Composite Membranes for Seawater Desalination by Reverse Osmosis

R. L. RILEY, H. K. LONSDALE,* and C. R. LYONS,

Gulf General Atomic Company, San Diego, California 92112

Synopsis

A composite reverse-osmosis membrane has been developed for seawater desalination having a 400-Å semipermeable barrier. The membrane is prepared by directly forming a very thin film of a polymer, generally cellulose triacetate, upon the finely porous surface of a supporting membrane. The composite membrane, capable of desalinating seawater in a single pass, has demonstrated improved flux stability at high pressures over modified membranes currently used to desalinate brackish water.

INTRODUCTION

The major factor in the rapid advance of the reverse osmosis process has been the development of the modified cellulose acetate membrane by Loeb and Sourirajan[1] and later improvements made by others.[2,3] At present, most large reverse osmosis plants operate on brackish waters with membranes of this type. Seawater desalination by this process, however, has been slowed due to membrane deficiencies. The membrane, clearly the most fundamental element of the process, exhibits insufficient selectivity, marginal chemical stability, and decreasing permeability with time.

During the past several years, the reverse osmosis performance as well as the intrinsic permeability properties, the physical structure, and, to a lesser extent, the mechanism of transport through these membranes have come to be understood.[4] These studies led to the discovery that the modified cellulose 2.45-acetate (39.8% acetyl) membrane is a two-layered structure consisting of a thin, dense, semipermeable barrier typically 2000 Å thick and of a finely porous substructure that serves essentially as a support.[5] The high water fluxes attainable through these membranes are possible because the membranes are effectively very thin. The membrane, then, can be viewed as a very thin film supported on an integral porous support.

Soon after the modified membrane was developed it became apparent that the method of preparation would not generally be applicable to other polymer systems, a conclusion that subsequent research has amply demonstrated. As a result, a novel method of preparing composite membranes was developed whereby a thin film of a polymer, generally cellulose triacetate, is formed upon the precoated surface of a supporting membrane.

* Present address: Pharmetrics, Inc., Palo Alto, California 94304.

DEFINITION AND PRINCIPLES

It is now generally agreed that dense cellulose acetate membranes obey a solution–diffusion model of membrane transport. That is, the movement of water and simple salts through the membrane is described as solution and subsequent diffusion of the species within the membrane. The phenomenologic equation for water flow is

$$J_1 = \frac{D_1 C_1 \bar{V}_1}{RT} \frac{(\Delta P - \Delta \pi)}{\Delta X} \equiv A(\Delta P - \Delta \pi) \tag{1}$$

where J_1 is the water flux (grams per cm²-sec); D_1 is the diffusion coefficient of water (cm² per sec); C_1 is the water content (grams per cm³; $\bar{V}_1$ is the partial molar volume of water in the external phase (cm³ per mole); $\Delta P - \Delta \pi$ is the net pressure difference in atmospheres across the membrane (applied pressure less osmotic pressure); ΔX is the effective membrane thickness in centimeters across which ΔP and $\Delta \pi$ are exerted; and R and T are the gas constant (cm³-atm per mole-degree Kelvin) and absolute temperature, respectively. The proportionality factor A, referred to as the membrane constant, is a measure of the water flux per unit net pressure (grams per cm²-sec-atm).

Likewise, a similar phenomenologic equation exists for solute flow J_2 (grams per cm²-sec) through imperfection-free membranes,

$$J_2 = D_2 K \frac{\Delta \rho_2}{\Delta X}, \tag{2}$$

where D_2 is the diffusion coefficient (cm² per sec); K is the distribution coefficient for the solute species (grams solute per cm³ membrane/grams solute per cm³ solution); and $\Delta \rho_2$ is the difference in concentration of solute in the solutions separated by the membrane (grams per cm³).

Equations (1) and (2) are working relations for the transport of water and simple salts through the composite membrane discussed in this work. The salt rejection, S, in reverse osmosis is usually defined as

$$S = (\rho_2' - \rho_2'')/\rho_2' \tag{3}$$

where the supersripts prime and double prime refer to the solutions on the high-pressure and low-pressure side of the membrane, respectively. Assuming diffusive flows, the concentration of solute in the permeate is determined only by the relative water and salt fluxes in reverse osmosis. Thus, $\rho_2'' = J_2 \rho_1''/J_1$, and

$$S = \left[1 + \frac{D_2 K R T \rho_1''}{D_1 C_1 \bar{V}_1 (\Delta P - \Delta \pi)}\right]^{-1} \tag{4}$$

where ρ_1'' is the water concentration of the permeate.

