in studying the hyperfiltration properties of many different polymers. Organic and

* Research conducted at the Oak Ridge National Laboratory and jointly sponsored by the U.S. Atomic Energy Commission and the Office of Saline Water, U.S. Department of the Interior.

inorganic materials, cast as films or dynamically deposited, are being studied. Criteria for separating the economically-promising materials from the unpromising ones have not been available. Clearly, membranes giving very low intrinsic rejections ($< 50\%$) and having very low permeabilities ($< 0.5 \text{ gal/day} \cdot \text{ft}^2 \cdot \text{atm}$) can be classed as unpromising. The classification of moderately rejecting membranes with high permeabilities is an objective of this work. Optimum operating conditions for many combinations of membrane rejection, permeability and feed concentration are presented also.

In hyperfiltration, the passage of water through membranes which reject salt causes accumulation of salt near the membrane surface. Therefore, the observed rejection

$$R_{\text{obs}} = 1 - \frac{m_w}{m_t} \quad (1)$$

must be distinguished from the intrinsic rejection of the membrane

$$R = 1 - \frac{m_w}{m_\alpha} \quad (2)$$

Here m is the salt molality, and the subscripts w and α refer to the membrane surfaces (low and high pressure sides, respectively). The subscript t refers to the turbulent core of fluid. This polarization increases the salt concentration of the product and decreases the water flux through the membrane (by decreasing the effective pressure drop across the membrane). Concentration polarization can be reduced by establishing turbulent crossflow of the salt solution parallel to the membrane surface. Increasing the pressure on the salt solution increases flux and tends to decrease surface area requirements, but also increases the polarization effect. An optimal design requires a balance between the energy costs of pumping and the capital costs associated with pumps and membrane surface area requirements.

The existence of an optimum membrane permeability for a given membrane rejection was shown by Griffith, Keller and Kraus (1). Increasing the permeability causes a higher product rate at fixed operating pressure, but also increases the concentration polarization. Therefore, higher crossflow velocities are required to maintain the product concentration as membrane permeability increases. At some point the decreasing capital costs (due to lower membrane area requirements) are more than offset by increasing energy costs.

Perona, Pickel and Kraus (2) showed that the addition of a second stage increased the optimum permeability and resulted in lower product water costs than could be obtained with the same membrane rejection-permeability combinations of economic interest.

FLOWSHEET

A conventional single-entry cascade was the general scheme used (Fig. 1). The number of enriching stages is computed by the program for each case. Since the product concentration from a stage is not known *a priori*, the computer compares the product concentration with the product specification after the calculations for each stage are completed, and adds stages until the specification is met. Similarly, stripping stages (*i.e.*, stages operating on brine above the feed concentration) are added until the specified reject stream concentration is reached.

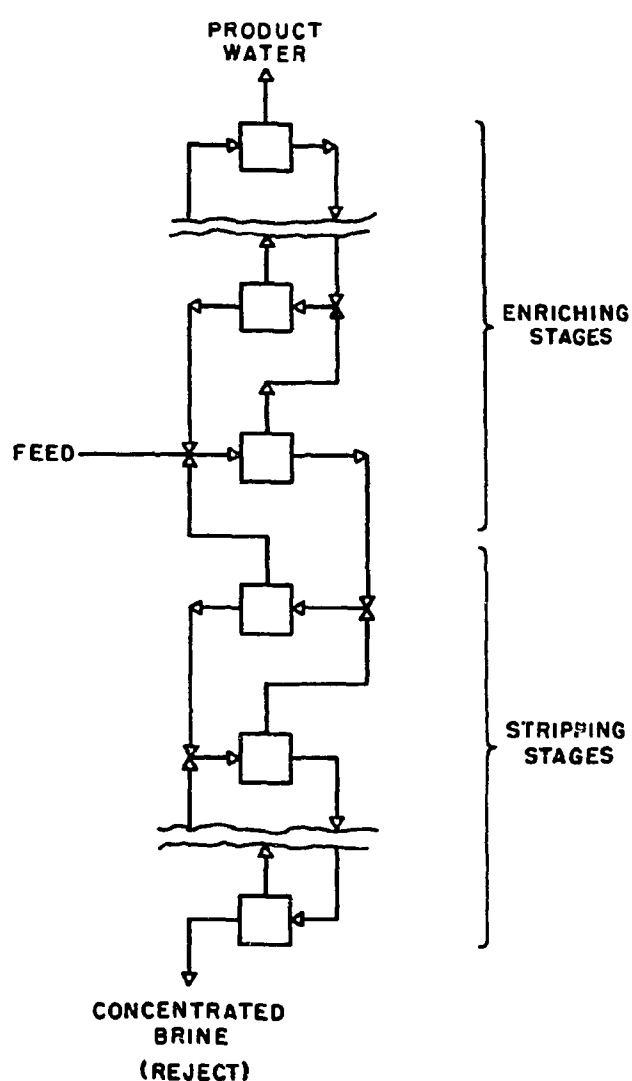


Fig. 1. Flowsheet of a multistage hyperfiltration plant.

Each stage can be divided into an arbitrary number of sections (Fig. 2). Pumps between the sections permit repressurizing the salt solution. Therefore, the inlet pressure for each section can be specified independently. Each section is composed of a number of membrane-lined tubes in parallel. The numbers of tubes in the sections are independent of each other, so that inlet velocities are independently variable.

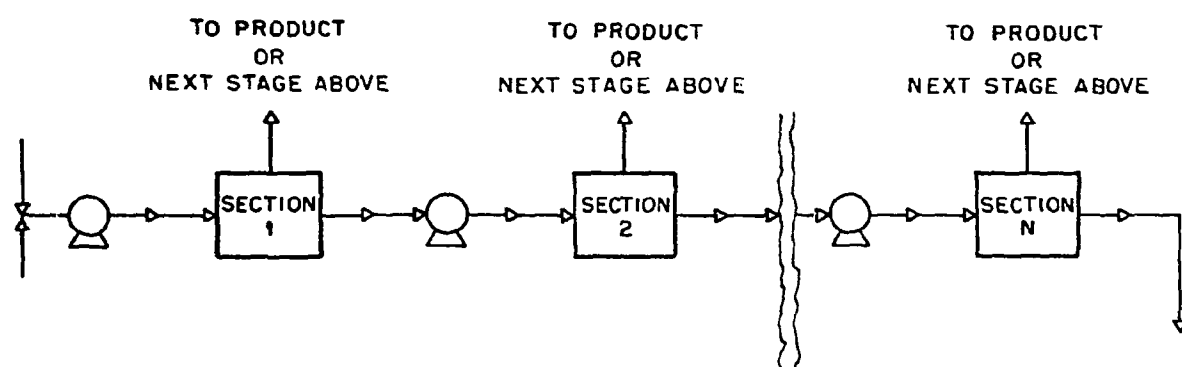


Fig. 2. Flowsheet of a stage divided into sections.

A stage can be divided into sections in various ways. The method used throughout most of this work was to keep the difference between entrance and exit concentrations constant for each stage. This method resulted in progressively decreasing section tube lengths as the concentration increased along a stage. Another method used was to maintain an equal ratio of outlet to inlet concentration for the various sections in a given stage. The latter method resulted in approximately equal section lengths, but product costs were only slightly lower for the second method.

If the product from at least one section of an enriching stage has a lower concentration than the product specification, and if one or more sections yield product at concentrations higher than specification, the products are blended to produce a stream at specification which is withdrawn from the cascade. The remaining product is fed to the next higher stage and the process continued until no over-specification product is generated.

The stream returning to the feed stage from the first stripping stage is blended into the section of the feed stage where its concentration is most closely matched. This concentration matching procedure is not used in the enriching section since it greatly lengthens computation time and did not decrease costs in the two-stage study (2).

MEMBRANE MODEL

The membrane model is very similar to the one in the two-stage code (2). The product of coupling coefficient β and the salt distribution coefficient D^* were related to concentration by

$$\beta D^* = A + B m_\alpha + C m_\alpha^2 + D m_\alpha^3 \quad (3)$$

Eq. 3 allows great flexibility in the membrane behavior through the choice of the constants A , B , C and D . The dependence of salt rejection on water flux J_1 through the membrane and to βD^* are given by

$$\frac{1}{R} - 1 = \left(\frac{e^{\beta\sigma}}{e^{\beta\sigma} - 1} \right) \left(\frac{\beta D^*}{1 - \beta D^*} \right) \quad (4)$$

where σ is a function of J_1 , the membrane thickness l and the diffusion coefficient of salt in the membrane D_2^* , namely

$$\sigma = \frac{J_1 l}{D_2^*} \quad (5)$$

Values of l and D_2^* for use in Eq. 5, and the effect of system variables on these values, are not well enough known to permit a detailed representation of Eq. 5. With dynamically-formed membranes, l is probably affected by hydrodynamic variables. As an expedient, Eq. 5 was reduced to

$$\sigma = K \cdot [P - (\pi_\alpha - \pi_w)] = K \cdot P_{\text{eff}} \quad (6)$$

where P is pressure, π is osmotic pressure, and α and w refer to the membrane surfaces (high and low pressure sides, respectively). Considerations which led to Eq. 6 are

$$J_1 \propto \mathcal{P} \cdot P_{\text{eff}} \quad (7)$$

where $\mathcal{P}$ is the membrane permeability, and

$$l \propto \frac{1}{\mathcal{P}} \quad (8)$$

and therefore $J_1 l$ is proportional to the effective pressure, P_{eff} . A value of unity was assumed for β . As σ becomes large, $(e^{\beta\sigma}/e^{\beta\sigma} - 1)$ approaches unity and R approaches a limiting value R_∞ . From Eq. 4, $1 - R_\infty = \beta D^*$. A value of K of 0.0415 atm^{-1} was used, which gives values of R/R_∞ at an effective pressure of 30 atm of 0.98 for $R_\infty = 0.95$, 0.90 for $R/R_\infty = 0.75$, and 0.85 for $R_\infty = 0.55$. The membrane model in the two-stage code (2) differs from the present model only in the method of calculating σ . Values of R/R_∞ for a gross value of R_∞ are slightly smaller with the present model.

ALGORITHM FOR A SECTION OF A STAGE

The following independent variables must be specified: inlet pressure, inlet velocity, recycle ratio, feed rate, tube diameter, concentrations of the salt solution entering and leaving the section, and membrane characteristics. The product rates and concentrations were calculated by an iteration of the following steps:

(1) The inlet pressure was taken as a first approximation to the average effective pressure in calculating the superficial velocity of water through the membrane, v , by

$$v = \mathcal{P} \cdot P_{\text{eff}} \quad (9)$$

and in calculating σ by Eq. 6.

(2) m_w was calculated from Eq. 4 and

$$\frac{1}{R_{\text{obs}}} - 1 = \exp \left[25 \frac{v}{\bar{u}} N_{\text{Re}}^{1/4} N_{\text{Sc}}^{2/3} \right] \left(\frac{1}{R} - 1 \right) \quad (10)$$

using the inlet value for $\bar{u}$ as a first approximation. Eq. 10, which was developed by Shor *et al.* (3), relates m_i and m_x through concentration polarization theory.

(3) The flow rates of the product stream and the concentrated stream were calculated by material balance.

(4) The membrane area was calculated from the product flow rate and v .

(5) The tube length was calculated from the membrane area, the number of tubes, and the tube diameter.

(6) The outlet velocity was calculated from the flow rate and the average squared velocity was calculated from

$$(\bar{u}^2)_{\text{av}} = \frac{\bar{u}_2^2 + \bar{u}_2 \bar{u}_1 + \bar{u}_1^2}{3} \quad (11)$$

where subscripts 1 and 2 refer to the inlet and outlet of a section. Eq. 11 was developed by Perona *et al.*, (2).

(7) The pressure drop across the section and outlet pressure were calculated. The friction factor was calculated from the Blasius equation, $f = 0.079(N_{\text{Re}})^{-1/4}$.

(8) The arithmetic average effective pressure in the section was calculated.

(9) v and σ were recalculated using the average effective pressure.

(10) m_x and m_w were recalculated, using an average value for $\bar{u}$.

(11) Steps 3 through 10 were repeated until successive values of v agreed within 10^{-4} gal/day ft².

MAIN HYPERFILTRATION PROGRAM

The main program first calculates the product rate and product concentration of each section in the feed stage. Then the product concentrations are compared with the feed concentration to the plant. If any are larger, they are compared to the feed concentrations to the sections of the first stage and blended with the one which has a concentration most nearly like it. Thus, sections whose products are recycled in this way become stripping stages, and the original number of sections in the feed stage is diminished. If the products of more than one section are recycled to the same point, a multisection stripper stage is created.

If the testing of product concentrations reveals that a stripping stage is required, the subsequent blending of the recycle stream changes the original feed concentration and flow rate to the feed stage, which affects all streams in the feed and stripper stages. Therefore, an iteration procedure must be set in motion which is continued until the error in the material balances is small.

The need for enriching stages is ascertained by comparing the product

concentrations from all sections of the feed stage with the product specification. If none of the product streams meet the specification, they are blended into a single stream which becomes the feed stream to the first section of the first enriching stage. If some but not all of the product concentrations are lower than the product specification, the streams are blended to produce one stream exactly at specification, which is withdrawn from the cascade, and another stream (if there is anything left) which is fed to the next higher stage in the enriching section.

The product from each enriching stage is blended and compared with the specification, and when all of the product from a stage meets the specification no more enriching stages are added. If the number of enriching stages (including the feed stage) exceeds 2, the flow rates must be adjusted to account for the increase in feed rates due to recycle streams from the higher stages. If the number does not exceed 2, the feed rate to the plant is reduced by the amount of the recycle stream from the first enriching stage, thereby eliminating the need for iterating the material balances.

With cost per kilogallon of product water as the objective function, optimum inlet pressures, inlet velocities and recycle ratios of each section of each stage were found for each case with a general optimization program developed for constrained nonlinear problems by Kephart and Cross (4, 5). This program, which was applied successfully to the two-stage code, uses a gradient search technique, with refinements for recognizing patterns in the response surfaces, and boundaries on the variables. The response surface of the hyperfiltration program contained many local optima, some caused by the use of the iteration technique, and each case was run with several different starting values to assure that global optima had been found. The number of stages in a plant is dependent on the set of pressures, velocities and recycle ratios chosen; therefore, in finding the optimum set, the computer program also finds the optimum number of stages.

COST ESTIMATION

Three costs were added to obtain a total cost for the product water. They are (a) a capital and operating cost proportional to membrane area, C_A , (b) energy costs of pumping, C_E , and (c) the capital costs of pumps. Design studies reported in the literature have resulted in capital and operating costs excluding pumps and energy of about 1 cent/ft² · day (6, 7), which was used in most of the calculations reported here.

The energy cost of pumping was obtained by summing the power delivered by the pumps, dividing by an efficiency of 70 percent to convert to the power required by the pumps, and applying an electrical power cost, C_E , of 0.5 cents/kWh.

Prices of multistage centrifugal pumps made of stainless steel (with motor included) were obtained from vendors and correlated with discharge pressure and flow rate by an equation of the form

$$\text{Pump cost} = A (\text{pressure, psi})^B (\text{flow rate, gal/min})^C \quad (12)$$

For pump sizes ranging from 35 to 5600 gal/min and for discharge pressures ranging from 1000 to 3000 psi, the values of the constants were $A = 70$, $B = 0.3$, and $C = 0.5$.

OPTIMUM MEMBRANE PERMEABILITIES FOR MULTISTAGE PLANTS

Costs for 75% and 95% rejecting membranes ($R_\infty = 0.75, 0.95$) as functions of membrane permeability are given in Fig. 3 for 5000 ppm feed. Values for other

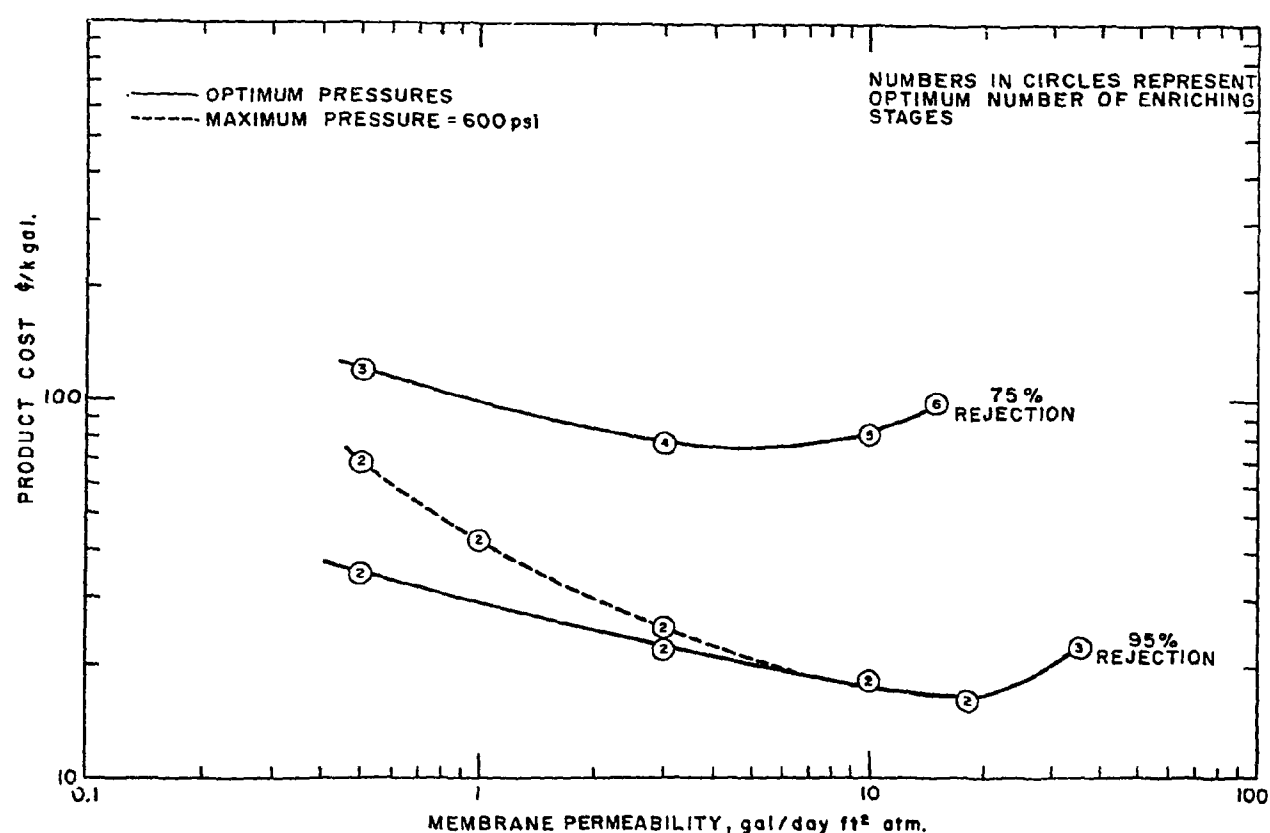


Fig. 3. The effect of membrane permeability on water cost at optimum water recoveries. Feed concentration 5000 ppm.

parameters are listed in Table I. As the permeability of the 75% membrane increased from 0.5 to 15 gal/day $\cdot$ ft² $\cdot$ atm, the optimum number of enriching stages increased from 3 to 6. The lowest cost results with a membrane permeability of 5 gal/day $\cdot$ ft² $\cdot$ atm. The optimum permeability for a 95% rejecting membrane is 18 gal/day $\cdot$ ft² $\cdot$ atm, with two enriching stages. If the 95% membrane can be operated at optimum pressure, water costs are much lower even with a very low permeability than using a 75% membrane at its optimum permeability. However, if the 95% membrane with a permeability of 0.5 is considered to represent the characteristics of cellulose acetate, and therefore must be limited to a maximum

TABLE I

PARAMETERS MOST COMMONLY USED

Number of sections in the first stage	3
Tube diameter	0.25 in.
Feed rate to first stage	10^7 gal/day
Product concentration	500 ppm
Cost per unit membrane area	1 cent/ft ² · day
Energy cost	0.5 cent/kWh
Membrane characteristics:	
$A =$	0.05, 0.25, 0.50
$B = C = D =$	0
$K =$	0.0415 atm ⁻¹
Pump efficiency	70%
Amortization rate for pump costs	10%/year
Plant load factor for pump costs	90%

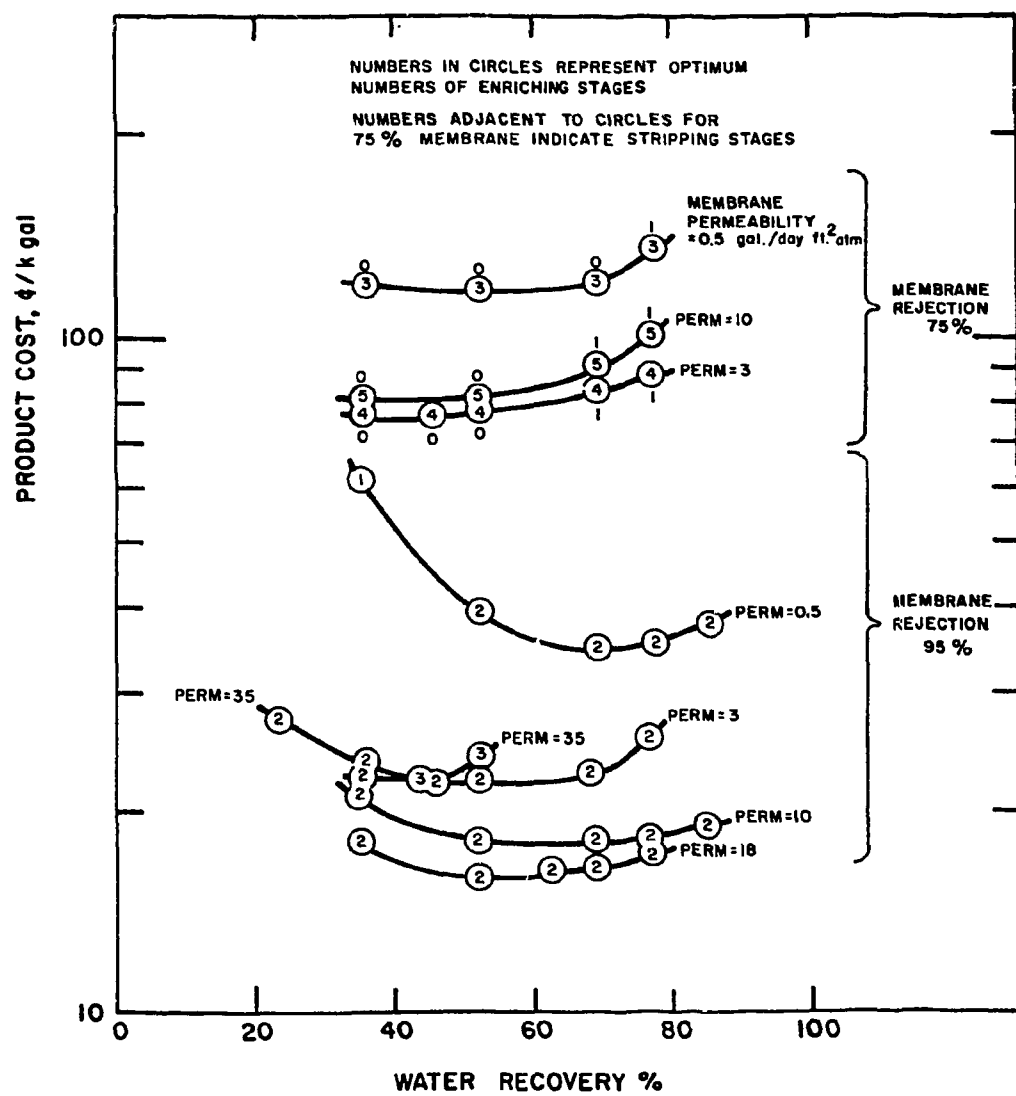


Fig. 4. The dependency of water cost on water recovery. Feed concentration 5000 ppm.

pressure of about 600 psi, then the costs with the 75% membrane at its optimum permeability are about the same as the costs with cellulose acetate.

The costs in Fig. 3 were calculated at optimum water recoveries. Water recovery is the percentage of feed converted into product. The effects of water recovery on cost are shown in Fig. 4. In general, the curves are not very steep, and operation at recoveries ten and in some cases even twenty percent greater than optimum would not increase product costs significantly. Optimum recoveries for the 75% membrane ranged 55 to 40% as permeability increased from 0.5 to 10, and for the 95% membrane ranged from 70 to 45% as permeability increased from 0.5 to 35. A stripping stage was required at the higher water recoveries for the 75% membrane. Costs were higher with a stripping stage, which is reasonable since no pretreatment or brine disposal costs were assumed.

The use of moderately-rejecting membranes with a very low feed concentration was investigated. With 1000 ppm feed, optimum permeabilities were 5 gal/day · ft² · atm for $R_{\infty} = 0.5$ and 4 gal/day · ft² · atm for $R_{\infty} = 0.75$ (Fig. 5).

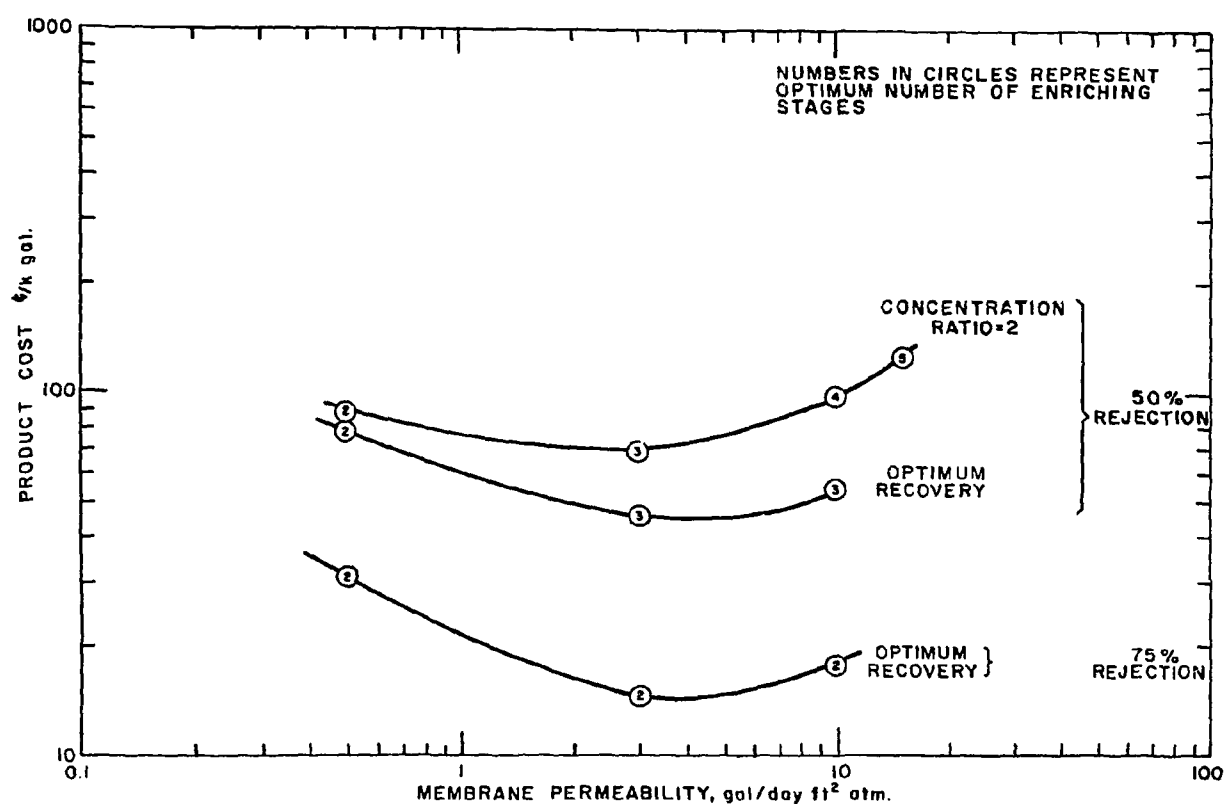


Fig. 5. The effect of membrane permeability on water cost. Feed concentration 1000 ppm.

The cost versus water recovery curves were steeper for these cases than for 5000 ppm feed. The large penalty incurred for operating with a concentration ratio of 2.0 (~50% recovery) with the 50% membrane is shown in Fig. 5. Optimum recoveries for the 50% membrane ranged from 45 to 30% and for the 75%

membrane from 80 to 35%, as permeability increased from 0.5 to 10 gal/day · ft² · atm.

In order to establish the effect of equal section lengths on plant economics, several runs were made holding the ratio of outlet to inlet salt concentration constant for each section in a stage. Costs at optimum water recoveries for a membrane with a 75% rejection were 76¢/kgal for a permeability of 10 and 89¢/kgal for a permeability of 15 gal/day · ft² · atm. These costs are slightly lower than those for a plant with sections of constant concentration difference.

EFFECT OF THE COST PARAMETER C_A

The same value of C_A ($= 1.0\text{¢/ft}^2 \cdot \text{day}$) was used in all of the preceding calculations. Firm values for C_A must await design and construction experience on much larger plants than have been built up to now. However, there is some basis for selecting a value in the neighborhood of 1.0 for cellulose acetate plants; namely, two design studies which have been reported (6, 7). Values of C_A for membranes with higher permeabilities than 0.5 gal/day · ft² · atm are even less certain, with not even one design study to serve as an indicator. Some support materials (e.g., porous canvas) which are being tested with dynamically-formed membranes could lead to much lower values of C_A . Costs were calculated over a

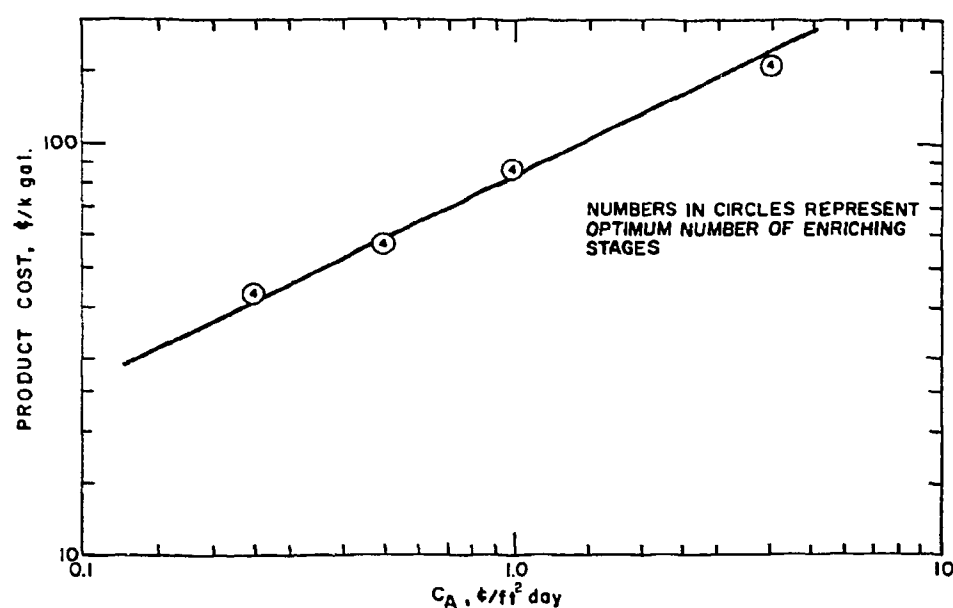


Fig. 6. The relationship between C_A and water cost for $R_\infty = 0.75$, Feed concentration 5000 ppm, Permeability 3 gal/day ft² atm, and Optimum water recovery.

range of C_A from 0.25 to 4.0¢/ft² · day for the 75% membrane at a permeability of 3.0 gal/day · ft² · atm (Fig. 6). The product cost was proportional to $C_A^{1/2}$ for this four-stage plant, as it was shown to be for one- and two-stage plants over a wide range of conditions (2). The relationship is a useful approximation whenever

TABLE II

FLOW VELOCITIES AND PRESSURES IN OPTIMUM PLANTS¹

Feed conc., ppm	Intrinsic membrane rejection %	Membrane permeability gal/day ft ² · atm	Optimum water recovery, %	Average entering flow Velocity in stage, ft/sec					Maximum inlet pressure in stage, psi					Pump capital cost, ¢/kgal	Energy cost Total cost	Product cost, ¢/kgal
				1	2	3	4	5	1	2	3	4	5			
1000	40	3.0	30	17	17	16	16		900	1000	1010	620		4.7	0.52	77
	50	0.5	50	12	9				2240	2300				2.0	0.52	79
		3.0	30	20	20	20			950	1000	1000			2.7	0.59	46
		10.0	30	25	25	25			630	630	670			4.9	0.64	55
	75	0.5	80	7	5				1860	1010				0.3	0.39	31
		3.0	65	17	15				950	680				0.5	0.47	15
		10.0	35	20	20				490	670				1.6	0.62	18
	90	3.0	92	12	20				1090	600				0.3	0.41	11
	50	3.0	25	20	19	19	19	19 ²	1050	1060	1100	1130	1090 ²	11.7	0.57	272
	75	0.5	55	13	13	8			2160	2180	2520			4.3	0.50	117
5000		3.0	45	15	16	15	15		940	1530	910	1240		3.1	0.53	78
		10.0	40	29	25	23	23	22	800	750	690	670	830	5.0	0.65	81
	90	3.0	50	14	13				930	1120				0.9	0.53	30
	95	0.5	70	10	4				1890	1330				0.7	0.42	35
		0.5	52	5	5				600	600 ³				0.9	0.09	68
		1.0	50	6	3				600	600 ³				1.0	0.16	43
		3.0	60	16	15				970	1020				0.9	0.56	22
		10.0	60	15	15				640	490				0.9	0.47	18
		18.0	55	20	20				550	600				1.0	0.55	16
		35.0	45	40	38				640	610				1.7	0.77	22

¹ Parameters in Table I.² For the last three stages of this 8-stage plant, velocities were 18, 19, 18 ft/sec, pressures were 1150, 1060, 1190 psi.³ Upper limit on pressure set at 600 psi.

nearly all of the capital and operating costs (exclusive of energy costs) are comprised of the cost based on membrane area.

OPTIMUM FLOW VELOCITIES AND PRESSURES

The optimization program determined the optimum inlet flow velocity and optimum inlet pressures for each section of each stage. The space required to present all of these for the preceding results is not warranted, with four main parameters (feed concentration, membrane rejection, membrane permeability, and water recovery) and with up to 10 sections per stage. Average inlet velocities per stage are meaningful, because optimum inlet velocities of different sections within a stage did not vary significantly. These are presented in Table II. Optimum inlet pressures of different sections within a stage did vary by as much as a factor of ~ 2 , and the highest pressure for each stage was chosen as the most meaningful for presentation in Table II.

Optimum inlet velocities increased with membrane permeability, but were not affected by membrane rejection or feed concentration over the ranges studied. For the lowest permeability studied, $0.5 \text{ gal/day} \cdot \text{ft}^2 \cdot \text{atm}$, inlet velocities were generally in the neighborhood of 5 to 10 ft/sec. For the highest permeability of 35 with the 95% membrane, inlet velocities were around 40 ft/sec.

Optimum inlet pressures also were not affected by membrane rejection or feed concentration. For the permeability of 0.5, inlet pressures were generally in the neighborhood of 2000 psi or higher; for permeabilities of 10 or higher, pressures were in the range of 500 to 800 psi.

CONCLUSION

The operating conditions which result in a minimum cost for a given membrane (*i.e.*, for a given R_{∞} and permeability) and feed concentration often do not coincide with the use of a minimum number of stages. The number of stages can be decreased usually by taking low water recoveries, but even with no pre-treatment or brine disposal charges minimum stages often does not lead to minimum cost.

When membrane permeability was allowed to vary, the number of stages increased with permeability. In these cases also, optimum permeability and minimum cost do not correspond with minimum stages.

