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Evaluation of Military Field-Water Quality

Volume 7. Performance Evaluation of the 600-GPH Reverse Osmosis Water Purification Unit (ROWPU): Reverse Osmosis (RO) Components

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February 1986

Lawrence Livermore National Laboratory

Supported by
U.S. Army Medical Research and Development Command
Fort Detrick, Frederick, MD 21701-5012
Project Order 82PP2817
Project Officer: Dr. Stephen A. Schaub

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Project Officer: S. A. Schaub

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UNCLASSIFIED
SECURITY CLASSIFICATION OF THIS PAGE

REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1a. REPORT SECURITY CLASSIFICATION
UNCLASSIFIED

1b. RESTRICTIVE MARKINGS

2a. SECURITY CLASSIFICATION AUTHORITY

2b. DECLASSIFICATION/DOWNGRADING SCHEDULE
-----

3. DISTRIBUTION/AVAILABILITY OF REPORT
Approved for public release;
distribution unlimited

4. PERFORMING ORGANIZATION REPORT NUMBER(S)
UCRL-21008 Vol. 7

5. MONITORING ORGANIZATION REPORT NUMBER(S)

6a. NAME OF PERFORMING ORGANIZATION
Lawrence Livermore National
Laboratory

6b. OFFICE SYMBOL *(If applicable)*

7a. NAME OF MONITORING ORGANIZATION
U.S. Army Biomedical Research and
Development Laboratory

6c. ADDRESS *(City, State, and ZIP Code)*
Environmental Sciences Division
P.O. Box 5507 (L-453)
Livermore, CA 94550-0617

7b. ADDRESS *(City, State, and ZIP Code)*
ATTN: SGRD-UBZ-C
Fort Detrick (Bldg. 568)
Frederick, MD 21701-5010

8a. NAME OF FUNDING/SPONSORING ORGANIZATION U.S. Army Medical
Research and Development Command

8b. OFFICE SYMBOL *(If applicable)*

9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER
Army Project Order 82PP2817

8c. ADDRESS *(City, State, and ZIP Code)*
Fort Detrick
Frederick, MD 21701-5012

10. SOURCE OF FUNDING NUMBERS

PROGRAM ELEMENT NO.	PROJECT NO.	TASK NO.	WORK UNIT ACCESSION NO.
62787A	3M1-62787A875	AG	DA300881

11. TITLE *(Include Security Classification)*
Evaluation of Military Field-Water Quality. Volume 7. Performance Evaluation of the 600-GPH Reverse Osmosis Water Purification Unit (ROWPU): Reverse Osmosis (RO) Components

12. PERSONAL AUTHOR(S)
B.J. Mariñas, Z. Ungun, R.E. Selleck

13a. TYPE OF REPORT
Final

13b. TIME COVERED
FROM 11-82 TO 2-86

14. DATE OF REPORT *(Year, Month, Day)*
February 1986

15. PAGE COUNT
227

16. SUPPLEMENTARY NOTATION

17. COSATI CODES

FIELD	GROUP	SUB-GROUP
24	07	
06	11	

18. SUBJECT TERMS *(Continue on reverse if necessary and identify by block number)*
Reverse Osmosis, 600-gph ROWPU, Hyperfiltration,
Field Operation, Evaluation, Field-water-quality Standards

19. ABSTRACT *(Continue on reverse if necessary and identify by block number)*

The primary purpose of this work is to ascertain whether the performance of the current 600-gph reverse osmosis water-purification unit (ROWPU) is adequate to meet the water-quality standards recommended in Volume 4 of this study. A secondary objective is to review the design of the treatment units used in the ROWPU, as well as the prescribed mode of operation, and to make constructive recommendations.

Reverse osmosis (hyperfiltration) is a complicated water-treatment process that is not described easily with a few process parameters. Furthermore, published literature on the type of membrane currently used in the ROWPU was scarce. Therefore, we required a mathematical model that could be used to extrapolate existing information to different operating conditions. It was successful for seawater and single-salt solutions, but it proved to be unsuccessful for just any mix of salts that might be encountered in nature.

20. DISTRIBUTION/AVAILABILITY OF ABSTRACT
☐ UNCLASSIFIED/UNLIMITED ☒ SAME AS RPT ☐ DTIC USERS

21. ABSTRACT SECURITY CLASSIFICATION
UNCLASSIFIED

22a. NAME OF RESPONSIBLE INDIVIDUAL
Mary Frances Bostian

22b. TELEPHONE *(Include Area Code)*
301-663-7325

22c. OFFICE SYMBOL
SGRD-RMI-S

DD Form 1473, JUN 86 *Previous editions are obsolete.*

SECURITY CLASSIFICATION OF THIS PAGE
UNCLASSIFIED

This report is the seventh volume of a nine-volume study entitled Evaluation of Military Field-Water Quality. Titles of the other volumes are as follows: Vol. 1, Executive Summary; Vol. 2, Constituents of Military Concern from Natural and Anthropogenic Sources; Vol. 3, Opportunity Poisons; Vol. 4, Health Criteria and Recommendations for Standards; Vol. 5, Infectious Organisms of Military Concern Associated with Consumption: Assessment of Health Risks, and Recommendations for Establishing Related Standards; Vol. 6, Infectious Organisms of Military Concern Associated with Nonconsumptive Exposure: Assessment of Health Risks, and Recommendations for Establishing Related Standards; Vol. 8, Performance of Mobile Water Purification Unit (MWPU) and Pretreatment Components of the 600-GPH Reverse Osmosis Water Purification Unit (ROWPU) and Consideration of Reverse Osmosis (RO) Bypass, Potable-Water Disinfection, and Water-Quality Analysis Techniques; and Vol. 9, Data for Assessing Health Risks in Potential Theaters of Operation for U.S. Military Forces.

FOREWORD

This report is the seventh volume of a nine-volume study entitled Evaluation of Military Field-Water Quality. Titles of the other volumes are as follows: Vol. 1, Executive Summary; Vol. 2, Constituents of Military Concern from Natural and Anthropogenic Sources; Vol. 3, Opportunity Poisons; Vol. 4, Health Criteria and Recommendations for Standards; Vol. 5, Infectious Organisms of Military Concern Associated with Consumption: Assessment of Health Risks, and Recommendations for Establishing Related Standards; Vol. 6, Infectious Organisms of Military Concern Associated with Nonconsumptive Exposure: Assessment of Health Risks, and Recommendations for Establishing Related Standards; Vol. 8, Performance of Mobile Water Purification Unit (MWPU) and Pretreatment Components of the 600-GPH Reverse Osmosis Water Purification Unit (ROWPU) and Consideration of Reverse Osmosis (RO) Bypass, Potable-Water Disinfection, and Water-Quality Analysis Techniques; and Vol. 9, Data for Assessing Health Risks in Potential Theaters of Operation for U.S. Military Forces.

The nine volumes of this study contain a comprehensive assessment of the chemical, radiological, and biological constituents of field-water supplies that could pose health risks to military personnel as well as a detailed evaluation of the field-water-treatment capability of the U.S. Armed Forces. The scientific expertise for performing the analyses in this study came from the University of California Lawrence Livermore National Laboratory (LLNL) in Livermore, CA; the University of California campuses located in Berkeley (UCB) and Davis (UCD), CA; the University of Illinois campus in Champaign-Urbana, IL; and the consulting firms of IWG Corporation in San Diego, CA, and V.J. Ciccone & Associates (VJCA), Inc., in Woodbridge, VA. Additionally a Department of Defense (DoD) Multiservice Steering Group (MSG), consisting of both military and civilian representatives from the Armed Forces of the United States (Army, Navy, Air Force, and Marines), as well as representatives from the U.S. Department of Defense, and the U.S. Environmental Protection Agency provided guidance, and critical reviews to the researchers. The reports addressing chemical, radiological, and biological constituents of field-water supplies were also reviewed by scientists at Oak Ridge National Laboratory in Oak Ridge, TN, at the request of the U.S. Army. Furthermore, personnel at several research laboratories, military installations, and agencies of the U.S. Army and the other Armed Forces provided technical assistance and information to the researchers on topics related to field water and the U.S. military community.

ACKNOWLEDGMENTS

The authors extend their appreciation to the scientists and staff of the Environmental Sciences Division at the Lawrence Livermore National Laboratory, as well as to Dr. Stephen A. Schaub and his colleagues at the U.S. Army Biomedical Research and Development Laboratory (USABRDL), for their cooperation and assistance. A special thank you is extended to the scientists and staff of the Sanitary Engineering and Environmental Health Research Laboratory at the University of California, Richmond Field Station, and at the University of California, Berkeley, for their efforts in preparing this document. The authors also express their gratitude to those individuals and organizations in the reverse osmosis industry who provided information about reverse osmosis technology that was intrinsic to our research.

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PRINCIPAL SYMBOLS AND ABBREVIATIONS

A	Membrane parameter, length/(time-pressure)
B	Solute transport parameter, length/time
c	Concentration, mass or moles/volume of solution
D	Molecular diffusivity, $(\text{length})^2$/time
d_p	Particle diameter, length
d_t	Tube diameter, length
h	Brine water carrier height, length
J	Mass flux, mass/(area-time)
k	Mass-transfer coefficient, length/time
K_t	Temperature coefficient, K
ℓ	Channel length, length
m	Solution molality, g-moles/kg of solvent
$\underset{\sim}{M}$	Solution molarity, g-moles/L of solution
n	Water flux compaction factor, dimensionless
p	Pressure, force/area
PR	Product-water recovery (see Eq. 10)
Q	Volumetric flow, $(\text{length})^3$/time
R	Ideal gas constant
SP	Solute passage (see Eq. 12)
SR	Solute rejection (see Eq. 11)
t	Time
T	Temperature
U	Product-water approach velocity, length/time
U_b	Brine-water approach velocity, length/time
w	Concentration, mass fraction

Greek letters

δ	Fixed film thickness, length
ν	Kinematic viscosity, $(\text{length})^2$/time
π	Osmotic pressure, force/area
ρ	Density, mass/$(\text{length})^3$
ϕ	Osmotic coefficient, dimensionless
α	Temperature coefficient, dimensionless
γ	Slope of curves in Fig. 24 and Eq. 34

Subscripts

b	Brine
f	Feed
p	Product (downstream side of membrane)
s	Solution or salt
w	At the membrane surface wall (upstream side of membrane)
o	Condition at time 0 (see Eq. 34)

Superscripts

'	Molar or mass quantity
1	Refers to any salt other than NaCl (see Eqs. 22 and 23)

Common unit abbreviations

gpd	gal/d
gph	gal/h
gpm	gal/min
kW	kilowatt
psi	lb/in^2
psid	lb/in^2 with respect to drop in pressure
psig	lb/in^2 with respect to atmospheric pressure
cpm	concentration polarization modulus
NTU	nephelometric turbidity units
TDS	total dissolved solids

The dimensions in this report are those used by authors of various publications referenced herein. The dimensions commonly used were English, and no attempt generally was made to convert them to SI metric. Some of the conversion factors are presented on the following page.

PRINCIPAL DIMENSIONAL CONVERSIONS

To convert from	to	Multiply by
psi	kPa	6.895
atm	kPa	101.3
gpd	m^3/s	4.381×10^{-8}
$gal/(d \cdot ft^2)$	m/s	4.716×10^{-7}
ft/d	m/s	3.528×10^{-6}
$gal/(d \cdot ft^2 \cdot atm)$	$m/(s \cdot kPa)$	4.773×10^{-5}
cm^2/s	m^2/s	1.000×10^{-4}
		Solve
degree Celsius (°C)	Kelvin (K)	$T_K = T_C + 273.15$
degree Fahrenheit (°F)	degree Celsius (°C)	$T_C = (T_F - 32)/1.8$

EVALUATION OF MILITARY FIELD-WATER QUALITY

Volume 7. Performance Evaluation of the 600-GPH Reverse Osmosis Water Purification Unit (ROWPU): Reverse Osmosis (RO) Components

PREFACE

This work is Volume 7 of the series, Evaluation of Military Field-Water Quality, and it is concerned primarily with the reverse osmosis (RO) components of the ROWPU that were available in 1986. Appendix A contains tables concerning osmotic coefficients and chemical removals with RO membranes composed of cellulose acetate. Appendix B provides descriptions of the CALIBRATOR and PREDICTOR models. Appendix C contains background information that we did not use directly in the RO modeling. Volume 8 of the series is concerned with pretreatment, RO bypass, and other considerations related to field-water treatment. Together, these two volumes represent an assessment of the treatment, disinfection, and water-quality analysis procedures now used by U.S. military forces.

ABSTRACT

The primary purpose of this work is to ascertain whether the performance of the current 600-gph reverse osmosis water-purification unit (ROWPU) is adequate to meet the water-quality standards recommended in Volume 4 of this study. A secondary objective is to review the design of the treatment units used in the ROWPU, as well as the prescribed mode of operation, and to make constructive recommendations.

Reverse osmosis (hyperfiltration is a complicated water-treatment process that is not described easily with a few process parameters. Furthermore, published literature on the type of membrane currently used in the ROWPU was scarce. Therefore, we required a mathematical model that could be used to extrapolate existing information to different operating conditions. It was successful for seawater and single-salt solutions, but it proved to be unsuccessful for just any mix of salts that might be encountered in nature.

BACKGROUND AND DESCRIPTION OF THE 600-GPH ROWPU

Development of the U.S. Armed Forces' current water-supply and purification unit, the 600-gph Reverse Osmosis Water Purification Unit (ROWPU), dates back to the 1960's when dissatisfaction was expressed with the ERDLATOR, a water-purification device that could be used to treat fresh water only. The U.S. Army then acknowledged the need for a more "universal" water-purification device. The period also coincides with the development of reverse osmosis and ultrafiltration technology.[1]

Work on the membranes to make reverse osmosis (RO) desalination feasible was first performed by Reid at the University of Florida in the mid-1950's and later by Dow Chemical Co.[2,3] However, none of the membranes developed at that time was commercially successful because of low water flux. In the late 1950's, Loeb and Sourirajan discovered a way to make an effectively thin cellulose-acetate membrane with much greater water flux and compatible salt rejection.[2,3] It consisted of a thin salt-rejecting cellulose-acetate (CA) barrier supported by a finely porous substrate. After this breakthrough by Loeb and Sourirajan, RO became an economical desalination technique.

In the years following the introduction of the Loeb-Sourirajan membranes, membrane research was expedited with the objectives of (1) describing the salt- and water-flux relationships through membranes, (2) measuring the equilibrium and transport properties of the membranes, and (3) searching for materials superior to cellulose acetate. These investigations led to the development of a new class of reverse osmosis membrane materials--"thin-film composite" membranes.

According to Cadotte and Petersen,[4] it was P. S. Francis, at the North Star Research and Development Institute, who first sought an alternative to the Loeb-Sourirajan membrane. The approach was to fabricate the dense barrier layer and the porous substructure of the membrane separately and then laminate them together. Each of these layers could then be optimized individually for maximum performance.

The first thin-film composite membranes were made of cellulose acetate. Low water flux and compaction under sustained high pressure were the main problems.[4] In 1966, Cadotte used polysulfone in the substructure. Polysulfone increased the resistance to compaction so that fluxes could be increased to 10 to 15 gal/(d • ft^2).[1] Later, in 1970, Cadotte developed an RO membrane that contained an ultrathin aryl-alkyl polyurea formed in situ on a microporous polysulfone support. This development represents the first noncellulosic membrane; most thin-film composite membranes since that time have been noncellulosic.[4]

These developments in membrane technology led the U.S. Army to consider RO as a feasible alternative. Consequently, in the early 1970's, the U.S. Army began sharing information with the U.S. Department of the Interior (Office of Water Research and Technology or OWRT, formerly the Office of Saline Water), the prime supporter of RO research and development prior to the 1970's.

The Army's principal investigators were Richard P. Schmitt, Allen Ford, Jr., Vincent J. Ciccone, Robert P. Carnahan, and Don C. Lindsten; later, Gerald R. Eskelund became involved.[1] The first prototype RO unit investigated had a target product flow of 360 gph. The pretreatment process consisted of chlorine and cationic polymer addition, followed by a coal-sand-gravel multimedia filtration. The commercial UOP-ROGA-4100 (4-in. diam., 33-in. long) spiral-wound module (Universal Oil Products, Inc., San Diego, CA) with cellulose-acetate (CA) membrane was used in the prototype RO unit. Two of these elements were placed in series in a single pressure vessel. Six such pressure vessels were then arranged in a 3-2-1 step-down series designed to give a 60% product-water recovery with fresh water. Each ROGA element had an effective membrane area of 65 ft^2, yielding a total membrane area of 780 ft^2.

Over the years following its introduction, numerous modifications have been made to the ROWPU. The modifications included changes in the membrane material, module size, and pretreatment system. After being tested extensively, the resulting 600-gph ROWPU unit now in service has been used frequently. Currently, a much larger 3000-gph unit is being developed. Studies are also under way to increase the capacity of the 600-gph unit.

The mobile 600-gph ROWPU was designed to operate for two 10-h periods a day with interruption only to refuel, backwash filters, and perform routine maintenance and operational checks.[5] The product-water flow rate was to be 600 gph when treating fresh water (less than 500 ppm total dissolved solids [TDS] at 77°F), and 400 gph when treating seawater (approximately 35,000 ppm TDS at 77°F). The actual potable-water production from seawater is greater than this because of optimal component configuration.[5]

The ROWPU consists of (1) a 30-kW generator power source (only 22 kW is required), (2) a pretreatment system, and (3) an RO system and a post-treatment system.[6] These parts are contained in a flatbed cargo trailer (see Fig. 1) with an overall weight of 8-1/2 tons, a length of 230 in., a width of 96 in., and a height of 97 in. These specifications allow for ROWPU transportation by train, road, or air. The system is also designed to withstand a deceleration of 24 g for parachute delivery.

A diagram of a typical field installation of the ROWPU is shown in Fig. 2, and a schematic illustration of the equipment mounted on the trailer is presented in Fig. 3.

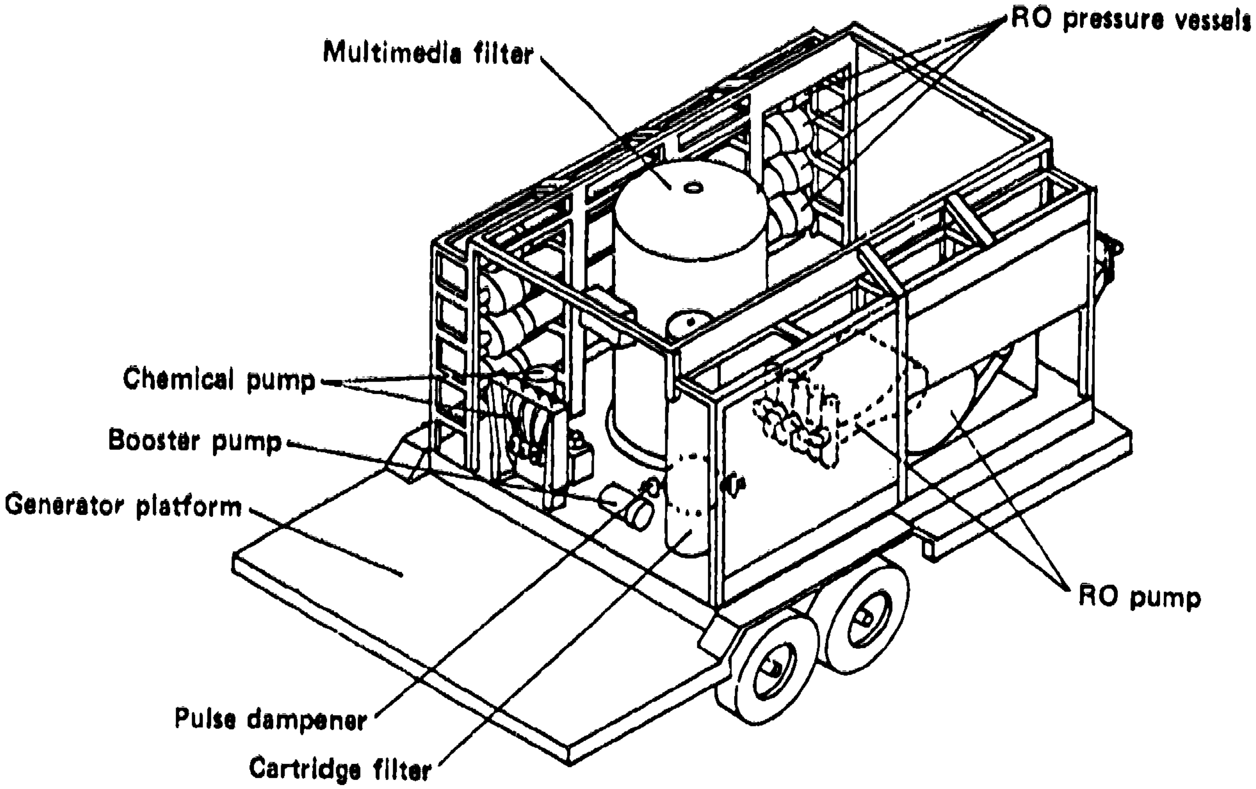


Figure 1. Rear view of 600-gph ROWPU (generator removed) and transport trailer used by U.S. Army. Reprinted from U.S. Army Training Manual, TM 5-4610-215-10, 1982.[6]

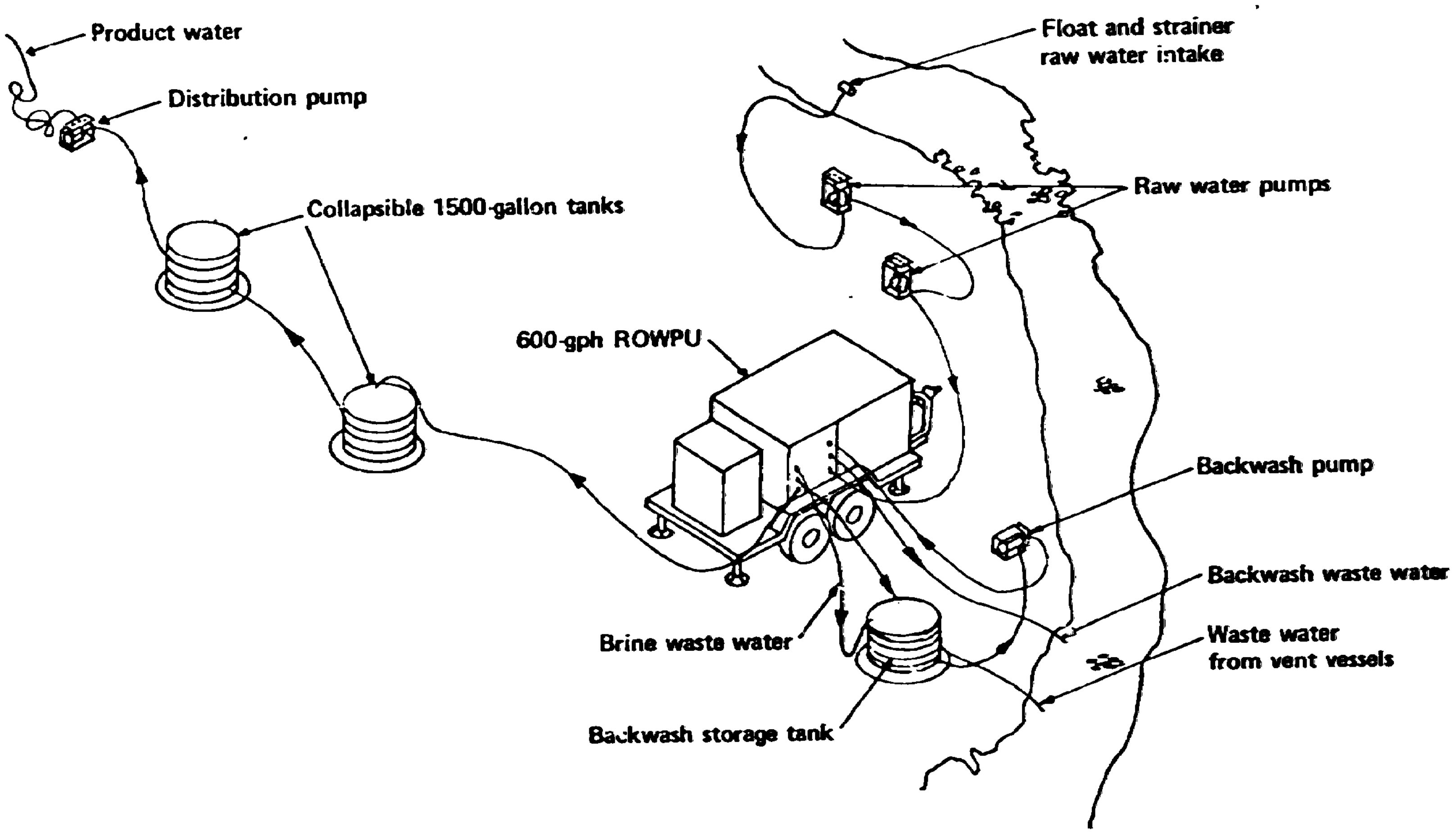


Figure 2. Typical field installation of 600-gph ROWPU. Reprinted from U.S. Army Training Manual, TM 5-4610-215-10, 1982.[6]

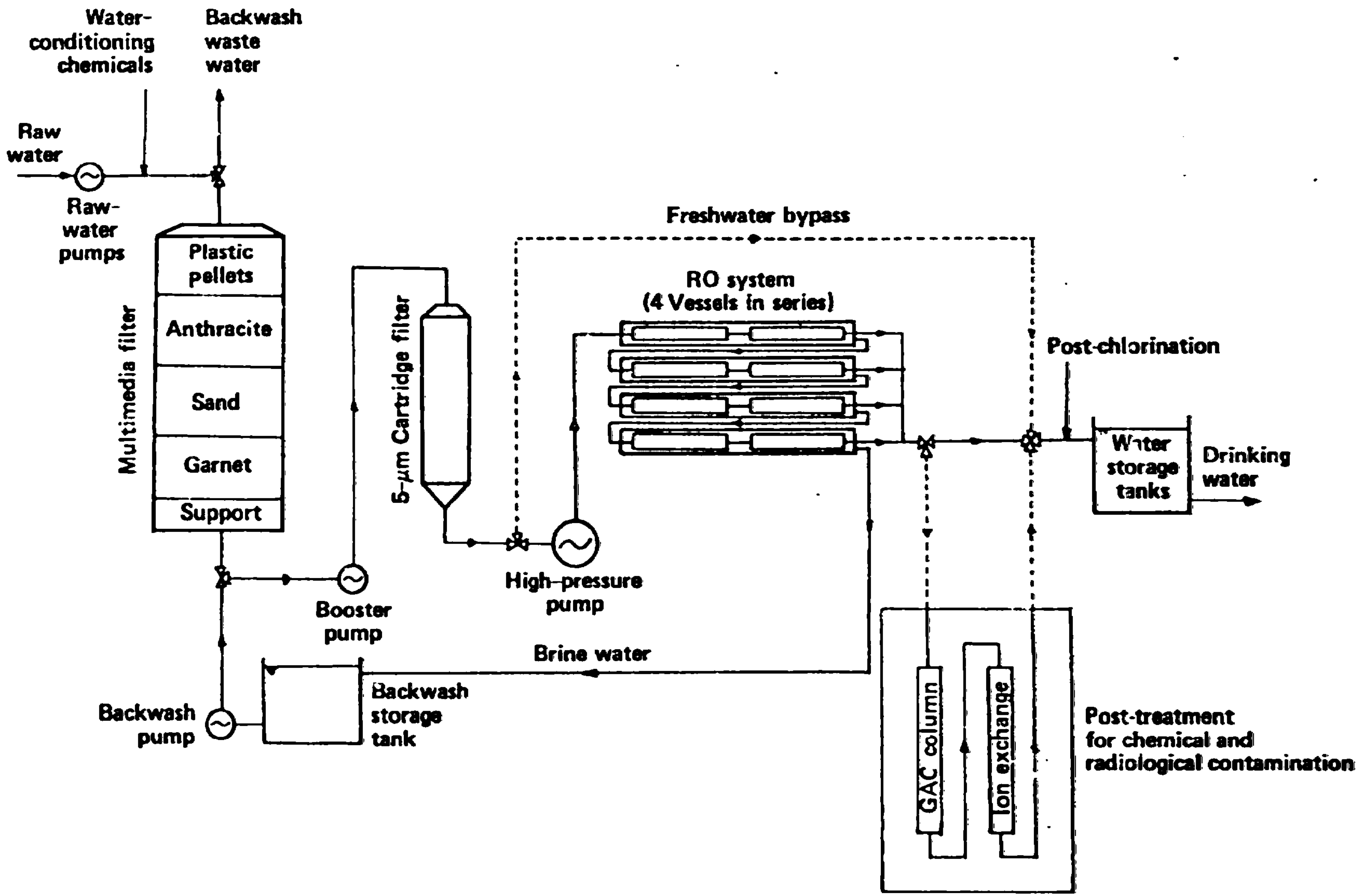


Figure 3. Schematic diagram of 600-gph ROWPU. After Carnahan et al., 1979.[7] (GAC = granular activated carbon).

Two raw-water pumps connected in series draw water from the source and pump it under pressure into the ROWPU pretreatment system. The suction lift of these pumps is limited to 10 ft. Specifications for the pumps used in the ROWPU are summarized in Table 1. A float and strainer installed at the end of the water-intake hose keeps leaves, plants, stones, fish, and dirt out of the pumps and filters of the ROWPU.

Water-conditioning chemicals are pumped into the water just before it enters the filtration unit. A citric acid solution is used to keep acid-soluble substances, such as metal hydroxides and calcium carbonate, in solution. Sodium hexametaphosphate is used to remove organic substances and microbiological slimes that are not acid-soluble.

Because of restrictions imposed by the ROWPU's dimensions, a conventional clarification system could not be used. Direct filtration (without using separate flocculation and coagulation basins) was employed with a cationic polyelectrolyte coagulant (Cat-Floc T1). The quality of the filtrate was less sensitive to polymer dose than expected; therefore, a maximum dosage of 5 mg/L of cationic polymer was established, regardless of the raw-water quality.[7]

The dimensions of the multimedia filter (Culligan Model MD20 mixed media) are shown in Fig. 4. The filter contains four media (plastic pellets, anthracite coal, calcined aluminum silicate, and garnet sand) and two support media (small and medium garnet gravel). Specific gravities, uniformity coefficients, densities, and some geometrical specifications of the media are also given in Fig. 4.[8]

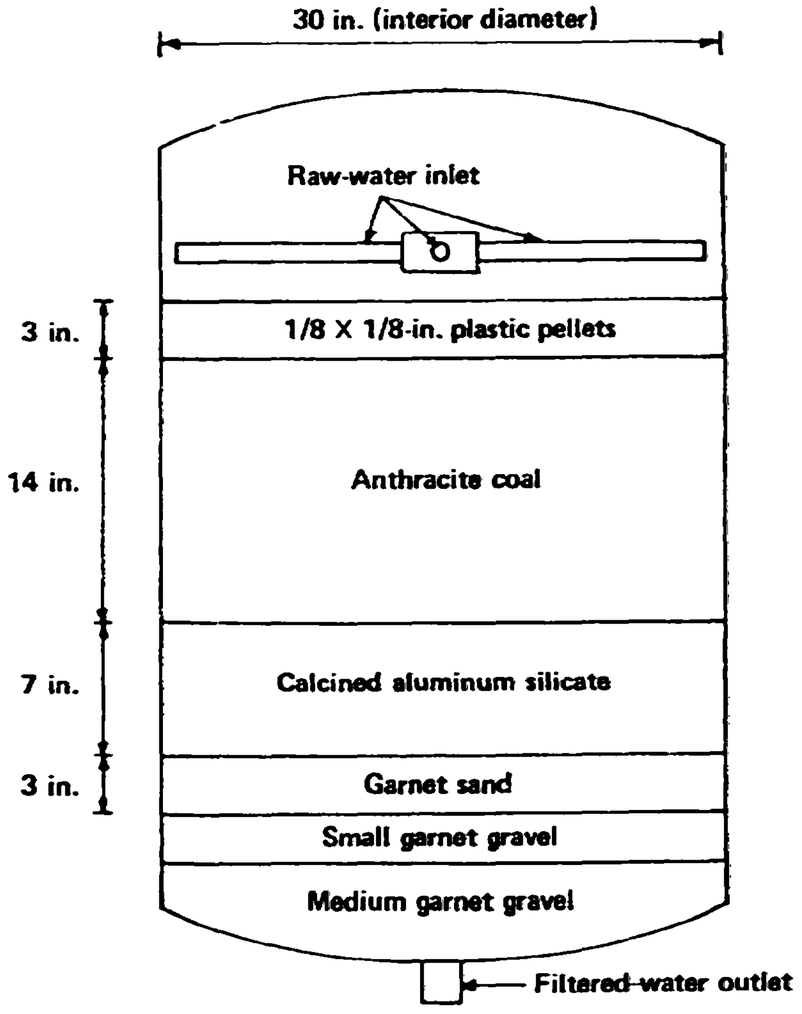
The range in the filter loading rate is 5 to 10 gpm/ft^2, with the nominal value being 6.5 gpm/ft^2. This range allows a nominal flow rate of 30 gpm at a minimum entering pressure of 25.0 psig. Backwash of the filter is performed after 20 h of operation or when the head loss increases 5 psid (pounds per square inch drop in pressure) above an initial value of 2 psid.[7] Brine water is used for the backwash operation. This process is automatic and is completed in 20 min.[7] The backwash flow rate increases automatically from 0 to 70 to 120 gpm to accommodate washing and rinsing cycles.

The effluent from the multimedia filter is then pumped through a cartridge filter by a booster pump. A diagram of the cartridge filter is shown in Fig. 5. This filter houses eight 5- µm filter tubes of woven polypropylene. Each 5- µm filter tube is 40 in. long and has a diameter of 2-3/4 in.[8] The overall surface area is 19.2 ft^2 (2.4 ft^2 for each tube), and the nominal flow rate is 35 gpm. Cartridge filters are changed when the differential pressure rises above 20 psid.

The effluent from the cartridge filter is forced through the RO system under high pressure by a positive-displacement pump. A pulse dampener, located behind the cartridge filter, reduces the shock caused by the piston of the RO pump. The specifications of the displacement pump are summarized in Table 1.

Table 1. Summary and specifications for pumps used in 600-gph ROWPU.[6]

Number of pumps	Pumps	Pump type	Driving motor power (hp)	Revolutions (rpm)	Pump		Operation
					Capacity (gpm [m^3/hr])	Pressure (psig [kPa])	
2	Raw water	Single-stage centrifugal self-priming	2	3500	30 [6.8]	45.5 [314]	continuous
4	Chemical feed	Positive-displacement	1/3	--	0.053 [0.012]	--	continuous
1	Backwash	Centrifugal	10	3500	120 [27.2]	70.0 [483]	intermittent
1	Booster	Centrifugal	1	3500	30 [6.8]	21.7 [149]	continuous
1	RO	Positive-displacement	20	500 (maximum)	51 [12]	980 [6760]	continuous
1	Distribution	Single-stage centrifugal self-priming	2	3500	30 [6.8]	45.5 [314]	intermittent



	Effective diameter (mm)	Specific gravity	Uniformity coefficient	Density (lb/ft^3; kg/m^3)
1/8 X 1/8-in. plastic pellets	—	1.2	—	45; 720
Anthracite coal	0.80	1.5	2	52; 830
Calcined aluminum silicate	0.42	2.5	1.74	—
Garnet sand	0.30	3.95	1.2	135; 2160

Figure 4. The 600-gph ROWPU multimedia filter. From Small *et al*., 1982.[8]

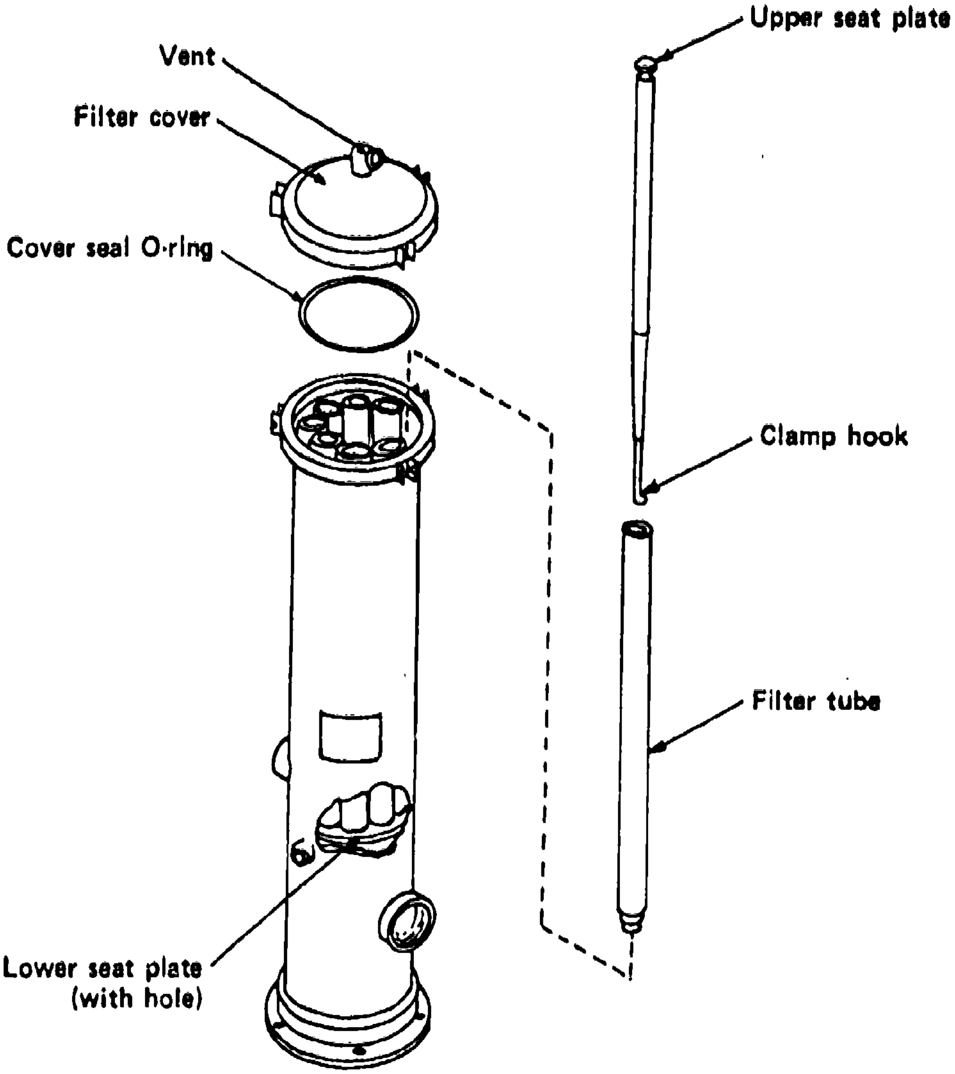


Figure 5. Diagram of ROWPU cartridge filter. From U.S. Army Training Manual, TM 5-4610-215-10, 1982.[6]

The RO system consists of four pressure vessels connected in series (see Fig. 3). Each pressure vessel contains two membrane elements (a complete description of the RO system is presented in this report).

In the event of chemical and/or radiological contamination, granular activated-carbon (CAC) and mixed-bed ion-exchange columns can be incorporated as post-treatment for the RO process. These columns are designed for an average 3-d operational capacity.[7] If required, one of the two raw-water pumps is used to force the water through these two columns.

If nuclear and chemical warfare agents are not present in raw fresh water (TDS concentration is much less than that of seawater), ideally the feed would not require demineralization. Lindsten[9] has proposed a "freshwater bypass" (see Fig. 3) of the RO system for this situation. A main advantage of using such a bypass procedure allows a maximum flow rate of 1800 gph. This flow rate is three times greater than the design flow with the RO system included in the treatment chain.

Finally, the product water coming out of the RO system is post-chlorinated. Two collapsible 1500-gal tanks connected in series permit a minimum of 5 h contact time for disinfection. If the RO elements are bypassed, the recommended contact time for the disinfection is 100 min. A distribution pump sends the product water to any point desired. The brine water is disposed of downstream from the raw-water intake, or it is stored for use in backwash.

All of the equipment described in this section is carried in the ROWPU and is included in the overall size and weight specifications.

PRINCIPLES OF HYPERFILTRATION

Reverse osmosis (RO) or hyperfiltration removes molecules in the size range of 1 to 10 Å (0.0001 to 0.001 μm) from water as shown in Fig. 6 (molecules ranging from 1 to 10 times the size of water molecules).[10] The RO membranes remove most electrolytes effectively. As a result, the difference between osmotic-pressures on either side of the membrane becomes appreciable, especially in the case of high initial salt concentration. Thus, the amount of external pressure applied to the upstream side may have to be significantly large to overcome the osmotic-pressure gradient across the membrane. The pressure applied across an RO membrane may range from about 20 to 100 bars (300 to 1500 psi), depending on the salt content of the water being demineralized.[11]

The RO membranes are thin enough to obtain good water flows per unit area of membrane surface. These delicate membranes are supported usually by a backing of

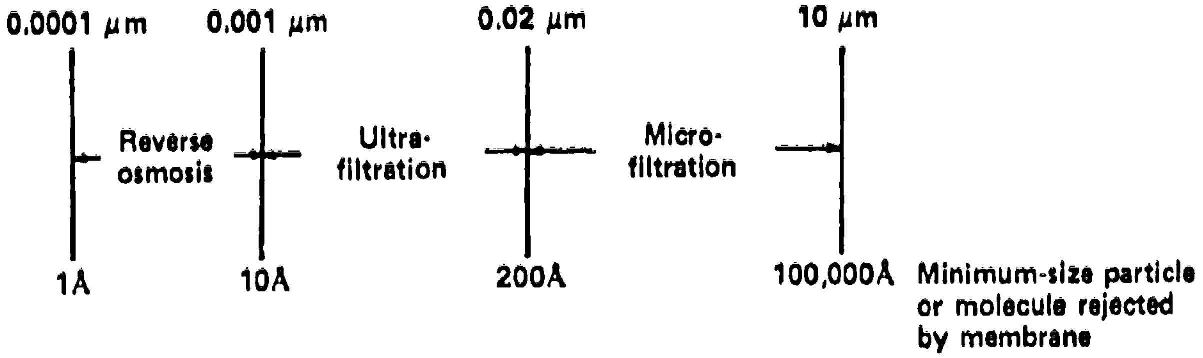


Figure 6. Classification of pressure-driven membrane separation processes. From Lonsdale, 1982.[2]

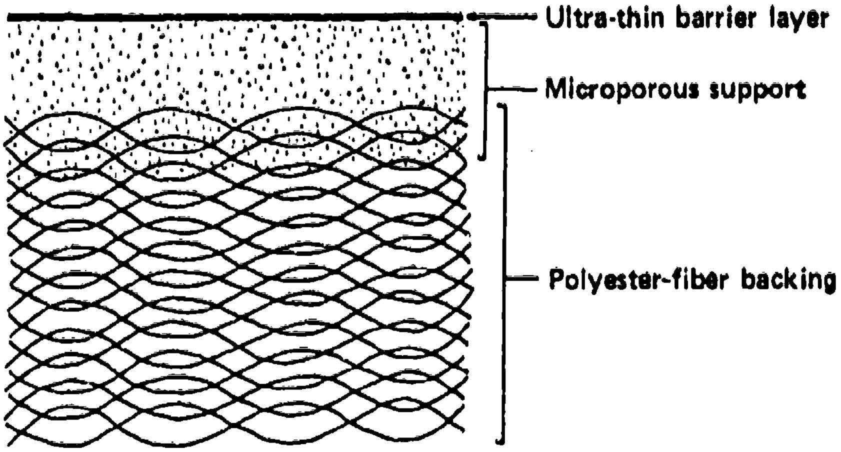


Figure 7. Schematic drawing of a thin-film composite membrane. From Cadotte and Petersen, 1981.[4]

tough fibers as illustrated in Fig. 7.[4] This backing may be in multilayers with the layers having little or no RO properties. Membranes of this type are referred to as asymmetric, composite, or anisotropic.

Particles and molecules greater than about 10 Å (0.001 μm) in size are removed with asymmetrical membranes containing micropores. The mechanisms of removal are sieving and sorption[11]; the process is called ultrafiltration (UF). Most of the dissolved salts pass through UF membranes; the decrease in osmotic pressure, which can be ascribed to the salts, is negligible. Thus, the pressures that have to be exerted across UF membranes are considerably less than those exerted across RO membranes. They range from about 0.5 to 5 bars (approximately 7 to 75 psi) in practice.[11]

The foregoing does not mean, however, that macromolecules or particle suspensions cannot exert osmotic pressures. Belfort and Altena[12] emphasize that such substances can exert significant osmotic pressures when present in high concentration.

When the minimum size of the particles rejected is about 0.02 μm according to one report[2] or 0.1 μm according to another,[11] the sieving process is called microfiltration (MF). Microfiltration membranes are usually symmetric; the pressures exerted across the membrane commonly range from about 0.1 to 1 bar (approximately 1.5 to 15 psi) in practice.[11]

Neither UF nor MF membranes contain pores of a uniform size. With the single exception of the Nuclepore MF membrane, all of these membranes contain a spectrum of pore sizes; this means that the cutoff in the sizes of the particles and molecules passing through the membrane is not sharply defined.[2]

MASS-TRANSPORT EQUATIONS AND MATERIAL BALANCES

The mass-transport equations used herein were obtained from general thermodynamic principles.[3,13] Assumptions made in the derivations include steady-state, isothermal conditions; no coupling between water and solute flow through the membrane; concentrations sufficiently small in the membrane to meet all dilute-solution laws; and a linear membrane solute-adsorption isotherm. The equations are

$$J = A' \cdot (\Delta p - \Delta\pi) \text{ , and} \tag{1}$$

$$J_s = B \cdot \Delta c \text{ ,} \tag{2}$$

in which p = hydraulic pressure; π = osmotic pressure; J and J_s are the mass fluxes of the water and solute through the membrane, respectively; A' and B are coefficients referred to as the water-permeability and solute-transport parameters, respectively; and c = solute concentration. The gradient terms represented by the Δ symbol are $(\Delta p - \Delta\pi) = (p_w - p_p) - (\pi_w - \pi_p)$ and $\Delta c = (c_w - c_p)$, in which the subscripts w and p refer to the upstream and downstream sides of the membrane proper, respectively.

Dividing Eq. 1 by the density (ρ) of pure water gives

$$U = A \cdot (\Delta p - \Delta\pi) \text{ ,} \tag{3}$$

in which U = the approach velocity of the water, and $A = A'/\rho$. The English dimensions used in this report for U, A, and B are gal/(d • ft^2), gal/(d • ft^2 • atm), and ft/d, respectively. The solute concentrations are expressed in terms of molarity (mole per unit volume of solution).

The solute rejected at the membrane wall has to be returned to the bulk feed solution. This can be accomplished only by molecular diffusion as shown in Fig. 8. The expression commonly used to relate the solute concentration at the membrane wall with that existing in the bulk feed solution is[14]

$$U/k = \ln \frac{c_w - c_p}{c_b - c_p} , \qquad (4)$$

in which k is a mass-transfer coefficient, and c_b is the solute concentration in the bulk feed solution (the brine concentration). This expression is based on fully developed, turbulent-flow conditions existing in the feed-water carrier as shown in Fig. 8. The expression simplifies to

$$\frac{c_w}{c_b} = e^{U/k} , \qquad (5)$$

when $c_p = 0$ (complete rejection of the solute). The ratio c_w/c_b is called the concentration polarization modulus (cpm).

The membrane is supported within an assembly called a module or element. The overall material-balance equations for the element are

$$\rho_{s,f}Q_f = \rho_{s,p}Q_p + \rho_{s,b}Q_b , \qquad (6)$$

and

$$c_fQ_f = c_pQ_p + c_bQ_b , \qquad (7)$$

in which the Q and ρ_s terms are the volumetric flows and densities of the solutions, respectively. The subscripts f, p, and b indicate feed, product, and brine, respectively. A schematic of flows and concentrations entering and leaving the element is shown in Fig. 9.

The densities of salt solutions were estimated empirically with the polynomial

$$\rho_s(\text{g/cc}) = 1 - 4.62 \times 10^{-6}T^2 + 10^{-3} \bullet (\alpha - \beta T + \gamma T^2) \bullet w$$

$$+ (p-1) \bullet (4.88 - 2.58 \times 10^{2}T + 4.30 \times 10^{-4}T^2) \bullet 10^{-5} , \qquad (8)$$

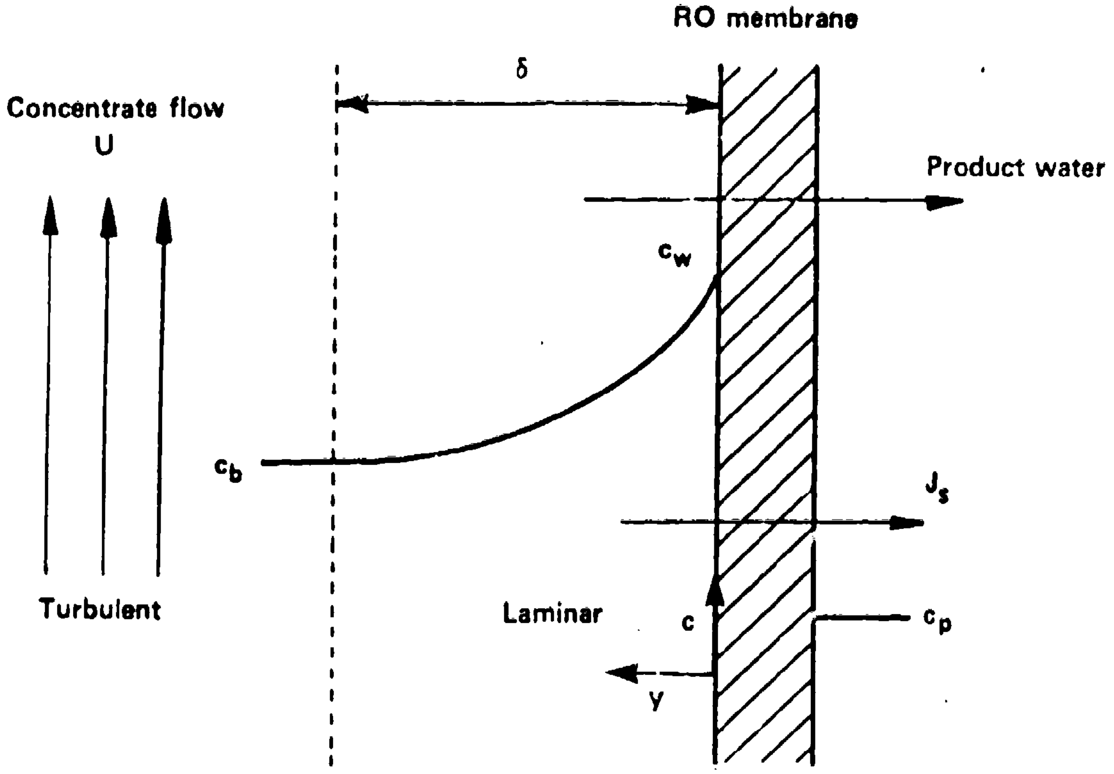


Figure 8. Idealized sketch of concentration polarization in a continuous-flow device with turbulent concentrate flow; (y denotes scale for axis, defining increasing distance from membrane wall; c denotes scale for axis, defining increasing concentration of salts approaching membrane wall as a result of concentration polarization; $c_w > c_b > c_p$). From Matthiasson and Sivik, 1980.[14]

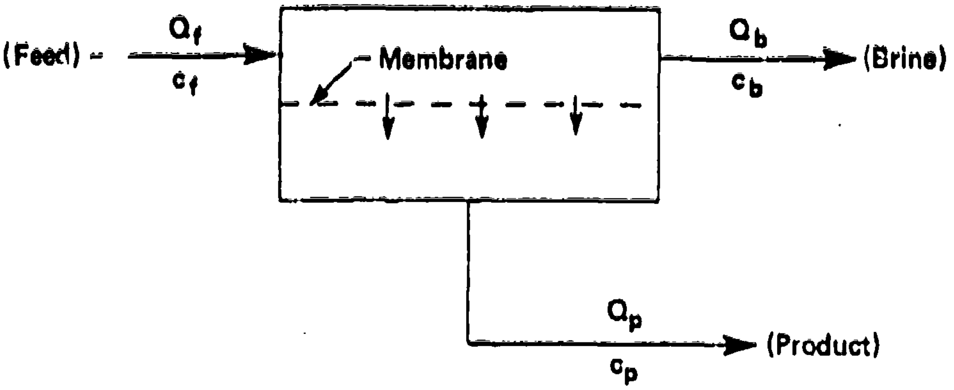


Figure 9. Material balance about an RO element.

in which w = the TDS in percent by weight; T = temperature in °C; p = the absolute pressure in atm; and α, β, and γ are coefficients that change with the salt composition. The values of the coefficients are α = 7.59, β = 0.0307, and γ = 0.000247 for NaCl; and α = 8.08, β = 0.0258, and γ = 0.000260 for standard seawater. The relationship between c and w is

$$c = \rho_s w/100 \ . \tag{9}$$

The performance of an RO system is judged frequently in terms of the product-water recovery (PR), the product-water flow Q_p or flux U, and the solute rejection (SR). The PR and SR are defined customarily as

$$PR = Q_p/Q_f \text{ and} \tag{10}$$

$$SR = 1 - c_p/c_f \ , \tag{11}$$

or perhaps

$$SR = 1 - w_p/w_f \ .$$

(The technical literature is not always clear as to which measure of concentration, c or w, was used to compute the solute rejection.) Sometimes the solute passage (SP) is used in lieu of SR, with

$$SP = 1 - SR \ . \tag{12}$$

OSMOTIC PRESSURE

An equation commonly used to compute the osmotic pressure (π) of a single strong electrolyte is

$$\pi = i\,RT\,m\,\phi \ , \tag{13}$$

in which i = the number of moles of ions produced with the complete dissociation of one mole of the salt, ϕ is an osmotic coefficient that corrects for the nonideal behavior of the electrolyte, m = the molality of the salt, and RT = the product of the ideal gas constant and the absolute temperature. Values of ϕ at 25°C and molalities ranging from 0.001 to 6 are given in Appendix A (Table A-1) for the salts NaCl, KCl, $MgCl_2$, $CaCl_2$, Na_2SO_4, $MgSO_4$, and a mix of sodium and magnesium sulfates.[15-20] Values of ϕ for temperatures other than 25°C may be obtained from the references given in the table. Alternatively, the variation in π with temperature may be estimated with reasonable accuracy from Eq. 13, assuming ϕ to be constant with respect to temperature.

The osmotic-pressure exerted by a mixture of salts is not determined easily. Of special interest is the mix represented by standard sea salts. The concentrations of the major ions in standard seawater (w = 3.5%) are shown in Table 2. The concentrations of these ions may be prepared by adding the substances shown in Table 3 to water at 25°C.

The results of osmotic pressure determinations made on standard seawater diluted to various degrees with pure water are shown in Table 4.[23] A polynomial was adjusted to fit the 25°C data shown in the table. The result was

$$\pi\,(\text{atm}) = 0.0289 + 6.86w + 0.121w^2 \ , \tag{14}$$

in which w = TDS in percent by weight. The increase in osmotic pressure with temperature was in accord with Eq. 13.

A similar equation was also fitted to the NaCl data shown in Appendix A (Table A-1).[15,16] The results demonstrated that the NaCl osmotic pressures were about 10% greater than the osmotic pressures exerted by standard sea-salt solutions at the same temperature and TDS weight concentration, or

$$\pi\,(\text{NaCl}) = 1.10 \cdot \pi\,(\text{sea salt}) \ . \tag{15}$$

Table 2. Major constituents for 3.5-wt% standard seawater.[21]

Constituent	Concentration (wt%)
Cl^-	1.9353
Na^+	1.076
$SO_4^=$	0.2712
Mg^{++}	0.1294
Ca^{++}	0.0413
K^+	0.0387
HCO_3^-	0.0142
Br^-	0.0067
Sr^{++}	0.0008

Table 3. Chemical composition of substitute ocean water.[a,b,c]

Compound	Concentration (g/L)
NaCl	24.53
$MgCl_2$	5.20
Na_2SO_4	4.09
$CaCl_2$	1.16
KCl	0.695
$NaHCO_3$	0.201
KBr	0.101
H_3BO_3	0.027
$SrCl_2 \cdot 6H_2O$	0.025
NaF	0.003

---

[a] Chlorinity (the weight of silver ion required to completely precipitate the halides in 0.3285 kg of water) is 19.38.