The transport properties of dense cellulose acetate membranes of varying acetyl contents were measured in an earlier study.[4] It was shown that the permselectivity increases while the water permeability decreases as the
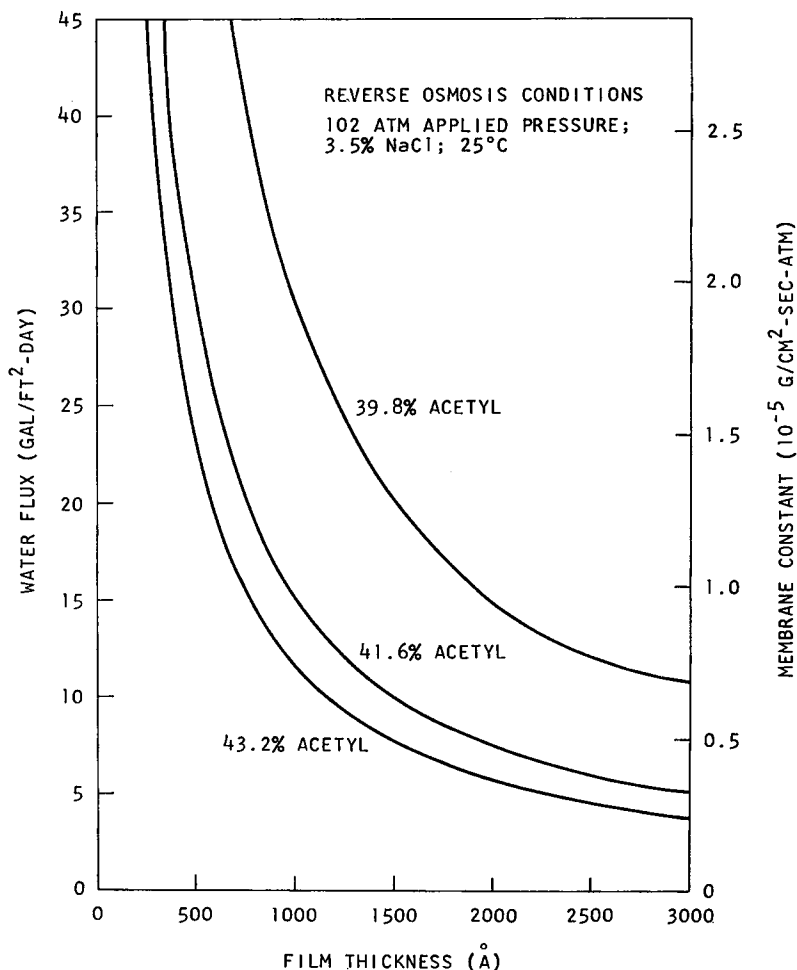
Fig. 1. Expected water flux in reverse osmosis as a function of thin-film thickness for 39.8%-, 41.6%-, and 43.2%-acetyl cellulose acetate.

acetyl content of the membrane increases.   Based on intrinsic water permeability measurements by direct osmosis and eq. (1), the expected water flux can be calculated for membranes of different thickness and acetyl content. Such a relation is shown by Figure 1 for 39.8%-, 41.6%-, and 43.2%-acetyl cellulose acetate membranes in reverse osmosis at an applied pressure of 102 atm with a 3.5 wt-% sodium chloride brine at 25°C.   Similarly, based on the intrinsic salt permeability, the expected salt rejection of sodium chloride for imperfection-free membranes is given in Table I.   The expected salt rejection is not absolute, however, since the salt permeability of cellulose acetate membranes is variable, depending upon casting conditions and postpreparation treatment of the membrane.   It should be noted, based on eq. (4), that the salt rejection is independent of the thickness of the mem-

TABLE I
Expected Sodium Chloride Rejection in Reverse Osmosis[a]

Cellulose acetate		Salt permeability D_2K, (cm²/sec) × 10^{-11}	Salt rejection, %
Acetyl, %	Degree of substitution		
39.8	2.45	3.4[b]	99.76
41.6	2.65	0.92[c]	99.87
43.2	2.83	0.33[c]	99.94

[a] $\Delta p - \Delta \pi = 74$ atm; 3.5 wt-% sodium chloride; 25°C.
[b] Membrane cast from acetone.
[c] Membrane cast from chloroform.

brane. In contrast, the water flux is inversely proportional to the membrane thickness. It is apparent, then, that the semipermeable layer of the membrane should be as thin as possible.