Ranges of membrane rejection exist where the cost is not appreciably lowered by increasing rejection for a given feed concentration and permeability. For low feed concentrations, these ranges can reach fairly low rejections. Examples with 1000 and 5000 ppm concentrations are shown in Fig. 7 for a membrane permeability of $3 \text{ gal/day} \cdot \text{ft}^2 \cdot \text{atm}$. Increasing rejection above 75% has very little

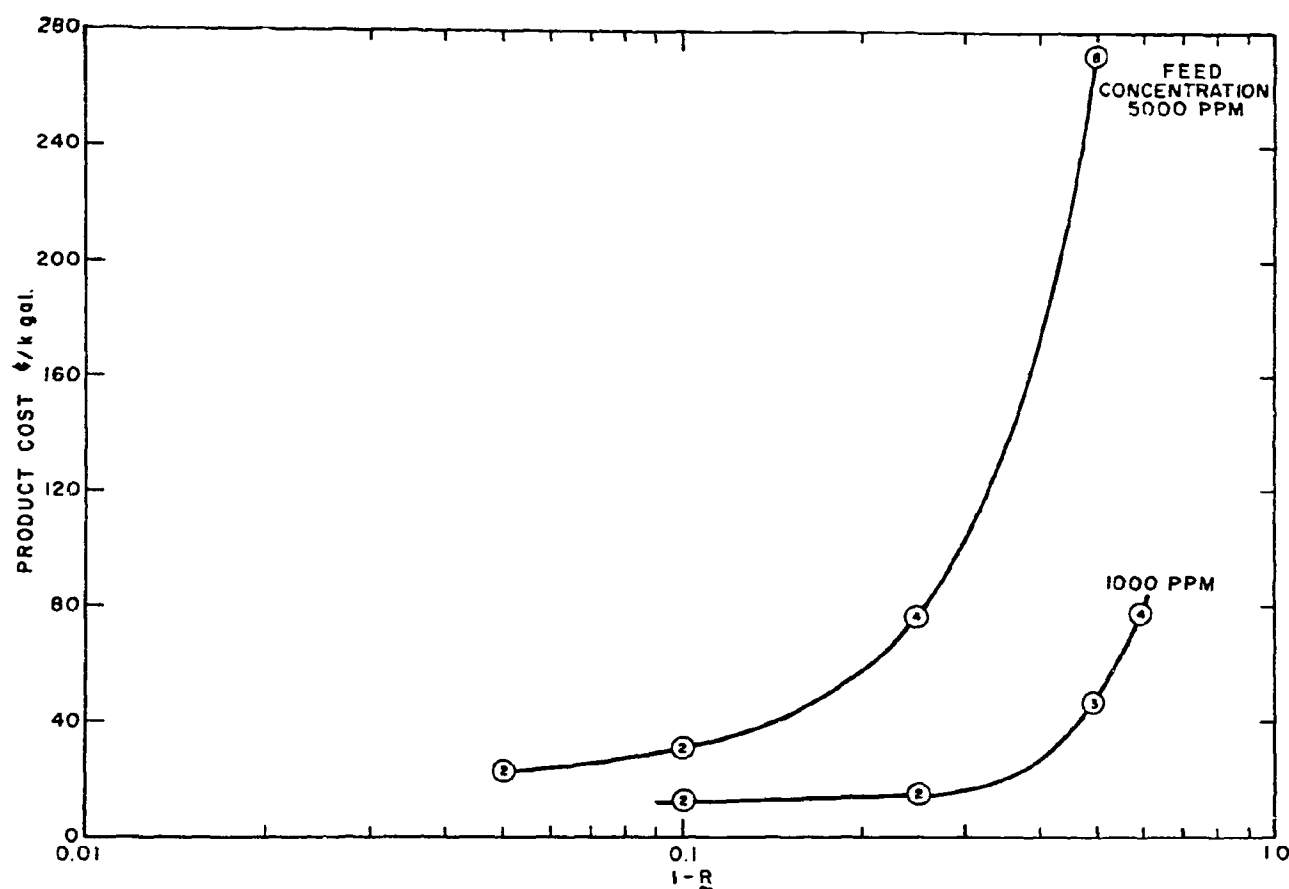


Fig. 7. The effect of intrinsic membrane rejection on water cost. Membrane permeability 3 gal/day ft² atm.

effect on product cost with 1000 ppm feed, and for 5000 ppm feed rejections higher than 95% would offer very little cost advantage with no brine disposal cost.

A correlation of product cost with intrinsic rejection and feed concentration is presented in Fig. 8 for a membrane permeability of 3. Though empirical, this correlation may be useful for obtaining approximate costs for other combinations of intrinsic rejection and feed concentration than those presented earlier. Similar correlations can be made for other membrane permeabilities. The curve for a permeability of 0.5 is roughly parallel to the one shown, but with costs about one-third higher. The curve for a permeability of 10 coincides almost exactly with the one shown. The group $[(1 - R)/R] \cdot [\text{Feed Conc}]$ seems to provide a measure of the difficulty of the separation job and a criterion for judging when staging lowers costs. We have observed that for values of the group in the range of 100–200 one and two-stage plants achieve about equal product costs, but for higher values of the group (corresponding to a more difficult separation job) the optimal number of stages is greater than one.

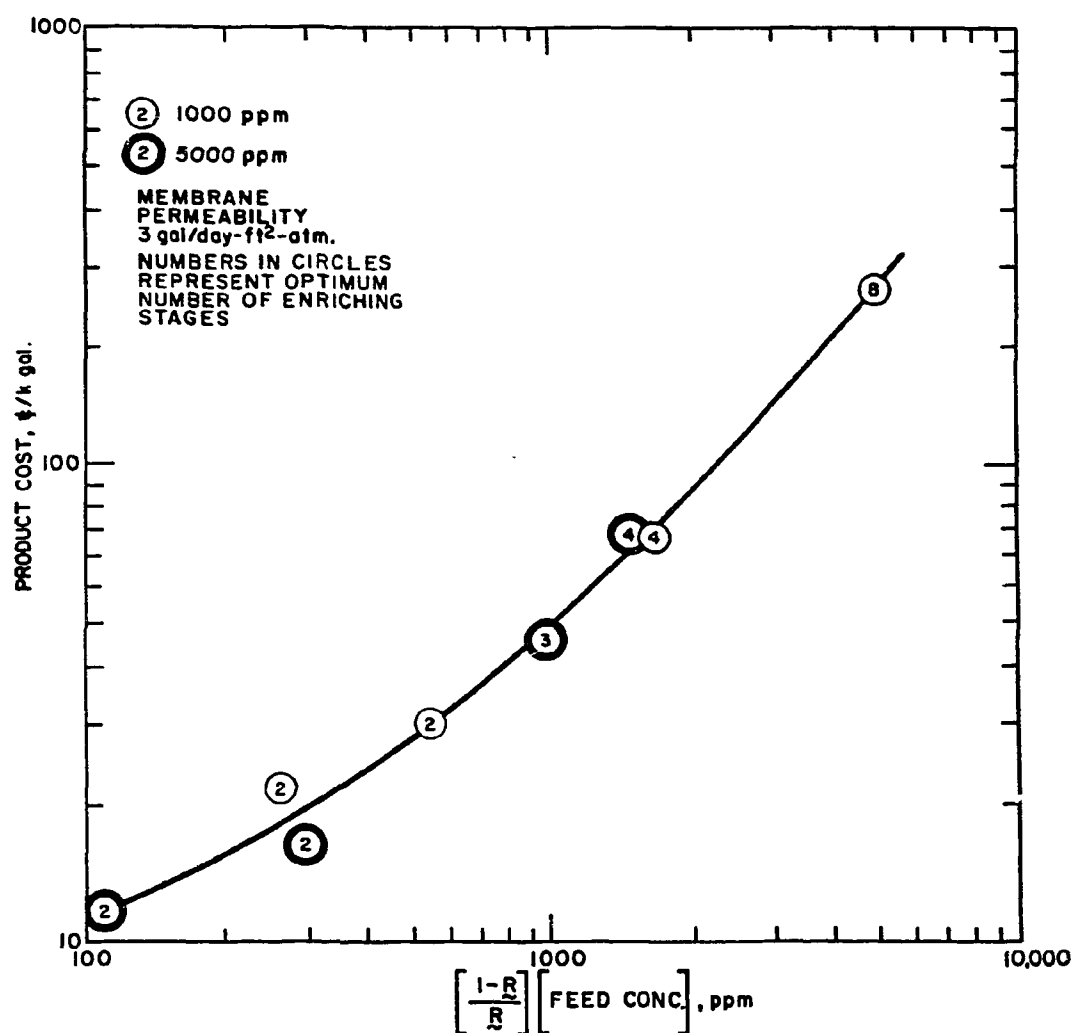


Fig. 8. Minimum cost correlated with intrinsic membrane rejection and feed concentration.

ACKNOWLEDGMENT

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6.3 PRELIMINARY ECONOMIC ANALYSIS OF DONNAN SOFTENING

Lawrence Dresner

Donnan softening (Eisenmann and Smith, 1970; Smith, 1971) is the name given to a dialytic method (Wallace, 1964, 1966, 1967) of removing divalent cations from the feed water of desalination plants. The feed to the plant and the brine from it flow countercurrent to each other in adjacent channels, the common wall of which is a cation exchange membrane. Divalent cations migrate from feed to brine, while univalent cations migrate in the opposite direction. In a variation of the process, the brine is enriched in a salt of the univalent cation

from an external source. Donnan softening of the feed water would be extremely valuable in suppressing scale formation in desalination plants. It is the purpose of this paper to estimate the cost of this pretreatment.

Description of Process, Simplifying Assumptions, and Notation

Figure 1 shows a schematic diagram of the process. Two channels are shown, one marked "feed" and the other "brine."



The Nernst-Planck equations are used to describe ionic transport in the membrane.

Mass Balance

Let us begin by making mass balances only over the plant proper. The volume entering the plant proper per unit time (and per unit length in the y -direction) is q . The words "per unit length in the y -direction" will be omitted henceforth. The volume leaving as product is $(K - 1)q/K$; the difference, q/K , is divided between the waste stream and the stream going to the brine makeup tank. The amounts, $(1 - \theta)q/K$, is the volumetric flow rate of the waste stream, $\theta q/K$ that of the brine makeup stream. Since only salt is added in the brine makeup tank, the volumetric flow rate in the brine channel is also $\theta q/K$.

The ionic concentrations in the product stream are $1 - R$ times those in the treated feed stream—this is the definition of R . The ionic concentrations in the waste stream are the same as those in the brine-makeup stream. A mass balance over any of the three ions shows that the ionic concentrations in the waste and brine-makeup streams are $(K - 1)R + 1$ times greater than those in the treated feed stream.

Let us make an overall mass balance for the univalent cation. The amount entering the overall plant per second is $c_{1\alpha}q$ at point α , and cq at the brine-makeup tank. The amount leaving per second is $(K - 1)q(1 - R)c_{1\beta}/K$ in the product, $(1 - \theta)q[(K - 1)R + 1]c_{1\beta}/K$ in the waste, and $\theta qc_{1\omega}/K$ in the brine. Thus

$$c_{1\alpha} + c = \left[\frac{K - 1}{K}(1 - R) + (1 - \theta) \frac{(K - 1)R + 1}{K} \right] c_{1\beta} + \frac{\theta}{K} c_{1\omega} \quad (1a)$$

A similar overall mass balance for the divalent cation gives

$$c_{2\alpha} = \left[\frac{K - 1}{K}(1 - R) + (1 - \theta) \frac{(K - 1)R + 1}{K} \right] c_{2\beta} + \frac{\theta}{K} c_{2\omega} \quad (1b)$$

For the anion, the overall mass balance reads

$$1 + c = \left[\frac{K - 1}{K}(1 - R) + (1 - \theta) \frac{(K - 1)R + 1}{K} \right] + \frac{k\theta}{K} \quad (1c)$$

Only two of the three equations (1a, b, c) are independent owing to the conditions of electroneutrality $c_{1\alpha} + 2c_{2\alpha} = c_{1\beta} + 2c_{2\beta} = 1$ and $c_{1\omega} + 2c_{2\omega} = k$.

We can also make a mass balance over the part of the overall plant beyond the plane $x = L$ (L = length of the membrane)—i.e., the plant proper and the brine-makeup tank. The amount of univalent cation entering this part of the overall plant is $qc_{1\beta} + qc$; the amount leaving is $(K - 1)q(1 - R)c_{1\beta}/K$ in the product, $(1 - \theta)q[(K - 1)R + 1]c_{1\beta}/K$ in the waste, and $\theta qc_{1\gamma}/K$ in the fresh brine. Then

$$c_{1\beta} + c = \left[\frac{K - 1}{K}(1 - R) + (1 - \theta) \frac{(K - 1)R + 1}{K} \right] c_{1\beta} + \frac{\theta}{K} c_{1\gamma} \quad (2a)$$

Similarly

$$c_{2\beta} = \left[\frac{K - 1}{K}(1 - R) + (1 - \theta) \frac{(K - 1)R + 1}{K} \right] c_{2\beta} + \frac{\theta}{K} c_{2\gamma} \quad (2b)$$

When the first of these equations is added to twice the second, we recover Equation 1c.

In addition to these overall mass balances, we can make local mass balances over the parts of the feed and brine channels lying between the planes x and $x + dx$. For example, the flow of univalent ion into the volume of the feed channel between these planes is $qc_{1f}(x) + j_1(x)dx$, where the subscript f denotes the feed channel, and j_1 is the flux of univalent ion through the membrane. The flow of univalent ion out of the same volume is $qc_{1f}(x + dx)$. In the steady state, these flows are equal; thus,

$$j_1(x) = q \frac{dc_{1f}(x)}{dx} \quad (3a)$$

The flow of univalent ion into the volume of the brine channel between the planes x and $x + dx$ is $(\theta q/K)c_{1b}(x + dx)$, where the subscript b refers to the brine channel. The flow out is $(\theta q/K)c_{1b}(x) + j_1(x)dx$. Thus,

$$j_1(x) = \frac{\theta}{K} q \frac{dc_{1b}(x)}{dx} \quad (3b)$$

An identical set of equations holds for the divalent cation:

$$j_2(x) = q \frac{dc_{2f}(x)}{dx} \quad (4a)$$

$$j_2(x) = \frac{\theta}{K} q \frac{dc_{2b}(x)}{dx} \quad (4b)$$

Equations 4a and 4b are identical to Equation 3a and 3b owing to the conditions of electroneutrality, $j_1 + 2j_2 = 0$, $c_{1f} + 2c_{2f} = 1$, $c_{1b} + 2c_{2b} = k$.

If we subtract Equation 4b from Equation 4a and Equation 3b from Equation 3a, the right-hand sides of the resulting equations can be integrated:

$$c_{2\alpha} - \frac{\theta}{K} c_{2\omega} = c_{2\beta} - \frac{\theta}{K} c_{2\gamma} = c_{2f}(x) - \frac{\theta}{K} c_{2b}(x) \quad (5a)$$

$$c_{1\alpha} - \frac{\theta}{K} c_{1\omega} = c_{1\beta} - \frac{\theta}{K} c_{1\gamma} = c_{1f}(x) - \frac{\theta}{K} c_{1b}(x) \quad (5b)$$

The left-hand sides of Equations 5a and 5b are constants of integration whose values have been determined by setting $x = 0$ and $x = L$, respectively.

Flux Through the Membrane

To complete the theory, we need an expression for the ionic fluxes, j_1 and j_2 , through the membrane in terms of the ionic concentrations in the feed and brine channels. These expressions we get by integrating the Nernst-Planck equations, which we use to describe ionic transport through the membrane:

$$j_1 = -\mathcal{D}_1 \frac{dc_1}{dz} + \mathcal{D}_1 c_1 \epsilon \quad (6a)$$

$$j_2 = -\mathcal{D}_2 \frac{dc_2}{dz} + 2\mathcal{D}_2 c_2 \epsilon \quad (6b)$$

where ϵ is the electric field divided by RT/F , c_1 and c_2 are the ionic concentrations in the membrane, and $\mathcal{D}_1$ and $\mathcal{D}_2$ the ionic diffusion coefficients in the membrane. If we eliminate ϵ from these two equations and use the conditions

of electroneutrality $j_1 + 2j_2 = 0$ and $dc_1/dx + 2 dc_2/dx = 0$, we get

$$j_2 = -\frac{\mathcal{D}_1 \mathcal{D}_2 (4c_2 + c_1)}{4\mathcal{D}_2 c_2 + \mathcal{D}_1 c_1} \cdot \frac{dc_2}{dz} \quad (7a)$$

or

$$j_2 = -\frac{\mathcal{D}_1 \mathcal{D}_2 (X + 2c_2)}{4\mathcal{D}_2 c_2 + \mathcal{D}_1 (X - 2c_2)} \cdot \frac{dc_2}{dz} \quad (7b)$$

since $c_1 = X - 2c_2$. Here X is the concentration of fixed charge in the membrane. Equation 7b can be integrated to yield

$$\frac{-j_2 l}{\mathcal{D}_2} = \left[\frac{2}{A} c_2 + \frac{A-2}{A^2} X \ln (Ac_2 + X) \right]_{z=0}^{z=l} \quad (8)$$

where $A = 4(\mathcal{D}_2/\mathcal{D}_1) - 2$ and l is the membrane thickness.

The values of $c_2(0)$ and $c_2(l)$ are determined from the conditions of Donnan equilibrium at the two interfaces $z = 0$ and $z = l$. If D_f is the distribution coefficient of the univalent cation between the membrane and the feed solution, then D_f^2 is the distribution coefficient for the divalent cation. For, when all activity coefficients are taken equal to 1, $D_f = \exp(-F\phi/RT)$ for univalent cations and $D_f = \exp(-2F\phi/RT)$ for divalent cations, where ϕ is the difference in electrical potential between a point just inside the membrane and a point just outside the membrane. Since anion invasion of the membrane is assumed to be negligible,

$$D_f c_{1f} + 2D_f^2 c_{2f} = X \quad (9a)$$

or

$$D_f = \frac{-c_{1f} + (c_{1f}^2 + 8c_{2f}X)^{1/2}}{4c_{2f}} \quad (9b)$$

A similar equation holds for the distribution coefficient of the univalent cation at the brine-membrane interface.

Method of Solution

We wish to find the length, L , of the channel. To solve the equations we have developed accurately, numerical treatment is necessary. We begin this treatment by listing the independent variables: $K, R, \theta, c, c_{2\alpha}, c_{2\beta}, X, \mathcal{D}_1, \mathcal{D}_2, l$, and q . All other quantities are determined by these given eleven. However, l occurs only in the combination $\mathcal{D}_2/l$, and $\mathcal{D}_1$ only in the combination $\mathcal{D}_2/\mathcal{D}_1 = (A+2)/4$ (Equation 8). We can replace the three variables $\mathcal{D}_1, \mathcal{D}_2$, and l by the two variables A and $\mathcal{D}_2/l$. The quantity $\mathcal{D}_2/l$ has the dimensions (length) (time)⁻¹ and q has the dimensions (length)² (time)⁻¹. All the other independent variables are dimensionless. The only dimensionless groups we can form from L , a length, $\mathcal{D}_2/l$, and q , is $L\mathcal{D}_2/ql$. Thus

$$\frac{L\mathcal{D}_2}{ql} = G(K, R, \theta, c, c_{2\alpha}, c_{2\beta}, X, A) \quad (10)$$

where G is an as yet undetermined equation.

The first way of finding values of G that might come to mind is the following. Using Equations (1a-c) we find values of the ionic concentrations at point ω in terms of those at points α and β . Then we have initial values with which to integrate one of the Differential Equations 3 and 4, say Equation 4a (with the help of Equations 5, 8, and the equations of electroneutrality). We integrate in the direction of feed flow until $c_{2f} = c_{2\beta}$; the corresponding value of x is L . Each integration thus gives us one point of the function G .

If we integrate in the direction opposite to the feed flow, on the other hand, each integration gives us an entire line of points on G . Using Equations 2a,b, we can find the ionic concentrations at point γ in terms of those at point β . Then we have initial values with which to integrate Equation 4a in the direction opposite to the feed flow. So far, we have not chosen $c_{2\alpha}$ —each value of c_{2f} in turn may serve as $c_{2\alpha}$. Hence, as we integrate, we produce a curve of $L\mathcal{D}_2/ql$ vs. $c_{2\alpha}$ for the already chosen values of $K, R, \theta, c, c_{2\beta}, X$, and A .

In spite of the simplifications introduced above, we still must perform a seven-parameter family of numerical integrations in order fully to explore the function G . This is a formidable task, which might be avoided if we could find some approximate solutions to our equations that show explicitly the dependence of $L\mathcal{D}_2/ql$ on the various arguments of G .

Membrane Substantially in Univalent Form

Suppose we consider a feed water in which the proportion of divalent cation is so low that the membrane is substantially in the univalent form everywhere—i.e., suppose that $c_2 \ll c_1 \approx X$ for all x and z . To lowest order in c_2 , Equation 8 becomes

$$\frac{-j_2 l}{\mathcal{D}_2} = c_2(l) - c_2(0) \quad (11)$$

For the membrane to be substantially in the univalent form, c_{2f} must be $\ll c_{1f}$ and $c_{2b} \ll c_{1b}$ since the distribution coefficient of divalent ions is greater than that of univalent ions. But then $c_{1f} \approx 1$ and $c_{1b} \approx k$. Thus, Equation 9b becomes

$$D_f = \frac{X}{c_{1f}}, D_b = \frac{X}{c_{1b}} \quad (12)$$

and

$$\frac{-j_2 l}{\mathcal{D}_2} = \left(\frac{X}{c_{1f}}\right)^2 c_{2f} - \left(\frac{X}{c_{1b}}\right)^2 c_{2b} = X^2 \left(c_{2f} - \frac{c_{2b}}{k^2}\right) \quad (13)$$

If we eliminate j_2 and c_{2b} among Equations 4a, 5a, and 13, we get

$$\frac{-ql}{\mathcal{D}_2 X^2} \frac{dc_{2f}}{dx} = c_{2f} \left(1 - \frac{K}{\theta k^2}\right) + \frac{K}{\theta k^2} \left(c_{2\beta} - \frac{\theta}{K} c_{2\gamma}\right) \quad (14)$$

Integration of Equation 14 gives

$$c_{2f} = -\frac{K}{\theta k^2 - K} \left(c_{2\beta} - \frac{\theta}{K} c_{2\gamma}\right) + B \exp \left[-\left(1 - \frac{K}{\theta k^2}\right) \frac{\mathcal{D}_2 X^2}{ql} x \right] \quad (15)$$

When $x = 0$, $c_{2f} = c_{2\alpha}$, so that

$$B = c_{2\alpha} + \frac{K}{\theta k^2 - K} \left(c_{2\beta} - \frac{\theta}{K} c_{2\gamma}\right) \quad (16)$$

When $X = L$, $c_{2f} = c_{2\beta}$. Using Equations 15 and 16, we find that

$$\frac{L\mathcal{D}_2}{ql} = \frac{1}{X^2} \frac{\theta k^2}{\theta k^2 - K} \ln \left[\frac{c_{2\alpha} + \frac{K}{\theta k^2 - K} \left(c_{2\beta} - \frac{\theta}{K} c_{2\gamma}\right)}{c_{2\beta} + \frac{K}{\theta k^2 - K} \left(c_{2\beta} - \frac{\theta}{K} c_{2\gamma}\right)} \right] \quad (17)$$

Membrane Substantially in Divalent Form

Suppose we consider a feed water in which the proportion of divalent cations is so high that the membrane is sub-

stantially in the divalent form everywhere—i.e., suppose that $c_1 \ll c_2 \approx X/2$ for all x and z . To lowest order in c_1 , Equation 8 becomes

$$-\frac{j_1 l}{\mathcal{D}_1} = c_1(l) - c_1(0) \quad (18)$$

For the membrane to be substantially in the divalent form it is not necessary for c_{1f} to be $\ll c_{2f}$ and c_{1b} to be $\ll c_{2b}$ because the distribution coefficient of divalent cations is greater than that of univalent cations. In the interest of simplicity, we restrict ourselves to this case. When $c_{1f} \ll c_{2f}$ and $c_{1b} \ll c_{2b}$, $c_{2f} \approx 1/2$ and $c_{2b} \approx k/2$. Furthermore, Equation 9b gives

$$D_f = \left(\frac{X}{2c_{2f}} \right)^{1/2} = X^{1/2} \quad (19a)$$

and

$$D_b = \left(\frac{X}{2c_{2b}} \right)^{1/2} = \left(\frac{X}{k} \right)^{1/2} \quad (19b)$$

Thus

$$-\frac{j_1 l}{\mathcal{D}_1} = X^{1/2} \left(c_{1f} - \frac{c_{1b}}{k^{1/2}} \right) \quad (20)$$

If we eliminate c_{1b} and j_1 from among Equations 20, 5b, and 3a, we get

$$-\frac{ql}{\mathcal{D}_1 X^{1/2}} \frac{dc_{1f}}{dx} = \left(1 - \frac{K}{\theta k^{1/2}} \right) c_{1f} + \frac{K}{\theta k^{1/2}} \left(c_{1\beta} - \frac{\theta}{K} c_{1\gamma} \right) \quad (21)$$

Solving Equation 21 as we did Equation 14, we find

$$\frac{L\mathcal{D}_1}{ql} = \frac{1}{X^{1/2} K - \theta k^{1/2}} \ln \left[\frac{c_{1\beta} + \frac{K}{\theta k^{1/2} - K} \left(c_{1\beta} - \frac{\theta}{K} c_{1\gamma} \right)}{c_{1\alpha} + \frac{K}{\theta k^{1/2} - K} \left(c_{1\beta} - \frac{\theta}{K} c_{1\gamma} \right)} \right] \quad (22)$$

Membrane in Divalent Form at Feed Interface and Univalent Form at Brine Interface

When a salt of the univalent cation is added to the brine, the membrane may be in the divalent form at the feed interface and the univalent form at the brine interface. Equation 8 then becomes

$$-\frac{j_2 l}{\mathcal{D}_2} = X \left[\frac{1}{A} + \frac{A-2}{A^2} \ln \left(1 + \frac{A}{2} \right) \right] \quad (23)$$

from which it follows at once that

$$\frac{L\mathcal{D}_2}{ql} = \frac{c_{2\alpha} - c_{2\beta}}{X \left[\frac{1}{A} + \frac{A-2}{A^2} \ln \left(1 + \frac{A}{2} \right) \right]} \quad (24)$$

Since the driving force for dialysis is greatest in this case, Equation 24 should give a lower limit to $L\mathcal{D}_2/ql$ for given values of $c_{2\alpha}$, $c_{2\beta}$, X , and A .

Special Case $R = 1$, $c = 0$, $\theta = 1$

The value $R = 1$ means perfect salt rejection and $c = 0$ means no salt addition, in which case $\theta = 1$ minimizes the

length of membrane required for a given change of concentrations. Under these circumstances,

$$k = K \quad (25a)$$

$$c_{2\omega} = K c_{2\alpha} \quad (25b)$$

$$c_{1\omega} = K c_{1\alpha} \quad (25c)$$

$$c_{2\gamma} = K c_{2\beta} \quad (25d)$$

$$c_{1\gamma} = K c_{1\beta} \quad (25e)$$

$$c_{1b} = K c_{1f} \quad (25f)$$

$$c_{2b} = K c_{2f} \quad (25g)$$

as we see from Equations 1 and 2. Equations 17 and 22 become, respectively,

$$\frac{L\mathcal{D}_2}{ql} = \frac{1}{X^2} \frac{K}{K-1} \ln \left(\frac{c_{2\alpha}}{c_{2\beta}} \right) \quad (17a)$$

$$\frac{L\mathcal{D}_1}{ql} = \frac{1}{X^{1/2}} \frac{1}{K^{1/2}-1} \ln \left(\frac{c_{1\beta}}{c_{1\alpha}} \right) \quad (22a)$$

It should be highly instructive to apply Equations 17a and 22a to estimating membrane requirements L/q for softening with ordinary electrodialysis membranes. The L/q expressed in appropriate units is the number of square feet of membrane required per day, kilogram of water softened. Since these equations deal with limiting cases, we need some rough criteria of when these limiting cases apply.

The membrane will be substantially in the $\left\{ \begin{array}{l} \text{univalent} \\ \text{divalent} \end{array} \right\}$ form at a solution-membrane interface if

$$D^2 c_2 \ll D c_1 \quad \left\{ \begin{array}{l} \text{univalent} \\ \text{divalent} \end{array} \right\} \quad (25)$$

If we use Equation 9b for D , we find this criterion becomes

$$c_2 X \ll 3 c_1^2 \quad \left\{ \begin{array}{l} \text{univalent} \\ \text{divalent} \end{array} \right\} \quad (26)$$

Suppose

$$c_{2\alpha} X \ll 3 c_{1\alpha}^2 \quad (26a)$$

Then the membrane is substantially in the univalent form at the feed-membrane interface at the head of the feed channel. Since the proportion of divalent to univalent cations decreases as we go down the feed channel, the membrane is substantially in the univalent form throughout the feed channel. From Equations 23f and 23g, we see that the ionic concentrations in the brine channel are K times those in the feed channel. Since $K > 1$, if Equation 26 holds with the upper sign in the feed channel it also holds with the upper sign in the brine channel. Hence the condition $c_{2\alpha} X \ll 3 c_{1\alpha}^2$ is a sufficient condition for the membrane to be substantially in the univalent form throughout—i.e., for Equation 17a to be applicable.

To make cost estimates using Equation 17a we shall have to choose values of the various parameters in it. The conductances per unit surface area σ of wet electrodialysis membranes in the univalent form are ~ 200 msho cm^{-2} , and their ion exchange capacities C are ~ 1 mol l^{-1} (wet) (Spiegler, 1966, pp 209-11). Now,

$$\frac{l}{\mathcal{D}_1} = \frac{F^2 C}{RT\sigma} \quad (27)$$

so that with the values of the capacity and conductance given above $l/\mathcal{D}_1 \sim 1.88 \times 10^4 \text{ sec cm}^{-1} = 880 \text{ ft}^2/\text{daily kgal at } 25^\circ\text{C}$.

The degree of softening is given by the ratio $c_{2\alpha}/c_{2\beta}$. Since this ratio appears as the argument of a logarithm, L/q is not very sensitive to its value. We take $c_{2\alpha}/c_{2\beta} = 10$ for the purposes of estimation; this corresponds to 90% softening.

High water recovery is desirable in desalting plants. The ratio $K/(K-1)$ is rather insensitive to the percent recovery if the latter is high. For 50% recovery $K/(K-1) = 2$; for 80%, $K/(K-1) = 1.25$, and for 100% recovery, $K/(K-1) = 1$. We choose $K/(K-1) = 1.5$ ($K = 3$) for the purposes of estimation.

For moderately cross-linked cation exchangers of sulfonated polystyrene (~5% DVB), the self-diffusion coefficient of Zn^{2+} is ~0.3 that of Na^+ (Soldano, 1953). Accordingly, we take $\mathcal{D}_1/\mathcal{D}_2$ to be $1/0.3 = 3.33$ for the purposes of estimation.

As we recall, X is the ion exchange capacity expressed in units of the feed anion concentration. Since we have already chosen the capacity to be 1 mol l^{-1} , choosing X is equivalent to choosing the total anion concentration of the feed. Table I shows costs of L/q vs. feed anion concentration. Also included in the table are costs based on an assumed cost of membrane area of $0.32\text{¢ ft}^{-2} \text{ day}^{-1}$, obtained as explained below, as well as the permissible divalent cation concentrations in the feed, estimated from the relationship $c_{2\alpha} \ll 3/X$.

Recent guidelines for cost estimates put the cost of active electro dialysis membrane area at $\$3.00 \text{ ft}^{-2}$ and the membrane lifetime at 5 years (Prenn and McGaugh, 1970, p 16). At 4% interest (22.5% fixed charges) and a 330-day year (90% load factor), this puts the daily cost of membrane surface at $0.204\text{¢ ft}^{-2} \text{ day}^{-1}$ on stream. To this cost must be added at least the cost of the equipment necessary to support the membranes. If the membranes are mounted in stacks similar to electro dialysis stacks, we can use the costs of the latter as a guide. Clark (1970) gives a detailed cost breakdown of electro dialysis stacks in a recent cost analysis of six desalting processes. For a 1-mgd plant, the cost of his stacks, excluding membranes, is $0.185\text{¢ ft}^{-2} \text{ day}^{-1}$, but 40% of this cost is for electrical equipment and instrumentation. If we assume this electrical equipment and instrumentation is absent in the dialysis stacks, we obtain a cost of $0.111\text{¢ ft}^{-2} \text{ day}^{-1}$. The total daily cost of membrane area is then $0.315\text{¢ ft}^{-2} \text{ day}^{-1}$.

It is clear that when the anion concentration of the feed is low, the permissible divalent cation concentration in the feed for which Equation 17a is still valid, is so small that there is hardly any need for softening (first and second columns in Table I). When the feed anion concentration is high (third and fourth columns of Table I) the cost is high, and we must try to reduce it by adding salt to the brine.

The addition of salt to the brine is not without an economic penalty because at the very least the added salt must be paid for. Furthermore, salt addition may complicate the waste disposal problem since it increases the total amount of salt being dumped. We try to minimize the amount of salt we have to add by making θ less than 1. However, this reduces the volume of the brine stream into which the divalent ion is migrating, thereby increasing the concentration in the brine of the divalent cation. We must therefore briefly re-examine the question of when the membrane is in the univalent form at the brine-membrane interface.

The proportion of divalent cation in the brine stream is greatest at point ω . According to Equations 1a and 1b, when $R = 1$,

Table I. Cost Estimates for Cases in Which Membrane Is Substantially in Univalent Form Throughout—Ordinary Electro dialysis Membranes

Feed anion concentration (mol/l.)	0.01	0.03	0.1	0.3
L/q (ft ² /daily kgal)	1.01	9.09	101	909
Membrane cost (¢/kgal)	0.320	2.88	32.0	288
Maximum divalent cation concentration in feed	$\ll 0.03$	$\ll 0.09$	$\ll 0.3$	$\ll 0.9$

$$c_{2\omega} = \frac{K}{\theta} [c_{2\alpha} - (1 - \theta)c_{2\beta}] \quad (28a)$$

$$c_{1\omega} = \frac{K}{\theta} [c_{1\alpha} - (1 - \theta)c_{1\beta} + c] \quad (28b)$$

Inserting these expressions into Equation 26 with the upper sign, we find

$$X[c_{2\alpha} - (1 - \theta)c_{2\beta}] \ll 3 \left(\frac{K}{\theta} \right) [c_{1\alpha} - (1 - \theta)c_{1\beta} + c]^2 \quad (29)$$

Equation 29 is a separate criterion, additional to Equation 26a, for the membrane to be in the univalent form throughout except when $\theta = 1$, when it is clear that Equation 29 is satisfied if Equation 26a is. We can simplify Equation 29 somewhat by observing that if the feed water is well softened, $c_{2\beta} \ll c_{2\alpha}$, and the feeds we are considering have $c_{2\alpha} \ll 1$. Thus $c_{1\alpha}$ and $c_{1\beta} \approx 1$, and Equation 29 can be written:

$$Xc_{2\alpha} \ll 3 \frac{K}{\theta} (c + \theta)^2 \quad (30)$$

as long as $\theta \gg c_{1\alpha} - c_{1\beta}$. Comparing this with Equation 26a with $c_{1\alpha} = 1$, we see that Equation 29 will be satisfied if Equation 26a is as long as

$$\frac{K}{\theta} (c + \theta)^2 \gtrsim 1 \quad (31)$$

i.e., as long as

$$c \gtrsim \left(\frac{\theta}{K} \right)^{1/2} - \theta \quad (31a)$$

The maximum value of the right-hand side of Equation 31a for any value of θ is $1/4 K$; hence if

$$c \gtrsim \frac{1}{4K} \quad (31b)$$

the membrane will be in the univalent form throughout, irrespective of the value of θ as long as $\theta \gg c_{1\alpha} - c_{1\beta}$.