[b] The pH (after adjustment with 0.1 N NaOH solution) is 8.2.

[c] From Ref. 22.

Table 4. Osmotic pressures of standard sea-salt solutions.[23]

Temp. (°C)	Osmotic pressure (atm) for solutions with sea-salt content (wt%) of:					
	1.00	2.00	3.45[a]	5.00	7.50	10.0
25	7.11	14.29	25.15	37.49	59.30	83.97
40	7.42	14.93	26.34	39.35	62.41	88.53
60	7.80	15.70	27.74	41.51	65.98	93.69
80	8.13	16.37	28.94	43.32	68.89	97.82
100	8.42	16.94	29.92	44.79	71.17	100.97

[a] 3.45-wt% solids was taken as standard value for seawater.

The errors in Eqs. 14 and 15 are less than 1.8% for TDS concentrations ranging from about 0.04 to 7.5% by weight.

MEMBRANE TESTING

The properties of RO membranes are measured frequently in flat-leaf test cells similar to the one shown in Fig. 10. These test cells are designed deliberately to have a small concentration polarization or product recovery so that $Q_b = Q_f$, and $c_w = c_b = c_f$. With the assumption that $J_s = Uc_p$, Eqs. 2 and 3 simplify to

$$U = B\,(c_f - c_p)/c_p = A\,(p - \Delta\pi) \quad , \tag{16}$$

in which p = pressure reading on the monitoring gauge.

Figure 11 shows a diagram of changes in the product-water flux and solute rejection with applied pressure for the case of a constant feed-water salt concentration. The solid lines represent the results for no concentration polarization ($k = \infty$), and the dashed lines represent the results for a modest concentration polarization. At a pressure gradient equal to π_b, the product-water flux begins to increase dramatically, and it increases in proportion to $(p - \pi_b)$ for either case when $p > \pi_b$. The concentration polarization decreases the product-water flux significantly, and the solute rejection only marginally, at least in the case shown in the diagram.

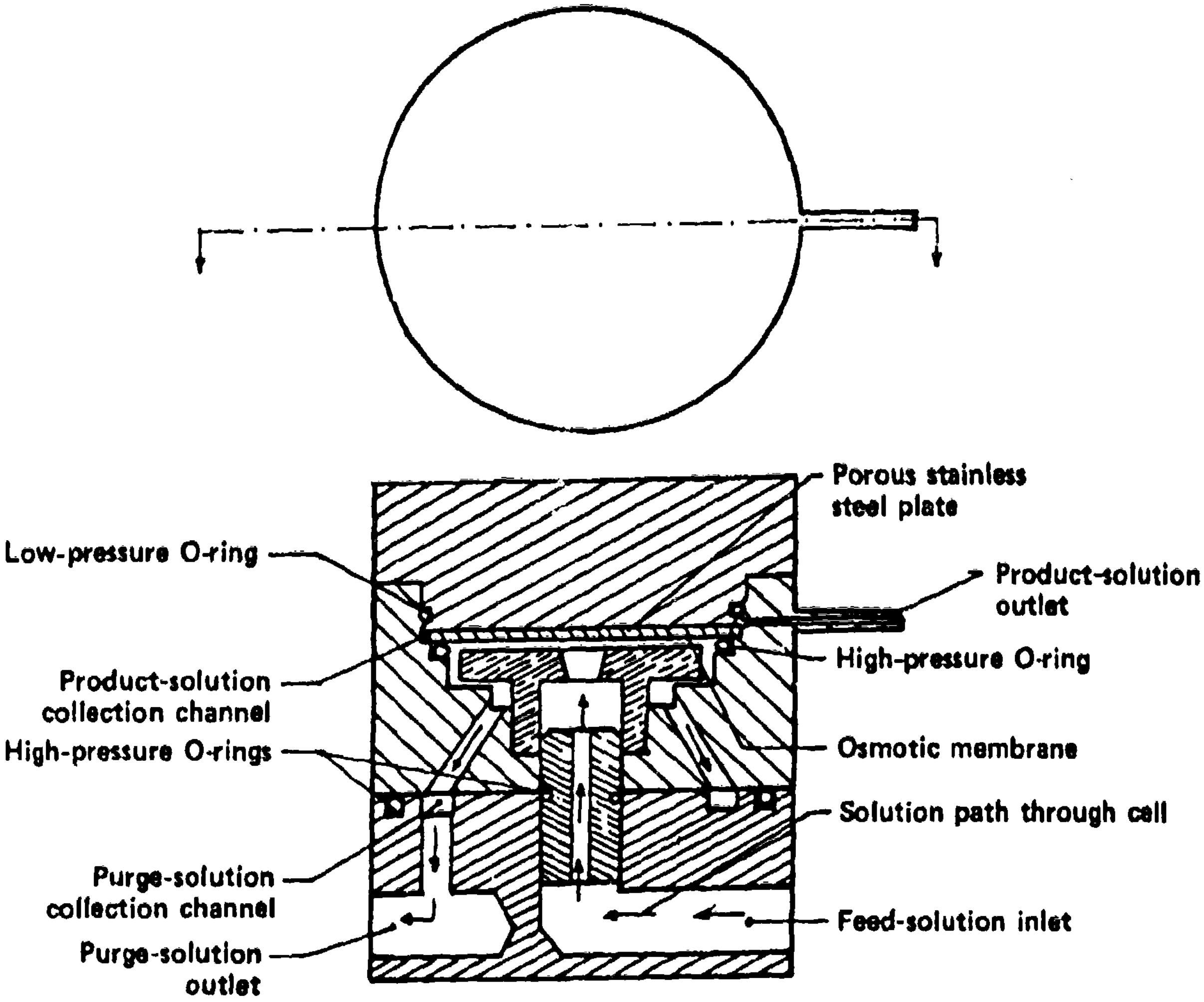


Figure 10. Details of RO test cell to accommodate 45-r .-diameter membrane disk. From McCray *et al.*, 1981.[24]

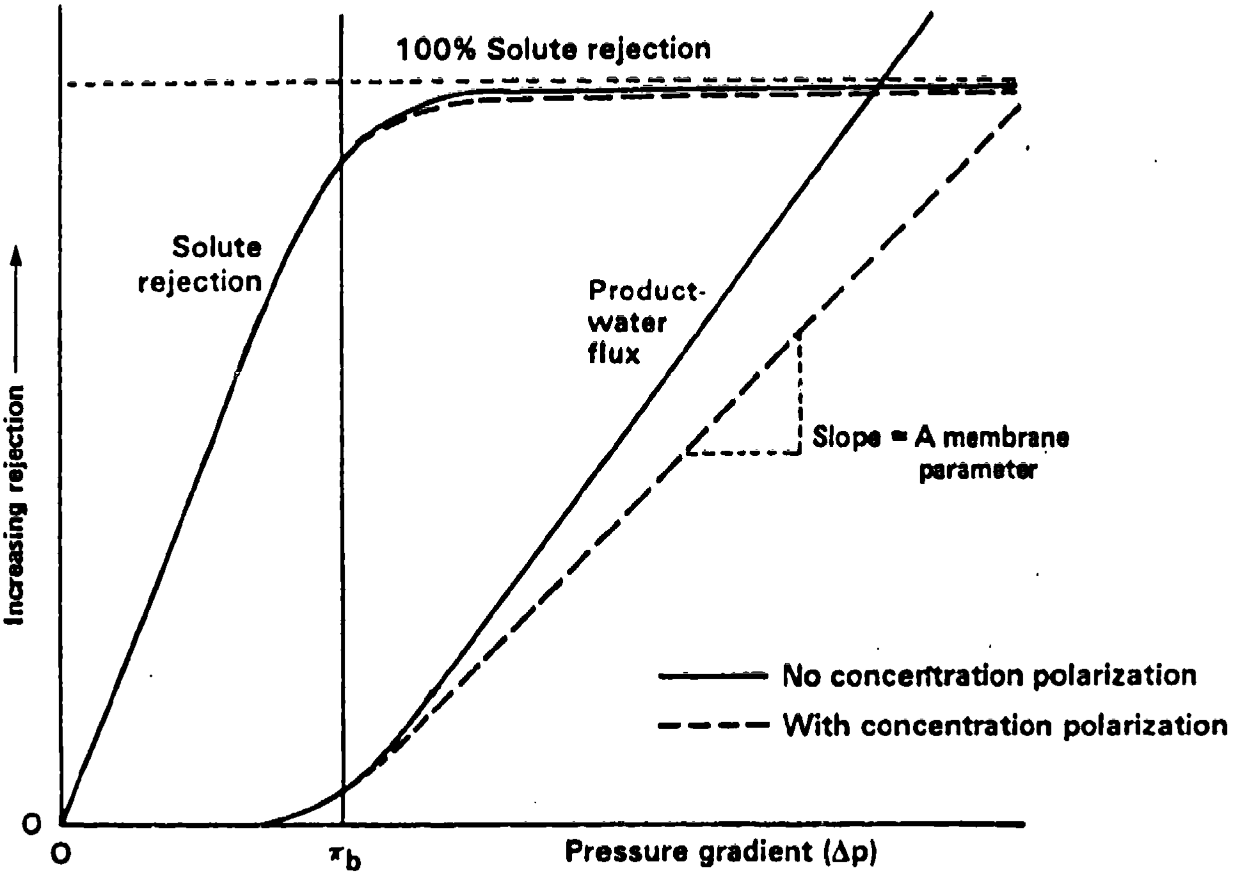


Figure 11. Generalized plot of mass-transport equations for flat-leaf tests. Note, that at a pressure gradient equal to π_b, the product-water flux begins to increase dramatically.

Figures 12 and 13 show the results of flat-leaf tests performed on a modern composite RO membrane (FT-30, FilmTec Corporation, Minnetonka, MN).[25] This membrane contains three layers: an ultrathin polyamide barrier layer (cross-linked aromatic polyamide), a microporous plastic sublayer, and a reinforcing web.[26] The total product-water recovery was about 0.1% for six 3-in.-diameter test cells placed in series. The feed water tested was a substitute seawater (see Table 3).

The shapes of the solute-rejection and product-water flux curves shown in Fig. 12 are similar to those depicted schematically in Fig. 11. Furthermore, Eqs. 14, 15, and 16 can be used to validate that the A parameter is a function of the applied pressure. For example, the A parameter decreases from about 1.3 gal/(d • ft^2 • atm) at 400 psig to 0.70 gal/(d • ft^2 • atm) at 1000 psig. Moreover, assuming that the TDS rejections shown were computed from weight concentrations, we confirmed that the TDS B parameter remained approximately constant at about 0.020 ft/d.

Figure 13 shows the results of various dilutions of substitute seawater when subjected to a constant pressure of 1000 psig. In this case, Eqs. 14, 15, and 16 validate that the A parameter decreases from about 0.87 to 0.65 gal/(d • ft^2 • atm) when the TDS concentration of the feed solution is increased from 0.05 to 6.0% by weight. The TDS B parameter, however, also decreases from about 0.050 to 0.020 ft/d as the feed-water TDS concentration increases from 0.05 to 6.0%.

These results appear to be typical for the thin-film composite membranes. The A parameter decreases with applied pressure, and the B parameter may be independent of the pressure. Both parameters decrease with increasing feed-salt concentration.

SPIRAL-WOUND ELEMENTS

A spiral-wound element consists of porous support material with a membrane on each side.[27] These sheets are formed into rectangles called leaves. A leaf is connected to a porous tube and wound around the tube, together with spacers to maintain the desired distance between the membranes. The feed solution flows axially along the wound cylinder in the spaces provided between the leaves, as shown in Figs. 14[28] and 15.[29] The product water flows in a spiral to the center tube.[14] The plastic netting that maintained space between the membranes for concentrate flow commonly had thicknesses ranging from 0.015 to 0.045 in. in the early days of UOP-ROGA spiral-wound element design.[29]

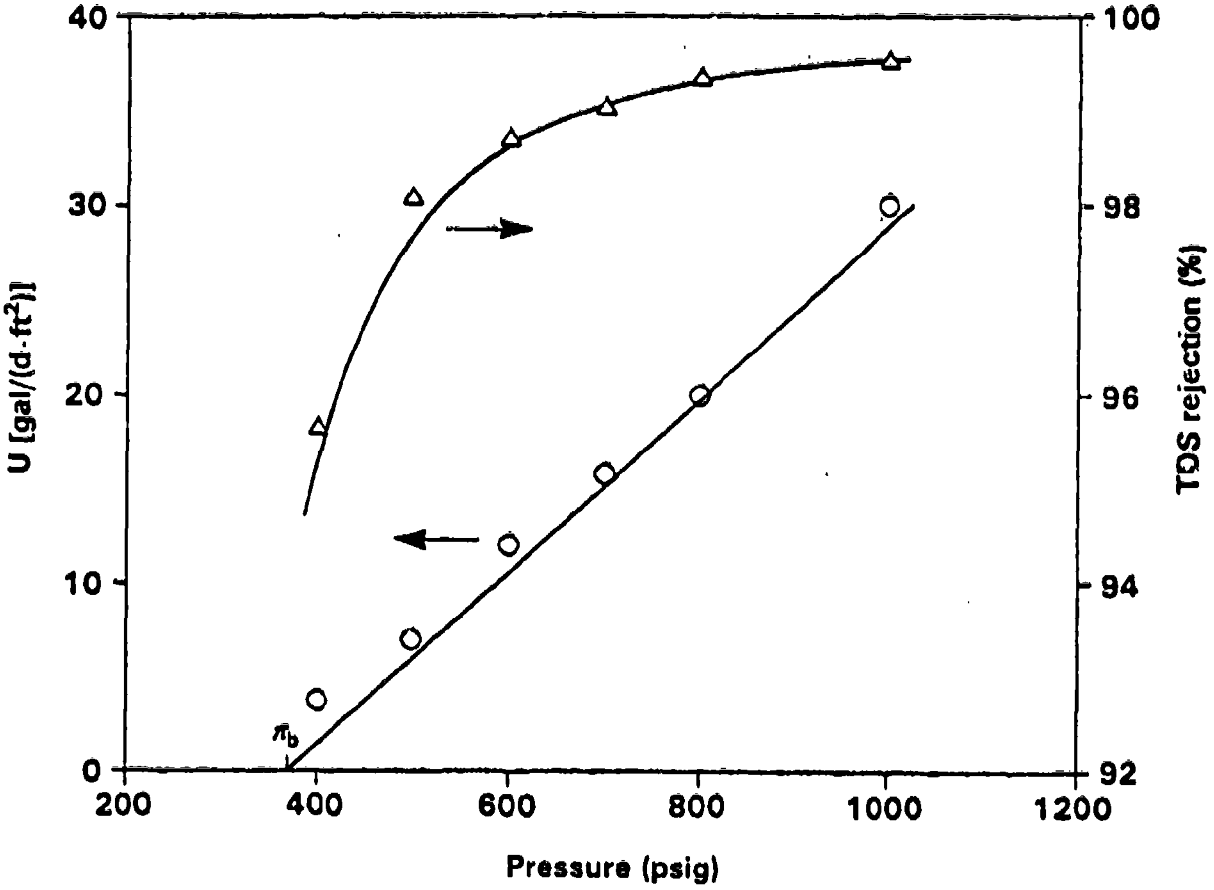


Figure 12. FT-30 flat-leaf membrane product-water flux and total dissolved solids (TDS) rejection as a function of operating pressure for a 3.5% substitute seawater feed solution at 25°C. Adapted from Cadotte et al., 1980.[25] Arrows point to applicable scale. Note, that at π_b the product-water flux begins to increase.

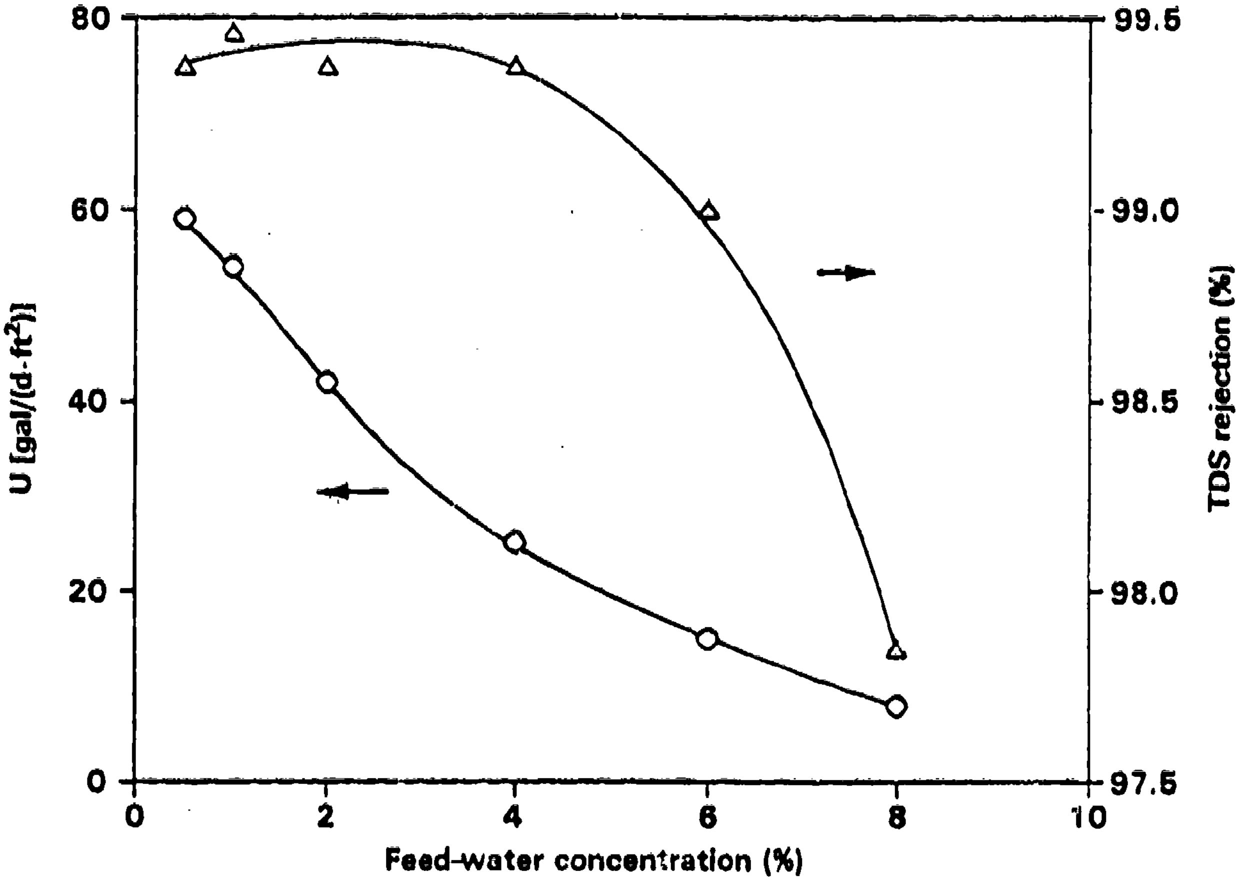


Figure 13. FT-30 flat-leaf membrane product-water flux and TDS rejection as a function of feed-water concentration for substitute seawater at 25°C and 1000-psig operating pressure. Adapted from Cadotte <u>et al.</u>, 1980.[25] Arrows point to applicable scale.

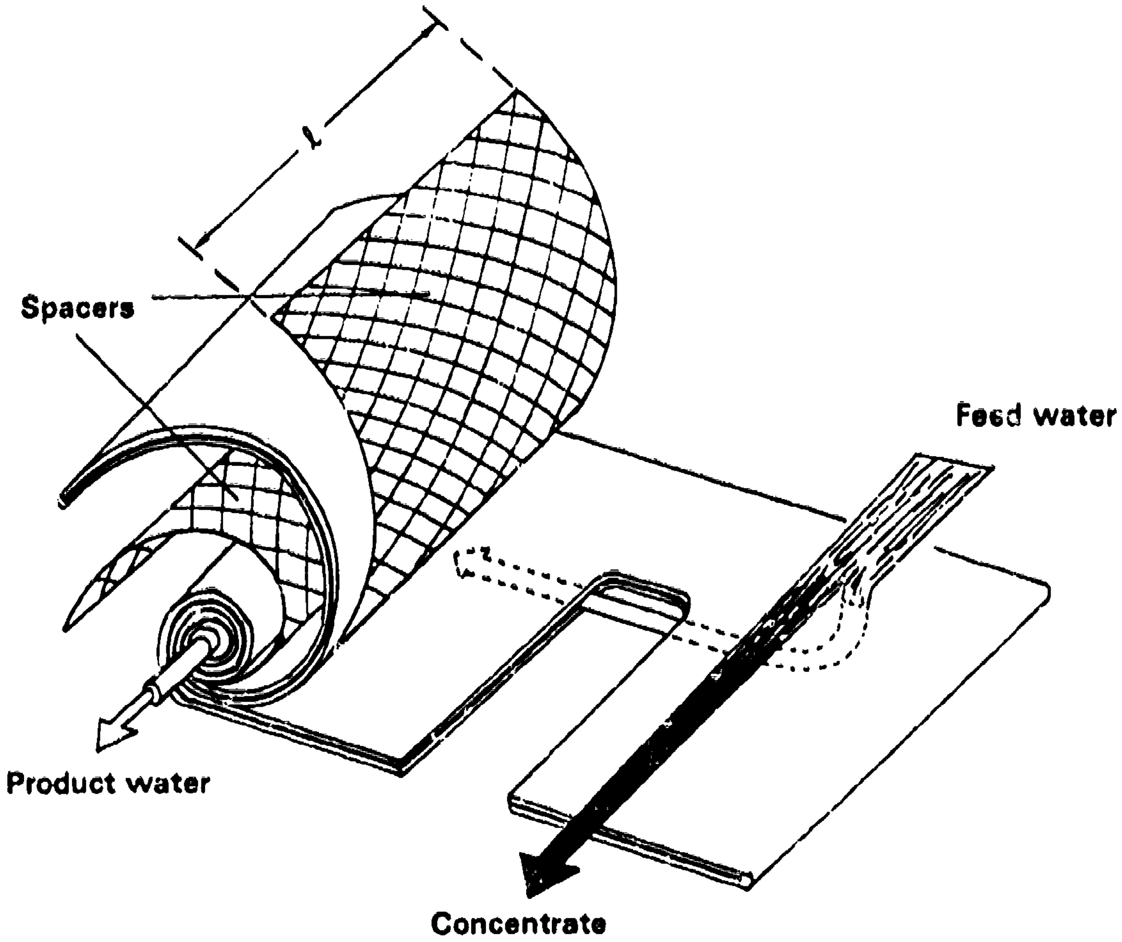


Figure 14. Schematic of spiral-wound element where ℓ is the channel length. After Bairinji et al., 1983.[28]

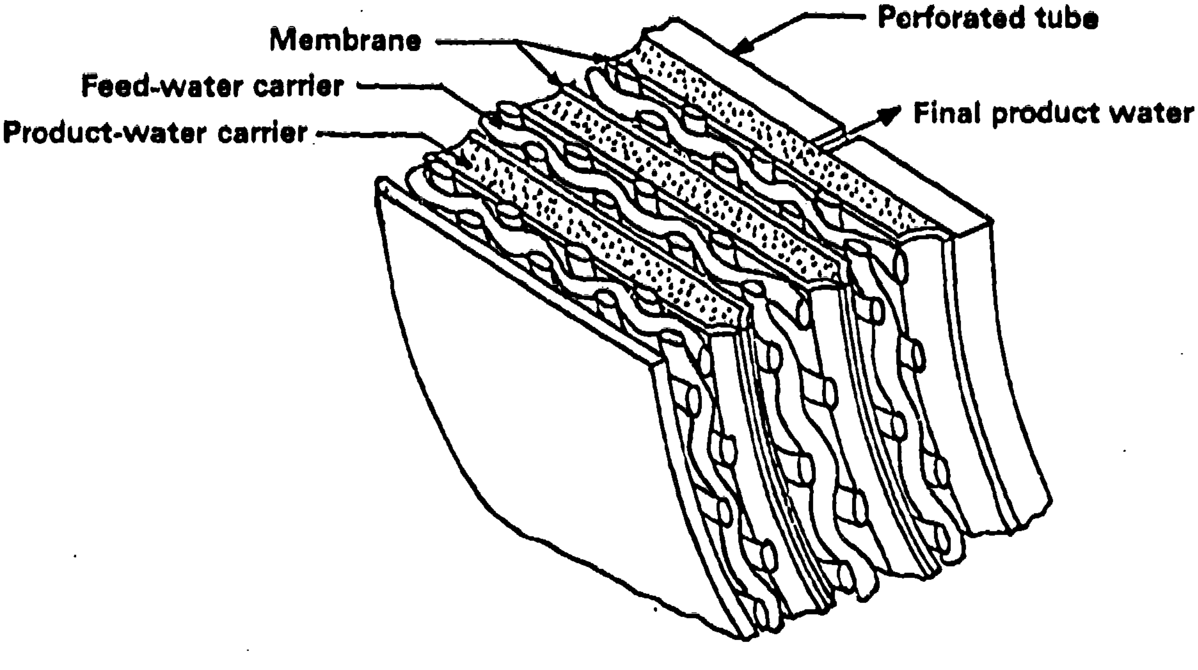


Figure 15. Structure of spiral-wound element. From Sirkar et al., 1982.[29]

Dimensions

The UOP Model 1501 spiral-wound element is used in the 600-gph ROWPU. This element has an overall length of 40 in., with a total diameter of 5.97 in. as shown in Fig. 16.[30] The effective membrane area is about 158 ft^2. The model numbers and dimensions of other spiral-wound elements manufactured by UOP are listed in Table 5.[31]

An open-mesh nylon webbing maintains a spacing of about 0.037 in. in the brine-water (concentrate) channel as shown in Fig. 17.[1] Dacron cloth maintains a spacing of about 0.032 in. in the product-water channel proper. The overall thickness of the thin-film composite (TFC) membrane is about 100 µm.[1]

Two 1501 elements are installed commonly in series in a single pressure-containment vessel. An expanded view of a pressure vessel in the 600-gph ROWPU is shown in Fig. 18. According to data furnished by H. B. G. Goettsch[32] of UOP, Inc., the drop in the brine-water pressure across a single pressure vessel containing two 1501 elements is about

$$\Delta p\ (\text{psid}) = 0.087 \cdot [Q_b\ (\text{gpm})]^{1.6} \ , \qquad (17)$$

for brine flows ranging from about 25 to 33 gpm.

We gave special attention to the UOP 1501 element because this is the element used in the 600-gph ROWPU. The dimensions and general characteristics of this element do not differ greatly from any other 6-in.-diameter spiral-wound element manufactured in the United States.[32] The competition exists in the type of membrane housed in the element.

Concentration Polarization

According to the manufacturer of the UOP Model 1501 spiral-wound element, the sodium chloride concentration polarization modulus (cpm) for 3-ft-long elements can be obtained from the expression

$$\text{cpm} = \exp\ (0.675\ Q_p/Q_b) \ , \qquad (18)$$

in which Q_b is the mean brine flow in the element and Q_p is the the product-water flow.[30] This expression may be written in a form corresponding more to Eq. 5, or

$$\text{cpm} = \exp\ (KU/U_b) \ , \qquad (19)$$

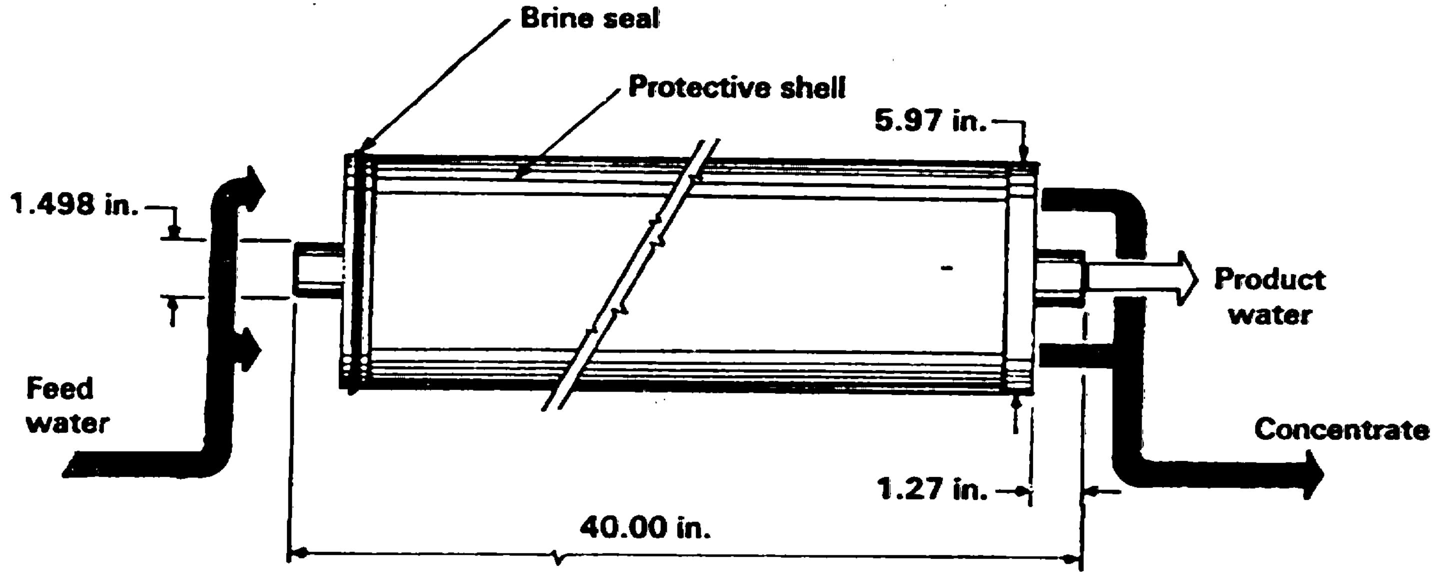


Figure 16. Diagram of UOP TFC-1501 spiral-wound element. From UOP, Inc., 1982.[30]

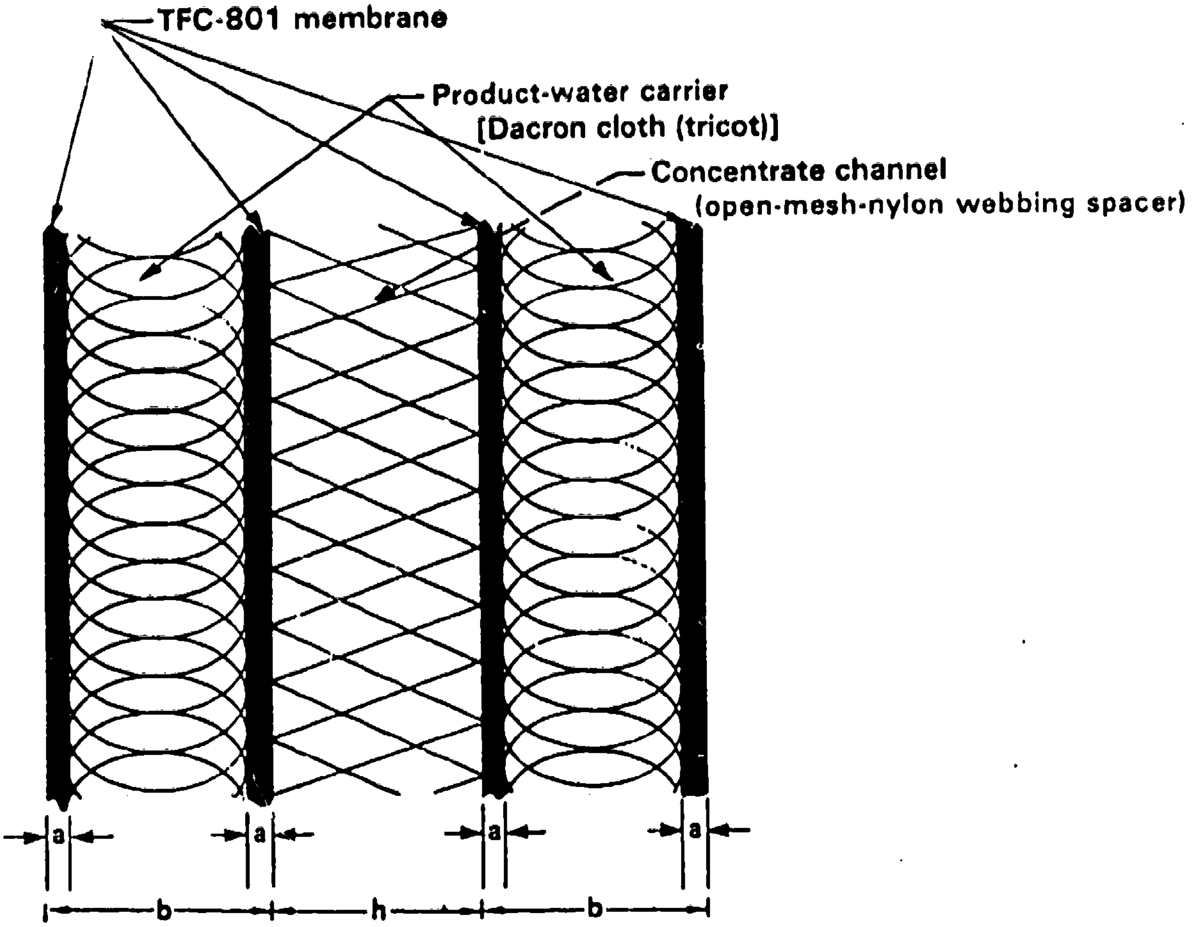


Figure 17. Cross section of a UOP 1501 element obtained from direct measurement on an element used in 600-gph ROWPU, where the dimension of the membrane wall "a" is 0.004 in., the dimension of the product-water-carrier channels "b" is 0.040 in., and the dimension of the concentrate channel "h" is 0.037 in. From Ciccone, 1983.[1]

Table 5. Model designation and physical dimensions of UOP TFC-801 spiral-wound elements.[31]

Model number	Diameter (in.)	Length (in.)	Approximate membrane surface area (ft^2)
7005	2.5	21	8.4
701	2.5	40	18.5
1001	4	40	65
1501[a]	6	40	158

[a] Model currently being used in 600-gph ROWPU in U.S. Army and U.S. Marine Corps inventories.

in which the coefficient $K = 0.675(2\ \ell/h)$ and ℓ and h are the length and height of the brine-water carrier, respectively (see Figs. 14 and 17).[33] The mass-transfer coefficient appearing in Eq. 5 is, therefore,

$$k = U_b/K = U_b h/(1.35 \cdot \ell) \ , \tag{20}$$

in which $\ell = 3$ ft by definition.

The Reynolds number, Re, used for flow between parallel plates is $Re = U_b h/\nu$, in which ν = the kinematic viscosity of the brine water. Comparison of this definition of Re (i.e., $Re \propto U_b$) with Eq. 20 where $k \propto U_b$) indicates that k was set directly proportional to Re in the derivation of Eq. 18.

The flow of water delivered to an RO element may range from 13.5 gpm (the minimum recommended by UOP) to 34.5 gpm (the output of the positive-displacement pump used in the 600-gph ROWPU). The corresponding range in the 20°C Re is about 105 to 270 based on a brine-water-carrier height of 0.037 in. (Fig. 17) and cross-sectional area of 0.081 ft^2. These values are sufficiently small to yield laminar flow if the brine-water carrier is free of obstructions. The plastic webbing that maintains the distance between membrane leaves in the element also serves to promote turbulence.

Many investigators have published empirical expressions of the form

$$Sh = \alpha\ Re^{\beta}\ Sc^{1/3} \ , \tag{21}$$

in which

Sh = kh/D (Sherwood number)

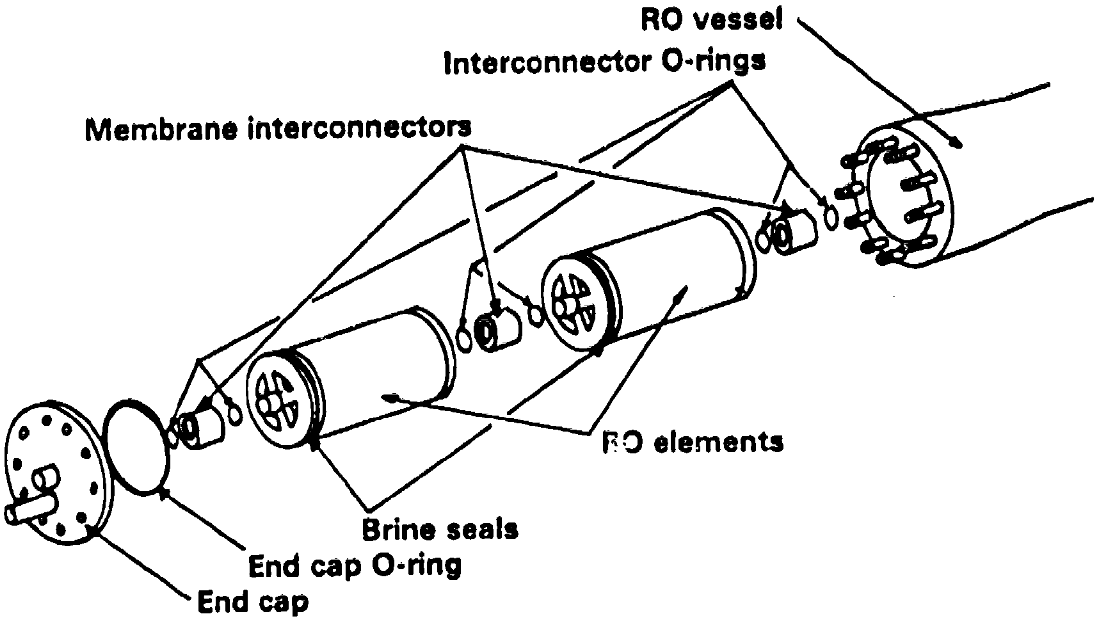


Figure 18. Expanded view of a pressure vessel used in 600-gph ROWPU. From U.S. Army Training Manual TM 5-4610-215-10, 1982.[6]

and

$$Sc = \nu/D \text{ (Schmidt number)},$$

for flow between parallel plates containing turbulence promoters.[34,35] The coefficients, α and β, are valid only for a specific spacer webbing as well as a specified range in the Reynolds number, but the power on the Schmidt number is always 1/3. Some observations of electrodialysis reported in the technical literature indicate that the power on Re may be unity ($\beta = 1$) for $100 < Re < 400$.[35] This supports the statement made in Eq. 20 that k is proportional to Re for $105 < Re < 270$.

The mass-transfer coefficient decreases rapidly for Reynolds numbers less than about 100. Tweddle et al.[36] observed a k of about 2.8 ft/d at an $Re \approx 50$ in a UOP-ROGA-4000 element, or about 8.6 times less than that obtained from Eq. 20 for the minimum recommended Reynolds number of 105. This observation indicates that the study was performed in the laminar flow regime where D can be expected to be small.

Equation 20 is valid for NaCl only. Equation 21 indicates that the mass-transfer coefficient k should be proportional to D taken to the two-thirds power. This relationship can be used to adjust cpm for salts other than NaCl, or

$$cpm^1 = \exp 0.675 \left[\frac{Q_p}{\bar{Q}_b} \left(\frac{D}{D^1} \right)^{2/3} \right], \tag{22}$$

in which D = the molecular diffusivity of NaCl (1.6×10^{-5} cm^2/s at 25°C)[3], and the superscript 1 refers to any salt other than NaCl. This expression was also used to adjust the cpm's for temperatures other than 25°C because D is directly proportional to the absolute temperature.[37]

Values of the ratio D/D^1 for various single salts may be obtained from Appendix A (Table A-2) that was prepared from calculations by Sourirajan and Matsuura,[38] because

$$\left(\frac{D}{D^1} \right)^{2/3} = \frac{k}{k^1}. \tag{23}$$

For example, the table shows that $k = 20 \times 10^{-4}$ cm/s for NaCl and 13×10^{-4} cm/s for $MgSO_4$. The ratio D/D^1 taken to the two-thirds power is, therefore, 20/13 = 1.54. If we assume that $Q_p = 1.25$ gpm per element and $Q_b = 28.5$ gpm (35% product-water recovery) in the 600-gph ROWPU, Eq. 22 gives a cpm of 1.03 for NaCl and 1.05 for $MgSO_4$. These small cpm values indicate an almost negligible sea-salt concentration polarization in the 600-gph ROWPU. This stems in part from the exceptionally large feed flow of the ROWPU.

TEMPERATURE AND pH

Both product flow and solute rejection are sensitive to temperature. H. B. G. Goettsch of UOP, Inc.,[32] has expressed the temperature dependencies of the parameters A and B in terms of Arrhenius law, or

$$A_2/A_1 = \exp(\alpha)\text{, and} \tag{24}$$

$$B_2/B_1 = \exp(2\alpha)\text{, in which} \tag{25}$$

$$\alpha = K_t \left[\frac{1}{T_2} - \frac{1}{T_1}\right],$$

where K_t and T are the Arrhenius temperature coefficient and absolute temperature, respectively. The subscripts 1 and 2 represent two different temperatures. The value of K_t ranges from 2000 to 3000 K, depending on the membrane type and geometry.[32]

Subsequently, UOP[33] has expressed Eq. 24 in terms of the total product-water flow, or

$$Q_{p,2}/Q_{p,1} = \exp(\alpha)\text{,} \tag{26}$$

in which $K_t = 3470$ K for all TFC® RC elements. It should be noted that Eqs. 24 and 26 are not equivalent except for the very special case of $(\Delta p - \Delta\pi)_2 = (\Delta p - \Delta\pi)_1$ (constant net driving force).

H. B. G. Goettsch[32] has expressed the variation in sodium chloride rejection with feed-water pH as a function of the sodium chloride B parameter, or

$$B = B_s \cdot (1 + 0.15\ [\mathrm{pH}_f - 5.7])\text{,} \tag{27}$$

in which B_s is the value of B at a pH of 5.7. This expression is valid at 25°C, and no correction is to be made for a pH less than 5.7. It also has been expressed in terms of the sodium chloride rejection for a particular value of B_s,[32] or

$$SR_{NaCl} = 0.993 - 0.00105\ (\mathrm{pH}_f - 5.7)\ . \tag{28}$$

The B_s corresponds to a 99.3% NaCl rejection at a pH of 5.7.

Six 3-in. diameter flat-leaf test cells were placed in series to obtain the test results shown in Fig. 19 for the FilmTec FT-30 membrane.[25] A pressure of 1000 psig may have compressed the membrane with a decrease in product flux at the higher temperatures. However, the properties of the membrane returned to normal levels when the temperature was returned to 25°C. We interpreted this to mean that the temperature effects were reversible.[25]

The FT-30 membrane was also housed in a small spiral-wound element (dimensions not reported).[40] The product recovery was about 1.8% at 25°C for a feed-water NaCl concentration of 3.2% by weight and an applied pressure of 800 psig. The variation in the transport properties with temperature is shown in Fig. 20 for $10°C < T < 35°C$. Again the increase in product flow with temperature did not appear to follow the Arrhenius relationship.

Larson et al.[40] state that additional data (not published) obtained on spiral-wound elements using temperatures as high as 50°C showed slight changes in product-water flow and salt rejection when the temperature was returned to 25°C. These changes indicate damage in either the membrane or the spacers, etc., used in the construction of the spiral-wound element. They concluded that the damage did not occur in the membrane per se because the flat-leaf tests indicated no membrane damage with temperature as high as 60°C (see Fig. 19).

The NaCl rejection shown in Fig. 20 either increased or remained constant when the temperature increased. This behavior is not predicted by Eq. 25. Larson et al.,[40] postulated that a drop in salt rejection at the lowest temperatures investigated stemmed from the small product-water fluxes observed at those temperatures.

The performance of the FT-30 membrane does not change much with changing pH as illustrated by the data shown in Fig. 21. Flat-leaf tests demonstrated some membrane damage at pH levels below 3 and greater than 11. According to Petersen et al.,[26] the FT-30 membrane can be exposed to very high or very low pH cleaning solutions without damage if no appreciable pressure is applied to the RO elements.

STABILITY

Most RO membranes will compress or creep slowly with time when subjected to high pressure. This activity causes a decrease in the product-water flux with time. The rate of decrease in the flux is usually more rapid for membranes with higher initial flux, and it is strongly dependent on the applied pressure.[41] The decrease in the flux is most rapid during the initial hours of operation, but it continues indefinitely at a decreasing pace.

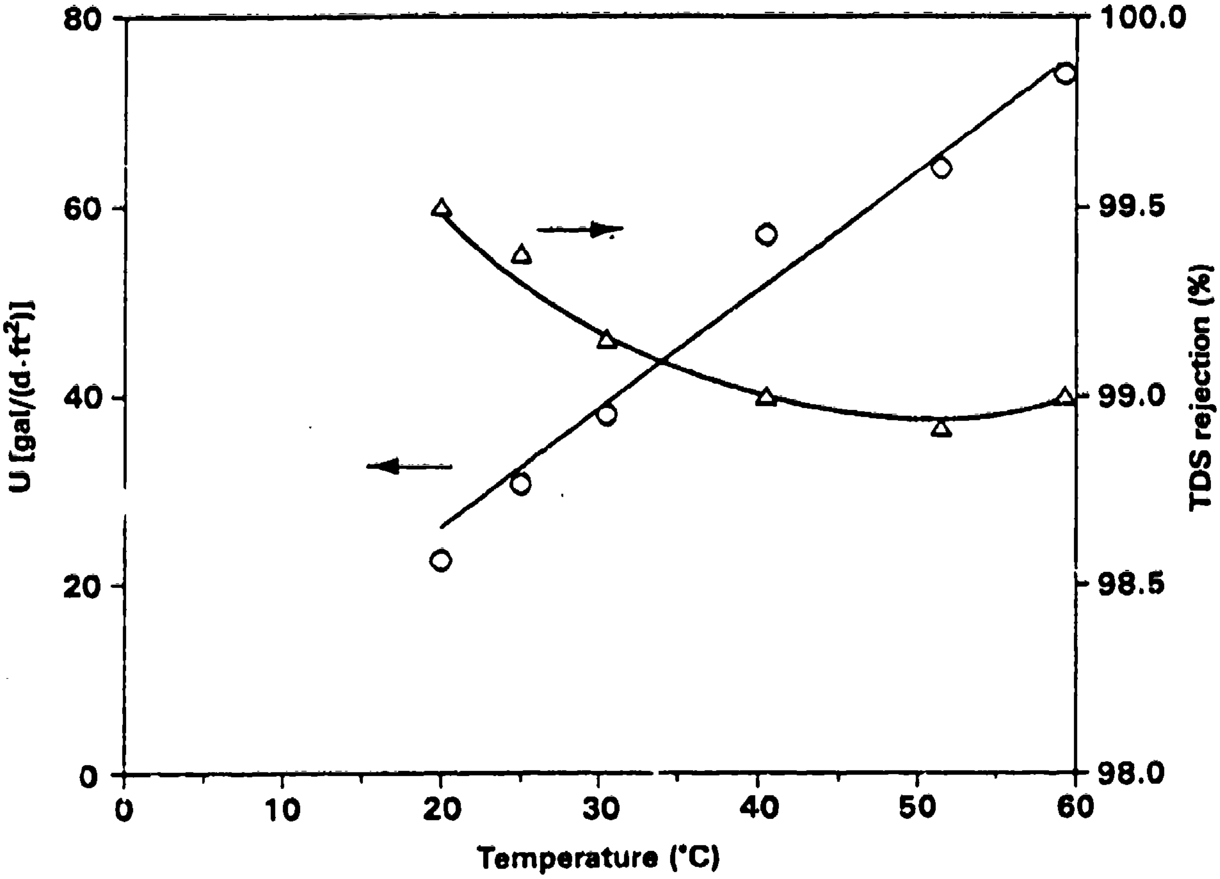


Figure 19. FT-30 flat-leaf membrane product-water flux and TDS rejection as a function of water temperature for a 3.5%-substitute-seawater feed solution at 1000-psig operating pressure. Adapted from Cadotte et al., 1980.[25] Arrows point to applicable scale.

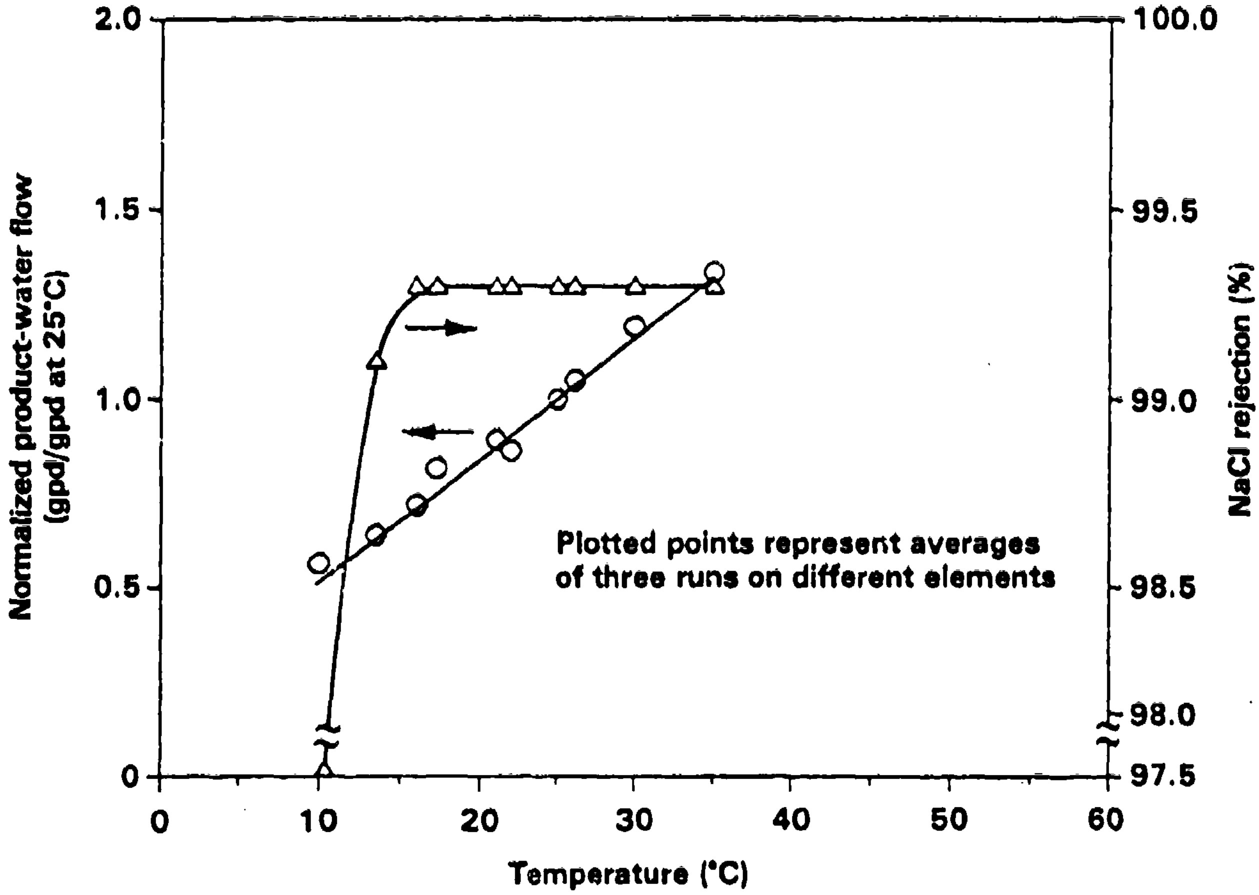


Figure 20. FT-30 spiral-wound membrane element salt rejection and normalized product-water flow as a function of feed-water temperature for a 3.2%-sodium-chloride feed solution at a pH = 7, 800-psig applied pressure, and 1.75-gpm feed-water flow. Adapted from Larson, et al., 1981.[40] Arrows point to applicable scale.

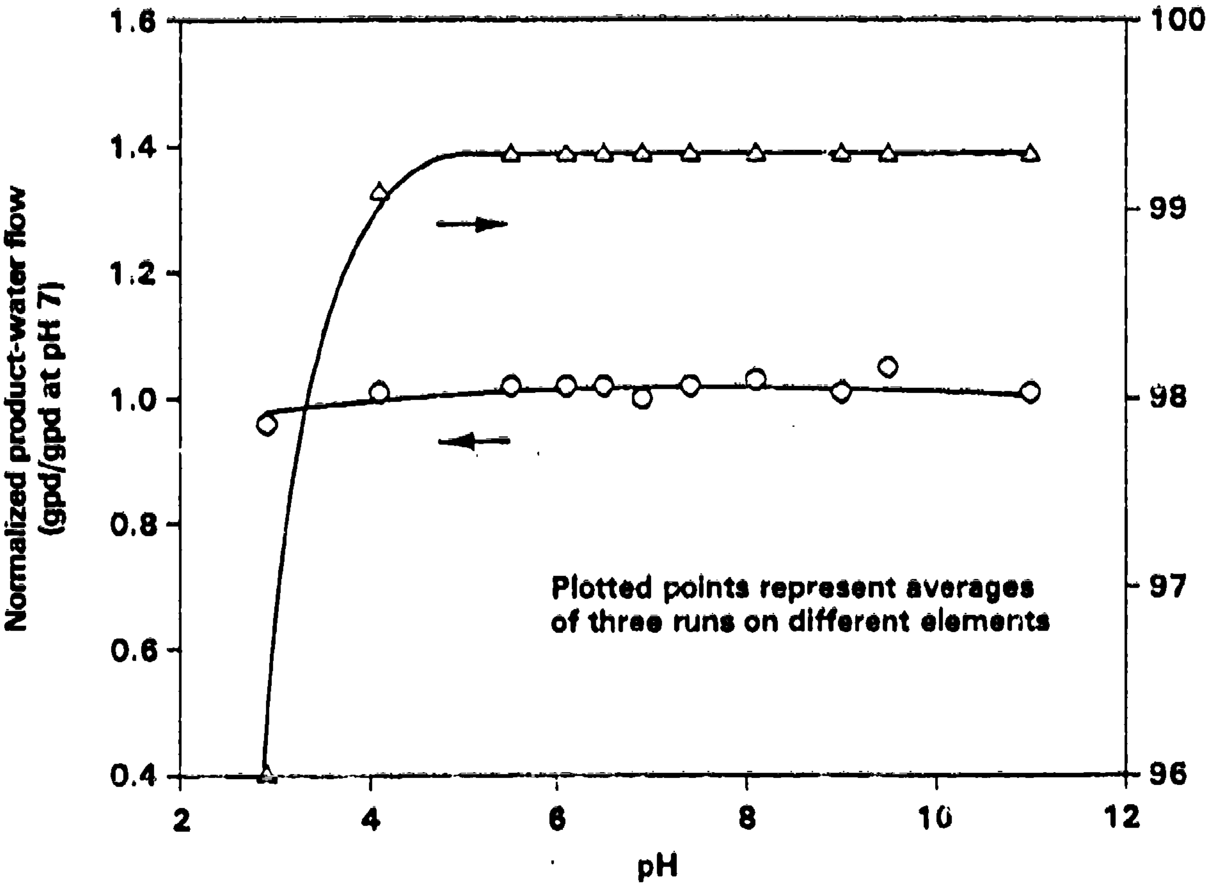


Figure 21. FT-30 spiral-wound membrane element salt rejection and normalized product-water flow as a function of feed-water pH for a 3.2%-sodium-chloride feed solution at 25°C, 800-psig applied pressure, and 1.75-gpm feed-water flow. Adapted from Larson, et al., 1981.[40] Arrows point to applicable scale.

The effect of compaction on product-water flux is expressed customarily as a power function of the run time,[41] or

$$U_t = U_1 \cdot t^n \ , \qquad (29)$$

in which t is in hours ($t \geq 1$), n is a compaction factor, and U_1 is the value of the product-water approach velocity (U) at one hour. The membrane parameter A may be used in lieu of U in this expression. This equation, while useful for extended operating times, does not define what happens during the first hour of rapid membrane compaction.