REVERSE OSMOSIS MEMBRANES

For seawater desalination to be practical, it is necessary to have reasonably high water recoveries. This makes it necessary for the membrane to reject about 99.5% of the sodium chloride to yield potable water in a single pass. In practice, the selectivity of the modified membrane has consistently been less than 99%. Typically, the seawater rejection at an applied pressure of 102 atm is 97% to 99%. The failure to achieve the expected salt rejections is attributed to the existence of imperfections in the thin semipermeable barrier through which salt water can pass more rapidly than through the rest of the membrane. Recently, it has been reported that the permselectivity of the modified membrane can be increased sufficiently by using cellulose acetates having a higher degree of substitution.[6] This finding is consistent with the fact that permselectivity increases with increasing degree of substitution.[4]

It is well established that the modified membrane undergoes long-term deleterious effects. At high pressures, the membrane permeability tends to decline with time. This decline is believed to be the result of a gradual collapse of the porous substructure and the resultant increase in the effective membrane thickness. It has been found, in the time range over which it has been studied, that the water flux depends on time according to a power law,

$$\log A = -m \log t, \tag{5}$$

where the constant m (the compaction slope) depends on membrane type, pressure, and operating temperature.

Another long-term effect to which cellulose acetate membranes are subject is hydrolysis.[7-9] It has been shown that the hydrolysis rate of the cellulose ester is strongly pH dependent and that the rate is significant at pH 8, that of seawater. As the membrane hydrolyzes, the degree of acetylation of

the cellulose ester decreases, thereby increasing the rate of salt permeation. Consequently, the lifetime of the membrane, defined as the period over which potable water is obtained, is strongly dependent on the extent of membrane hydrolysis. This effect can, however, be partially controlled by pH adjustment of the brine.

Each of the limitations cited for the modified membrane has serious implications to the design and performance of reverse osmosis plants. These problems have been recognized for some time, and considerable effort has been expended to effect solutions, but these have had only limited success.

It is likely that a quantum improvement in membrane properties will result from a more general method of preparing membranes than that of Loeb and Sourirajan.[1] Such a method, described and used in this work, is a composite method. The method evolved from earlier studies[10] in which ultrathin cellulose acetate films (nominally 1500 Å thick) were prepared on the surface of glass plates, floated off onto the surface of water, and subsequently supported on a finely porous supporting membrane. It was found, however, that it was quite difficult to transfer large areas of the thin film from the water trough onto the porous supporting membrane without introducing imperfections into the thin film. Furthermore, this method of preparing membranes is impractical for a large-scale continuous process. As a result, an integral method was developed in which the thin semipermeable barrier is formed directly on the porous supporting membrane. This method provides several additional degrees of freedom in membrane preparation. First, the thin film and the porous supporting membrane can be individually optimized for their specific functions. Second, the thin-film thickness can be readily varied and controlled. Third, it may be possible to prepare membranes from new and improved membrane materials.

EXPERIMENTAL

To prepare a composite membrane, the thin film, generally cellulose triacetate, is formed on the poly(acrylic acid)-coated surface of the porous supporting membrane by dipping into a dilute solution. The detailed procedure is described elsewhere.[11] The thickness of the thin film is controlled by the withdrawal rate and the concentration of the polymer in the dilute solution.[12] The porous supporting membrane is prepared from a mixture of cellulose nitrate and cellulose acetate by the "gelation" or "multiple solvent" method.[13-15] The membrane constant of the porous supporting membrane used in this study was 2000×10^{-5} g/cm^2-sec-atm at 2.7 atm applied pressure. The composites were tested at 25°C with seawater at an applied pressure of 102 atm. The seawater used for each of the experiments was taken from the Pacific Ocean several hundred yards offshore from the Scripps Institution of Oceanography at La Jolla, California, and filtered through a 5-μ filter. At this location, the composition of the ocean varies because of coastal dilution. Experiments were performed with the seawater both as received and with pH adjustment. The pH was reduced