When the membrane is substantially in the univalent form throughout, addition of a salt of the univalent cation to the brine is not of much help, especially when the percentage of water recovery is high. To see this, we show now that the values of L/q one would calculate from Equation 17 are never less than $K/(K-1)$ times the values one calculates from Equation 17a. Suppose we consider the limiting form of Equation 17 as $c \rightarrow \infty$ with all other parameters fixed. We see from Equation 1c that $k \rightarrow \infty$ also, while Equation 2b

Table II. Cost Estimates (in ¢/kgal.) for Cases in Which Membrane Is Substantially in Univalent Form Throughout—Ordinary Electrodialysis Membranes—Salt Added to Brine

Feed anion concn, mol/l.		0.01	0.03	0.1	0.3
$c = 0, \theta = 1$		0.320	2.88	32.0	288
$c = 0.1$	$\theta = 1$	0.463	3.16	31.1	270
	$\theta = 0.3$	0.573	4.15	42.2	370
	$\theta = 0.1$	0.707	5.35	55.6	490
$c = 0.3$	$\theta = 1$	0.771	3.94	31.7	257
	$\theta = 0.3$	0.773	3.96	31.9	260
	$\theta = 0.1$	0.752	3.77	29.8	241
$c = 1$	$\theta = 1$	1.91	7.14	40.1	260
	$\theta = 0.3$	1.90	7.06	39.1	251
	$\theta = 0.1$	1.90	7.00	38.5	246
Max divalent cation concn in feed		$\ll 0.03$	$\ll 0.09$	$\ll 0.3$	$\ll 0.9$

Table III. Cost Estimates for Cases in Which Membrane Is Substantially in Divalent Form Throughout—Ordinary Electrodialysis Membranes

Feed anion concn- tration, mol/l.	0.01	0.03	0.1	0.3
L/q , ft ² /daily kgal	276	478	874	1510
Membrane cost (¢/kgal)	88.2	153	279	484

shows that $c_{2\gamma}$ does not change. The limiting form of Equation 17 is then

$$\left(\frac{L\mathcal{D}_2}{ql}\right) = \frac{1}{X^2} \ln \left(\frac{c_{2\alpha}}{c_{2\beta}}\right) \quad (32)$$

which is the same as Equation 17a except for the factor $K/(K - 1)$. In the case we have been considering ($K = 3$), the maximum possible reduction in membrane area is thus 33%.

We take the cost of NaCl to be \$7.00 per ton = 0.0446¢/mol (Eisenmann and Smith, 1970, p 69). (A cost of \$7.00 per ton equals 35¢/cwt. Costs are quoted in the recent *Chemical Marketing Reporter* for rock salt in 100-lb bags fob New York of 97¢/cwt. A 40¢/cwt discount is indicated for bulk salt, bringing the cost fob New York to 57¢/cwt. A 28¢/cwt reduction in price is available for Kansas salt, and if we take the 40¢/cwt discount for bulk buying, we find a price of 29¢/cwt. The cost of 35¢/cwt thus seems a reasonable average value to use.) If we add 0.03 mol of NaCl to the brine per liter of feed softened, the salt cost per kgal is 5.05¢. Now in order to do any appreciable good, the amount of salt added to the brine must be at least comparable with the amount of salt in the brine originating from the feed. Thus c should be comparable with unity. Roughly speaking then, the cost of the added salt should vary linearly with feed anion concentration; we already know from Equation 17a that the membrane cost without salt addition varies as the square of the feed anion concentration. Consequently, salt addition can only be of value for the more concentrated feeds.

Another way of looking at this is the following: In the case represented by the second column of Table I, the maximum savings we can create by adding salt to the brine is $\frac{1}{3} \times 2.88¢ = 0.960¢/\text{kgal}$. This saving would buy only 0.00571 mol of NaCl per kgal of water softened, which is probably far too little to attain the savings in membrane cost. In this case, then, salt addition should result in an increase in cost. In the case represented by the fourth column, however, the

Table IV. Membrane Cost Estimates for Cases in Which Membrane Is in Univalent Form at Brine Interface and Divalent Form at Feed Interface—Ordinary Electrodialysis Membranes

Feed anion concn, mol/l.	0.01	0.03	0.1	0.3
L/q , ft ² /daily kgal				
(upper bound based on $c_{1\beta} = 1$)	13.5	40.5	135	405
Membrane cost, ¢/ kgal	4.32	13.0	43.2	130
Total cost, ¢/kgal, $c = 1$	6.00	18.1	60.0	181

maximum savings is $\frac{1}{3} \times 288¢ = 96¢/\text{kgal}$, enough to buy 0.571 mol of NaCl per kgal. Since this is probably more salt than is needed, salt addition should result in a decrease in cost. These conclusions are borne out in the results of computations using Equation 17 shown in Table II.

Next we turn to Equation 22a, which is valid when the membrane is substantially in the divalent form throughout. The criterion for this is Equation 26 with the lower sign. The point at which the relative proportion of divalent to univalent cations in the membrane is least is γ . Using Equations 25d and 25e, we can write Equation 26 at point γ as

$$c_{2\beta} X \gg 3 K c_{1\beta}^2 \quad (33)$$

Equation 33 sets a limit on how far we can soften the feed before the conditions of applicability of Equation 22a are violated.

The concentration ratio $c_{1\beta}/c_{1\alpha}$ only enters Equation 22a in the argument of a logarithm, so that L/q is not very sensitive to its precise value, which we take to be 10 for the purposes of estimation. Using our previous values for $L/\mathcal{D}_1$, the ion exchange capacity, and K , we find the costs shown in Table III.

These costs are extremely high, but in this case the total cost can be sharply reduced by adding salt to the brine. In fact, if we add enough salt to the brine, we can put the membrane in the univalent form at the brine interface. Then we can use Equation 24 to estimate the membrane requirements. Such estimates are shown in the first three rows of Table IV.

The estimates in the third row, Table IV, are incomplete because they lack an estimate of the cost of the added salt. This we estimate using Equation 29. If θ is small enough, Equation 29 will be satisfied if c is slightly greater than $-c_{1\alpha} +$

Table V. Feed Water Composition at Well 49, Yuma, Ariz.

Ion	Ppm	Mol/l.
Ca^{2+}	213	0.00533
Mg^{2+}	85	0.00354
Na^+	1030	0.0448
K^+	15	0.00039
SO_4^{2-}	1300	0.0135
Cl^-	1142	0.0322
HCO_3^-	(Equiv to 184 ppm CaCO_3)	0.00184

$(1 - \theta)c_{1\beta}$. [The value of c must always be $\geq -c_{1\alpha} + (1 - \theta)c_{1\beta}$ since $c_{1\omega} \geq 0$; cf. Equation 28b.] In the case we are considering (Equation 22a), $c_{1\alpha}$ is small compared to unity. If the softening process is effective, $c_{1\beta}$ will be of the order of unity. Since θ is small, $c \gtrsim (1 - \theta)c_{1\beta} - c_{1\alpha} \approx 1$. The salt costs corresponding to $c = 1$ have been added to the costs in the third row of Table IV to get the costs shown in the fourth row.

The rough estimates of this section suggest the following three conclusions regarding Donnan softening with electrodialysis membranes:

The process is likely to be feasible for feed waters of low salinity, roughly those having a total anion concentration $\lesssim 0.03M$.

When the feed has a high proportion of divalent cations, a salt of the univalent cation *must* be added to the brine to make the process feasible.

When the feed has a low proportion of divalent cations, salt need not be added to make the process feasible.

Well 49—Yuma, Ariz.

When we keep in mind the exploratory survey given in the last section, the best chance of economic success would appear to be with a feed water of low salinity with a low proportion of divalent cations. The water from Well 49 at Yuma, Ariz. is such a water (Saline Water Conversion Report, 1970-71, Table 2-42, p 131). Table V shows its composition. The total feed anion concentration is 0.0629 equiv/l.; the proportion of divalent cations in the feed is 28 equiv. %.

Shown in Figures 2a, b, and c are values of $L\mathcal{D}_2/lq$ computed by numerical integration of Equation 4a. The $L\mathcal{D}_2/lq$ is plotted against X for three values of the water recovery [20% ($K = 1.25$), 50% ($K = 2$), 80% ($K = 5$)], three values of A [2 ($\mathcal{D}_2/\mathcal{D}_1 = 1$), -0.8 ($\mathcal{D}_2/\mathcal{D}_1 = 0.3$), -2 ($\mathcal{D}_2 \ll \mathcal{D}_1$)], and three degrees of softening ($= 1 - c_{2\beta}/c_{2\alpha}$) (50%, 90%, 99%). In these computations, $R = 1$, $c = 0$, and $\theta = 1$. If we use our previous estimate for $L/\mathcal{D}_1$, we find that $L/q = 880 \times 4/(A+2) \times L\mathcal{D}_2/lq$ ft²/daily kgal. The lowest price for any of the cases considered is for 80% water recovery ($K = 5$) and 50% softening. If we again take a capacity of 1 mol/l., $X = 15.9$, and we find values of $L\mathcal{D}_2/lq$ of 0.035 and 0.018 for $A = 2$ and -0.8 , respectively. These values correspond to membrane requirements of 30.8 and 52.8 ft²/daily kgal., respectively, and costs of 9.85¢ and 16.9¢/kgal. The corresponding figures for 90% softening are 18.3¢ and 34.6¢/kgal.

The capacity of 1 mol/l. and the conductance of 200 mmho cm^{-2} we have been using are good average values for electrodialysis membranes, but not as good as the best values available. The Tokuyama Soda Co. of Japan manufacturers a cation exchange membrane with a dry capacity of about 2.0-2.5 meq/g, a gel water when wet of about 33% on a dry basis, and a conductance of about 370-430 mmho cm^{-2} (Spiegler,

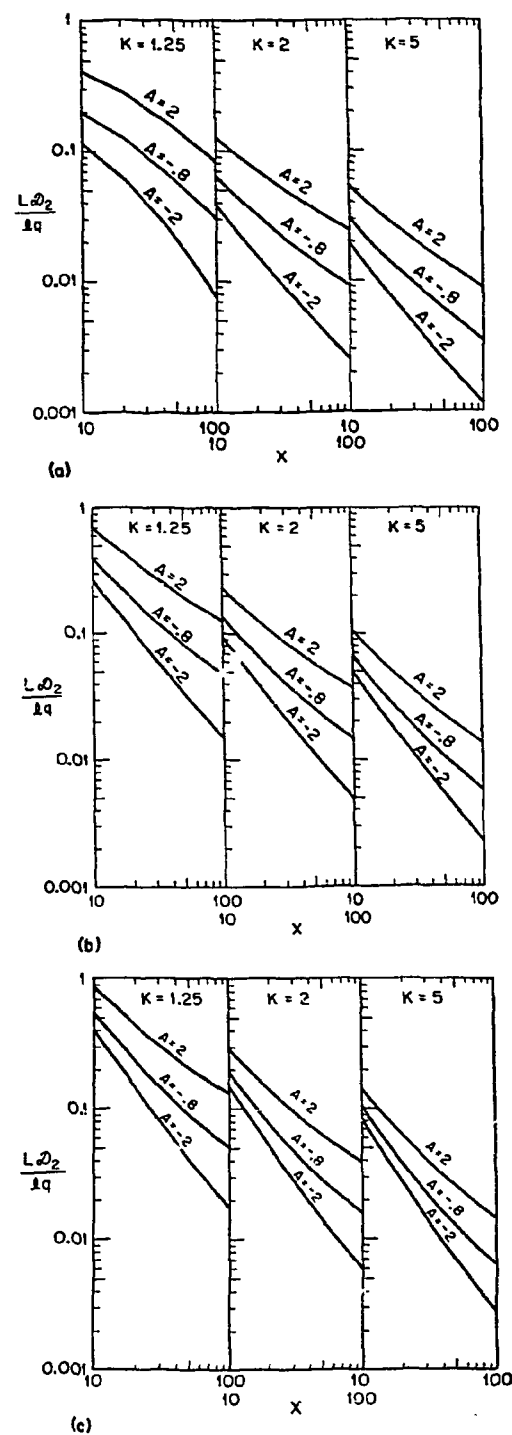


Figure 2a,b,c. Results of Donnan softening calculations for feed water at Yuma, Ariz.

Figure 2a is for 50% softening, 2b for 90% softening, and 2c for 99% softening. No salt has been added to brine ($c = 0$); $R = 1$; $\theta = 1$

1966, pp 209-11). Using the highest capacity (2.5/1.33 mol/l.), we find $X = 30$. In such membrane $\mathcal{D}_2/\mathcal{D}_1 = 0.3$ ($A = -0.8$) is most reasonable. For these values we find $L\mathcal{D}_2/lq = 0.0096$ and 0.018 for 50% and 90% softening, respectively. Using a conductance of 430 mmho cm^{-2} , we find $L/\mathcal{D}_1 = 770$ ft²/daily kgal., and cost items of 7.87¢ and 14.7¢ per kilogallon respectively, for 50% and 90% softening.

Next we inquire to what extent these costs might be lowered by adding salt to the brine. Shown in Figure 3 are the results of the appropriate calculations of $L\mathcal{D}_2/lq$ plotted against θ for several salt additions. Two sets of curves are shown arranged in pairs, one curve for $R = 1$ and one curve for $R = 0.8$. The upper curve of each pair corresponds to $R = 0.8$. The close agreement of the curves of each pair shows that dependence of $L\mathcal{D}_2/lq$ on R is only slight.

The strange behavior of the curves marked $c = 0.25$ for the case of 90% softening comes about in the following way.

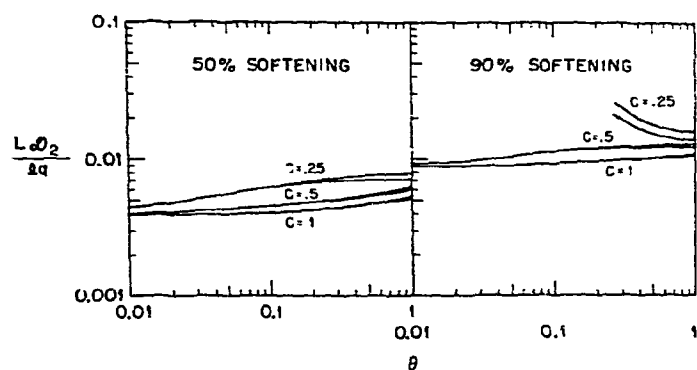


Figure 3. Results of Donnan softening calculations for feed water at Yuma, Ariz., when salt is added to brine

$X = 30$; $K = 5$; $A = -0.8$. Upper curve of each pair corresponds to $R = 0.8$, lower curve to $R = 1$

Table VI. Costs for Softening Yuma Water with Salt Addition to Brine

c	50% softening			90% softening		
	Mem. cost	Salt cost	Total cost	Mem. cost	Salt cost	Total cost
0.25	3.70	2.64	6.34	...	...	...
0.50	3.36	5.28	8.64	7.95	5.29	13.23
1.00	3.28	10.56	13.84	7.30	10.56	17.86

Suppose we decrease θ without adding any salt to the brine. The divalent cations that pass through the membrane enter a smaller and smaller stream as θ decreases. This tends to decrease the driving force for diffusion near points α and ω . On the other hand, fewer divalent cations are introduced into the brine channel from the plant proper as θ decreases. This second effect tends to increase the driving force. If the degree of softening is high, this second effect is small compared with the first, and the membrane requirements will go up as θ decreases. This clearly can also happen if too little salt is added.

θ is certainly limited from below by the requirement that the brine stream not be saturated in NaCl, for then further reduction of θ does not increase the chemical potential of NaCl in the brine stream. Since the curves in Figure 3 are rather flat, we do not need very accurate estimates of θ . We use Equation 2a and set $c_{17} \approx 100$ (corresponding roughly to 6.3 m/l., since the feed anion concentration is 0.0629 m/l.). Since θ will be small, we have $Kc/c_{17} \approx 0.05c$ as the limiting value of θ . Using this value of θ , we obtain the costs as shown in Table VI. In both cases, addition of salt to the brine decreases the cost slightly.

For purposes of comparison, cost of chemicals for 100% softening of this water by the soda-lime process [0.00446 m/l. Ca(OH)_2 and 0.0441 m/l. Na_2CO_3] is about 7.65¢/kgal. [Costs: Na_2CO_3 @ \$31/ton, CaO @ \$16/ton (Battey et al., 1971, p 12).] Fifty percent softening could be accomplished by addition only of the Ca(OH)_2 at a cost of only 1.67¢/kgal.

Well at Webster, S.D.

Our next example is based on the feed water available in Webster, S.D., the composition of which is taken to be that shown in Table VII (Eisenmann and Smith, 1970, Figure 32, p 71). The total feed anion concentration is 0.025 equiv/l.; the proportion of divalent cations in the feed is 80 equiv %.

Shown in Figure 4a, b, and c are values of $L\cdot D_2/qL$ plotted vs. X for $K = 1.25, 2, 5$; $A = 2, -0.8, -2$; and 50%, 90%,

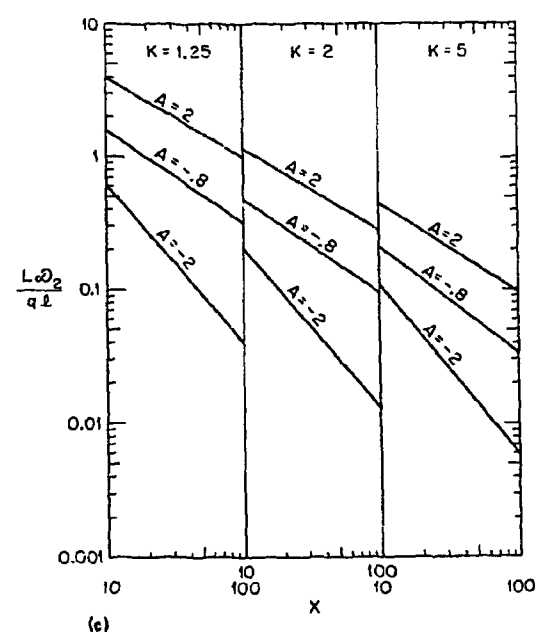
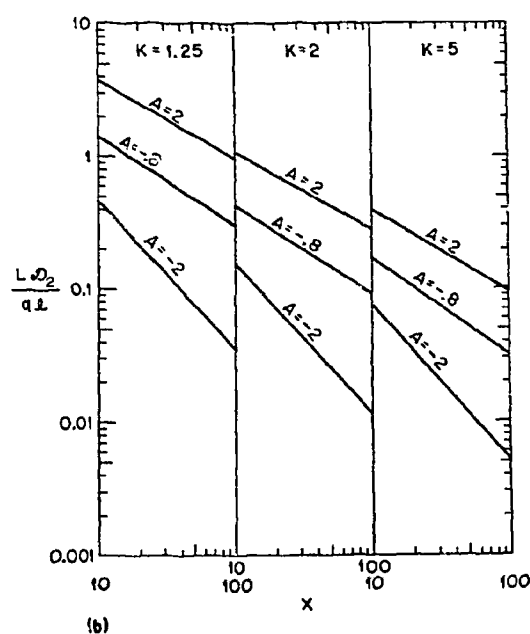
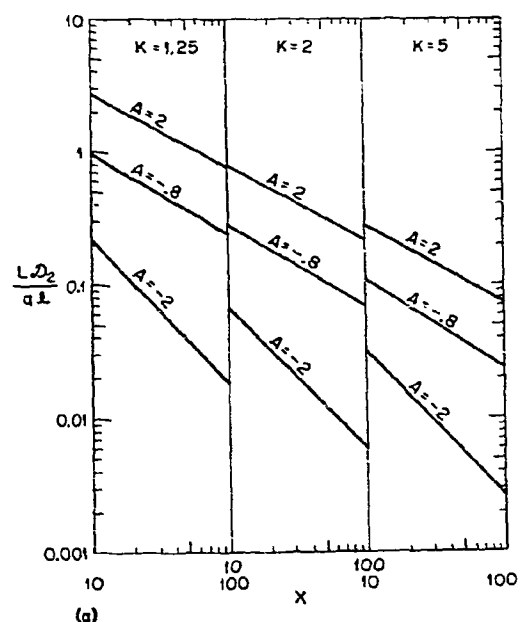


Figure 4a,b,c. Results of Donnan softening calculations for feed water at Webster, S.D.

Figure 4a is for 50% softening, 4b for 90% softening, and 4c for 99% softening. No salt has been added to brine ($c = 0$); $R = 1$; $\theta = 1$

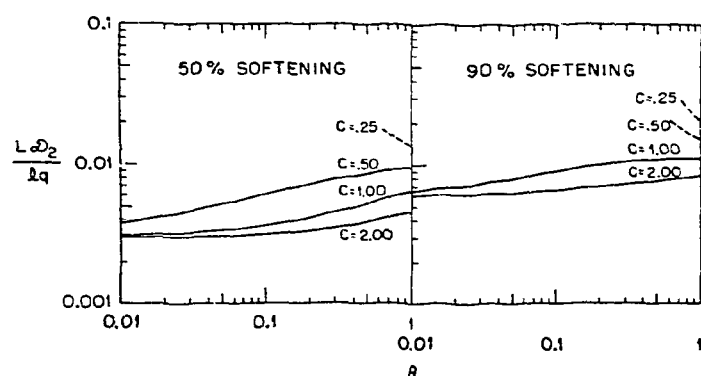


Figure 5. Results of Donnan softening calculations for feed water at Webster, S.D., when salt is added to brine

$$X = 75; K = 5; A = -0.8; R = 1$$

Table VII. Feed Water Composition at Webster, S.D.

Ion	Ppm	Mol/l.
Ca ²⁺	400	0.010
Na ⁺	115	0.005
SO ₄ ²⁻	960	0.010
Cl ⁻	178	0.005

and 99% softening. In these computations, $R = 1$, $c = 0$, and $\theta = 1$. As before, the lowest costs correspond to the highest water recoveries ($K = 5$). Using the Tokuyama membrane as the basis for the softening process, we find $X = 75$ and $l/D_1 = 770$ ft²/daily kgal. Using $A = -0.8$, we find $L D_2 / l q = 0.029$ for 50% softening, and 0.039 for 90% softening. The respective costs for these two degrees of softening are 23.8¢ and 32.0¢/kgal.

Next we examine the extent to which these costs may be reduced by adding salt to the brine. Shown in Figure 5 are plots of $L D_2 / l q$ vs. θ for several salt additions for 50% and 90% softening. If θ is again limited from below by the requirement that the brine channel not be saturated in NaCl, and if we choose $c_1 \approx 250$ (corresponding to 6.25 m/l. since the feed anion concentration is 0.025 m/l.), then $\theta \geq 0.02 c$. Using the limiting value of $0.02 c$ for θ , we find the costs as shown in Table VIII. Thus the minimum costs for 50% and 90% softening are about 5.14¢ and 9.87¢/kgal., respectively, compared with 23.8¢ and 32.0¢/kgal. without brine addition. The cost reduction due to salt addition is greater in this case than in the case of Yuma water because of the higher proportion of divalent cations in the Webster feed. For comparison, the cost of Na₂CO₃ to completely soften this feed is 13.6¢/kgal.

Synthetic Seawater

Our next example is a synthetic seawater (Smith, 1971, p 22) composed of 0.45M NaCl and 0.01M CaCl₂. The total feed anion concentration is 0.47 equiv/l.; the proportion of divalent cations in the feed is 4.26 equiv %. Shown in Figure 6 are plots of $L D_2 / l q$ vs. X for $K = 1.25, 2$, and 5; $A = 2, -0.8$, and -2 ; and 50, 90, and 99% softening. These curves refer to $R = 1$, $c = 0$, and $\theta = 1$. The dotted curves are the results of computations based on Equation 17a, which we expect to apply since $c_2 X \ll 3 c_1 a^2$ for all points in Figure 6.

Again we consider the case of 80% recovery ($K = 5$), the Tokuyama membrane ($X = 4$, $A = -0.8$), and 50 or 90% softening. The membrane costs in these two cases are 49.4¢ and 156¢/kgal., respectively. Since the approximate theory

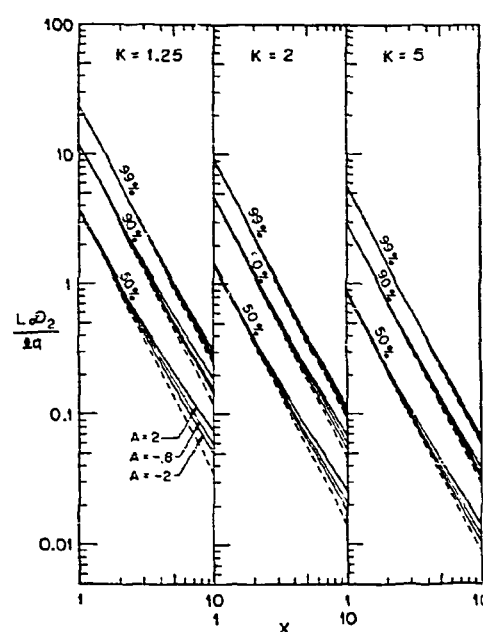


Figure 6. Results of Donnan softening calculations for synthetic seawater

No salt has been added to brine ($c = 0$); $R = 1$; $\theta = 1$. A-values correspond to three curves in each triple in way shown for triple at lower left. Dotted curves were calculated using Equation 17a

Table VIII. Costs for Softening Webster Water with Salt Addition to Brine

c	50% softening			90% softening		
	Mem. cost	Salt cost	Total cost	Mem. cost	Salt cost	Total cost
0.25	11.3 ^a	1.05	12.35	17.2 ^a	1.05	18.25
0.50	3.04	2.10	5.14	12.7 ^a	2.10	14.80
1.00	2.60	4.20	6.80	5.67	4.20	9.87
2.00	2.48	8.40	10.88	5.10	8.40	13.50

^a $\theta = 1$.

based on the assumption that the membrane is substantially in the univalent form throughout is valid, we see that a savings in membrane cost of at most 20% is possible. Moreover, the cost of the salt necessary to effect this savings would vastly outweigh the savings, so we expect salt addition to be of very little help. This point is brought out somewhat more fully by the results shown in Table IX. These results are based on Equation 17. In the case of 50% softening, no cost reduction appears possible; in the case of 90% softening, a cost reduction of about 8% appears to be possible. (The membrane costs were obtained by correcting the costs for $c = 0$, $\theta = 1$ obtained above by the ratio of the cost for (c, θ) to that for $c = 0$, $\theta = 1$ given by Equation 17.)

The cost of Na₂CO₃ to soften this synthetic seawater is 13.6¢/kgal.

Well at Roswell, N.M.

Our last example is based on the well water in Roswell, N.M., the composition of which is given in Table X (Saline Water Conversion Report, 1970-71, Table 1-1, p 13). The total feed anion concentration is 0.255 equiv/l.; the proportion of divalent cations in the feed is 15.7 equiv %.

Shown in Figure 7 are values of $L D_2 / l q$ plotted vs. X for $K = 1.25, 2, 5$; $A = 2, -0.8, -2$; and 50, 90, and 99% softening. In these computations $R = 1$, $c = 0$, $\theta = 1$. As before, the lowest costs correspond to the highest water recoveries ($K = 5$). Using the Tokuyama membrane, we find $X = 7.35$

Table IX. Effect of Salt Addition on Cost of Softening Synthetic Seawater

Degree of softening	c	θ	Mem. cost	Salt cost	Total cost
50%	0	1	49.4	0	49.4
50%	0.05	1	48.3	3.95	52.2
		0.1	59.0	3.95	63.0
		0.01	47.4	3.95	51.3
50%	0.1	1	47.2	7.9	55.1
		0.1	48.1	7.9	56.0
		0.01	41.5	7.9	49.4
50%	0.2	1	45.9	15.8	61.7
		0.1	42.9	15.8	58.7
		0.01	40.0	15.8	55.8
90%	0	1	156	0	156
90%	0.05	1	152	3.95	156
		0.1	361	3.95	365
		0.01	197	3.95	201
90%	0.1	1	150	7.9	158
		0.1	190	7.9	198
		0.01	139	7.9	147
90%	0.2	1	145	15.8	161
		0.1	146	15.8	162
		0.01	128	15.8	144
90%	0.3	1	142	23.7	165
		0.1	136	23.7	160
		0.01	126	23.7	150

Table X. Well Water Composition at Roswell, N.M.

Ion	Ppm	Mol/l.
Ca^{2+}	521	0.013
Mg^{2+}	170	0.007
Na^+	4950	0.215
SO_4^{2-}	1530	0.016
Cl^-	7810	0.220
HCO_3^-	195	0.003

Table XI. Costs for Softening Roswell Water with Salt Addition to Brine

c	50% softening			90% softening		
	Mem. cost	Salt cost	Total cost	Mem. cost	Salt cost	Total cost
0.1	23.8 ^a	4.30	28.1	63.1 ^a	4.30	67.4
0.2	19.5	8.60	28.1	59.0 ^a	8.60	67.6
0.3	18.1	12.90	31.0	55.0	12.90	67.9
0.5	17.5	21.50	39.0	51.0	21.50	72.5

^a $\theta = 1$.

and $L/D_1 = 770$ ft²/daily kgal. Using $A = -0.8$, we find $L/D_2/lq = 0.031$ for 50% softening and 0.081 for 90% softening. The respective costs for these two degrees of softening are 25.4¢ and 66.5¢/kgal.

If we add salt to the brine, we may reduce these costs. Shown in Figure 8 are values of $L/D_2/lq$ vs. θ for several values of c . If θ is again limited from below by the requirement that the brine channel not be saturated in NaCl, and if we choose $c_{17} = 25$ (corresponding to 6.38 m/l.), then $\theta \geq 0.2c$. Table XI shows the costs based on this value of θ (with exceptions noted). In neither case is salt addition of any help. The cost of chemicals to soften this water 100% [0.0085 m/l. $\text{Ca}(\text{OH})_2$ and 0.0115 m/l. Na_2CO_3] is 18.8¢/kgal.

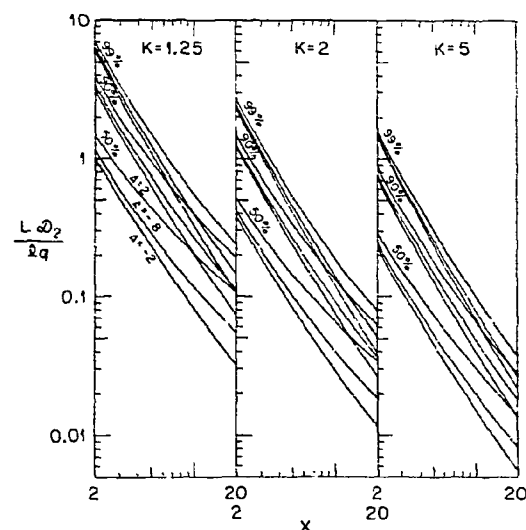


Figure 7. Results of Donnan softening calculations for feed water at Roswell, N.M.

No salt has been added to brine ($c = 0$); $R = 1$; $\theta = 1$. A-values correspond to three curves in each triple in way shown for triple at lower left

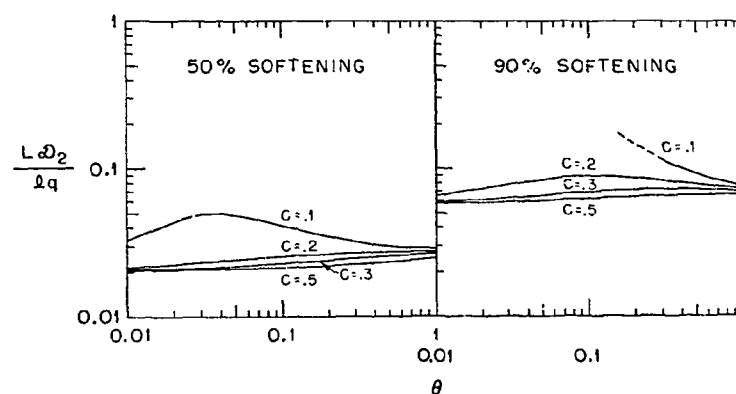


Figure 8. Results of Donnan softening calculations for feed water at Roswell, N.M., when salt is added to brine

$X = 7.35$; $K = 5$; $A = -0.8$; $R = 1$

Table XII. Summary of Cost Estimates

Feed		50% softening, ¢/kgal.	90% softening, ¢/kgal.	Cost of chemicals for soda-lime softening	
				50%	100%
Yuma	No salt	7.87	14.7	1.67	7.65
	Salt	6.34	...	...	...
Webster	No salt	23.8	32.0	6.80	13.6
	Salt	5.14	9.87	...	...
Syn. sea-water	No salt	49.4	156	6.80	13.6
	Salt	...	144	...	...
Roswell	No salt	25.4	66.5	5.20	18.8
	Salt	...	...	...	...

Cost Summary and Recommendations

Shown in Table XII is a summary of the costs we have estimated in the examples just discussed together with the cost of chemicals for 50 and 100% softening by the soda-lime process. As anticipated earlier, Donnan softening with present-day electrodialysis membranes is too costly for use with feed waters of high salinity—e.g., seawater or the water at Roswell. Even with less saline waters like those at Yuma or Webster, Donnan softening does not always compete favorably with the soda-lime process. It seems fair to say

that with present-day electrodialysis membranes, Donnan softening is not interesting economically. However, a drastic reduction in membrane cost—e.g., by a factor of ten—would make Donnan softening an attractive candidate for intensive development.

The most hopeful avenue for drastically reducing membrane costs is to make the membranes thinner. The typical thickness of a present-day electrodialysis membrane is 200 μ . A tenfold reduction in thickness to 20 μ , for example, would permit a tenfold reduction in membrane area required. This would be reflected in a tenfold reduction in cost when no salt is added to the brine, and when the cost per unit area is the same for the thinner as for the thicker membrane. The savings could conceivably be even greater because the thinner membrane would have only a tenth as much material per unit surface area as the thicker membrane. With a very cheap membrane surface, salt addition to the brine would probably not produce any savings. This is good because adding salt may complicate the brine disposal problem of inland desalting plants. Finally, it may be noted that ordinary dialysis membranes are often manufactured in the form of tubes, and such a configuration appears an excellent choice for Donnan softening.

Nomenclature

$$A = 4(\mathcal{D}_2/\mathcal{D}_1) - 2$$

c_1, c_2 = concentration of univalent (divalent) cations divided by feed anion concentration

c = amount of salt added to brine-makeup water per unit volume of feed treated divided by feed anion concentration

C = volumetric ion-exchange capacity of wet membrane
 D = distribution coefficient of univalent cations across membrane-solution interface

$\mathcal{D}_1, \mathcal{D}_2$ = diffusion coefficient of univalent (divalent) cations in membrane

F = Faraday

j_1, j_2 = current of univalent (divalent) cations through membrane divided by feed anion concentration

k = anion concentration in brine channel divided by feed anion concentration

$K(K-1)/K$ is fraction of feed water recovered as product

l = membrane thickness

L = length of membrane in x -direction

q = volumetric flow rate in feed channel per unit length in y -direction

R = salt rejection of desalting plant

R = universal gas constant

T = absolute temperature

X = C divided by feed anion concentration

x, y, z = length coordinates in directions specified in Figure 1

GREEK LETTERS

ϵ = electric field divided by RT/F

σ = conductance per unit area of wet membrane

θ = fraction of water not recovered as product that is used in brine makeup

SUBSCRIPTS

$\alpha, \beta, \gamma, \omega$ = points whose locations are shown in Figure 1

b = brine

f = feed

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7. Theoretical Studies

Summary

Transport through membranes has been one of the main interests of the Water Research Program since its inception. During the biennium of this report, support of transport studies has come from the National Science Foundation/RANN, as well as from OSW/Research. Two papers of L. Dresner in the category are reproduced here: one, (7.1), concerned with the theory of mosaic membranes and piezodialysis, and the other, (7.2), dealing with analysis of transport through ion-exchange membranes when more than one salt is present. For completeness, we list, but do not reproduce, a third paper supported by NSF/RANN: L. Dresner, "Stability of the Extended Nernst-Planck Equation in the Description of Hyperfiltration through Ion-Exchange Membranes," J. Phys. Chem., 76, 2256 (1972).

Another activity, in which NSF/RANN also shared support, was the revision of a chapter, "Hyperfiltration (Reverse Osmosis)," for the second edition of Principles of Desalination, edited by K. S. Spiegler and A. D. K. Laird, to be published by Academic Press. Much besides theory was reviewed, as the Table of Contents reproduced here (7.3) indicates. We shall discuss only one topic treated in the chapter, selected for relevance to the other papers included in this section, as well as Water Research Program's interests over the years (see Ref. 30, p. 1). This involves estimates from literature data of coupling between solute and solvent fluxes in ion-exchange membranes (7.4).