The data published for some thin-film composite membranes contained in spiral-wound elements indicate a relatively slow rate of compaction. In an early study, Riley et al.[42] reported a value of n of -0.01 for a UOP PA-300 membrane exposed to seawater at a temperature of 25°C and a pressure of 990 psig for 500 h. A similar test performed with clean water for 200 h at 55°C and a pressure of 390 psig yielded an n of -0.012.

The power on the time t in Eq. 29 increases with the applied pressure. The absolute value of n was approximately proportional to the applied pressure for a series of flat-leaf tests performed on a cellulose acetate homopolymer membrane ($p > 200$ psig).[41] The effects of pressure recycling on membrane compaction have not been studied extensively, but relaxation and hysteresis effects have been noted.[41]

The concensus is that membrane compression has little or no effect on salt rejection, although not much has been published on this topic.[41] If the salt rejection is constant with time, Eq. 16 shows that the ratio B/U must also be constant with time, or

$$B/U = c_p/\Delta c = SP/SR = \text{a constant} \ . \qquad (30)$$

The membrane material may also react chemically with species contained in the feed water, or with water itself. A well-known example of the latter is the hydrolysis of cellulose acetate membranes. The replacement of acetate with hydroxyl in the polymer chain causes an increase with time in the product-water flux and salt passage. The rate of membrane hydrolysis increases rapidly with temperature, and it is directly dependent on the OH^- concentration at pH levels in excess of about 5.0.[43] According to Sammon,[41] the logarithms of the membrane parameters A and B increase linearly with time subsequent to an initial lag period.

FOULING

The product-water flux may be decreased by the formation of gels or precipitates on the high-pressure side of the membrane. This is called membrane fouling. Other causes of membrane fouling include products of corrosion, scaling, biological films, and freezing.[14]

Concentration polarization and large product-water recoveries enhance any tendency for membrane fouling. The profound effect of the former may be illustrated by the following example.

> The apparent diffusion coefficient imparted by Brownian motion for spherical particles is about
>
> $$D^1\ (\mathrm{cm}^2/\mathrm{s}) \simeq 5 \times 10^{-9}/d_p \quad , \tag{31}$$
>
> in which d_p = the particle diameter in units of µm. The size of the particle most likely to pass through the 600-gph ROWPU pretreatment system is about 2 µm. The above, therefore, gives a $D^1 \simeq 2.5 \times 10^{-9}\ \mathrm{cm}^2/\mathrm{s}$ at ambient temperatures. Equation 22 gives a cpm^1 of 4600 for this size particle when $Q_p = 1.25$ gpm and $Q_b = 34.5$ gpm. This may be compared with the NaCl cpm of only 1.02 computed previously for the same operating conditions.

Membrane fouling may be caused also by dissolved or colloidal organic compounds as well as suspended solids. Some early tests performed on tubular elements indicated that 0.01 M solutions of organic solutes caused appreciable decreases in the product-water flux when the solutes contained five or more carbon atoms. The product-water flux was restored completely when the solutes were removed from the feed water.[41] This demonstrates that this type of membrane fouling is reversible, unlike the effects of chemical degradation discussed previously.

Sparingly soluble salts may precipitate out onto the membrane wall. The most troublesome salts appear to be calcium carbonate, calcium sulfate, and silica.[44] The precipitation of strontium and barium salts is also possible. Reduced forms of the heavy metals such as iron and manganese may also precipitate if the feed water contains dissolved oxygen.[44]

This type of fouling by precipitates can be controlled to some extent by adding chemicals to the feed water or to a cleaning solution. Citric and ethylenediaminetetraacetic (EDTA) acids (buffered to a pH of 8) are used frequently to dissolve calcium sulfate precipitates, if precipitation is discovered at an early stage.[44] Deposits of calcium carbonate and oxidized heavy-metal ions can be removed with citric acid buffered to a pH of 4. The colloidal films and gels can be removed with hydrochloric acid (pH 2), sodium hydroxide (pH 12), and enzymatic detergents added singly or sequentially.

Some types of films, such as the glycoprotein films produced by microorganisms (biofouling), cannot be removed once they have formed on the membrane.[45] Droplets of oil dispersed in water will also move to the membrane wall, in accord with the principles of concentration polarization, and coat the membrane surface.[12] It is best to avoid oily feed waters.

We did not consider membrane fouling of any type in our calculations for the 600-gph ROWPU tests because (1) the expected life of the elements is relatively brief (2000 h), and (2) the RO elements are cleaned frequently.

MEMBRANE SELECTIVITY

The mass-transport equations (i.e., Eqs. 1-12) were derived from thermodynamic relationships written about the membrane. The solute rejection, on the other hand, cannot be predicted a priori without knowledge of the exact mechanisms by which the solute is separated from the water. Many separation theories have been postulated, including: (1) the solution-diffusion model of Lonsdale; (2) the sieve-transport theory of Banks and Sharples; (3) the pore transport-preferential sorption theory of Sourirajan; (4) the interstitial sieve theory of Schultz and Asunmaa; (5) the dynamic pore theory of Hoenn and co-workers; and (6) various water-clustering theories.[46] The same general form of the mass-transport equations may be obtained from any of these theories, but the mechanisms of solute rejection differ significantly.

According to the model of Lonsdale that was mentioned above, the separation of a solute from water is caused by differences in the solubilities and diffusivities of the solute and water molecules within an isotropic, homogeneous membrane. In the case of the Sourirajan model also mentioned above, the membrane is porous. Both the solvent and solute can be transported through the pores if the pores are not too small. The separation occurs by preferential sorption onto the membrane material.

Transmission electron micrographs of the active skin of RO membranes generally show a nonhomogeneous, clumped or globular structure.[46] This led to the barrier models of Schultz and Asunmaa, and Hoenn and co-workers. In the case of the Hoenn model, the polymeric membrane contains impervious crystalline regions interspersed with amorphous regions. The polymers in the amorphous regions can have thermal motion and can be shoved aside to make room for the permeating molecules. Solute molecules are left behind if the permeability of the solute molecules in the membrane is less than the permeability of the water molecules. Large macromolecules or particles will be rejected at the surface of the membrane.[10]

These physical models do not suffice to explain the details of the molecular processes that may occur at the solid-liquid interface, and it is precisely this knowledge that is required to predict solute rejection.[46] To date, this has not been accomplished, and our knowledge of solute rejection is based primarily on empirical observation.

Strong Electrolytes

The passage of a single salt through an RO membrane may vary with the salt and type of membrane, but the relative ranking of the passage in terms of other single salts remains virtually unchanged regardless of the type of membrane. Sourirajan and Matsuura have attempted to model the barrier to strong electrolytes in dilute solution.[38] In this case, the primary barrier parameters were taken to be the polar interfacial free energies of the ions. The results of this type of analysis are shown in Appendix A (Table A-2) for a cellulose acetate membrane.

Riley and Milstead[31] investigated the effect of salt type and concentration on the transport properties of the UOP TFC membrane housed in the element Model 7005. The electrolytes used in this experiment were NaCl, Na_2SO_4, $MgCl_2$, and $MgSO_4$. The feed concentration of each salt was adjusted to obtain a constant net driving force. The results are shown in Table 6.

The salt passage increased with a decrease in the salt concentration, in agreement with the previous observation for the FT-30 membrane. The salt passage also decreased with an increase in the valence of the ions comprising the salt. The rankings of the salts in terms of decreasing rejection are compared with the predictions of Sourirajan and Matsuura[38] in Table 7. Also shown are the manufacturer's predictions for the type of membrane presently used in the 600-gph ROWPU.[32]

The rankings are identical except for the bicarbonate ion (HCO_3^-). The presence of the bicarbonate ion makes solute rejection predictions difficult because the ionic concentration is constantly changing to maintain equilibrium with the CO_2 and carbonate dissolved in the water. The situation is much more complex when a mix of salts is present in the feed water. Electrical neutrality must be preserved in mixtures of salts as well as

Table 6. Passage of single salts through UOP TFC-801 membrane (Model 7005 element, pH 5.6, 25°C temperature, 1.9-gpm feed flow, and an applied pressure of 400 psig).[a]

Salt	Feed concentration (M)	(mg/L)	Net driving force (psi)	Product-water recovery (%)	Product-water flux (gal/[d • ft^2])	Salt passage (%)
NaCl	0.171	10,000	286	3.3	10.4	0.63
	0.017	1,000	389	3.7	13.9	1.40
Na_2SO_4	0.140	19,890	286	3.2	10.0	0.26
	0.014	1,990	389	4.8	14.8	0.74
$MgCl_2$	0.121	11,520	286	3.2	10.0	0.27
	0.012	1,150	389	4.7	15.0	0.79
$MgSO_4$	0.282	33,950	286	3.1	9.8	0.17
	0.028	3,395	389	4.5	14.3	0.29

[a] Adapted from Riley and Milstead.[31]

Table 7. Comparison of single-salt rejections of the UOP TFC-801 membrane and a cellulose-acetate membrane at 25°C.

Solute	Anticipated by manufacturer[a]	Study of Riley and Milstead[b]	Sourirajan and Matsuura[c]
$MgSO_4$	99.7	99.7	>99.9
Na_2SO_4	99.5	99.3	99.8
$MgCl_2$	99.2	99.2	99.2
$CaCl_2$	99.2	---	99.1
NaF	98.9	---	98.4
NaCl	98.9	98.6	96.8
$NaHCO_3$	98.7	---	98.6
KCl	98.7	---	96.6
$NaNO_3$	98.3	---	93.5

[a] TFC-801 membrane, 400-psi net driving force, pH - 5.7, 10% water recovery, brackish water.[32]

[b] TFC-801 membrane, 389-psi net driving force, pH - 5.6, 3 to 5% water recovery, dilute solutions.[31]

[c] Cellulose acetate, 405-psig applied pressure and dilute solutions (see Table A-2 in Appendix A).[38]

with a single salt, but the degrees of freedom on the system increase by one for every new ionic species added to the system. The salt composition can thus change from one side of the membrane to the other.

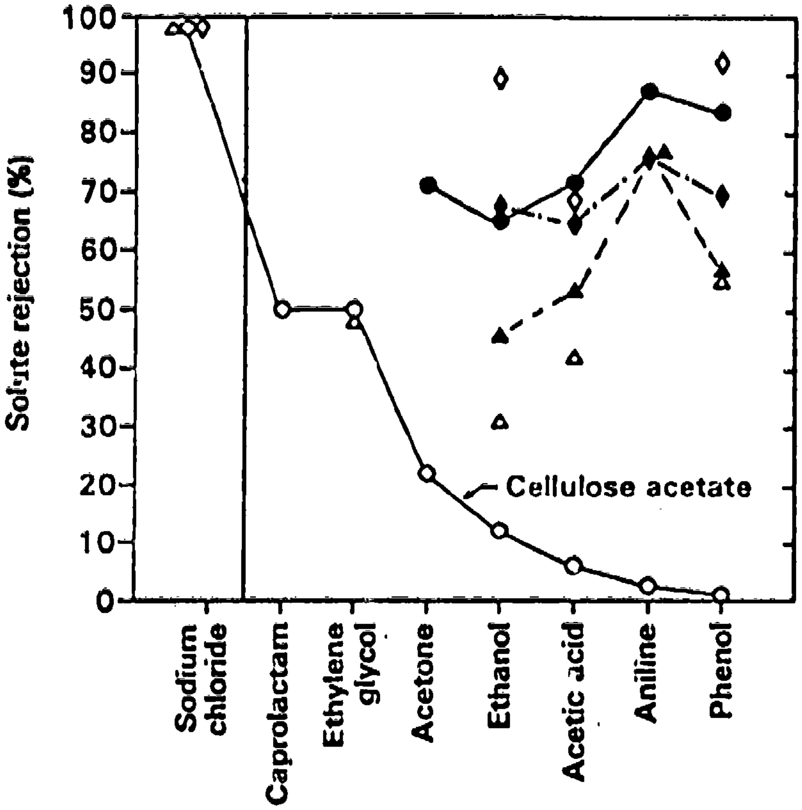
A few of the simpler mixed-solute systems were analyzed by Sourirajan and co-workers for cellulose acetate membranes. These include (1) mixtures including a common ion (NaCl, Na_2SO_4, Na_2CO_3, etc.),[47] (2) mixtures of un-ionized organic compounds with no mutual solute-solute reactions,[48] (3) a mixture of two uni-univalent salts without a common ion,[49] and (4) a mixture of one uni-univalent salt with one divalent-univalent salt.[50] The approach used in mixed-solute systems (1) and (2) consisted simply of treating each solute independently using the basic mass-transport equations. The requirement of electrical neutrality was added to the approach used in mixed-salt systems (3) and (4), increasing the computational effort significantly.

Organic Compounds

As illustrated in Fig. 22, the rejection of organic compounds decreases with decreasing polarity of the compound for cellulose acetate membranes.[32,51] This does not occur for the noncellulosic membranes as evidenced by the other curves in Fig. 22. Some information on the rejection of organic compounds is shown in Table 8 for two types of polyamide membranes (Du Pont B-9 and UOP PA-300). Primarily, the results were similar. Methyl orange was rejected most by both membranes; formaldehyde was rejected least.

Sourirajan and Matsuura[38] computed the rejections of organic compounds expected with a polyamide membrane as shown in Table 9. The results of those computations are important because the organic compounds were classed according to structure (alcohols, ketones, etc.). In general, the rejection increases with the molecular weight for a homologous series of compounds.

Some flat-leaf test results are shown in Table 10 for the composite membranes manufactured by UOP. The composition of the membrane (i.e., polyurea, poly[ether/urea], polyamide, or poly[ether/amide]), was not given; however, according to Goettsch, all of these membranes behave similarly as far as the organic compounds are concerned.[32] The rejections shown are much larger than those in Table 8, but the test conditions differ significantly. Primarily, the rejections appear to be excellent, but Petersen[51] emphasizes that a flat-leaf test rejection should be at least 90%; otherwise, the rejections may be much less in an RO system with an appreciable product-water recovery.



		Temperature (°C)	Pressure (psig)	Product recovery (%)	Ref.
○ CA	(Toray)[a]	25	430	0.5 - 1	b
△ PA	(DuPont)	20	400	0.05 - 0.2	b
▲ PA	(DuPont)	25	600	—	c
◊ PA-300	(UOP)	25	1,000	0.01 - 0.2	b
♦ PA-300	(UOP)	25	600	—	c
● FT-30	(FilmTec)	25	800	0.1 - 1	b

[a] Toray Industries, Japan.
[b] Adapted from Petersen.[51]
[c] Adapted from Goettsch.[32]

Figure 22. Comparison of rejection of some organic compounds by various types of RO membranes. Adapted from Petersen, 1983.[51] Circles indicate cellulose acetate; other symbols indicate noncellulosic membranes.

Table 8. Rejection of organic compounds with two types of polyamide membranes (100-mg/L feed concentration, 600-psig applied pressure, 25°C temperature).[a]

		Rejection (%)	
Chemical group	Solute	UOP PA-300	Du Pont B-9
Aromatic amines	p-Aminodiphenylamine	84.4	90.6
	Aniline	75.8	76.9
	o-Toluidine	75.0	71.0
Alkyl halides	Trichloroethylene	57.3	74.2
	Chloroacetic acid	55.8	61.1
Esters, epoxides, carbamates	Vinyl acetate	75.8	50.3
	Methyl carbamate	45.0	46.0
Pesticides	Malathion	96.1	80.6
Nitro aromatics	p-Nitrophenol	68.2	47.7
Alkyl amines and amides	Di-n-propylamine	92.3	94.0
	Urea	69.5	55.2
Organic acids	Acetic acid	64.5	53.2
Fungal toxins and antibiotics	Gibberellic acid	85.1	88.9
Azo dyes and diazo compounds	Methyl orange	100.0	100.0
Solvents	Ethanol	67.4	45.7
	Formaldehyde	23.6	8.8
	Phenol	69.5	56.9
Detergent	Dodecyl sodium sulfate	96.0	87.7

[a] Adapted from Goettsch.[32]

Table 9. Calculated rejections of organic compounds for a polyamide membrane. Based on theory of Sourirajan and co-workers (450-psig applied pressure and dilute solutions).[a]

Solute	k x 10^4 (cm/s)[b]	Rejection (%)
NaCl	20	98.4[c]
<u>Organic Compound</u>		
Methanol	22.6	25.3
Ethanol	18.7	70.0
1-Propanol	16.5	80.2
1-Butanol	15.0	83.9
1-Pentanol	13.9	89.4
3-Hexanol	13.0	94.7
1-Heptanol	12.3	92.6
1-Octanol	11.7	90.8
Acetone	17.0	64.6
2-Pentanone	14.0	85.5
3-Pentanone	14.0	78.4
Methyl acetate	16.3	81.6
Methyl propionate	14.8	86.4
Methyl butyrate	13.7	93.3
Methyl pentanoate	12.9	94.7

[a] Adapted from Sourirajan and Matsuura.[38]

[b] k = mass-transfer coefficient.

[c] Observed.

Table 10. Rejections of various organic compounds with flat-leaf UOP TFC membranes (1000-psig applied pressure, 25°C temperature).[a]

Solute	Solute concentration (ppm)	pH	Rejection (%)
Urea	1,250	4.9	80 - 85
Phenol	100	4.9	93^{b}
	100	5.5	73
	100	12.0	$>99^{b}$
Glycine	1,350	6.0	99.8
	1,400	5.6	99.7
d,1-Aspartic acid	1,440	3.2	98
Ethyl alcohol	700	4.8	7'
	700	4.7	90
Ethyl acetate	366	6.0	93.8 - 95.3
Methyl ethyl ketone	465	5.2	92 - 94
Acetic acid	190	3.8	65 - 75
Acetonitrile	425	6.3	11 - >25
Acetaldehyde	660	5.8	70 - 75
Dimethyl phthalate	37	6.2	>95
2,4-Dichlorophenoxyacetic acid	130	3.3	88 - >98.5
Citric acid	10,000	2.6	99.5 - 99.9
Alcozyme (soap)	2,000	9.3	99.3
o-Phenylphenol	156	3.5	91.8
	110	6.5	>99
Tetrachloroethylene	104-105	5.9	>93
Trichlorobenzene	100	6.2	>90
Butyl benzoate	220	5.8	99.3

---

[a] Adapted from Goettsch.[32]

[b] The superscript "b" indicates that the membrane used was of the same composition in both cases.

Gases

The concensus is that hyperfiltration does not remove dissolved gases.

PERFORMANCE SPECIFICATIONS

The requirements of the military for reverse osmosis membranes and elements are described in this section, along with the reported specifications for the RO membranes of the three U.S. manufacturers that can now meet the military specifications.

MILITARY SPECIFICATIONS

Military specifications for the 6-in. spiral-wound element presently include (1) a minimum salt rejection of 99% based on the chloride ion for a substitute ocean water containing no heavy metals, (2) a product-water flow rate of 2100 gpd (+450, -250), and (3) a minimum product recovery of 6% per element.[52] The composition of the substitute ocean water is given in Table 3. The pertinent operating conditions are

- Applied pressure: 800 ± 10 psig,
- Feed-solution temperature: 25°C ± 1°C,
- Feed-solution pH: adjusted to 7.0 ± 0.2 with NaOH or HCl.

The elements must be operated for 7 h before measuring the salt rejection.

A minimum RO element life expectancy of 2000 h has been established. Currently, no data are available to determine the actual mean operating life of the Army RO elements.[53]

MANUFACTURER'S SPECIFICATIONS

The manufacturers of the RO membranes are continually improving their products. The most recent results are generally proprietary, however, making the procurement of such information difficult for membrane-comparison purposes. The products of at least three American manufacturers can now meet the military specifications presented in this section. These are the UOP TFC-1501 PA, FilmTec FT-30, and Hydranautics 600 C-2210 CPA elements.[52]

UOP TFC-1501 PA

Today, the Universal Oil Products, Inc. (UOP) TFC-801 membrane is used in the 600-gph ROWPU. This poly(ether/urea) composite membrane was designated by UOP as RC-100 in the early days of its development. During the same period, the UOP polyamide thin-film composite (TFC) membrane was designated as PA-300. The nomenclature used by UOP has changed and can be summarized as follows.[31]

> The first digit in the membrane number indicates the operating pressure (e.g., 8 = 800 psig, 4 = 400 psig, and 2 = 200 psig). The last digit indicates the membrane type where 0 stands for polyurea, 1 for poly(ether/urea), 2 for polyamide, and 3 for poly(ether/amide).

With this systematic terminology, the four types of composite seawater desalination membranes (i.e., polyurea, poly[ether/urea], polyamide, and poly[ether/amide] composites) are designated as TFC-800, TFC-801, TFC-802, TFC-803, respectively. Similarly TFC-400, TFC-401, TFC-402, TFC-403 are the four types of composite membranes used in the high-rejection brackish water systems; and TFC-200, TFC-201, TFC-202, TFC-203 are those used for low-pressure brackish water demineralization.

UOP also uses model numbers to differentiate between the different sizes of spiral-wound elements as shown in Table 5. Model 1501 is currently being used in the 600-gph ROWPU. Today, the tendency is simply to designate all UOP 6-in. elements as TFC-1501 PA and not to identify the composition of the membrane (e.g., 800, 802, etc.). However, in earlier manufacturer's publications, the tendency was to identify the elements only as TFC-1501.

The method used to manufacture the membrane proper is to deposit a thin layer of an aqueous solution of epichlorohydrinethylenediamine condensate (epiamine) on a finely porous surface of polysulfone support and subsequently contacting the epiamine layer with a "water-immiscible solution" of diisocyanate. It was observed that the membrane transport properties varied significantly with changes in composition of this thin-film composite membrane. The advantages claimed for the TFC-801 membrane are good product-water flux and solute rejection, affinity for salt-rejection restoratives, chemical stability, and long-term durability.[31]

Past specifications advertised for the UOP TFC-1501 elements are shown in Table 11, and the most recent are in Table 12. Both are presented here because we are aware that the military purchased a stock of elements when the old specifications were still in force.[32]

Table 11. Former UOP (Fluid Systems Division, Universal Oil Products, Inc., San Diego, CA) specifications for TFC-1501 PA spiral-wound element.[51]

Spiral-wound element specifications	
Element type	TFC-1501 PA
Water source	seawater
Salt rejection	98.9% (98.5% minimum)
Product water flow	2200 gpd
Test conditions	
Salt solution	3.5% NaCl
Pressure	800 psig
Temperature	25°C
Recovery ratio	7%
Solution pH	5.0 to 6.0
Operation time prior to data collection	30 min
Operating conditions	
Applied pressure	820 psig (1000-psig maximum)
Temperature	45°C maximum
pH range	5.5 (4.0 to 6.5)
Feed-water chlorine concentration	0 mg/L
Feed-water turbidity	<0.2 NTU[a] (1-NTU maximum)

[a] NTU = nephelometric turbidity units.

FilmTec FT-30

The FilmTec FT-30 membrane is a composite membrane consisting of three layers: (1) an ultrathin polyamide barrier layer (cross-linked aromatic polyamide), (2) a microporous plastic sublayer, and (3) a reinforcing web.[26] The polyamide barrier contains free carboxylic acid groups and is slightly anionically charged at neutral or alkaline pH levels.[26] Spiral-wound elements up to 8 in. in diameter have been developed by the FilmTec Corporation during the last 4 years for single-pass, seawater and brackish water desalination. The specifications advertised for their 6-in. element are listed in Table 13.

Table 12. Most recent UOP specifications for TFC-1501 PA element for 32,800-mg/L NaCl feed solution, 25°C temperature, pH = 5.7 (after 30 min of operating time).[54]

	Nominal	Minimum	Maximum
Feed-water flow rate (gpm)	22.5	13.5	27.5
Product-water flow rate (gpd)	2200	1875	2550
NaCl rejection (%)	99.3	98.9	--
Operating pressure (psig)	820	--	1000
Pressure drop (psid)	4	--	10
Cleaning flow rate (gpm)	17.5	--	20.0
Cleaning time (min)	45	--	--
Feed-water turbidity (NTU)	<0.2	0	1

Hydranautics 600 C-2210 CPA

Table 14 shows the only published information we located on the Hydranautics membrane or elements.

DISCLAIMER

Rapid improvements in membrane manufacturing techniques date performance data quickly; consequently, the data presented in Tables 11, 12, 13, and 14 may already be dated.

MODE OF OPERATION AND ELEMENT CLEANING

The RO operational limits established by the U.S. Army for the 600-gph ROWPU are summarized in Table 15. The product flow shall not exceed 12 gpm for salt water, or 13.5 gpm for brackish and fresh water. The product flow shall be at least 6 gpm for salt water. The applied pressure shall not exceed 800 psig for salt water, or 500 psig for fresh water. These limits are referred to herein as the "limits of feasible operation" and will be discussed further.

The Marine Corps operates the 600-gph ROWPU differently from trouble-point conditions given in Table 15 for salt water. For example, the U.S. Marine trainees at Camp LeJeune, NC, are instructed to stop applying pressure to the RO elements when product-water flow reaches 10 gpm or the pressure reaches 800 psig, whichever occurs first.[55]

Table 13. FilmTec (FilmTec Corporation, Minnetonka, MN) specifications for FT-30 6-in. diameter spiral-wound element.[51]

Spiral-wound element specifications		
Element type	SW30-6040	BW30-6040
Water source	seawater	brackish water
Salt rejection	98.9% (98.6% minimum)	97.0% (96.0% minimum)
Product-water flow	3000 gpd	3000 gpd
Test conditions		
Salt solution	3.5% NaCl	0.2% NaCl
Pressure	800 psig	225 psig
Temperature	25°C	25°C
Recovery ratio	10%	10%
Solution pH	8.0	8.0
Operation time prior to data collection	30 min	30 min
Operating conditions		
Applied pressure	800 psig (1000 psig maximum)	225 psig (1000 psig maximum)
Temperature	45°C maximum	45°C maximum
pH range	3-11 (1-12 maximum)	3-11 (1-12 maximum)
Feed-water chlorine concentration	0 mg/L[a]	0 mg/L[a]
Feed-water turbidity	≤1 NTU	≤1 NTU

[a] Manufacturer claims that this composite membrane can withstand up to 500 mg/L-h chlorine exposure in brackish water and 1000 mg/L-h in seawater.

The Department of the Army recommends two methods for cleaning the RO elements, with objectives of improving solute rejection and reducing operating pressure. The most common method is to flush citric acid solution through the pressure vessels. An alternative method is to flush the vessels with Triton X-100 soapy cleaning solution. These solutions remove unwanted material from the membrane. According to the U.S. Army Technical Manual TM 5-4610-215-10, the ROWPU RO elements should be cleaned according to the following schedule[6]:

Table 14. Hydranautics (Hydranautics, Goleta, CA) specifications for 600 C-2210 CPA 6-in. diameter spiral-wound element.[51]

Spiral-wound element specifications	
Element type	600 C-2210 CPA
Water source	--
Salt rejection	99.0% (98.5% minimum)
Product-water flow	2200 gpd
Test conditions	
Salt solution	3.5% NaCl
Pressure	800 psig
Temperature	25°C
Recovery ratio	7%
Solution pH	5.0 to 6.0
Operation time prior to data collection	30 min
Operating conditions	
Applied pressure	800 psig (1000 psig maximum)
Temperature	45°C maximum
pH range	5.0 to 6.0 (4.0 to 8.5 maximum)
Feed-water chlorine concentration	0 mg/L
Feed-water turbidity/silt density index	<1 NTU/4.0 SDI

Table 15. Normal and trouble-point gauge readings for the 600-gph ROWPU.[a]

Gage/indicator	Normal reading	Trouble-point reading[b]
Cartridge filter	1 to 20 psid	Over 20 psid
Multimedia filter	0 to 10 psid	5 psid over first reading
Raw-water flow	27 to 33 gpm	Drop to 25 gpm or less
Brine flow	16 to 24 gpm	Below 15 gpm
Product-water flow		
Salt water	6 to 12 gpm	Above 12 gpm
Fresh water	Up to 13.5 gpm	Above 13.5 gpm
Brackish water	Up to 13.5 gpm	Above 13.5 gpm
RO pressure		
Salt water	Not to exceed 800 psig	Above 800 psig
Fresh water	Not to exceed 500 psig	Above 500 psig
RO vessels	50 to 100 psid	Above 100 psid
Product-water TDS	Below 1500 ppm	Above 1500 ppm

[a] Reproduced from U.S. Army Technical Manual TM 5-4610-215-10.[6]

[b] Point at which pressure to RO elements should no longer be applied.

- Once a week; or
- After 140 h of operation; or
- Whenever pressure in the RO vessels rises to either 900 psi for seawater or 600 psi for fresh water; or
- When product-water output drops several gallons per min, with no change in temperature; or
- When brine flow increases noticeably, and the adjustment of the product-flow valve does not correct the product-water flow.

The cleaning procedures recommended by the manufacturer of the Model 1501 elements are similar to those employed by the U.S. Army.[30] Citric acid or phosphoric acid, adjusted to pH 2.5 with ammonium hydroxide (NH_4OH), are recommended for the removal of acid-soluble substances such as metal hydroxides and calcium carbonate. This solution may cause a temporary increase in membrane salt passage and/or water flux beyond specifications, but this condition should not last more than 24 h.

A caustic solution representing a mixture of borax, a sodium salt of EDTA (Dow Chemical-Versene 200, or equivalent) and trisodium phosphate (TSP) is specified for organic substance and microbiological slime removal. Sodium tripolyphosphate (STPP) may be substituted in part or entirely for the TSP. The manufacturer also recommends that, in general, the acidic solution be applied before the caustic solution.

Both solutions may be used at temperatures up to 50°C for 45 min. System pressure should not exceed 60 psig. The recommended cleaning feed-flow rate for the UOP Model 1501 element is 4.0 $m^3/(h \cdot tube)$.

PERFORMANCE DATA PERTINENT TO 600-GPH ROWPU

Using a mathematical model called CALIBRATOR, which we developed for this project, we analyzed data published relative to the 600-gph ROWPU, or the elements contained therein. The general approach was to adjust the A and B parameters until the computed product-water flows and salt passages matched those observed. A brief description of CALIBRATOR is given in Appendix B.

STUDY ON UOP ELEMENTS

Riley and Milstead published the results of field tests performed on various UOP elements at the Office of Water Research and Technology (OWRT) Seawater Test Facility at Wrightsville Beach, NC.[31] The purposes of the tests were to evaluate (1) new adhesives and membrane substrates; (2) effects of citric acid cleaning; (3) continuous addition of chlorine dioxide, sodium bisulfite, and rejection restoratives; and (4) effects of long-term operation on element stability. The latter included the TFC-1501 elements currently used in the 600-gph ROWPU. Six such elements were installed in series in a single pressure vessel and subjected to a feed-water pressure of 800 psi for 10,000 h.

The pretreatment methods included

- Screen filtration (1 in.),
- Chlorine addition at intake,
- Screen filtration (#40 mesh),
- Clarification (20 mg/L alum),
- Dual-media sand filtration,
- Manganese-zeolite filtration (iron removal),

Table 16. Early data reported by Riley and Milstead[31] for UOP TFC-1501 element (800-psi applied pressure, 18-gpm feed flow, pH 5.2 to 5.7, seawater).

Time (h)	Temp. (°C)	TDS in feed (%)	Product flow (gpm)	TDS passage (%)	A (gal/[ft^2 • d • atm])	B(TDS) (ft/d)
400	28	3.77	6.8	1.67	0.48	0.017
800	27	3.43	6.2	1.81	0.41	0.018
1200	30.8	3.44	6.2	2.13	0.40	0.021
1600	31.7	3.47	6.25	2.20	0.47	0.022
2000	31.5	3.50	6.3	2.16	0.47	0.021
2400	27	3.24	5.8	2.08	0.39	0.019
2800	31	3.28	5.9	2.20	0.42	0.021
1[a]	22.5				0.52	

[a] Estimated from results of tests performed on some elements prior to long-term testing.[31]

- Activated charcoal (chlorine removal),
- Sulfuric acid injection, and
- Cartridge filtration (5 μm).

The pH was decreased to a level between 5.7 to 5.2 with sulfuric acid. The salt concentration and temperature of the feed water varied with the season. The TFC-801 membranes contained in the elements were cleaned only once during the 10,000 h of operation.

CALIBRATOR was used to compute the A and B parameters for the first 2800 h of operation when the temperature was fairly constant at about 30°C. The results are shown in Table 16.

TEST OF ROWPU ELEMENTS AT ABERDEEN PROVING GROUND

Carmer[56] presents the results of a recent study performed by the U.S. Army at the Aberdeen Proving Ground, Aberdeen, MD, for the U.S. Army Belvoir Research and Development Center (formerly U.S. Army Mobility Equipment Research and Development

Table 17. Summary of results of diisopropylmethyl phosphonate (DIMP) studies with UOP TFC-1501 element (400-psig applied pressure; averages for four samples per run).[a]

	Run number		
	1	2	3
Test water	Tap	Tap	Tap + 5000 ppm NaCl
Temperature (°F)	70-76	76-81	76-79
Feed flow (gpm)	14	14.8-15	15
Product flux (gal/[d • ft^2])	18	18	16
Product recovery (%)	14.3	13.3-13.5	11.7
Concentrations			
DIMP (mg/L)			
Feed water	23.53	22.6	22.0
Permeate	0.100	0.120	0.080
Alkalinity as $CaCO_3$ (ppm)			
Feed water	26	26	27
Permeate	1.8	0.25	0.16
Concentrate	29.9	28.5	29
TDS (ppm)			
Feed water	245	243	3388
Permeate	<10	<10	46
Concentrate	280	273	3625
pH			
Feed water	7.69	7.70	7.44
Permeate	5.58	5.32	5.66
Concentrate	7.61	7.62	7.42
Solute rejections (%)			
DIMP	99.6	99.5	99.6
TDS	--	--	98.6
Membrane parameters			
A (gal/[d • ft^2 • atm])	0.68	0.68	--
B (ft/d)[b]	--	--	--

[a] Adapted from Carmer.[56]

[b] B is the TDS transport parameter.

Command) at Fort Belvoir, VA. The primary objective of this work was to determine the removals of three chemical warfare agents and one pesticide with the UOP TFC-1501 PA element. The removal of TDS was also recorded. The chemicals tested were

Table 18. Summary of results of Sarin (GB) studies with UOP TFC-1501 element (400-psig applied pressure; NaCl added to tap water; averages for four samples per run).[a]

	Run number	
	1	2
Temperature (°F)	81-84	74-79
Feed flow (gpm)	14.9	14.8
Product flux (gal/[d • ft^2])	16.4	15.5
Product recovery (%)	12.1	11.5
Concentrations		
GB(mg/L)		
Feed water	17.34	18.44
Permeate	0.37	0.36
Alkalinity as $CaCO_3$ (ppm)		
Feed water	23	22
Permeate	2.3	2.3
Concentrate	25	24
TDS (ppm)		
Feed water	6664	6347
Permeate	68.2	66.9
Concentrate	7157	7186
pH		
Feed water	7.51	7.37
Permeate	6.68	6.36
Concentrate	7.32	7.30
Solute rejections (%)		
GB	97.85	98.0
TDS	99.0	98.9
Membrane parameters		
A (gal/[d • ft^2 • atm])	--	0.72
B (ft/d)[b]	--	0.020

---

[a] Adapted from Carmer.[66]

[b] B is the TDS transport parameter.

Table 19. Summary of results of Soman (GD) studies with UOP TFC-1501 element (400-psig applied pressure; NaCl added to tap water; averages for six samples per run).[a]

	Run number	
	1	2
Temperature (°F)	76–79	76–79
Feed flow (gpm)	14.8	14.8
Product flux (gal/[d • ft^2])	13.7	13.7
Product recovery (%)	10.1	10.1
Concentrations		
GD (mg/L)		
Feed water	21.50	17.83
Permeate	0.022	0.029
Alkalinity as $CaCO_3$ (ppm)		
Feed water	25	22
Permeate	6	3
Concentrate	29	25
TDS (ppm)		
Feed water	6279	6018
Permeate	71.3	41.1
Concentrate	7137	6783
pH		
Feed water	7.74	7.65
Permeate	6.78	6.24
Concentrate	7.84	7.71
Solute rejections (%)		
GD	99.90	99.86
TDS	98.9	99.3
Membrane parameters		
A (gal/[d • ft^2 • atm])	0.63	0.62
B (ft/d)[b]	0.019	0.011

[a] Adapted from Carmer.[56]

[b] B is the TDS transport parameter.

Table 20. Summary of results of VX studies with UOP TFC-1501 element (400-psig applied pressure; NaCl added to tap water; averages for six samples per run).[a]

	Run number	
	1	2
Temperature (°F)	72-86	70-72
Feed flow (gpm)	14.6-15	14.7
Product flux (gal/[d • ft^2])	10-14	10
Product recovery (%)	7.5-10	7.5
Concentrations		
VX (mg/L)		
Feed water	21.0	24.7
Permeate	0.21	0.18
Alkalinity as $CaCO_3$ (ppm)		
Feed water	25	26
Permeate	3	2.3
Concentrate	28	27
TDS (ppm)		
Feed water	5660	6384
Permeate	74	68
Concentrate	6193	7167
pH		
Feed water	7.60	9.08
Permeate	5.50	6.04
Concentrate	7.64	8.69
Solute rejections (%)		
VX	99.1	99.3
TDS	98.7	98.9
Membrane parameters		
A (gal/[d • ft^2 • atm])	0.53	--
B (ft/d)[b]	0.019	--

---

[a] Adapted from Carmer.[56]

[b] B is the TDS transport parameter.

- DIMP (diisopropylmethyl phosphonate)--pesticide,
- GB (Sarin)--nerve gas, chemical warfare agent,
- GD (Soman)--nerve gas, chemical warfare agent, and
- VX [o-ethyl s-(2-diisopropylaminoethyl) methylphosphonothioate]-- nerve agent.

The feed water was a dechlorinated tap water with an alkalinity of about 26 ppm as $CaCO_3$ and a TDS of about 245 ppm, as shown in Runs 1 and 2 of Table 17. The tap water was seeded generally with NaCl to increase the TDS to brackish-water levels, and one element was tested during each run. The applied pressure, temperature, and feed flow were held as constant as possible at 400 psig, 25°C (77°F), and 15 gpm, respectively. All process streams were sampled hourly over a test period of 6 h. The results of these tests are summarized in Tables 17 to 20. The solids balances were checked with Eqs. 6 and 8, and the A and B parameters were computed for those runs having errors in the solids balances of less than about 5%. The A and B parameters are also shown in the tables.

HIGH-TEMPERATURE STUDIES ON ROWPU ELEMENTS

Goto[57] studied the high-temperature capability of the UOP TFC-1501 element at ~130°F (54°C), which was significantly higher than the maximum operating temperature of 113°F (45°C) recommended by the manufacturer Potomac River water was filtered through a pressurized diatomaceous earth filter and used as the test-feed water. The water was fortified with dehydrated sea salt (99% NaCl) [sic] to produce a TDS ranging from about 17,900 to 23,700 mg/L. The temperature of the feed water was controlled by a chiller (10-hp Koolant Chiller, Model AF 10000). The elements were operated 10 to 12 h/d for a period sufficient to yield a total operating time of 200 h at the high temperature. When the element was not in operation, the high-temperature feed water was circulated through the system to maintain the feed-water temperature. As a result, the elements were exposed to a high-temperature NaCl solution for over 400 h (but not to the pressure).

Two elements were housed in a single pressure vessel of the type used in the ROWPU. The test was begun at an applied pressure of 700 psig and the ambient temperature. As the feed-water temperature was raised to 130°F, the pressure was lowered to 600 psig in order not to exceed the ROWPU design production rate of 1.5 gpm per element (12 gpm for the ROWPU) as shown in Fig. 23. The feed flow was maintained approximately constant at 20.6 to 20.9 gpm.

Toward the end of the high-temperature run, a sample of the feed water was analyzed gravimetrically for TDS. The results showed a TDS of 26,186 mg/L as compared with the 17,900 to 23,700 mg/L determined by conductivity. The method used to measure

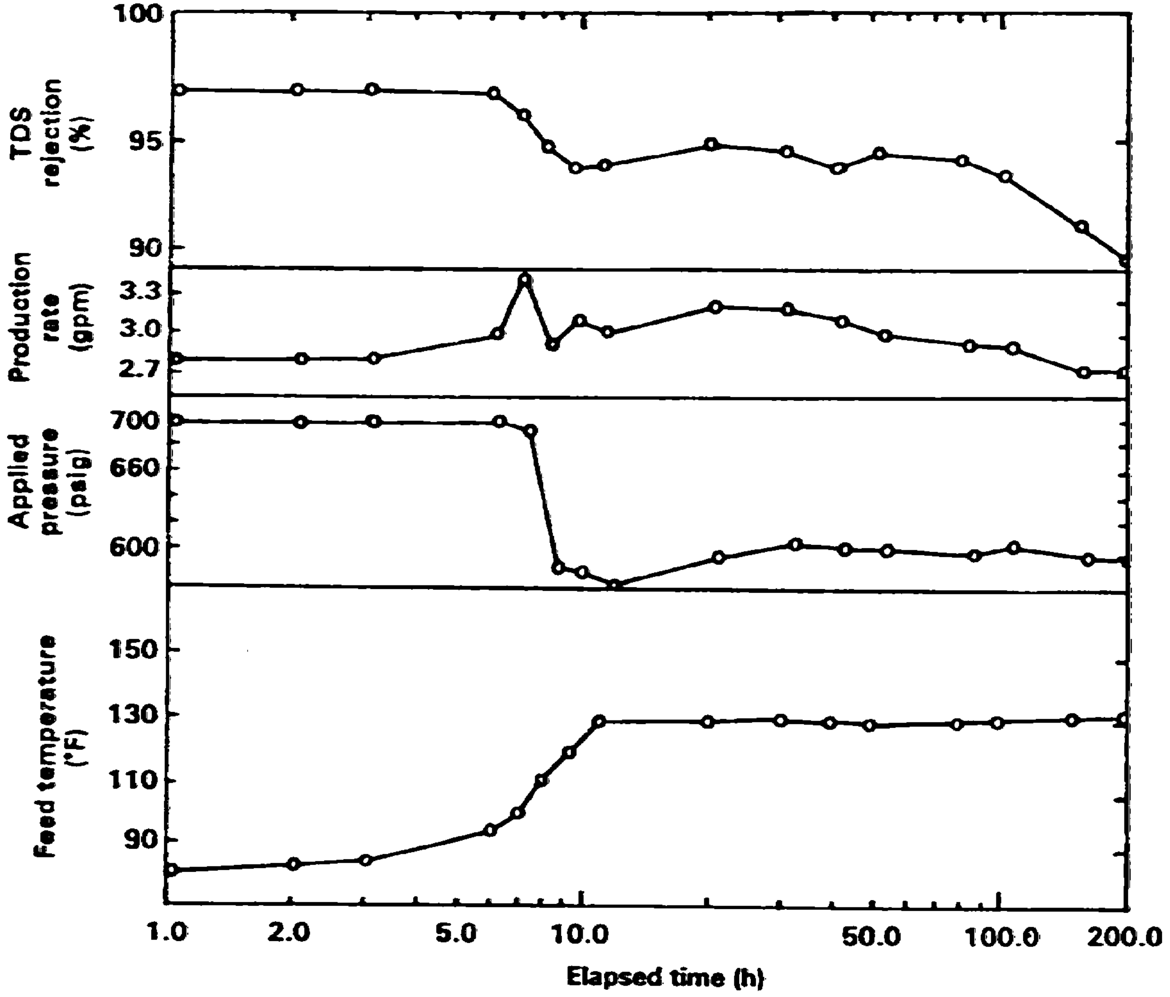


Figure 23. High-temperature performance of two UOP TFC-1501 elements in series. Reprinted from Goto, 1982.[57]

Table 21. Chemical analysis of the Potomac River water and RO feed-, product-, and brine-water samples for high-temperature (130°F) run.[a]

Characteristic	Potomac River	Feed	Product	Brine
pH	7.8	7.6	5.6	7.8
Turbidity (NTU)	3.3	0.3	0.06	0.23
TDS (mg/L)	160	26,186	2,069	31,735
Chloride (mg/L)	20	15,500	1,230	17,500
Cu (mg/L)	<0.01	0.20	<0.01	0.26
Fe (mg/L)	<0.01	0.10	0.05	0.12

[a] From Goto.[57]

Table 22. Element performance at room temperature after 200 h of high-temperature testing (average of 1-h operation, feed flow of 20 gpm, feed-salt concentration of 26,500 mg/L).[a]

	Element number	
	78690	78761
Temperature (°F)	83	80
Applied pressure (psig)	815	803
Product-water flow (gpm)	1.1	1.2
Salt passage (%)	1.89	2.04
A (gal/[d • ft^2 • atm])	0.30	0.34
B (ft/d)	0.024	0.029

[a] Data from Goto.[57]

TDS with conductivity was then revised so that the TDS measurement would correspond to the linear portion of the conductivity-concentration calibration curve. The chemical analysis of the water tested during this high-temperature run is shown in Table 21.

The two elements were then pulled out of the pressure-containment vessel and inspected; one of the elements had telescoped slightly. The elements were tested separately, and the results are shown in Table 22. Goto[57] concluded that the performance of the telescoped element had not been degraded seriously.

Table 23. A and B parameters for high-temperature data of Goto.[57]

Elapsed time[a] (h)	Temp. (°F)	A (gal/[d • ft^2 • atm])	B (TDS) (ft/d)
10	129	0.93	0.062
20	130	0.94	0.059
30	129	0.91	0.067
40	129	0.87	0.069
50	122	0.88	0.062
60	124	0.85	0.072
70	129	0.85	0.063
80.5	131	0.81	0.077
90.5	130	0.82	0.074
100.5	126	0.77	0.055
110.5	126	0.73	0.069
120.5	131	0.73	0.081
130.5	125	0.75	0.066
140	132	0.77	0.089
150	130	0.75	0.084
160	129	0.72	0.073
170	130	0.76	0.090
180	131	0.78	0.104
190	131	0.76	0.105

[a] After attaining high temperature.

CALIBRATOR was used to compute the A and B parameters during the high-temperature experiment and after the elements were pulled from the pressure vessel. A constant feed concentration of 26,186 mg/L (25,780 ppm) was assumed for the high-temperature run as indicated in Table 21. The parameters are shown in Tables 22 and 23. With time, the A parameter decreased significantly and the B parameter increased (Table 23).

TEST OF 600-GPH ROWPU AT COURTHOUSE BAY, NC (DECEMBER 1982)

Engineers from V. J. Ciccone and Associates, Inc. (VJCA), Woodbridge, VA, conducted three tests on a 600-gph ROWPU at the U.S. Marine Corps Engineer Training

Table 24. Courthouse Bay water-quality analyses (14-16 December 1982).[a]

Constituent	Concentration
Chloride (mg/L)	15,800
Sulfate (mg/L)	1,375
Magnesium (mg/L)	980
Calcium (mg/L)	676
Alkalinity (mg/L as $CaCO_3$)	97
Conductivity (µmho/cm)	44,200-50,400
TDS (mg/L)	23,300-31,846
pH	7.6

[a] Adapted from VJCA.[58]

Facility adjacent to Courthouse Bay in Camp LeJeune, NC. Estuarine water from Courthouse Bay was used in these tests. The reported composition of this water is shown in Table 24.

Details follow for each of the three tests, which ranged from 3 to 6 h in duration.

14 December: Operation in accordance with existing operations manual except that no calcium hypochlorite was added to product water (Table 25).

- Polymer dosage: 1.5 mg/L
- Sodium hexametaphosphate dosage: 1.8 mg/L
- Range for product-flow rate: 8.26 to 10 gpm
- Pressure: 810 to 775 psig
- Temperature range: 7 to 9°C (pressure had to be reduced to keep product-flow rate constant when feed-water temperature increased during tests).

15 December: As above, plus the addition of citric acid to the feed water (Table 26).

16 December: As on 14 December plus an increase in applied pressure to 800 psig to obtain overall 35% product recovery. Rainfall decreased salinity of feed-water during this run (Table 27).

On 14 December, the observed RO membrane performance was stable with respect to the quantity and quality of water produced for more than 6 h. However, the 8.26-gpm

Table 25. Summary of operating and performance data for 600-gph ROWPU, Courthouse Bay, NC (14 December 1982).[a,b]

Item	Feed	Brine	Product
Flow (gpm)	34.25	25.98	8.26
Operating pressure (psig)	787	--	--
Temperature (°C)	7.0	--	8.2
pH	7.6	--	7.5
Turbidity (NTU)	1.7	0.5	0.2
Alkalinity (mg/L)	97	--	7
Total hardness (mg/L)	6,360[c]	--	9
Sulfate (mg/L)	1,375	--	Trace
Chloride (mg/L)	16,780	--	221
Sodium (mg/L)	--	--	144[d]
Total dissolved solids (mg/L)	31,846[c]	--	--
Conductivity (μmho/cm)	50,400	66,132	847
Product recovery (%)	24.1		

Membrane parameters

$A = 0.37$ gal/(d • ft^2 • atm)

B(TDS) = 0.013 ft/d

B(Cl$^-$) = 0.015 ft/d

---

[a] Adapted from VJCA.[58]

[b] Citric acid was not added to feed water, and no calcium hypochlorite was added to product water.

[c] Reported by U.S. Army Mobility Equipment Research and Development Command Laboratory as backup to VJCA analysis.

[d] Estimated by VJCA.[58]

product-flow rate was higher than envisaged (6.5 gpm) at a feed-water temperature of 7.0°C. We believe that this may have been caused by a feed-flow rate greater than the design value of 30 gpm; this proved to be correct (see Tables 25, 26, and 27). (The feed-water rate could not be adjusted by the operator because the shaft speed of the positive-displacement RO pump determined the volumetric delivery to the RO elements.)

Table 26. Summary of operating and performance data for 600-gpm ROWPU, Courthouse Bay, NC (15 December 1982).[a,b]

Item	Feed	Brine	Product
Flow (gpm)	34.68	26.18	8.58
Operating pressure (psig)	744	--	--
Temperature (°C)	9.0	--	9.8
pH	7.3	5.9	5.4
Turbidity (NTU)	2.2	1.1	0.2
Alkalinity (mg/L)	97	--	3
Total hardness (mg/L)	--	--	9
Sulfate (mg/L)	--	--	Trace
Chloride (mg/L)	14,200	--	149
Sodium (mg/L)	--	--	98[c]
Total dissolved solids (mg/L)	28,952[c]	--	--
Conductivity (μmho/cm)	46,825	60,550	582
Product recovery (%)	24.7		

Membrane parameters

$A = 0.40$ gal/(d • ft^2 • atm)

B(TDS) = 0.010 ft/d

B(Cl$^-$) = 0.012 ft/d

---

[a] Adapted from VJCA.[58]

[b] Citric acid was added to feed water in accordance with manufacturer's recommendations, and no calcium hypochlorite was added to product water.

[c] Estimated by VJCA.[58]

The product-water flow increased slightly on 15 December. This increase was attributed to the increase in feed-water temperature from 7.0 to 9.0°C, and to possible variation in operator adjustment of the flow-rate indicator. The chloride rejection increased as a result of a decreased feed-water pH as anticipated.

A comparison of Tables 26 and 27 shows that the salt content (as measured by conductivity) of the product water increased (from 582 to 836 μmho/cm) as did the product-flow rate (from 8.6 to 12 gpm) as a result of increasing the operating pressure

Table 27. Summary of operating and performance data for 600-gph ROWPU, Courthouse Bay, NC (16 December 1982).[a,b]

Item	Feed	Brine	Product
Flow (gpm)	34.21	22.24	11.98
Operating pressure (psig)	857	--	--
Temperature (°C)	13	--	14
pH	7.4	--	7.2
Turbidity (NTU)	6.0	1.4	0.4
Alkalinity (mg/L)	78	--	4
Total hardness (mg/L)	5,060[c]	--	8
Sulfate (mg/L)	--	--	Trace
Chloride (mg/L)	15,952	--	230
Sodium (mg/L)	--	--	150[d]
Total dissolved solids (mg/L)	28,300[c]	--	--
Conductivity (μmho/cm)	45,867	66,667	836
Product recovery (%)	35.0		

Membrane parameters

$A = 0.45$ gal/(d • ft^2 • atm)

$B(TDS) = 0.019$ ft/d

$B(Cl^-) = 0.021$ ft/d

---

[a] Adapted from VJCA.[58]

[b] Citric acid was not added to feed water.

[c] Reported by U.S. Army Mobility Equipment Research and Development Command Laboratory as backup to VJCA analysis.

[d] Estimated by VJCA.[58]

from 744 to 857 psig. The temperature of the feed water was also highest in the third run (13°C). However, even at this high product-flow rate, the researchers indicated that the product water was acceptable for drinking.[58]

CALIBRATOR was used to compute the A and B parameters shown in Tables 25 to 27. The B parameter for TDS was estimated from the observed chloride ion concentrations by assuming that the salt in the product water was virtually all NaCl. This approximation is good because most of the ions that are separated from the product water are divalent, strong electrolytes, and thus are better rejected than sodium and chloride.

FIELD OPERATIONS OF 600-GPH ROWPU AT ASCENSION ISLAND (NOVEMBER THROUGH DECEMBER 1982)

Two 600-gph ROWPU's were operated on Ascension Island without trouble for a total of 105 h during the period 15-26 November 1982 by the U.S. Air Force.[59] The salt passage then increased dramatically (>5000 ppm), and the ROWPU's were shut down and repaired. The ROWPU's were operated again for 35 h during 3-4 December 1982, and then were shut down until 16 December 1982. Another failure was evidenced at that time with the passage of large salt concentrations. The system was repaired and the ROWPU's were operated successfully for another 81 h until 21 December 1982. The system failures apparently were caused by leaks into the product-water tubes owing to structural failure of an end-cap product-water seal.[59]

The ROWPUs' operational and performance data were taken on an hourly basis whenever possible by the Air Force personnel. Unfortunately, water temperature and feed-water TDS could not be ascertained until 16 December 1982 because of logistical problems.[59] The data for one of the two 600-gph ROWPU's were averaged for two periods, 18 November to 4 December 1982 and from 16 to 21 December 1982, as shown in Table 28. Observations made during system failures were not included in these averages.

The feed and product waters were sampled for independent quality analyses on 20 and 21 December 1982.[60] The results of those analyses are summarized in Table 29. The salt composition was typical for seawater, except that the calcium was greater and the magnesium was less than might be expected. The gravimetric TDS of the feed water was significantly greater than the conductivity TDS reported by the ROWPU operator (3.85 vs 3.4%). An ion balance between the cation and anion concentrations shown in Table 29, assuming that the ratios of Na^+ and K^+ to total TDS were the same as encountered in standard seawater, checks within 2.3% for the feed water. Likewise, the sum of the weights of all of the ions checks within 2.2% of the TDS data shown in the table. It was concluded that the water-quality analyses are reasonable.

CALIBRATOR was used to compute A and B parameters for the data shown in Table 28. It may be noted that the gravimetric TDS data yield a significantly higher estimate of the water-flux parameter A, which demonstrates that the accuracy of the water-quality analyses can be important when assessing the performance of the ROWPU.

Table 28. Summary of operating and performance data for one of the two 600-gph ROWPU's operated at Ascension Island (34- to 35-gpm feed flow).[a]

Item	1982 18 November-4 December	1982 16-21 December
Run time (h)	121	81
Feed water		
Pressure (psig)	747	798
Temp. (°C)	25[b]	25.9
pH	Citric acid added	Citric acid added
TDS (%)	3.4[b]	3.4 3.851[c]
Product water		
Flow (gph)	420	520
pH	6.7	6.1
TDS (%)	0.0477	0.0460 0.0421[c]
Membrane parameters		
A (gal/[d • ft^2 • atm])	0.41	0.46 0.58[c]
B(TDS) (ft/d)	0.013	0.015 0.012[c]

[a] Data from VJCA.[59]

[b] Assumed value.

[c] Based on separate gravimetric analysis for TDS (see Table 29).