TABLE II
Composition of Seawater

	Seawater as received	Seawater after pH adjustment
Conductivity, umho/cm	45,000	47,500
Salinity, ppm	28,800	30,500
Sodium chloride, ppm	25,300	25,950
Na^+, ppm	9,950	10,200
Cl^-, ppm	19,850	19,700
Divalent ion as Mg^{2+}, ppm	1,555	1,580
pH	8.0	6.0
Osmotic pressure, atm	19.1	21.4

from 8.0 to 6.0 by the addition of 0.11 g concentrated sulfuric acid per liter of seawater. The composition of the seawater varied as shown by Table II.

The ion concentrations in both the feed and the product were determined with an Orion Model 801 digital pH meter equipped with specific ion electrodes. The salinity, a measure of dissolved solids, was obtained from the total conductivity;[16] the osmotic pressure was calculated from the salinity.[17]

RESULTS AND DISCUSSION

As received, the pH of the seawater was 8.0. At this pH, it is possible that the performance of the cellulose-acetate thin film would be affected by hydrolysis.[8,9] Consequently, two experiments are presented, one with as-received seawater and one after pH adjustment.

For the reverse osmosis experiment with as-received seawater, composites having 750-Å thin films of Eastman 416-3 cellulose 2.65-acetate were used. A modified membrane, prepared according to the method of Sourirajan and Govindan,[2] was included for comparison. The results observed after 24 and 336 hr are presented in Table III. Long-term fluxes in excess of 7 gal/ft²-day were generally observed, with high salt rejections. The composites prepared with the more permeable CN-CA support (nos. 10 and 11 in Table III) exhibited higher water fluxes, lower salt rejections, and slightly increased compaction rates. The effect of hydrolysis on the modified membrane is reflected by a decrease in salt rejection between 24 and 336 hr. For the composite membranes, the effect is not readily apparent. That is, the salt rejections after 336 hr were, on the average, approximately unchanged. Nevertheless, it is assumed that the composites also hydrolyzed slightly, since the characteristic increase in salt rejection exhibited by composites with increasing time was not observed. The water flux decline for the composite membranes after 336 hr, expressed by the compaction slope, was quite low. With the use of eq. (5), the water flux decline can be extrapolated to even longer periods of time.

Four composite membranes having nominal 400-Å thin films of Eastman 432-130-B cellulose 2.83-acetate were tested with seawater adjusted for pH to 6.0. A modified membrane, similar to that described in the previous ex-

TABLE III

Reverse Osmosis Results for Composite Membranes at pH 8.0[a]

Composite membrane no.	Membrane constant, (g/cm²-sec-atm) × 10⁻⁵		Water flux, gal/ft²-day		Rejection, %								Compaction slope after 336 hr (log A vs. log time)
					Na+		Cl-		Divalent ions		Total conductivity		
	24 hr	336 hr	24 hr	336 hr	24 hr	336 hr	24 hr	336 hr	24 hr	336 hr	24 hr	336 hr	
1	0.45	0.44	7.8	7.6	99.37	99.38	99.48	99.39	99.81	99.81	99.51	99.16	−0.011 ± 0.003
2	0.43	0.43	7.5	7.3	99.68	99.64	99.73	99.67	99.96	99.95	99.60	99.53	−0.009 ± 0.003
3	0.42	0.42	7.4	7.3	99.03	99.01	99.14	99.0	99.65	99.60	98.9	99.11	−0.006 ± 0.003
4	0.32	0.32	5.6	5.5	99.68	99.68	99.73	99.71	99.61	99.94	99.60	99.60	−0.009 ± 0.003
5	0.51	0.50	8.8	8.7	99.63	99.50	99.68	99.50	99.92	99.90	99.56	99.33	−0.005 ± 0.004
6	0.45	0.44	7.7	7.6	99.05	99.18	99.16	99.18	99.75	99.76	98.9	98.9	−0.006 ± 0.004
7	0.46	0.44	8.2	7.6	98.8	99.38	99.0	99.36	99.85	99.92	98.8	99.22	−0.031 ± 0.004
8	0.47	0.46	7.9	8.0	99.46	99.43	99.52	99.44	99.91	99.90	99.38	99.31	+0.003 ± 0.005
9	0.45	0.44	8.0	7.6	99.53	99.48	99.59	99.48	99.94	99.93	99.44	99.33	−0.022 ± 0.004
10[b]	0.71	0.67	12.7	11.5	99.08	99.12	99.26	99.09	99.85	99.84	99.0	98.9	−0.037 ± 0.005
11[b]	0.70	0.65	12.4	11.2	98.8	98.9	99.0	98.9	99.73	99.76	98.9	98.7	−0.041 ± 0.004
Modified membrane	0.67	0.56	11.6	9.7	98.3	97.9	98.7	97.9	99.91	99.92	98.2	97.6	−0.068 ± 0.005