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7.1 GEOMETRIC EFFECTS IN PIEZODIALYSIS THROUGH CHARGE-MOSAIC MEMBRANES*

L. Dresner

SUMMARY

An explicit but highly schematic theory of the effect of the heterogeneity of charge-mosaic membranes on piezodialysis is given. An effect exists because the ions being transported through different parts of the membrane leave the feed bath at different points and also arrive in the filtrate bath at different points. The effect is always to reduce the salt flux through the membrane. The amount of reduction has been calculated for two geometric arrangements of the parts of the mosaic membrane, namely, alternating strips and a checkerboard of squares.

SYMBOLS

- A_n — expansion coefficient
- B_n — expansion coefficient
- c — concentration
- $\mathcal{D}$ — ionic diffusion constant (same for all ions)
- $\mathcal{D}_e$ — eddy diffusion constant
- E — electric field vector
- f — Fanning friction factor
- $\mathcal{F}$ — the Faraday
- h — width of an ion-exchange strip or side of an ion-exchange square
- h^+ — $h\nu_*/\nu$
- i — electric current density
- I — average magnitude of the electric current density i over a patch
- j — ionic current density
- J — average water flux vector
- l — membrane half-thickness
- L — phenomenological coefficient

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- p — pressure
 P — a function defined in Eq. (18)
 $\mathbf{q}$ — water flux vector
 R — universal gas constant
 T — absolute temperature
 U — mean stream velocity
 v — time-averaged water flow velocity at any point
 v_* — wall-shear velocity $= U(f/2)^{1/2}$
 v^+ — v/v_*
 $\bar{V}$ — specific volume of water
 x — distance coordinate parallel to the solution-membrane interfaces
 X — ion-exchange capacity per unit mass of water in the membrane
 y — distance coordinate perpendicular to the solution-membrane interfaces
 z — ionic charge in units of the proton charge ($z_1 = +1$, $z_2 = -1$)
 $\alpha = \frac{1}{2\pi} \frac{h}{l} \frac{\sigma_m(\sigma_f + \sigma_p)}{\sigma_f \sigma_p}$
 β — convective coefficient for counterions (see ref. (4))
 ε — membrane efficiency
 ε — (Appendix) electrical permittivity of water
 ν — kinematic viscosity
 ρ — electric charge density
 σ — conductivity
 ϕ — electrical potential
 ω — a number that is $+1$ for a cation exchanger and -1 for an anion exchanger

Subscripts

- f — high-pressure solution (feed)
 i — $i = 1$ denotes cations, $i = 2$ denotes anions
 m — membrane
 p — low-pressure solution (permeate)
 s — solution
 1 — (sec. 4) denotes water
 2 — (sec. 4) denotes counterions
 1 — (Appendix) denotes diffusive contribution to electric current
 2 — (Appendix) denotes contribution to electric current from migration in the electric field
 3 — (Appendix) denotes convective contribution to electric current

1. INTRODUCTION

Charge-mosaic membranes are membranes made up of alternating patches of anion and cation exchangers. When such a membrane is placed in a hyperfiltration cell, the filtrate may be enriched in salt compared to the feed (1-3). This process has been called piezodialysis. If the salt enrichment of the filtrate were great enough, piezodialysis could represent an interesting membrane process for the desalination of brackish water.

Piezodialysis is one of many possible processes involving transport through composite membranes, *i.e.*, membranes made of patches of different materials. An elaborate general theory of such membranes has been given by Kedem and Katchalsky (4), but it ignores geometric effects arising from the heterogeneity of the membrane. These geometric effects arise because the ions being transported through different patches of membrane leave the feed bath at different points and also arrive in the filtrate bath at different points. In the theory of Kedem and Katchalsky this "mixing" and "unmixing" is treated as though it takes place instantaneously, whereas in fact it does not. The purpose of this paper is to generalize the theory of Kedem and Katchalsky to include geometric effects.

The next section is devoted to a detailed physical description of piezodialysis. The following six sections cover the mathematical details of the theory. The last section contains a discussion of the results.

2. DESCRIPTION OF PIEZODIALYSIS

To see how piezodialysis works, let us first consider how hyperfiltration with an ordinary ion-exchange membrane works. To begin with, imagine the membrane immersed in pure water. If we exert pressure on the water on one side of the membrane, water flows through the membrane. The water exerts a frictional force on the mobile counterions in the membrane, tending to propel them in the direction of water flow. In the first instants of flow, there is a downstream shift of the counterions. An excess of counterions appears at the low-pressure face of the membrane, a paucity at the high-pressure face. This charge separation creates an electric field, which opposes further counterion flow. The electric field is the source of the well-known streaming potential. It serves to prevent a steady separation of electric charge.

If the water on the high-pressure side of the membrane contains salt, coions invade the membrane. Now a steady flux of counterions through the membrane is possible, accompanied by a flux of coions carrying an equal but opposite charge. Since counterions are much more numerous in the membrane than coions, pure convection would produce a counterion flux that far outweighed the coion flux. The streaming potential retards the counterions and accelerates the coions so that electroneutrality of the filtrate is maintained. The salt flow is limited by the extent

of coion invasion, and if the latter is sufficiently low, the filtrate will be salt-poor compared with the feed (hyperfiltration).

If the patches of anion and cation exchanger in a mosaic membrane are close together, the counterion currents through different patches could neutralize one another and prevent buildup of a streaming potential. Ideally, the counterion currents could approach the convective limit, *i.e.*, the limit in which the counterions are dragged along by the permeating water unhampered by any electric field. Since the counterion concentration in the ion-exchange patches is much larger than in the high-pressure solution (feed), the salt concentration of the filtrate would be much higher than the salt concentration of the feed. The water remaining on the high-pressure side of the membrane would be desalted and kept as product, while the filtrate would be rejected (piezodialysis).

This ideal situation is not achieved because the two counterion currents reach the low-pressure surface of the mosaic membrane in different places. In order to neutralize one another, ions of opposite charge must migrate through the low-pressure bath toward one another. If the path is long or the conductivity low, the counterions coming through each patch at first build up in concentration at the low-pressure surface of the patch. Owing to the depletion of counterions at the high-pressure surface of each patch, an equivalent excess of coions appears there. Electric charges of opposite sign thus appear on opposite faces of each patch, creating a streaming potential across the patch. This streaming potential retards the counterion flow through the patches, slowing the buildup of charge on the faces of the patches. The electric charges on the faces of the patches also create an electric field in the external solutions. This electric field drives ions of opposite signs toward one another and opposes the buildup of charge on the faces of the patches. The electric charges build up on the faces of the patches until a steady state is reached. In this steady state, the ionic flows drive electric currents into one patch and out of the adjacent ones, the circuits being completed in the two solutions (5). The steady-state currents through the patches are less than they would be in the convective limit owing to the buildup of electric charges on the faces of the patches. For maximum efficiency of piezodialysis, the resistance of the solution paths should be kept as low as possible.

Since the filtrate is more concentrated than the feed, salt tends to diffuse back through the membrane from the low-pressure bath to the feed. This back-diffusion of salt also limits the effectiveness of piezodialysis. The effectiveness of piezodialysis is thus determined by a competition between convection, back-diffusion, and retardation of counterions by the streaming potential.

In the following sections of this paper, the foregoing qualitative description of piezodialysis will be rendered into quantitative terms. In doing this, it will prove an enormous simplification to assume (1) *that the ion-exchange patches are identical in all regards save for the signs of their charge and that the same is true for the mobile ions* (we consider only one uni-univalent salt). We shall henceforth refer to

these assumptions as the assumption of charge symmetry. In addition to the assumption of charge symmetry, we assume (2) *that coions are completely excluded from the ion-exchange patches*, and (3) *that salt buildup or depletion (concentration polarization) at the membrane faces can be ignored*. Assumption (3) will be discussed at some length in section 9. Furthermore, (4) *we ignore all activity coefficients*. Finally, in this paper we deal with two geometric arrangements of the patches, namely, *alternating strips* and a *checkerboard of squares*.

One further item needs discussion before we turn to the quantitative aspects of the theory, namely, the size of the potential difference between the two solutions. When two solutions are separated by an ion-exchange membrane, a distribution of electric potential arises in each of them. Sufficiently far from the membrane, the potential in each solution becomes uniform (potential of the bulk solution). When an ordinary homogeneous ion-exchange membrane separates two solutions of different concentration, there is a difference of potential between the bulk solutions. However, when a charge-symmetric mosaic membrane with either of the geometric arrangements of patches considered in this paper separates solutions of a charge-symmetric electrolyte, *there is no potential difference between the bulk solutions*.

This conclusion is purely a consequence of the assumptions of charge and geometric symmetry we have made, as we can see in the following way. There are certain lines (which we identify explicitly below) perpendicular to the surface of the membrane around which the distribution of electric charge is antisymmetric under inversion. By antisymmetry of electric charge under inversion around a line L we mean the following. Consider pairs of points P and P' such that the line L intersects the line segment PP' at right angles in the midpoint of PP' . If the electric charge densities at P and P' have opposite signs for every pair of points P and P' , then the electric charge density is said to be antisymmetric under inversion around the line L . In the strip membrane, the lines L are any lines perpendicular to the membrane through the boundaries between adjacent patches. In the checkerboard membrane, the lines L are the lines perpendicular to the membrane through the midpoints of the sides of the square patches. Along these lines, the electric field vector points parallel to the membrane surface. If we move a test charge along one of these lines from one solution to the other, it experiences no force, and therefore no change in potential. Hence the two bulk solutions are at the same potential. Since the zero of potential can be chosen arbitrarily, we choose it now to be the potential of the bulk solutions.

3. LAPLACE'S EQUATION FOR THE POTENTIAL; SYMMETRY CONDITIONS

It follows from assumptions 1 and 3 that the electrical potential in the aqueous phases satisfies Laplace's equation. To see this we begin by writing the Nernst-Planck equation for the ionic currents

$$j_i = -D \text{grad } c_i + \frac{D\mathcal{F}}{RT} z_i c_i E. \quad (1)$$

If we multiply Eq. (1) by $z_i \mathcal{F}$ and sum over i , we get

$$i = \sum_{i=1}^2 j_i z_i \mathcal{F} = -\mathcal{F} D \text{grad} \left(\sum_{i=1}^2 z_i c_i \right) + \frac{D\mathcal{F}^2}{RT} \left(\sum_{i=1}^2 z_i^2 c_i \right) E. \quad (2)$$

Electroneutrality requires that

$$\sum_{i=1}^2 z_i c_i = 0.$$

In the steady state $\text{div } i = 0$, for otherwise there would be a steady accumulation of charge. Since

$$\sum_{i=1}^2 z_i^2 c_i$$

does not vary from point to point according to assumption 3, the vanishing of $\text{div } i$ implies $\text{div } E = 0$. Since $E = -\text{grad } \phi$,

$$\nabla^2 \phi = 0 \quad (3)$$

in the aqueous phases.

Similar considerations hold in the interior of an ion-exchange patch. Since coions are completely excluded from the patches (assumption 2), only counterions are available to neutralize the fixed charge. Because the fixed charge is uniformly distributed through each patch, the counterion concentration in the interior of each patch is also spatially uniform. Thus there is no diffusion of counterions, and the transport of counterions is due solely to convection and migration in the electric field (6):

$$j_i = \beta J X + \frac{D\mathcal{F}}{RT} z_i X E \quad (4)$$

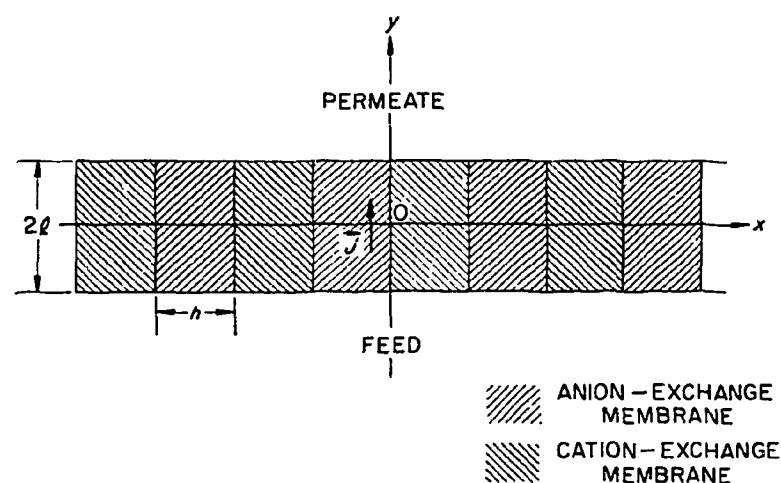


Fig. 1. Schematic diagram of the mosaic membrane showing the coordinate system used.

Again $z_i \mathcal{F} \operatorname{div} \mathbf{j}_i = \operatorname{div} \mathbf{i} = 0$ in the steady state. Continuity of fluid flow requires that $\operatorname{div} \mathbf{J} = 0$, so that $\operatorname{div} \mathbf{E}$ again equals zero. Thus (3) also holds in the interior of each ion-exchange patch.

Let us now consider a specific kind of membrane, one made up of alternating strips of anion- and cation-exchange patches. (Such membranes have actually been constructed (7)). The setup we are considering is shown in Fig. 1. The x -coordinate measures distance parallel to the faces of the membrane and normal to the planes of lamination; the y -coordinate measures distance in the direction perpendicular to the membrane. The origin 0 is chosen in the midplane of the membrane at a point lying on the interface between two adjacent patches. Owing to the periodicity and geometric symmetry of the situation, the potential ϕ obeys the following conditions

$$\phi(x + 2h, y) = \phi(x, y) \quad (5a)$$

$$\phi(-x, y) = -\phi(x, y) \quad (5b)$$

$$\phi(h - x, y) = \phi(x, y) \quad (5c)$$

4. BOUNDARY CONDITIONS; UNIQUENESS OF SOLUTION

We apply the following boundary conditions

$$\phi = 0 \quad \text{when} \quad y = \pm \infty \quad (6a)$$

$$\phi = 0 \quad \text{at} \quad x = Nh \quad \text{when} \quad |y| > l, N = 0, \pm 1, \pm 2, \dots \quad (6b)$$

$$\left(\frac{\partial \phi}{\partial x} \right)_{x=Nh} = 0 \quad \text{when} \quad |y| < l, N = 0, \pm 1, \pm 2, \dots \quad (6c)$$

$$\left. \begin{aligned} -\sigma_p \left(\frac{\partial \phi}{\partial y} \right)_{y=l+0} &= \omega \beta J X \mathcal{F} - \sigma_m \left(\frac{\partial \phi}{\partial y} \right)_{y=l-0} \\ -\sigma_f \left(\frac{\partial \phi}{\partial y} \right)_{y=-l-0} &= \omega \beta J X \mathcal{F} - \sigma_m \left(\frac{\partial \phi}{\partial y} \right)_{y=-l+0} \end{aligned} \right\} \quad (6d)$$

$$\left. \begin{aligned} \phi(y = l + 0) &= \phi(y = l - 0) + \omega \frac{RT}{\mathcal{F}} \ln \left(\frac{X}{c_p} \right) \\ \phi(y = -l - 0) &= \phi(y = -l + 0) + \omega \frac{RT}{\mathcal{F}} \ln \left(\frac{X}{c_f} \right) \end{aligned} \right\} \quad (6e)$$

where ω is a function of position that equals +1 for a cation exchanger and -1 for an anion exchanger.

Eq. (6a) is the condition that the potential vanish far from the membrane already discussed in section 2. Eq. (6b) is a consequence of the continuity of the potential in the external phases and (5b) and (5c). Eq. (6c) says that no electric current crosses the boundary between two patches. Eqs. (6d) are the conditions of continuity of the normal component of electric current at the boundaries between the membrane and the external solutions. Eqs. (6e) say that the potential suffers a jump equal to the Donnan potential at the boundaries between the membrane and the solutions.

Eqs. (6) define a *unique* solution of Laplace's equation. To see this, suppose there were two different solutions of Laplace's equation, ϕ_1 and ϕ_2 , that satisfy (6a-e). Their difference $\psi = \phi_1 - \phi_2$ also satisfies Laplace's equation as well as boundary conditions (6a-c). Eqs. (6d) and (6e) become for ψ

$$\left. \begin{aligned} \sigma_p \left(\frac{\partial \psi}{\partial y} \right)_{y=l+0} &= \sigma_m \left(\frac{\partial \psi}{\partial y} \right)_{y=l-0} \\ \sigma_f \left(\frac{\partial \psi}{\partial y} \right)_{y=-l-0} &= \sigma_m \left(\frac{\partial \psi}{\partial y} \right)_{y=-l+0} \end{aligned} \right\} \quad (7a)$$

$$\left. \begin{aligned} \psi(y = l + 0) &= \psi(y = l - 0) \\ \psi(y = -l - 0) &= \psi(y = -l + 0) \end{aligned} \right\} \quad (7b)$$

Thus in the strip $0 < x < h$ (which is really all we need to consider), ψ is the potential that would be present if (i) the permeate were replaced by an electronic conductor P of conductivity σ_p , (ii) the membrane were replaced by an electronic conductor M of conductivity σ_m , (iii) the feed solution were replaced by an electronic conductor F of conductivity σ_f , (iv) the surfaces $x = 0, h, |y| > l$ were covered with a thin layer of a perfect, grounded conductor, and (v) the surfaces $x = 0, h, |y| < l$ were covered with a thin layer of a perfect insulator.

Now if $\nabla\psi \neq 0$ at some point in the strip PMF, the electrical energy being dissipated into heat per unit volume at that point would be $\mathbf{i} \cdot \mathbf{E} = \sigma (\nabla\psi)^2$. But since the strip PMF is not connected to an external source of energy, there cannot be any steady dissipation of energy. Thus $\nabla\psi$ must vanish everywhere. Then $\psi = \text{constant}$. The constant must be zero since, for example, ψ vanishes at $x = 0, |y| > l$. Hence the difference between ϕ_1 and ϕ_2 must vanish, and there cannot be two different solutions of Laplace's equation obeying the boundary conditions (6a-e).

5. FOURIER SERIES

Functions obeying the symmetry conditions (5a–c) have Fourier series of the form

$$\phi = \sum_{n=1,3,5,\dots} \phi_n(y) \sin \left(\frac{n\pi x}{h} \right) \quad (8a)$$

with Fourier coefficients $\phi_n(y)$ given by

$$\phi_n(y) = \frac{2}{h} \int_0^h \phi(x, y) \sin \left(\frac{n\pi x}{h} \right) dx \quad (8b)$$

If we differentiate (8b) twice with respect to y we find that

$$\frac{d^2 \phi_n}{dy^2} = - \frac{2}{h} \int_0^h \frac{\partial^2 \phi(x, y)}{\partial x^2} \sin \left(\frac{n\pi x}{h} \right) dx \quad (9)$$

since $\partial^2 \phi(x, y) / \partial y^2 = -\partial^2 \phi(x, y) / \partial x^2$. Integrating once by parts we get

$$\frac{d^2 \phi_n}{dy^2} = - \frac{2}{h} \left[\frac{\partial \phi(x, y)}{\partial x} \sin \left(\frac{n\pi x}{h} \right) \right]_0^h + \frac{2n\pi}{h^2} \int_0^h \frac{\partial \phi(x, y)}{\partial x} \cos \left(\frac{n\pi x}{h} \right) dx \quad (10)$$

The integrated term vanishes because the sine vanishes at both limits. Integrating again by parts we find

$$\frac{d^2 \phi_n}{dy^2} = \frac{2n\pi}{h^2} \left[\phi(x, y) \cos \left(\frac{n\pi x}{h} \right) \right]_{0+0}^{h-0} + \frac{2(n\pi)^2}{h^3} \int_0^h \phi(x, y) \sin \left(\frac{n\pi x}{h} \right) dx \quad (11a)$$

$$= - \frac{4n\pi}{h^2} \phi(0 + 0, y) + \left(\frac{n\pi}{h} \right)^2 \phi_n(y) \quad (11b)$$

since $\phi(0 + 0, y) = \phi(h - 0, y)$ by Eq. (5c).

$\phi(0 + 0, y) = 0$ for $|y| > l$ by (6b). Then $\phi_n(y)$ is most generally a linear combination of $\exp(n\pi y/h)$ and $\exp(-n\pi y/h)$. Since ϕ vanishes at $y = \pm \infty$ [Eq. (6a)],

$$\phi_n = A_n'' \exp \left(- \frac{n\pi y}{h} \right) \quad y > l \quad (12a)$$

$$\phi_n = A_n' \exp \left(\frac{n\pi y}{h} \right) \quad y < -l \quad (12b)$$

so that

$$\phi = \sum_{n=1,3,5,\dots} A_n'' \exp\left(-\frac{n\pi y}{h}\right) \sin\left(\frac{n\pi x}{h}\right) \quad y > l \quad (12c)$$

$$\phi = \sum_{n=1,3,5,\dots} A_n' \exp\left(\frac{n\pi y}{h}\right) \sin\left(\frac{n\pi x}{h}\right) \quad y < -l \quad (12d)$$

Inside the membrane, ϕ is not continuous across the boundaries between adjacent patches and $\phi(0+0, y) \neq 0$. (To see that $\phi(0+0, y) \neq 0$, note that if $J = 0$ and the external solutions have identical compositions, then $\phi(0+0, y) = (-RT/\mathcal{F}) \ln(X/c_s)$, the Donnan potential.) In general we do not know $\phi(0+0, y)$, so we cannot specify $\phi_n(y)$ when $|y| < l$. In spite of this, there is value in continuing the analysis in a general way.

The potential given by (12c, d) in the external phases already satisfies (6a) and (6b). We satisfy (6c) in the following way. Because according to (6c) no current can cross the boundary between a cation- and an anion-exchange patch, the average electric current density flowing through a cation-exchange patch (amps cm^{-2}) is given by either one of the following two equivalent expressions:

$$I = -\frac{1}{h} \int_0^h \sigma_p \left(\frac{\partial \phi}{\partial y} \right)_{y=l+0} dx = \frac{2\sigma_p}{h} \sum_{n=1,3,5,\dots} A_n'' e^{-n\pi l/h} \quad (13a)$$

$$I = -\frac{1}{h} \int_0^h \sigma_f \left(\frac{\partial \phi}{\partial y} \right)_{y=-l-0} dx = -\frac{2\sigma_f}{h} \sum_{n=1,3,5,\dots} A_n' e^{-n\pi l/h} \quad (13b)$$

Thus (6c) implies

$$\sigma_p A_n'' = -\sigma_f A_n' \quad (13c)$$

The average electric current density flowing through an anion-exchange patch is $-I$.

Eqs. (6d) and (6e) can be written

$$\sigma_p A_n'' \left(\frac{n\pi}{h} \right) \exp\left(-\frac{n\pi l}{h}\right) = \left(\frac{4}{n\pi} \right) \beta J X \mathcal{F} - \sigma_m \left(\frac{d\phi_n}{dy} \right)_{y=l-0} \quad (14a)$$

$$-\sigma_f A_n' \left(\frac{n\pi}{h} \right) \exp\left(-\frac{n\pi l}{h}\right) = \left(\frac{4}{n\pi} \right) \beta J X \mathcal{F} - \sigma_m \left(\frac{d\phi_n}{dy} \right)_{y=-l+0} \quad (14b)$$

$$A_n'' \exp\left(-\frac{n\pi l}{h}\right) = \phi_n(y=l-0) + \frac{4}{n\pi} \frac{RT}{\mathcal{F}} \ln\left(\frac{X}{c_p}\right) \quad (14c)$$

$$A_n' \exp\left(-\frac{n\pi l}{h}\right) = \phi_n(y=-l+0) + \frac{4}{n\pi} \frac{RT}{\mathcal{F}} \ln\left(\frac{X}{c_f}\right) \quad (14d)$$

since the Fourier expansion of ω is

$$\omega = \sum_{n=1,3,5,\dots} \frac{4}{n\pi} \sin\left(\frac{n\pi x}{h}\right) \quad (15)$$

If we subtract (14d) from (14c) and replace A'_n by $-(\sigma_p/\sigma_f)A''_n$, we get

$$\left(1 + \frac{\sigma_p}{\sigma_f}\right) A''_n \exp\left(-\frac{n\pi l}{h}\right) = \Delta\phi_n - \frac{4}{n\pi} \frac{RT}{\mathcal{F}} \ln\left(\frac{c_p}{c_f}\right) \quad (16)$$

where $\Delta\phi_n$ is an abbreviation for $\phi_n(y=l-0) - \phi_n(y=-l+0)$. Using (14a) and (16), we can show that

$$\frac{2\sigma_p}{h} A''_n \exp\left(-\frac{n\pi l}{h}\right) = \frac{8}{\pi^2} \frac{\beta J X \mathcal{F} - b_n \frac{\sigma_m}{2l} \frac{RT}{\mathcal{F}} \ln\left(\frac{c_p}{c_f}\right)}{n \left(n + b_n \frac{h}{2\pi l} \frac{\sigma_m(\sigma_p + \sigma_f)}{\sigma_p \sigma_f} \right)} \quad (17a)$$

where*

$$b_n = \frac{2l}{\Delta\phi_n} \left(\frac{d\phi_n}{dy} \right)_{y=l-0} \quad (17b)$$

Formulas (17a) and (17b) are *exact*, but not yet of much direct help since they contain the unknown quantities b_n .

6. APPROXIMATE SOLUTION FOR I

Let us consider first a membrane in which h is very large compared with l , and let us focus our attention on a tube of current emerging from the central portions of a patch. The resistance of the outer parts of the tube (the parts in the external solutions) is large compared with the resistance of the inner parts of the tube (the parts in the membrane), assuming σ_m is not $\ll \sigma_p, \sigma_f$. In that case, conditions in the tube near and within the membrane resemble the conditions in an ordinary ion-exchange membrane of the same type as the patch. Only a small current flows in the tube compared with the current that would flow in the absence of external resistance. The electric field is nearly parallel to the y -axis and the electric field strength E is close to $-\omega\beta J X \mathcal{F} / \sigma_m$. For such a field, $2l(\partial\phi/\partial y)_{y=l-0} \approx \Delta\phi$.

These relations cannot hold for all current tubes. In particular, they fail for those emerging from the patches sufficiently close to the boundaries between patches that the resistance of the outer parts of the tubes is less than or comparable with the resistance of the inner parts of the tubes. Such tubes emerge from the patches up to a distance x from the boundaries given roughly by $\pi x[(1/\sigma_p) +$

* Note that it follows from (13c), (14a), and (14b) that $(d\phi_n/dy)_{y=l-0} = (d\phi_n/dy)_{y=-l+0}$.

$(1/\sigma_f)] \sim (4l/\sigma_m)$. We conclude from this reasoning that the relation $2l(\partial^2\phi/\partial y^2)_{y=l-0} = \Delta\phi$ is a good approximation everywhere on a patch surface except possibly in a region of width $2x$ symmetrically located around each boundary. We further note that

$$\frac{x}{h} = \frac{l}{\pi h} \frac{4\sigma_p\sigma_f}{\sigma_m(\sigma_p + \sigma_f)} \ll 1.$$

When two periodic functions with the same period differ substantially only over a small interval of each period, their Fourier coefficients only differ substantially when the wave length becomes comparable with or shorter than the width of the interval. Hence we expect $2l(d\phi_n/dy)_{y=l-0} \approx \Delta\phi_n$ and $b_n \approx 1$ for

$$n \lesssim \frac{h}{x} = \frac{\pi h}{l} \frac{(\sigma_p + \sigma_f)\sigma_m}{4\sigma_p\sigma_f}.$$

Now if we examine the terms (17a) in the series (13a) for I , we see that the main contribution comes from small n , i.e., from values of n for which $b_n \approx 1$. By way of approximation, we set $b_n = 1$ for all n . We expect this approximation to be better, the larger the value of $(\pi h/l)[(\sigma_p + \sigma_f)\sigma_m/4\sigma_p\sigma_f]$, since then the terms in (13a) for which $b_n = 1$ is a good approximation, account for a larger fraction of the total value of the sum.

Now let us consider a membrane in which h is very small compared with l . If h is small enough, the resistance of the outer parts of any current tube is then much smaller than the resistance of its inner part. Conditions are then nearly the same as they would be if the conductivity of the external solutions were infinite. The outer surfaces of the membrane ($y = l + 0$, $y = -l - 0$) are surfaces of zero potential. Inside the membrane, the electric field is uniform, parallel to the y -axis, and of magnitude $-(\omega/2l)(RT/\mathcal{F}) \ln(c_p/c_f)$.^{*} Again, $b_n = 1$ is a good approximation. We expect, therefore, that $b_n = 1$ is always a good approximation, no matter what the size of h compared with l .

Calculating I from Eq. (13a), we find

$$I = \left(\beta J X \mathcal{F} - \frac{\sigma_m}{2l} \frac{RT}{\mathcal{F}} \ln \frac{c_p}{c_f} \right) \sum_{n=1,3,5,\dots} \frac{8/\pi^2}{n \left(n + \frac{h}{2\pi l} \frac{\sigma_m(\sigma_f + \sigma_p)}{\sigma_f\sigma_p} \right)} \quad (18)$$

Eq. (18) is the central result of this paper. On the left-hand side appears the quantity I which equals the electric current density (amps cm^{-2}) through the cation-exchange patches. The electric current density through the anion patches is $-I$. The total salt flux (moles $\text{cm}^{-2} \text{sec}^{-1}$) through the membrane is $I/2\mathcal{F}$. The factor of 2 arises because an equivalent of cations flowing through a cation-exchange patch and an equivalent of anions flowing through an anion-exchange

^{*} See the discussion in section 9.

patch combine to give one mole of salt. In other words, two units of electric current are needed to provide one unit of salt flux.

The first term in the parentheses on the right-hand side of (18) is the convective contribution to the electric current density in the absence of any streaming potential.* The second term in the parentheses is the contribution from back-diffusion, also in the absence of any streaming potential. It is the product of the electric potential $(RT/\mathcal{F}) \ln(c_p/c_f)$ and the membrane conductance per unit area $\sigma_m/2l$. The difference of these two terms is the current that would flow in the absence of any streaming potential. This current we call the limiting current. The limiting current is multiplied by an infinite sum which depends on the dimensions h and l as well as on the various conductivities. We call this infinite sum the membrane efficiency ε : it specifies the attainable fraction of the limiting current.

7. EVALUATION OF ε

In order to evaluate I , we need to know the value of ε , which we can write as

$$\varepsilon = \frac{8}{\pi^2} \sum_{n=1,3,5,\dots} \frac{1}{n(n+\alpha)} \quad (19a)$$

$$\alpha = \frac{h}{2\pi l} \frac{\sigma_m(\sigma_p + \sigma_f)}{\sigma_p \sigma_f}. \quad (19b)$$

When $\alpha = 0$, $\varepsilon = (8/\pi^2)(1 + 1/3^2 + 1/5^2 + \dots)$. This latter series is well known (8) and has the value $\pi^2/8$, so that $\varepsilon(0) = 1$ as expected. To find ε for any other value of α , we introduce the function.

$$P(x, \alpha) \equiv \sum_{n=1,3,5,\dots} \frac{x^{n+\alpha}}{n+\alpha}. \quad (20a)$$

Then

$$\varepsilon = \frac{8}{\pi^2} \cdot \frac{P(1, 0) - P(1, \alpha)}{\alpha} \quad (20b)$$

From (20a) it follows that

$$\frac{dP}{dx} = x^2(1 + x^2 + x^4 + \dots) = \frac{x^2}{1 - x^2} \quad (21a)$$

so that

$$P(x, \alpha) = \int_0^x \frac{x^2 dx}{1 - x^2}. \quad (21b)$$

* The physical meaning of the various terms in (18) given here is discussed at length in section 9.

Then

$$\varepsilon = \frac{8}{\pi^2} \frac{1}{\alpha} \int_0^1 \frac{1-x^2}{1-x^{2\alpha}} dx \quad (22)$$

(22) can easily be evaluated when $\alpha = 1$. Then $\varepsilon = 8\ln 2/\pi^2 = 0.562$. When α equals any even integer $2N$,

$$\frac{1-x^2}{1-x^{2N}} = \frac{1-x^{2N}}{1-x^2} = 1 + x^2 + x^4 + \dots + x^{2N-2}. \quad (23)$$

Thus

$$\varepsilon(\alpha = 2N) = \frac{8}{\pi^2} \cdot \frac{1}{2N} \cdot \left(1 + \frac{1}{3} + \frac{1}{5} + \dots + \frac{1}{2N-1} \right). \quad (24)$$

For $N \geq 1$, the finite series in parentheses in (24) can be approximated by the expression $1 + \frac{1}{2} \ln N$ with an accuracy of about 1%. Thus for $\alpha \geq 2$, we may write with good accuracy

$$\varepsilon = \frac{8}{\pi^2} \cdot \frac{1 + \frac{1}{2} \ln(\alpha/2)}{\alpha} \quad (\alpha \geq 2) \quad (25)$$

A similar calculation can be carried out for a checkerboard membrane, *i.e.*, one in which the patches are squares of side h . The result for I is again a product of two factors: the first is the parenthesis in (18), the second is given by the infinite double sum

$$\varepsilon = \frac{64}{\pi^4} \sum_{\substack{n=1,3,5,\dots \\ m=1,3,5,\dots}} \frac{(n^2 + m^2)^{\frac{1}{2}}}{n^2 m^2 [(n^2 + m^2)^{\frac{1}{2}} + \alpha]} \quad (26)$$

where α is again given by (19b). When $\alpha = 0$, $\varepsilon = [(8/\pi^2)(1 + 1/3^2 + 1/5^2 + \dots)]^2 = 1$, as it should. When $\alpha \neq 0$, the series in (26) is not as easy to evaluate as the series in (19a). It has been evaluated by summing on a computer. The results are

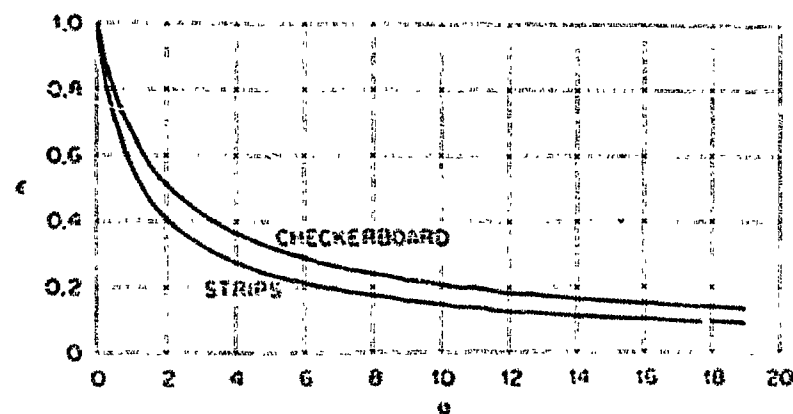


Fig. 2. The efficiency of the strip and checkerboard membranes.

shown in Fig. 2 along with ϵ for the strip membrane [Eq. (19a)]. The efficiency of the checkerboard membrane is somewhat higher than that of the strip membrane for the same value of α . This is to be expected since for equal values of h , the average distance an ion must travel to the adjacent patches of opposite sign is shorter for the checkerboard membrane than the strip membrane.

8. CONSISTENT TREATMENT OF THE SOLUTE-SOLVENT INTERACTION

In the theory developed so far, the solute-solvent interaction is not treated consistently: the effect of water flow on ionic flow (convection) has been taken into account, but the effect of ionic flow on water flow (electroosmosis) has been neglected. A theory that treats the solute-solvent interaction consistently can be obtained from the thermodynamics of irreversible processes. At any point in the membrane, the current densities of water and electricity are given by

$$q = L_{11} \bar{V} \text{grad } p + \omega L_{12} E \quad (27a)$$

$$i = \omega L_{21} \bar{V} \text{grad } p + L_{22} E \quad (27b)$$

$$L_{12} = L_{21}. \quad (27c)$$

since owing to assumption 2 (complete coion exclusion) there are no gradients of concentration in the membrane. L_{22} is clearly the same as σ_m , the conductivity of the wet membrane. $L_{11} \bar{V}/2l$ is the hydraulic permeability. At this point it is convenient to relate the cross coefficient L_{12} and the convection coefficient β . The connection between the two is

$$\omega \beta X \mathcal{F} = \left(\frac{i}{q} \right)_{E=0} = \omega \frac{L_{12}}{L_{11}} \quad (27d)$$

This equation is to be understood as a definition of β .