FIELD OPERATION OF 600-GPH ROWPU AT BEIRUT, LEBANON (1983)

Two 600-gph ROWPU were used by the U.S. Marines to treat a fresh-to-brackish well water in Beirut, Lebanon.[59] The operating and performance data reported by the ROWPU operators are summarized in Table 30. The applied pressures and feed-water temperatures were not recorded, making it difficult to judge the performance of the

Table 29. Ascension Island water-quality analyses (20-21 December 1982).[60]

Characteristic	Raw water	Product water[a] Unit #1	Product water[a] Unit #2
pH	7.4	6.0	6.1
TDS (mg/L)			
(Myron L-Meter)	39,000	370	420
(gravimetric)	39,564	388	464
Conductivity (μmho/cm)	47,800	650	780
Chloride (mg/L)	22,334	255	311
Sulfate (mg/L)	3,300	0	0
Alkalinity (mg/L as $CaCO_3$)	106	4	2
Calcium (mg/L)	590	2.4	2.4
Magnesium (mg/L)	1,287	3.4	5.3

[a] Two 600-gph ROWPU's were operated.

ROWPU's with this type of feed water. The assumed values of 400 psig for applied pressure and 24°C for temperature shown in the table were recommended by VJCA.[59] Apparently, citric acid was added continuously to the feed water. No information was provided concerning RO failures, if any, for these units.

The results of analyses performed on feed- and product-water samples of the Beirut well water (collected on 5 May 1983) are summarized in Table 31. The gravimetric TDS concentrations shown in Table 31 were substantially less than those reported by the ROWPU operators during the same period of time (1019 mg/L vs 2800 ppm, respectively, for the feed water, and 19 mg/L vs 55 ppm, respectively, for the product water). The number of ions analyzed in the laboratory were insufficient to permit an accurate evaluation of the gravimetric TDS data. Also, the alkalinity represents a fair portion of the total ions, and the feed water pH was lowered with citric acid. This means that the true feed-water TDS actually encountered by the membrane differed appreciably from the raw-water TDS shown in the table.

The estimates of the parameters A and B obtained using CALIBRATOR are shown for the ROWPU equipment operated in Beirut in Table 30. The values of A and B increased through the summer and then decreased abruptly after 16 October 1983. This activity indicates some kind of seasonal trend associated with temperature. A constant temperature of 24°C was assumed because the temperature of the ground water

Table 30. Summary of operating and performance data for 600-gph ROWPU, Beirut, Lebanon (1983).[a]

	30 April-3 Sept.	4 Sept.-15 Oct.	16 Oct.-12 Nov.
Run time (h)	621	118.5	72
Feed water			
Pressure (psig)	400[b]	400[b]	400[b]
Temp. (°C)	24[b]	24[b]	24[b]
pH		Citric acid added	
TDS (%)	0.261 0.102[c]	0.241	0.245
Product water			
Flow (gph)	600	760	480
pH	5.5	5.5	5.5
TDS (%)	0.0055 0.0019[c]	0.0076	0.0041
Membrane parameters			
A (gal/[d • ft^2 • atm])	0.51 0.48[c]	0.64	0.41
B(TDS) (ft/d)	0.026 0.024[c]	0.048	0.016

[a] Data from VJCA.[59]

[b] Assumed value, recommended by VJCA.

[c] Based on separate gravimetric analysis for TDS (see Table 31).

should not alter much with the season.[59] It appears now that the water pumped from the aquifer was stored above ground before treatment.[62] In this case, the water temperature would vary with the season.

Table 31. Water-quality analyses, Beirut, Lebanon (5 May 1983).[61]

Characteristic	Raw water	Product water[a]	
		Unit #14	Unit #30
pH	6.7	5.2	5.2
TDS (mg/L)			
(Myron L-Meter)	1000	21	21
(gravimetric)	1019	--	19
Conductivity (μmho/cm)	1410	28.5	27
Chloride (mg/L)	346	3.5	3.5
Sulfate (mg/L)	44.2	--[b]	--[b]
Alkalinity (mg/L as $CaCO_3$)	274	1.0	1.0
Calcium (mg/L)	170	2.4	2.4
Magnesium (mg/L)	6.24	1.5	1.5

[a] Two 600-gph ROWPUs were operated.

[b] Below detectable limits.

TESTING OF 600-GPH ROWPU AT CAMP LEJEUNE, NC (FALL OF 1982)

Two 600-gph ROWPUs were tested at Camp LeJeune, NC, during the period 30 August to 29 October 1982.[59] The results of these tests are significant because TDS concentrations as high as 1500 ppm were found in the product water as illustrated in Table 32.

The feed water was pumped from Courthouse Bay into feed-water storage tanks. The composition of this water matches that of the estuarine seawater for this location reported in Table 24. The TDS ranged from 35,000 to 50,000 ppm during the test period, and the product water TDS was commonly less than 1000 ppm, except for the period October 4-8, 1982, shown in Table 32. The TDS concentrations were estimated in the field with a conductivity meter; samples were not collected for an independent water-quality analysis in a laboratory.

CALIBRATOR did not converge to a solution for the data listed in Table 32. It appears that the reported product-water flows were too large for the observed pressures, temperatures, and feed-water salt concentrations.

Table 32. Operating and performance data for one of the two 600-gph ROWPUs operated at Camp LeJeune, NC, during two periods in the fall of 1982.[a]

	Periods of operation			
	September 10-17		October 4-8	
Run time (h)	11	11	11	11
Feed water				
Pressure (psig)	740	770	880	895
Temp. (°C)	34.4	34.1	25.0	25.0
pH	Not recorded		Not recorded	
TDS (%)	5.0	5.0	5.0	5.0
Product water				
Flow (gph)	720	720	720	720
pH	Not recorded		Not recorded	
TDS (%)	0.090	0.095	0.150	0.150
Membrane parameters				
A (gal/[d • ft^2 • atm])	No computer solution possible			
B (TDS) (ft/d)	No computer solution possible			

[a] Data from VJCA.[59]

FLAT-LEAF TEST OF UOP RC-100 MEMBRANE

High-temperature flat-leaf tests were performed on samples of the UOP RC-100 membrane by Leban and Wydeven.[63] The feed water contained 1000 mg/L sodium chloride, and the membrane samples were subjected to a pressure of 600 psig and a temperature of 74°C for 200 h (no pH data given). The product recoveries were less than 0.1% for two 15-cm^2 test cells placed in series.

The observed membrane compaction factor "n" (Eq. 29) was -0.090.[63] No change in salt rejection was claimed, but a close inspection of the data plot given in their paper indicates a slight decline in NaCl rejection with time.

PARAMETRIC ADJUSTMENTS

The observed A and B parameters must be corrected to some standard operating conditions before they can be used for comparative or predictive purposes.

pH

The B parameters were adjusted for pH with Eq. 27. The A parameter was assumed to be independent of pH.

TEMPERATURE

The A and B parameters were corrected for temperature with Eqs. 24 and 25. At first, the manufacturer of the TFC-1501 PA elements recommended an Arrhenius law temperature coefficient of 2000 to 3000 K for A and twice that for B.[32] Subsequently, a temperature coefficient of 3470 K was recommended for the product flow (Eq. 26).[39]

Table 33 shows a check on these values for the data of VJCA (Courthouse Bay),[58] Goto,[57] and Leban and Wydeven.[63] In the latter two studies, the values of A and B were determined based on data taken immediately before and after termination of the high-temperature runs when the temperatures were changed suddenly. The Courthouse Bay study was performed at relatively low temperatures over a period of a few operating hours. It was assumed that accompanying compaction and membrane fouling would be minimal in this case. Based on the results shown in the table, a K_T of 3000 K was selected for the A parameter and 5000 K for the B parameter.

STABILITY

The data contained in Table 23, as well as the work of Leban and Wydeven, demonstrate significant decreases in the A parameter over a period of relatively few hours. This could have been caused by compaction.[63]

Equation 29 was used to evaluate the effects of compaction on product-water flux. The equation was modified to eliminate the mathematical discontinuity, or

$$A = A_0 \ (1 + t)^n \ , \qquad (32)$$

in which A_0 is the value of A at time zero. The compaction factor n was then computed for the data for Riley and Milstead[31] and Goto,[57] as shown in Fig. 24.

Table 33. Observed Arrhenius-law temperature coefficients.

Study	Ref.	K_t coefficient (K) For A	K_t coefficient (K) For B
Courthouse Bay	58	2650	5350[a] (Cl^- ion)
Goto	57	3130	4950 (NaCl)
Leban and Wydeven[b]	63	3000	5200 (NaCl)

[a] Corrected for pH.

[b] Temperature was decreased to "room" temperature (20°C assumed).

The absolute values of n shown in the figure are much larger than those reported in the technical literature for spiral-wound elements (-0.01 at 25°C and 990 psig, and -0.012 at 55°C and 390 psig).[42] Leban and Wydeven,[63] on the other hand, report an n of -0.090 for the RC-100 membrane at 74°C and 600 psig. It may be expected that the compaction observed by those investigators would have been greater if the RC-100 membrane had been mounted in a spiral-wound element because the product-water carrier would also have been compressed. This could increase the resistance to flow in the product-water carrier.

The elements were not cleaned during the Riley and Milstead study period (Fig. 24). Membrane fouling may have contributed to the observed decrease in the A parameter. Based on these considerations, the expression

$$n = -2.17 \times 10^{-5} \cdot p \cdot (1.076)^{T-25} \tag{33}$$

was used to estimate the compaction factor herein. The pressure p is in psig and the temperature T in °C.

The consensus is that the ratio B/U is a constant (Eq. 30).[41] Plots of B/U against operating time are given in Fig. 25 for data of Goto,[57] Leban and Wydeven,[63] and Riley and Milstead.[31] The B/U ratio increased significantly with time in all of the studies except, possibly, the work of Riley and Milstead (the regression was not significant); or

$$B/U = \frac{B_o}{U_o} + \gamma t , \tag{34}$$

in which the subscript o represents conditions at time zero and γ is the slope of the plot.

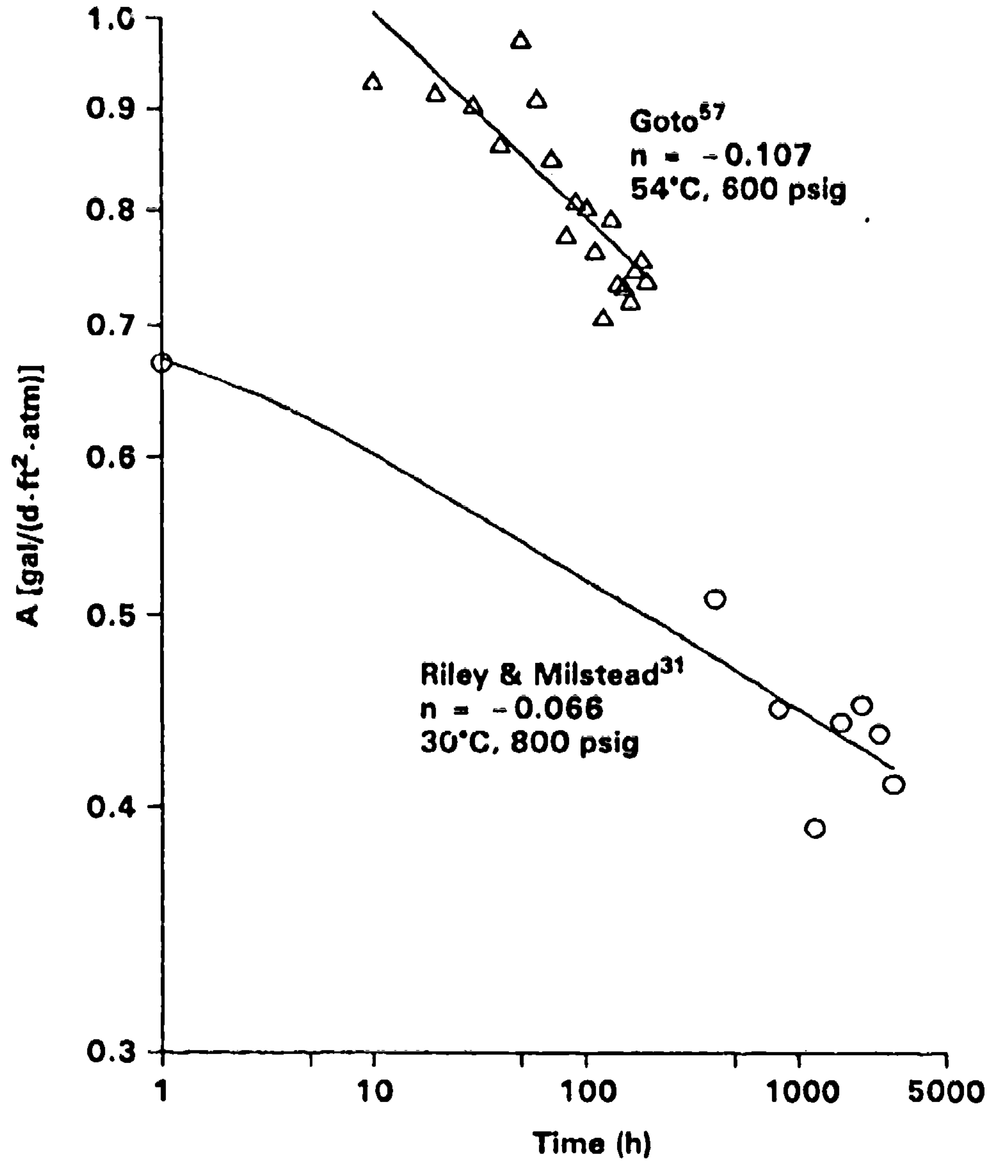


Figure 24. Observed decreases in product-water flux with time for UOP TFC-1501 PA elements.

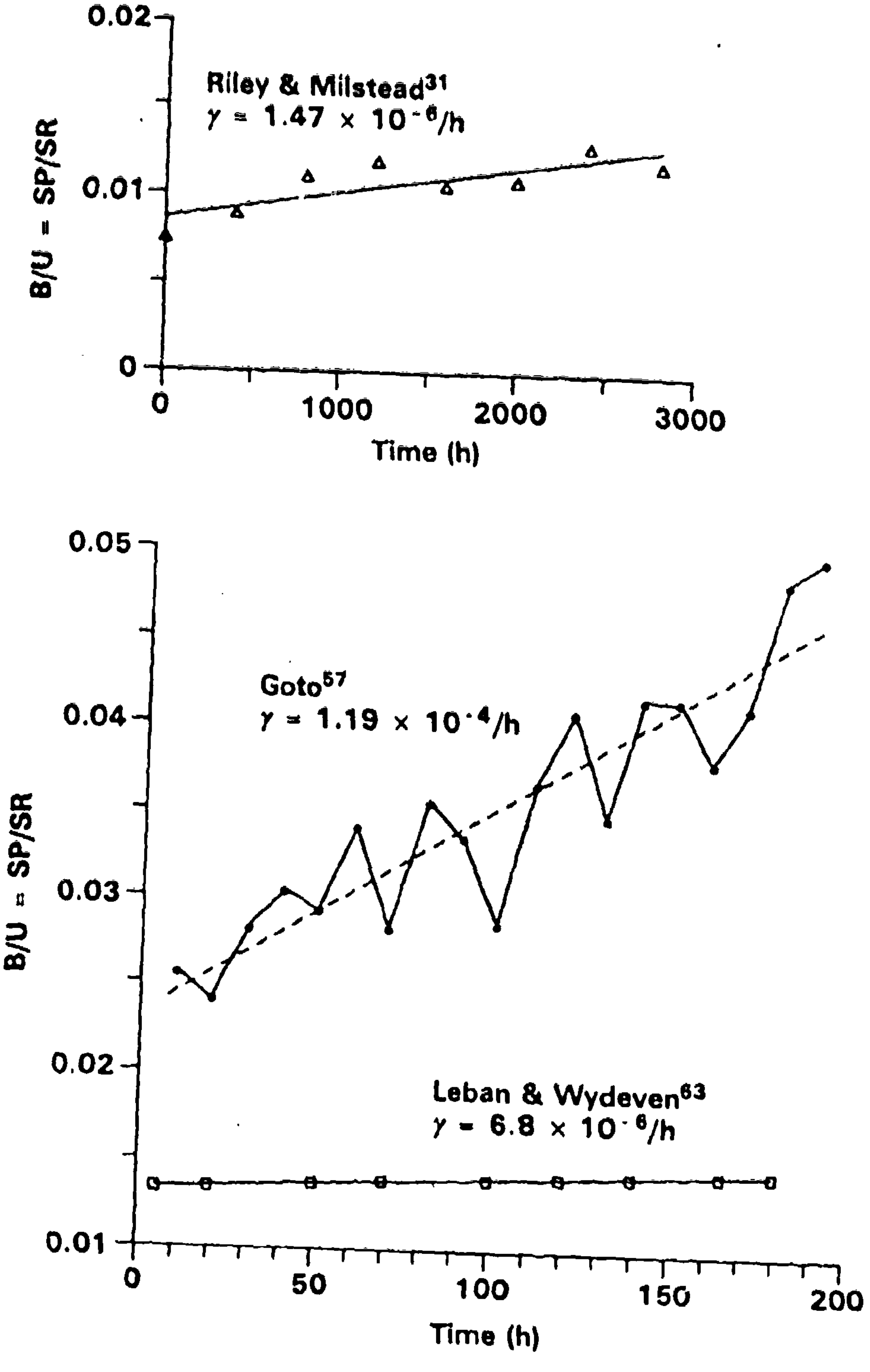


Figure 25. Observed increases in the B/U ratio with time for UOP RC-100 membrane and UOP TFC-1501 PA elements.

The magnitude of γ was much smaller for the flat-leaf data of Leban and Wydeven at 74°C than for the data of Goto at 54°C. This suggests that the large increase in B/U with time was caused by some gradual failure in the RO elements, or the pressure housing installation, rather than the membrane itself. The data (not shown) also demonstrated that the original flux capabilities of the element were not restored when the pressures and temperatures were decreased to standard conditions; i.e., primarily, these effects are irreversible.

All that is known about the coefficient γ is that it may be appreciable at 54°C and virtually nil at 30°C. Assuming that the observations of Goto are valid, some type of equation, which would meet these conditions, had to be proposed for this coefficient. An action similar to that observed for the hydrolysis of cellulose acetate membranes[41] was assumed, or

$$\gamma \text{ (per hour)} = 4.1 \times 10^{-7} \cdot 10^{(T-25)/11.7}, \qquad (35)$$

where T is expressed in °C. This expression may also be dependent on pH and pressure, but we were not able to substantiate it by the meager data available for this study.

SELECTIVITY

A literature search revealed no theory we could use to predict the B parameter for each ion found in standard seawater, and we made no attempt herein to do so; rather, a greatly simplified approach was used. The salts comprising seawater were assumed to be rejected independently of each other. This simplifies the computations because the charge and mass balances are obeyed automatically.

According to the data shown in Appendix A (Table A-2), the rejections of the salts of calcium and magnesium are almost equivalent. The Ca^{++} and Mg^{++} ions were replaced by a pseudo-divalent (Ca • Mg) ion having a molecular weight appropriate for the proportion of calcium to magnesium found in standard seawater. Two pseudosalts, $(Ca \cdot Mg)Cl_2$ and $(Ca \cdot Mg)SO_4$, were then used to account for all of the Ca^{++}, Mg^{++}, and $SO_4^{=}$ found in sea salts. Sodium chloride was used to fulfill the Na^+ and additional Cl^- requirements. (The fraction of NaCl was increased slightly to compensate for the contribution of the potassium ion.) All of the major ions found in seawater could thus be accounted for with just three salts.

The B parameters were obtained empirically for the three salts. The Ascension Island data (Tables 28 and 29) were used, and the results are shown in Table 34. The B ratios of the two pseudosalts with respect to NaCl were assumed to hold for all concentrations of sea salts; i.e., $B((Ca \bullet Mg)Cl_2)/B(NaCl) = 0.51$, and $B((Ca \bullet Mg)SO_4)/B(NaCl) = 0.044$.

OSMOTIC PRESSURE AND CONCENTRATION POLARIZATION

Equations 14 and 15 were used to compute the osmotic pressures of the brine and product waters. Adjustments were made to account for an increase in the better rejected salts in the brine water, as well as their loss from the product water. These adjustments are not discussed herein because their overall effect on the answers obtained with the computer models was relatively minor.

Using Eqs. 4 and 22, we considered the concentration polarization effects. Again, adjustments were made for the accumulation of the better rejected ions at the membrane wall. These adjustments are not discussed herein because their effects on the answers obtained with the computer models were minor.

DATA EVALUATIONS

The A and B parameters obtained from CALIBRATOR were corrected for pH and temperature (but not compaction). The results are presented in Table 34, together with the advertised parameters given by the manufacturer of the TFC-1501 element.

The Ascension Island results fall about midway between the past and present manufacturer's specifications. Some of the elements contained in the ROWPU's had been operated for about 180 h when the data shown in Table 29 were taken. Rough estimates obtained with Eqs. 32 through 35 indicate that the performance of these elements initially matched the manufacturer's past specifications.

The A and B parameters for the Courthouse Bay study are high compared to what was observed elsewhere and what was advertised by the manufacturer. This could be interpreted to mean that the Arrhenius law temperature coefficients used herein, as well as those recommended by the manufacturer, decrease with decreasing temperature. It could also mean that a leak existed in the ROWPU system, or that the temperatures actually existing at the membrane wall were greater than those reported for the brine water.

The A parameter calculated from Goto's data after the elements were removed from the high-temperature apparatus was about half of that expected for the older UOP elements. The elements, once compacted, did not recover at the lower temperature. At

Table 34. Comparison of A and B parameters with UOP specifications for TFC-1501 PA elements (standardized to 25°C and a pH of 5.7).

Study	A [gal/(d • ft^2 • atm)]	B (ft/d)
Manufacturer's specs.		
Past	0.59	0.0190 (NaCl)
Present	0.50	0.0123 (NaCl)
Ascension Island[a]	0.56	0.0123 (TDS) 0.0144 (NaCl) 0.000318 [(Ca • Mg)SO_4] 0.00730 [(Ca • Mg)Cl_2]
Aberdeen[a]	0.65	0.013 (NaCl)
Courthouse Bay[b]	0.68	0.031 (Cl^- ion)
Goto (after heating)	0.29	0.018 (NaCl)
Beirut, Lebanon	0.50	0.025 (TDS)

[a] Average for six elements.

[b] Average for 3 d of operation.

first glance, the B parameter appears correct, but it should have decreased in relation to the A parameter. Some irreversible degradation of the elements is thus demonstrated.

The A parameter from Beirut, Lebanon, appears too small, considering the low solids content of the feed water. The true operating temperature may have been lower than the 24°C assumed for those data (Table 30). The B parameter shown is virtually meaningless because the raw water was a fresh water. The proportion of alkalinity contained in the raw water was large. Decreasing the pH with citric acid alters the salt composition of such waters significantly.

The Aberdeen Proving Ground studies yielded an exceptionally large A parameter. This could have been caused, at least in part, by the low pressure (400 psig) and low feed-water salt concentrations employed in those studies.

PREDICTED PERFORMANCE OF 600-GPH ROWPU

The ROWPU product water must meet the most stringent field water-quality standards now in existence. For example,

- TDS = 1500 mg/L,
- Cl^- = 600 mg/L,
- Mg^{++} = 150 mg/L, and
- $SO_4^=$ = 400 mg/L.

are among these existing standards.[64] This also should hold true for the most stringent field water-quality standards that are adopted. These recommended standards appear in Volume 4 of this study[65] and include

- TDS = 1000 mg/L,
- Cl^- = 600 mg/L,
- Mg^{++} = 30 mg/L, and
- $SO_4^=$ = 100 mg/L.

Furthermore, the water-quality standard for chloride in the product water is the most critical standard for the 600-gph ROWPU to achieve. This is because NaCl will comprise the vast majority of the TDS concentration in the product water. Consequently, the chloride and TDS standards are virtually interchangeable. The limits of feasible operation for the 600-gph ROWPU with sea salt solutions are expressed in terms of normal and trouble-point gauge readings in Table 15 for a maximum product-water flow of 12 gpm, a minimum product-water flow of 6 gpm, and a maximum applied pressure of 800 psig.

A mathematical model, referred to herein as PREDICTOR, was used to obtain predictions of the ROWPU performance for a variety of input conditions. (PREDICTOR is similar to CALIBRATOR, except that the ROWPU performance output is computed for a stated set of input conditions including the A and B parameters. Brief descriptions of both models are presented in Appendix B.) The predictions were based on the following four major assumptions:

- The feed water contains sea salts only,
- The input and operating conditions are constant with time,
- No membrane fouling occurs, and
- The past specifications of the element manufacturer apply (Table 11).

The predictions could have been made for the current specifications (Table 12), but this would have doubled the effort without changing the results substantially.

The input conditions required for PREDICTOR include feed-water salt concentration, flow, and temperature; applied pressure; pH; time of operation or element age; membrane performance specifications; effective membrane area per element; and element staging (see Fig. B-3 in Appendix B). The last two items are fixed, of course, for the current 600-gph ROWPU. An example of the output obtained from PREDICTOR is shown in Table 35 for one set of input conditions. As previously stated, the most important output information of immediate concern are the weighted-mean Cl^- ion concentration (the critical contaminant) and the total product-water flow. These are depicted in Figs. 26 through 37 for feed-water sea-salt concentrations of 0.5, 2.0, 3.5 and 5.0% by weight; operating temperatures (water temperatures at the membrane wall; feed-water temperatures may be lower) of 1, 25, 45, and 65°C; applied pressures of 600, 700, 800, 900, and 1000 psig; pH values of 5.7 and 8.2; operating times of 20, 200, and 2000 h; and a constant feed flow of 34 gpm. Also shown in the figures are the limits of feasible operation or the maximum permissible chloride concentration in the product water. The product-water flow should not exceed about 20.5 gpm for the 600-gph ROWPU; otherwise the brine flow in the last element of the chain will drop below the minimum of 13.5 gpm recommended by the manufacturer. This limit is indicated by the dashed lines shown in the product-flow figures (Figs. 26, 29, 32 and 36).

1°C TEMPERATURE

The predicted product-water flows are shown in Fig. 26 for this operating temperature. The effects of compaction are minor. The minimum specified flow of 6.0 gpm will not be met, or perhaps barely met, at the maximum allowable applied pressure of 800 psig for a feed-water sea-salt concentration of 3.5% by weight. The maximum product-water flow of 12 gpm will not be exceeded for almost any feed-water salt concentration or applied pressure up to the maximum of 980 psig, which can be attained with the present RO positive-displacement pump (Table 1).

Figures 27 and 28 indicate no problems in meeting the recommended chloride standard of 600 mg/L[64] at a pH of either 5.7 or 8.2.

25°C TEMPERATURE

The effects of compaction on product-water flows become apparent at this temperature, but the salt rejection remains virtually constant with time. The ranges in

Table 35. PREDICTOR output for 600-gph ROWPU (3.5% seawater; 34-gpm feed flow, 25°C temperature, 800-psig applied pressure, pH = 5.7; 200 h of operation; former UOP TFC-1501 PA specifications).

	Pressure vessel output				Total or weighted mean
	#1	#2	#3	#4	
Product water					
Flow (gpm)	3.06	2.59	2.13	1.71	9.49
Concentration (mg/L)					
Cl^-	184	238	312	414	270
Na^+	111	143	188	249	162
$SO_4^=$	0.8	0.9	1.2	1.6	1.1
Mg^{++}	3.9	5.1	6.7	8.8	5.7
Ca^{++}	1.2	1.6	2.1	2.8	1.8
TDS					441
Brine water					
Flow (gpm)	30.9	28.4	26.2	24.5	
Concentration (%)					
Cl^-	2.141	2.334	2.521	2.695	
Na^+	1.204	1.312	1.418	1.515	
$SO_4^=$	0.297	0.324	0.350	0.375	
Mg^{++}	0.143	0.156	0.168	0.180	
Ca^{++}	0.045	0.049	0.053	0.057	
TDS	3.83	4.18	4.51	4.82	

Product-water flow = 9.5 gpm.

Product-water Cl^- ion concentration = 270 mg/L.

Product recovery = 28%.

Pressure decrease = 75 psid.

Membrane parameter A = 0.54 gal/(d • ft^2 • atm) (after 200 h).

Membrane parameter B = 0.018 ft/d for the NaCl (after 200 h).

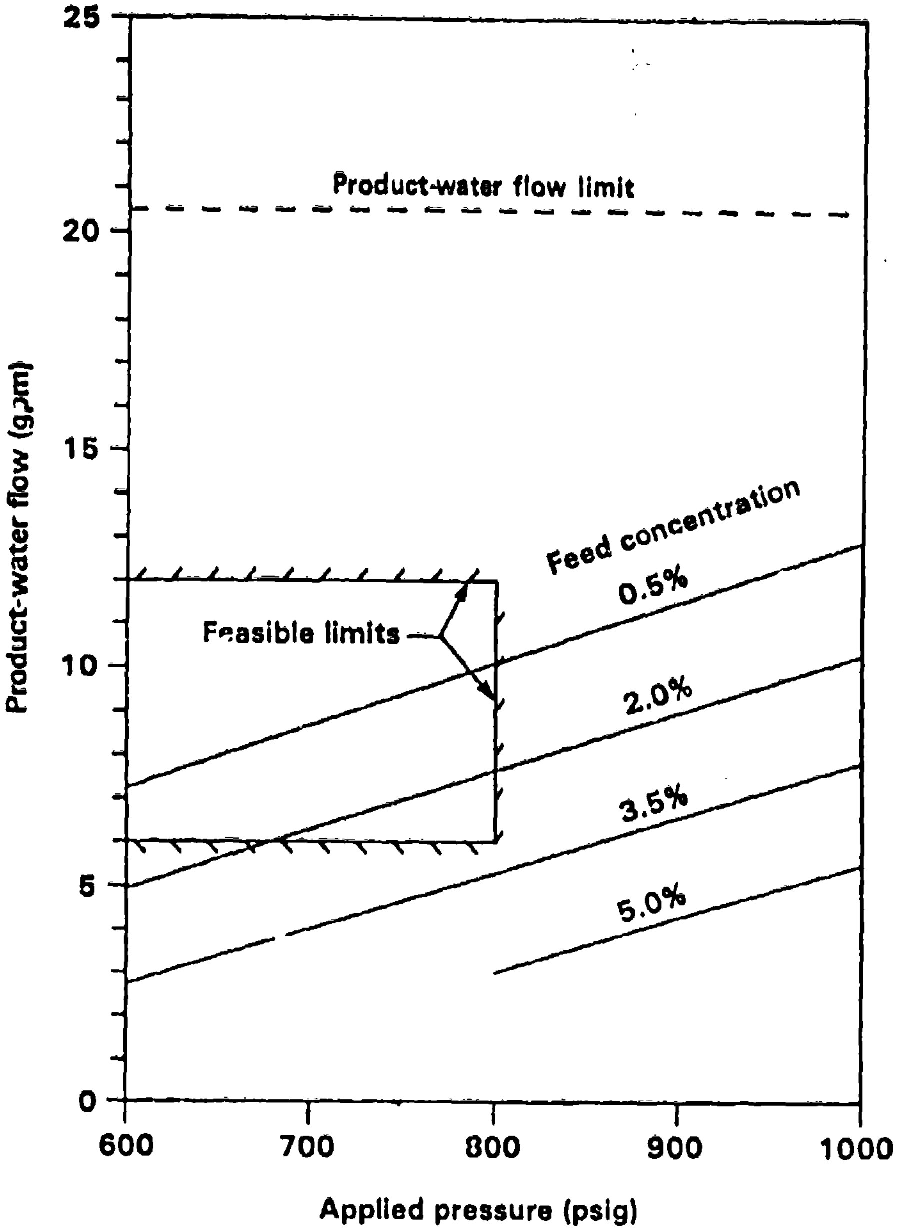


Figure 26. The 600-gph ROWPU product-water flows at operating temperature of 1°C and pH = 5.7.

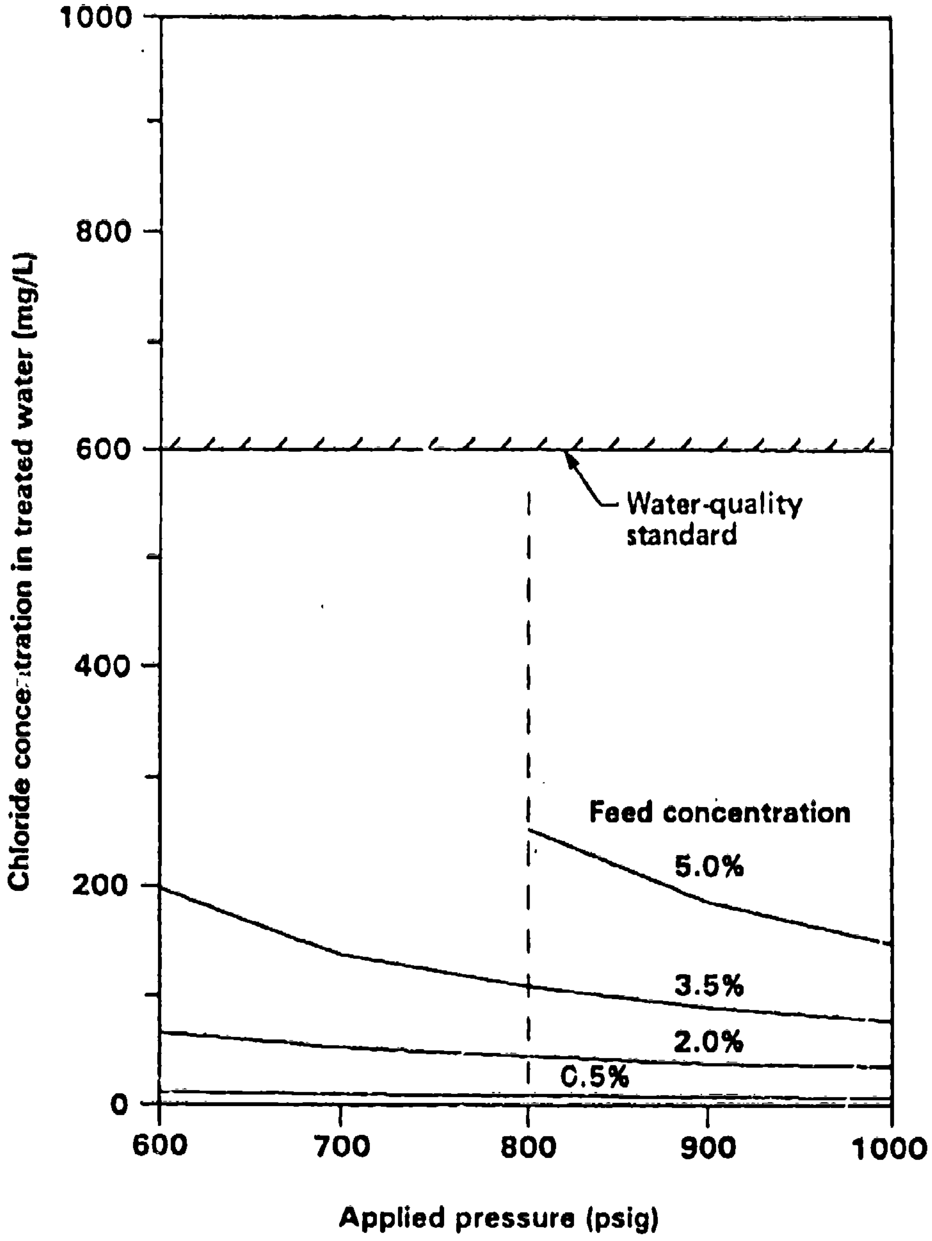


Figure 27. The 600-gph ROWPU product-water chloride concentrations at operating temperature of 1°C and pH = 5.7.

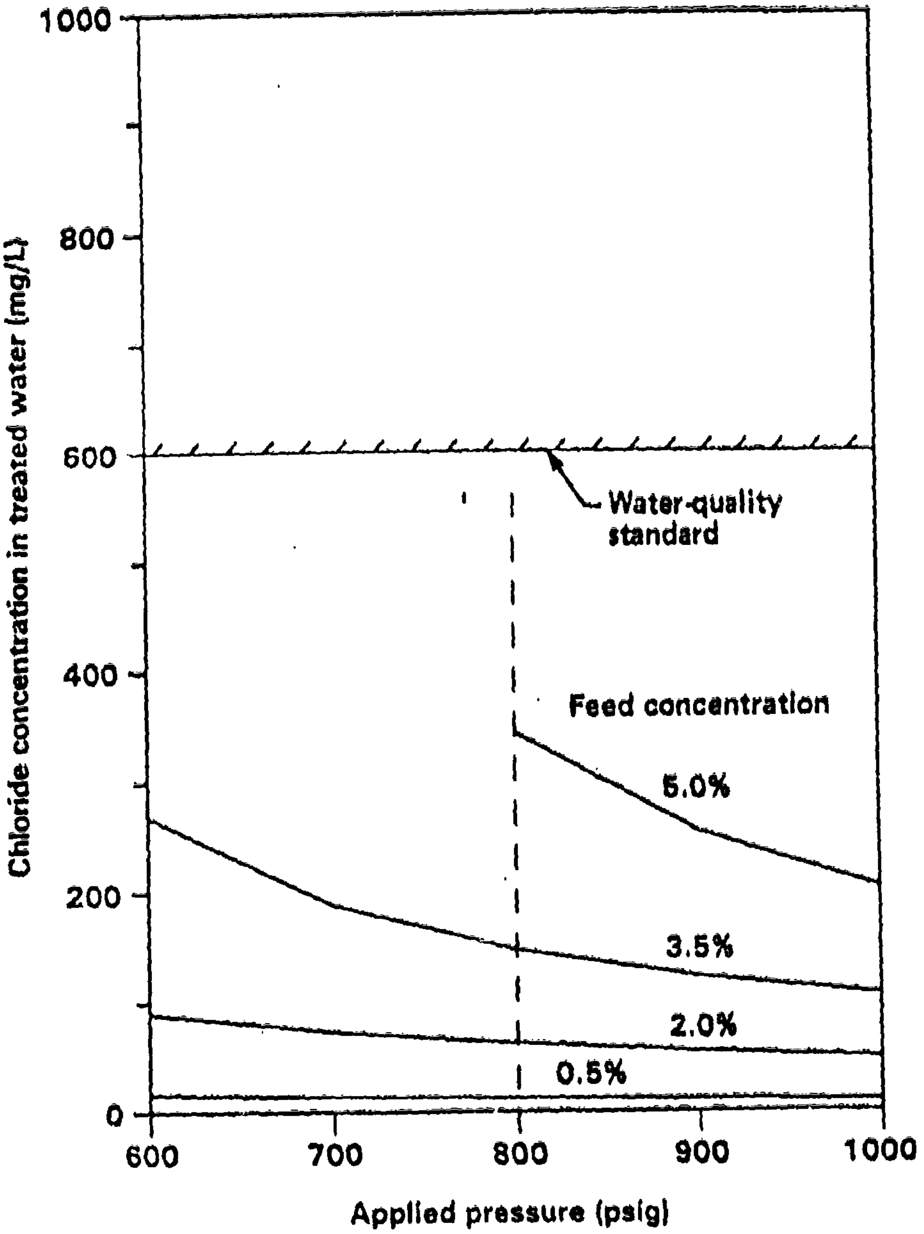


Figure 28. The 600-gph ROWPU product-water chloride concentrations at operating temperature of 1°C and pH = 8.2.

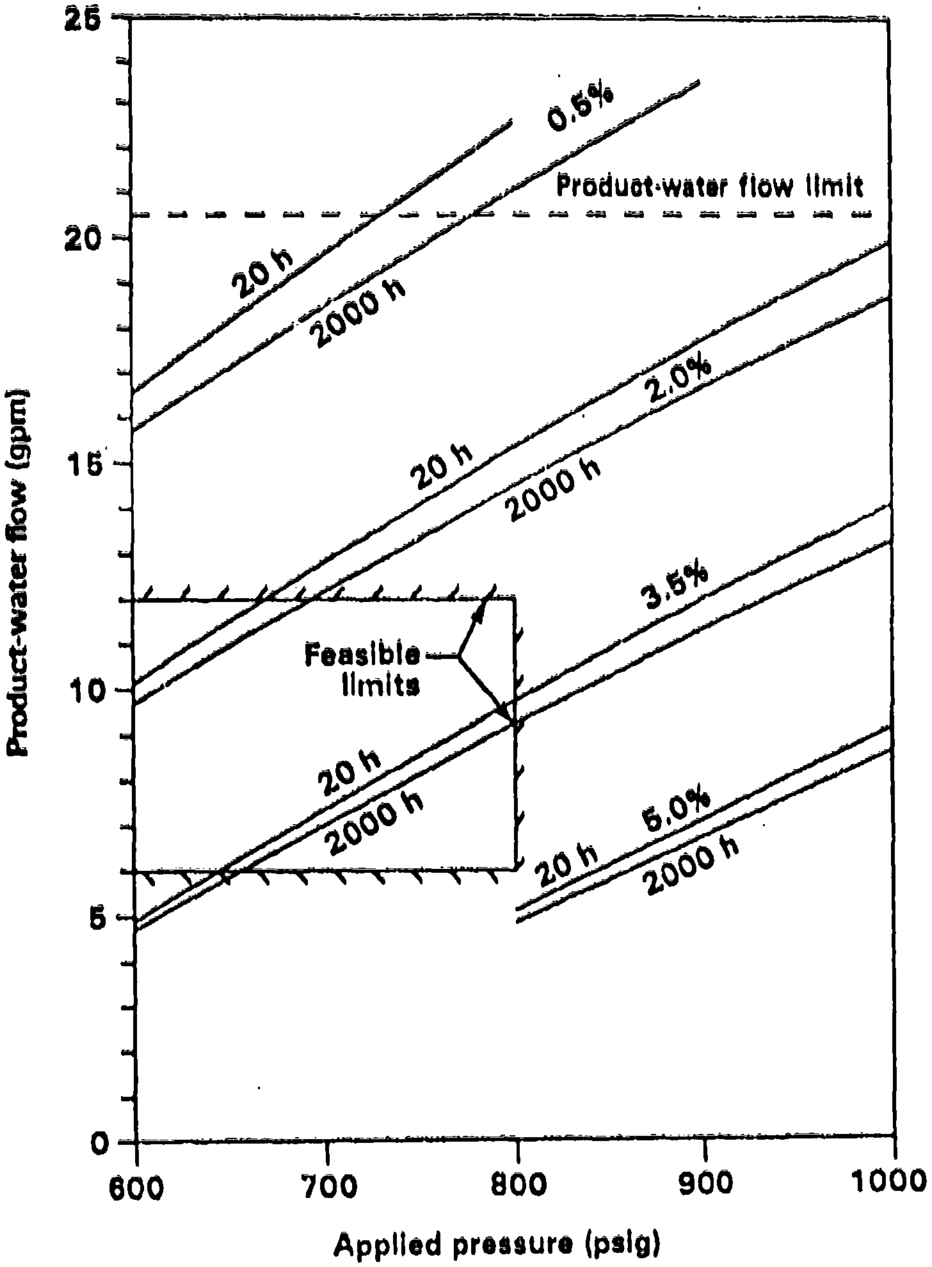


Figure 29. The 600-gph ROWPU product-water flows at operating temperature of 25°C, pH = 5.7, and run times of 20 and 2000 h.

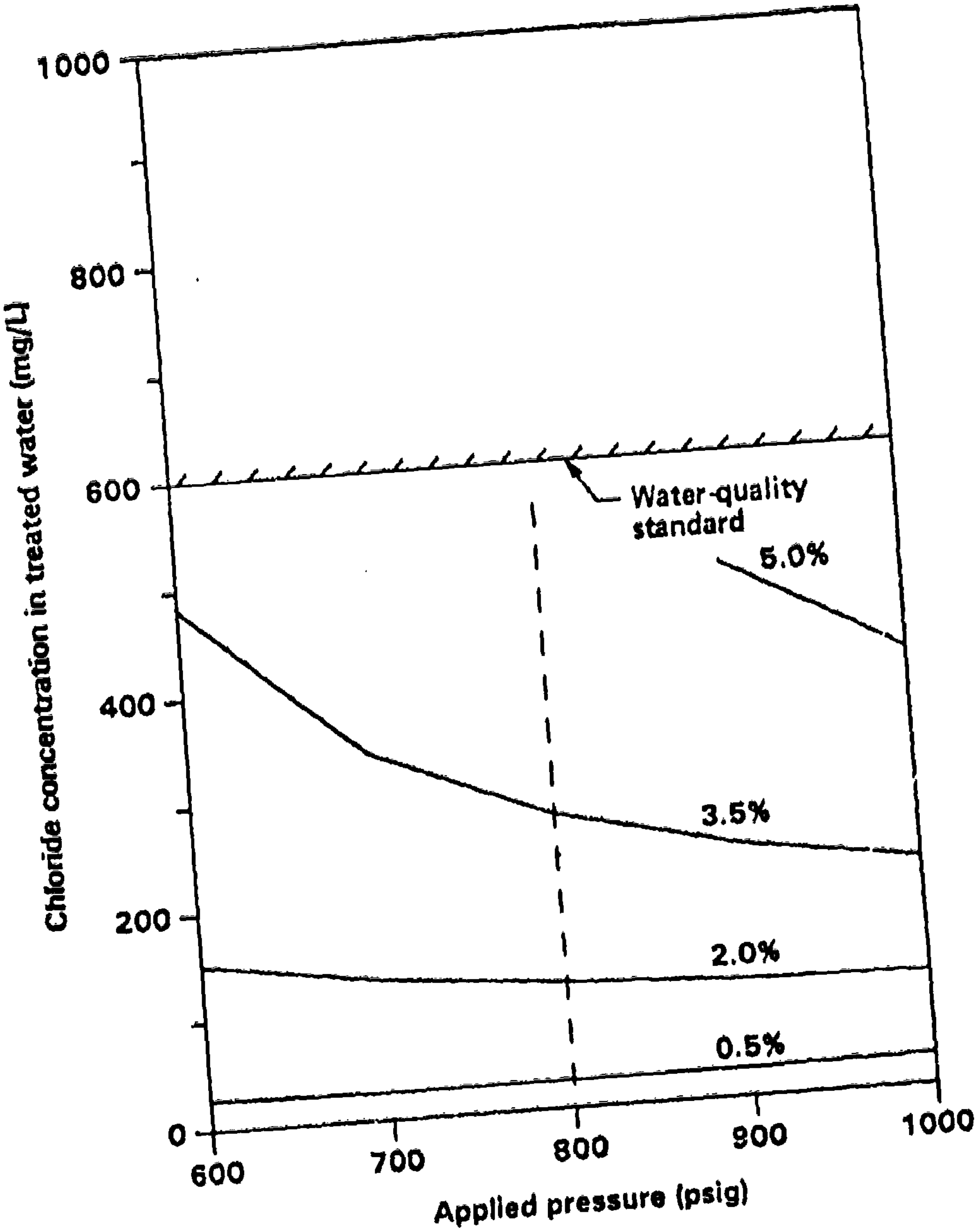


Figure 30. The 600-gph ROWPU product-water chloride concentrations at operating temperature of 25°C and pH = 5.7.

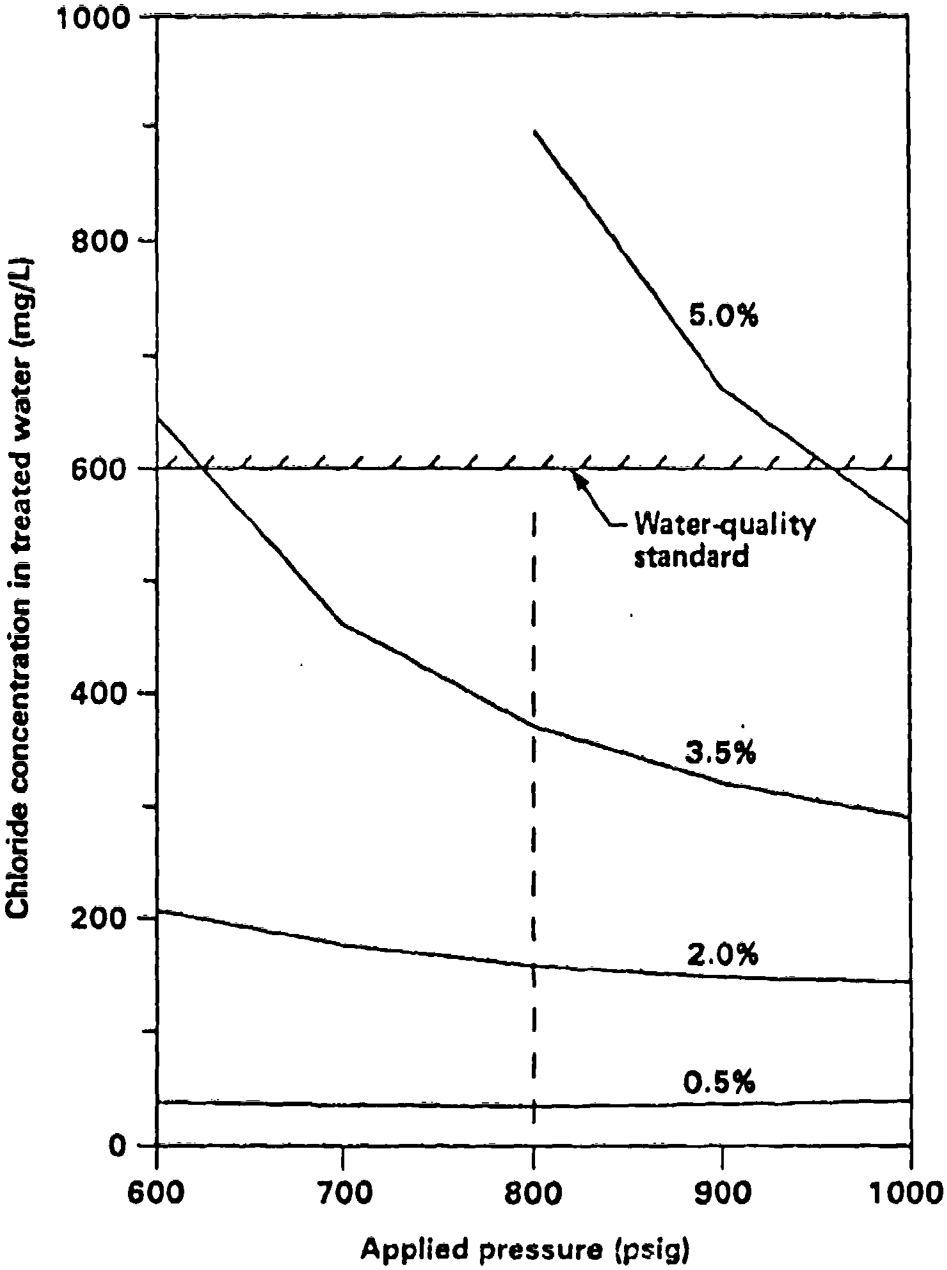


Figure 31. The 600-gph ROWPU product-water chloride concentrations at operating temperature of 25°C and pH = 8.2.

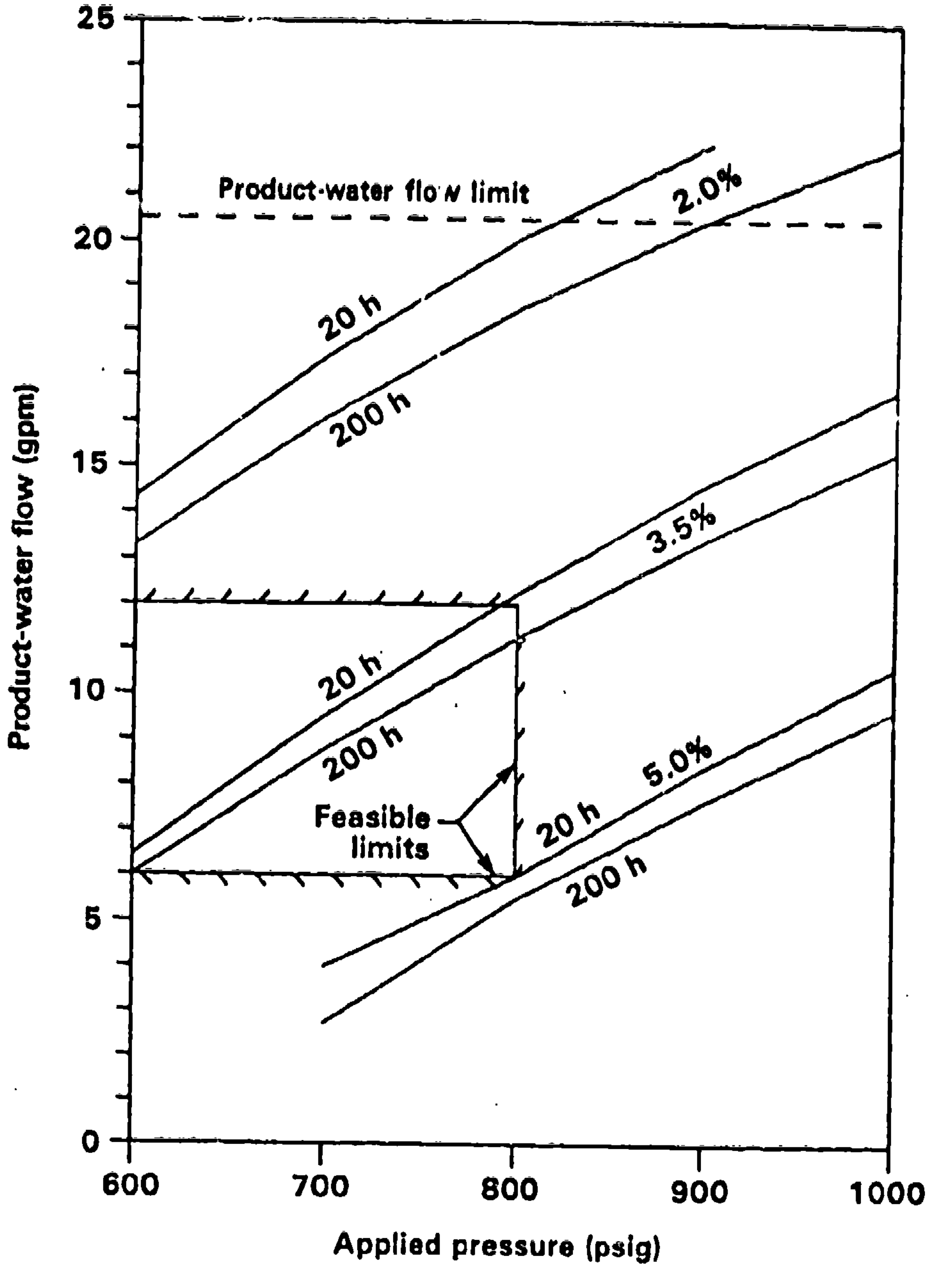


Figure 32. The 600-gph ROWPU product-water flows at operating temperature of 45°C, pH = 5.7, and run times of 20 and 200 h.

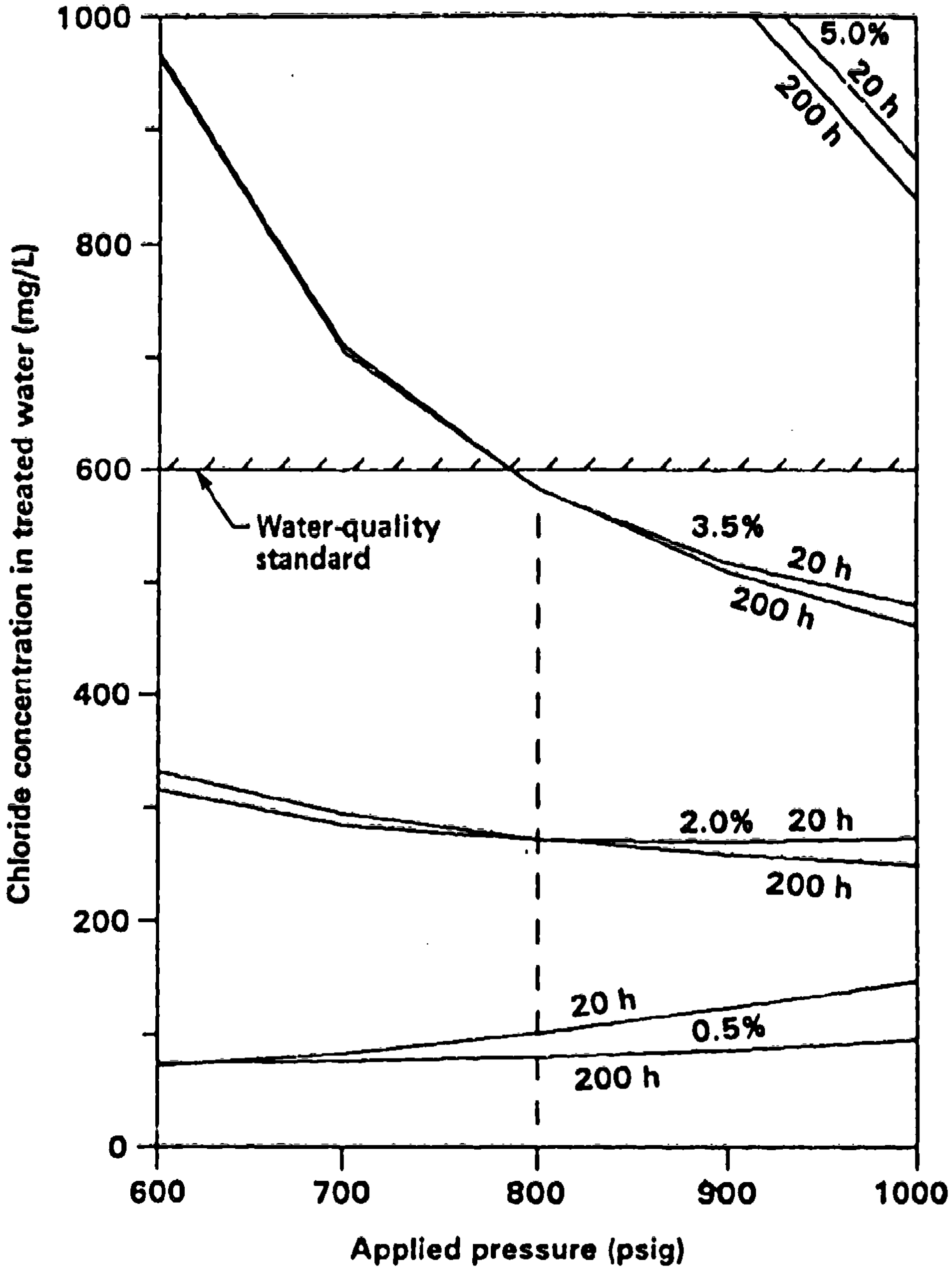


Figure 33. The 600-gph ROWPU product-water chloride concentrations at operating temperature of 45°C, pH = 5.7, and run times of 20 and 200 h.

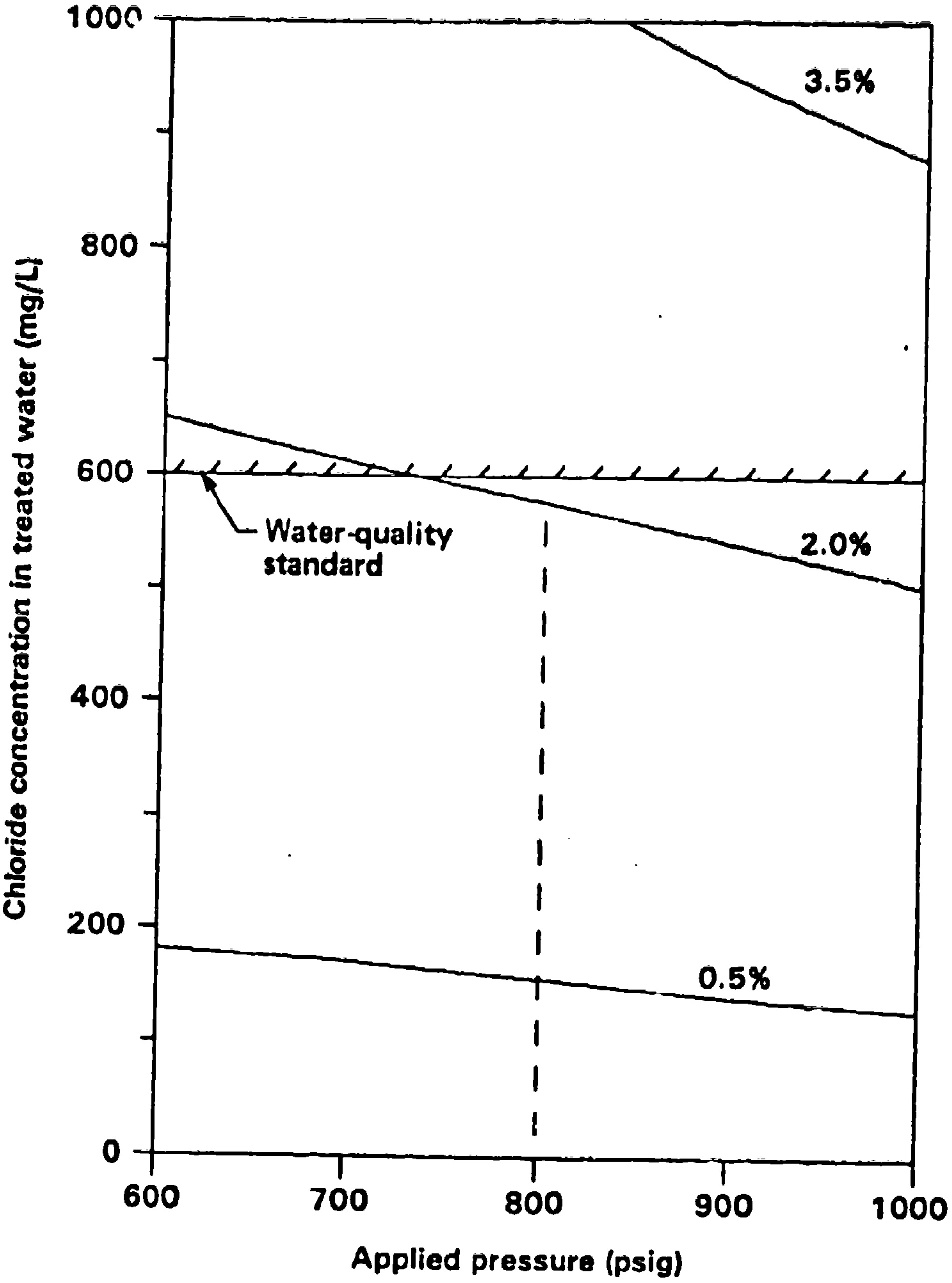


Figure 34. The 600-gph ROWPU product-water chloride concentrations at operating temperature of 45°C, pH = 5.7, and a run time of 2000 h.

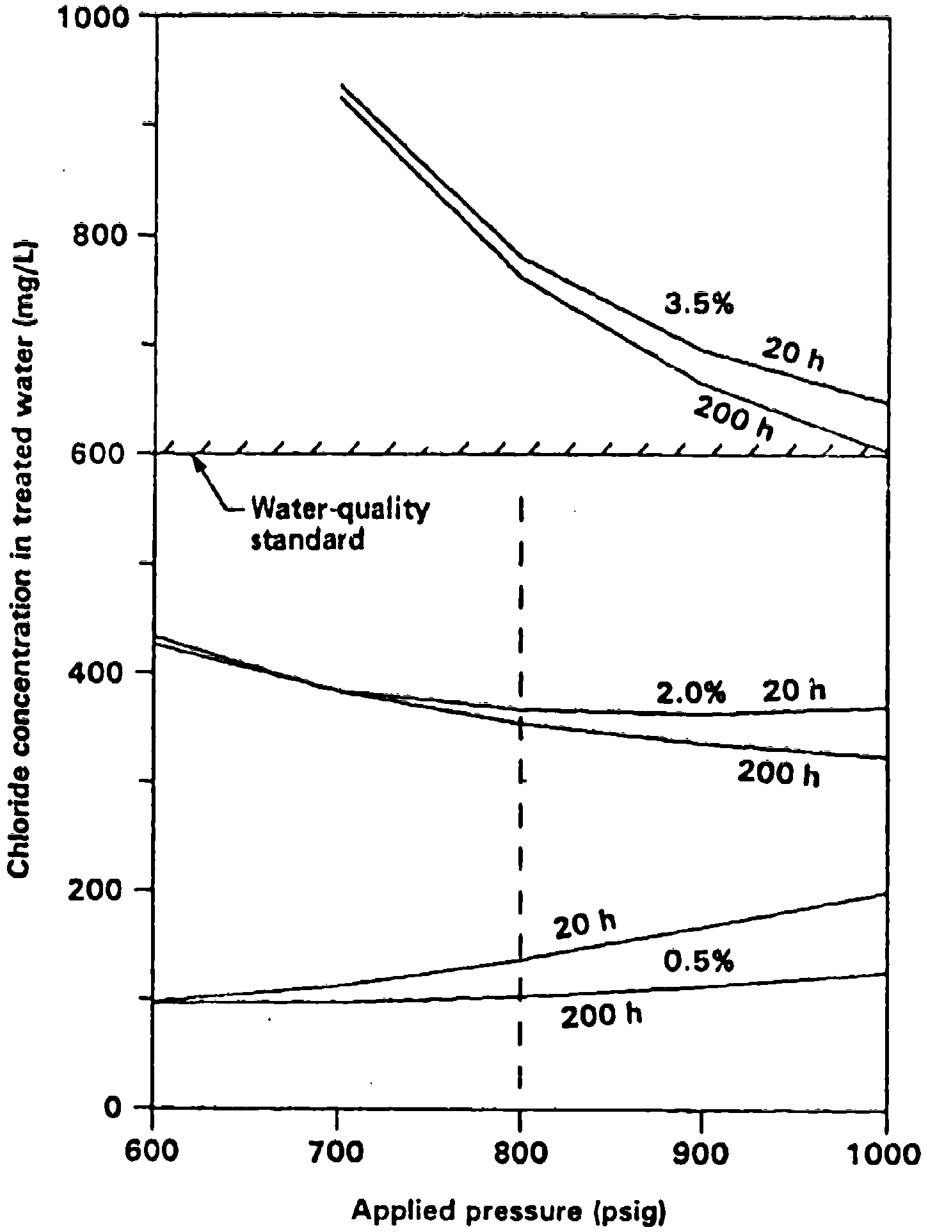


Figure 35. The 600-gph ROWPU product-water chloride concentrations at operating temperature of 45°C, pH = 8.2, and run times of 20 and 200 h.

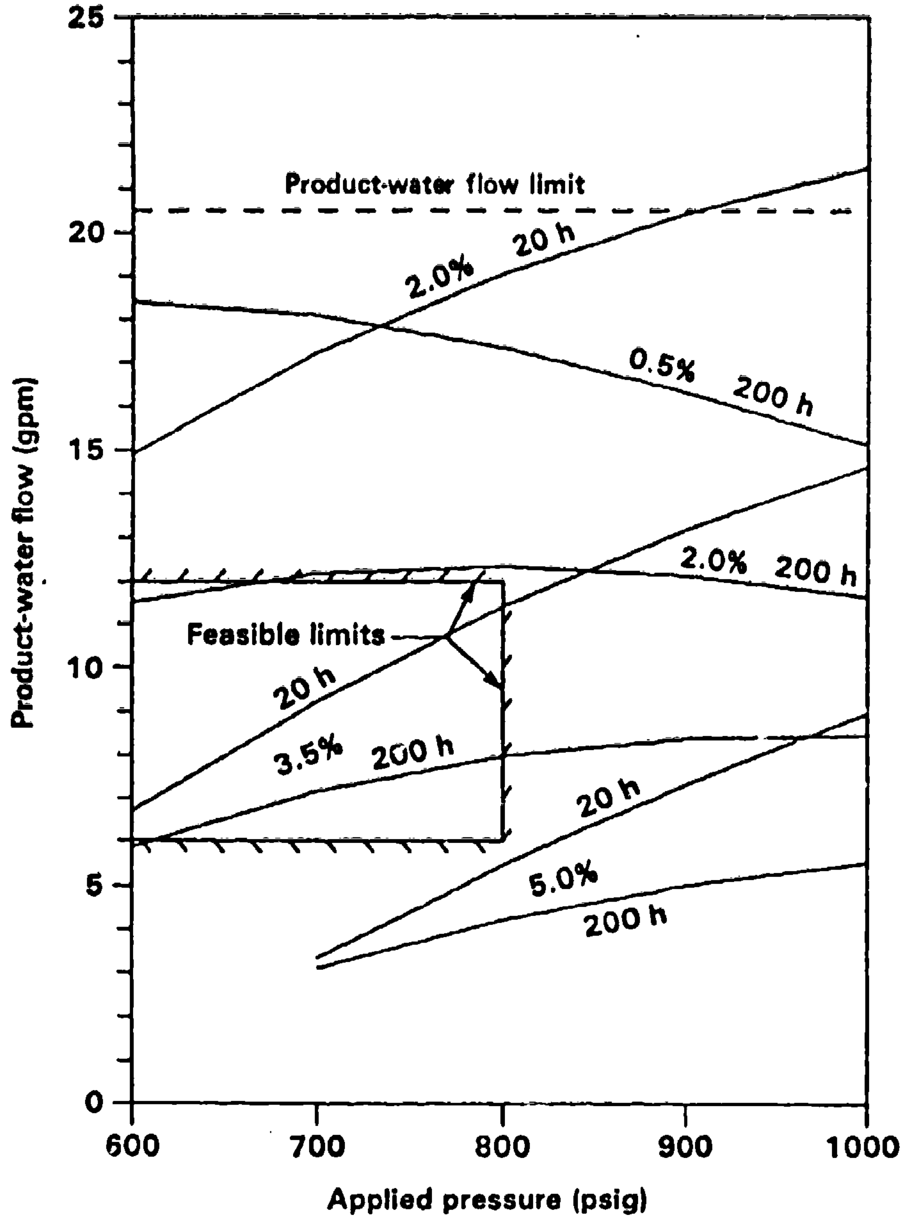


Figure 36. The 600-gph ROWPU product-water flows at operating temperature of 65°C, pH = 5.7, and run times of 20 and 200 h.

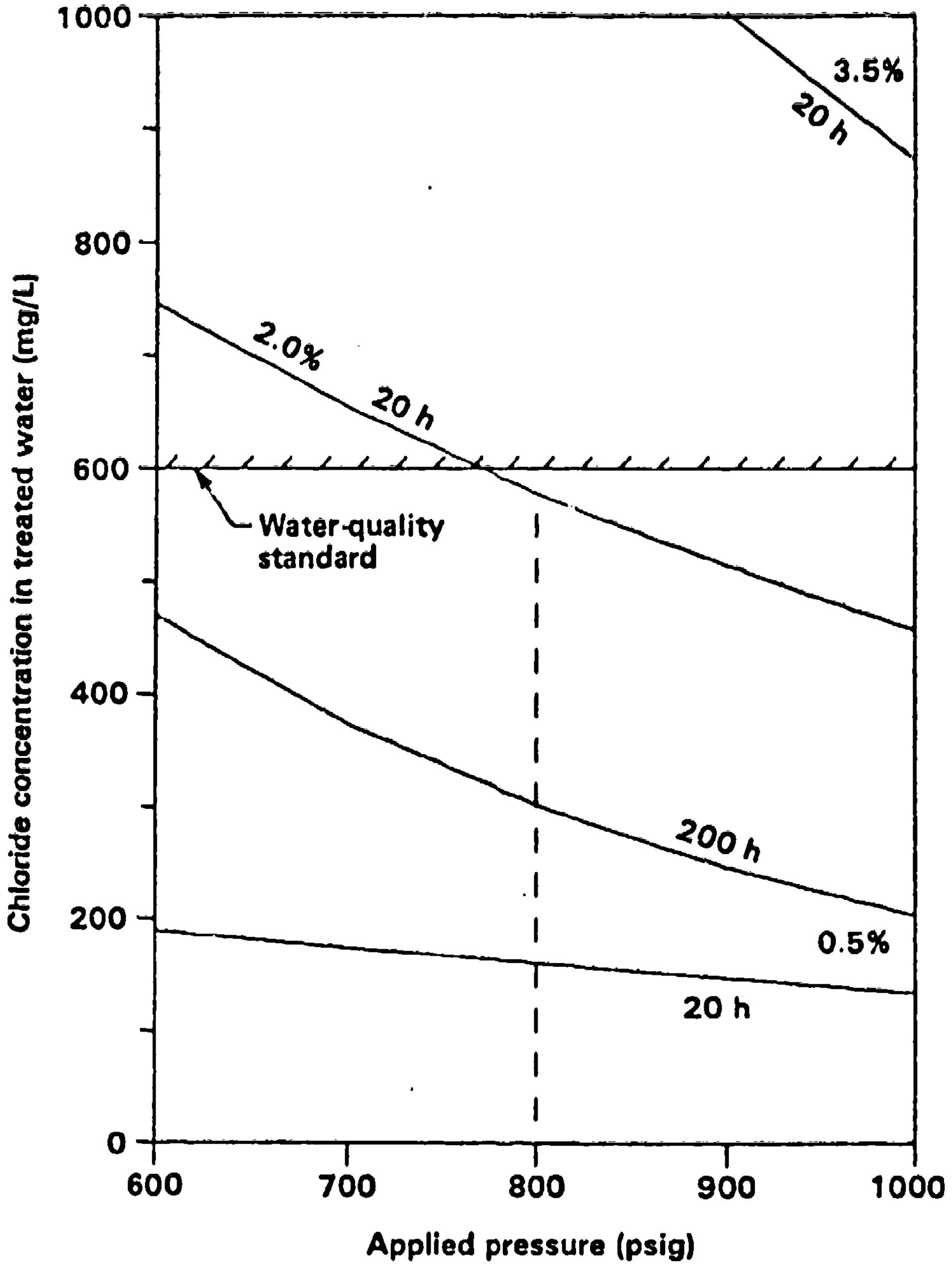


Figure 37. The 600-gph ROWPU product-water chloride concentrations at operating temperature of 65°C, pH = 5.7, and run times of 20 and 200 h.

the feed-water salt concentration, which fall within the prescribed product flows, are about 2.7 to 4.8% at 800 psig, and 1.6 to 3.2% at 600 psig (Fig. 29). Figure 30 indicates no problems with chloride breakthrough at a pH of 5.7. The water-quality standard for Cl^- will be exceeded at 800 psig and a pH of 8.2 when the feed-water salt concentration is greater than about 4.3% (Fig. 31).

45°C TEMPERATURE

The effects of stability become significant at this temperature. Compaction causes a significant decrease in product-water flow with time (Fig. 32), and element deterioration is evidenced by comparing the results shown in Figs. 33 and 34 for time and in Figs. 33 and 35 for increased pH. In general, either the maximum allowable product flow of 12 gpm (Fig. 32) or the water-quality standard for chloride (comparison of Figs. 33 and 34) will be exceeded. For example, Figs. 32 and 33 indicate that the product-water flow and chloride-ion concentration in the product water, respectively, for a feed-water salt concentration of 3.5% will almost be within acceptable limits when the operating pressure is 800 psig and the pH is 5.7; any other feed concentration will yield either too much product water or chloride-ion breakthrough. No feasible solution exists at a pH of 8.2 and a pressure of 800 psig for a 3.5% salt concentration in the feed water (Fig. 35).

The 2000-h results shown in Fig. 34 indicate a severe deterioration in the RO elements. Although this represents our greatest extrapolation of the data obtained from one short-term, high-temperature study,[57] the results do demonstrate that the elements may eventually deteriorate at this temperature.

65°C TEMPERATURE

Figures 36 and 37 demonstrate that the ROWPU cannot be operated within the prescribed limits of product-water flow and chloride concentration at this temperature. The effects of compaction are severe, and the RO elements deteriorate rapidly.

VARIABLE FEED-FLOW RATE

The feed-water flow rate reported for the 600-gph ROWPU is 34 to 35 gpm. This rate is significantly greater than the 22 to 23 gpm recommended by all manufacturers for the 6-in. spiral-wound element. The effect of feed-flow rate on ROWPU performance was investigated at three temperatures (1, 25, and 45°C) while maintaining the applied pressure, feed-water sea salt concentration, pH, and operating time at 800 psig, 3.5%, 5.7, and 200 h, respectively. The feed flows were set at 22.5, 26, 30, and 34 gpm. The results are shown in Figs. 38 and 39.

The effects of feed flow on product-water flow and chloride concentration, in general, were minimal for the range of feed flows investigated. The product-water chloride concentration did increase about 27% at 45°C when the feed flow was decreased from 34 to 22.5 gpm (Fig. 39).

ARSENIC AND CYANIDE

Currently, the military's most stringent arsenic water-quality standard is 0.05 mg/L.[64] This has been decreased to 0.02 mg/L according to the recommended standards (based on a maximum per capita water-consumption rate of 15 L/d for a period up to one year).[64] The corresponding cyanide standards are 0.5 mg/L (current) and 2 mg/L (recommended).[65] The rejection of these contaminants in the ROWPU is not easily ascertained because:

- The rejection depends on the chemistry of these contaminants as well as the feed-water pH.
- The rejection of the ionized species of these contaminants will vary with the concentration and composition of other salts that may co-exist with the contaminants in the feed water.
- Very few experiments have been performed with the noncellulosic thin-film composite membrane of interest herein, and those that have been performed were usually conducted at pH levels different from those of interest for ROWPU operation.

The information available in the technical literature concerning the removal of arsenic and cyanide with hyperfiltration (reverse osmosis) is summarized in the following sections.

ARSENIC

Schmitt[66] reports a series of tests performed in 1968 by the Army Mobility Equipment Research and Development Center at Fort Belvoir, VA, to demonstrate the ability of the RO process to remove arsenic, as well as chemical and biological warfare agents, from natural waters. The tests were conducted under controlled conditions, using

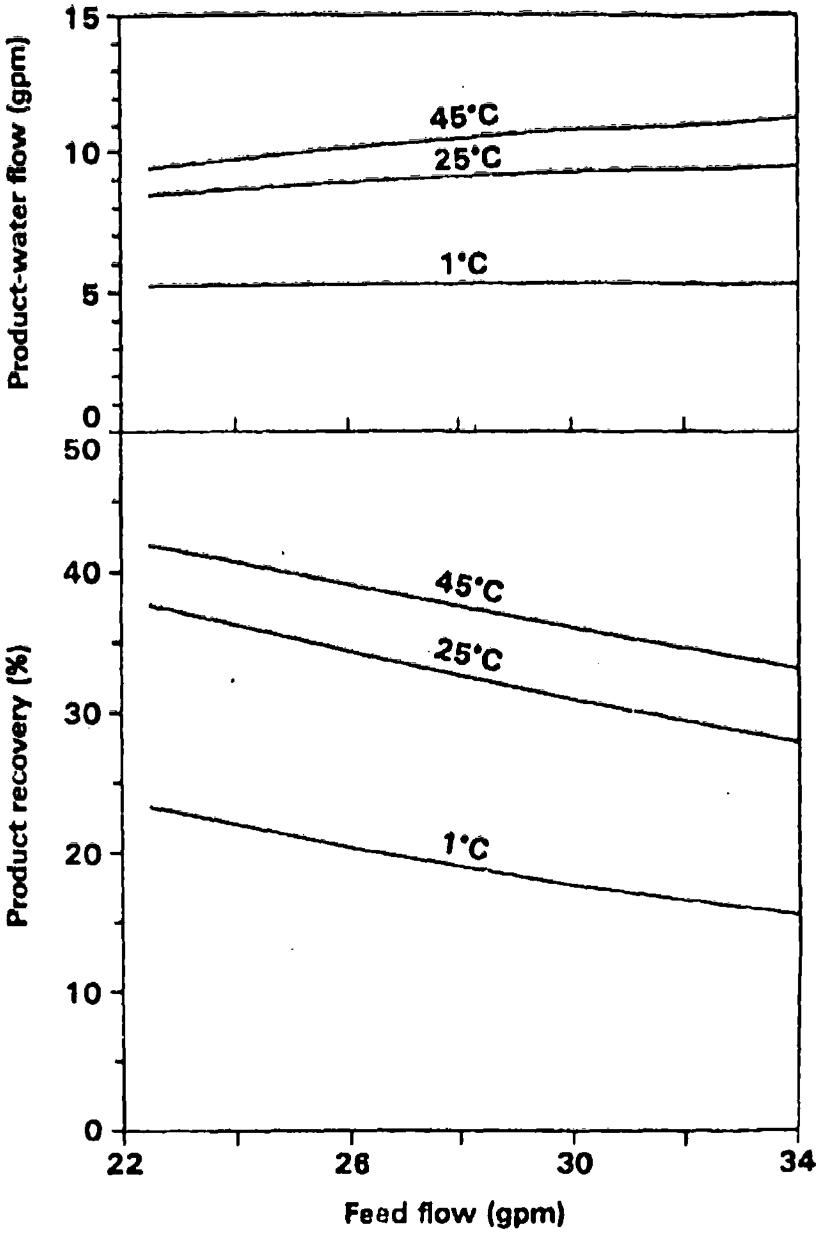


Figure 38. Effect of feed-flow rate on product-water flow and recovery for 600-gph ROWPU (concentration of feed = 3.5%, pressure = 800 psig, pH = 5.7, operating time = 200 h).

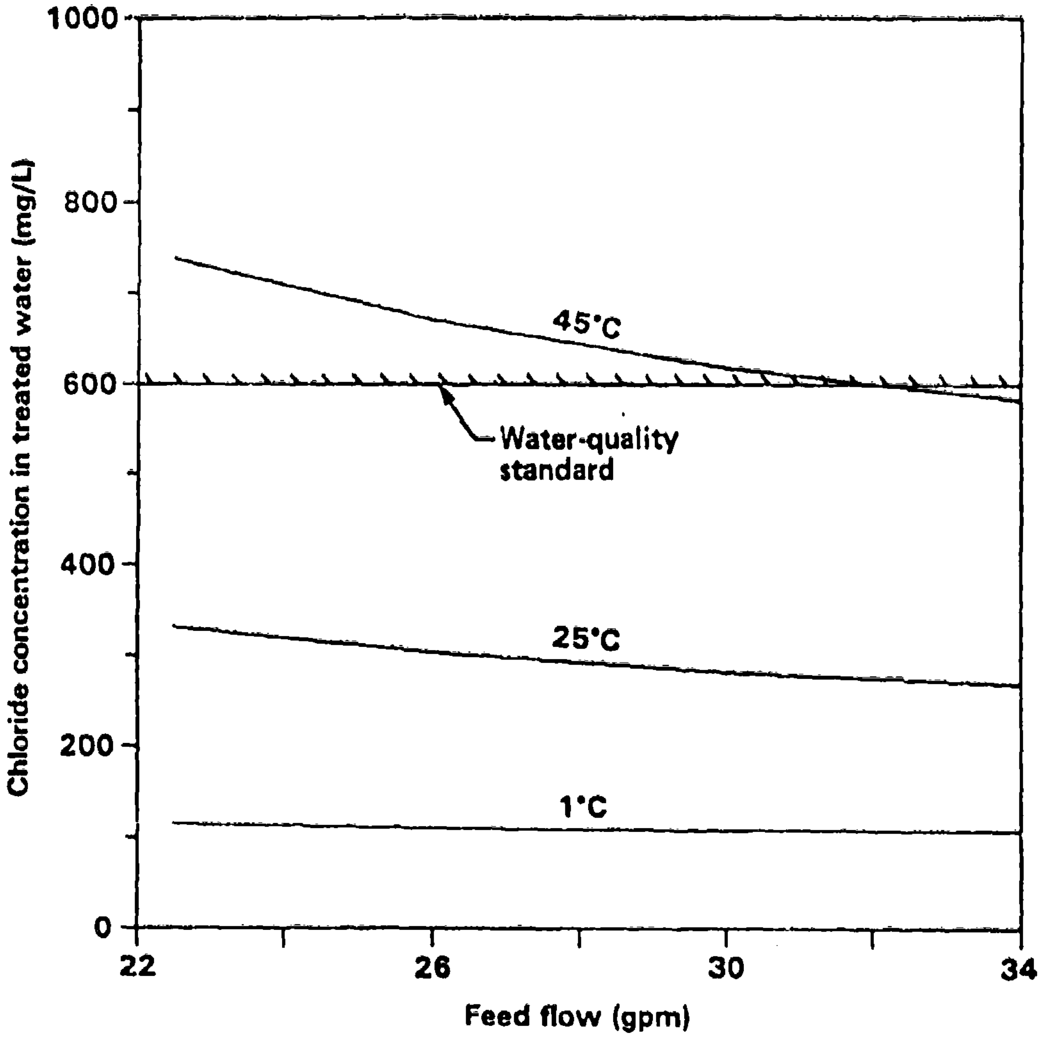


Figure 39. Effect of feed-flow rate on product-water chloride concentration for 600-gph ROWPU (concentration of feed = 3.5%, pressure = 800 psig, pH = 5.7, operating time = 200 h).

a turbid freshwater from a nearby stream. An arsenic compound was added to achieve an approximate level of 30 mg/L, and the contaminated water was pumped directly to the RO units without any pretreatment. Operating pressures were maintained at 600 psig, with the tests lasting from 6 to 24 h.

Three different grades of cellulose acetate membranes were investigated. It was found that the membrane with the lowest flux rate gave the best solute rejection. The results for arsenic are summarized in Table 36.

Clifford et al.[67] give a semiquantitative evaluation of the relative capabilities of various processes, including RO, to remove arsenic from ground water as shown in Table 37. This evaluation was based on the investigators' past experience and research.

Fox[68] reports a series of RO pilot-plant tests conducted to evaluate the technique required to remove trivalent and pentavalent arsenic, tetravalent and hexavalent selenium, fluoride, nitrate, lead, trivalent and hexavalent chromium, and cadmium from drinking water. Two separate RO units with different types of membranes were used. The two systems were operated under different conditions; therefore, membrane performance could not be compared.

A Du Pont polyamide hollow-fiber (HF) module was used in one of the units, and a spiral-wound (SW) element with a cellulose acetate membrane (Osmonic Sepralator, Osmonics Company, Minnetonka, MN) was used in the other.[68] The product-water flux increased and the solute rejection decreased in the cellulose acetate element after about 10 months of operation. This spiral-wound unit was then replaced by a larger Osmonic Sepralator, having a greater product-water delivery. The specifications for the three RO elements used in this study are given in Table 38.

The well water was obtained from Glendale, Ohio. A typical analysis of the untreated water is presented in Table 39. The water contained primarily carbonate hardness ions and some reduced iron. The iron may have been partially oxidized during the transport of the water to the test site. Pretreatment consisted of aeration and filtration through a diatomaceous earth filter to remove the oxidized iron. The filtered water was then pumped through a 5-μm cartridge filter and into the RO elements. The water was also acidified with a 10% (v/v) sulfuric acid solution to obtain a negative Langelier Saturation Index. The acidified water supplied to the RO units had a pH ranging from 4.6 to 6.5.

The raw water did not contain any of the contaminants investigated except for a low level of arsenic (0.010-0.016 mg/L); as a result, the contaminants had to be seeded along with $CaCl_2$ to increase the TDS of the test water. Arsenic (III) was added in the form of

Table 36. Summary of the arsenic rejections obtained using three grades of cellulose acetate membranes, Fort Belvoir, VA, 1968. Fresh water, 30-mg/L initial contaminant concentration (temperature and pH data not stated).[a]

Product-water flux (gal/[d • ft^2])	Arsenic removal[b] (%)
25	96
14	97
8	99

[a] Adapted from Schmitt.[66]

[b] Oxidation state unknown.

Table 37. Potential for arsenic removal by various processes.[a,b]

	Packed beds		Reverse osmosis	Electrodialysis
Contaminant	Activated alumina (pH 5.5-7.5)	Anion-exchange resins (pH 5-9)	Cellulose acetate or aromatic polyamides (pH 6-8)	(pH 6-8)
Arsenic (III)	P	P[c]	P/F	P/F
Arsenic (V)	G	P/G[d]	G	G

[a] Adapted from Clifford _et al._[67]

[b] Notes:

(1) G = good; F = fair; P = poor.

(2) For electrodialysis and reverse osmosis at 50 to 80% recovery: good means > 80% removal in typical ground water; fair means 40 to 80% removal; and poor means < 40% removal.

(3) For packed-bed processes: good means that the ion is a highly preferred ion relative to Cl^-; fair means that the ion is a preferred ion; and poor means that the ion is not a preferred ion.

[c] $HAsO_2$, the uncharged species, predominates at pH below 9.2.

[d] Poor at pH below 7 ($H_2AsO_4^-$); good at pH above 7 ($HAsO_4^=$), based on analogy to $HPO_4^=$.

Table 38. RO element specifications[a] used in EPA study of groundwater samples from Glendale, OH.[b]

	HF Membrane	SW Membrane #1	SW Membrane #2
Membrane material	aromatic polyamide	cellulose acetate	cellulose acetate
Product-water rated capacity (L/min)	1.31	0.18	0.38
Model number	0410-005	PV-52-97	PV-112-97
pH range	4-11	2-8	2-8
Salt passage	<10%[c]	<6%[d]	<6%[d]

[a] From manufacturer's literature.

[b] From Fox.[68]

[c] Based on operation with a feed of 1500 ppm NaCl at 200 psig, 77°F, and 50% recovery.

[d] Based on operation with a feed of 1000 ppm $CaCl_2$ at 400 psig, 77°F, and 10% recovery.

$NaAsO_2$ to yield feed-water concentrations ranging from 0.076 mg/L to 16.4 mg/L as As(III). Arsenic (V) was added in the form of $Na_2HAsO_4 \bullet 7\ H_2O$ to obtain concentrations ranging from 0.075 mg/L to 17.0 mg/L as As (V).

Test runs ranged from 4 to 14 h with an average of 8 h; a 1-h stabilization time was allowed before data collection. The feed flows were held constant at 5.1 and 2.5 L/min for the hollow-fiber and spiral-wound elements, respectively. The applied pressures ranged from 160 to 200 psig for the hollow-fiber unit, and 200 to 230 psig for the spiral-wound elements. The product-water recoveries were in the range of 40 to 50% for the hollow-fiber module, and 3 to 6% for the original spiral-wound element. The latter was increased to about 6 to 8% with the larger Osmonic Sepralator replacement element. The water temperatures were not reported. The specific conductance, pH, and flow rate were monitored routinely. Analyses were made according to the Environmental Protection Agency (EPA) standard methods, and the removals were averaged over each run.

The rejection of As(III) ranged from 60 to 72% for both types of RO systems (i.e., HF and SW). The individual data points are shown plotted on a double-log plot in Fig. 40. The line shown has a slope of 45°, which means that the product-water concentration was directly proportional to the feed-water concentration. An average of two-thirds of the As(III) was removed consistently. No significant change in rejection was noted for pH levels in the range of 4.8 to 6.4, operating pressures in the range of 170 to 250 psig, or when the TDS was increased to 1000 mg/L (data not shown).

Table 39. Analysis of raw well water (before arsenic was added) from Glendale, OH (13 February 1979) used in EPA study on RO removal of inorganic contaminants from drinking water.[a]

Constituent[b]	Concentration (mg/L)	Constituent[b]	Concentration (mg/L)
Ca	80.8	F	0.2
Mg	22.1	Cr	<0.005
Cl	<10.0	Ag	<0.03
SO_4	<15.0	Cu	<0.02
Na	10.4	Mn	0.07
Ba	0.2	Pb	<0.005
As	0.01	Fe	1.75
Se	<0.005	Cd	<0.002
Hg	<0.0005	Zn	<0.02

pH = 7.7

TDS = 285 mg/L

Specific conductance = 525 μmhos (25°C)

Hardness = 250 mg/L as $CaCO_3$

Alkalinity = 260 mg/L as $CaCO_3$

Turbidity = 14 NTU

Color = 4 color units[c]

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[a] From Fox.[68]

[b] Oxidation states not given.

[c] Assumed to be based on visual comparison method.

The rejection of As(V) ranged from 92 to 99% (see data points in Fig. 41). The concentration in the product water was below the analytical detectability limit of 0.005 mg/L of As(V) for feed concentrations less than 0.75 mg/L. As in the case of As(III), the rejection did not change significantly in either system (HF or SW) with changes in pH (4.8 to 6.5), pressure (170 to 250 psig), or TDS (up to 1000 mg/L).

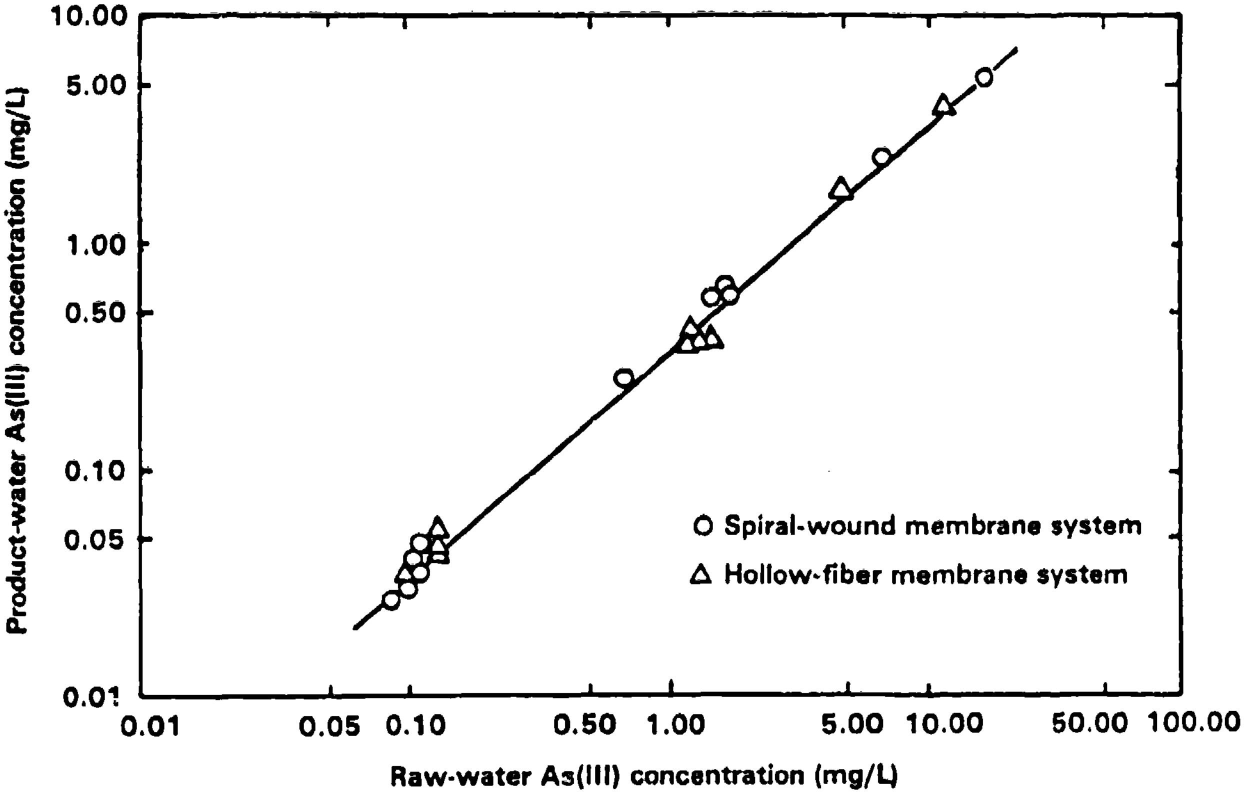

Figure 40. Product- vs raw-water arsenic [As(III)] concentration in EPA study on RO removal of inorganic contaminants from drinking water, Glendale, OH (170- to 230-psig operating pressure, pH range 4.6 to 6.5). From Fox, 1984.[68]

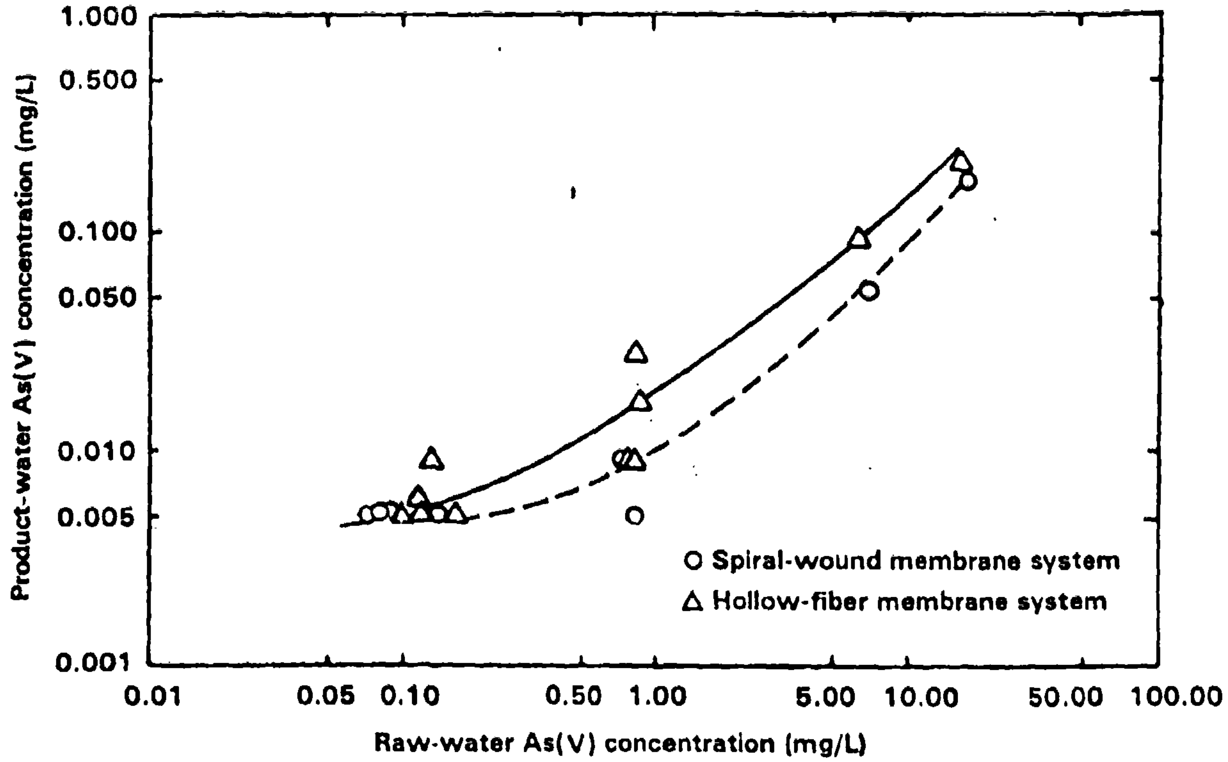

Figure 41. Product- vs raw-water arsenic [As(V)] concentration in EPA study on RO removal of inorganic contaminants from drinking water, Glendale, OH (170- to 230-psig operating pressure, pH range 4.6 to 6.5). From Fox.[68]

High concentration tests (6.0 to 16.0 mg/L) were run with both valences of arsenic to simulate some Alaskan ground water. Results were similar to the low concentration results in Figs. 40 and 41, with As(III) removals of 64-69% and As(V) removals of 98.6% and 99.0% for the hollow-fiber and spiral-wound elements, respectively.

Fox[68] concluded that the hollow-fiber and spiral-wound RO elements rejected As(III) to the same degree and that the spiral-wound unit was superior with As(V), as indicated in Figs. 40 and 41, respectively. The product recovery was considerably greater with the hollow-fiber elements, however. If we make allowance for this, it appears that the performance of the polyamide membrane was better than the cellulose-acetate membrane in terms of As(III) rejection, and that the performance of the polyamide membrane may have equaled the cellulose-acetate membrane as far as As(V) is concerned. It was also concluded by the author that the difference in the rejections noted for the two oxidation states of arsenic was produced by the predominant existence of the electromechanically neutral As(III) species, H_3AsO_3, in the pH range investigated.

Huxstep[69] conducted a series of tests to investigate the removals of fluoride, nitrate, two arsenic species, and selenium from ground water by RO. The pilot-plant RO system was housed in the Charlotte Harbor Water Association Water Treatment Plant facilities at Harbor Heights, FL. The pilot plant consisted of pretreatment, two RO systems, post-treatment, and a disposal pond for the spent test waters. The water sources were two deep wells (93 m and 139 m), and two shallow wells (9.1 m). During the initial testing program (October 1978 to March 1979), the deep-well test water consisted of a blend of the two wells. Analyses of water samples taken from each deep well during the period between October and November 1977, as well as a blended-water analysis performed later, are summarized in Table 40. The shallow well waters were lower in TDS and higher in color, but this supply was contaminated by acid in May 1979, and could not be used for further testing.

Pretreatment consisted of granular multimedia filtration, pH adjustment to a range of 5 to 6 with sulfuric acid, addition of hexametaphosphate, and 5-µm cartridge filtration. Two separate RO units were operated in parallel: (1) a conventional low-pressure system (330 psig) and (2) a less conventional very-low-pressure system (180 psig) referred to subsequently as the membrane barrier (MB) system. Each was originally designed to produce 1.97 L/s of product water with 75% product recovery, but the entire system was irreversibly fouled, and the membrane elements had to be replaced. The capacities of the new elements were decreased to 1.3 L/s and 0.98 L/s for the low-pressure and membrane-barrier systems, respectively.

The original low-pressure RO system contained two stages with 12 first-stage and 6 second-stage permeators (RO elements) arranged in a 6-6-3-3 array. The system was

Table 40. Water-quality analysis of raw water (before arsenic was added) for EPA study of inorganic contaminant removal from drinking water by RO at Harbor Heights, FL.[a]

Item	Deep well No. 1 (11/16/77)[b]	Deep well No. 2 (10/8/77)[b]	Source-water blend of deep wells 1 and 2[c]
pH	7.5	7.4	7.5
TDS (mg/L)	1156	1378	1104
Hardness (mg/L as $CaCO_3$)	460	490	428
Alkalinity (mg/L as $CaCO_3$)	108	106	109
Sulfate (mg/L)	152	210	105
Chloride (mg/L)	460	510	467
Calcium (mg/L)	76	96	82
Magnesium (mg/L)	66	60	54
Fluoride (mg/L)	1.3	1.2	--
Carbon dioxide (mg/L)	7	8	8
Color (units)	<5	5	3.2

[a] Reprinted from Huxstep.[69]

[b] Water samples were obtained and analyzed during the period between October and November 1977; the testing program occurred between October 1978 and March 1979.

[c] Average of 9 to 27 samples.

modified after fouling by reducing the total number of permeators to 12 and rearranging to a 4-4-2-2 array. Each permeator contained three 4-in. diameter UOP ROGA 4160 HR cellulose-acetate elements placed in series.

The membrane-barrier system was also designed originally as a two-stage system with 12 permeators, each containing three UOP ROGA 4160 LP cellulose-acetate elements. The original configuration was eight permeators in the first stage and four in the second, structured in a 4-4-2-2 array. The modified low-pressure system had only six permeators arranged in a 2-2-1-1 array. The performance data for both the low- and high-pressure systems are summarized in Table 41.

Arsenic (III) and As(V) as sodium salts were added to the test waters. Total arsenic was determined with a graphite-furnace atomic absorption apparatus. The initial concentrations and removals of both forms of arsenic are summarized in Fig. 42 and Table 42. The rejection of As(III) ranged from 63 to 73% for the conventional

Table 41. Summary of RO and membrane-barrier (MB) systems performance data. EPA study for removal of inorganic contaminants from drinking water by RO, Harbor Heights, FL.[a]

	Day 20 to 27 11/31/78 to 12/7/78			Day 28 to 69 1/29/79 to 3/28/79		
Item	Pressure (psig)	Flow (L/s)	Conductivity (μmho/cm)	Pressure (psig)	Flow (L/s)	Conductivity (μmho/cm)
RO system						
Feed	339	2.6	1862	359	1.73	1816
Product	8	1.99	105	6	1.30	127
Reject	31	0.6	5562	319	0.43	5245
Product recovery (%)	--	75.1	--	--	75.1	--
TDS rejection (%)[b]	--	--	94.6	--	--	93.0
MB system						
Feed	184	2.62	1862	187	1.32	1815
Product	--	1.96	1030	5	0.99	1019
Reject	124	0.66	4634	135	0.33	4719
Product recovery (%)	--	74.9	--	--	75.1	--
TDS rejection (%)[b]	--	--	--	--	--	43.9

[a] Reprinted from Huxstep.[69]

[b] Based on conductivity.

low-pressure RO system, and much less for the MB arrangement. These results are almost identical to those reported by Fox[68] for cellulose-acetate membranes. It should be noted, however, that the product-water recovery was much greater in this study (75% vs 6 to 8% for the Fox[68] study). The rejection of As(V) increased with the feed concentration as noted previously by Fox.[68] The percent rejections in the study by Huxstep[69] were less than those noted in the previously described study by Fox,[68] but this may be attributed, at least in part, to the much greater product recovery.

The results indicated that the high-pressure RO system outperformed the low-pressure MB system. Although rejections were significantly different between the two systems, the order of removal effectiveness for four of the contaminants studied was about the same: As(V) > F^- > As(III) > NO_3^- for the MB system, and As(V) > F^- > NO_3^- > As(III) for the RO system.

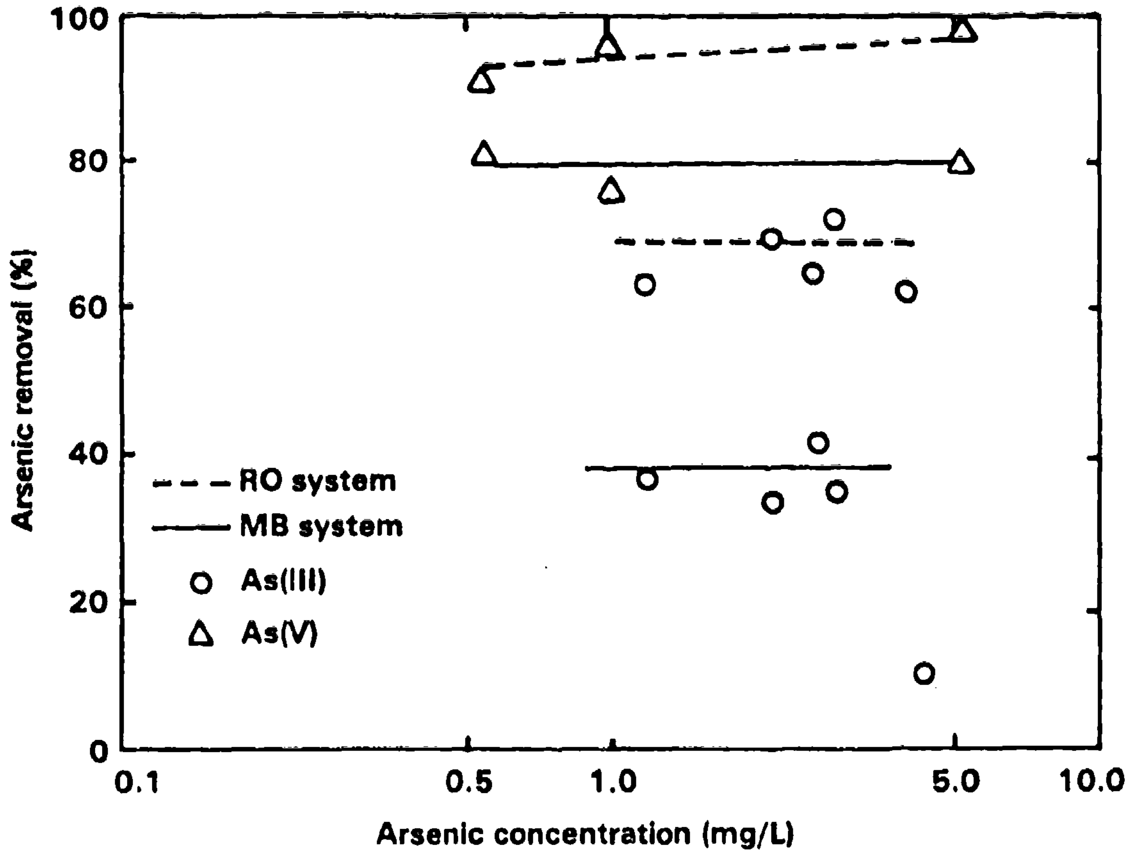

Figure 42. Removal of arsenic by low- and high-pressure RO systems (EPA study for removal of inorganic contaminants from drinking water by RO). Adapted from Huxstep, 1981.[69]

Table 42. Reported removal of As(III) and As(V). EPA study for removal of inorganic contaminants from drinking water by RO, Harbor Heights, FL.[a]

Days of operation[b]	As species and concentration (mg/L)	RO System			MB System		
		Product (mg/L)	Concentrate (mg/L)	Removal (%)	Product (mg/L)	Concentrate (mg/L)	Removal (%)
26	As(III)-4.20	1.55	13.6	63.1	3.70	9.75	11.9
27	As(III)-1.14	0.39	3.4	65.8	0.72	3.25	36.8
29-30	As(III)-2.12	0.64	5.5	69.8	1.40	5.13	34.9
32-35	As(III)-2.59	0.92	7.2	64.4	1.50	4.26	42.1
36	As(III)-2.80	0.76	7.0	72.9	1.81	6.46	35.4
47-48	As(V)-0.54	0.05	1.98	90.7	0.10	2.18	81.5
50	As(V)-1.0	0.05	3.44	95.0	0.23	3.66	77.0
51	As(V)-5.31	0.08	17.4	98.5	1.03	18.8	80.6

[a] Reprinted from Huxstep.[69]

[b] Consecutive.

The EPA[70] conducted an investigation to determine the source of arsenic contamination in groundwater supplies of New Hampshire. They also monitored the effectiveness of various home water-treatment units in removing arsenic from drinking water. They investigated the following processes:

- RO
- RO with an activated alumina cartridge (RO + AA)
- RO with an ion-exchange cartridge (RO + IX)
- Fractional distillation (FD)
- Two modules of activated carbon (AC)
- Ion exchange (IX)
- Activated alumina (AA)

The RO system was evaluated independently by installing a sampling tap between the RO unit and the AA cartridge. No information was given concerning the type of membrane or element employed in these studies. Also, the operating pH, temperature, and type of arsenic [As(III) or As(V)] were not reported.

The RO + AA system was operated at a minimum pressure of 40 psig. The product-water recovery was about 50%, and the product flow was 2 to 4 gpd. The RO membrane and the AA cartridge were replaced when the system became clogged; this resulted in a decrease in product recovery. The RO + IX system was similar, except that an IX cartridge was installed in place of the AA cartridge.

The arsenic was determined by atomic absorption with a graphite furnace. The concentrations in the feed water ranged from 0.135 to 0.240 mg/L, with an average of 0.180 mg/L. The results of the RO, RO + AA, and RO + IX experiments are shown in Fig. 43. The other methods are not reviewed in this study.

According to the investigators, the RO unit of the RO + AA system removed an average of 40% of the arsenic from the water. The rejection varied from about 16 to 50% (Fig. 43). The total RO + AA system lowered the concentration to or below the detectable limit of 0.005 mg/L. The RO + IX system removed arsenic to the detectable limit subsequent to an initial lag period of several weeks. Reasons for the observed lag time were not given by the investigators.

Huxstep[71] reports 69.08% rejection of As(III) with a FilmTec BW-30 4021 element. The concentration of As(III) in the potable water was decreased from an average of 0.097 to 0.032 mg/L. The operating conditions recommended for this element are 160 to 180 psig of applied pressure, a feed-water temperature <30°C, and a pH in the range of 4 to 10. The details of the arsenic removal test are not given in the report.

Arsenic (V) removal was studied with a Toray SC 3100 spiral-wound, modified cellulose-acetate element. Test conditions included operating pressure of 30 kg/cm^2, temperature of 25°C, NaCl feed-water concentration of 0.15%, and a pH in the range of 5 to 6. The product-water recovery ranged from 25 to 30%. Data obtained after an hour of operation indicated an average salt rejection of 97% with a minimum of 96%, and an average product-flow rate of 4.4 m^3/d. The As(V) concentration was decreased from 0.347 to 0.002 mg/L or less. The average rejection was thus greater than 98.95%.

Effectiveness of RO treatment was tested on two types of textile wastewaters containing arsenic (scour bath and dye) at a textile finishing plant for woven fabric.[72] Three types of RO membranes were tested: poly(ether/amide) (PEA); cellulose acetate (CA); and a dual-layer, hydrous zirconium oxide (ZrO)-polyacrylate dynamic membrane devised by Clemson University. The manufacturers of the two commercial membranes (PEA and CA) were not specified.

The dye wastewaters were derived from dyeing operations. Typically, these waters had a pH of 6 to 8, conductivity of 200 to 1000 μmhos/cm, and TDS of 400 to 2800 mg/L.