In a consistent theory, the right-hand side of (27b) should replace $\omega \beta J X \mathcal{F} + \sigma_m E$. Since $L_{22} = \sigma_m$, this is the same as saying that $L_{12} \bar{V} |\text{grad } p|$ should replace $\beta J X \mathcal{F}$. If we substitute for L_{12} its value from (27d), we find that $L_{12} \bar{V} |\text{grad } p| = \beta J_0 X \mathcal{F}$, where $J_0 \equiv L_{11} \bar{V} |\text{grad } p|$ is the water flux that would occur if the back-diffusion of salt exerted no retarding force on the water. Thus J_0 should replace J in a consistent theory.

We can find the *actual* water flux by eliminating E between Eqs. (27a) and (27b):

$$L_{22} q - \omega L_{12} i = \left(1 - \frac{L_{12}^2}{L_{11} L_{22}} \right) L_{22} L_{11} \bar{V} \text{grad } p = L_{22} \left(1 - \frac{L_{12}^2}{L_{11} L_{22}} \right) J_0 \quad (28a)$$

If we average this over a patch, we get

$$J - \frac{L_{12}}{L_{22}} I = \left(1 - \frac{L_{12}^2}{L_{11}L_{22}} \right) J_0 \quad (28b)$$

Eqs. (18) (with J replaced by J_0) and (28b) now give a theory of piezodialysis in which the solute-solvent interaction is treated consistently. When the efficiency $\varepsilon = 1$, this theory is equivalent to that of Kedem and Katchalsky for a charge-symmetric system.

9. DISCUSSION

We now consider in greater detail the physical meanings given on page 59 to the various terms in (18). There is no difficulty identifying the infinite sum as a factor of reduction due to the buildup of charge on the faces of the patches, for it is the only term containing h , the linear dimension of a patch. In the limit as h becomes zero, the infinite sum approaches unity; the terms in parentheses remain the same. We know that in the same limit, the charge buildup on the faces of the patches disappears. Thus the two terms in parentheses represent the contributions to the electric current density in the absence of any streaming potential. It is easy to identify the first term as the convective term since it alone contains J , the water flux. By elimination, we could conclude that the second term in parentheses is the contribution from back-diffusion. It is easy to see that this is so directly, since of the two terms in parentheses, only the second contains the concentrations of the low- and high-pressure solutions.

It is possible to identify the second term in parentheses as the back-diffusion term directly in the following way. When $h = 0$ and there is no charge buildup on the faces of the patches, the two solutions are at a uniform (zero) potential right up to the faces of the membrane. On the other hand, except at the junctions of different patches, there is a jump in potential across the membrane surface, the Donnan potential. The Donnan potentials at the two surfaces of the membrane are not equal when the concentrations of the two solutions are not equal. The only way the two solutions can be at the same uniform potential is for an electric field to exist in the membrane which creates a potential difference across the interior of the membrane equal to the difference in Donnan potentials. This electric field points from the more concentrated solution to the more dilute solution in the cation-exchange patches, and in the opposite direction in the anion-exchange patches, as consideration of the size and sign of the Donnan potentials will show. Thus the electric field tends to drive ions of both signs from the more concentrated to the more dilute solution. In the event that activity coefficients are ignored, the difference in Donnan potentials can easily be shown to be $(RT/\mathcal{F}) \ln (c_p/c_f)$. Thus the back-diffusion term, as previously noted, is the product of the difference of Donnan potentials and the membrane conductance per unit area $\sigma_m/2l$.

One additional item has been reserved for further discussion here, namely, assumption 3 that salt buildup or depletion (concentration polarization) at the membrane faces can be ignored. This local buildup or depletion is usually overcome by having the solutions flow across the faces of the membrane. Turbulent flow is more effective for this purpose than laminar flow. When there is turbulent flow across the membrane faces, the question arises as to whether it affects the transport of the mobile ions. In the theory worked out in this paper, mobile ions of opposite sign diffuse toward one another solely under the action of the electric field. If mobile ions of opposite sign were mixed to any substantial degree by the turbulent eddies, the theory presented above would need to be changed. This question has been studied in detail in the Appendix to this paper and turbulent mixing has been shown to have a negligible effect.

To sum up: the theory presented here is highly schematic, being based on the restrictive assumptions of good coion exclusion, charge symmetry, and neglect of activity coefficients; but it gives for the first time simple expressions for the performance of mosaic membranes in terms of their structural characteristics.

APPENDIX

When ions move in a turbulent fluid, their motion is made up of four parts: molecular diffusion, eddy diffusion, convection, and migration in any electric field that is present. The ionic currents are given by an extension of Eq. (1):

$$j_i = -(\mathcal{D} + \mathcal{D}_e) \text{grad } c_i + \frac{\mathcal{D}\mathcal{F}}{RT} z_i c_i E + v c_i \quad (\text{A1})$$

If we multiply (A1) by $z_i \mathcal{F}$ and sum over i , we get

$$\begin{aligned} i = \sum_{i=1}^2 j_i z_i \mathcal{F} = & -\mathcal{F} (\mathcal{D} + \mathcal{D}_e) \text{grad} \left(\sum_{i=1}^2 z_i c_i \right) \\ & + \frac{\mathcal{D}\mathcal{F}^2}{RT} \left(\sum_{i=1}^2 z_i^2 c_i \right) E + \mathcal{F} \left(\sum_{i=1}^2 z_i c_i \right) v \end{aligned} \quad (\text{A2})$$

The first terms on the right-hand sides of (A1) and (A2) are the respective contributions to j_i and i from molecular and eddy diffusion, the second terms are the respective contributions from migration in the electric field, and the last terms are the respective contributions from convection. In the development of section 3 leading to Eq. (3),

$$\sum_{i=1}^2 z_i c_i$$

was taken equal to zero in (A2) on the basis of the condition of electroneutrality.

Strictly speaking,

$$\sum_{i=1}^2 z_i c_i = \rho / \mathcal{F},$$

where ρ is the electric charge density. While small compared with c_i , $\rho / \mathcal{F}$ may not vanish, so that the diffusive and convective terms in (A2) do not drop out. What we propose to show here is that these terms are very small compared with the term involving the electric field in circumstances of interest.

Let us denote the three terms on the right-hand side of (A2) by i_1 , i_2 , and i_3 . Now

$$\operatorname{div} i_2 = \frac{\mathcal{D} \mathcal{F}^2}{RT} \left(\sum_{i=1}^2 z_i^2 c_i \right) \operatorname{div} E \quad (\text{A3})$$

if we assume that the ionic strength

$$\sum_{i=1}^2 z_i^2 c_i$$

is kept virtually constant by the turbulent flow. Furthermore,

$$\operatorname{div} E = \frac{\rho}{\epsilon} \quad (\text{A4})$$

and

$$i_1 = -(\mathcal{D} + \mathcal{D}_e) \operatorname{grad} \rho \quad (\text{A5})$$

Thus,

$$\operatorname{grad} \operatorname{div} i_2 = - \frac{\left(\sum_{i=1}^2 z_i^2 c_i \right) \mathcal{F}^2}{RT\epsilon} \cdot \frac{\mathcal{D}}{\mathcal{D} + \mathcal{D}_e} \cdot i_1 \quad (\text{A6})$$

Since the electric current changes from its minimum to its maximum value over a spatial extension of the order of h , the left-hand side of (A6) is of the order of magnitude of i_2/h^2 . Thus

$$\frac{i_2}{i_1} \sim \frac{\left(\sum_{i=1}^2 z_i^2 c_i \right) \mathcal{F}^2 h^2}{RT\epsilon} \cdot \frac{\mathcal{D}}{\mathcal{D} + \mathcal{D}_e} \quad (\text{A7})$$

The first factor on the right-hand side of (A7) is the square of the ratio of h to the Debye length of a solution the ionic strength of which is

$$\sum_{i=1}^2 z_i^2 c_i.$$

If we choose an ionic strength of $0.2 \text{ moles liter}^{-1}$ ($z_i = \pm 1$, $c_i = 0.1 \text{ mole liter}^{-1}$),

$T = 293^\circ\text{K}$, and $\varepsilon = 80 \times$ the permittivity of free space $= 80 \times 8.854 \times 10^{-12}$ farad m^{-1} , then the Debye length

$$\left[\frac{RT\varepsilon}{\left(\sum_{i=1}^2 z_i^2 c_i \right) \mathcal{F}^2} \right]^{1/2} = 9.65 \text{ \AA} \quad (\text{A8})$$

Thus if $h \sim 1\mu$, the first factor on the right-hand side of (A7) is of the order of 10^6 .

In order to estimate the second term in (A7) we need the eddy viscosity $\mathcal{D}_e$. To find it, we need to know the hydrodynamic conditions—these we specify as follows: fully developed turbulent channel flow across the face of the membrane, mean stream velocity $U = 100 \text{ cm sec}^{-1}$, Reynolds number $\text{Re} = 10^4$, kinematic viscosity $\nu = 0.01 \text{ cm}^2 \text{ sec}^{-1}$. The Fanning friction factor $f = 0.08 (\text{Re})^{-1/4} = 0.008$, and the wall-shear velocity $v_* = (f/2)^{1/2} U = 6.33 \text{ cm sec}^{-1}$. We are interested in finding $\mathcal{D}_e$ in that region of space in which electric current is flowing, *i.e.*, in a region of thickness h adjacent to the membrane. To find $\mathcal{D}_e$ a distance h from the membrane, we form the dimensionless quantity $h^+ = hv_*/\nu = 0.0633$. Points with $h^+ \ll 5$ are well within the laminar sublayer where $\mathcal{D}_e \ll \nu$. (Deissler's expression for $\mathcal{D}_e/\nu$ in terms of h^+ ($= 0.0633$) gives $\mathcal{D}_e/\nu = 4.05 \times 10^{-9}$. $\mathcal{D}_e/\nu \sim 0.002$ for most salts, so that $\mathcal{D}_e \ll \mathcal{D}$.) Thus the second factor in (A7) is very close to unity and $i_2 \gg i_1$. Even if h were 1000μ , the second factor in (A7) would only be 8.75×10^{-5} , while the first factor would be of the order of 10^{12} . Only when h is comparable with the Debye length can i_2 be comparable with i_1 ; if it is much larger, $i_2 \gg i_1$.

Let us now consider the ratio of i_3 to i_1 . We begin by noting that

$$\text{div } i_3 = v \cdot \text{grad } \rho = - \frac{v \cdot i_1}{\mathcal{D} + \mathcal{D}_e} \quad (\text{A9})$$

since $\text{div } v = 0$ in incompressible flow. Thus,

$$\frac{i_3}{i_1} \sim \frac{hv}{\mathcal{D} + \mathcal{D}_e} < \frac{hv}{\mathcal{D}} \quad (\text{A10})$$

To find v , we use the universal velocity profile which gives the dimensionless quantity $v^+ = v/v_*$ in terms of h^+ . When $h = 1\mu$, $v^+ = 0.0633$, and $v = 0.4 \text{ cm sec}^{-1}$. Then if $\mathcal{D} = 2 \times 10^{-5} \text{ cm}^2 \text{ sec}^{-1}$ ($\mathcal{D}/\nu = 0.002$), $i_3/i_1 = 2$, so that $i_3 \ll i_2$. When $h = 1000\mu$, $v^+ = 16.2$, and $v = 102 \text{ cm sec}^{-1}$. Then $i_3/i_1 = 1020$. i_3 is thus $\gg i_1$, but still $\ll i_2$.

We see by these arguments that in practical circumstances $i_2 \gg i_1$ and i_3 , so that the procedure of section 3 is justified even in the presence of turbulent flow.

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7.2 SOME REMARKS ON THE INTEGRATION OF THE EXTENDED NERNST-PLANCK EQUATIONS IN THE HYPERFILTRATION OF MULTI-COMPONENT SOLUTIONS*

L. Dresner

SUMMARY

A new method is suggested for the integration of the extended Nernst-Planck equations in the hyperfiltration of multicomponent solutions through ion-exchange membranes. The method is based on the assumption of good coion exclusion. It yields the asymptotic solute rejections with comparatively little computational labor. The new method is compared with several older methods. Some circumstances, hitherto unnoticed, are described under which negative rejection of a solute may occur.

SYMBOLS

c_i	— molality of the i th ion (moles per kg water)
$\mathcal{D}_i^*$	— product of the diffusion constant of the i th ion in the membrane and the density of water in the membrane ($\text{kg m}^{-1} \text{sec}^{-1}$)
E	— electric field (volt m^{-1})
F	— the Faraday (96,500 coulombs)
j_i	— flux of the i th ion through the membrane ($\text{moles m}^{-2} \text{sec}^{-1}$)
J	— water flux through the membrane ($\text{kg m}^{-2} \text{sec}^{-1}$)
l	— thickness of membrane (m)
L_{ik}, L'_{ik}, L_{ik}	— phenomenological coefficients ($\text{mole}^2 \text{m}^{-3} \text{sec kg}^{-1}$)
N	— number of ions present in feed solution
q	— sign of the fixed charge (+ 1 for an anion exchanger; — 1 for a cation exchanger)
R	— universal gas constant ($8.32 \text{ joules mole}^{-1} \text{deg}^{-1}$)
T	— absolute temperature (deg)
x	— distance coordinate in the membrane (m)
X	— fixed charge density (equiv per kg water)

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z_i	— charge of the i th ion in units of the proton charge
β_i	— convective coupling coefficient (see sec. 3 and the Appendix)
γ_i	— practical activity coefficient of the i th ion
ϵ	— electrical permittivity of the membrane phase (farads m^{-1})
λ_D	— $(\epsilon RT/F^2 X \rho_w)^{1/2}$, Debye length (m)
μ	— chemical potential (joules mole^{-1})
$\tilde{\mu}$	— electrochemical potential (joules mole^{-1})
ρ	— electric charge (coulombs)
ρ_w	— density of water in the membrane phase (kg m^{-3})
ϕ	— electrical potential (volts)

Subscripts

1	— counterions
2	— coions
i	— identifies the i th ion
(r)	— refers to the membrane phase
α	— refers to the feed solution
ω	— refers to the effluent solution (filtrate)

1. INTRODUCTION

Schlögl (1), among others, has described ionic transport in ion-exchange membranes using an extension of the Nernst-Planck equations that includes convection. These extended Nernst-Planck equations are attractive candidates for a phenomenological description of ionic transport in membranes, representing, as they do, a highly simplified version of the equations of irreversible thermodynamics, yet still taking into account the three main mechanisms of ionic transport in membranes: diffusion, migration in an electric field, and convection. In spite of their simplicity from the physical point of view, the extended Nernst-Planck equations are highly complicated from a mathematical point of view because they are nonlinear. Thus in trying to decide just how well the extended Nernst-Planck equations describe ionic transport, we are faced with the difficult problem of solving these equations or at least of getting information about their solutions. It is this latter, purely mathematical problem that is the subject of this paper. Furthermore, as noted in the title, this paper is restricted to the problem of hyperfiltration (reverse osmosis).

The only problem of hyperfiltration for which a solution of the extended Nernst-Planck equations in terms of elementary functions is known is the problem of hyperfiltration of two-component solutions (water plus one binary electrolyte) (1-3). No general solution in terms of elementary functions is known for multicomponent solutions. The extended Nernst-Planck equations for multicomponent solutions may be dealt with by the method of finite differences, but this method has

two drawbacks. First, it is time-consuming; second, it often fails to reveal in an obvious way important general properties. For these reasons, several approximate methods of solving the Nernst–Planck equations or getting information about their solutions have been proposed.

One method is based on the following observation regarding the exact solution in the two-component case. When the membrane is sufficiently thick or the water flux sufficiently high, the ionic concentrations in the membrane become nearly independent of position near the feed–membrane interface. The concentration gradient terms in the extended Nernst–Planck equations then drop out, and the equations become a set of coupled *algebraic* equations rather than a set of coupled differential equations. The hyperfiltration problem can then be solved easily, and the rejection of the solute by the membrane can be related to the composition of the feed solution and the properties of the membrane. The value approached by the solute rejection when the water flux becomes large or the membrane becomes thick is called the asymptotic rejection. For a two-component solution, then, the asymptotic rejection of the solute can be calculated by solving algebraic rather than differential equations.

The asymptotic rejections of the solutes in a multicomponent solution may sometimes, but unfortunately not always, be found by solving algebraic equations. When the feed solution contains several electrolytes, the ionic concentrations in the membrane do not always become independent of position near the feed–membrane interface as the membrane becomes thick or the water flux high. The reduction to algebraic equations fails for feed solutions for which there is sufficiently good coion exclusion. Because feed solutions for which there is good coion exclusion are the most important in hyperfiltration, finding asymptotic rejections by solving the algebraic form of the extended Nernst–Planck equations often fails to give us much useful information. This is made clearer by example below.

Schlögl (2) has suggested a method of solving the extended Nernst–Planck equations approximately based on a method of Goldman's (4) for dealing with the original Nernst–Planck equations. Both Goldman and Schlögl make the assumption that the electric field strength is constant in the membrane. I show below that this assumption can be badly violated in quite typical hyperfiltration problems. Thus the Schlögl–Goldman method, too, is limited in its usefulness.

A new method for obtaining the *asymptotic rejections* of the solutes from the extended Nernst–Planck equations is suggested in this paper. The new method is based on the assumption of good coion exclusion, and resembles the Schlögl–Goldman method in that a guess is made for the electric field. This guess is better motivated physically than the guess of Schlögl–Goldman (see section 2 below). A detailed argument given below indicates that the new method should always give good results when there is good coion exclusion—comparison of the results of the new method with exact results in certain test problems bears this expectation out.

Finally, the new method has the advantage of requiring only a small amount of calculation, even when several ions are present.

2. PHYSICAL DESCRIPTION OF HYPERFILTRATION WITH AN ION-EXCHANGE MEMBRANE

To see how hyperfiltration with an ion-exchange membrane works, let us first begin by imagining that there is complete exclusion of coions from the membrane. If we exert pressure on the water on one side of the membrane, water flows through the membrane. The water exerts a frictional force on the mobile counterions in the membrane, tending to propel them in the direction of water flow. In the first instants of flow, there is a downstream shift of the counterions. An excess of counterions appears at the low-pressure face of the membrane, a shortage at the high-pressure face. This charge separation creates an electric field, which opposes further counterion flow. The electrical force on the counterions exactly balances the frictional force, stopping the flow of the counterions and preventing a *steady* separation of charge.

Now suppose instead that a few coions and counterions invade the membrane. A steady flux of counterions through the membrane is now possible, accompanied by a flux of coions carrying an equal but opposite charge. Since counterions are much more numerous in the membrane than coions, pure convection would produce a counterion flux that would far outweigh the coion flux. Again, an excess of counterions appears on the low-pressure face of the membrane, a shortage at the high-pressure face. This charge separation creates an electric field, which retards the counterions and accelerates the coions, until in the steady state the counterion and coion fluxes carry equal but opposite charges. The counterion and coion fluxes are then in the stoichiometric ratio and together are equivalent to a salt flow.

This salt flow is limited by the coion flow. The coion flow is small if there is very little coion invasion of the membrane. The counterion flow must then be equally small. The only way this can happen is for the flow of the vastly more numerous counterions to be *nearly stopped* by the action of the electric field. Thus the electric field is very close to the electric field that exists when no salt current flows through the membrane.

The small difference between the actual electric field and the one that would exist when no salt current flows, is crucial if we want to calculate the flux of counterions. This is because the counterion flux is determined by the difference between two forces that are nearly equal, the frictional force and the electrical force. A small error in one of them can produce a very large error in their difference. But the coion flux is determined by the *sum* of the electrical and the frictional forces since the electrical force on coions is in the direction opposite to the electrical force on counterions, while the frictional force is in the same direction for both of them. Thus a small error in the electrical force hardly affects the coion flux at all.

For this reason, we can estimate the coion flux accurately using the "no-current" field, but not the counterion flux.

Of course, the two fluxes are equal. Once we have an estimate of the coion flux we also have an estimate of the counterion flux. Using this estimate of the counterion flux, we could compute a correction to the electric field. We could then improve our estimate of the coion flux, and so on. This iteration is possible in principle, but in practice we use the first estimate of the coion flux.

This physical description is oversimplified for two reasons: it omits mention of diffusion, and it tacitly assumes that only two kinds of ions are present. In spite of these drawbacks it makes clear the basic rationale of the new method, namely, estimation of the coion fluxes using the electric field that would exist in the total absence of coions in the membrane. With this picture in mind, we now turn to the quantitative theory.

3. BASIC EQUATIONS

In his book (1) Schlögl gives the extended Nernst-Planck equations as

$$j_i = Jc_{i(r)} - \mathcal{D}_i^* \frac{dc_{i(r)}}{dx} + z_i c_{i(r)} \mathcal{D}_i^* \frac{FE}{RT} - c_{i(r)} \mathcal{D}_i^* \frac{d \ln \gamma_{i(r)}}{dx} \quad (1)$$

j_i is the flux of the i th kind of ion through the membrane. In the steady state, it is independent of x , as we can see by considering the equation of continuity for the i th ion: $\partial c_{i(r)}/\partial t + \partial j_i/\partial x = 0$. The right-hand side of Eq. (1) expresses j_i as the sum of several terms, each of which is capable of a simple physical interpretation. The first term represents convection; the second and fourth, diffusion; the third, migration in the electric field.

Schlögl obtained (1) by reduction from the equations of irreversible thermodynamics. But in the thermodynamic equations with which he started, he assumed that the membrane material is thermodynamically inactive and has no other physical effect than that of keeping the fixed charges stationary. This is too restrictive, and lifting this assumption leads to a slightly modified equation for j_i . The mathematical details are given in Appendix A, but the upshot is that the convective term Jc_i is replaced by $\beta_i Jc_i$, where β_i is defined as the ratio of certain phenomenological coefficients in the equations of irreversible thermodynamics. In order to integrate the extended Nernst-Planck equations we assume the β_i , like the $\mathcal{D}_i^*$, are independent of concentration. How good an assumption this is, is a question that cannot be answered here. In any case, the new method we propose in this paper applies as well to Eq. (1) when $\beta_i \neq 1$ as it does when all the $\beta_i = 1$.

From a physical standpoint, the β_i account for the possibility that in pure convection the ions might not be swept along with the velocity of the permeating water. For example, if there were transitory binding of the counterions by the

fixed charges, the instantaneous concentration of *mobile* counterions would be smaller than the total concentration of counterions, and convection would be reduced. Thus β_i for counterions would be < 1 . Another kind of effect could occur in a porous ion-exchange membrane in which the pore diameter is comparable with the thickness of the electrical double layer. The mobile counterions would be concentrated near the charged walls of the pores where the water flow velocity is below average, while the coions would be concentrated away from the walls where the water flow velocity is above average. Thus β_i for counterions would be < 1 , while β_i for coions would be > 1 .

In view of these possible effects, we choose for our phenomenological description of hyperfiltration not the restricted Eq. (1) but the equations derived in the Appendix:

$$j_i = \beta_i J c_{i(r)} - \mathcal{D}_i^* \frac{dc_{i(r)}}{dx} + z_i c_{i(r)} \mathcal{D}_i^* \frac{FE}{RT} - c_{i(r)} \mathcal{D}_i^* \frac{d \ln \gamma_{i(r)}}{dx} \quad (2)$$

For the purpose of simplifying his investigations of the mathematical properties of the extended Nernst-Planck equations, Schlögl took all activity coefficients equal to 1. We restrict ourselves in this regard, too, but not as severely: we take each activity coefficient to be constant in each phase, but permit its value to change across phase boundaries.

In addition to Eq. (2), we have the equations of electroneutrality* in the membrane

$$\sum_i z_i c_{i(r)} + qX = 0 \quad (3)$$

and in the external solutions

$$\sum_i z_i c_i = 0 \quad (4)$$

Since no electric current flows in hyperfiltration,

$$\sum_i z_i j_i = 0 \quad (5)$$

The condition of thermodynamic equilibrium at each membrane-solution interface takes the form

$$\frac{c_{i(r)} \gamma_{i(r)}}{c_i \gamma_i} = \exp \left(- z_i \frac{F \Delta \phi}{RT} \right) \quad (6)$$

where $\Delta \phi$ is the potential difference between a point just inside the membrane and the contacting solution (Donnan potential). Finally, it is important to note ex-

* A discussion of some subtleties connected with the use of Eq. (3) is given in Appendix B.

plicitly that in hyperfiltration the composition of the effluent solution (filtrate) is determined by the fluxes j_i and J :

$$c_{i\infty} = \frac{j_i}{J} \quad (7)$$

4. ELECTRIC FIELD WHEN THERE IS COMPLETE COION EXCLUSION

If coions were completely excluded from the membrane, no current of any counterion could flow in the steady state, for then a steady separation of charge would occur. Thus j_i would vanish for each counterion, and Eq. (2) could easily be solved:

$$\frac{1}{c_{i(r)}} \frac{dc_{i(r)}}{dx} = \frac{\beta_i}{\mathcal{D}_i^*} J + z_i \frac{FE}{RT} \quad (\text{counterions only}) \quad (8a)$$

$$\ln c_{i(r)} = \frac{\beta_i}{\mathcal{D}_i^*} Jx - z_i \frac{F\phi}{RT} + \text{constant} \quad (\text{counterions only}) \quad (8b)$$

where $E \equiv -d\phi/dx$ is the electrical potential at x . For convenience, let us choose the feed-membrane interface as the origin $x = 0$, and let us choose the positive x -direction to be the direction of water flow. At $x = 0 +$ (the notation $0 +$ denotes the coordinate of a point just inside the membrane at the feed-membrane interface),

$$\ln c_{i(r)}(0+) = -z_i \frac{F\phi(0+)}{RT} + \text{constant} \quad (\text{counterions only}) \quad (9)$$

so that Eq. (8b) can be written

$$c_{i(r)}(x) = c_{i(r)}(0+) \exp \left(\frac{\beta_i}{\mathcal{D}_i^*} Jx - z_i \frac{F[\phi(x) - \phi(0+)]}{RT} \right) \quad (\text{counterions only}) \quad (10)$$

The electrical potential ϕ is defined only to within a constant; therefore, with no loss of generality, we can take $\phi = 0$ in the feed solution. According to Eq. (6),

$$c_{i(r)}(0+)\gamma_{i(r)} = c_{ia}\gamma_{ia} \exp \left(-z_i \frac{F\phi(0+)}{RT} \right) \quad (11)$$

so that Eq. (10) becomes

$$c_{i(r)}(x)\gamma_{i(r)} = c_{ia}\gamma_{ia} \exp \left(\frac{\beta_i}{\mathcal{D}_i^*} Jx - z_i \frac{F\phi(x)}{RT} \right) \quad (\text{counterions only}) \quad (12)$$

If the activity coefficients $\gamma_{i(r)}$ in the membrane are taken as known constants, we can find $\phi(x)$ by applying the equation of electroneutrality (3) to Eq. (12):

$$\sum_i' z_i c_{iz} \frac{\gamma_{iz}}{\gamma_{i(r)}} \exp \left(-\frac{\beta_i}{\mathcal{D}_i^*} Jx - z_i \frac{F\phi(x)}{RT} \right) = \sum_i' z_i c_{i(r)} = -qX \quad (13)$$

Here the prime on the summation indicates a sum *only over the counterions*. Eq. (13) is a polynomial equation for the quantity $\exp(F\phi/RT)$ from which we can determine the electric potential $\phi(x)$ at any point in the membrane.

5. COION CURRENTS

We now assume, as explained in section 2, that the coion currents can be calculated using the electric potential found in the last section. When $\phi(x)$ is a known function, Eq. (2) is an ordinary, first-order differential equation, the solution of which can be obtained by standard methods (5):

$$c_{i(r)}(x) \gamma_{i(r)} \exp \left(-\frac{\beta_i}{\mathcal{D}_i^*} Jx + z_i \frac{F\phi(x)}{RT} \right) =$$

$$c_{iz} \gamma_{iz} - \frac{j_i}{\mathcal{D}_i^*} \gamma_{i(r)} \int_{0+}^x \exp \left(-\frac{\beta_i}{\mathcal{D}_i^*} Jx + z_i \frac{F\phi(x)}{RT} \right) dx$$

(14)

(coions only)

That Eq. (14) gives a solution may be verified by substitution into Eq. (2). It can also be verified by setting $x = 0+$ that Eq. (14) satisfies the boundary condition (6) at the feed-membrane interface.

Let us now inquire what happens when either J or x or both increase so that the terms $(\beta_i/\mathcal{D}_i^*)Jx$ become very large. Since the sum in Eq. (13) is only over counterions, all the terms have the same sign, namely, $-q$. To keep the sum bounded, all the exponentials must individually remain bounded. This means that for large enough J or x , $F\phi/RT$ must take the same algebraic sign as the charge of the counterions ($-q$) and must increase in magnitude as rapidly as $|\beta_k/z_k \mathcal{D}_k^*| Jx$, where subscript k refers to the counterion with the *largest* value of $|\beta_k/z_k \mathcal{D}_k^*|$. For, in the first place, if $F\phi/RT$ took the sign of q for large Jx , all the exponentials on the left-hand side of Eq. (13) would become infinite, which is impossible. Second, if $F\phi/RT$ had the sign of $-q$ and increased less rapidly than $|\beta_k/z_k \mathcal{D}_k^*| Jx$, at least one of the exponentials would become infinite as Jx did, which is again impossible. On the other hand, if $F\phi/RT$ had the sign $-q$ and increased more rapidly than $|\beta_k/z_k \mathcal{D}_k^*| Jx$, all the exponentials would vanish, which is also impossible. But if $F\phi/RT$ had the sign $-q$ and were to increase exactly as rapidly as $|\beta_k/z_k \mathcal{D}_k^*| Jx$, the term on the left-hand side of Eq. (13) for which $i = k$ would

have a finite limit as Jx became infinite, whereas all other terms ($i \neq k$) would vanish. This is a satisfactory state of affairs, and since it is the only possibility left, it must occur.

If we examine Eq. (12) in the light of this last conclusion, we see that $c_{i(r)}(x)$ approaches zero as Jx approaches infinity for all $i \neq k$. Thus far from the feed-membrane interface, the fixed charges are neutralized almost entirely by the k -counterions. This means that in the limit of large J or x or both, only these k -counterions come through the membrane—all other counterions are completely rejected. It should be remembered that this conclusion is based on an approximate theory; in practice we might expect that the rejection of counterions with $i \neq k$ would be close to 100%, and that the coions would be accompanied mostly by k -counterions.

We have seen that $F\phi/RT$ takes the algebraic sign $-q$ far from the feed-membrane interface, i.e., when $(\beta_i/\mathcal{D}_i^*)Jx$ is very large. Since Eq. (14) refers to coions only, the z_i appearing in it all have the sign $+q$. Then the terms $z_i(F\phi/RT)$ in Eq. (14) are negative for large enough $(\beta_i/\mathcal{D}_i^*)Jx$. If we now let J or x or both approach infinity, the left-hand side of Eq. (14) vanishes, and Eq. (14) becomes

$$c_{i\infty} \gamma_{i\infty} = \frac{j_i}{\mathcal{D}_i^*} \gamma_{i(r)} \int_{0+}^{\infty} \exp \left(-\frac{\beta_i}{\mathcal{D}_i^*} Jx + z_i \frac{F\phi}{RT} \right) dx \quad (15)$$

(coions only; limit of large J or x)

From Eq. (15) we can calculate the j_i , and from Eq. (7) the $c_{i\infty}$. The quantity $1 - (c_{i\infty}/c_{i2})$ is then the asymptotic rejection of the i th coion. The coion currents are accompanied by a current of the k -counterion carrying an equal but opposite charge. No other counterion passes through the membrane. These remarks complete the quantitative statement of the approximate theory.

6. EXAMPLE: ONE BINARY ELECTROLYTE

We can check the correctness of the foregoing theory by comparing the result with the exact result in the case of a two-component feed solution. When there is only one binary electrolyte in the feed solution, there is only one counterion, and the sum in Eq. (13) contains only one term. It is then easy to solve Eq. (13) for the electric potential ϕ . Eq. (15) then gives

$$j_2 = Jc_{22} \frac{\gamma_{22}}{\gamma_{2(r)}} \left(\beta_2 - \beta_1 \frac{z_2 \mathcal{D}_2^*}{z_1 \mathcal{D}_1^*} \right) \cdot \left(\frac{-qX \gamma_{1(r)}}{z_1 c_{12} \gamma_{12}} \right)^{z_2/z_1} \quad (16)$$

where the subscript 2 denotes coions and the subscript 1 denotes counterions. Using the condition of membrane equilibrium, Eq. (6), we can show that

$$c_{2(r)}(0+) = c_{22} \frac{\gamma_{22}}{\gamma_{2(r)}} \left(\frac{c_{1(r)}(0+) \gamma_{1(r)}}{c_{12} \gamma_{12}} \right)^{z_2/z_1} \quad (17)$$

Using Eq. (17), we can transform Eq. (16) into

$$j_2 = Jc_{2(r)}(0+) \left(\beta_2 - \beta_1 \frac{z_2 \mathcal{D}_2^*}{z_1 \mathcal{D}_1^*} \right) \cdot \left(\frac{-qX}{z_1 c_{1(r)}(0+)} \right)^{z_2/z_1} \quad (18)$$

Eq. (18) gives the coion current in the limit as J or x or both become infinite, *i.e.*, the asymptotic coion current.

As mentioned in section 1, the *asymptotic* rejection, and therefore the asymptotic coion current, may be calculated for a two-component solution by solving Eqs. (2) without the gradient terms. An easy calculation shows that

$$j_2 = Jc_{2(r)}(0+) \left(\beta_2 - \beta_1 \frac{z_2 \mathcal{D}_2^*}{z_1 \mathcal{D}_1^*} \right) \cdot \left(1 + \frac{z_2^2 \mathcal{D}_2 c_{2(r)}(0+)}{z_1^2 \mathcal{D}_1^* c_{1(r)}(0+)} \right)^{-1} \quad (19)$$

Eq. (19) is an *exact* consequence of Eqs. (2) in the limit as J or x or both become infinite. It differs from the approximate result (18) only in the last factor. It is easy to see that in both cases the last factor approaches 1 as coions are better and better excluded from the membrane. Clearly, then, the approximate and exact results for the asymptotic coion current draw closer together, the better the exclusion of coions from the membrane.

7. EXAMPLE: TWO BINARY ELECTROLYTES WITH A COMMON COION

Next we consider a somewhat more complicated example in which the feed solution contains two binary electrolytes with a common coion. In this example, we must solve Eqs. (2) as well as (13) and (15) numerically. We choose the hyperfiltration of HCl-MgCl₂ solutions through a cation-exchange membrane. Various feed solutions with different ratios of [H⁺] to [Mg⁺⁺] are considered, but all have a Cl⁻ concentration equal to 0.1 X , *i.e.*, one-tenth the ion-exchange capacity of the wet membrane. Since we are only interested in verifying the accuracy of an approximate method of solution of Eqs. (2), we are at liberty to choose any reasonable values for the β_i , $\mathcal{D}_i^*$, and the activity coefficients. We choose $\beta_i = 1$, $\gamma_{i\alpha} = \gamma_{i(r)} = 1$ and take the $\mathcal{D}_i^*$ to be proportional to the values they would have in dilute aqueous solution.*

Shown in Fig. 1 are asymptotic rejections of Mg⁺⁺ and Cl⁻ calculated using Eqs. (13) and (15). On the theory underlying these equations the rejection of H⁺ is 100%. For pure HCl solutions, the rejection of H⁺ and Cl⁻ is 87.8% on the good-exclusion theory. This point is plotted at the extreme right-hand side of Fig. 1. (Because of the approximate nature of the theory of Eqs. (13) and (15), it predicts a discontinuous change in the rejection of H⁺ from 100% to 87.8% as the concentration of Mg⁺⁺ approaches zero. Such a discontinuity is physically nonsensical, and in reality is replaced by a rapid but continuous change.) For pure MgCl₂

* Only the ratios of the $\mathcal{D}_i^*$ enter the theory of Eqs. (13) and (15) as we can see by introducing in place of x the dimensionless variable $Jx/\mathcal{D}_m^*$, where m is any one of the values assumed by i .