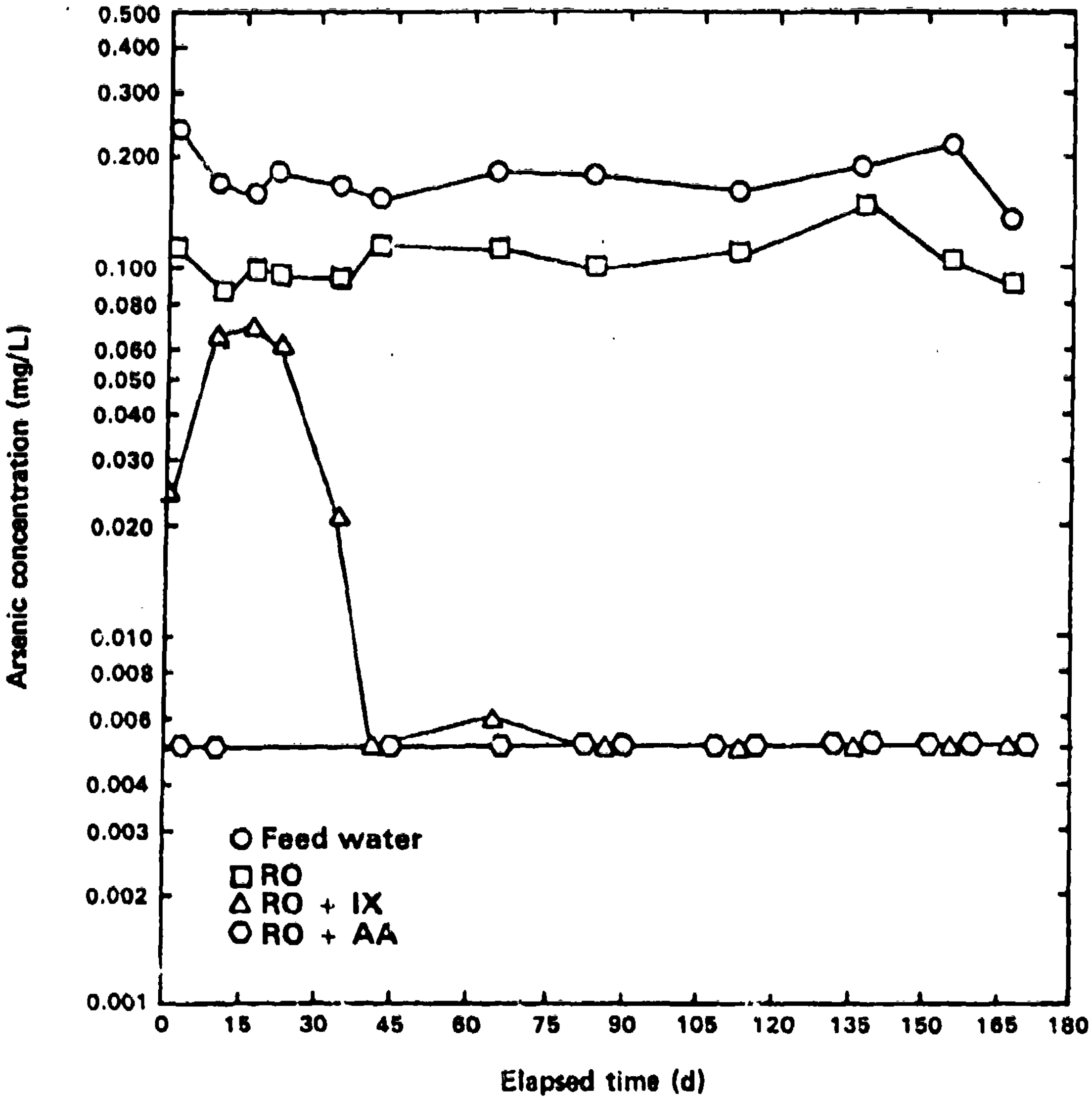

Figure 43. Comparison of arsenic removal by RO, RO + IX, and RO + AA systems (40-psig applied pressure, 0.135- to 0.240-mg/L initial arsenic concentration, 50% water recovery). Adapted from U.S. Environmental Protection Agency, 1982.[70] Detectable lower limit of arsenic concentration was 0.005 mg As/L water.

They also contained thickener and dispersing-wetting agents in addition to the dyes. The scour-bath wastewaters were derived from the washer, and the scour pad contained hydrogen peroxide, sodium carbonate, and a dispersing-wetting agent.[72] The pH was typically 8 to 10.

The wastewater feed samples were passed through a 1-μm polypropylene cartridge filter before they were introduced to the RO unit. The PEA and CA membranes were tested in series, resulting in two product samples and one final brine sample per feed tested. No information was given relative to membrane area, element length or diameter, oxidation state of the arsenic compounds, or the type of element placed first in the series.

The tests utilized the scour-bath and dye waste waters; were performed at 400-psig applied pressure and 46°C temperature; and the feed flow for these tests was approximately 15 L/min. The variations of product-water flows with time are shown in Fig. 44 for both types of wastewaters tested.

The dye wastewater had a pH of 6.5, conductivity of 271 μmhos/cm, and a TDS of about 400 mg/L. The reported overall product-water recovery was 86.3%, with 48.4% from the PEA and 37.9% from the CA membranes. The arsenic concentration in the dye waste (feed) was about 35 μg/L. The PEA product water contained 15 μg/L of arsenic, and the CA permeate had less than 1 μg/L of arsenic (Table 43).

The scour-bath waste had a pH of 9.7, a conductivity of 710 μmhos/cm, and a TDS of 730 mg/L. The reported overall product recovery was 89%, with 47.2% from the PEA and 41.8% from the CA membrane. The arsenic concentrations were less than 1 μg/L for the PEA and about 1 μg/L for the CA (Table 43).

All RO arsenic rejection data found in the technical literature are summarized in Table 44. In the pH range investigated (4.5 to 9.7), As(III) rejections commonly ranged from 60 to 73%. One exception was the EPA study with the unconventional, low-pressure, membrane-barrier system where the As(III) rejections ranged from only 12 to 42%. Arsenic rejection was also unusually low in the study conducted by EPA on ground water located in New Hampshire.[70] The oxidation state of arsenic in the ground water used in that study was not identified, but As(III) should be expected. Arsenic (V) was well removed in all of the conventional RO systems tested.

Most of the published data summarized in Table 44 were obtained with CA membranes; however, the rejections observed with the Du Pont polyamide membrane and the noncellulosic FilmTec BW-30 membrane were comparable. It is difficult to draw any conclusions from the study on textile wastes because a PEA and a CA membrane were used in series. Moreover, these wastes contained various waste substances that could have affected the arsenic removals.

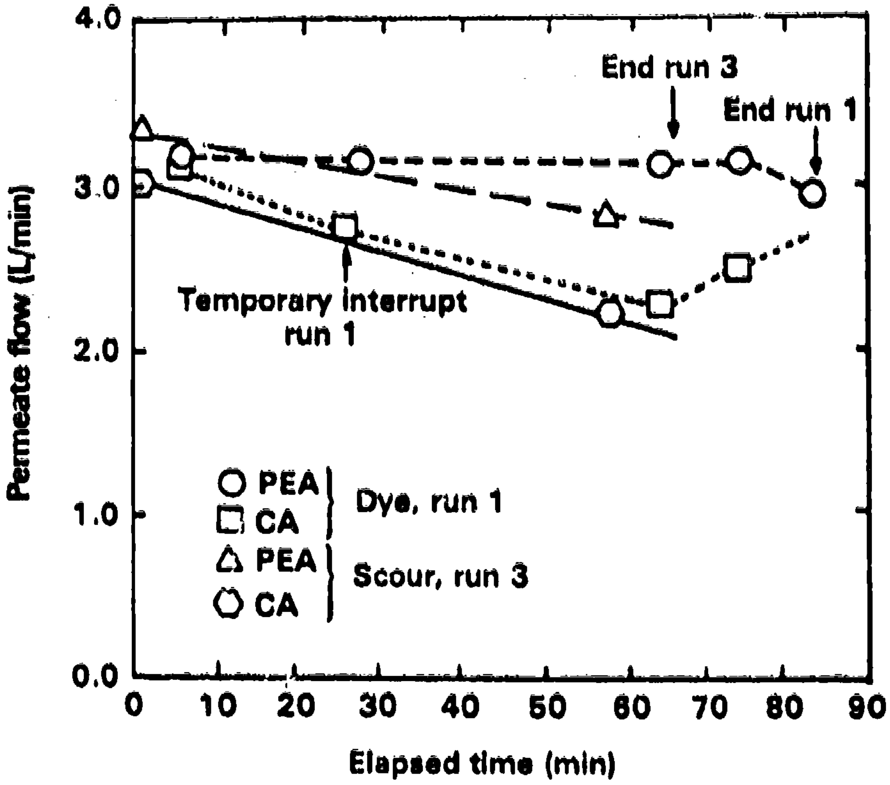

Figure 44. Permeate (product-water) flow rates for "cast" membranes during testing at 2800-kPa (400-psig) applied pressure, 46°C temperature, and 15-L/min feed flow. Adapted from Gaddis and Spencer, 1979.[72]

Table 43. The removal of total arsenic from two types of textile wastewaters with cellulose acetate (CA) and poly(ether/amide) (PEA) RO membranes (400-psig operating pressure and 45°C temperature).[a]

Stream	pH	TDS (mg/L)	TDS rejection (%)	As (µg/L)	As rejection (%)
Dye, feed	6.5	462[b]		35	
Dye, PEA permeate	6.9	15	98	15	75
Dye, CA permeate	6.7	45	94	<1	>98
Dye, concentrate	7.6	2670		221	
Scour, feed	9.7	730		19	
Scour, PEA permeate	7.2	105	93	<1	>98
Scour, CA permeate	7.7	32	98	1	98
Scour, concentrate	9.8	6020		160	

[a] Adapted from Gaddis and Spencer.[72]

[b] Feed was concentrated by 15% before feed sample was obtained. Estimated actual feed-solids concentration was 391 mg/L.

The difference in rejection of As(III) and As(V) probably stems from the predominant form of As(III) being the nonionic species H_3AsO_3 at the pH range common to most of the published studies (4.5 to 6.5). Arsenic(V), on the other hand, carries a charge within the same pH range, improving the rejection with RO membranes. Arsenic removal is enhanced for the same reason in some other arsenic-removal techniques such as conventional coagulation and lime softening.[73]

CYANIDE

The removal of cyanide from electroplating wastewaters with RO membranes has been studied extensively.[74-78] Unfortunately, all of these studies were performed under alkaline conditions (pH = 10 to 13). Under these conditions, more than 90% of the cyanide should be in the form of CN^-. The observed rejections of free cyanide with various commercial RO membranes at a high pH are summarized in Table 45.

Table 44. Summary of arsenic removal achieved by RO treatment.

Study (or group)	Water	Feed pH	Membrane type	As oxidation state	Water recovery (%)	Initial As concentration (mg/L)	As rejection (%)
MERADCOM[64,a]	fresh	N.I.[b]	cellulose acetate	N.I.	N.I.	30	96
	fresh				N.I.	30	97
	fresh				N.I.	30	99
			Du Pont Permasep (aromatic polyamide)	III	40–50	0.08–16.0	60–72
						6.0–16.0	64–69
				V	40–50	0.075–17.0	92–99
						6.0–16.0	99
EPA (Fox[68])	well water (brackish)	4.6–6.5	Osmonic Sepralator (cellulose acetate)	III	3–6 (original)	0.076–16.4	60–72
					6–8 (replacement)	6.0–16.0	64–69
				V	3–6	0.075–17.0	92–99
					6–8	6.0–16.0	99
EPA (Huxstep[69])	well water (TDS 2000–3000)	5–6	ROGA 4160 HR (cellulose acetate)	III	75.1	1.1–4.2	63.1–72.9
				V	75.1	0.54–5.31	90.7–98.5
			ROGA 4160 LP (cellulose acetate)	III	74.9	1.1–4.2	11.9–42.1
				V	75.1	0.54–5.31	77–81.5
EPA (unpublished[70])	New Hampshire ground water	N.I.	RO (not identified)	N.I.	50	0.135–0.24	40
			RO + activated alumina	N.I.	50	0.135–0.24	>97
			RO + ion exchange	N.I.	50	0.135–0.24	>97
EPA (Huxstep[71])	potable	5–6	FilmTec BW 30	III	N.I.	0.032	69.08
			Toray SC 3100 (modified cellulose acetate)	V	25–30	0.347	>98.95
Gaddis and Spencer[72]	textile dye waste	6.5	poly(ether/amide)	N.I.	48.4	0.035	75
			cellulose acetate	N.I.	37.9	0.035	>98
	textile scour waste	9.7	poly(ether/amide)	N.I.	47.2	0.019	98
			cellulose acetate	N.I.	41.8	0.019	98

[a] Formerly U.S. Army Mobility Equipment Research and Development Command, Fort Belvoir, VA; now U.S. Army Belvoir Research and Development Center, Fort Belvoir, VA.

[b] N.I. = no information presented.

The range and arithmetic mean for rejection and product-water flux values shown in the table were obtained over a test period of 500 h. The high alkalinity caused the collapse of several of these membranes during the test period. The pH of the wastewater solutions could not be lowered to prevent this because under such conditions the cyanide began to precipitate out as cyanide salts (especially zinc cyanide). For example, this was observed when the pH was about 9.[75,76]

A single-solute study using NaCN dissolved in clean water was performed by Lonsdale et al.[79] An initial concentration of NaCN of 1370 mg/L was supplied to a CA membrane at a pH of 10.8. At this pH, about 98% of the total cyanide should be in the form CN^- (approximately 1340 mg/L). The time of exposure of the membrane to this solution was limited to 1 h to minimize membrane deterioration, and the cyanide rejection observed under these conditions was 95.3%.

As shown in Table 45, the rejection of cyanide was 90% or better for most of the membranes tested when the pH was in excess of about 10. Typically, the pH of feed water supplied to the RO elements of the 600-gph ROWPU is adjusted to between 5 and 6 with citric acid.[6] For cyanide, this will either cause a shift to the un-ionized form or the precipitation of insoluble cyanide salts, depending on the composition and concentration of the salts contained in the feed water. In the former case, the rejection should decrease because the rejection of un-ionized forms is expected to be less than that of the ionic forms.[80] In the latter case, the precipitation of cyanide salts eventually will foul the membrane.

Table 45. Rejection of cyanide ion from various electroplating wastewaters. Exposure time 500 h; 328 to 420 mg/L CN^- in CuCN solution at a pH range = 9.9 to 12.6 unless otherwise noted.[a]

Type of Membrane	Membrane material and configuration	Operating pressure (atm)	Feed flow (L/min)	Free CN^- rejection (av %) (range)	Product-water flux (arithmetic mean and range) $\frac{L}{m^2 \cdot h}$ (range)
PA-300[b]	Poly(ether/amide) flat-sheet	54.4	1.1	98.0 (96.7-99.2)	19 (15-25)
PBIL[b]	Polybenzimidazolone flat-sheet	54.4	1.1	96.8 (94.3-98.8)	17 (14-22)
NS-100	Polyethyleneimine tubular	40.8	1.9	91.9 (90.0-94.3)	9.7 (8.7-11)
NS-200	Polyfurfuryl alcohol tubular	40.8	1.9	93.2 (91.8-94.8)	23 (20-25)
NS-200	Polyfurfuryl alcohol hollow fiber	54.4	1.9	97.4 (96.7-98.6)	54 (51-58)
SPPO	Polyphenylene oxide flat-sheet	40.8	0.19	87.0 (79.9-92.8)	5.7 (4.4-7.5)
B-9	Aromatic polyamide hollow fiber	27.2	0.19	98.1 (97.0-98.8)	1.8 (1.7-2.0)

[a] Adapted from McNulty and Hoover.[77]

[b] 840 to 1200 mg/L CN^- in CuCN solutions, pH range = 11.0 to 11.9.

SUMMARY AND CONCLUSIONS

SEA SALTS (STRONG ELECTROLYTES)

Water pumped from the ocean, ocean embayments, and estuaries essentially contains sea salt. The following summary and conclusions regarding RO components apply to such waters or to solutions of sodium chloride.

- The composition of sea salt and the current drinking-water-quality standards for TDS, Cl^-, Mg^{++}, and $SO_4^=$ are such that the chloride ion has to be removed to the greatest extent to meet the standards. Of the substances specified, the chloride ion is removed the least with RO membranes. The chloride standard is thus the critical standard; achieving this standard will ensure that the other standards are met. The same is true for achieving the recommended standards in Volume 4. The chloride and TDS standards are virtually interchangeable because the TDS content of product water is composed almost entirely of sodium and chloride ions (e.g., a TDS concentration consisting of 1000 mg NaCl/L of water = 600 mg of Cl^-/L of water).

- The standard recommended for chloride in Vol. 4 of this study has not been changed from the current standard of 600 mg/L.[64] The proposed revised standards in Vol. 4 for TDS, Mg^{++}, and $SO_4^=$ thus have no impact on ROWPU operation as far as sea-salt or NaCl solutions are concerned.

- In most cases with the 600-gph ROWPU, the greater the product-water flow, the less the chloride-ion concentration in the product water. This applies especially to operating temperatures of 45°C or less. The ROWPU should thus be operated at the greatest product flow possible to achieve maximum performance for operating temperatures up to 45°C.

- The maximum permissible product-water flow should be based on evaluations of membrane fouling, element stability, and concentration polarization, rather than the performance specifications published by the membrane manufacturers (Tables 11 through 14). The brine-water flow should never be decreased much below 13.5 gpm for any 6-in. spiral-wound element. This gives a maximum permissible product-water flow of about 20 gpm, or about 60% product recovery for the ROWPU as presently configured. It may be noted that this is significantly greater than the 12 gpm established by the military for salt water.

- The maximum permissible applied pressure specified by the military is 800 psig for salt water. According to the results of PREDICTOR, increasing this limit to the maximum attainable of 980 psig for the ROWPU increases the product-water flow at temperatures less than 45°C, and this in turn decreases the concentration of chloride ions in the product water.

- Increasing the permissible limits on product-water flow and applied pressure to 20 gpm and 980 psig, respectively, extends the range in feed-water quality that can be treated successfully with UOP TFC-1501 PA elements (former specifications). For example, with the restrictions currently placed on maximum product flow and applied pressure, virtually no sea-salt concentration (except possibly a 3.5% solution) can be treated adequately for the first 200 h of operation at 45°C. The range in feed-water concentration that can be treated successfully expands to about 2.5 to 4.0% at 980 psig and a maximum feed flow of 20 gpm.

- The U.S. Army has stipulated that the useful life of a spiral-wound element in the 600-gph ROWPU should be at least 2000 h. Tests performed on UOP TFC-1501 PA elements indicated that the elements compacted and deteriorated rapidly at about 54°C and 600-psig pressure when the pressure was applied 10 to 12 h daily for a total run time of about 200 h. The product-water flux dropped about 50%, and the ratio of salt passage to rejection increased about 80% during that time. This indicates that the elements would have been useless after 2000 h of operation. (It should be noted that the maximum feed-water temperature recommended by all the manufacturers of spiral-wound elements is 45°C.)

- Based on the results of the high-temperature study, as well as other studies of a proprietary nature, it appears that the elements will deteriorate so rapidly at 65°C that practically no sea-salt concentration can be treated adequately after 200 h of operation. The results from PREDICTOR also indicate that the spiral-wound elements may deteriorate to some extent within 200 to 2000 h of operation at 45°C.

- Interpolation of the PREDICTOR output indicates that the treated-water standards will be exceeded when the product-water flow is less than about 5 to 8 gpm at 25°C, and 10 to 13 gpm at 45°C. Virtually no lower limit exists at 1°C. The minimum permissible product flow of 6 gpm established by the military for salt water thus helps to ensure compliance with the water-quality standards at a temperature of 25°C, but not at 45°C. The limit placed on the minimum product flow is unnecessarily restrictive at 1°C.

- The feed-flow rate recommended by all of the manufacturers of the 6-in. spiral-wound element is in the range of 22 to 23 gpm. Field tests show that the actual feed-flow rate used for the ROWPU is 34 to 35 gpm. The effect of feed-flow rate on ROWPU performance was checked with PREDICTOR by decreasing the flow in stages from 34 to 22.5 gpm for a constant feed-water salt concentration of 3.5% and a constant applied pressure of 800 psig. The results demonstrated that the feed-flow rate does not change the product-water flow or salt passage appreciably within this feed-flow range at temperatures of 1, 25, and 45°C.

- The amount that the feed-flow rate can be decreased is controlled by the minimum brine flow stipulated for the elements. The feed flow should not be decreased to less than 24 gpm for the particular input conditions investigated (3.5% feed-water concentration and 800-psig applied pressure).

- Based on the foregoing, it is apparent that the performance of the RO components of the 600-gph ROWPU can be improved significantly for salt water simply by modifying the restrictions placed on maximum and minimum product-water flow, and the maximum applied pressure.

- The performance of the entire 600-gph ROWPU unit can be improved significantly by decreasing the feed-water flow to the unit. The advantages of this approach are manifest and include the following: a greater product-water recovery; longer run times on the multimedia and cartridge filters; improved multimedia filter removal efficiency; a smaller, lighter, and cheaper RO positive-displacement pump; and a decrease in the rate of consumption of the feed-water conditioning chemicals.

MIXTURES OF STRONG ELECTROLYTES OTHER THAN SEA SALTS

- No conclusions can be drawn concerning the performance of the ROWPU with fresh and brackish surface and ground water except to say that the rejections of TDS, Cl^-, Mg^{++}, and $SO_4^=$ should be adequate in nearly all cases to meet the current or recommended water-quality standards. The problem here lies with the scaling and fouling of the membrane surfaces. Many cases can be cited of surface or ground water containing saturated concentrations of the sparingly soluble salts. Such salts would precipitate out immediately onto the membrane surfaces with the slightest product-water recovery. Sodium hexametaphosphate and citric acid are added continuously to the feed water to help alleviate this problem, but their effectiveness with the almost infinite variety of water qualities that might be encountered anywhere on earth defies rational analysis.

WEAK ELECTROLYTES (ARSENIC AND CYANIDE)

- Published data are scarce relative to the removal of the weak electrolytes with noncellulosic thin-film composite membranes. Arsenic studies performed with CA membranes and polyamide hollow fibers indicate that As(V) probably will be well rejected at most pH levels. As(III), on the other hand, may be poorly rejected if citric acid is added to the ROWPU feed water. Co-precipitation may also occur with other compounds, depending on the feed-water chemistry.

- The rejection of hydrocyanic acid (HCN) apparently has not been investigated in any study. Cyanide probably will pass through a membrane with little or no rejection if citric acid is added to the ROWPU feed water, or it will precipitate out, depending on the feed-water chemistry.

RECOMMENDATIONS

- The chloride standard of 600 mg/L should always be used to check compliance with the drinking-water standards for Mg^{++}, $SO_4^=$, TDS, and Cl^-.

- The permissible limits established by the military for the operation of the 600-gph ROWPU with seawater should be modified significantly. The maximum limit on product-water flow should be increased to 20 gpm, the restriction on maximum applied pressure should be raised to the maximum attainable of 980 psig, and the minimum limit on product-water flow should be increased with the operating temperature.

- No recommendations can be made concerning the maximum product-flow rate or applied pressure that should be permitted for waters containing mixtures of salts other than sea salt or NaCl solutions.

- Based on what appears to be the complete lack of knowledge for hydrocyanic acid and the wrong kind of information available for As(III), we recommend that it be assumed that both cyanide and As(III) will not be removed in the RO section of the 600-gph RCWPU when citric acid is added to the feed water.

- The conductivity meter used to determine the TDS in the product water should be calibrated against a NaCl solution if the feed-water salts are primarily sea salts. For a NaCl solution, a 1000 mg/L TDS concentration approximately equals a Cl^- concentration of 600 mg/L.

- The life of pressure-vessel seals might be prolonged if a valve is devised to increase and decrease the pressure on the RO elements gradually, regardless of the actions of the ROWPU operator.

- The temperature of the product-water stream should be registered automatically on the control panel. This is needed to operate the ROWPU properly.

- Information obtained by the U.S. Army relative to the stability of spiral-wound elements of various manufacturers should be made available for publication.

- Some thought should be given to the redesign of the RO portion of the ROWPU. This should include a complete evaluation of the effects of decreasing the feed-water flow and, possibly, the staging (i.e., arrangement of elements in ROWPU) of smaller elements to improve product-water recovery while maintaining the stipulated minimum brine flow. Staging was not evaluated in this study.

APPENDIX A

COMPREHENSIVE DATA CONCERNING OSMOTIC COEFFICIENTS AND CHEMICAL REMOVALS WITH RO MEMBRANES OF CELLULOSE ACETATE

The tables presented in this appendix were too lengthy to include in the main body of the text. They are presented here for the convenience of the reader. Table A-1 contains empirically determined osmotic coefficients (ϕ) for computing osmotic pressures of strong electrolytes. Table A-2 contains information concerning relative removals of single salts, based on calculated rejections for a cellulose acetate membrane.

Table A-1. Osmotic coefficients for aqueous inorganic salt solutions at 25°C.

	Osmotic coefficients (ϕ)						
Solution molality (m)	$NaCl^{a,b}$	$KCl^{a,c}$	$MgCl_2$ ^{c,d}	$CaCl_2$ ^{d,e}	Na_2SO_4 ^{f}	$MgSO_4$ ^{f}	Na_2SO_4-$MgSO_4$ ^{f} $\frac{1}{1}$ molalities
0.001	0.9884	0.9883	0.9623	0.9621	--	--	--
0.005	0.9760	0.9755	0.9278	0.9275	--	--	--
0.01	0.9679	0.9671	0.9085	0.9075	--	--	--
0.05	0.9425	0.9396	0.8664	0.8617	--	--	--
0.1	0.9313	0.9255	0.8606	0.8525	0.7885	0.5934	0.6829
0.2	0.925	0.913	0.877	0.8594	0.7505	0.5578	0.6444
0.4	0.920	0.902	0.919	0.8943	0.7077	0.5286	0.6149
0.6	0.923	0.898	0.976	0.9381	0.6793	0.5188	0.6104
0.8	0.929	0.897	1.036	0.9878	0.6586	0.5199	0.6217
1.0	0.936	0.897	1.108	1.0426	0.6435	0.5291	0.6460
1.2	0.943	0.899	1.184	1.1021	0.6329	0.5448	0.6822
1.4	0.951	0.901	1.264	1.1656	0.6263	0.5663	0.7293
1.6	0.962	0.904	1.347	1.2327	0.6230	0.5931	0.7869
1.8	0.972	0.908	1.434	1.3028	0.6226	0.6249	0.8544
2.0	0.983	0.912	1 523	1.3756	0.6249	0.6616	0.9315
2.2	0.995	--	--	1.4508	0.6295	0.7032	--
2.4	1.007	--	--	1.5278	0.6361	0.7496	--
2.6	1.019	--	--	1.6065	0.6448	0.8010	--
2.8	1.032	--	--	1.6666	0.6553	0.8575	--
3.0	1.045	0.937	--	1.7678	0.6675	0.9193	--
4.0	1.116	0.965	--	2.1807	--	--	--
5.0	1.192	--	--	2.5739	--	--	--
6.0	1.271	--	--	2.8908	—	--	--

References: a = 15, b = 16, c = 17, d = 18, e = 19, f = 20.

Table A-2. Calculated rejections of strong electrolytes for a cellulose acetate membrane, using theory of Sourirajan and Matsuura.[38] (Operating conditions: dilute solutions and a pressure of 405 psig.)

Solute	k x 10^4 (cm/s)	Separation (%)	Solute	k x 10^4 (cm/s)	Separation (%)
NaCl	20	96.8	$Cu(NO_3)_2$	16.6	97.4
			$CuSO_4$	17.1	99.1[a]
Inorganic solutes			$FeCl_2$	16.9	98.6
$Al(NO_3)_3$	14.5	99.5	$Fe(NO_3)_2$	16.7	93.7
NH_4Br	23.3	95.8	$Fe(NO_3)_3$	15.4	99.7
NH_4Cl	23.0	96.4	$LaCl_3$	17.3	99.4
NH_4I	23.1	94.5	$La(NO_3)_3$	16.7	94.3
NH_4NO_3	22.5	92.6	$Pb(NO_3)_2$	18.3	97.5
$BaBr_2$	18.3	99.1	LiBr	18.0	96.2
$BaCl_2$	18.2	99.4	LiCl	17.9	96.7
BaI_2	18.2	98.5	LiF	16.5	97.9
$Ba(NO_3)_2$	17.7	97.2	LiI	18.0	95.0
$Cd(NO_3)_2$	17.2	96.5	$LiNO_3$	17.6	93.2
$CdSO_4$	13.1	99.9[a]	$MgBr_2$	17.0	98.9
$CaBr_2$	17.8	98.7	$MgCl_2$	16.9	99.2
$CaCl_2$	17.6	99.1	MgI_2	16.9	98.1
CaI_2	17.7	97.8	$Mg(NO_3)_2$	16.5	96.5
$Ca(NO_3)_2$	17.2	95.9	$MgSO_4$	13.0	>99.9[a]
$Ce(NO_3)_2$	16.9	99.4	$Mn(NO_3)_2$	16.6	96.9
CsBr	23.6	96.7	$MnSO_4$	13.1	>99.9[a]
CsCl	23.5	97.2	$Ni(NO_3)_2$	16.6	97.2
CsI	23.5	95.7	$NiSO_4$	13.1	>99.9[a]
$CsNO_3$	22.9	94.2	K acetate	18.2	99.2
$Cr(NO_3)_3$	16.7	98.8	K anisate	15.6	98.9
$Co(NO_3)_2$	16.8	96.3	K benzoate	16.4	98.8
$CoSO_4$	12.6	>99.9[a]	KBr	23.3	96.0

Table A-2. (Continued)

Solute	k x 10^4 (cm/s)	Separation (%)	Solute	k x 10^4 (cm/s)	Separation (%)
$KBrO_3$	20.6	97.8	KOH	29.3	99.4
K butyrate	16.8	99.2	K phenylacetate	16.0	98.8
K o-chlorobenzoate	16.5	99.5	K 4-phenylbutyrate	14.2	99.0
K p-chlorobenzoate	16.4	98.8	K β-phenylpropionate	14.5	99.0
KCl	23.0	96.6	K pivalate	16.3	99.7
$KClO_3$	21.7	95.3	K propionate	17.0	99.3
$KClO_4$	22.1	92.5	K_2SO_3	18.7	99.8
K_2CO_3	18.5	>99.9[a]	K_2SO_4	19.4	99.8[a]
$K_2C_2O_4$	11.7	99.9	$K_2S_2O_3$	19.7	>99.9
K_2CrO_4	19.5	99.9	K toluate	16.4	98.9
$K_2Cr_2O_7$	18.7	98.3	K valerate	16.6	99.3
K cyclohexylcarboxylate	16.3	99.4	RbBr	23.7	96.2
KF	20.6	97.8	RbCl	23.5	98.8
KCOOH	20.5	97.5	RbI	23.5	96.1
$KHCO_3$	18.9	98.5	$RbNO_3$	23.0	93.3
KH phthalate	20.1	97.1	Na acetate	16.5	99.2
KH_2PO_4	18.0	99.3	Na anisate	14.4	99.0
$KHSO_4$	19.8	99.4	Na benzoate	15.0	98.9
K hydroxybenzoate	16.4	98.8	NaBr	20.1	96.3
KI	23.1	94.8	$NaBrO_3$	18.3	97.9
KIO_3	18.2	98.9	Na butyrate	15.4	99.3
$K_3Fe(CN)_5$	19.0	>99.9[a]	Na o-chlorobenzoate	15.1	99.5
$K_4Fe(CN)_6$	18.8	>99.9[a]	Na p-chlorobenzoate	15.0	98.9
K isobutyrate	16.8	99.3	$NaClO_3$	19.1	95.6
K m-nitrobenzoate	18.5	99.1	$NaClO_4$	19.3	93.0
K o-nitrobenzoate	16.5	99.6	Na_2CO_3	16.1	>99.9[a]
K p-nitrobenzoate	16.5	99.1	$Na_2C_2O_4$	10.9	99.9
KNO_2	20.9	94.0	Na_2CrO_4	16.9	99.9
KNO_3	22.5	93.0	$Na_2Cr_2O_7$	14.8	98.6

Table A-2. (Continued)

Solute	k x 10^4 (cm/s)	Separation (%)	Solute	k x 10^4 (cm/s)	Separation (%)
Na cyclohexylcarboxylate	14.9	99.4	Na toluate	12.0	98.8
NaF	18.3	98.0	Na valerate	15.2	99.3
NaHCOO	18.2	97.7	$SrBr_2$	17.8	98.9
$NaHCO_3$	16.9	98.6	$SrCl_2$	17.6	99.2
NaH phthalate	17.9	97.3	SrI_2	17.7	98.1
NaH_2PO_4	16.3	99.4	$Sr(NO_3)_2$	17.3	96.4
$NaHSO_4$	17.8	39.4	$Th(NO_3)_4$	11.1	99.9
Na hydroxybenzoate	15.0	98.9	$Zn(NO_3)_2$	16.5	96.3
NaI	20.0	95.2	$ZnSO_4$	13.0	>99.9[a]
$NaIO_3$	16.4	99.0			
$Na_3Fe(CN)_6$	16.3	>99.9[a]			
$Na_4Fe(CN)_6$	16.0	>99.9[a]			
Na isobutyrate	15.4	99.3			
Na m-nitrobenzoate	15.0	99.2			
Na o-nitrobenzoate	15.0	99.6			
Na p-nitrobenzoate	15.0	99.2			
$NaNO_2$	18.5	94.4			
$NaNO_3$	19.6	93.5			
NaOH	15.1	99.4			
Na phenylacetate	14.6	98.9			
Na 4-phenylbutyrate	13.2	99.1			
Na β-phenylpropionate	13.5	39.1			
Na pivalate	14.9	99.7			
Na propionate	15.5	93.3			
Na_2SO_3	10.0	99.8			
Na_2SO_4	16.7	99.8[a]			
$Na_2S_2O_3$	17.1	>99.9			

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[a] Separation shown corresponds to solute concentrations of 200 mg/L in feed water.

APPENDIX B

BRIEF DESCRIPTION OF CALIBRATOR AND PREDICTOR MODELS

A simple mathematical model describing RO behavior was devised to permit a performance evaluation of the 600-gph ROWPU under a variety of conditions. The mixing portion of the model consisted of a completely stirred tank reactor (CSTR) element on the brine-water side of the membrane, as shown in Fig. B-1. We used Eqs. 1, 2, 4, 6, 7, and 22 to establish a relationship between the CSTR element and the product-water side. The CSTR elements were also linked to form a CSTR cascade on the brine-water side of the membrane. Other major features of the model included a brine-water-carrier pressure drop (Eq. 17) and polynomial expressions for osmotic pressure (Eqs. 13 to 15). These comprise the main features of the model called CALIBRATOR.

CALIBRATOR was verified to some extent by comparing its output with a computer model used by the Fluid Systems Division of UOP, Inc., to model the 600-gph ROWPU.[32] First, the A and B parameters were computed for the data listed in Table 12 related to the advertised performance of the UOP TFC-1501 PA element. The results are shown in Table B-1. According to CALIBRATOR, A = 0.50 gal/(d • ft^2 • atm) and B = 0.0167 ft/d for NaCl at 25°C and a pH of 8.1.

The A and B parameters were then computed again with CALIBRATOR, using stated input and output conditions obtained for the UOP computer model. The stated input conditions were a feed water similar in composition to seawater, except that the sulfate-ion concentration was adjusted to give a B parameter for TDS approximately equal to the B for pure NaCl at 850-psig applied pressure, 25°C, and a pH of 8.1. The results shown in Table B-1 compare closely with those obtained from the manufacturer's specifications; i.e., the model used in this study would give about the same total product-water flow and TDS rejection as the UOP model for the 600-gph ROWPU when A and B are set equal to 0.50 gal/(d • ft^2 • atm) and 0.017 ft/d, respectively.

Empirical input and output data from the literature were used with CALIBRATOR to calibrate the mathematical mixing model shown in Fig. B-1. The corrections for pH, temperature, salt selectivity, compaction, etc. were then included in the mixing model. Next, the name of the model was changed to PREDICTOR, and PREDICTOR was used to calculate the expected output for different input data (i.e., different from those used for calibration). Schematic diagrams of the CALIBRATOR and PREDICTOR models are shown in Figs. B-2 and B-3, respectively. These schematic diagrams summarize the input and output data for each model and indicate the equations used for each model.

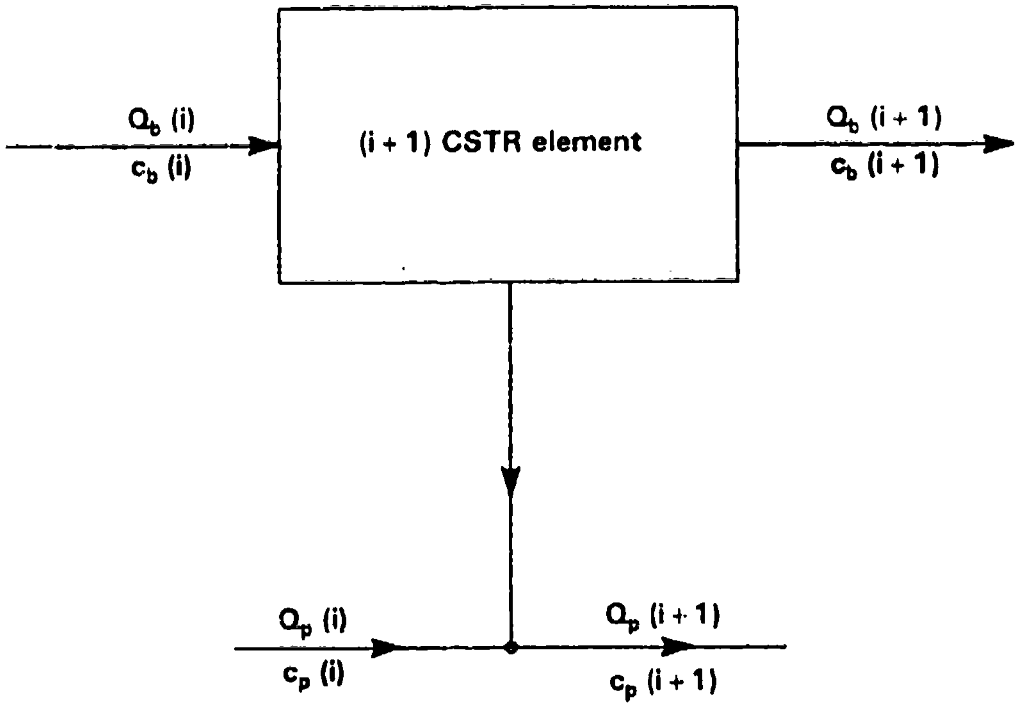

Figure B-1. Diagram of mixing portion of the model used for CALIBRATOR and PREDICTOR--(i + 1) finite mixing element (20 such elements used per pressure vessel). (CSTR - completely stirred tank reactor; i - integer.)

Table B-1. Comparison of A and B parameters obtained with CALIBRATOR (25°C, pH = 8.1).

Data Source	Computed A (gal/[d • ft^2 • atm])	 B (ft/d x 10^2)
Output statement for the UOP computer model[32] (600-gph ROWPU)	0.51	1.6 (TDS)
Present UOP TFC-1501 PA specifications	0.50	1.7 (NaCl)

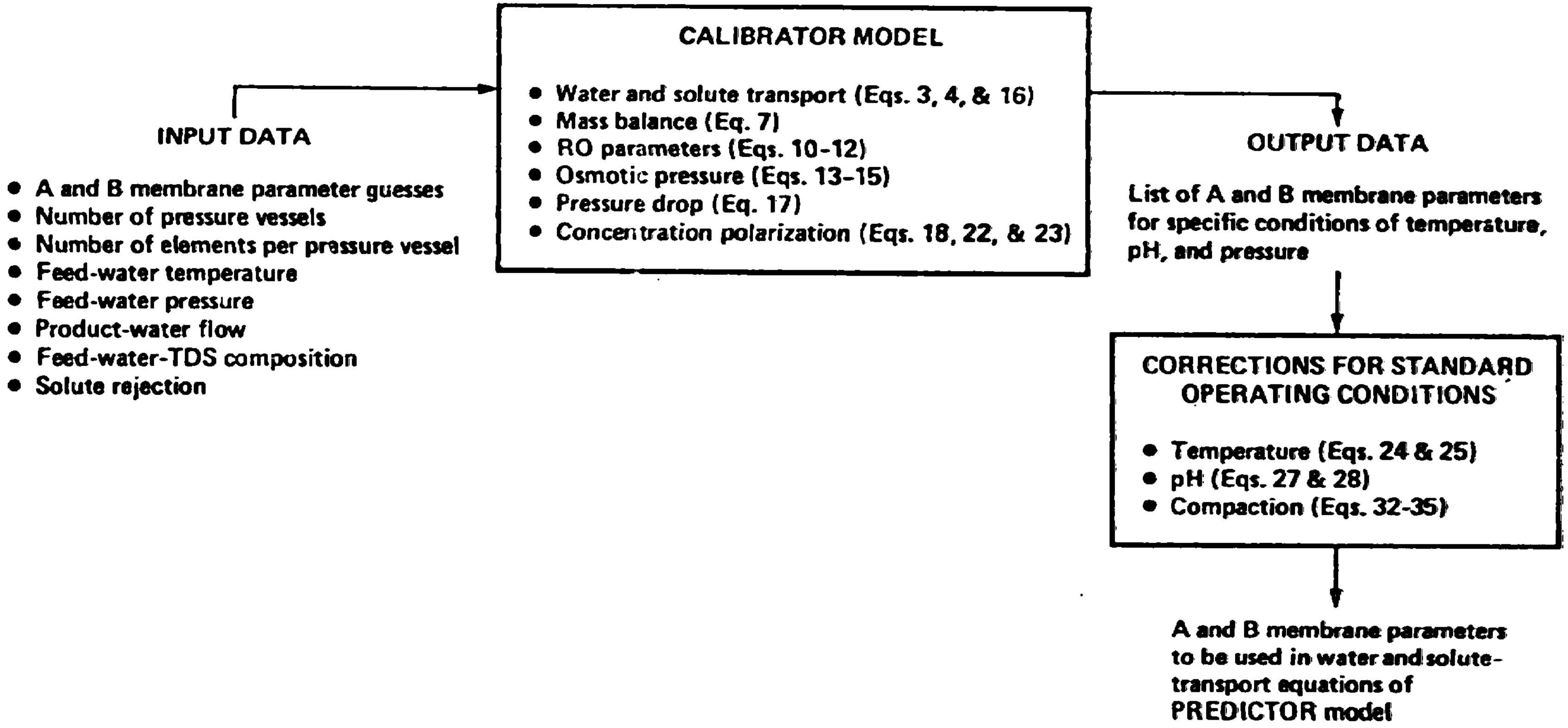

Figure B-2. Schematic diagram summarizing procedure to obtain the membrane parameters A and B. Standard operating conditions: temperature = 25°C; pH = 5.7.

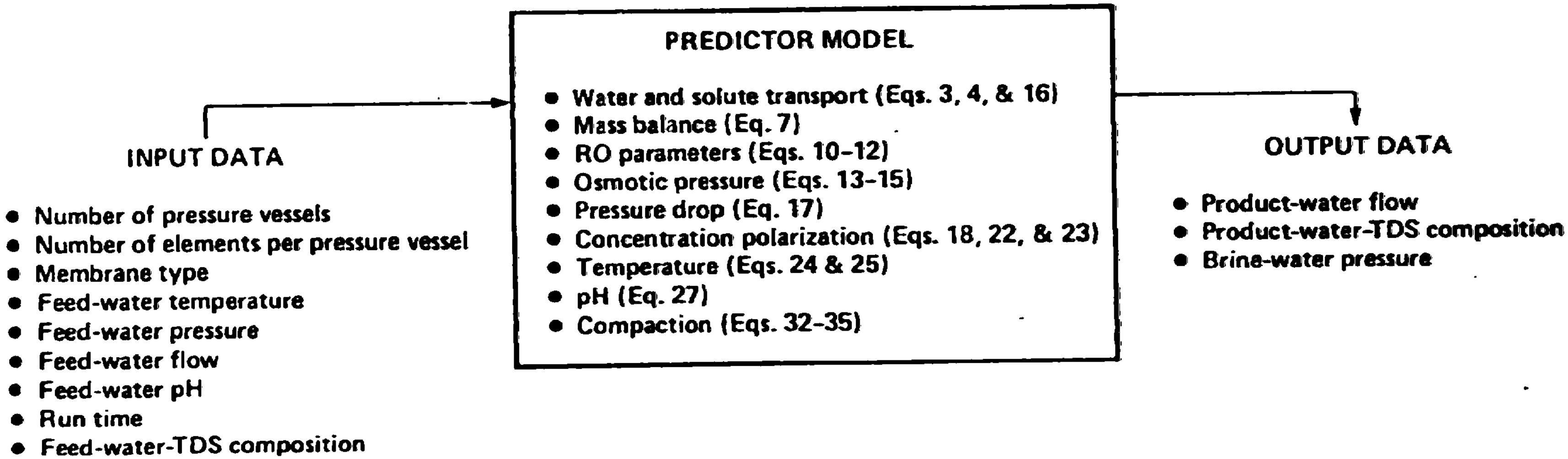

Figure B-3. Schematic diagram summarizing procedure to predict the performance characteristics of the 600-gph ROWPU. The A and B membrane parameters, which were determined using the CALIBRATOR model, are used in the water- and solute-transport equations of the PREDICTOR model.

APPENDIX C
SUPPLEMENTAL DATA

INTRODUCTION

One of the requirements for this study was a comprehensive literature review. Most of the background information that we did not use directly in the reverse osmosis (RO) modeling described in the main text of this volume is presented in this appendix. This information includes virtually all data relative to membrane fouling and control, ion-selectivity theory, performance of thin-film composite membranes not presently used in the 600-gph ROWPU, freshwater performance of the UOP TFC-1501 PA element, arsenic and cyanide water chemistry, and data that have been judged obsolete.

MEMBRANE FOULING AND CLEANING

The concentration of the salt in the concentrate (i.e., brine) increases with the product-water recovery and concentration-polarization modulus. The sparingly soluble salts will precipitate onto the membrane surface if the solubility limits of the salts are exceeded at the membrane wall. Macromolecules and particles will also collect at the membrane wall in accord with the principles of concentration polarization. If the concentration at the wall becomes too great, the macromolecules and colloids will gel out onto the surface of the membrane. In this case, the product-water flux will become independent of the applied pressure (i.e., increasing the pressure will not increase the product-water flux).[14]

Some well waters contain significant concentrations of reduced metal ions such as iron and manganese. These ions will precipitate out when exposed to dissolved oxygen that is introduced naturally in the RO pretreatment units. The limits on iron concentration, as described in Table C-1, are recommended by Caracciolo and co-workers[44] for the Du Pont B-9 hollow-fiber element.

Reactions between a solute and the membrane material will also cause membrane fouling. Most problems of this type have been encountered in the ultrafiltration of wastes containing high concentrations of serum-plasma protein, cationic electrocoat paints, surfactants, sulfite, etc. Oil dispersions will also coat the membrane surface; this decreases product-water flux.[12]

Table C-1. Iron-concentration limits in RO feed water for different pH and dissolved-oxygen conditions recommended for the Du Pont B-9 hollow-fiber element.[a]

pH	Dissolved oxygen (mg/L)	Maximum iron concentration (mg/L)
<7	0	5
5.5 to 6.5	1 to 5	0.5
>7	5 to 10	<0.1

[a] Adapted from Caracciolo *et al.*[44]

Riley and Milstead[31] studied the effects of cleaning agents, surfactants, and scale inhibitors on the transport characteristics of the TFC-801 membrane. The following test conditions were employed. Spiral-wound elements with 2.5 in. diameter (Models 7005 and 701) and membrane-surface areas of 8.4 ft^2 and 18.5 ft^2, respectively, were used in a two-element, recirculating test loop. The applied pressure was 800 psig. The feed-water flow rate was maintained at 2 gpm. The pH of the feed water was 5.5 to 5.7, and the TDS concentration was 35,000-mg/L NaCl. The product-water recovery ranged between 9 and 15%. Caustic solutions (mixtures of EDTA, borax, and sodium tripolyphosphates or trisodium phosphate) were effective in restoring the product-water flux with either no effect or very little effect on membrane performance.

Rover Rust Remover (a mixture of sodium bisulfite and sodium hydrosulfite manufactured by Hach Chemical Company, Ames, IA), a commercial cleaning agent for iron removal, had no adverse effect on the membrane. Also, enzyme cleaners, Rhozyme H39 and Rhozyme PF (manufactured by Rohm and Haas Chemical Company, Philadelphia, PA), that were used for protein removal were effective in cleaning and had no adverse effects on the membrane. However, Biz detergent (manufactured by Procter and Gamble Chemical Company, Cincinnati, OH), containing sodium perborate, destroyed the membrane.[31]

The effects of surfactants in trace amounts were tested in a laboratory. Two spiral-wound elements were operated in parallel at an applied pressure of 400 psig with a feed water containing 5000-ppm NaCl and pH between 5.5 and 8.0. Baseline performance was determined by operating for several hours prior to surfactant addition. The system was allowed to stabilize for 1 h or more after surfactant addition to obtain the new product-water flux and salt-rejection data. The elements were then flushed with clean water, and the transport properties were measured again to determine whether there were any permanent effects of the surfactant addition.[31]

The tests indicated that anionic materials decrease both water and salt transport through the membrane. The effect was more pronounced on polyurea than on polyamide membranes because of the greater cationic character of the former membrane, especially at the low pH. Generally, anionic materials can be removed from the membrane surface by caustic cleaning.[31]

The cationic surfactants did not affect membrane performance. This lack of effect was attributed to repulsion by the cationic nature of the membrane. The effects of nonionic surfactants were not investigated by Riley and Milstead.[31] In general, nonionic surfactants have the least effect, followed by the cationics.[31]

Scale inhibitors can eliminate acid handling and reduce corrosion problems by making it possible to operate RO systems at the natural pH of pretreated seawater (pH 7.8 to 8.2). Riley and Milstead[31] tested the effect of a polyacrylate-polymer scale inhibitor, Cyanamer P-70 (manufactured by American Cyanamid Company, Wayne, NJ). Little effect was observed at pH 7.9. At pH 5.7, the salt transport was reduced by approximately 35% with a constant product-water flux. It was concluded that Cyanamer P-70 could be used at pH 7.9.

Riley and Milstead[31] also investigated the effects of Pfizer Flocon-100 (manufactured by Pfizer Chemical Company, New York, NY), another antiscalant. After the antiscalant was added to a feed of pH 5.5, the pH was raised to 8.0. A small decrease in product-water flux and solute rejection consistent with that observed in the absence of the antiscalant was observed. Consequently, Pfizer Flocon-100 was also considered as a potential candidate for field testing.

Riley and Milstead[31] also reported the results of the field testing of the TFC-801 membrane at the Office of Water Research and Technology (OWRT) Seawater Test Facility at Wrightsville Beach, NC. Tests were initiated in 1976, and approximately 80,000 cumulative hours of testing were completed. Both 4-in. and 6-in. spiral-wound elements were tested. The elements were arranged in series of four 4-in. diameter and six 6-in. diameter elements. For seawater, the applied pressure ranged between 800 and 1000 psig, with the product-water recovery ranging from 23 to 33%, depending on the seasonal variation in water temperature. These tests produced some important findings.

- Citric acid cleaning at 200-h intervals was applied to four TFC-801, Model 1001, elements in series. The elements were operated for a total of 3898 h. After 2500 h of operation at 800-psig applied pressure, the plant exhibited single-stage capability (defined as 99% TDS rejection) and 23 to 30% product-water recovery. Subsequently, the plant was shut down several times and flushed with chlorinated water, which caused a deterioration in performance.

- The possibility of permanently maintaining single-stage desalination capability was investigated. A 50-ppm Colloid 189 rejection restorative was added to the feed stream for several minutes immediately after cleaning with citric acid. For the initial 2400 h (after restorative was added), single-stage capability was observed with 99.4% TDS rejection and 24% product-water recovery at 800-psig applied pressure. Data on further performance could not be obtained because the system was shut down.

In a different experiment, the continuous addition of 8 ppm of the rejection restorative fouled the membrane. The product-water flux dropped from the baseline value of 7.1 gpd/ft^2 to approximately 4.0 gpd/ft^2, with a corresponding increase in solute rejection from 98.2 to 99.4%. When the addition of the rejection restorative was stopped, the transport properties remained unchanged. Commercial acidic cleaning compounds were effective, however, in restoring product-water flux and salt rejection.

ELEMENT STABILITY

Riley and Milstead[31] also made some pertinent observations concerning element stability while conducting long-term field tests. The product-water carrier (see Fig. 15 in main text) that is used in the membrane is hydrolyzed under acidic conditions. This carrier was replaced by a product-water-carrying simplex impregnated with epoxy, but the membrane performance deteriorated because of frequent shutdowns. A third material was tested for the product-water-carrying simplex. It was a membrane-support fabric made of nonwoven Pellon polyester, and it was cured at high temperature and impregnated with melamine formaldehyde. This third material demonstrated satisfactory performance despite frequent shutdowns.

A loss of 37% in product-water flux was observed after the standard TFC-801, model 1601, element was operated over 4500 h without cleaning. A 33% decrease in product-water flux was observed for the 4-in. element (TFC-801, model 1001) after it was operated at 1000 psig of applied pressure for 20,774 h. It was cleaned only once during this period (with acid). Analysis of one of the elements was performed by taking some samples from the uncleaned element and testing them in flat-leaf RO cells. The membranes exhibited product-water flux and salt-rejection values close to the initial values for the element. It was concluded that the decrease in product-water flux was caused by the collapse of the channel material of the product-water-carrying simplex. The lower salt rejection exhibited by the element was attributed to osmotic blistering, which occurs by osmotic backflow through the membrane from the permeate to the feed side at the time of shutdown.

Riley and Milstead[31] were also concerned about the effects of testing the elements prior to using them in the field. The following results were reported by these investigators:

- Membrane performance evaluated in flat-leaf test cells was not realized in the spiral-wound element configuration, regardless of the size of the element. Both product flux and salt rejection generally were lower during the initial testing of the element.

- Element performance deteriorated further upon retesting, with an increase in product-water flux accompanied by a decrease in salt rejection.

Several factors were investigated and it was concluded that the procedure used to depressurize the elements after the initial testing might influence subsequent element-transport characteristics. For instance, elements that were slowly depressurized showed a smaller increase in water and salt flux upon retesting.

An extensive program of investigation was then performed to ascertain whether the problem was with the membrane proper or with the installation of the membrane leaves within the module. The results indicated that the problem was primarily with the membrane itself.[31] Flat-leaf tests were performed in test cells under the following conditions: (1) a 32,000-ppm NaCl feed-water solution, (2) pH of 5.5, (3) 800-psig applied pressure, and (4) 25°C temperature. The tests indicated that the greatest change in the membrane-transport properties occurred with the first depressurization. The changes in the transport properties were relatively insignificant with subsequent depressurizations. The investigators found that the detrimental effects of the first depressurization could be mitigated significantly if the elements were slowly depressurized with the simultaneous dilution of the feed water.[31]

BIOFOULING STUDIES

One of the common causes of membrane fouling is the development of microbiological films on the membrane surfaces. Winters and Isqueth[45] reported the results of studies on the development of biofilms in RO equipment used to desalt seawater. The process usually consists of four steps.

1. The rapid absorption of polymerized substances on the immersed membrane surfaces, followed by the absorption and concentration of low-molecular-weight substances that can be used as a carbon or energy source by bacteria.
2. Colonization by rod-shaped bacteria from a seawater source.
3. Colonization by other bacteria and microorganisms (fungi, protozoans, etc.).
4. Collection of debris, detritus, and inorganic particles on the primary biofilm.