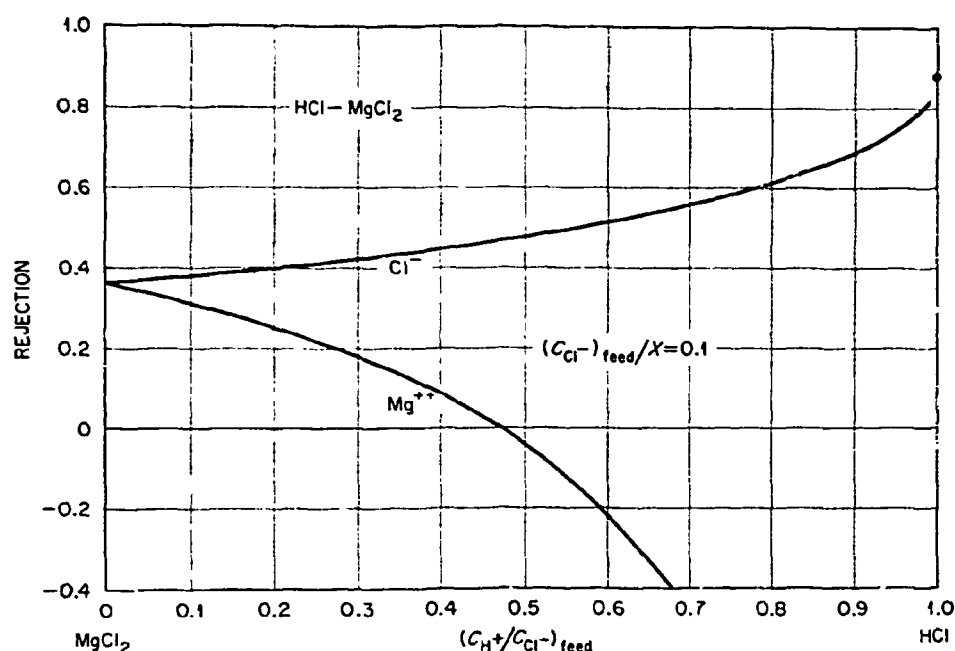


Fig. 1. Solute rejections for the HCl-MgCl₂ system according to the good-exclusion theory.

solutions, the rejection of Mg⁺⁺ and Cl⁻ is 36.1% on the good-exclusion theory. In both of these limiting cases of two-component solutions, the asymptotic rejection can be calculated exactly from Eqs. (2) without the concentration gradient terms—the respective values are 27.5% and 88.0%.

In order to compare the results in Fig. 1 with results of numerical integration of Eqs. (2), we must choose a value of x out to which we integrate. Since Fig. 1 is based on $Jx = \infty$, the value of Jx in the numerical calculations should be sufficiently large. We have chosen a value large enough to make the solute rejections for pure MgCl₂ solutions and pure HCl solutions very close to the respective exact asymptotic rejections noted above. For this purpose, the value $(Jx/\mathcal{D}_{Cl^+}) = 3$ is sufficient. Fig. 2 shows rejection of H⁺, Mg⁺⁺, and Cl⁻ calculated by numerical integration* of Eqs. (2), again for feed solutions having a Cl⁻ concentration of 0.1

* Perhaps a word should be said about the manner in which the numerical results were obtained. The numerical integration of Eqs. (2) is a straightforward matter; I used the Runge-Kutta method. The difficulty arises from the necessity of choosing the effluent (in order to have definite values of the j_i) and calculating the feed. In order to obtain results for constant feed chloride concentration, one proceeds best as follows. Calculations are performed for several effluent chloride concentrations and several effluent compositions. The H⁺, Mg⁺⁺, and Cl⁻ rejections are plotted on separate graphs with rejection as ordinate, effluent chloride concentration as abscissa, and effluent composition as parameter. A straight line on the chloride rejection plot having an intercept on the rejection axis of 100% and an intercept on the effluent chloride concentration axis of c , intersects the various curves of the family in points all of which correspond to *feed* solutions with a chloride concentration c . Each intersection point determines an effluent chloride concentration and an effluent composition. Looking these points up on the various graphs gives the rejections of the various ions, from which the compositions of the various feed solutions can be determined. Enough information is now available to plot rejections as functions of composition for a fixed feed chloride composition.

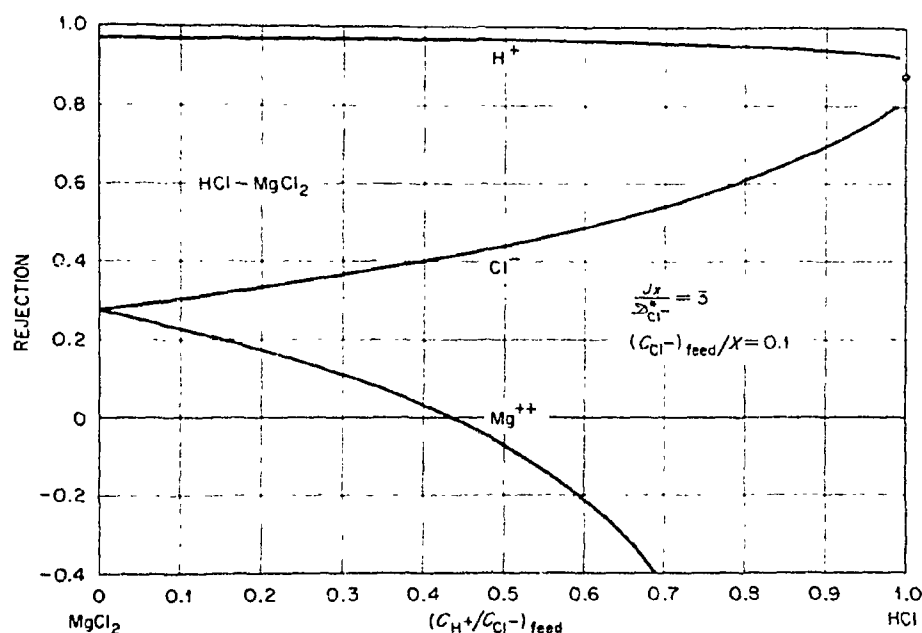


Fig. 2. Solute rejections for the HCl-MgCl₂ system determined by numerical integration of the extended Nernst-Planck equations.

X . The strong resemblance of Figs. 1 and 2 is unmistakable and shows that the method of Eqs. (13) and (15) can be quite accurate, even when the total chloride rejection is as low as 40 %.

One striking feature of Figs. 1 and 2 is the negative rejection of Mg^{++} in feed solutions with a low ratio of $[Mg^{++}]$ to $[H^+]$. (Negative rejection of an ion means that the filtrate is more concentrated in the ion than the feed.) This negative rejection comes about because in this example Mg^{++} is the k -counterion, *i.e.*, the counterion with the largest value of $\beta_k/z_k\mathcal{D}_k^*$. The phenomenon is general: according to the approximate good-exclusion theory, when the concentration of the k -counterion in the feed is low enough, its asymptotic rejection becomes negative. This we prove as follows.

If we multiply Eq. (8a) by $z_i c_{i(r)}$ and sum i over all *counterions*, we find using Eq. (3) and the assumption of complete coion exclusion, that

$$0 = \frac{d}{dx} (-qX) = \frac{d}{dx} \left(\sum_i' z_i c_{i(r)} \right) = J \sum_i' \frac{z_i \beta_i c_{i(r)}}{\mathcal{D}_i^*} + \frac{FE}{RT} \sum_i' z_i^2 c_{i(r)} \quad (20)$$

E is the electric field when there is complete coion exclusion. It follows from Eq. (20) that

$$\frac{FE}{RT} = - \frac{J \sum_i' \frac{z_i \beta_i c_{i(r)}}{\mathcal{D}_i^*}}{\sum_i' z_i^2 c_{i(r)}} \quad (21)$$

Thus FE/RT always has the sign opposite the sign of the charge of the counterions, *i.e.*, the same sign as q . (Thus the electric field always retards counterions and

accelerates coions.) Since coions also have the same sign of charge as q , it follows that $z_i(FE/RT) > 0$ for coions. By integrating this inequality between $0+$ and x , we find that

$$z_i \frac{F\phi(x)}{RT} < z_i \frac{F\phi(0+)}{RT} \quad (i = \text{coion}) \quad (22)$$

(remember $E \equiv -d\phi/dx$). From Eq. (22) we see that replacement of $\phi(x)$ in Eq. (15) by $\phi(0+)$ leads to *too small* a value of j_i since it will overestimate the integral. Making this replacement and carrying out the integral, we find

$$c_{i\omega} = \frac{j_i}{J} > \beta_i c_{i\alpha} \frac{\gamma_{i\alpha}}{\gamma_{i(r)}} \exp\left(-z_i \frac{F\phi(0+)}{RT}\right) = \beta_i c_{i(r)}(0+) \quad (\text{coions only}) \quad (23)$$

Here we have used Eqs. (6) and (7). When the concentration of the k -counterion in the feed is small compared with the concentration of the other ions, it has little effect on $\phi(0+)$. The lower limits to the coion concentrations in the effluent, $c_{i\omega}$, given in Eq. (25) are then nearly independent of $c_{k\alpha}$. Since only the k -counterion neutralizes the coions in the effluent solution, it follows from Eqs. (4) and (23) that

$$c_{k\omega} > \sum_i'' \left(-\frac{z_i}{z_k}\right) \beta_i c_{i(r)}(0+) \quad (24)$$

Here the double prime on the summation indicates a sum only over the coions. If $c_{k\alpha}$ is below the limiting value on the right-hand side of Eq. (24), the rejection of the k -counterion must be negative.

8. DISCUSSION OF THE SCHLÖGL-GOLDMAN METHOD

As we have seen previously, for large x , $(F\phi/RT)$ varies as $(\beta_k/z_k \mathcal{D}_k^*)Jx$, so that

$$\frac{1}{J} \frac{FE(\infty)}{RT} = -\frac{\beta_k}{z_k \mathcal{D}_k^*} \quad (25)$$

From Eq. (21) it follows that

$$\frac{1}{J} \frac{FE(0+)}{RT} = -\frac{\sum_i' \frac{\beta_i}{z_i \mathcal{D}_i^*} z_i^2 c_{i(r)}(0+)}{\sum_i' z_i^2 c_{i(r)}(0+)} \quad (26)$$

We can show that $|E(\infty)| \geq |E(0+)|$ from Eqs. (25) and (26) by observing that the right-hand side of Eq. (26) represents an average value of $\beta_i/z_i \mathcal{D}_i^*$ for counterions with the weights $z_i^2 c_{i(r)}(0+)$, whereas the right-hand side of Eq. (25) is the largest value of $\beta_i/z_i \mathcal{D}_i^*$ for counterions, and therefore has an absolute value $\geq$ the absolute value of the average. Equality occurs only if (i) all the $\beta_i/z_i \mathcal{D}_i^*$ are equal

or (ii) there is only one counterion. Otherwise $|E(\infty)| > |E(0+)|$. If

$$\left| \frac{\beta_k}{z_k \mathcal{D}_k^*} \right| > \left| \frac{\beta_i}{z_i \mathcal{D}_i^*} \right| (i \neq k),$$

the difference between $|E(\infty)|$ and $|E(0+)|$ can be quite large. For example, let us consider the hyperfiltration of HCl–NaCl solutions through a cation-exchange membrane. Let us assume purely for the sake of illustration that $\beta_i = 1$, $\gamma_{i\alpha} = \gamma_{i(r)} = 1$, and the $\mathcal{D}_i^*$ are proportional to their values in dilute aqueous solution. Then, Na^+ is the k -counterion, its ratio $\beta_i/z_i \mathcal{D}_i^*$ being 6.93 times the corresponding ratio for H^+ . Since we have assumed the activity coefficients to be 1, $[\text{H}^+]/[\text{Na}^+]$ is the same just inside the membrane as it is in the feed solution. Then for a mole fraction of NaCl in the feed of 90%, $|E(\infty)|/|E(0+)| = 1.09$; for a mole fraction of NaCl in the feed of 50%, $|E(\infty)|/|E(0+)| = 1.75$; and for a mole fraction of NaCl in the feed of 10%, $|E(\infty)|/|E(0+)| = 4.35$. In this example, the Schlögl–Goldman assumption of constant electric field is in considerable error for all feed solutions except those with small mole fractions of HCl.

A somewhat different situation prevails regarding the example of Figs. 1 and 2. There Mg^{++} is the k -counterion; its ratio of $\beta_i/z_i \mathcal{D}_i^*$ is 6.59 times the corresponding ratio for H^+ . When the feed solution has mole fractions of HCl of 10%, 50%, 90%, and 98%, $|E(\infty)/E(0+)| = 1.025, 1.10, 1.53$, and 2.62, respectively. In this example, the Schlögl–Goldman assumption of constant electric field is in considerable error only for feed solutions with small mole fractions of MgCl_2 . The reason for this is the following. As we can see from Eqs. (25) and (26), $E(\infty)/E(0+)$ is substantially larger than 1 only when the concentration of H^+ in the exchanger is much larger than the concentration of Mg^{++} . Since the uptake of Mg^{++} is much greater than that of H^+ when there is good chloride exclusion, it is only for feed solutions with a very small mole fraction of MgCl_2 that the concentration of H^+ in the exchanger is much larger than that of Mg^{++} .

From these examples, we see that the Schlögl–Goldman method is sometimes valid and sometimes not and that it can fail for problems of practical interest. The domain of its applicability depends in a complicated way on the values of the ionic parameters, the membrane capacity, and the composition of the feed solution. Perhaps the best criterion for its applicability is the value of the ratio $|E(\infty)/E(0+)|$ that one calculates from Eqs. (25) and (26).

9. REDUCTION TO ALGEBRAIC EQUATIONS

We mentioned in the Introduction that as J or x or both become large, the ionic concentrations sometimes (but not always) become independent of position near the feed–membrane interface. When the concentrations do become independent of position, the extended Nernst–Planck equations reduce from differential to algebraic equations. We now discuss the circumstances under which this

reduction is *not* possible. This we do by seeing under what circumstances such a reduction leads to absurd results.

When the gradient terms drop out of Eq. (2), it becomes

$$j_i = \beta_i J c_{i(r)}(0+) + z_i c_{i(r)}(0+) \mathcal{D}_i^* \frac{FE}{RT} \quad (27)$$

Using Eq. (5), we find that

$$\frac{FE}{RT} = -J \frac{\sum_i z_i \beta_i c_{i(r)}(0+)}{\sum_i z_i^2 c_{i(r)}(0+) \mathcal{D}_i^*} \quad (28)$$

Then by substituting Eq. (28) into Eq. (27) and rearranging, we get

$$j_i = \beta_i J c_{i(r)}(0+) \left[1 - \frac{z_i \mathcal{D}_i^*}{\beta_i} \frac{\sum_i (\beta_i / z_i \mathcal{D}_i^*) z_i^2 c_{i(r)}(0+) \mathcal{D}_i^*}{\sum_i z_i^2 c_{i(r)}(0+) \mathcal{D}_i^*} \right] \quad (29a)$$

$$= \beta_i J c_{i(r)}(0+) \left[1 - \frac{\langle \beta_i / z_i \mathcal{D}_i^* \rangle}{\beta_i / z_i \mathcal{D}_i^*} \right] \quad (29b)$$

where $\langle \rangle$ denotes the average of the quantity it encloses over all ions with the weights $z_i^2 c_{i(r)}(0+) \mathcal{D}_i^*$.

It is not difficult to find sets of possible and reasonable z_i , $\mathcal{D}_i^*$, β_i , and $c_{i(r)}(0+)$ for which the bracket in Eqs. (29) is negative for at least one value of i . For this i , j_i , and J have the opposite signs, *i.e.*, they are oppositely directed. However, in hyperfiltration no j_i can be oppositely directed to J . This means that for the particular feed solution leading to the $c_{i(r)}(0+)$ being considered, the reduction to algebraic equations is impossible, and the ionic concentrations do not become independent of position near the feed-membrane interface as J or x become infinite.

Fig. 3 shows an example based on the hyperfiltration of HCl-MgCl₂ through a cation-exchange membrane. Again we take $\beta_i = 1$, $\gamma_{i\alpha} = \gamma_{i(r)} = 1$, and assign to the $\mathcal{D}_i^*$ values proportional to those they have in dilute aqueous solution. The axes in Fig. 3 show the concentrations of H⁺ and Mg⁺⁺ in the feed expressed as multiples of the concentration of fixed charge in the membrane. All feed solutions inside the region labeled "Region of No Constant Solution" are feed solutions for which the reduction of the extended Nernst-Planck equations to algebraic equations fails. In this example, the region of no constant solution covers virtually the entire region of practical interest, so that calculations based on the reduction of the extended Nernst-Planck equations to algebraic equations give us very little useful information.

It is no accident that the region of no constant solution in this example covers the region of feed solutions for which there is good coion exclusion. To see

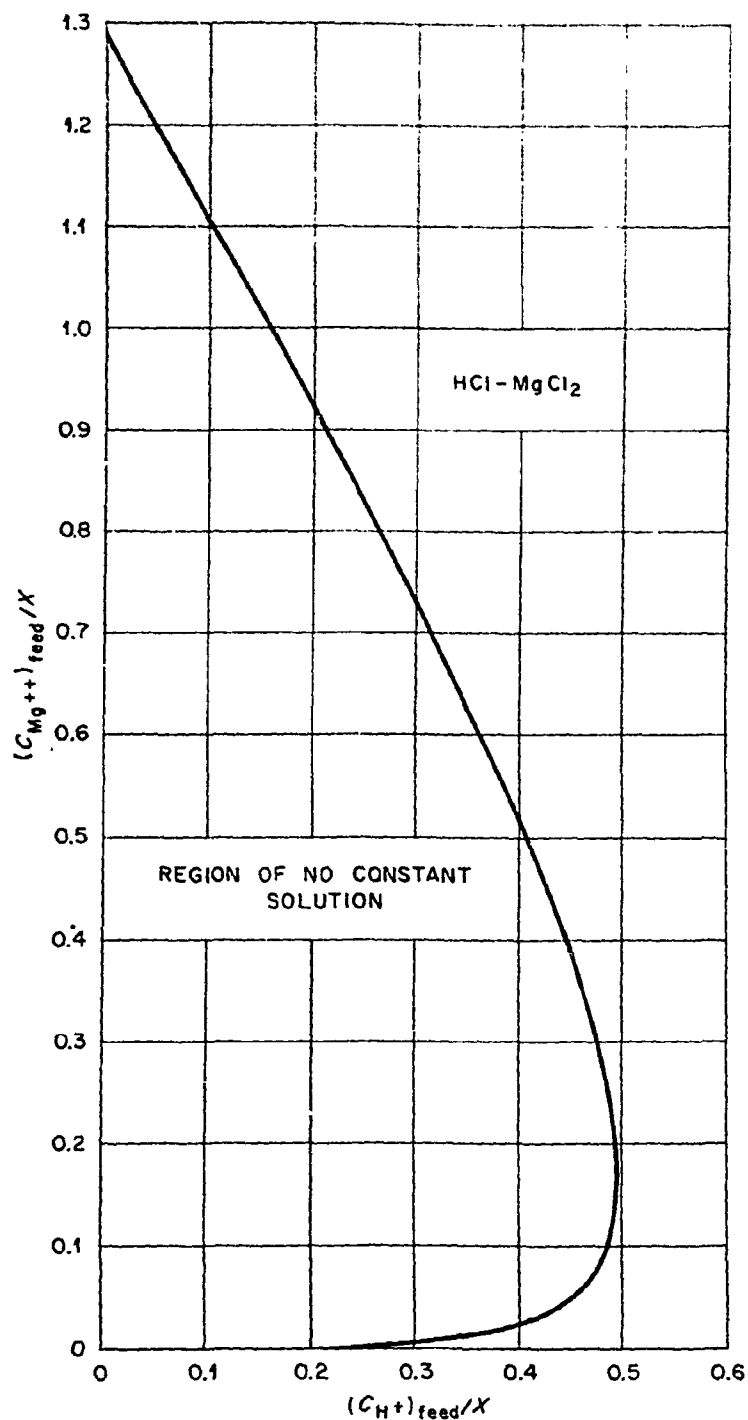


Fig. 3. The region of no constant solution for the HCl-MgCl₂ system. All feed solutions inside the region of no constant solution are feed solutions for which the reduction of the extended Nernst-Planck equations to algebraic equations fails.

this, let us note that when there is good coion exclusion, the sums in Eq. (29a) may be considered as extending only over counterions. The average in Eq. (29b) is then the average of $\beta_i/z_i\mathcal{D}_i^*$ over just the counterions with the weights $z_i^2c_{i(r)}(0+)\mathcal{D}_i^*$. If we let the subscript m denote the counterion with the *smallest* value of $\beta_m/z_m\mathcal{D}_m^*$, then clearly

$$\left\langle \frac{\beta_i}{z_i \mathcal{D}_i^*} \right\rangle \geq \frac{\beta_m}{z_m \mathcal{D}_m^*},$$

equality occurring only if (i) all the $\beta_i/z_i \mathcal{D}_i^*$ for counterions are equal or (ii) there is only one counterion. If equality does not occur, the bracket in Eq. (29b) is negative, and j_m and J have opposite signs, *i.e.*, are oppositely directed. Thus we expect quite generally that reduction of the extended Nernst–Planck equations to algebraic equations in the limit of large J or x fails for multicomponent feeds for which there is sufficiently good coion exclusion.

APPENDIX A

In this Appendix we discuss the effect on the convective term in Eqs. (1) and (2) of taking the membrane material to be a thermodynamic component. We shall see below that when we do not, the equations of irreversible thermodynamics allow us no latitude regarding the value of β_i : it must be 1. On the other hand, if we do consider the membrane material to be a thermodynamic component, we shall see below that we are freed from this constraint.

To simplify the discussion, we consider only thermodynamic systems in which the condition of mechanical equilibrium is fulfilled. The condition of mechanical equilibrium can be stated in two equivalent ways: (1) the velocity of the local center of mass of the components is independent of position, or (2) the pressure gradient equals the sum of the applied external forces. If the density of the wet membrane does not change from point to point, form (1) of the condition of mechanical equilibrium follows from the requirement of continuity. The external forces mentioned in form (2) of the condition of mechanical equilibrium are the elastic forces applied to each element of the membrane phase by those adjacent to it or by the clamping and supporting structure.

When the condition of mechanical equilibrium is fulfilled, we can transform the linear equations of irreversible thermodynamics from the frame of reference fixed with respect to the local center of mass of the components (barycentric frame of reference) to a frame of reference fixed with respect to any one of the components. In this latter frame of reference, we again have linear equations connecting the fluxes and forces, and the matrix of coefficients is again symmetric (Onsager's relation). The details of such transformations have been exhaustively discussed by S. R. de Groot and P. Mazur (7).

In Schlögl's analysis, there are $N + 1$ thermodynamic components, N dissolved ions and water.* The fluxes of the N dissolved ions in a frame of reference fixed with respect to the water are given by

$$j_i = - \sum_{k=1}^N L_{ik} \frac{d\tilde{\mu}_k}{dx}, \quad L_{ik} = L_{ki} \quad (i = 1, \dots, N) \quad (\text{A1})$$

* See the remarks at the end of Appendix B regarding the use of individual ions as components.

Schlögl simplifies these equations by assuming that the off-diagonal elements of the matrix L_{ik} vanish, while the diagonal elements are given by the equation $L_{ii} = \mathcal{D}_i^* c_{i(r)} / RT$. The physical meaning of these assumptions is that the ions interact only through the electric field and not directly by collision or by affecting the motion of the water molecules. With these assumptions, Eqs. (A1) becomes

$$j_i = - \mathcal{D}_i^* \frac{dc_{i(r)}}{dx} + z_i \mathcal{D}_i^* c_{i(r)} \frac{FE}{RT} - \mathcal{D}_i^* c_{i(r)} \frac{d \ln \gamma_{i(r)}}{dx} \quad (\text{A2})$$

We must remember now that the j_i appearing in Eqs. (A2) are the ionic fluxes in a frame of reference fixed with respect to the water. In order to get the ionic fluxes in a frame of reference fixed with respect to the laboratory, we have to add the term $Jc_{i(r)}$, which leads at once to Eqs. (1).

Suppose now we begin again and this time consider the membrane material as a thermodynamic component. Then there are $N + 2$ components, N dissolved ions, water, and membrane. The fluxes of the N dissolved ions and water in a frame of reference fixed with respect to the membrane material are given by

$$j_i = - L'_{i0} \frac{d\mu_0}{dx} - \sum_{k=1}^N L'_{ik} \frac{d\tilde{\mu}_k}{dx}, \quad L'_{ik} = L'_{ki} \quad (i = 0, 1, \dots, N) \quad (\text{A3})$$

Here the subscript 0 refers to the water. If we use the equation for $i = 0$ to eliminate $d\mu_0/dx$ in favor of $j_0 \equiv J$, the equations for $i = 1, \dots, N$ take the form

$$j_i = - \sum_{k=1}^N \mathcal{L}_{ik} \frac{d\tilde{\mu}_k}{dx} + \beta_i J \quad (i = 1, \dots, N) \quad (\text{A4a})$$

$$\mathcal{L}_{ik} = L'_{ik} - \frac{L'_{i0} L'_{0k}}{L'_{00}} = \mathcal{L}_{ki}, \quad \beta_i c_i = \frac{L'_{i0}}{L'_{00}} \quad (\text{A4b})$$

If we again make Schlögl's assumption that $\mathcal{L}_{ik} = 0$ ($i \neq k$) and $\mathcal{L}_{ii} = \mathcal{D}_i^* c_{i(r)} / RT$, we find that Eqs. (A4) are the same as Eqs. (2). We see then how the inclusion of the membrane material as an additional thermodynamic component leads to greater generality in the form of the convective term, for nothing in the theory now demands that $\beta_i = 1$.

APPENDIX B

Eq. (3), the equation of electroneutrality, cannot be strictly valid since the existence of an electric field in the membrane generally implies a non-vanishing charge density. But, to use the words of Kirkwood and Oppenheim, "the deviation from electroneutrality produces macroscopically imperceptible composition changes." (6) To see that this is so, we estimate the changes in composition that arise from departures from strict electroneutrality. If we anticipate the results derived in section 8, we see that when there is good coion exclusion, the change in

$(F|E|/RT)$ across the membrane is less than $(J\beta_k/|z_k|\mathcal{D}_k^*)$, where k denotes the counterion with the largest value of $(\beta_k/|z_k|\mathcal{D}_k^*)$. The charge density required to produce this field can be estimated from Maxwell's equation

$$\frac{|\rho|}{\varepsilon} = |\operatorname{div} E| \sim \frac{|E|}{l} = \frac{RT}{F} \frac{J\beta_k}{|z_k|\mathcal{D}_k^*} \quad (\text{B1})$$

If we express this charge density as a concentration $\Delta c = (|\rho|/F\rho_w)$, we find that

$$\frac{\Delta c}{X} \sim \frac{\beta_k}{|z_k|} \frac{J}{\mathcal{D}_k^* l} \frac{\varepsilon RT}{F^2 X \rho_w} \quad (\text{B2})$$

Now the quantity $\varepsilon RT/F^2 X \rho_w$ is the square of a Debye length, λ_D , so that we can write finally

$$\frac{\Delta c}{X} \sim \frac{\beta_k}{|z_k|} \frac{Jl}{\mathcal{D}_k^*} \left(\frac{\lambda_D}{l} \right)^2 \quad (\text{B3})$$

The left-hand side of Eq. (B3) is a measure of the departure from electroneutrality in the membrane. In a membrane with an ion-exchange capacity of 1 mole per kg water, containing 50 vol-% water, and having an electrical permittivity one-tenth that of water, $\lambda_D = 1.9 \text{ \AA}$. If we take $l = 1 \text{ micron}$, $J = 4.7 \times 10^{-4} \text{ g cm}^{-2} \text{ sec}^{-1}$ ($= 10 \text{ gal ft}^{-2} \text{ day}^{-1}$), and $\mathcal{D}_k^* = 5 \times 10^{-7} \text{ g cm}^{-1} \text{ sec}^{-1}$, $(Jl/\mathcal{D}_k^*) = 0.094$. Thus $(\Delta c/X) \sim 3.8 (\beta_k/|z_k|) \times 10^{-9}$ and is very small as expected. No reasonable alteration of the numbers changes this conclusion.

We can proceed therefore by solving the extended Nernst-Planck equations under the condition of strict electroneutrality, treating both E and the ionic concentrations as unknowns. When we have determined E , we can compute the charge density required to produce it. This charge density requires, as we have just seen, only the smallest alteration of the concentrations, so that the values obtained in the first step more than suffice for practical purposes. The error in the electric field E is also of the same order as the error in the ionic concentrations (*cf.*, *e.g.*, Eq. (21)). The electric field and the concentrations calculated in this way change very little over a Debye length λ_D , as we expect in the interior of a homogeneous phase. Thus we expect that the use of the strict equation of electroneutrality will cause negligible error in describing the variation of the ionic concentrations and the electric field in the membrane.

In this problem, however, we must extend the interior solution of the extended Nernst-Planck equations across the two phase boundaries into the exterior aqueous phases. In order to do this we must cross the electrical double layers that exist at the phase boundaries. In these double layers, the concentrations and the electric field do change appreciably over a Debye length, and electroneutrality is no longer a good approximation as it is in the interior of a homogeneous phase. The theory employed in the body of this paper is thus invalid over an interval a few Debye lengths wide on each side of a phase boundary.

However, we do not need to know the detailed variation of electric field and ionic concentrations in the double layer as long as we know how to go from a point P in an exterior phase just *outside* the double layer to a point P' in the membrane just *outside* the double layer.

At P and P' , electroneutrality is a good approximation. We make the passage from P to P' by employing the assumption of membrane equilibrium: we assume that each small element of volume in the double layer is in thermodynamic equilibrium with those adjacent to it. Thus the states at P and P' are in thermodynamic equilibrium, and we can use Eqs. (3), (4), and (6) to calculate the change in ionic concentrations and electric potential across the double layer.

We see from the above discussion that the assumption of strict electroneutrality in the problem under discussion in this paper is an excellent approximation.

The fact that electroneutrality is not *strictly* true is what justifies using individual ions as thermodynamic components in Appendix A. If electroneutrality were strictly true, the amounts of the different ions present in a phase could not be varied independently, which is the condition that must be met for a constituent of a phase to be a component in the Gibbsian sense. However, electroneutrality is only an approximation, and no fundamental reason exists why we cannot add individual ions to a phase (e.g., by shooting them in with a particle accelerator). Another way of looking at this situation is to begin by noting that none of the theorems of thermodynamics, either equilibrium thermodynamics or the thermodynamics of irreversible processes, depends in any way on the *size* of the charge on the proton. In a universe in which the size of the proton charge were, say, 10^{20} times smaller than in our universe, electroneutrality would be a very poor approximation, yet one would have the same thermodynamics and in particular the same identification of Gibbsian components.

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7.3 REVISED REVIEW ARTICLE ON HYPERFILTRATION

During the biennium, the review article "Hyperfiltration (Reverse Osmosis)", originally published as Chapter 8 in Principles of Desalination, edited by K. S. Spiegler and published by Academic Press in 1966, was revised. The revised chapter is to be published in the second edition of Principles of Desalination, with Spiegler and A. D. K. Laird as editors. An impression of the scope of the chapter can be obtained from the table of contents of the revision given below.

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7.4 COUPLING OF SOLUTE AND SOLVENT FLUXES IN ION-EXCHANGE MEMBRANES (ADAPTED FROM MATERIAL IN CHAPTER REFERRED TO IN (7.3)).

Transport through membranes can be discussed in terms of several different sets of variables. We have chosen to break the subject into the distribution of solute between membrane and aqueous phases, diffusion of solutes under their concentration gradients in the membrane phase, the flux of solvent, and the coupling between solvent and solute fluxes. Information on the first three is relatively accessible experimentally. There is, however, little in the way of data from which one can estimate the degree of coupling for ion-exchange membranes. The usual practice, followed in Section 7.1 and 7.2, is to make the plausible assumption of complete coupling (expressed as a value of 1 for the coupling coefficient, β) between the individual ions and water. With neutral membranes of high rejection (for example, cellulose acetate), evidence seems compelling that coupling is small, with β approaching zero, since a "solution-diffusion" model adequately represents results. Ion-exchange membranes, however, since their water content is usually much higher than that of neutral membranes of high rejection, might be expected to have higher coupling. Because of streaming potential effects, assumption of $\beta = 1$ for the individual ions would imply a value of β greater than 1 for the overall salt coupling coefficient. Such values lead to predictions of negative rejection with two-component systems in certain cases, particularly with hyperfiltration of concentrated solutions of acids by anion-exchange membranes.⁵¹ Hoffer and Kedem found negative rejection of acids in hyperfiltration with loose anion-exchange membranes, prepared by cross-linking albumin in a collodion matrix. Negative rejection occurred for both sulfuric and hydrochloric acids for sufficiently concentrated solutions. The effect, as they expected, was more pronounced and covered a wider concentration range for sulfuric acid than for hydrochloric acid.

⁵² Pusch reports similar observations for HCl and H₂SO₄ with Asahi anion-exchange membranes, the negative rejections being much more pronounced for H₂SO₄. However, he also reports high distribution coefficients for sulfuric acid, $\underline{D}^*$ (moles of solute per kg of water in membrane phase ($\underline{m}^*$)/moles of solute per kg water solution phase ($\underline{m}$)) being about 5 for half-molar solution

compositions. Similar high values of $\underline{D}^*$ were earlier found by Nelson and Kraus⁵³ for anion-exchange beads, and were explained on the basis of sulfate-bisulfate equilibrium.⁵⁴ With such high distribution coefficients, the overall $\beta_{\text{H}_2\text{SO}_4}$ appears to be less than unity.

Shor, et al.¹³ have measured asymptotic rejections of various salts by dynamically formed hydrous zirconium (IV) oxide membranes at low pH (3 to 4) where the membrane is an anion exchanger. They found values of R_{∞} in the range of 70-80% for feeds composed of 0.025 molar NaCl, CsCl, NaBr, NaNO₃, or NaClO₄. The asymptotic rejection, R_{∞} , is the value approached with increasing flux, and is related to solute distribution at the membrane-brine interface (α) and to coupling of fluxes in the membrane of the solute component and water by the equation

$$R_{\infty} = 1 - \beta_{\text{salt}} \frac{D^*}{-\alpha} \quad (7.4.1)$$

Such asymptotic rejections indicate values of β of the salt of at least 0.2-0.3, and probably much higher, since $\frac{D^*}{-\alpha}$ in these cases should be well below 1. Shor et al. were able to fit their data on the asymptotic rejection of NaCl and MgCl₂ over a considerable range of feed concentrations with the choice of $\beta = 1$ for the salt component. If this value is correct, it implies β 's of considerably less than unity for the individual ions.

There is one ion exchanger, Zeo-karb 315, for which enough information recently became available to determine β for NaBr, Na⁺, and Br⁻. The membrane is a phenol-formaldehyde condensate with -CH₂SO₃⁻ groups on about 1/5 of the aromatic rings.⁵⁵ Meares and Foley,⁵⁶ as a result of exhaustive studies on this exchanger, have evaluated phenomenological L -coefficients relating cation flow, volume flow, and electric current to the gradients of osmotic pressure, hydrostatic pressure, and electric potential. From these coefficients and other data they present, we can estimate values of β for the ions and NaBr (Table 7.1).

One method (Column 3, Table 7.1) utilizes the L -coefficients of Meares and Foley and the equation

$$10^{-3} \beta_{\text{NaBr}} \frac{m_{\text{NaBr}}^*}{m_{\text{NaBr}}} = \left(\frac{\phi_1}{\phi_v} \right)_{\pi=0} = \frac{L_{\pi p} L_E - L_{\pi E} L_{Ep}}{L_p L_E - L_{pE} L_{Ep}} \quad (7.4.2)$$

where ϕ_1 is the counterion (here cation) flux (mole cm⁻¹ sec⁻¹); ϕ_v , the

volume flux (cm sec^{-1}); i , the electric current density (amps cm^{-2}); and the symbols p , π , and E represent, respectively, the differences in pressure (joules cm^{-3}), osmotic pressure (joules cm^{-3}), and electric potential (volt). The L 's are the phenomenological coefficients given by Meares and Foley in the units given by them.

The other method utilizes a form of Equation (7.4.1) derived in the chapter* for ion-exchange membranes, from which in the present case

$$\beta_{\text{NaBr}} = \frac{\beta_{\text{Br}^-} + \frac{D_{\text{Br}^-}}{D_{\text{Na}^+}} \beta_{\text{Na}^+}}{1 + \frac{m^*}{m} \frac{D_{\text{Br}^-}}{C}} \quad (7.4.3)$$

TABLE 7.1
TRANSPORT COEFFICIENTS OF NaBr IN ZEO-KARB 315
DETERMINED FROM THE MEASUREMENTS OF MEARES AND FOLEY

External Concen- tration (moles/ liter)	Internal Concen- tration (moles/ kg wet resin)	β_{NaBr} (Eq. 7.4.2)	β_{Na^+}	β_{Br^-}	$10^6 \times D_{\text{Na}^+}$ ($\text{cm}^2 \text{sec}^{-1}$) (Ref. 55)	$10^6 \times D_{\text{Br}^-}$ ($\text{cm}^2 \text{sec}^{-1}$) (Ref. 56)	β_{NaBr} (Eq. 7.4.3)
.100	.0360	1.08	.385	.600*	4.1	8.22	1.20**
.200	.0837	1.16	.521	.617	4.6	8.89	1.26
.300	.137	1.27	.708	.600	4.85	8.89	1.35
.500	.255	1.20	.765	.602	5.2	8.89	1.20
1.00	.593	1.10	.745	.600*	5.6	8.92	.951**

*Assumed value.

**Calculation based on assumed value of β_{Br^-}

The ionic β 's (Columns 4 and 5 of Table 7.1) were obtained by

$$10^{-3} \beta_{\text{Na}^+} \frac{m^*}{m} = \left(\frac{\phi_1}{\phi_v} \right)_{\pi=0, E=0} = \frac{L_{\pi p}}{L_p}$$

$$10^{-3} \beta_{\text{Br}^-} \frac{m^*}{m} = \left(\frac{\phi_2}{\phi_v} \right)_{\pi=0, E=0} = \left(\frac{\phi_1}{\phi_v} \right)_{\pi=0, E=0} - \frac{i/F}{\phi_v} \pi=0, E=0 = \frac{L_{\pi p} - (L_{Ep}/F)}{L_p}$$

*See Section 7.3.

Here ϕ_2 represents the coion (bromide) flux (moles $\text{cm}^{-2} \text{sec}^{-1}$). Further

$$\underline{m}_{\text{Br}^-}^* = \underline{m}_{\text{NaBr}}^* \quad \text{and} \quad \underline{m}_{\text{Na}^+}^* = \underline{m}_{\text{NaBr}}^* + \underline{C}^*.$$

Meares and Foley indicate that the ion-exchange capacity $\underline{C}^*$ is 0.72 eq per kg water in the exchanger; $\underline{f}_w$, the weight fraction of water in the exchanger, is 0.667. The resin-phase concentration, $\underline{m}_{\text{NaBr}}^*$, and the diffusion coefficient $\mathcal{D}_{\text{Br}^-}$ have been measured by Meares and Foley. The diffusion coefficient $\mathcal{D}_{\text{Na}^+}$ has been measured by McHardy, Meares, and Thain.⁵⁵

The β 's in Table (7.1) are given only for the range of external concentrations for which Meares and Foley quote internal salt concentrations as a function of salt concentration in the external solution. The values of β_{NaBr} given by the two methods of computation agree within about 10%, and appear to slightly exceed unity, presumably from streaming potential effects. However, although solute and solvent fluxes in the membrane are clearly coupled, coupling between individual ions and solvent is not complete in Zeo-karb 315, since β_{Na^+} and β_{Br^-} are both less than unity.

8. Enhanced Heat Transfer

In earlier biennia, see for example Ref. 15, p. 305 ff, and Ref. 30, p. 153 ff, we published several accounts showing that heat transfer in distillation was enhanced considerably by the attachment of wires or fins to the heat transfer surface. During the current biennium, D. G. Thomas published an article in Desalination⁵⁷ in which he gives an estimated limit on the performance of enhanced heat transfer surfaces. The article is reprinted here.

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8.1 PROSPECTS FOR FURTHER IMPROVEMENT IN ENHANCED HEAT TRANSFER SURFACES* **

D. G. Thomas

SUMMARY

The current state-of-the-art of commercial enhanced surfaces for thin film evaporation and condensation on vertical tubes is exemplified by fluted tubes having overall heat-transfer coefficients of 1300 to 2000 Btu/hr ft² °F at atmospheric pressure. Experimental surfaces have been tested which gave overall coefficients up to 5000 Btu/hr ft² °F.

Oxidative fouling factors as small as 10^{-4} (Btu/hr ft² °F)⁻¹ have been reported for fluted enhanced surfaces. It is hypothesized that such small fouling factors occur because high shear forces developed in the thin-film region prevent formation of all except very thin oxide films. Limited data also suggest that the fouling resistance may decrease with increasing heat-transfer coefficient (*i.e.*, with increased shear rate); if true this would provide an important incentive for development of improved enhanced heat transfer surfaces.

Although the mechanism responsible for high performance on the condensing side of fluted or finned tubes seems relatively well understood and upper limits can be estimated, the mechanism on the evaporating side seems to be much more complicated. Consequently an upper limit for heat transfer rates on the evaporative side was estimated assuming that the upper limit occurred when the water film thickness was just sufficient to prevent dry spot formation. Assuming a metal wall resistance of 0.00004 and upper limits of 18,000 and 14,200 Btu/hr ft² °F on the condensing and evaporative sides, respectively, gives an estimated upper limit on performance of enhanced surfaces of ~6000 Btu/hr ft² °F.

SYMBOLS

$\mathcal{A}$ — Constant in Eq. (3) = 1.72×10^{-6} , dimensionless

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c_p	— Specific heat, Btu/lb _m
d	— Wire diameter or fin width, ft
D	— Tube diameter, ft
D_c	— Initial nucleus diameter, ft
D_p	— Particle diameter, ft
e	— Penetration, ft
g_c	— Conversion factor, (lb _m ·lb _f) (ft/hr ²)
g_L	— Gravitational acceleration, ft/hr ²
h	— Heat-transfer coefficient with wires or fins, Btu/hr ft ² °F
h_0	— Heat-transfer coefficient of smooth tube, Btu/hr ft ² °F
h_c	— Thin-film region condensing coefficient, Btu/hr ft ² °F
h_e	— Thin-film region evaporating coefficient, Btu/hr ft ² °F
h_{fg}	— Latent heat of condensation, Btu/lb
k	— Thermal conductivity, Btu/hr ft ² °F/ft
L	— Length, ft
l	— Amplification length, ft
N	— Number of wires or fins, dimensionless
N_{Re}	— Reynolds number, $4\Gamma/\mu$, dimensionless
N_{Pr}	— Prandtl number
n	— Number of ions formed on dissociation
M	— Molecular weight
P	— Wetted perimeter, ft
p	— Pitch, ft
Δp	— Pressure difference, lb _f /ft ²
q/A	— Heat flux, Btu/hr ft ²
R_1, R_2	— Radius of curvature, ft
R	— Gas constant
R_B	— Bond resistance, lb _f /ft ²
R_{B0}	— Bond resistance of protective oxide film, lb _f /ft ²
S/S_∞	— Supersaturation, dimensionless
T	— Temperature, °K
t_σ	— Characteristic time for surface tension effects, sec
u_∞	— Surface velocity, ft/sec
u_*	— Friction velocity, $(g_c \tau_w/\rho)^{1/2}$, ft/sec
u_T	— Particle settling velocity, ft/sec
u_σ	— Local velocity due to surface tension effects, ft/sec
U	— Overall heat-transfer coefficient, Btu/hr ft ² °F
x	— Metal wall thickness, ft
x_f	— Oxide layer thickness, ft
x_{f0}	— Protective oxide film thickness, ft
y	— Fraction of surface covered by thin film
z	— Height, ft

Greek letters

α	— Degree of dissociation
Γ	— Mass flow per unit perimeter, lb _m /hr ft
δ	— Film thickness, ft
λ	— Interfacial free energy, ergs/cm
ρ	— Density, cm/cc
τ_w	— Fluid shear stress at surface, lb _f /ft ²
φ_d	— Deposition rate
φ_r	— Removal rate
μ	— Viscosity, lb _m /ft sec
ν	— Kinematic viscosity, ft ² /hr
ρ	— Density, lb _m /ft ³
σ	— Surface tension, lb _f /ft

INTRODUCTION

The rate of evaporation and condensation from thin films of water falling down vertical tubes is markedly increased by introducing many fine axial grooves into the smooth surface (1–12). Typically the grooves have a pitch of ~ 0.3 cm and penetration of ~ 0.1 cm. Such enhanced surfaces are often referred to as fluted or corrugated. Frequently, fluted tubes have given overall heat-transfer coefficients as large as 2000 Btu/hr ft² °F when evaporating water at atmospheric pressure. In contrast the overall coefficient for thin film evaporation and condensation obtained with smooth tubes under similar conditions (13–15) is ~ 650 Btu/hr ft² °F.

As Kays (18) has pointed out, the reduction in water costs when using enhanced surfaces would be expected to occur largely through reduction of capital costs. Since heat transfer area contributes some 40% to overall capital costs of long tube vertical evaporator distillation plants (16), use of enhanced heat-transfer surfaces affords an attractive possibility of reducing water costs. Clearly because of their high heat-transfer coefficients, enhanced surfaces permit a reduction in heat transfer area requirements and in addition, some plant components such as pressure vessel can be made smaller. Another option is to increase the number of stages by reducing the temperature difference across each stage, thereby increasing the plant performance ratio (17–18). Of course, realization of the cost reductions depends on developing economical methods for producing enhanced surfaces and operating procedures for ensuring that high heat-transfer coefficients can be maintained in practice (17).

FLUTED ENHANCES SURFACES

Gregorig's original fluted surface design (1) had grooves with rounded bottoms and ridges with rounded tops, a pitch of 0.2 cm and a penetration of

0.07 cm. Since then surfaces have been tested which had grooves with round bottoms and ridges with flat tops, with vee-shaped grooves, and with grooves formed by corrugating flat sheet (5). The pitch has been varied from 0.3 cm to 1.5 cm and the penetration from 0.06 to 0.23 cm (7). Despite the range of shapes and dimensions the overall heat-transfer coefficient (after subtracting the metal wall resistance) varied only from 1330 to 1900 Btu/hr ft² °F at atmospheric pressure, with a ΔT of 12°F and a Reynolds number, $(4\Gamma/\mu)$, of ~ 8000 . The principal factor affecting the magnitude of the overall coefficient appeared to be (7) the ratio of groove pitch, p , to penetration, e , with maximum values of the coefficient at a value of $p/e = 2.8$. The nature of the surface shape seemed to have only a secondary effect (7). Other factors which cause increased coefficients with fluted tubes are surfactants and salt at sea water concentrations (5), with overall coefficients in the range 2000 to 3000 Btu/hr ft² °F often observed in atmospheric pressure tests.

The principal development effort on enhanced surfaces for vertical tube evaporators has been on variants of the fluted tube surface in which the shape of the grooves and ridges are roughly mirror images. A variety of such shapes are now commercially available from tubing manufacturers and the performance described above can be considered the current state-of-the-art for present day plant designs utilizing enhanced surfaces.

In a recent survey (18), it was found that whereas seamless tubes cost slightly less than \$1.00 per pound, doubly fluted tube costs were roughly \$2.00 per pound. Since heat-transfer coefficients for the two types of surfaces at atmospheric pressure are 650 to 700 and 1300 to 1800 Btu/hr ft² °F, respectively, the cost of enhancement largely cancels any benefits from the increased heat-transfer coefficient of doubly fluted tubes. Consequently, to realize the full benefits of enhanced surfaces either the cost of enhanced surfaces must be decreased or the overall heat-transfer coefficient must be increased with no additional cost penalty.

ADVANCED ENHANCED SURFACES

Subsequent to the discovery of the marked effect of fluted surfaces on the rate of evaporation and condensation from thin films on vertical surfaces, a variety of experimental surfaces were developed which had substantially larger heat-transfer coefficients than conventional fluted tubes (19–24). The chronology of these events is illustrated in Fig. 1, in which the range of overall heat-transfer coefficients for the different surfaces is shown plotted against the approximate time that the new surface was discovered. (The references cited on the figure do not necessarily coincide with the date of discovery but are literature sources describing the surfaces.)

In 1967 Linde announced (19, 25) that a specially textured surface markedly increased the evaporating heat-transfer coefficient; little information is available on the nature of the textured surface. When the textured surface was combined

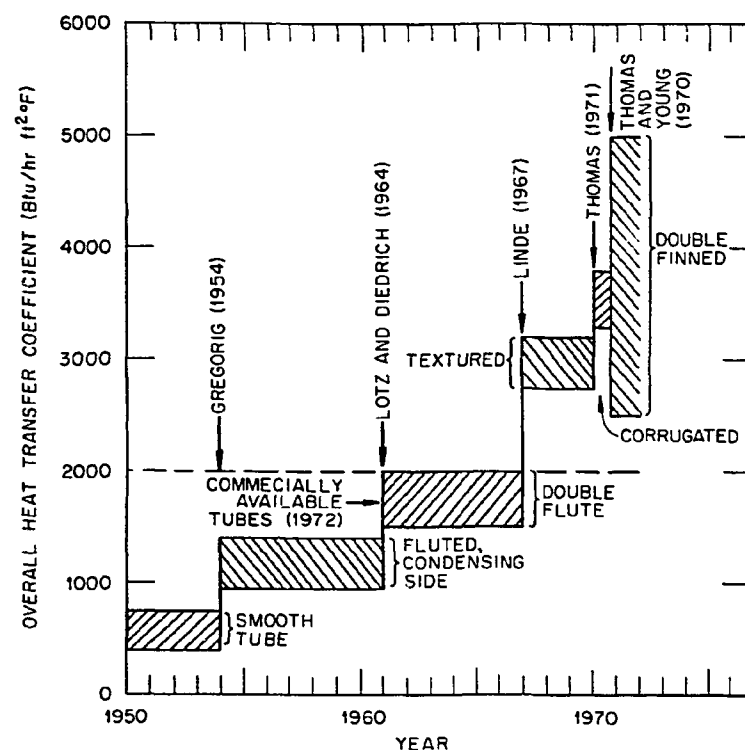


Fig. 1. Chronology of development of enhanced heat-transfer surfaces for vertical tube evaporators.

with fluted, finned, or gold plated surfaces on the condensing side, overall coefficients were 2700 to 3200 Btu/hr ft² °F with fresh water feed at atmospheric pressure but the coefficients decreased to ~2400 Btu/hr ft² °F with salt water feed (5).

In 1967 it was also shown (26) that small axial wires increased the condensing coefficient up to 4.5 times when loosely strapped to the surface of vertical tubes. With this discovery it became clear that the configuration of the surface was not as important as providing regions at intervals around the tube where the bulk of the condensate could be drained off as a rivulet. Based on results of a simplified theoretical model, it was expected that further increases in condensing coefficient would be affected by reducing the amount of tube surface masked by the rivulet guide. When round wires were replaced by loosely attached fins, the condensing coefficient was increased by a factor of ~9 over the smooth tube values (20). When similar fins were placed on the evaporative side of a tube, the evaporative heat-transfer coefficient increased by up to a factor of 12 over the value for smooth tubes (21).

By combining fins on both the evaporative and condensing sides of a vertical tube, it was possible to achieve overall heat-transfer coefficients in the range 2500 to 5000 Btu/hr ft² °F with the higher heat-transfer coefficients occurring at a heat flux of 10⁴ Btu/hr ft².

Finally, based on concepts developed in the finned tube studies, a general corrugated surface configuration was designed (23). When one version was tested (22), overall coefficients for thin film evaporation and condensation were in the

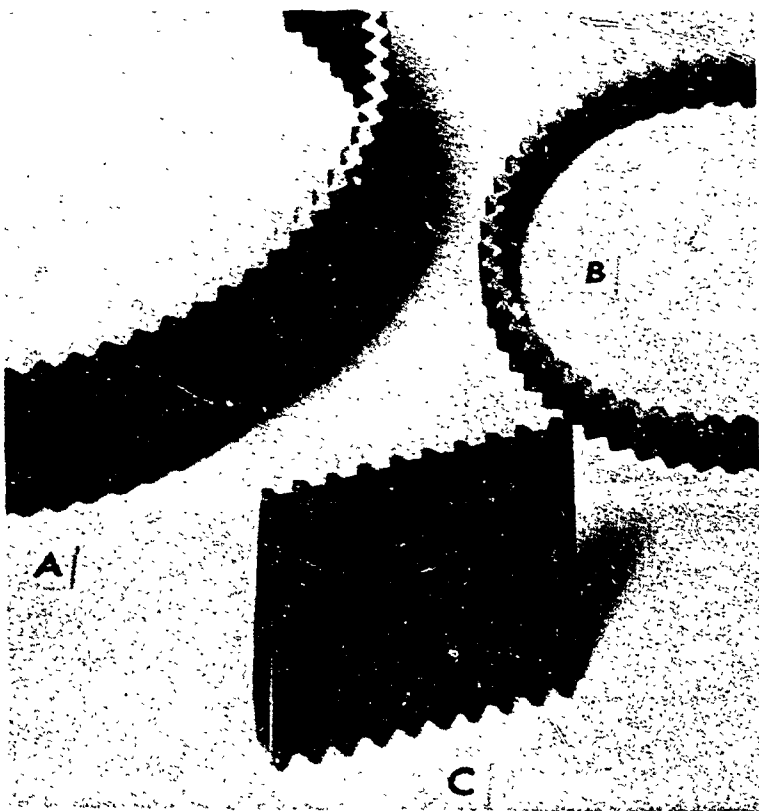


Fig. 2. Commercial and experimental enhanced surfaces for vertical tube evaporators. A. General electric profile 9, B. Anaconda Grob, C. Corrugated surface (Thomas, 1971) (23).

range 3300 to 3800 Btu/hr ft² °F. A sample of the corrugated surface is shown in Fig. 2, Item C. Also shown in this figure are portions of tubes fluted with General Electric profile 9 (Item A) characterized by ridges with flat tops and the Anaconda-Grob profile (Item B) characterized by vee-shaped grooves.

Both the double finned and corrugated surfaces share the special characteristics that (1) the thin evaporating film opposes the thin condensing film so that the heat flow path through the metal wall is minimized and (2) the ratio of rivulet guide circumferential width to thin-film heat transfer circumferential width is the minimum consistent with the water-carrying capacity required for the rivulet guide.

The response of different heat-transfer surfaces to the temperature difference, ΔT , between the evaporating tube side and the condensing tube side is illustrated in Fig. 3. For smooth tubes (5, 24), the value of U is substantially independent of ΔT . This is also true for both the fluted (5) and corrugated (22, 23) tubes when the evaporative film flow rate is ~ 1400 lb/hr ft. On the other hand the overall coefficient of fluted tubes (27) and double ribbed tubes (24) increased markedly as ΔT decreased when the evaporative film flow rates were 630 and ~ 340 lb/hr ft, respectively. This behavior may have important consequences in the design of high performance plants in which the number of stages must be increased to improve the performance ratio (17).

The object of this paper is to examine prospects for further improvement in

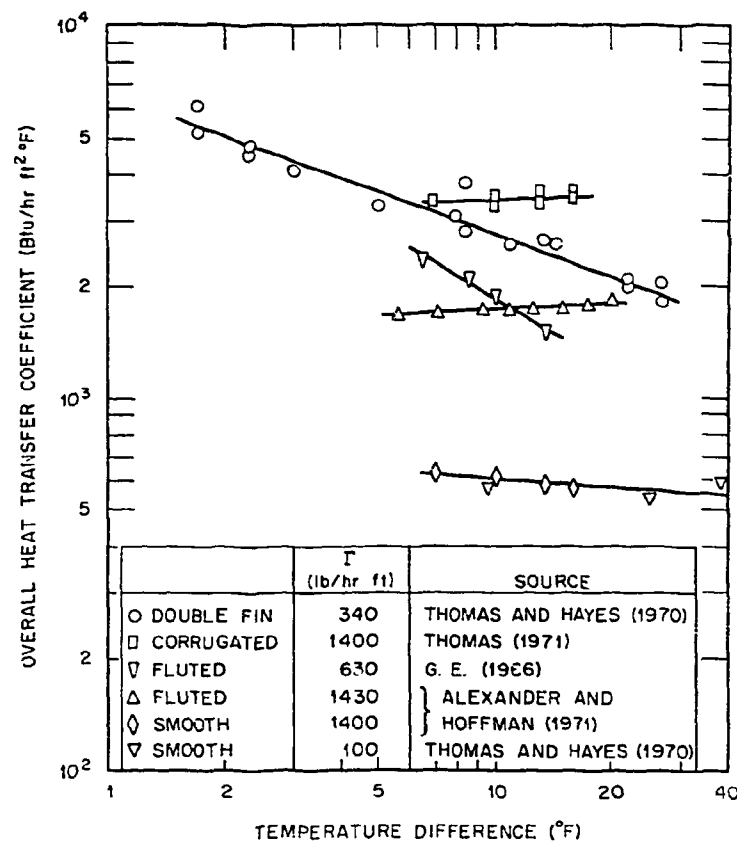


Fig. 3. Effect of overall temperature difference on overall heat transfer coefficient in thin film evaporation and condensation.

enhanced heat-transfer surfaces. From the point of view of current state-of-the-art of manufacturing capability, double fluted tubes must serve as the baseline for comparison. At atmospheric pressure, overall heat-transfer coefficients of ~ 1700 Btu/hr ft² °F are being specified in designs of large VTE plants (28) which will use doubly fluted tubes made from a Cu-Fe alloy, [$k = 150$ Btu/hr ft² (°F/ft)].

Based on the results shown in Fig. 1 and 3, it is clear that experimental test surfaces exist which have 1.5 to 2 times greater overall heat-transfer coefficient. However, as far as is known, these surfaces are not available commercially. In the light of our poor understanding of the mechanisms responsible for these high coefficients, it would seem prudent to make additional studies of temperature dependence of the heat-transfer coefficient, susceptibility of the surface to scaling or fouling etc., before attempting to go into commercial production.

In attempting to assess whether there are prospects for further improvement in enhanced heat-transfer surfaces, there are two somewhat different but related questions.

1. What is the optimum shape for "conventional" fluted surfaces and is there a special configuration that will lead to heat-transfer coefficients well above 2200 Btu/hr ft² °F?

2. Can a surface shape be developed that will represent a marked improve-

ment over current experimental surfaces? Of interest would be surfaces which either have heat-transfer coefficients markedly greater than the 3500–5000 Btu/hr ft² °F indicated in Fig. 1 and 3, or tubes which are practical, inexpensive and easy to manufacture and have heat-transfer coefficients near the upper limit given by existing experimental surfaces.

In view of the large number of “conventional” fluted surfaces that have been tested (5), it seems likely that the most fruitful approach to answering question 1 would be from increased understanding of the mechanisms involved in producing the enhanced heat-transfer coefficients. Although the designs of some of the experimental surfaces (20–24) were based on simplified mathematical models, the models are far from complete. Consequently the answers to question 2 also appear to be most readily approached through improved models based on the fundamental mechanisms involved.

It should be emphasized that with overall coefficients as large as 5000 Btu/hr ft² °F, other factors may be of more importance than improving the thin film evaporation and condensation heat-transfer coefficients. For instance, a recommended fouling factor for fluted copper alloy surfaces is 0.0002 and a reasonable tube wall resistance may be as low as 0.000027. With these values and assuming that the evaporating and condensing film heat-transfer coefficients could be made infinite, the overall design coefficient would be only 4400 Btu/hr ft² °F. For the corrugated tube, made from 0.004-in.-thick stainless steel, such a fouling factor would reduce the observed experimental coefficient from 3400 Btu/hr ft² °F to a design coefficient of ~2400 Btu/hr ft² °F. This indicates that perhaps the greatest impact on enhanced surface VTE plant performance awaits increased understanding and control of the fouling problem.

MECHANISM OF SURFACE ENHANCEMENT

Condensing side

In this paper describing the effect of a grooved surface on thin film condensation, Gregorig (1) hypothesized that, because of the shape of the grooved tube, surface tension forces in the thin liquid film tend to draw condensate from the crests of the surface into the grooves between crests. The bulk of the condensate drains off in the grooves leaving a thin liquid film on the crests where heat-transfer coefficients can be extremely large.

The problem of obtaining an analytical solution for flow down a fluted surface is difficult, not only because of the well known problem in obtaining a solution to the equations of motion for a three dimensional flow situation but because the surface tension is introduced through the boundary condition at the vapor–liquid interface (31)

$$\Delta p - 2\mu \left(\frac{\partial u_i}{\partial X_k} + \frac{\partial u_k}{\partial X_i} \right) = \left(\frac{1}{R_1} + \frac{1}{R_2} \right) \sigma \quad (1)$$

and of course this boundary condition is just what determines the shape of the interface to which it is to be applied. Although no solutions have been reported for the equations of motion with fluted tube geometry and boundary conditions given by Eq. (1), it is interesting to note that, taking into account the pressure variation with height, the equilibrium at an interface between vapor and liquid is specified by (31)

$$\rho g_L Z - \sigma \left(\frac{1}{R_1} + \frac{1}{R_2} \right) = \text{constant.} \quad (2)$$

The only parameter that can be formed from the nongeometric quantities is $(\sigma/\rho g_L)^{1/2}$ with the dimensions of length. Batchelor (31) interprets this as being the length scale for which surface tension effects may be comparable with gravitational effects. For water this characteristic length varies from 0.27 to 0.24 cm in the temperature range 80 to 240°F. It is notable that the value of the parameter for water is substantially the same as the pitch of the grooves in many of the fluted tubes (7).

In his analysis of the condensation phenomenon, Gregorig (1) postulated two-dimensional flow, a constant film thickness over the crest and then assumed that the pressure gradient in the liquid film was given by $\Delta p = (\sigma/R)$. With those assumptions Gregorig was able to calculate an "optimum" surface shape as a function of film thickness. Since film thickness was a parameter in the calculation, heat-transfer coefficients were not obtained on an a priori basis. Subsequent studies (2) indicate that the magnitude of the condensing heat-transfer coefficients obtainable with grooved surfaces were not so much a function of surface shape as they were of pitch and depth of the grooves.

In analyzing film condensation results obtained with small wires or fins loosely attached to the surface of vertical tubes, Thomas (20, 26) divided the flow into two regions, a thin film between the wires or fins where the heat-transfer coefficient was high and a rivulet adjacent to the wires or fins. The bulk of the condensate was assumed to flow down the tube in the rivulet and heat transfer in the rivulet region was assumed to be negligible. After introducing the surface tension on dimensional grounds, it was possible to obtain an expression for the ratio of heat-transfer coefficient with fins (or cylinders) and the smooth tube heat-transfer coefficient, h/h_0 . For finned tubes the final expression was

$$\begin{aligned} (h/h_0) = & \left[1 - \left(\frac{Nd}{\pi D} \right) \left\{ 1 + 3.2 \left(\frac{\nu \Gamma D}{g_L \rho N d^4} \right)^{1/4} \right\} + \right. \\ & \left. 1.03 \times 10^{-3} \mathcal{A} \left(\frac{g_c \sigma L}{\nu \Gamma} \right)^{2/3} \left(\frac{\nu \Gamma N^3}{g_L \rho D^3} \right)^{5/8} \right]^{1/3} \times \\ & \left[1 - \left(\frac{Nd}{\pi D} \right) \left\{ 1 + 3.2 \left(\frac{\nu \Gamma D}{g_L \rho N d^4} \right)^{1/4} \right\} \right]. \end{aligned} \quad (3)$$

The value of $\mathcal{A}$, determined experimentally, was 1.72×10^{-6} . Differentiation of Eq. (3) to obtain the optimum fin spacing gave

$$\left(\frac{Nd}{\pi D}\right)_{\text{opt}} \approx \frac{5}{13} \left[\frac{1}{1 + 2.7 \left(\frac{\nu \Gamma D}{g_L \rho N d^4} \right)^{1/4}} \right] \quad (4)$$

substantially independent of the empirical constant $\mathcal{A}$ as well as the surface tension and viscosity of the fluid. At a heat flux of 5×10^4 Btu/hr ft², Eq. (4) indicates an optimum fin spacing of ~ 0.25 cm. This is about the same value as has been adopted for the pitch of grooves in a fluted surface (7) as well as being almost the same as the characteristic length obtained from Eq. (2).

Thomas (20) also suggested a criterion for flooding (*i.e.*, sharp decrease in heat-transfer enhancement) based on results for cylindrical wires loosely attached to the surface of vertical tubes. Flooding was predicted to occur on tubes with cylindrical wire fins when

$$4.77 \left(\frac{\nu \Gamma D}{g_L \rho N d^4} \right)^{1/4} > 1. \quad (5)$$

This criterion, adjusted for fin-type geometry by use of the constant 3.2 [Eq. (3)] instead of 4.77, was subsequently used (22, 23) to establish the height of corrugations for the surface shown as "C" in Fig. 2.

Alexander and Hoffman (7) have shown from their experimental studies that the optimum pitch-to-penetration, p/e , for fluted tubes (for maximum heat-transfer enhancement) is less than $(p/e) = 2.8$. If flooding is assumed to be responsible for the poorer performance of surfaces with $(p/e) > 2.8$, then for fluted surfaces the appropriate value of the numerical constant in Eq. (5) should be ~ 2.9 . The principal reason for the differences in numerical coefficient for different surfaces is believed to be due to the different rivulet shapes.

As shown in Fig. 4, the performance of the finned surface in enhancing film condensation follows the same trend with heat flux as does data for fluted tubes and furthermore the enhancement of film condensation by the finned surface is equal to or somewhat better than the highest values reported for fluted surfaces. Thus, for the two extremely different surface shapes (finned and fluted) the dimensions of the grooves or fins rather than the specific shape appear to be controlling.

Evaporating side

The principal difference between thin film evaporation and thin film condensation on corrugated, fluted or finned surfaces is that in evaporation liquid must be supplied continuously to the thin film to balance vaporization whereas in condensation the condensate is drawn from the thin film to the rivulet where it drains away. Although it is commonly accepted that surface tension forces play a

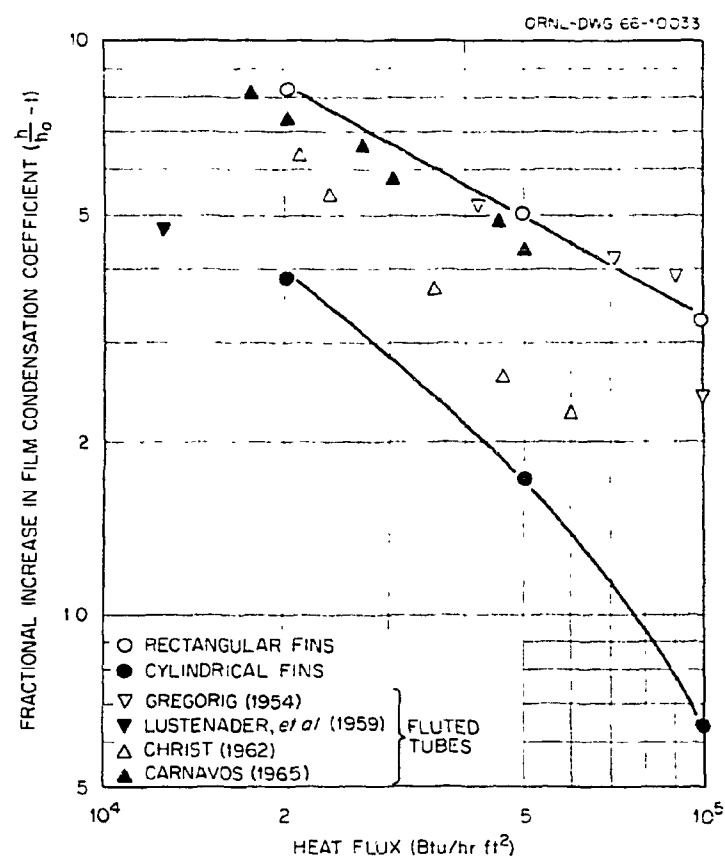


Fig. 4. Comparison of the maximum observed effect of fluted and finned tubes on the film condensation heat-transfer coefficient (after Thomas, 1968).

predominant role in drawing condensate to the rivulet, mechanisms on the evaporative side are not so well understood.

It does seem to be commonly accepted that on the evaporative side as on the condensing side, surface tension forces draw the liquid film into rivulets which flow down the tube either in the grooves on fluted surfaces or along the base of fins on finned surfaces. The principal problem in elucidating the evaporative side mechanism is explaining how the thin film of liquid between rivulets is continuously supplied to maintain high rates of evaporation.

Carnavos (3) and Diedrich and Lotz (2) proposed that nucleate boiling in the rivulet in the grooves kept the crests constantly wetted by splashes from the bubbling accompanying the boiling. However, Alexander and Hoffman (5) were unable to observe nucleate boiling on the evaporative side when the mass flow rate was 1400 lb/hr ft. Instead they observed roll waves moving down the surface of the tube with a wave velocity of ~ 140 cm/sec; the surface velocity of a completely laminar film falling down a smooth tube at the same mass flow rate was calculated to be ~ 160 cm/sec. The maximum frequency of waves was $\sim 16 \text{ sec}^{-1}$ and the amplitude of these waves was ~ 0.05 cm. Between the passage of waves the crests of the fluted tube surface was clearly visible indicating that after passage of a wave which wetted the crest, surface tension forces rapidly drew the liquid film

ing liquid into the grooves permitting high rates of evaporation from the crests. Even when nucleate boiling occurs, exploratory studies (49) indicate that Marangoni flows (surface tension induced flows) around the vapor bubbles may be one of the predominant heat transfer mechanisms.

In studies of evaporation from finned surfaces mass flow rates were ~ 300 lb/hr ft, much smaller than the value of 1400 lb/hr ft used in the fluted tube studies (21, 24). With these small flow rates it seems unlikely that roll waves would form, particularly since the fins had a height of ~ 0.25 cm. Consequently, Thomas and Young (21) postulated that the tube surface was continuously wetted by small waves analogous to those observed to precede dry spot formation at very low flow rates. The phenomenon has been named "roping" by Norman and McIntyre (30) who observed that as the flow rate down a tube was decreased to the order of $(4\Gamma/\mu) \sim 200$, the water film became thicker in several vertical bands spaced around the tubes. Although there was a tendency for dry patches to form between ropes, the patches were quickly covered over as the film became very disturbed.

Johnson *et al.* (8) studied evaporation from fluted surfaces at mass flow rates up to ~ 360 lb/hr ft. Under these circumstances, they postulated that Marangoni instabilities driven by surface tension gradients (which are caused by temperature and concentration gradients in the film between grooves and crests) were responsible for the rapid renewal of the thin film on the crest of the fluted surface. They estimated that surface velocities of ~ 500 cm/sec might accompany the Marangoni instabilities. Forced convection at these large lateral velocities could then account for the large evaporative heat-transfer coefficients observed with fluted tubes.