The result is the formation of a glycoprotein polymer that adheres effectively to solid surfaces and that is detrimental, even at low concentrations. Winters and Isqueth observed that the presence of surface runoff in the seawater enhanced the rate of biofouling.[45]

McCray and co-workers,[24] Glater and co-workers,[81] and McCutchan and Glater[82] compared the resistance of various commercial membranes to those chemicals (i.e., the halogens and chlorine dioxide) that are used commonly as disinfectants. The membranes were soaked in equimolar solutions (about 4.3×10^{-5} $\underline{M}$) of chlorine, bromine, or iodine for various periods of time and then tested by running a 5000-ppm sodium chloride feed-water solution across the membrane in a flat-leaf test cell. A similar test was performed using a 1.8×10^{-5}-$\underline{M}$ (1.2 mg/L) solution of chlorine dioxide. For all tests, the water temperature was held constant at 22°C during the soaking, and at 25°C during the assessment of operating behavior. Controls, membranes that were not soaked in a disinfectant solution, were always analyzed in parallel with those that received treatment by a disinfectant. The effective membrane area in all cases was 15.91 cm^2. Each of the membranes was first compacted at 800 psig for 1.5 to 2 h before being tested at a constant pressure of 600 psig.

Typical results for the UOP RC-100 membrane are shown in Fig. C-1 for a free-available-chlorine concentration of 3 mg/L. The product-water flux increased grossly after 16 h of soak time, but the salt rejection decreased significantly. In fact, the salt rejection decreased by 50% or more after 64 h of soak time in the disinfectant solution. A pH within the range of 3 to 8.6 did not alter appreciably the rate of

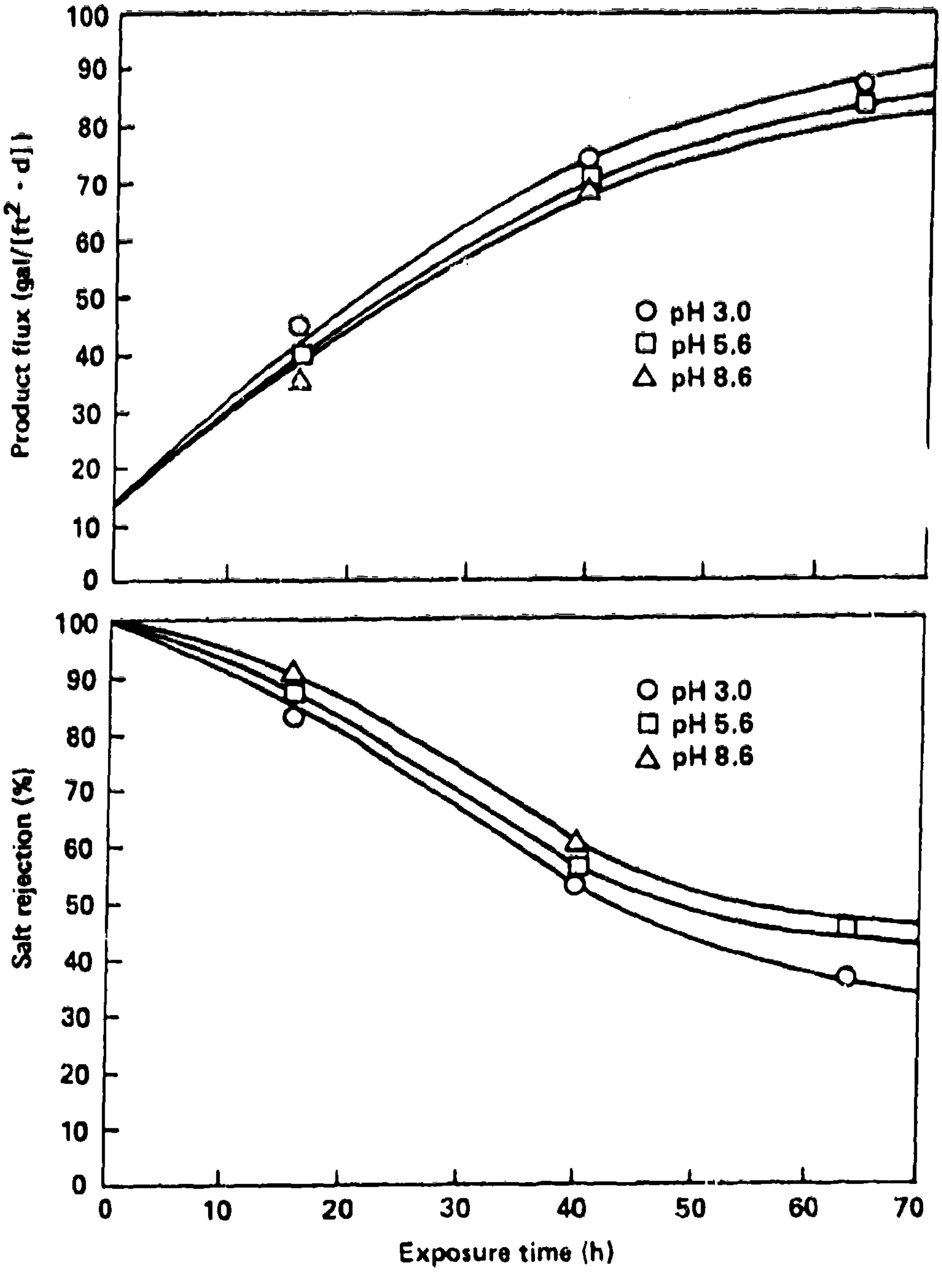

Figure C-1. Deterioration of RO performance of the RC-100 membrane after being soaked in a 3-mg/L solution of free-available chlorine. From McCray et al., 1981.[24]

membrane oxidation. This indicates that both hypochlorous acid (HOCl) and the hypochlorite ion (OCl^-) can effectively oxidize this membrane material.

Bromine oxidized the RC-100 membrane more rapidly than did chlorine under acidic conditions, and less so under basic conditions, as shown in Fig. C-2. Iodine oxidized the membrane only modestly during a 16-h exposure time. It should be noted that the results shown in Fig. C-2 are for a relatively short period of exposure to the halogens. The oxidation of the RC-100 membrane was severe after 64 to 88 h of soak time for all halogens, even at the different pH levels tested. Based on the results of this study, McCray and co-workers[24] ranked the oxidizing action of the various species of the halogens on the RC-100 membrane as follows:

$Br_2 > HOBr > HOCl > OCl^- > I_2 > HOI > OBr^-$ or $BrO_3^- > IO_3^-$.

Unlike the halogens, the rate of oxidation of the RC-100 membrane with chlorine dioxide increased with increasing pH as shown in Fig. C-3. Based on these results, as well as the smaller concentration of chlorine dioxide tested, it was concluded that chlorine dioxide reacts more rapidly with the RC-100 membrane than do any of the halogens.[24]

These investigators also determined the resistance of four other membrane materials to attack by free halogen and chlorine dioxide. The membranes tested were the Du Pont B-9, the γ-Hydranautics, the FT-30, and a blended cellulose acetate. The FT-30 membrane proved to be resistant to chlorine, iodine, and chlorine-dioxide oxidation under acidic conditions as shown in Fig. C-4. This membrane was oxidized more easily with bromine at low pH levels, and with all of the disinfectants except iodine at a pH of 8.6. McCray and co-workers[24] recommended an optimal operational pH of about 5.8 for the FT-30 membrane.

Larson and co-workers[40] also investigated the resistance of the FT-30 membrane to chlorine oxidation at several pH levels. The tests were performed in manners similar to those outlined for the experiments conducted by the University of California, Los Angeles (UCLA) researchers.[24,81,82] However, the concentration of free-available chlorine in the soaking solution was increased to 100 ppm, and the RO performance was measured using seawater at a standard pressure of 800 psig. The results shown in Fig. C-5 substantiate the findings of the UCLA investigators. The FT-30 membrane appears to be resistant to free chlorine as HOCl at a pH of about 5 or less. The deterioration in the membrane becomes noticeable at a pH of 6 and relatively severe at a neutral pH of 7. The membrane decomposes rapidly under basic conditions.

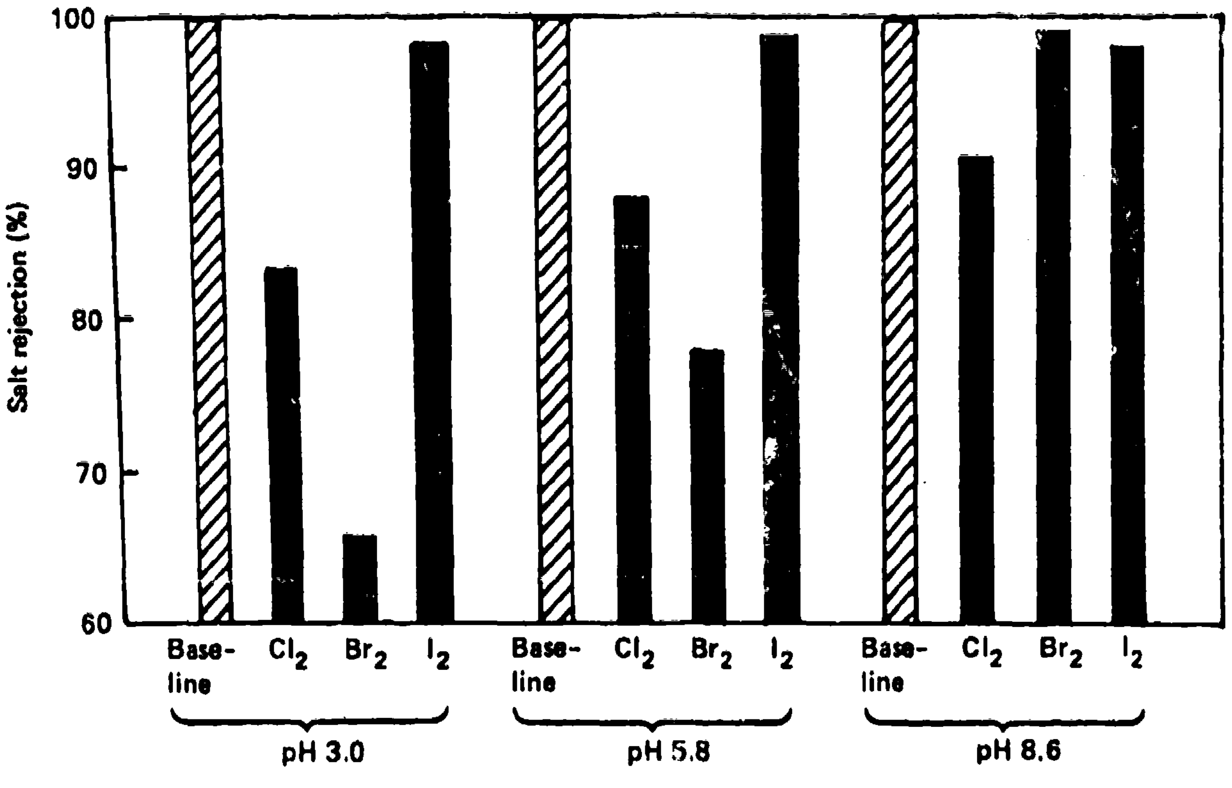

Figure C-2. Relative influence of the halogens (chlorine, bromine, and iodine) on the percent salt rejection of the RC-100 membrane. Membranes were soaked for 16 h in 4.3×10^{-5} M concentrations of the halogens at 22°C prior to assessment of RO operating behavior. From McCray et al., 1981.[24]

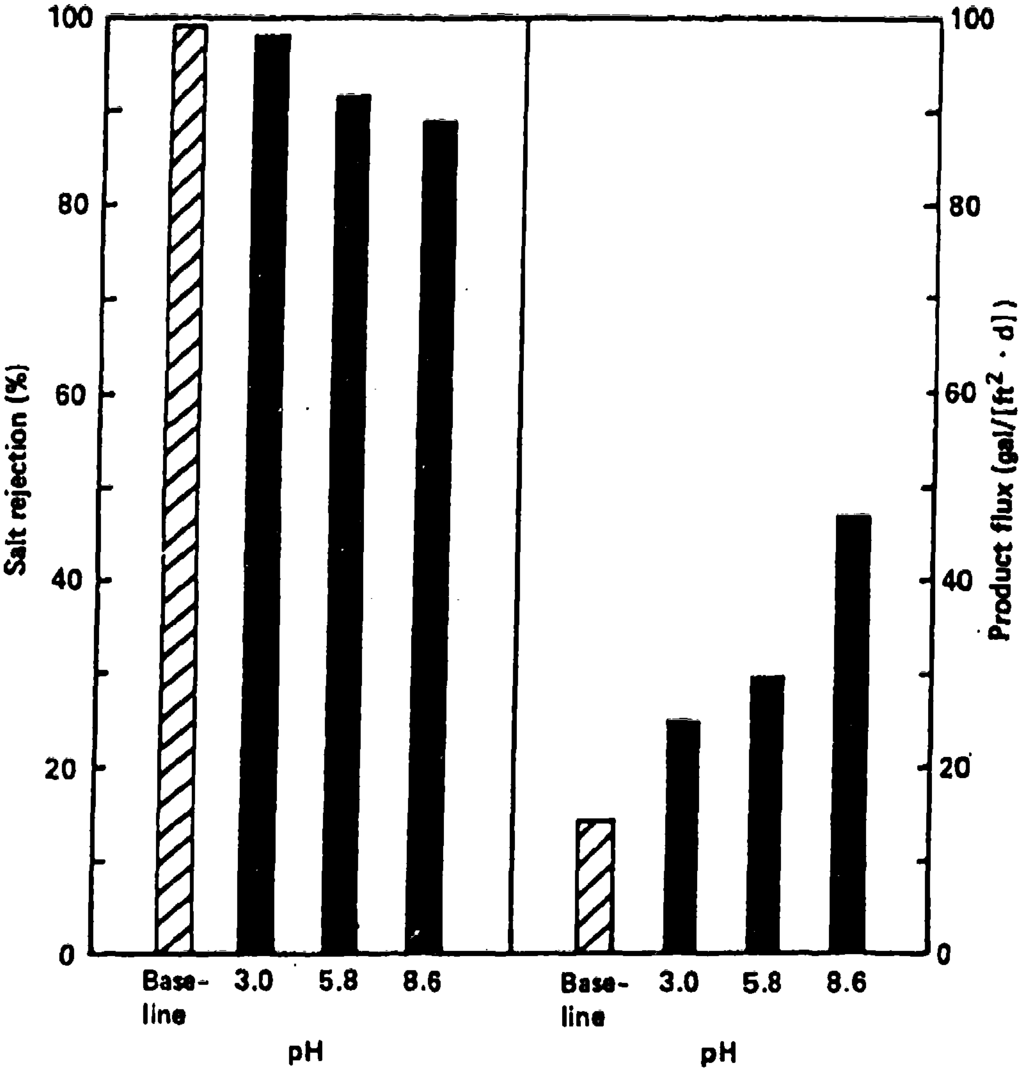

Figure C-3. Deterioration of RO performance of the RC-100 membrane. Membranes were soaked in a 1.2-mg/L solution of chlorine dioxide for 16 h prior to assessment of RO operating behavior. From McCray et al., 1981.[24]

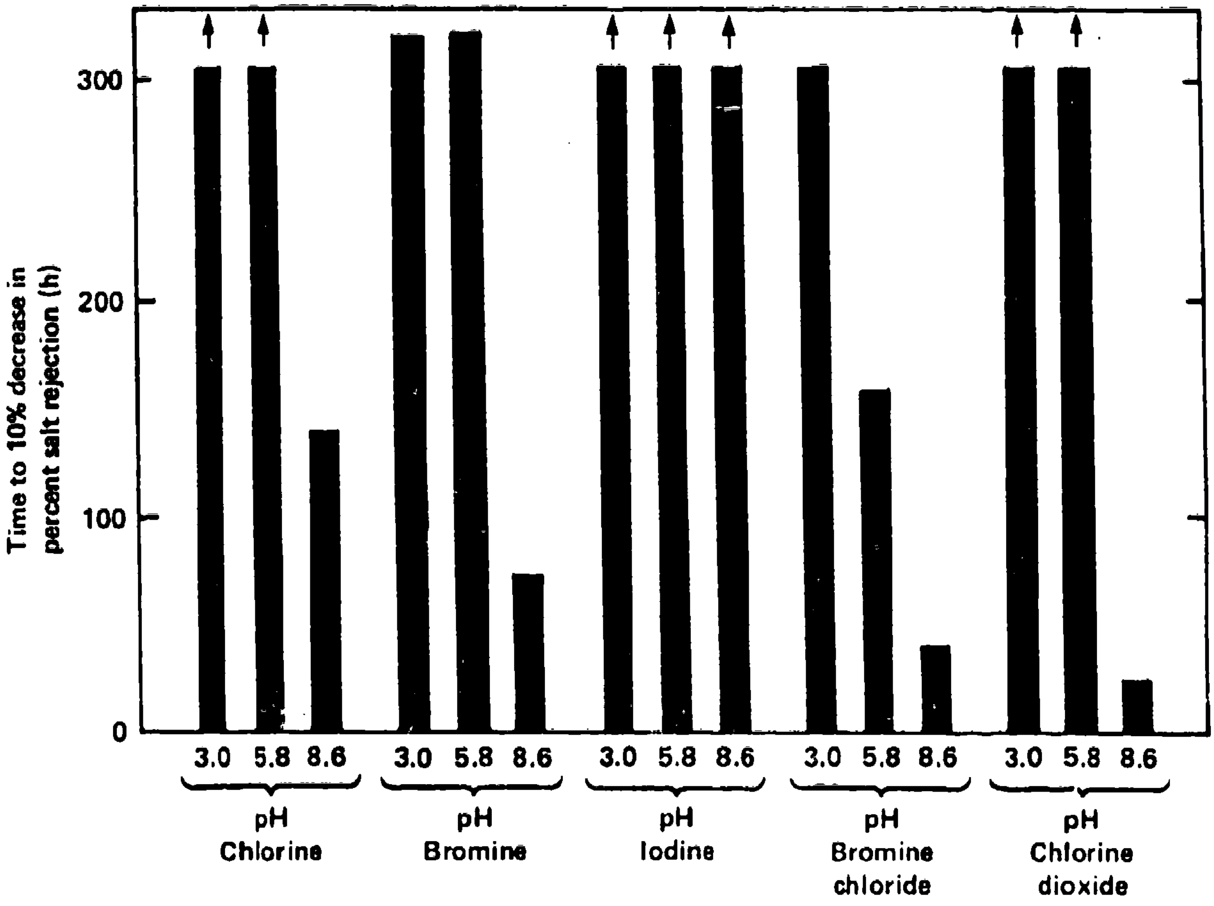

Figure C-4. Soaking time required to obtain a 10% decrease in salt rejection for the FT-30 membrane. From McCray et al., 1981.[24] Arrows (↑) indicate that a 10% decrease was not observed.

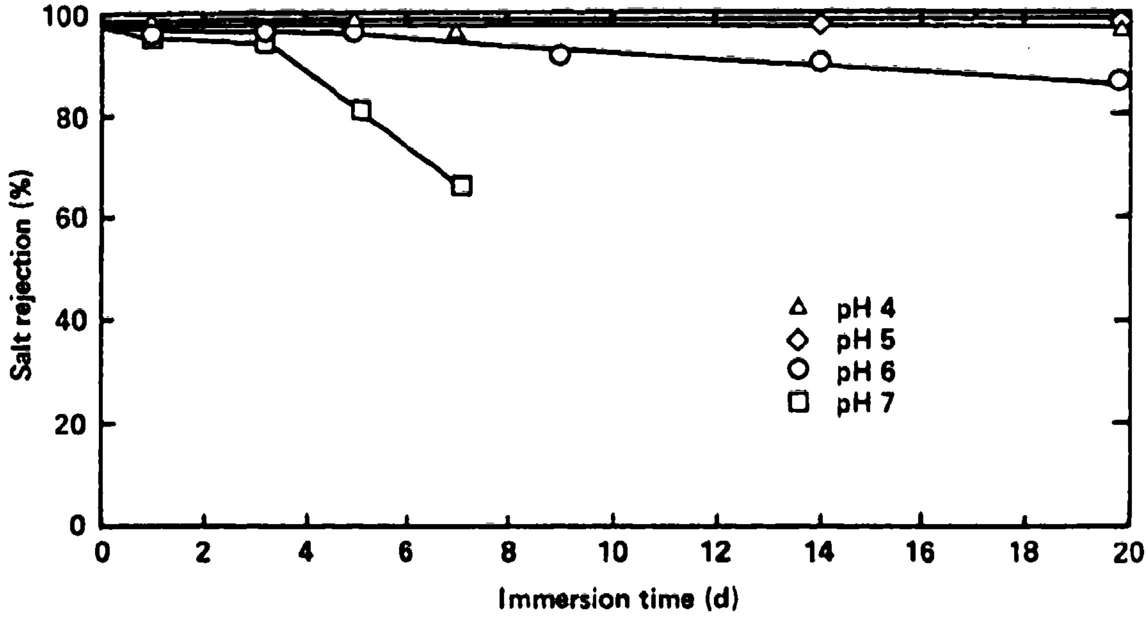

Figure C-5. Effect of pH on chlorine oxidation of FT-30 membranes (pH 4 to 7 and chlorine concentration 100 ppm). From Larson et al., 1981.[40]

Ozone is a powerful oxidizing agent, and it is unreasonable to expect that any organic RO membrane can withstand the attack of ozone for a long period. This was substantiated by McCutchan and Glater[82] who found that an exposure of the RC-100 membrane to approximately 0.4 to 0.8 mg/L of ozone decreased the solute rejection of the membrane to almost nothing within 40 h of exposure time. The results of this work were compared with those for free-chlorine exposure as shown in Fig. C-6.

Most of the foregoing membrane-oxidation studies were performed in the laboratory with the membrane first being soaked in solutions of the disinfectants. The situation was altered appreciably in continuous-flow tests, with the disinfectants being added either continuously or intermittently to the feed solution. Such studies were performed by Riley and Milstead[31] on spiral-wound elements containing different types of UOP membranes and concentrate-channel-spacer webbings. The particular membrane type of interest here is the TFC-801 membrane, which is similar in composition to the RC-100, as well as to the membrane now used in the military's 600-gph ROWPU. A 10,000-ppm solution of NaCl was tested in one series of experiments. The pressure applied to the elements was held constant at 400 psig. The water pH and temperature were also maintained constant at 5.6 and 25°C, respectively.

The results of chlorination are shown in Fig. C-7. The performance of the RO elements began to reflect the addition of the chlorine almost immediately, with the deleterious effects readily becoming apparent after about 170 h of intermittent chlorination. The deterioration in performance continued after all chlorination was terminated. The results for bromine chloride shown in Fig. C-8 were similar but much more pronounced.[31] This agrees with the observations of McCray and co-workers[24] who found that at a low pH, bromine oxidizes this particular membrane more readily than does chlorine.

Iodine was added continuously at a feed concentration of 1 to 1.6 mg/L to the RO elements for about 75 d. The process began to deteriorate after about 55 d (about 1300 h) as shown in Fig. C-9. Unlike chlorine, no further deterioration in process performance occurred after iodination was stopped.[31]

Figure C-10 shows the results when chlorine dioxide was added continuously to the NaCl feed solution for a period of about 14 d. The ClO_2 concentration and pH were about 4 to 5 ppm and 5.6, respectively. The chlorine dioxide appeared to have no effect on the performance of the TFC-801 membrane. This lack of effect contradicts the observations of McCray et al.[24] that are presented in Fig. C-3. The difference may stem, in part, from the fact that care was taken to generate a pure solution of ClO_2 in the Riley and Milstead[31] work. (The procedure commonly used to generate ClO_2 yields an

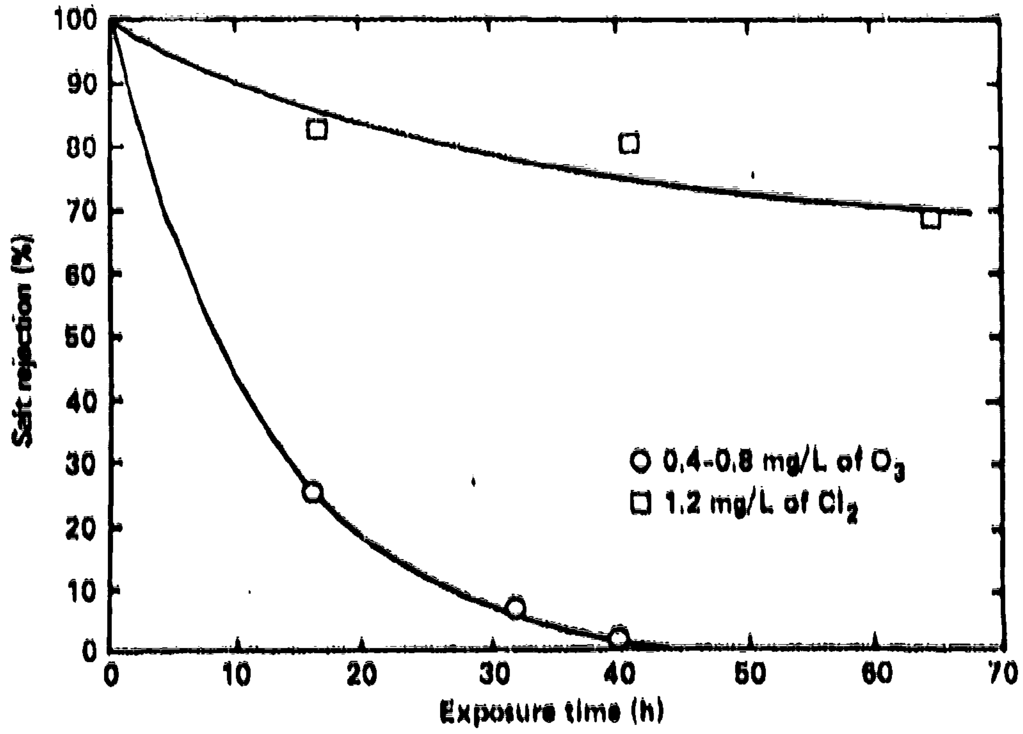

Figure C-6. Comparison of the decline rate of salt rejection for the RC-100 membranes exposed to equimolar concentrations of ozone and chlorine at pH 5.6. From McCutchan and Glater, 1980.[82]

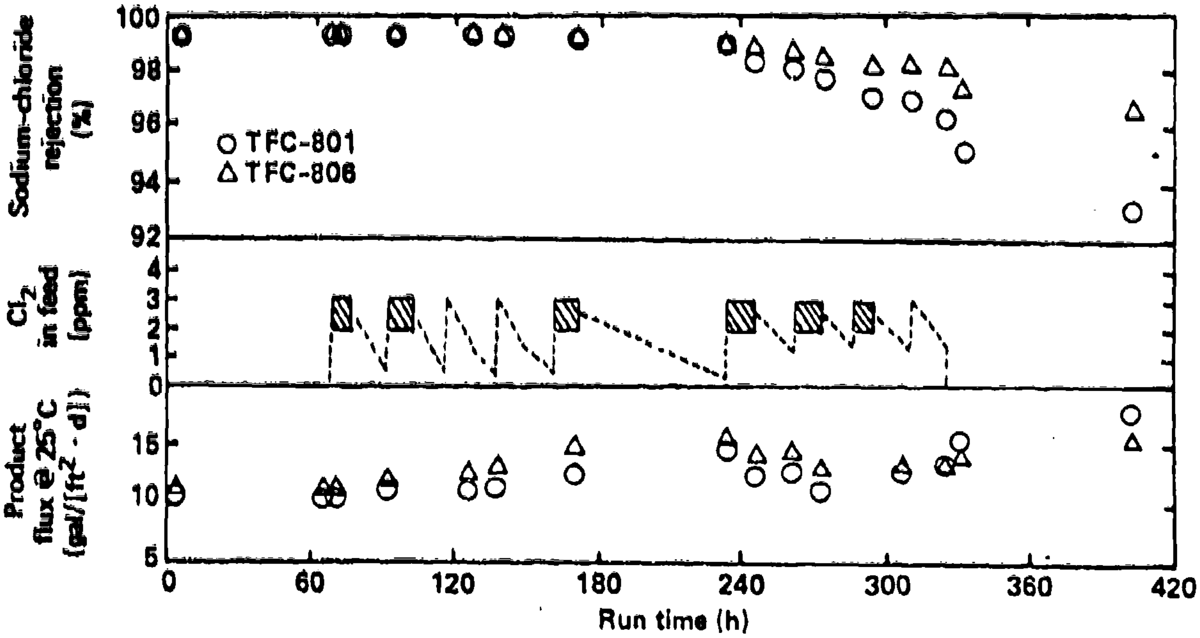

Figure C-7. The effects of chlorination on RO-process performance using either the TFC-801 or TFC-806 membranes (pH = 5.6); product flux = product-water flux. From Riley and Milstead, 1981.[31]

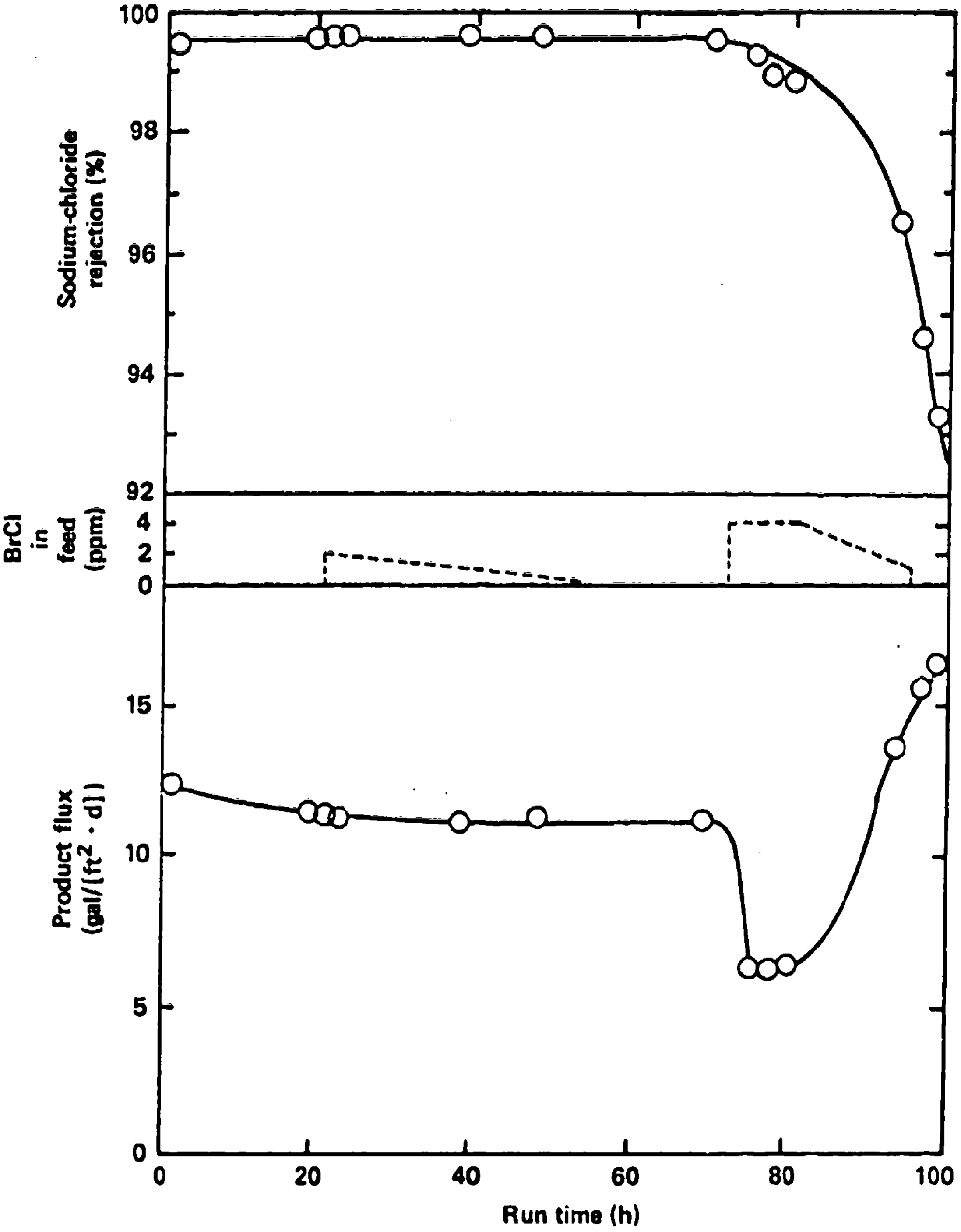

Figure C-8. The effects of bromine chloride on RO-process performance using the TFC-801 membrane (pH = 5.6); product flux = product-water flux. From Riley and Milstead, 1981.[31]

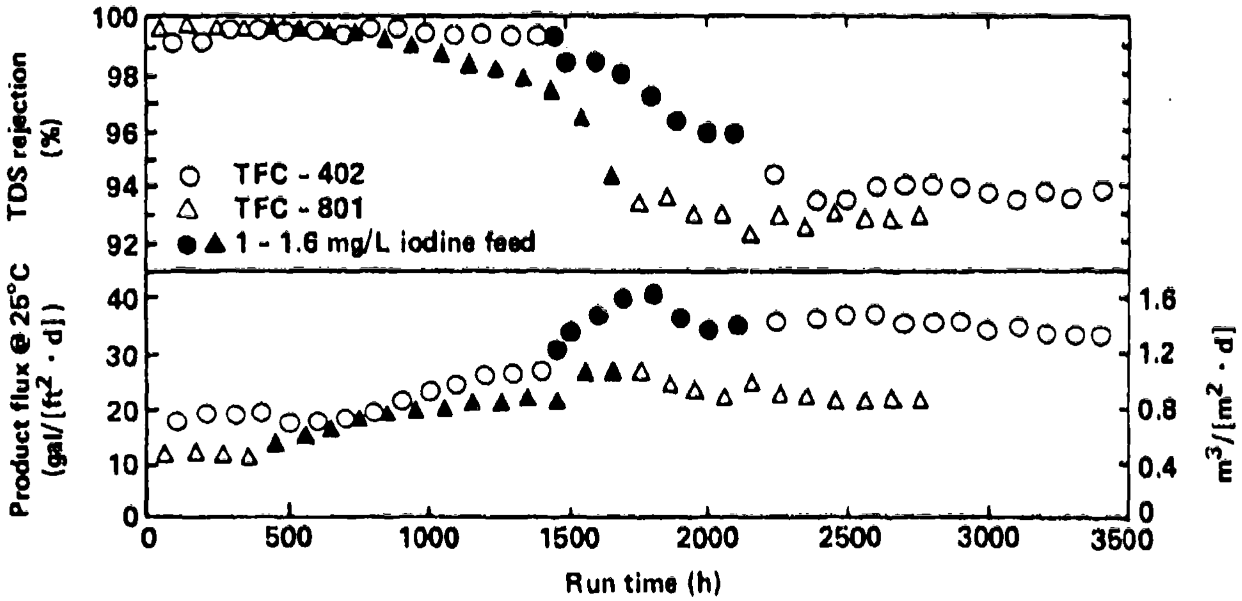

Figure C-9. The effects of iodine on RO-process performance using either TFC-801 or TFC-402 membranes (pH = 5.6); product flux = product-water flux. From Riley and Milstead, 1981.[31]

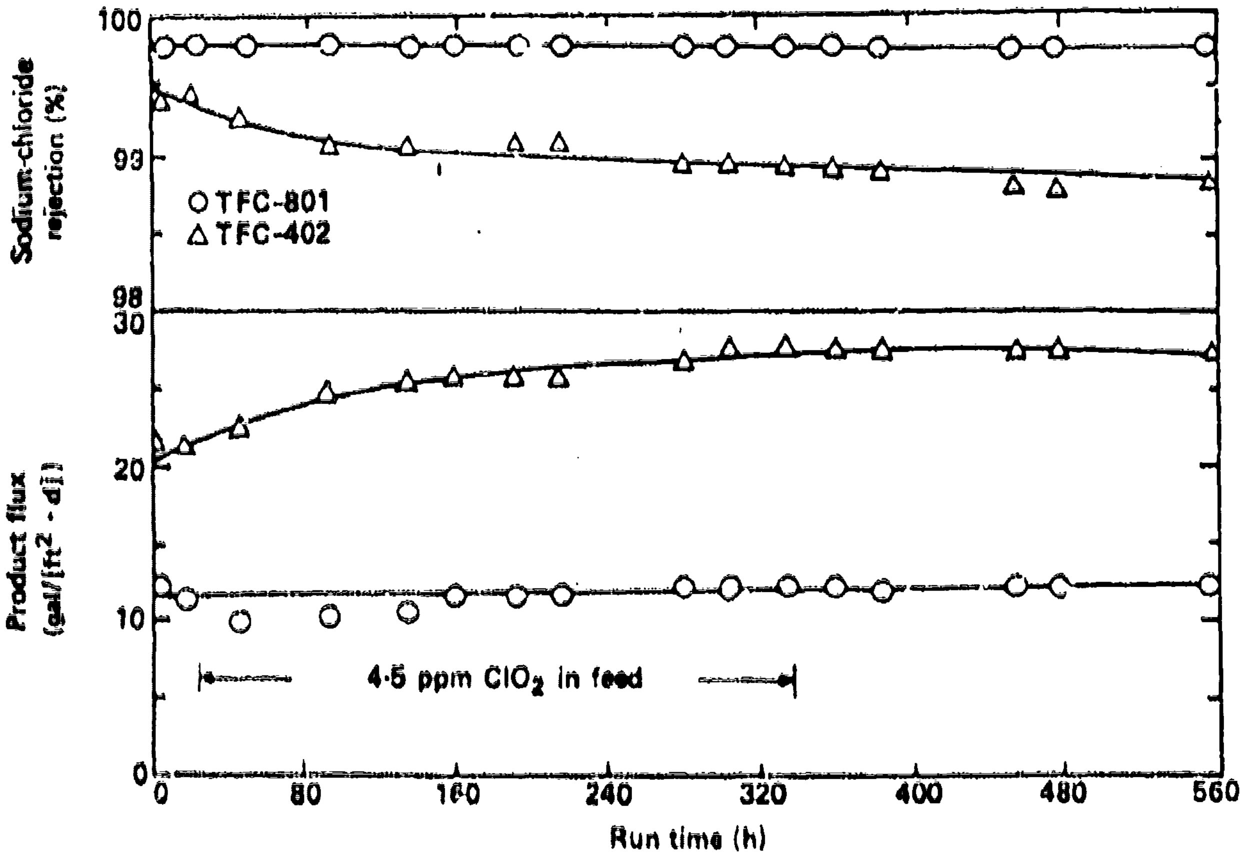

Figure C-10. The effects of "stabilized" (pure) chlorine dioxide on RO-process performance using either TFC-801 or TFC-402 membranes (pH = 5.6); product flux = product-water flux. From Riley and Milstead, 1981.[31]

excess of either chlorite ions or chlorine, depending on the reaction stoichiometry employed. The pure ClO_2 is called "stabilized" chlorine dioxide in Fig. C-10.)

Figure C-11 shows the results obtained when combined chlorine was added to the feed solution. No deleterious effects were noted when the combined chlorine was added in an irregular manner to the feed over a 5-d period. The combined chlorine concentration varied from about 0.5 to 15 mg/L as chlorine during that period. The fraction of chlorine that was added to ammonia to generate the combined residual was not given.[83]

Riley and Milstead[31] used spiral-wound modules containing the TFC-801 membrane to determine the effects of iodine, chlorine dioxide, Chloramine-T ($CH_3C_6H_4SO_2N(Cl)Na \cdot 3H_2O$) (manufactured by J. T. Baker Chemical Co., Phillipsburg, NJ), and two commercial biocides, Hyamine 3500 and 1622 (manufactured by Rohm and Haas) on the desalination of seawater. The pressure was maintained constant at 800 psig, and the seawater pH was decreased from around 8 to a range of 5 to 6 with sulfuric acid. The long-term response without any additives (the control) typically was a constant salt rejection with a modest decrease in product-water flux. The final conclusions of this work were as follows.

- The salt rejection remained essentially constant when iodine was added continuously to the feed water of the RO elements at a concentration of 3 mg/L and a temperature of 24°C for 75 d.

- The decrease in salt rejection approached 10% when stabilized chlorine dioxide was added to the feed water at a concentration of 2 mg/L and a temperature of 28°C for 141 d. The product-water flux in this test increased about 25%.

- The salt rejection remained unchanged, but the product-water flux decreased significantly when Chloramine-T was added to the feed water at a concentration of 1 mg/L and a temperature of 26°C for 22 d.

- The biocides decreased the product-water flux significantly and were not recommended for use under continuous-flow conditions.

The effects of sulfite on RO performance were also investigated by McCutchan and Glater[82] and Riley and Milstead.[31] Sulfite was of interest because it is used commonly to reduce strong oxidizing agents (the halogens and chlorine dioxide). It is also a component

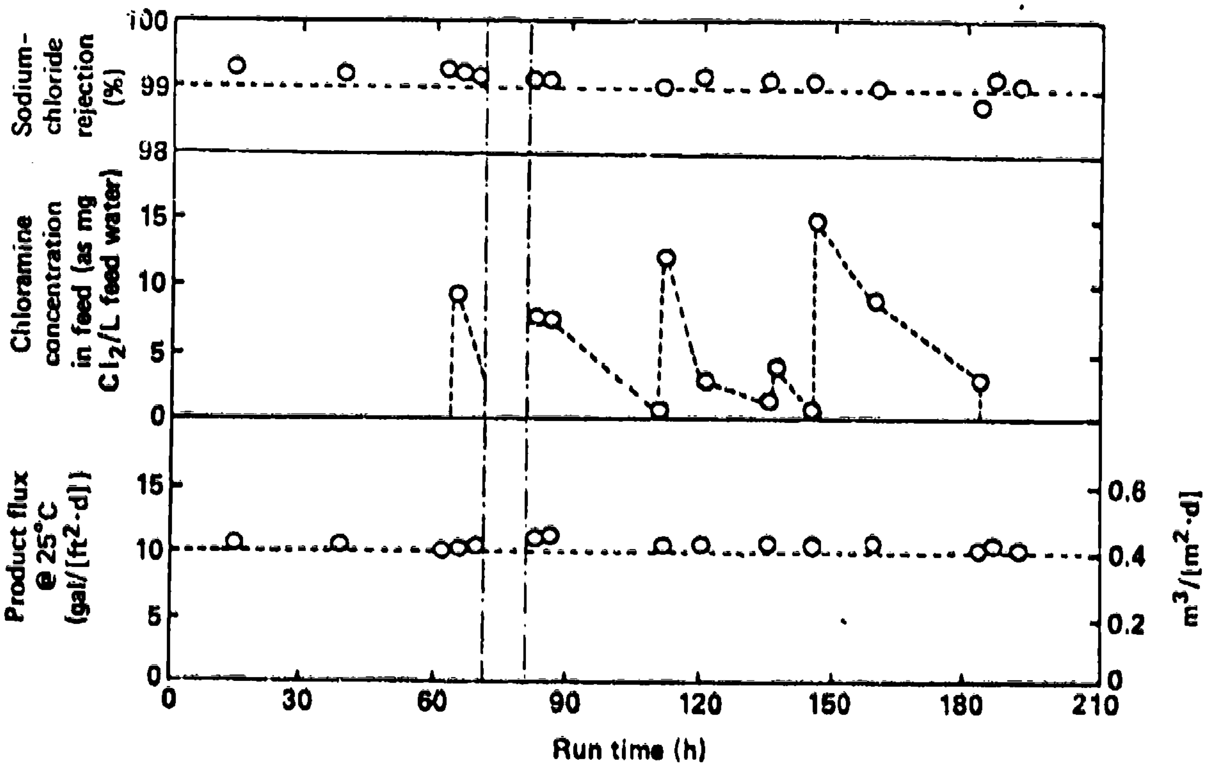

Figure C-11. The effects of combined chlorine on RO-process performance using the TFC-801 membrane (pH = 5.5); product flux = product-water flux. From Riley et al., 1980.[83]

of commercial RO membrane-cleaning compounds (e.g., Rover, manufactured by the Hach Chemical Company, Loveland, CO 80537).[31] Sulfite has been known to attack RO and ultrafiltration membranes when it is present in significant concentration.[84]

Laboratory soaking tests conducted by McCutchan and Glater[82] indicated that membranes susceptible to halogen attack are not affected by sodium bisulfite concentrations as large as 1000 ppm. Riley and Milstead[31] observed a small decrease in solute rejection and a 20% increase in product-water flux when sodium bisulfite was added to seawater to yield a feed concentration of 3 mg/L. The seawater was desalted in RO elements containing TFC-801 membranes for a period of 159 d at 28°C.

PERFORMANCE DATA

Data have been published on the performance of the UOP spiral-wound elements, which were not included in the preceding text of this report. A review of these studies is presented here. Also presented are performance data published for the FilmTec elements.

UOP MEMBRANES AND ELEMENTS

Riley et al.[83] state that the UOP TFC-801 membrane elements showed excellent performance in processing concentrated acid-mine-waste leachate with a TDS concentration of 45,000 mg/L and a pH of 2.0. In conjunction with studies at the Los Alamos National Laboratory, rejections greater than 99% were found for Al, Ca, Cd, Co, Cr, Cu, F, Fe, Mn, Ni, and Zn present in the leachate (oxidation states of these ions were not reported).

Riley et al.[83] also describe the performance of a hand-powered water-purification unit that uses a 2-in. diameter x 10.75-in.-long spiral-wound element made of TFC-801 membrane. The normal working pressures for this hand-powered unit are 1000 psi for seawater and 500 psi for brackish water. The rated productivity for seawater at a temperature of 25°C is 1.0 gph. The membrane rejects about 99% of the TDS for concentrations up to 20,000 mg/L. The investigators observed that the rejection also depends on speed and smoothness of pumping action. The typical performance of this unit is summarized in Table C-2.

Riley et al.[83] also report the results of the joint membrane-development program between the Office of Water Research and Technology (OWRT) and the U.S. Army Mobility Equipment Research and Development Command (now Belvoir Research and

Table C-2. Typical performance for the UOP TFC-801 membrane elements[a] used in the hand-powered, emergency seawater-desalination unit.[b] (Test conditions: 800-psig applied pressure; seawater feed; 2.0- to 2.4-gpm feed-water flow; 25°C feed-water temperature.)

		Performance		
Element	Feed pH	Product-water flux (gpd/ft^2)	Product TDS (mg/L)	TDS rejection (%)
1	5.5	6.0	49	99.86
2	5.5	6.0	35	99.90
3	5.5	7.7	66	99.81
4	5.5	8.0	66	99.81
5	8.5	5.4	203	99.42
6	8.5	8.0	189	99.46

[a] 2-in. diameter, 10.75-in. length, 3.0-ft^2 membrane area.

[b] Adapted from Riley *et al.*[83]

Development Center), which resulted in the development of the 600-gph ROWPU. The reported typical performance of the elements is summarized in Table C-3.

Riley and Milstead[31] reported a pilot study performed at Water Factory 21, the wastewater-reclamation plant of the Orange County Water District (OCWD) located at Fountain Valley, CA. The treatment at Water Factory 21 consisted of chemical clarification, ammonia stripping, recarbonation, multimedia filtration, carbon adsorption, and reverse osmosis that initially used cellulose-acetate membranes. The wastewater (the effluent from a secondary wastewater-treatment plant) received additional treatment in the form of pH adjustment, introduction of scale inhibitors, cartridge filtration, and chlorination prior to processing in the RO elements. The major objective of the study was to evaluate the feasibility of operating the reverse osmosis system on a feed-water stream at Water Factory 21 that would receive much less pretreatment, thus eliminating the ammonia stripping, multimedia filtration, and carbon adsorption processes.

The RO unit consisted of 4-, 3-, and 2-in. diameter elements containing approximately 71, 30, and 12 ft^2 of active TFC-401 membrane area, respectively. Six elements of each type were operated in series to obtain an overall product-water recovery of about 85%.

Table C-3. Performance of the UOP TFC-801 membrane element Model 1501 operated in the U.S. Army trailer-mounted multipurpose ROWPU.[a] (Test conditions: 800-psig applied pressure; seawater feed; pH 5.7; 12.5-gpm feed-water flow; about 10% product-water recovery; 21 to 24°C feed-water temperature.)

Test element number	Element flow (gpd)	Performance Product-water flux (gpd/ft^2)	Product TDS (mg/L)	Chloride rejection (%)
1	1670	10.6	346	99.01
2	1550	9.8	336	99.04
3	2210	14.0	420	98.8
4	1580	10.0	255	99.27
5	1360	8.6	227	99.35
6	1535	9.7	255	99.27

[a] Adapted from Riley _et al._[83]

Typical solute-rejection data for some individual ions are presented in Table C-4. A diagram of the overall performance of this pilot plant is shown in Fig. C-12. It was claimed that the product-water recovery and TDS rejection as determined by conductivity were stable during the 6500 h of testing. The following conclusions were drawn from this study by the researchers.

- The most effective membrane-cleaning procedure included phosphoric acid (pH 1.0) followed by trisodium phosphate (pH 12.0); the latter was also effective in removing $CaCO_3$ scale. Sodium hexametaphosphate was added to the feed water to inhibit $CaCO_3$ precipitation, but this approach was not always effective at Water Factory 21.

- An anionic polymer, Percol LT 26 (manufactured by Allied Colloid, Fairfield, NJ), was added at a rate of 0.1 mg/L to the water entering the chemical clarifier. A 70-h laboratory test indicated that this polymer did not cause any decline in water flux for polymer doses as great as 10 mg/L.

Table C-4. Typical salt rejection observed in the Water Factory 21 Pilot Plant, Orange County, CA, with TFC-401 RO membrane on secondary wastewater-treatment-plant effluent. Test conditions: 400-psig applied pressure; 1100- to 2000-mhos/cm feed conductivity; 4.1- to 7.3-gpm feed-water flow rate.[a]

Constituent	Feed water (mg/L)	Product water (mg/L)	Rejection (%)
Na^+	159	1.4	99.12
NH_4^+	0.5	<0.1	--
$SO_4^=$	320	1.0	99.70
Cl^-	186	7.5	96.0
NO_3^-	11	0.3	97.3
TDS	885	11	98.8
N as NH_3	2.0	not detected	>98.8

[a] Adapted from Riley and Milstead.[31]

- A sand filter was introduced into the study after 5000 h of operation. The filter was located between the lime clarifier and the reverse osmosis system. The sand filter contaminated the RO plant with a bacterial slime that made operation difficult throughout the last 1500 h of the test. The elements were cleaned several times during this last period with phosphoric acid, trisodium phosphate, an enzyme cleaner, and formaldehyde. None of the cleanings, however, was totally effective. As a result, the pressure drop across the elements increased to an unacceptable level, causing a decrease in salt rejection and product-water recovery. The test was discontinued in order to sterilize and clean the RO elements.

Muirhead et al.[85] describe the performance of the two-stage, 12,000-m^3/d, reverse osmosis seawater-desalination plant located in Jeddah, Saudi Arabia, for the first 2 y of its operation. The UOP TFC-1501 PA element is used in the plant. The operating conditions are given in Table C-5, and the raw- and product-water characteristics are shown in Table C-6. The performance data indicated that the addition of coagulants and coagulant aids was not needed before filtration. The first-stage RO system consists of

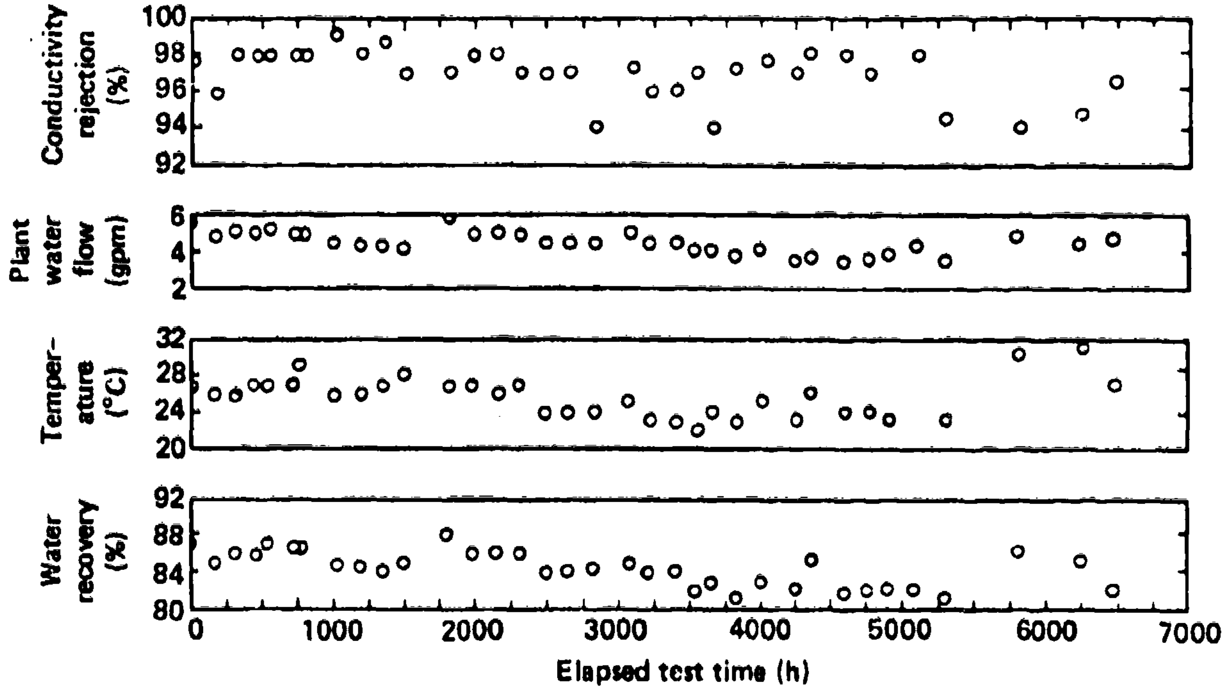

Figure C-12. Performance of an 8000-gpd RO pilot plant using a TFC membrane and operated on lime-clarified municipal wastewater at Water Factory 21, Orange County, CA. Test conditions: 400-psig applied pressure; 1100- to 2000-mhos/cm feed conductivity; 4.1- to 7.3-gpm feed flow. Reprinted with permission from Riley and Milstead.[31]

Table C-6. Operating conditions for the reverse osmosis seawater-desalination plant located at Jeddah, Saudi Arabia.[a]

Treatment order	Operating conditions
Pretreatment	Dual-media gravity filtration, anthracite and sand (periodic copper sulfate addition, 2 mg/L) Acid addition (sulfuric acid) Sodium hexametaphosphate scale inhibitor (2 mg/L) Cartridge filtration
First stage	Eight operating units; one standby unit 850-psig operating pressure 30% product-water recovery per vessel Feed-water pH = 6.0 to 6.1 Product-water concentration = 750- to 900-mg/L TDS
Partial second stage	Three operating units 400-psig operating pressure 85% product-water recovery Product-water concentration = 50-mg/L TDS (pH = 4.0)
Post-treatment	Lime addition Chlorine addition (1.0 to 1.5 mg/L)

[a] Adapted from Muirhead _et_ _al._[85]

9 units in parallel (one standby), each of which contains 56 elements. The three second-pass units are provided to maintain the TDS level at 1000 ppm or less. During the first 2 y of operation, the product-water TDS was always at or below 1000 mg/L. Chemical and fuel consumption were generally close to anticipated values. The results of the 5-d between acceptance test (performed between January 25 through 30, 1979) are given in Table C-7.

Corrosion, algae growth, and high-pressure piping and vessel failures were the main operational problems confronted at the Jeddah facility during the first 2-y period. Also, the process-monitoring data indicated some product-water flux and salt-rejection losses

Table C-6. Water characteristics for the reverse osmosis seawater-desalination plant at Jeddah, Saudi Arabia.[85]

Property of water	Red Sea water	Product water
Temperature	32°C (max)	--
pH	around 8	around 8.5
Lime saturation point	--	around 8.5
TDS (mg/L)	41,200	<1000
Chloride (mg/L)	22,000	<600
Total hardness (mg/L as $CaCO_3$)	7,400	70 to 140
Calcium (mg/L)	520	20 to 36
Magnesium (mg/L)	1,464	--
Total iron (mg/L)	0.2	--
Silica (mg/L)	0.4	--
Plugging index (%)	91 to 96	--
Turbidity (NTU)	0.5 to 0.6	<0.3

with time. These were caused by an inadequately cured product-water channel resin that either leached gradually out of the channel material or was softened by water absorption. This, in turn, caused a collapse in the product-water channels. As a result, most of the elements had to be replaced within 2 y.