Benjamin (36) has shown that even in the absence of surface tension gradients a falling liquid film on a vertical wall is unstable at all Reynolds numbers. The

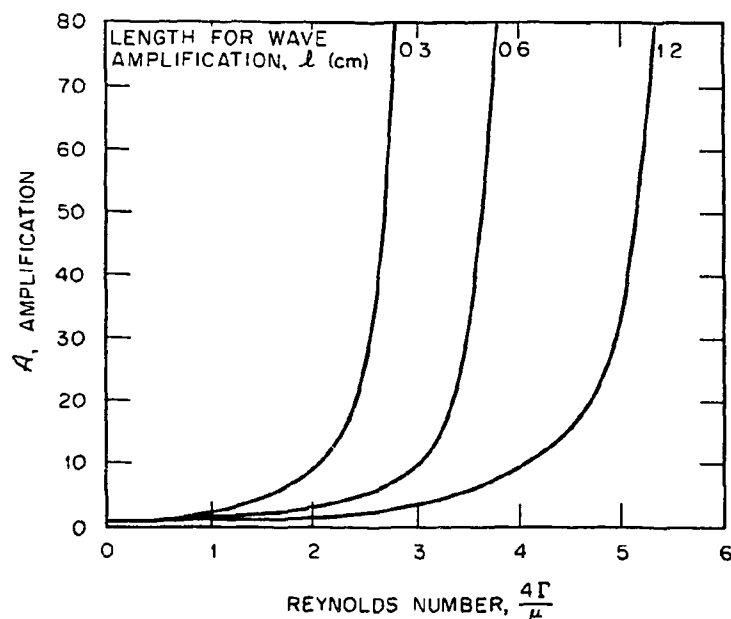


Fig. 5. The amplification experienced in a distance l by the most unstable wave on a vertical water film at saturation (after Benjamin, 1957).

analysis showed that as the Reynolds number becomes very small the rates of amplification also become small and the wave length becomes large. However, since the amplification is an exponential function of the square of the film Reynolds number, amplification becomes very large after a certain Reynolds number is exceeded. This for all practical purposes would appear as a "critical" Reynolds number for wave formation. Fig. 5 is a plot of amplification vs film Reynolds number with the distance for wave amplification as a parameter calculated from Benjamin's analysis for water at $\sim 100^\circ\text{C}$. Clearly amplification becomes very large at film Reynolds numbers greater than ~ 1.5 . Cerro and Whittaker (37) have shown experimentally that waves can be observed on water films at Reynolds numbers as low as 1.5. However, the first waves appeared ~ 1 cm below the top of the film. At a Reynolds number of 1.5 the film velocity is approximately 0.5 cm/sec; this implies an amplification time for waves at this low Reynolds number of ~ 3 seconds. This time seems much too large for the isothermal wave analysis of Benjamin to have any application to the problem at hand especially in view of the fact that Alexander and Hoffman (6) have observed high evaporative heat-transfer rates in the presence of roll waves which inundated the surface up to 16 times per second. This observation implies that the time scale for the thin film phenomena responsible for the high heat-transfer rates must be less than ~ 0.06 seconds.

Brian (38) has pointed out that under circumstances where a falling liquid film might develop Marangoni instabilities, there might be an interaction between the two modes of instability. Brian also suggested that such instabilities might manifest themselves in extremely short times.

With this in mind it would be instructive to attempt to estimate a characteristic time for surface tension induced flows. One such time could be obtained by dividing the length scale for surface tension effects deduced from Eq. (2) by the velocity induced in the thin film by surface tension effects:

$$t_\sigma = \frac{(\sigma/\rho g_L)^{1/2}}{u_\sigma}. \quad (6)$$

The problem is to obtain a value for the surface tension induced velocity. In the model for film condensation enhancement on finned surfaces developed by Thomas (20), this velocity was given by

$$u_\sigma = \frac{\alpha_1 g_c \sigma \delta}{2\mu R}, \quad (7)$$

where α_1 = empirical constant = 4×10^{-2} and

$$\delta = \left(\frac{3}{2\alpha_1} \right)^{1/3} \left(\frac{\pi \Gamma D R v}{g_c \sigma N L} \right). \quad (8)$$

Assuming that $\pi D/N$, (the fin or flute pitch) is given by the characteristic surface tension length, $(\sigma/\rho g_L)^{1/2}$, then Eq. (6) becomes

$$t_{\sigma} = 30 \frac{R^{1/2} L^{1/2}}{g_L^{1/2} (4\Gamma/\mu)^{1/2} (\sigma/\rho g_L)^{1/4}} \quad (9)$$

For $(4\Gamma/\mu) = 200$ (the value of the Reynolds number close to dry spot formation on short tubes according to Norman and McIntyre (32)), $L = 1$ cm (the value at which first waves were observed by Cerro and Whittaker (37)) and assuming that the radius of curvature of the fluid is 0.01 cm, then for water at 212°F, Eq. (9) indicates a characteristic time of ~ 0.01 seconds. This time is sufficiently small to indicate that interactions between two (or more) mechanisms must be involved on the evaporative side of enhanced surfaces.

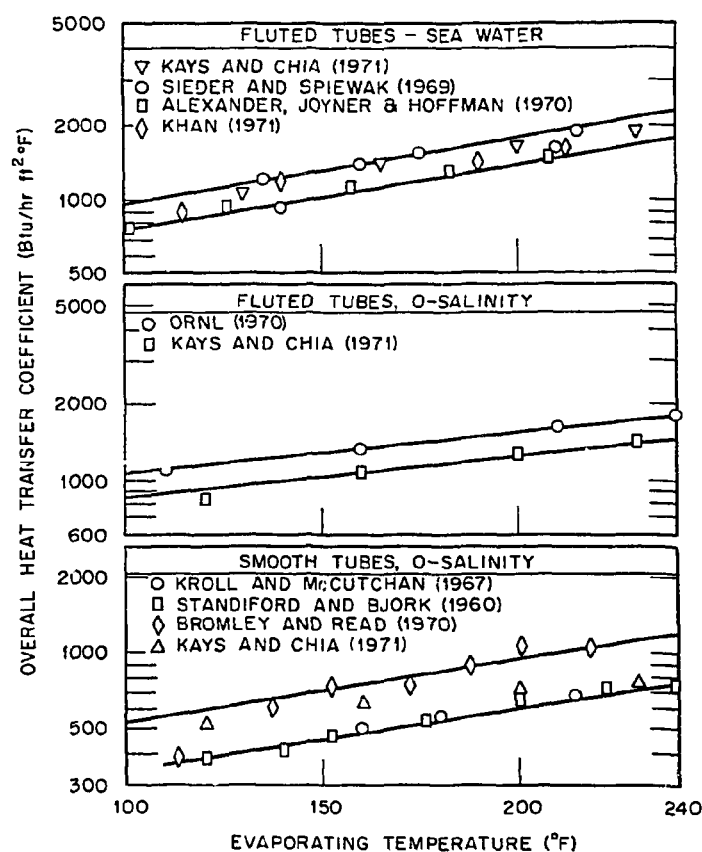


Fig. 6. Temperature dependence of overall heat-transfer coefficient.

Further indication of this is given by examination of the temperature dependence of the overall heat-transfer coefficient in thin film evaporation and condensation, Fig. 6. This figure is a plot of $\log U$ vs. T for smooth tubes with 0-salinity feeds, fluted tubes with 0-salinity feed and fluted tubes with sea water feed. It seems remarkable that, within each set of conditions, the slopes of the lines through results of different investigators are substantially the same. The straight line relation shown on Fig. 6 suggests that a temperature coefficient, B , for the different conditions might be defined by

$$\frac{\Delta U}{U} = C + B T. \quad (10)$$

The results shown on Fig. 6 give for B , (when T is in degrees F):

	$B \times 10^3$
Smooth tube, 0-salinity	5.7
Fluted tube, 0-salinity	3.9
Fluted tube, sea water	5.9
Nusselt parameter, $k(g_L/v^2)^{1/3}$	5.9
(Surface tension) $^{-1}$	1.3

Also included in the above list is the temperature coefficient for the Nusselt parameter for film condensation and that for the reciprocal of the surface tension. The good agreement of the temperature coefficient for the Nusselt parameter and for the smooth tubes indicate that substantially all of the loss in heat-transfer coefficient with smooth tubes as temperature is reduced, may be accounted for by variation of physical properties included in the Nusselt parameter. The markedly smaller value of B observed with fluted tubes and 0-salinity feed indicates that other physical properties are contributing. The low temperature coefficient for the reciprocal of the surface tension appears to be significant here. Finally, when feed to the evaporating side is sea water the temperature coefficient for fluted tubes is substantially greater than for the same type tubes with 0-salinity feed. This may indicate that Marangoni instabilities induced by concentration gradients are playing an additional role.

In all probability the mechanism of enhancement of the evaporative side is quite complicated with one or more of the phenomena described above making important contributions, and with the relative contribution of the mechanisms a function of mass flow rate. It has often been pointed out that in fluid mechanics discovery of a new phenomenon almost always precedes theoretical analysis. Theoretical explanations are often arrived at only after simplifying the equations of motion and boundary conditions to the greatest extent possible consistent with the particular phenomenon being analyzed. As a consequence, development of theoretical expressions which include all of the mechanisms described above (and others as yet unknown) seems to have a small probability of success. Perhaps more fruitful would be a combined experimental-theoretical approach. First, predominant mechanisms and the range of operating conditions for which they are controlling should be identified experimentally. Then simplified analytical models could be developed which are consistent with the physics of the individual processes and which, when appropriately combined, provide an adequate description of the overall process.

FUTURE PROSPECTS

At the present state of commercial development of enhanced surfaces, overall coefficients with clean fluted tubes are ~ 1800 Btu/hr ft² °F, is compared to ~ 650 Btu/hr ft² °F for smooth tubes. Kays (18) has pointed out that, at present,

fabrication costs at least partially cancel the benefits of the higher coefficients offered by fluted tubes. Furthermore, any fouling of high performance surfaces results in a further reduction in benefits. The present state of scale control in sea water evaporators containing conventional tubes has been reviewed recently and will not be discussed further (39, 40).

In the design of distillation plants it is common practice to account for all forms of fouling and introduce a factor of safety by using a fouling factor (18). The value recommended in the standards of the Tubular Exchanger Manufacturers Association is $0.001 \text{ (Btu/hr ft}^2 \text{ }^\circ\text{F)}^{-1}$. If this value is adopted, the design heat-transfer coefficient of fluted tubes is reduced from 1850 to 650 $\text{Btu/hr ft}^2 \text{ }^\circ\text{F}$, almost a 65% reduction. Even if Eissenberg's (29) recommended value of 0.0002 is used, the design coefficient must be decreased to 1350 $\text{Btu/hr ft}^2 \text{ }^\circ\text{F}$, a 25% reduction. Because fouling factors of this magnitude would be controlling if higher performance surfaces were developed, it is essential to examine fouling mechanisms taking into account the special hydrodynamic phenomena that occur on enhanced surfaces. Provided adequate fouling control can be achieved, it would be of some interest to then estimate possible upper limits on enhanced surface performance.

Fouling of enhanced surfaces

Fouling of heat transfer surfaces may occur as a result of oxidation of the metal tubes, by deposition of CaCO_3 , CaSO_4 etc. on the heat transfer surface or by depositions of particulate matter from a variety of sources on the heat transfer surface. In a pioneering paper Kern and Seaton (41) proposed that the rate of fouling layer accumulation, dx_f/dt , should be equal to the difference between the rate of deposition, φ_d , and the rate of removal, φ_r :

$$\frac{dx_f}{dt} = \varphi_d - \varphi_r \quad (11)$$

In general the deposition term will be different depending on whether chemical reaction, precipitation or deposition of solids is involved, while the removal term will depend on a balance between adhesive forces between both the deposit and the metal surface and the deposit and itself as well as on the magnitude of the shear forces in the particular flow situation being considered (41, 42). In general the removal term can be written as

$$\varphi_r = f(\tau_w/R_B), \quad (12)$$

where τ_w is the shear stress in the fluid at the fouled surface and R_B is the bond resistance of the deposit. Taborek *et al.* (42) postulate that the correct value of R_B should be that corresponding to the weakest plane of adhesion, that R_B increases with uniformity of deposit structure and, perhaps most important, that R_B may decrease with deposit thickness due to an increase in the number of planes

of potential weakness. Based on these qualitative arguments Taborek *et al.* (42) postulated that the bond resistance term would be expressed as

$$R_B = \psi(\tau_w)f(x_f), \quad (13)$$

where ψ is a function of the deposit structure which is primarily dependent on the flow velocity and f is a function which reflects the weakening of the deposit structure as its thickness increases.

With enhanced surfaces hydrodynamic conditions will be markedly different in the rivulet which carries the bulk of the fluid down the tube and in the thin film where the bulk of the evaporation and condensation occurs (20, 21, 26). In the following discussion of the effect of enhanced surface hydrodynamics on fouling, it will be assumed that the heat transfer rate in the thin-film region between rivulets is controlling and that modest accumulation of foulants in the rivulet region has negligible effect on the rate of heat transfer. In fact if the character of foulants is such as to initiate nucleate boiling, the net effect of modest fouling in the rivulet region may be to increase the overall heat-transfer coefficient.

Oxidative fouling

In distillation plants using chemical additives to control scale, oxidative fouling is one of the major reasons for decreased plant performance. Although the corrosion resistance of heat transfer surfaces is due to an oxide film, evidence such as color fringes on the metal are clearly indicative that the protective film is less

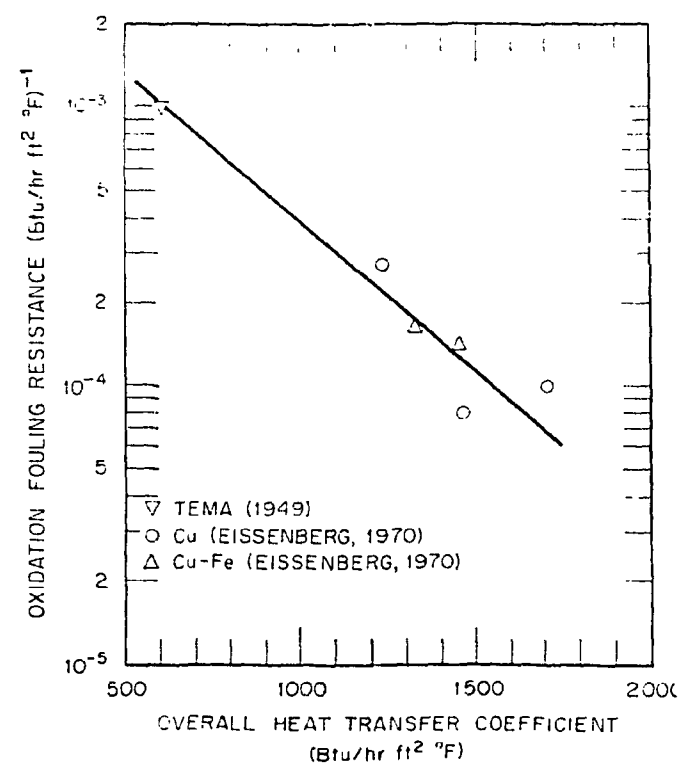


Fig. 7. Oxidative fouling resistance of smooth and fluted tubes.

than a micron thick, *i.e.*, a fouling resistance of less than 10^{-5} (Btu/hr ft² °F)⁻¹. Measurements of fouling resistances of oxidized Cu and Cu-Fe fluted tubes are at least an order of magnitude greater than that required for a protective film (29). Further, as shown in Fig. 7, the limited data indicate that the fouling resistance decreases as the overall heat-transfer coefficient increases; interestingly the fouling resistance recommended by TEMA (43) for smooth tubes is not inconsistent with a decrease in fouling resistance as the overall heat-transfer coefficient increases.

Although the data are limited, the results shown in Fig. 7 may be used to obtain some qualitative information on the nature of the bond resistance term, R_B . When the film thickness reaches its asymptotic value $\varphi_d = \varphi_r$. Assuming the deposition term is mass transfer controlled then the deposition term, φ_d , is proportional to the friction velocity, u_* . If it is further assumed that $\varphi_r \propto \tau_w/R_B$ then

$$\frac{\partial R_B}{\partial x_f} \frac{\partial x_f}{\partial u_*} \propto \frac{(\partial \tau_w / u_*)}{\partial u_*}. \quad (14)$$

Assuming that the overall heat-transfer coefficient, U , is proportional to the friction velocity, u_* , then from Fig. 10

$$\frac{\partial x_f}{\partial u_*} \propto - \frac{x_f}{\tau_w}. \quad (15)$$

After combining Eqs. (14) and (15) and integrating the bond resistance term is found to be

$$R_B \propto - \tau_w \ln \frac{x_f}{x_{f0}} + R_{B0}, \quad (16)$$

where the constant of integration has been taken as the bond resistance of the protective oxide film, R_{B0} , with thickness, x_{f0} .

The question then becomes, are hydrodynamic shear forces ever sufficiently large to approach the value of the bond resistance of the protective oxide film? Hydrodynamic removal of even the protective oxide film from stainless steel has been demonstrated experimentally (44), however, this required extremely large velocities in very thin channels; based on the data presented (44) it is estimated that at 250°C the water velocity required was 110 ft/sec in a channel 0.050×0.50 in. Clearly at the extremely high shear rates in that study, the removal term in Eq. (11) was completely dominant even though the protective oxide film was chemically bonded to the surface. At the other extreme, it has been shown (45) that the velocity required to prevent deposition of small particulates suspended in a turbulent shear flow is given by

$$\frac{u_T}{u_*} = 0.008 \left(\frac{D_p u_*}{\nu} \right)^3. \quad (17)$$

Intermediate between these two cases are experimental measurements (46)

which showed that the adhesive force (90% removal) between 2-micron metal-oxide particles and an oxidized substrate was ~ 0.003 dyne, while the adhesive force for 4-micron particles was ~ 0.006 dyne. This trend with particle diameter is consistent with theoretical predictions (47, 48) of the attractive force experience by small particles; since the theory applies only to perfectly spherical particles, the experimental values may represent practical values for the force required to remove irregular shaped particles from a surface. It should also be noted that with metal-oxides the oxygen atom is the primary potential determining ion (47), hence the above results may be taken as an order of magnitude estimate of adhesive forces for most metal oxides particles in contact with an oxidized substrate.

In order to compare the above data on a common basis, the fluid shear stress was calculated for the three situations assuming, where required, that the characteristic size of the particle was 1000 Å. The results are given in Table I.

TABLE I

ESTIMATED FORCES REQUIRED FOR PREVENTION OR REMOVAL OF DEPOSITS

	Friction velocity, (u_*), ft/sec	Wall shear stress, (τ_w)	
		lb _f /ft ²	dyne/cm ²
Prevention of deposition of suspended solids (45)	0.33	0.2	100
Removal of solids deposited on surface (46)	0.64	0.8	400
Removal of protective oxide film (44)	4.2	34	17000

Some perspective on the values given in Table I is afforded by results reported by Zuckerman (51) on fouling tests at Eilat where it was found that a friction velocity of ~ 0.3 ft/sec washed away oxide fouling deposits. Thus, although the above results are somewhat speculative they may represent order of magnitude results against which may be compared values of friction velocity developed in thin films on falling film heat transfer surfaces.

For boundary layer flows the heat-transfer coefficient is related to the friction velocity by (50)

$$u_*^2 = \frac{g_c \tau_w}{\rho} = \frac{u_w}{\rho c_p} h. \quad (18)$$

Assuming an average value of 0.005 for the friction factor then

$$u_* = \frac{20}{\rho c_p} h \quad (18a)$$

and for $h = 1000$ and $18,000$ Btu/hr ft² °F the friction velocity is 0.09 and 1.7

ft/sec, respectively. The smaller of these two friction velocities represents an order of magnitude estimate of the friction velocity for thin films on smooth, vertical heat transfer surfaces.

An estimate of the friction velocity on enhanced surfaces can be obtained from a material balance on unit length of surface between adjacent flutes or fins:

$$u \delta = \frac{(q/A) p y}{3600 h_{fg} \rho}. \quad (19)$$

Assuming that the friction velocity is related to the average velocity in the film by

$$u_*^2 = \frac{g_c \tau_w}{\rho} = \frac{3 \nu u}{\delta}, \quad (20)$$

and that the film thickness, δ , is given by the thermal conductivity of the water film, k , divided by the heat-transfer coefficient, h , then

$$u_* = \left(\frac{32 p y}{3600 k^2 \rho h_{fg}} \right)^{1/2} \left(\frac{q}{A} \right)^{1/2} h. \quad (21)$$

The value of y , the fraction of the surface covered by the thin film which experiences high shear forces, may be estimated from

$$\frac{1}{U} = \frac{1}{y} \left(\frac{1}{h_c} + \frac{1}{h_e} \right) + \frac{1}{k/x}, \quad (22)$$

which assumes that there is negligible heat transfer in the rivulet region and that the film heat-transfer coefficients are the maximum value for the thin-film region between rivulets. As will be shown in the following section these maximum values are 18,000 and 14,000 Btu/hr ft² °F for the condensing and evaporating sides, respectively. Values of y calculated from Eq. (22) for three enhanced surfaces are given in Table II. Also shown in Table II are the fraction of the surface covered by

TABLE II

ESTIMATED FRACTION OF SURFACE COVERED BY THIN EVAPORATING AND CONDENSING FILMS

Surface	Overall heat transfer coeff., Btu/hr ft ² °F	Fraction of surface covered by	
		Rivulet + Fin	Thin film
Fluted (7)	1850	Unknown	0.24
Corrugated (22, 23)	3500	0.50	0.48
Double Fin (24)	4500	0.32	0.63

the rivulet + fin for two of the three surfaces. For the corrugated surface this latter estimate is relatively accurate since it is based on surface geometry alone (see Fig. 2C). For the double fin surface the dimension of the rivulet, R , was calculated from

$$R = 1.6 \left[\frac{v \Gamma D}{g_L \rho N} \right]^{1/4} \quad (23)$$

as suggested in an earlier publication (20). The fact that 95 to 98 % of the surface is accounted for by this simple model for 2 out of 3 surfaces lends credence to its use with fluted tubes.

With the value for “ y ” given in Table II, the friction velocity for fluted tubes calculated from Eq. (21) is 2.1 ft/sec. Comparing the estimates of friction velocity for smooth and fluted tubes (~ 0.1 and 2 ft/sec, respectively) with the estimates for forces required to remove deposits from surfaces given in Table I, makes it reasonable to assume that the trend shown in Fig. 8 is real and that the oxidative fouling potential of enhanced surfaces is decreased as the overall heat-transfer coefficient is increased. Confirmation of this hypothesis of course awaits further experimental studies.

Fouling by deposition of scale

At present control of scaling by inverse solubility salts is avoided by either pH control or by limiting temperature and brine concentration (40). As a result there are few results available from large scale studies on fouling factors for either smooth or enhanced surfaces. More fundamental studies indicate that among factors which influence the rate of scale nucleation are the Reynolds number of the flow (52, 53), the nature and roughness of the surface (52), the heat flux (52), the contact time (54), and the extent of supersaturation at the heat-transfer surface (52). Of these factors the most important was the extent of supersaturation at the heat-transfer surface with the rate of deposition being proportional to the 6 to 10th power of the supersaturation. According to Bradley (54) the relation between supersaturation and nucleated particle radius is

$$(1 + \alpha + n\alpha) RT \log (S/S_\infty) = M\lambda/\rho D_c. \quad (24)$$

The interfacial free energy, λ , for $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ has been measured (55) as 370 ergs/sq cm; for supersaturations of 1.05 and 1.1, typical of those found in saline water films at moderate temperature differences, the nucleus diameters calculated from Eq. (24) were 0.47 and 0.24 microns, respectively. If these particles nucleate in the solution near the surface, then from Eq. (17), the friction velocities required to prevent deposition is 0.22 and 0.26 ft/sec, respectively. Of course if the particles nucleate on the surface then larger friction velocities would be required to remove the deposit as indicated in Table I. Further, Flint and Elliot (56) observed an oxide layer between the scale and the metal which was believed to both aid nucleation and increase the bond strength between the scale and the substrate.

To summarize: if, as hypothesized in the section on oxidative fouling, the high heat-transfer coefficients of enhanced surfaces are accompanied by friction velocities in the fluid film which are significantly greater than the friction velocities

on smooth tubes, then fouling factors for both oxidative fouling and for scale formation may be significantly smaller for enhanced surfaces than for smooth tubes. In other words, the tangential shear stress developed in the thin film on enhanced surfaces may be sufficiently large that thick fouling layers are prevented from forming resulting in relatively small fouling factors for these surfaces.

Upper limits on enhanced surface performance

Since existing theory seems unlikely to provide guidance to the upper limit on the rate of heat transfer with enhanced surfaces, resort must be made to experiment. On the condensing side film coefficients as large as 18,000 Btu/hr ft² °F have been observed with both fluted and finned surfaces (3, 20). This value will be adopted as a reasonable upper limit for performance of enhanced surfaces in film condensation.

Observed performance on the evaporating side is not in such good agreement. Carnavos (3) reported a maximum value of 7000 Btu/hr ft² °F in the early studies of fluted surfaces. Subsequently, Thomas and Young (21) obtained values as large as 10,000 Btu/hr ft² °F with finned surfaces and Johnson *et al.* (8) reported a maximum value of 12,600 Btu/hr ft² °F with a finely corrugated surface. Because of the complex mechanisms that may be involved on the evaporating side, it is not clear that these values represent an acceptable upper limit.

A clue to the magnitude of the upper limit may be obtained from the observation that unexpectedly large evaporative film coefficients occurred on very short smooth tube surfaces when the flow rate was reduced to values approaching that for which dry spot formation occurs (32). Norman and McIntyre's (32) results, obtained with tubes 8.2 and 23 cm long, are shown on Fig. 8 as $h/(kg_L^{1/3}/v^{2/3})$ vs. $4\Gamma/\mu$, coordinates suggested by Nusselt's analysis of film condensation.

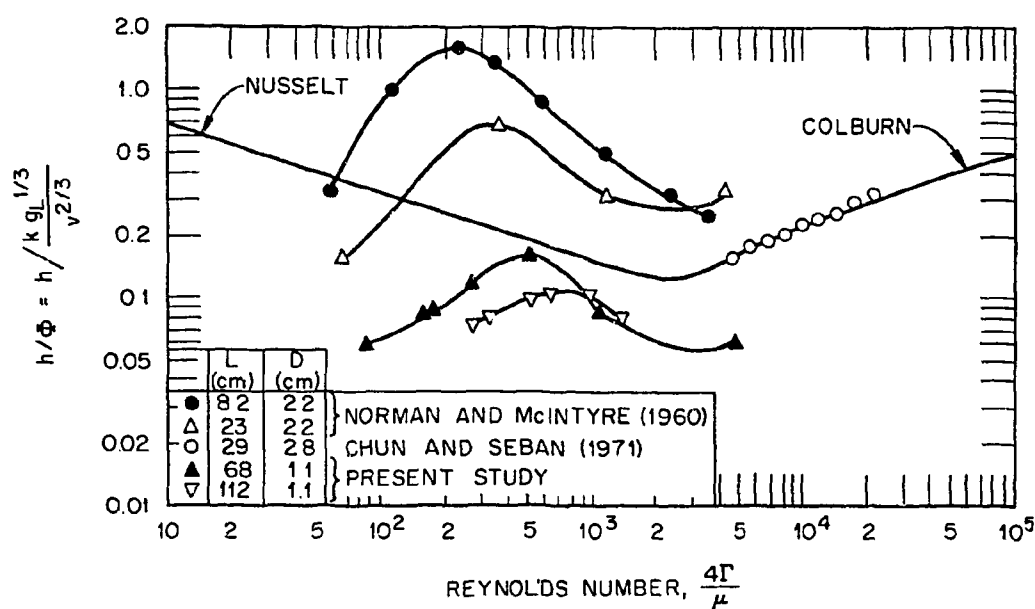


Fig. 8. Heat-transfer coefficient for thin evaporating films on vertical surfaces.

Also shown are new results for low flow rates with tubes of 68 and 112 cm length. Several aspects of these results are notable. All of the low flow rate results indicate a maximum in the evaporative film coefficient in the Reynolds number range 200 to 800. There is an orderly increase in the maximum heat-transfer coefficient as tube length is decreased and for the shortest tube the heat-transfer coefficient is over six times greater than the value expected for convection through a laminar film (*i.e.*, the result from Nusselt's analysis). This is indeed a remarkably large increase. In a review of turbulence promoter performance, it was shown that when the heat-transfer coefficient in single phase forced convection is increased a factor of 5 at constant Reynolds number by use of turbulence promoters there is an accompanying 100-fold increase in pressure drop (59). Secondary flows are also known to increase the rate of heat transfer. Fig. 9 shows the increase in the rate of heat transfer which is experimentally observed in thermal convection (58) and in flow between rotating cylinders (59). Results of both types of experiment were congruent up to a Raleigh-Taylor number of 10^5 , the upper limit of the rotating cylinder experiments. This indicates that the primary flow in the rotating flow case had little effect on the rate of heat transfer and that the secondary flow was controlling. It is of interest to note that a 6-fold increase in the rate of heat transfer occurred at a Raleigh-Taylor number of $\sim 3 \times 10^5$, one hundred times the threshold value and well above the break in the curve at $\sim 4 \times 10^4$ above which turbulence is often claimed to occur (58). In other words, extremely vigorous secondary flow type agitation is required to affect a 6-fold increase in the rate of heat transfer, and a superposed steady primary flow makes little contribution to the rate of heat transfer until fully developed turbulence occurs.

The maximum values of the heat-transfer coefficient from Fig. 8 are plotted

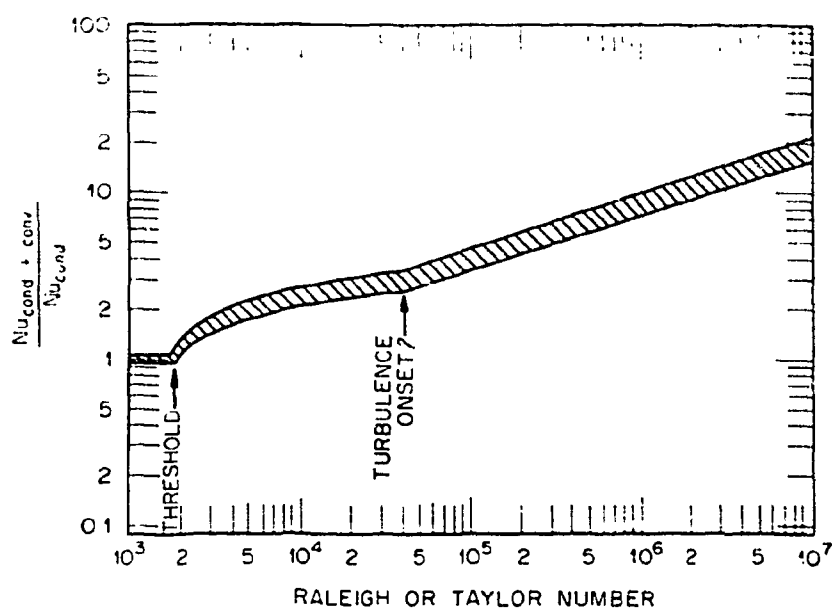


Fig. 9. Increased heat-transfer rates caused by secondary flow in thermal convection and in flow between rotating cylinders.

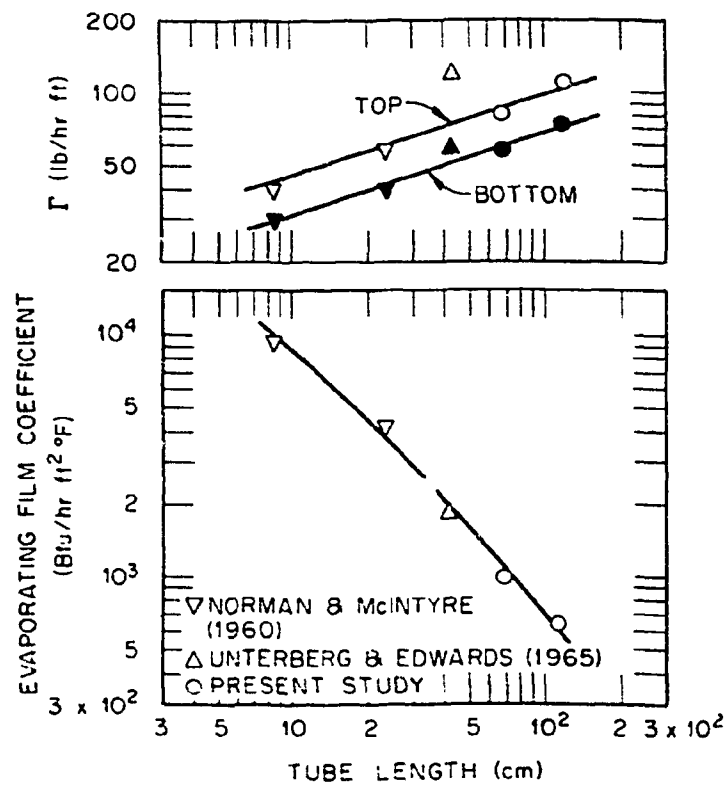


Fig. 10. Maximum evaporative film heat-transfer coefficient observable at low flow rates on smooth vertical tubes.

in Fig. 10 as h_{evap} vs. tube length; also shown are mass flow rates at the top and bottom of the tubes. It is clear that for short tubes and low mass flow rates there is a marked increase in evaporative heat-transfer coefficient as tube length is decreased and that as tube length is increased the mass flow rate must be increased to attain the maximum heat-transfer coefficient.

It seems likely that the vigorous (and as yet unexplained) agitation in thin films observed by Norman and McIntyre (32) is the principal reason for the unexpectedly large heat-transfer coefficients. Further, as tube length is increased feed rate to the tube must be increased to prevent dry spot formation and this increased feed rate must have a disproportionate effect on damping the agitation in the thin films.

Be that as it may, the results shown in Fig. 10 may be used to estimate the upper limit for evaporative film coefficients. To establish this upper limit it will be assumed that maximum evaporative heat transfer occurs when the water film thickness is just sufficient to prevent dry spot formation and that maximum film agitation occurs under these circumstances as suggested by Norman and McIntyre (32). Since available experimental results (Fig. 10) indicate that there is an optimum (low) flow rate for maximum evaporative heat-transfer coefficient with a given tube length and further that the value of the maximum heat-transfer coefficient increases as tube length decreases, the heat-transfer coefficient for zero tube length was obtained by extrapolation on a plot of $\log(1/h)$ vs. tube length. The value obtained

was 14,200 Btu/hr ft² °F at a feed rate of 30 lb/hr ft. Combining this value with the upper limit for film condensation given above (18,000 Btu/hr ft² °F) and assuming a metal wall resistance of 0.00004 gives an estimated upper limit for the overall heat-transfer coefficient of ~6000 Btu/hr ft² °F. This estimate is based on the assumption that a rivulet guide can be designed which occupies a negligible amount of surface. This coefficient is about 1.5 times the value obtained with corrugated tubes (22, 23) and only about 1.2 times the value obtained with doubly finned tubes (24) at heat fluxes of ~10⁴ Btu/hr ft².

CONCLUSIONS

The mechanism responsible for high performance on the condensing side of fluted or finned tubes seems relatively well understood, at least qualitatively. The mechanism on the evaporating side is apparently much more complicated and not at all well understood.

Estimates of the upper limits on film coefficients on the condensing side and on the evaporative side indicate that an upper limit on the overall coefficient for enhanced surfaces, as they presently are conceived, might be as large as 6000 Btu/hr ft² °F compared to a value of ~2000 Btu/hr ft² °F which represents the present state-of-the-art.

Limited data on oxidative fouling indicate that the fouling factors of enhanced heat transfer surfaces may be appreciably smaller than the values recommended by TEMA for smooth tubes. The data also suggest that the fouling factors may decrease as the enhanced surface heat-transfer coefficient increases. It is hypothesized that shear forces developed in the thin-film region are proportional to the magnitude of the heat-transfer coefficient and that these shear forces are sufficiently large that thick fouling layers are prevented from forming. Order of magnitude estimates of the fluid shear forces and bond resistances indicate qualitative support for the hypothesis. It seems worth noting that Kays (18) has suggested that rather than using a fixed numerical fouling factor "it may be more appropriate to specify that the design coefficient shall be reduced from the clean value by a fixed percentage, say 20 to 25 %." This is of course qualitatively consistent with the present hypothesis.

In the absence of a rigorous theoretical treatment, attempts to predict upper bounds on performance must be of a speculative nature. Nevertheless, the present review of presently available theory and data appear to indicate that significant improvements in enhanced heat-transfer surface performance may be possible and that the same factors which are responsible for high heat-transfer coefficients may also maintain fouling at acceptably low values. If these hypotheses prove true, then significant reductions in desalted water cost would result.

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