Data on the tests of the 150,000-gpd ROWPU in August and October 1983 at Fort Story, VA, were obtained by the U.S. Army Environmental Hygiene Agency.[86] These tests were performed on seawater, and the average results for two of the runs are given in Table C-8. No information was obtained concerning operating temperature, pH, or applied pressure.

FILMTEC MEMBRANES AND ELEMENTS

The intrinsic properties of the FT-30 membrane were evaluated in 3-in.-diameter flat-leaf test cells.[25] A reverse osmosis test loop with high-speed brackish water recirculation was used. Concentration polarization and product-water recovery were minimized by this arrangement. The product-water recovery was about 0.1% per cell for six test cells connected in series. These experiments were performed under the following nominal test conditions: 1000-psig operating pressure, 25°C feed-water temperature, and

Table C-7. Water analyses performed during the 5-d (January 25 through 30, 1979) acceptance test of the RO desalination plant at Jeddah, Saudi Arabia.[a] (Red Sea water, 850-psig applied pressure, approximately 30% product-water recovery, 13,033 m^3/d [3.44 million gpd] average product-water flow.)

	Combined first stage	Stabilized product (lime and chlorine added)	Raw seawater	RO feed	Brine	Percent rejection (based on 1st-stage product)
Calcium (mg/L)	1.0	8.0	225	224	313	99.54
Magnesium (mg/L)	2.3	1.7	742	737	1029	99.68
Sodium (mg/L)	316	249	14,255	14,237	19,676	99.73
Carbonate (mg/L)	0	0	1.9	0	0	--
Bicarbonate (mg/L)	1.4	40	146	96	130	98.54
Chloride (mg/L)	493	375	22,219	22,183	30,668	97.72
Sulfate (mg/L)	10	10	3078	3096	4348	99.67
TDS @180°C (mg/L)	746	576	39,884	39,475	55,365	98.06
pH @25°C	5.0	7.8	8.05	6.7	6.9	--
Conductivity @25°C (mhos/cm)	1065	1330	--	--	--	--

[a] Adapted from Muirhead *et al.*[85]

a 3.5%-salinity seawater-feed solution. The membrane performance was also evaluated for changes in pressure, temperature, pH, and salt concentration. A few flat-leaf tests were also performed with a feed-water sodium-chloride concentration of 0.5%.

The results of some of these tests are shown in Figs. 12 and 13 in the main text of this report. The purpose of this was to illustrate the general intrinsic properties of composite membranes of the type proposed for use in later versions of the ROWPU. Unlike the UOP membranes, the performance of the FT-30 membrane is not altered substantially by a pH less than 11.[25]

Much larger portions of the FT-30 membrane were tested in a spiral-wound element.[40] The tests of these membranes were conducted under the following standard conditions: 800-psig operating pressure; 25°C feed-water temperature; pH of about 7.0; 3.2%-NaCl feed-water solution; and 1.75-gpm feed-water flow. The pressure, temperature, pH, and salt concentration were varied, in turn, whereas the other test parameters were held constant. The dimensions of the elements were not given by the

Table C-8. Average ion-removal efficiencies for two runs of the 150,000-gpd ROWPU performed at Fort Story, VA, using seawater as the feed.[a]

Constituent	Test No. 1 Date: 26 Aug 83 (% removal)	Test No. 2 Date: 13 Oct 83 (% removal)
Mg^{2+}	99	99
Ca^{2+}	99	99
Na^{+}	95	94
Fe[b]	93	92
Zn[b]	NR[c]	>50

[a] Adapted from Doherty.[86]

[b] Oxidation state not given.

[c] Not reported.

authors of this study, and the results were normalized to standard operating conditions. Presenting the data in relative terms without stating the standard product-water flux (or membrane area) makes it impossible to compute the membrane product-water flux parameter A.

Most field applications of the FT-30 spiral-wound-element have been made in order to study the resistance of the membrane to disinfectant attack. Nevertheless, some studies were performed with unchlorinated feed waters.[26,87,88]

Three spiral-wound elements were tested with brackish feed water containing 3000-mg/L TDS. Although the operating pressure was 200 psig, the effective applied pressure in this set of elements was only about 188 psi because of pressure drops through elements and fittings. As shown in Fig. C-13, the salt rejection was initially 97.5%, rising to 97.8% during the first 700 h of operation and remaining in the range of 97.8 to 98.0% until the test was terminated at 14,000 h. An initial product-water flux of 16 gpd/ft^2 increased to a peak of 17.5 gpd/ft^2 after about 1500 h and then gradually decreased to about 15 gpd/ft^2 at 9900 h. At this point, microbiological tests showed the presence of microbiological growth and probable membrane biofouling. The test was stopped twice, and the RO elements were soaked in a sodium bisulfite cleaning solution. As a result of these treatments, the flux initially decreased to 13.3 gpd/ft^2 but recovered to yield about 15 gpd/ft^2 in 200 h.

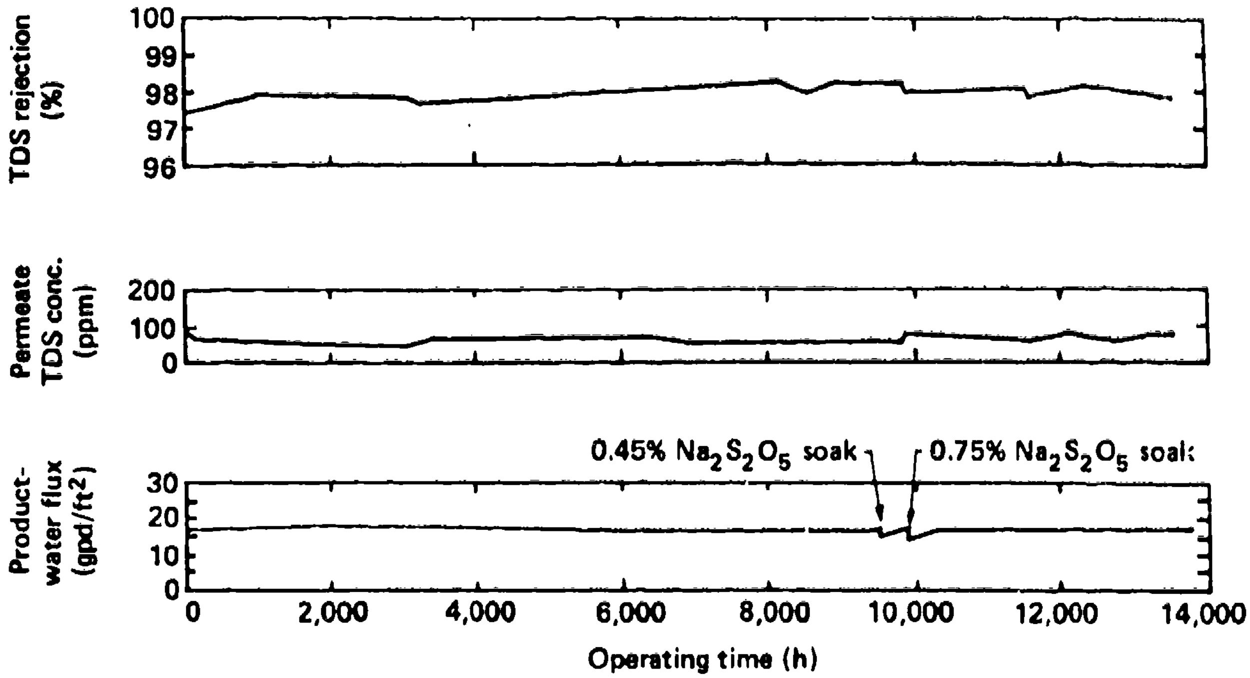

Figure C-13. Long-term test of FT-30 spiral-wound elements with brackish water (200-psig applied pressure and 3000-mg/L TDS feed-solution concentration); permeate - product water. Adapted from Petersen *et al.*, 1982.[26]

A set of three spiral-wound elements connected in series was operated at the Office of Water Research and Technology's (OWRT) Wrightsville Beach Test Facility located in North Carolina.[26] Pretreated seawater was fed at 800-psig applied pressure for an actual on-line time of 7000 h. As shown in Fig. C-14, the initial product-water flux (corrected to 25°C) was about 15 gpd/ft^2. The flux declined rapidly to about 12 gpd/ft^2 during the first 500 h of operation. A second sharp decline in flux occurred after about 1500 h of operation, and the flux eventually reached a minimum value of about 5 gpd/ft^2. It was suspected that the decrease in flux was caused by biofouling.

The salt rejection at first increased and then decreased to about 98.6% at the time of the second sharp decrease in product-water flux. After 3800 h of operation, the system was shut down for 6 wk to perform a major overhaul of the test facility's pretreatment units. After restarting with the new pretreatment system, the P.O elements responded with an increased salt rejection to 99.1%.

Another long-term test was carried out at the OWRT Wrightsville Beach Test Facility[87] using pretreated seawater feed. The average TDS concentration was 32,000 mg/L and the pH was about 5.6. Three spiral-wound elements, model SW30-2514 (2.5-in. diameter and 14-in. product-water-tube length), were connected in series. The product-water flux decreased slowly from about 15 gpd/ft^2 to 7.5 gpd/ft^2 during 2700 h of operation (see Fig. C-15). The TDS rejection decreased from about 99.4 to 98.8% during the same period of time.

Long-term test results on FT-30 8-in.-diameter RO elements (320-ft^2 effective membrane area) have not been reported; however, some short-term data have been made available.[88] A product-water flux of 16 gpd/ft^2 (corrected to 25°C by the author) and a salt rejection of about 96% were obtained for a feed-water TDS of 2000 ppm and an applied pressure of 200 psig. Elements having an effective membrane area of 290 ft^2 each, and operating on a seawater feed, produced water at a flux of 22 gpd/ft^2 (corrected to 25°C) and yielded a TDS rejection for seawater of about 99% at a pressure of 800 psig.

Some other long-term tests performed at the U.S. Department of the Interior Roswell Test Facility at Roswell, NM, and at the Island Water Association Facility at Sanibel Island, FL, and reported by the manufacturer[88] are summarized in Figs. C-16 and C-17, respectively.

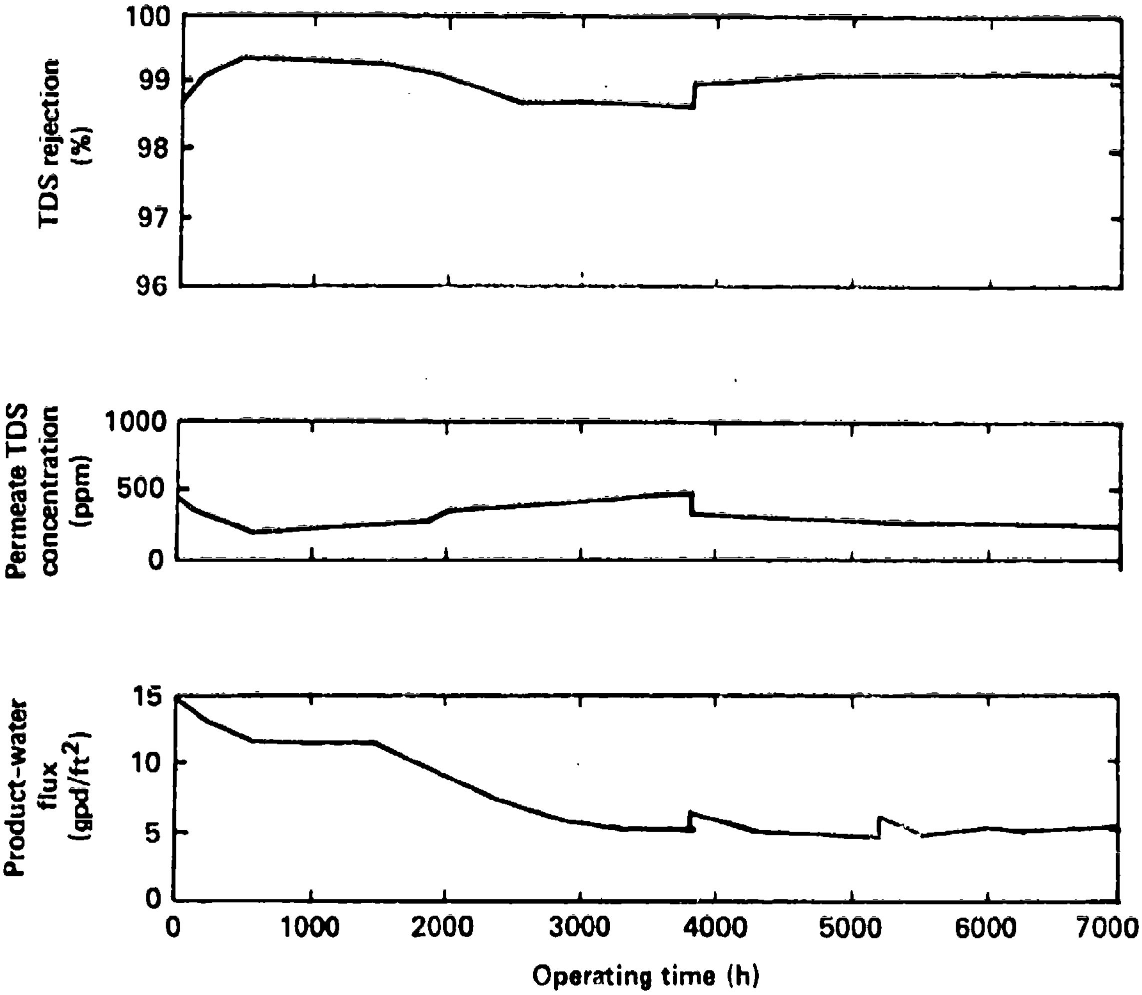

Figure C-14. Long-term test of FT-30 elements with seawater fed at 800 psig; permeate = product water. Adapted from Petersen et al., 1982.[26]

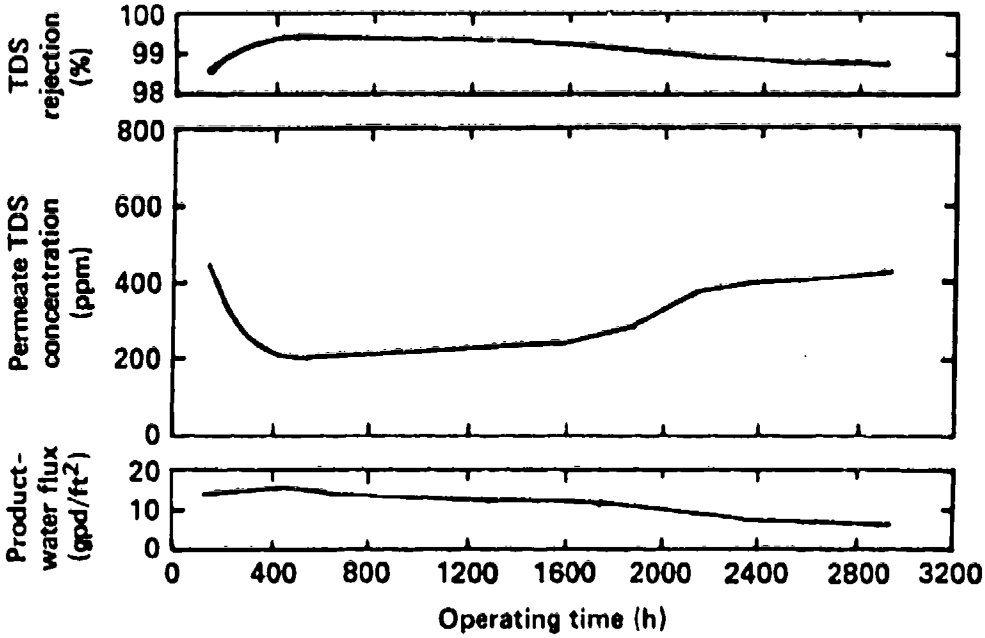

Figure C-15. Performance of FT-30 spiral-wound RO element in long-term testing on seawater at Wrightsville Beach test facility (32,000-ppm seawater-feed solution, pH 5.6, 800-psig applied pressure, 5% average water recovery, flux corrected to 25°C, average for three SW30-2514 elements); permeate - product water. Adapted from Larson et al., 1981.[87]

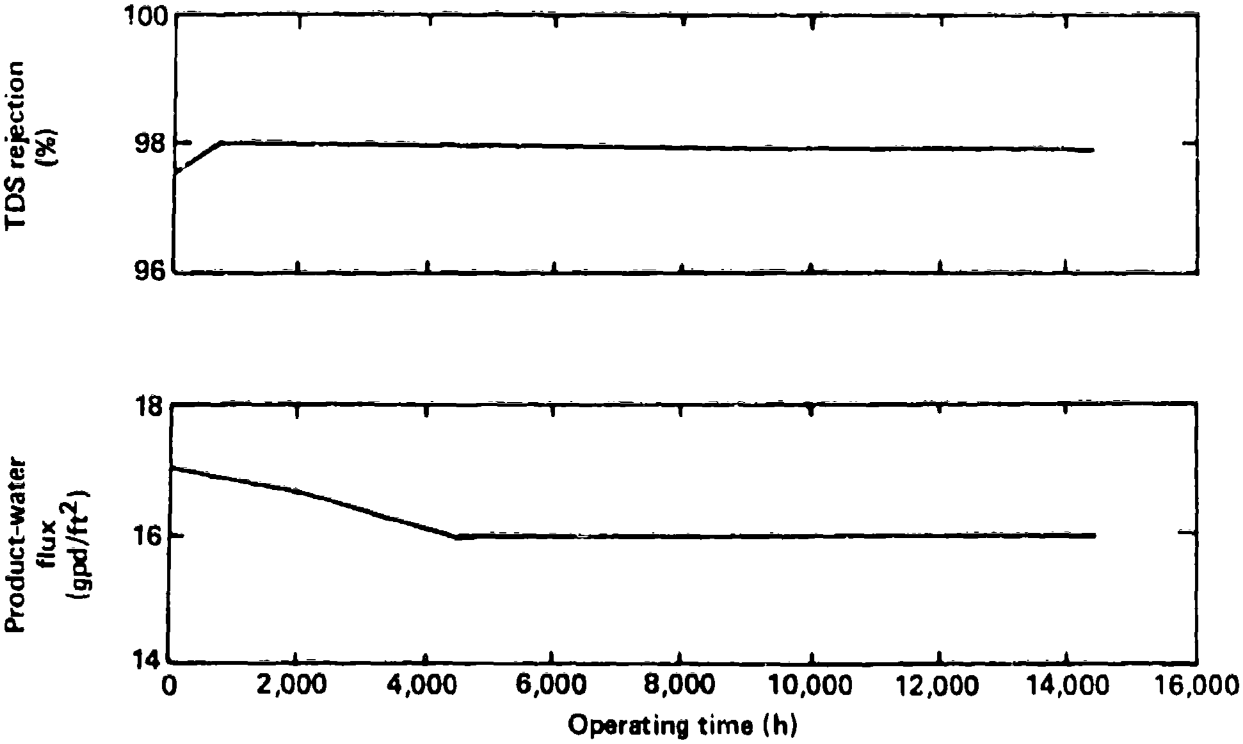

Figure C-16. Performance of FT-30 spiral-wound element under long-term test on brackish water at U.S. Department of the Interior Roswell Test Facility, Roswell, NM (3000-ppm feed TDS concentration, pH 6, 200-psig applied pressure, 8.5% average product-water recovery, flux corrected to 25°C, three BW30-2514 elements). Adapted from Larson et al., 1983.[88]

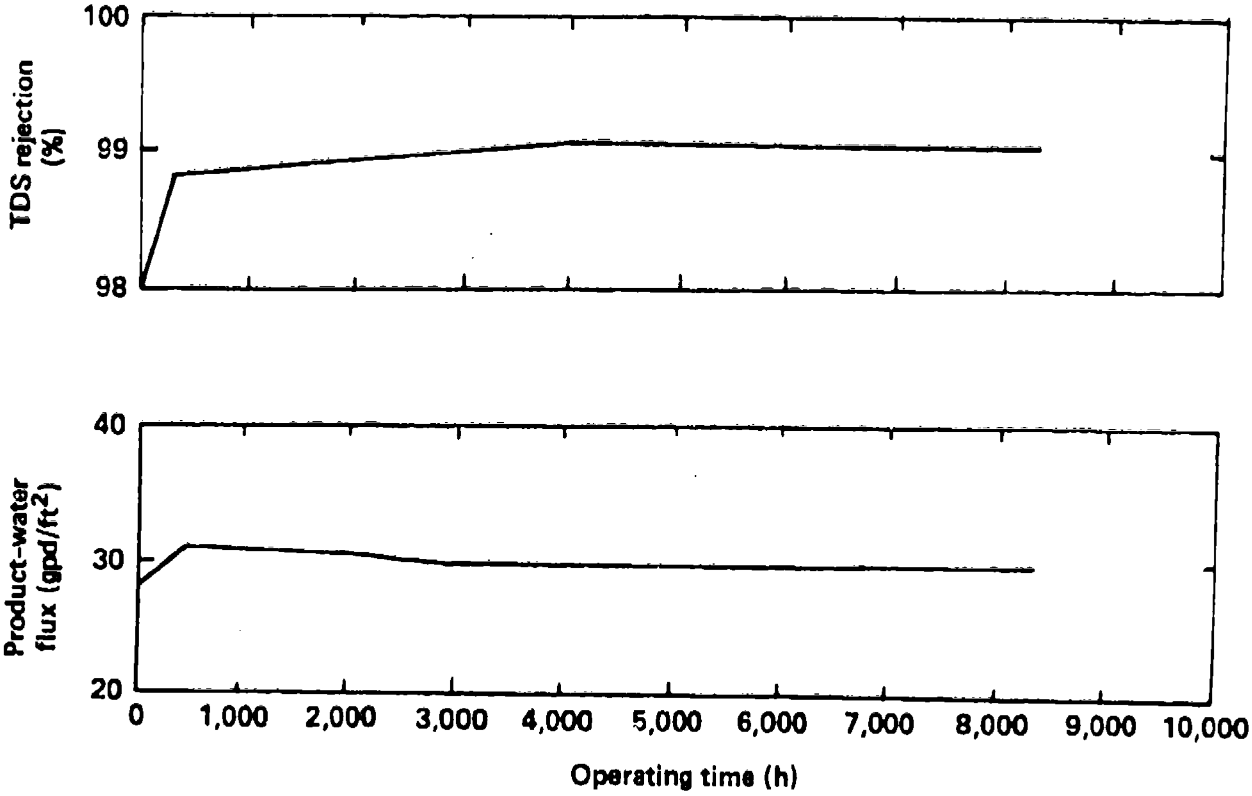

Figure C-17. Performance of FT-30 spiral-wound element under long-term test on brackish well water at the Island Water Association Facility, Sanibel Island, FL (3200-ppm feed TDS concentration, 350-psig applied pressure, 20% product-water recovery, flux adjusted to 25°C, two BW30-2514 elements). Adapted from Larson et al., 1983.[88]

REMOVAL OF WARFARE AGENTS

Lindsten and DesRoches[89] reported the results of an early Army study on the removal of chemical warfare (CW) and radiological warfare (RW) agents with reverse osmosis at the Edgewood Arsenal of Aberdeen Proving Ground in Maryland. Although it is an old study, the results explain why activated carbon and ion-exchange columns are now included as part of the 600-gph ROWPU package.

The CW agents were added to water obtained from Bush River, and the RW agents were added to water obtained from Winter's Run. The agents used are given in Table C-9. At the time of the study (1976), two banks of RO pressure vessels were utilized, with each bank containing five pressure vessels staged in a 2:2:1 arrangement. Each vessel contained two RO elements that measured 4 in. in diameter and 36 in. in length, with a membrane area of 65 ft^2 per element. Pretreatment consisted of the addition of 5 ppm of Cat-Floc cationic polymer and multimedia (coal-sand-garnet) filtration.

One pressure bank contained a cellulose acetate brackish-water membrane, and the other contained a polyamide seawater membrane (UOP PA-300). The pressure-vessel banks for the CW tests were operated at 430 psig and 75 to 80°F, and the pH of the raw-water feed ranged between 7.2 and 7.9. The pressure-vessel banks for the RW tests were operated at 400 psig and 62 to 80°F, and the pH of the raw-water feed ranged between 6.5 and 7.1. The overall product-water recoveries were about 50%. The polyamide membrane gave the larger average product-water flux with superior TDS rejection, as shown in Table C-9.

The effect of chlorinating the product water on the residual chemical warfare agent concentration was investigated in the GB and BZ tests by comparing the residual concentrations in the chlorinated and unchlorinated product-water samples. It was observed that chlorination had little effect on the concentration of the agents found in the product water.

The initial concentrations and rejections of the warfare agents tested are shown in Table C-10. The values of the rejections in the table represent averages of 5 runs per agent with 5 samples per run. None of the product-waters, except possibly BZ and VX for the polyamide membrane, met the drinking-water-quality criteria existing at the time.[89] Therefore, post-treatment with activated carbon was proposed for the CW agents, and ion exchange was proposed for the RW agents.[88] The results of a study in which carbon adsorption was used after the RO elements are shown in Table C-11.

Table C-9. Performance of an early version of the 600-gph ROWPU (CA = cellulose acetate membrane; PA = UOP PA-300 membrane; feed-water flow = 10 gpm).[a]

	Product-water flux [gal/(d • ft^2)]		Raw-water TDS range (mg/L)	TDS removal (%)	
Agent	CA	PA		CA	PA
Chemical warfare agents:					
GB	16	21	705 to 900	93.3[b]	92.0[b]
VX	20	24	867 to 1004	88.4	92.6
BZ	20	21	933 to 1583	89.4[b]	94.3[b]
Radiological warfare agents:					
^{131}I	21	22	44 to 72	96.3	97.5
^{85}Sr	22	22	45 to 52	87.3	95.8
^{134}Cs	21	20	78 to 84	90.7	97.9

[a] Adapted from Lindsten and DesRoches.[89]

[b] Average values for chlorinated product-water samples.

GENERAL DESCRIPTION OF RO ELEMENTS

The hollow-fiber RO element probably has the best product-water-recovery characteristics. The concept of this design is a low product-water flux coupled with a large membrane-surface area. The concentration polarization is held at a reasonable limit by the low product-water flux. The large membrane-surface area is provided by a bundle of fine tubes composed of the membrane material.

Many flow schemes can be used with the hollow-fiber element. The one used with the Du Pont B-9 element is shown in Fig. C-18. The feed water enters under pressure through the strands of the hollow-fiber bundle. The concentrate leaves through the annular-flow screen placed along the inner wall of the pressure vessel and then out the concentrate outlet. The product water moves inside the hollow fibers to the end of the element, where the tubes have been cut to permit free passage of the product-water.[44]

Table C-10. Removal of warfare agents from water with an early version of the 600-gph ROWPU (CA = cellulose acetate; PA = UOP PA-300).[a]

	Feed-water concentration		Percent rejected	
Contaminant	(mg/L)	(pCi/L)	CA	PA
Chemical warfare agents:				
GB	7.54[b]		32.1[b]	99.1[b]
VX	10.14		97.9	99.9
BZ	6.95[b]		74.3[b]	99.9[b]
Radiological warfare agents:				
^{131}I		297,000	93.5	95.5
^{85}Sr		322,000	98.9	99.7
^{134}Cs		173,000	89.8	98.8

[a] Adapted from Lindsten and DesRoches.[89]

[b] Average values for chlorinated product-water samples.

Table C-11. Concentration of chemical warfare agents in final effluent after post-treatment with activated carbon.[a]

	Final product water (mg/L)	
Agent	CA[b]	PA[c]
GB	<0.0006	<0.0005
VX	<0.000012	<0.0001
BZ	0.003	0.002

[a] Reprinted from Lindsten and DesRoches.[89]

[b] Cellulose acetate membrane.

[c] UOP PA-300 membrane.

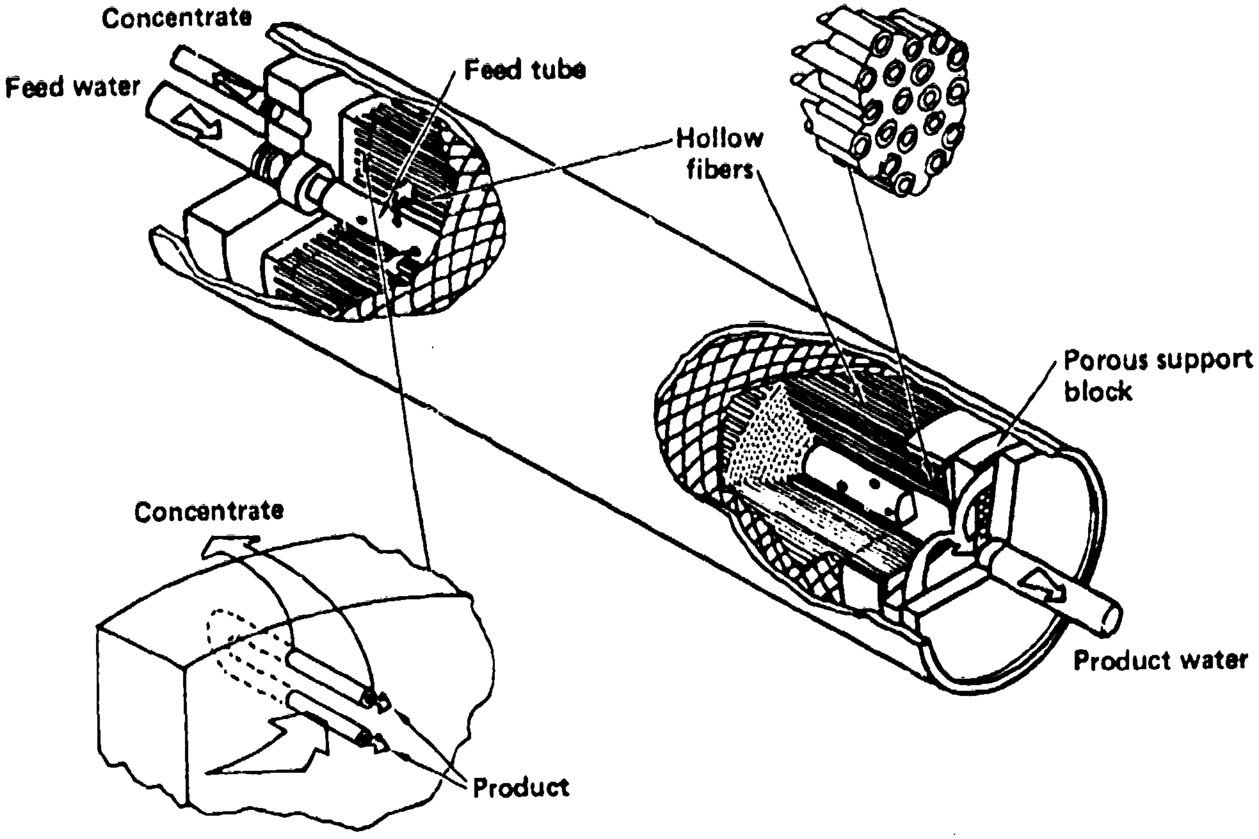

Figure C-18. Diagram of a Du Pont B-9 hollow-fiber element. Adapted from Lonsdale, 1982.[2]

The aromatic polyamide polymer used in the Du Pont hollow fibers has good salt-rejection characteristics. Thus, a reasonable salt rejection may be obtained with a large product-water recovery. The hollow fibers have an active length of 30 in. with an inside diameter of 41 μm and an outside diameter of 84 μm. The total effective membrane area contained in the 4-in. Du Pont B-9 hollow-fiber bundle (shell dimensions of 5.25-in. outside diameter and 47-in. length) is about 2000 ft^2. The gap between the fibers in the bundle averages about 25 μm.[44] Clogging of the bundle with suspended solids can be avoided by removing particles that measure 5 μm or greater from the feed water.[44]

The opposite approach to the hollow-fiber module design is a large product-water flux coupled with high turbulence in the concentrate channels that reduces concentration polarization. Examples of this design are tubular modules with the turbulence being generated hydraulically, by static or moving inserts, and by spinning the membrane tube inside a fixed annular ring.[12] The clear space for concentrate flow is commonly large in these types of elements, and the tendency for clogging is small. The concentrate channels also are relatively easy to clean by flow-surging, flow-reversal, and the insertion of balls into the feed stream, which helps to dislodge films that adhere to the membrane surfaces.[14] A major problem with this approach is the relatively small membrane-surface area, which gives a small product-water recovery per element.

A compromise between the hollow-fiber and the tubular elements is the spiral-wound element. The spiral-wound element is discussed in detail in the main text of this report. The clear passageway for the concentrate is significantly greater than in the case of the hollow-fiber element, but it is still relatively restricted as compared to tubular elements.

WATER CHEMISTRY OF ARSENIC AND CYANIDE

The effectiveness of RO in removing arsenic and cyanide from water supplies is dependent upon the species of the chemical that is present. For this reason, a brief discussion of the chemical behavior of arsenic and cyanide in natural waters is presented here.

ARSENIC

Arsenic is a naturally occurring element, chemically classified as a metalloid and generally referred to as a metal. A member of Group 5a of the periodic table, arsenic has five electrons in its outer shell, resulting in oxidation states of V, III, 0, and -III.[90] In natural water systems, arsenic has a complex chemistry, which includes oxidation-reduction, ligand exchange, precipitation, and adsorption reactions.[91]

Elemental arsenic is stable in the presence of water at all pH levels, if the water contains no oxidizing agents. Arsenic is slowly oxidized to the soluble arsenious anhydride, As_2O_3, if water contains dissolved oxygen. Muylder and Pourbaix[92] stated that, if a stream of air is passed through the water, the rate of oxidation is fairly rapid. The As_2O_3 is an amphoteric oxide that hydrolyzes in water at a pH of 1 to 8 to form arsenious acid, $HAsO_2$ (or H_3AsO_3). The 25°C solubility of As_2O_3 in this pH range remains constant at about 21 mg/L as As_2O_3. Elemental arsenic may also be oxidized to the soluble arsenyl cation, AsO^+ (+3 oxidation state), under the appropriate pH and concentration conditions.[91]

Arsenious acid dissociates immediately to yield the charged arsenite ions, as shown in Eq. C-1. The 25°C dissociation constant, pk_{a1} ($pk_{a1} = -\log k_{a1}$) is about 9.23.[93] The degree of dissociation with pH at 25°C is shown in Fig. C-19.

Under strong oxidation potentials, the arsenites can be oxidized to arsenic acid. Arsenic acid dissociates immediately to yield arsenate ions with various charges, depending on the pH, as shown in Eqs. C-2, C-3, and C-4. The degree of dissociation of this acid with pH at 18°C is shown in Fig. C-20.

$$HAsO_2 \xrightleftharpoons{k_{a1}} AsO_2^- + H^+ , \qquad \text{(C-1)}$$

$$H_3AsO_4 \xrightleftharpoons{k_{a1}} H_2AsO_4^- + H^+ , \qquad \text{(C-2)}$$

$$H_2AsO_4^- \xrightleftharpoons{k_{a2}} HAsO_4^{2-} + H^+ , \qquad \text{(C-3)}$$

$$HAsO_4^{2-} \xrightleftharpoons{k_{a3}} AsO_4^{3-} + H^+ , \qquad \text{(C-4)}$$

Elemental arsenic can be reduced to the gas arsine, AsH_3, or the highly insoluble solid hydrides, As_2H_2 or As_4H_2, under strong reducing conditions (highly negative potentials). According to Ferguson and Gavis,[91] arsine is only slightly soluble in water. The arsenates, once formed, can be reduced to the arsenites only under very acid conditions. The rate of reduction is infinitely slow under alkaline conditions.

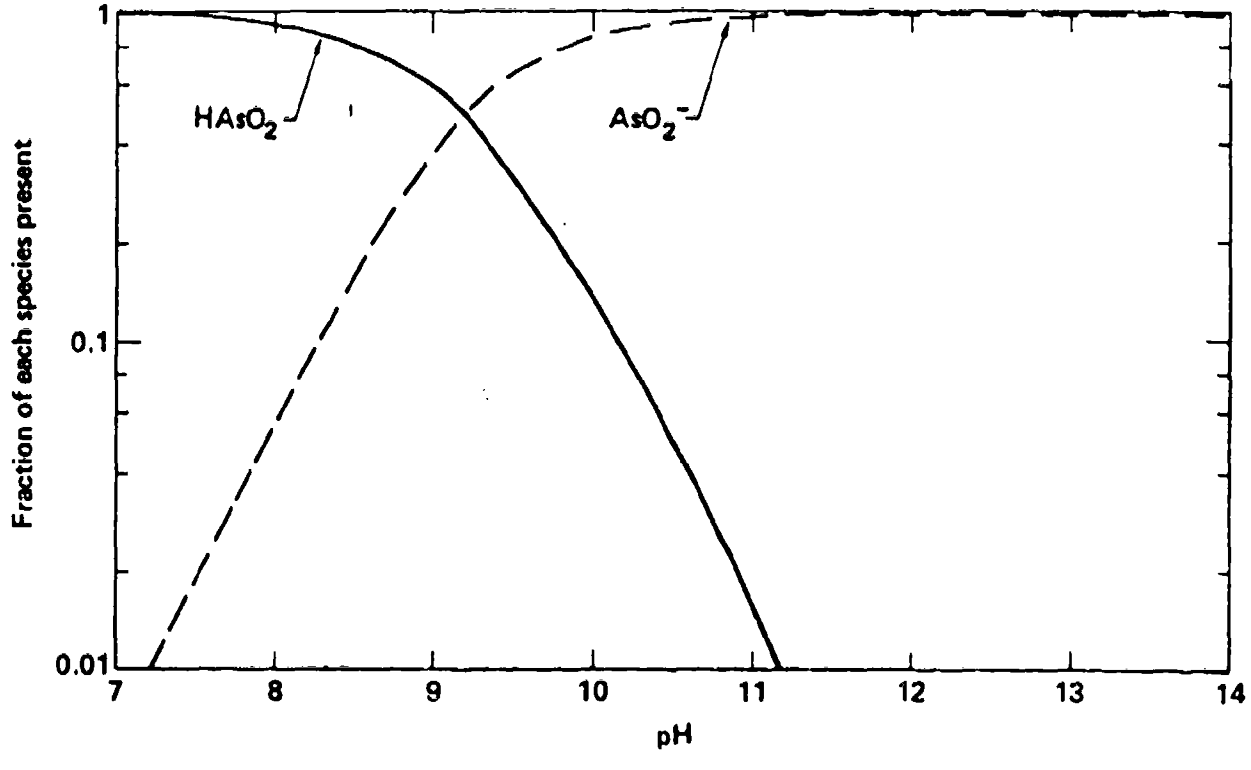

Figure C-19. Dissociation of arsenious acid in dilute solution at 25°C (pk_{a1} = 9.23).[93]

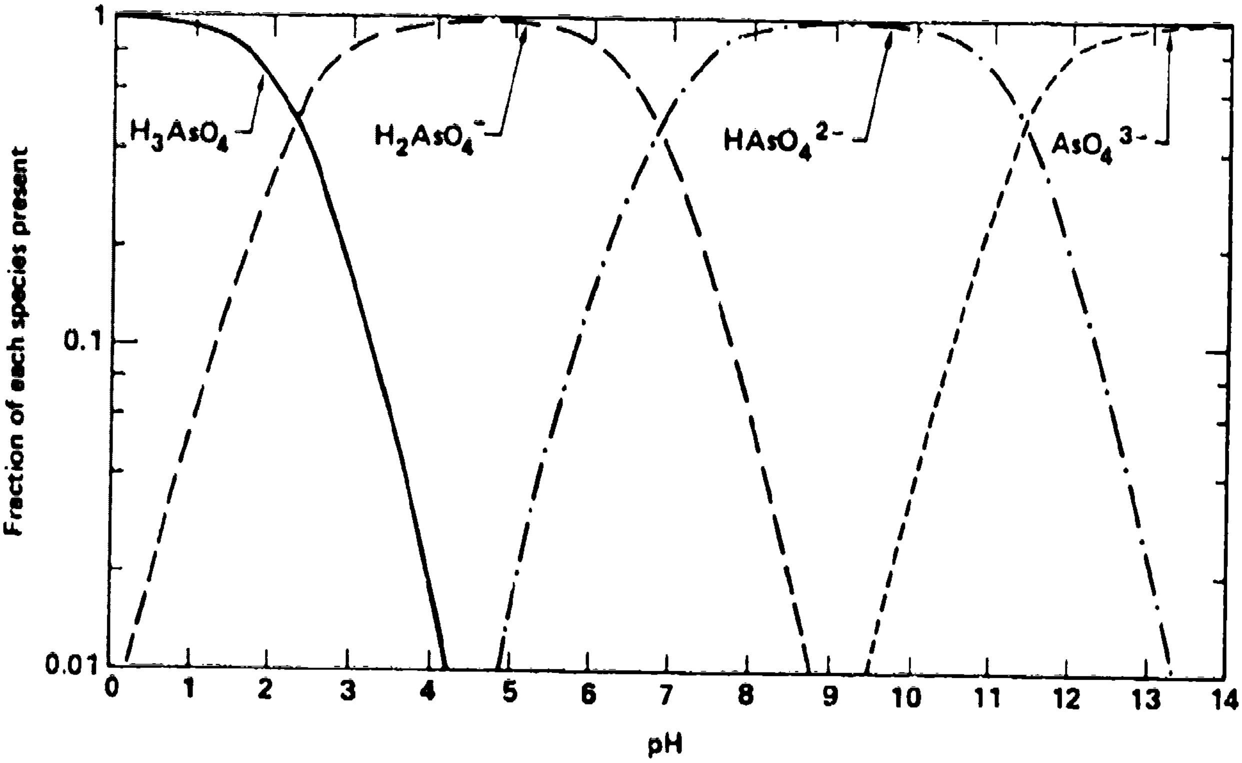

Figure C-20. Dissociation of arsenic acid at 18°C in dilute solutions ($pk_{a1} = 2.25$; $pk_{a2} = 6.77$; $pk_{a3} = 11.6$).[93]

The free energies of formation (ΔG_f^0) of most of the arsenic compounds discussed herein are given in Table C-12. The oxidation potentials required to oxidize elemental arsenic to the arsenates are significantly greater than those required to obtain the arsenites. Indeed, an appreciable over-potential is required. According to Muylder and Pourbaix,[92] dissolved oxygen alone, without the presence of a catalyst, is inadequate for this purpose. Stronger oxidizing agents, such as a halogen, one of its oxygen compounds, or chromic or nitric acid, are required.

The arsenate species can coprecipitate with or adsorb onto hydrous iron oxides, as well as onto aluminum hydroxide and clays. The arsenite species will also adsorb or coprecipitate with iron oxides. The arsenites also have a strong affinity for sulfur, readily absorbing or coprecipitating with metal sulfides. The free energies of formation of some of the sulfides of arsenic are also shown in Table C-12. All of the sulfides shown except AsS_2^- are virtually insoluble in water.

From the foregoing, one might deduce that As(III) would never be oxidized to As(V), nor would As(V) be reduced to As(III), in natural waters. However, this is not the case. Ferguson and Gavis[91] report that oxygen alone will oxidize arsenite to arsenate at a finite rate under either strongly alkaline or acid conditions. These authors also report that certain types of bacteria can readily oxidize As(III) to As(V). Johnson and Pilson[94] have postulated that As(V) is reduced to As(III) in seawater by biological actions, even under aerobic conditions. Finally, certain fungi, yeasts, and bacteria are known to methylate arsenic to derivatives of arsine, such as methyl, dimethyl, and trimethyl arsines. These are gaseous compounds with limited solubilities, but they transmit precipitated arsenic from anaerobic sediments back into the water column.

Johnson and Pilson[94] investigated the rate of oxidation of As(III) to As(V) in seawater. The empirical expression shown in Eq. C-5 was proposed by Johnson and Pilson to calculate the rate of production of As(V) in terms of $\mu M/(L \bullet d)$, where $R = 1.9872$ cal/(g-mole • K), T is the temperature expressed in K units, $C_{As(III)}$ is the concentration of As(III) in $\mu\underline{M}$, and S is the salinity expressed as parts per thousand). The reaction is strongly catalyzed by sunlight, with the observed rate of oxidation being increased 5 to 10 fold. The dissolved oxygen concentration did not have a significant effect on the reaction rate over the 100-fold range of oxygen concentration that was examined.

$$\log\left[-\frac{dC_{As(III)}}{dt}\right] = \left[\log \frac{dC_{As(V)}}{dt}\right] = \left(0.8356 - \frac{5847}{RT}\right) + \left[(0.6785)\,(\log C_{As\,(III)})\right] + \left[(0.7575)\,(pH)\right] + \left[(0.6721)\,(\log[S])\right], \qquad \text{C-(5)}$$

Table C-12. Free energies of formation for arsenic species at 25°C and one atmosphere (ΔG_f^o , kcal/mole).[a]

Name	Species	State[b]	ΔG_f^o
Arsenates	H_3AsO_4	aq	-184.0
	$H_2AsO_4^-$	aq	-181.0
	$HAsO_4^{2-}$	aq	-171.5
	AsO_4^{3-}	aq	-155.8
Arsenites	H_3AsO_3	aq	-154.4
	$H_2AsO_3^-$	aq	-141.8
	$HAsO_3^{2-}$	aq	-125.3
Sulfides	$HAsS_2$	aq	-11.61
	AsS_2^-	aq	-6.56
	AsS	s	-16.81
	As_2S_3	s	-40.25
Elemental arsenic	As	s	0
Arsine	AsH_3	aq	+23.8
	AsH_3	g	+16.5
Anhydrides	As_2O_3	s	-140.8
	As_2O_5	s	-186.9

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[a] Adapted from Ferguson and Gavis.[91]

[b] aq - aqueous; s - solid; g - gaseous

where

$C_{As\ (III)}$ = concentration of arsenic (III);
$C_{As\ (V)}$ = concentration of arsenic (V);
S = salinity (as parts per thousand);
R = gas constant;
T = temperature (K).

The expression gives an initial arsenite oxidation rate of 6.34 x 10^{-5} $\mu\underline{M}$ As(III)/(L • d), or 0.023 µM/(L • y), in water having a pH of 7.8, a salinity of 35 parts per thousand, a temperature of 4°C, and an initial arsenite concentration of 0.01 $\mu\underline{M}$. The arsenate concentration predicted after a year's time is within an order of magnitude of the total amount of arsenic normally found in the oceans. Because of the long duration of water detention in the oceans, all seawater arsenic ideally should be oxidized to arsenate; however, this is not the case. Ferguson and Gavis[91] state that the ratio of As(V) to total arsenic in seawater is commonly about 0.8. Johnson and Pilson[94] explain this by suggesting the likelihood of biologically mediated in situ reduction of As(V).

The natural cycling of the various species of arsenic in a stratified lake is shown in Fig. C-21. The As(III) will be oxidized to As(V) in the epilimnion, and As(V) will be reduced back to As(III) in the hypolimnion. Adsorption and coprecipitation of either As(III) or As(V) will occur in the hypolimnion, with the arsenic being stored in an insoluble form in anaerobic sediments. Methylation will redissolve the precipitated arsenic back into the overlying waters. Many forms of arsenic, therefore, can be encountered in natural surface waters. The As(III) predominates in anaerobic ground water.

Although arsenic removal from water supplies varies greatly according to the oxidation state, the state is not always identified. A major reason for this discrepancy is that the analytical techniques commonly used, such as atomic absorption, do not distinguish between valence states.[73]

CYANIDE

The cyanide ion hydrolyzes in water to form hydrocyanic acid:

$$CN^- + H_2O \overset{k_h}{\rightleftharpoons} HCN + OH^- \quad . \qquad C\text{-}(6)$$

The hydrolysis equilibrium constant is $k_h = 1.4 \times 10^{-5}$ at 25°C.[79] Therefore, about half of the total cyanide will be in the form of HCN at a pH of 9.2. The speciation of the free

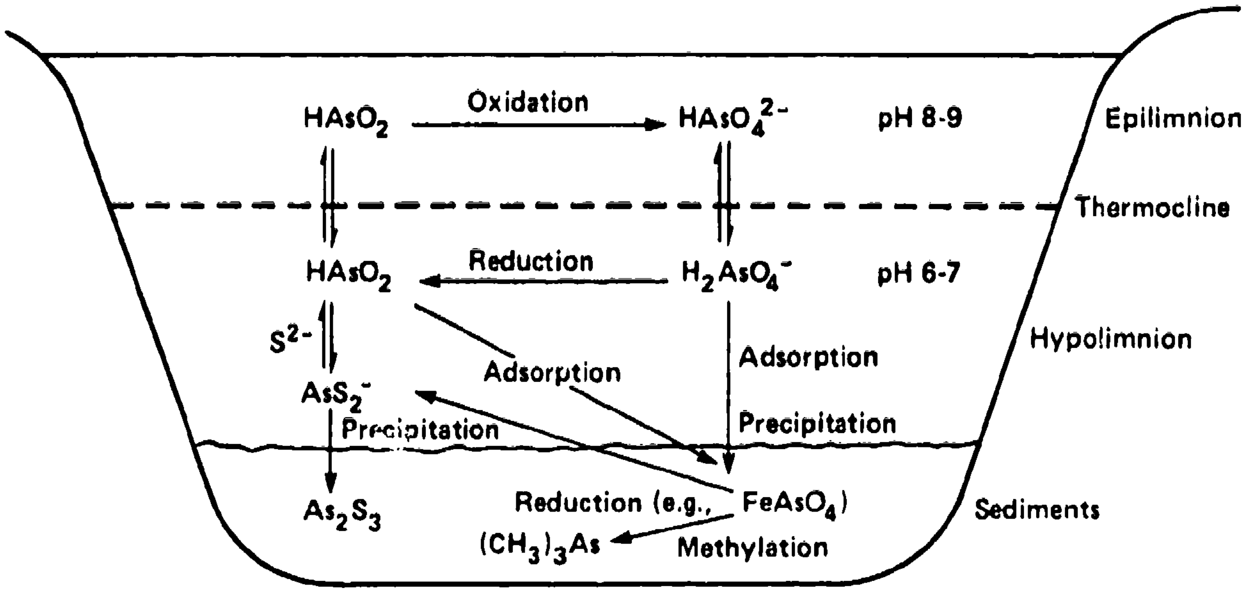

Figure C-21. Natural cycling of arsenic in a stratified lake. Reprinted with permission from Ferguson and Gavis.[91]

cyanide as a function of pH is shown in Fig. C-22. Hydrogen cyanide is a gas at a temperature of approximately 26°C and a pressure of one standard atmosphere. Although total solubility has not been reported, HCN is known to be very soluble in water.[95]

The cyanide ion CN^- forms complex cyanides with many metals such as Cu, Ag, Au, Zn, Cd, Hg, Mn, Fe, Ni, Co, etc. Some of these complexes, e.g., $Ag(CN)_2^-$, $Fe(CN)_6^{3-}$, are stable and do not decompose appreciably with a strong acid. Other cyanide complexes are decomposed quickly by strong acids to hydrocyanic acid.[95]

The toxicity of aqueous solutions of cyanide is attributed primarily to the undissociated hydrocyanic acid.[96,97] The toxicities of the cyanide ion and the metallocyanide complexes are apparently much less than that of molecular HCN.[98] Hydrocyanic acid is formed when simple or complex cyanide salts are added to water. In the case of a simple cyanide such as NaCN, the liberated cyanide ion is immediately hydrolyzed to HCN. Complex cyanide salts, e.g., $Na_yM(CN)_x$, first yield the complex cyanide ion $M(CN)_x^{y-}$ by dissociation. This reaction is followed by decomposition to the cyanide ion CN^- and then hydrolysis to HCN.[97,98]

The amount of undissociated hydrocyanic acid can be decreased by several mechanisms. Raising the pH of the solution will decrease the hydrogen-ion (H^+) concentration, displacing the equilibrium between HCN and CN^- in the direction of CN^- (see Eq. C-6). The addition of complex-forming metal ions to a cyanide solution will yield a similar effect. The metal ion will remove free CN^- and favor the formation of more CN^- from the reservoir of undissociated HCN.[96]

Historically, cyanide wastewaters have been treated by alkaline chlorination.[98,99] When chlorine is added to a cyanide solution such as sodium cyanide, the free cyanide oxidizes to cyanogen chloride:

$$NaCN + Cl_2 \rightleftharpoons CNCl + NaCl \,. \qquad C\text{-}(7)$$

Cyanogen chloride is a highly toxic gas (the toxicity of CNCl may exceed that of an equal concentration of HCN)[98]; however, CNCl possesses limited solubility in water. Under alkaline conditions (pH of 8.5 to 9.0), the CNCl is hydrolyzed to cyanate:

$$CNCl + 2\,NaOH \rightleftharpoons NaCNO + NaCl + H_2O \,. \qquad C\text{-}(8)$$

The cyanate ion is a much more stable and less toxic compound than cyanogen chloride.

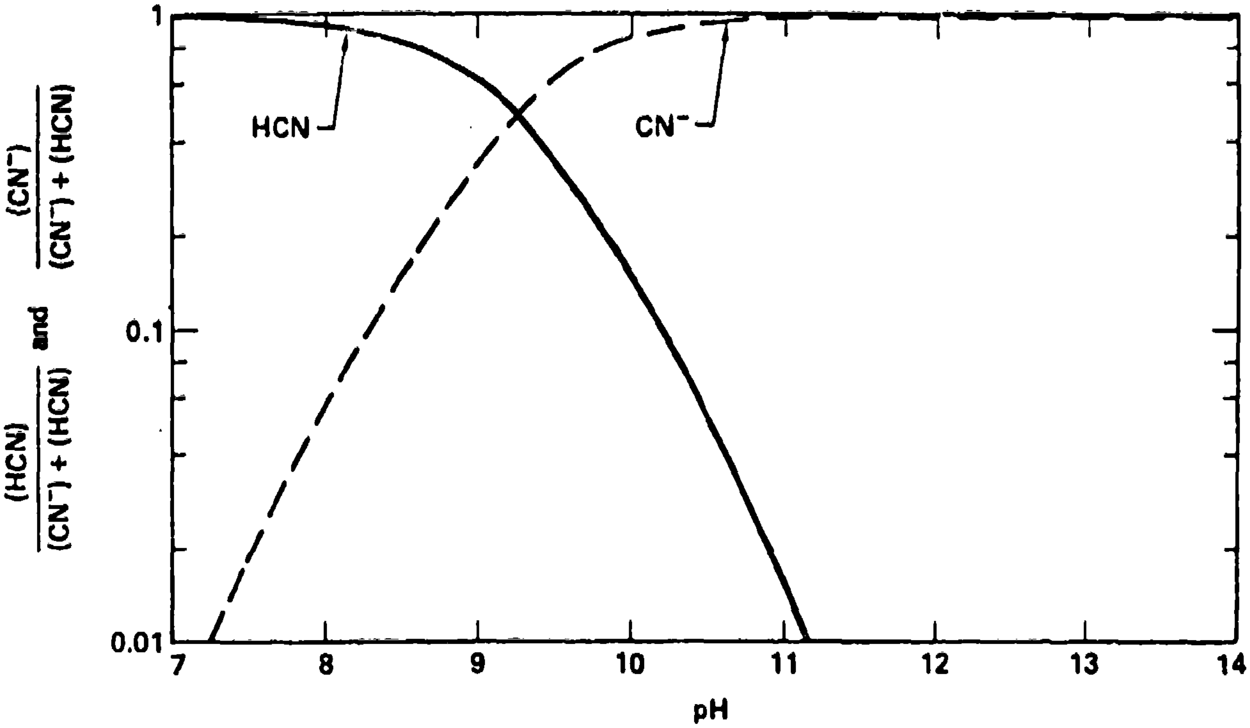

Figure C-22. Speciation of cyanide in water as a function of pH.

Almost complete conversion of free cyanide to cyanate occurs within 10 to 30 min at a pH of 8.5 to 9.0 when chlorine is added in excess. The reaction time decreases to a range of 5 to 7 min. at a pH of 10 to 11. Unhydrolyzed cyanogen chloride will appear at pH values below 8.0.[99] The stoichiometric amounts of chlorine and caustic required for the oxidation of free cyanides to cyanates are as follows: 2.73 parts by weight of chlorine for each part of free cyanide as CN, and 1.125 parts of caustic as NaOH per part of chlorine applied. In practice, the chlorine is always added in excess.[99]

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