[a] 750-Å Thin films of cellulose 2.65-acetate.

[b] Membrane constant of porous supporting membrane = 3000 × 10⁻⁵ g/cm²-sec-atm at 2.7 atm applied pressure.

TABLE IV

Reverse Osmosis Results for Composite Membranes at pH 6.0[a]

| Composite membrane no. | Membrane constant, (g/cm²-sec-atm) × 10⁻⁵ | Water flux, gal/ft²-day | Rejection, % | | | | Compaction slope after 143 hr (log A vs. log time) |
			Na⁺	Cl⁻	Divalent ions	Total conductivity	
1	0.73	12.5	99.62	99.62	99.89	99.49	−0.036 ± 0.002
2	0.78	13.2	99.45	99.47	99.81	99.26	−0.036 ± 0.002
3	0.78	13.3	99.54	99.54	99.84	99.37	−0.031 ± 0.002
4	0.75	12.7	99.45	99.47	99.84	99.26	−0.017 ± 0.008
Modified membrane	0.65	11.2	97.6	97.7	99.72	97.1	−0.064 ± 0.002

[a] 400-Å Thin films of cellulose 2.83-acetate.

periment, was again tested for comparison. The experimental results are given in Table IV. The sodium and chloride ion rejections ranged from 99.45% to 99.62% with water fluxes in excess of 12 gal/ft²-day. The compaction slopes were also low. These composites were superior in every respect to the modified membrane control sample. For each of the composites, the rejections increased with time.

It is clear that the salt rejection of the composite membranes in both experiments was quite ample for single-pass desalination, and, in some cases, water fluxes in excess of 10 gal/ft²-day were achieved after several days. It appears that pH adjustment of seawater may be necessary to maintain the high performance for extended periods.

CONCLUSIONS

A thin-film composite reverse osmosis membrane has been developed by forming a thin film of cellulose triacetate from dilute solution directly upon the precoated surface of a porous supporting membrane. The membrane, capable of desalinating seawater in a single pass, combines high flux and stability with excellent selectivity. The method of preparing the composite membrane may prove useful for thin-film materials other than cellulose acetate.

References

1. S. Loeb and S. Sourirajan, *Advan. Chem. Ser.*, **38**, 117 (1962).

2. S. Sourirajan and T. S. Govindan, in *Proceedings of the First International Symposium on Water Desalination*, Washington, D.C., October 3–9, 1965, Vol. 1, U.S. Government Printing Office, Washington, D.C., 1967, p. 251.

3. S. Manjikian, *Semipermeable Desalination Membranes from Organic Casting Solutions*, Report 65–13, University of California, Department of Engineering, Los Angeles, March 1965.

4. H. K. Lonsdale, U. Merten, and R. L. Riley, *J. Appl. Polym. Sci.*, **9**, 1341 (1965).

5. R. L. Riley, J. O. Gardner, and U. Merten, *Science*, **143**, 801 (1964).

6. D. L. Hoernschemeyer, C. W. Saltonstall, Jr., O. S. Schaeffer, L. W. Schollenback, A. J. Secchi, and A. L. Vincent, *Research and Development of Saline Water*, U.S. Department of the Interior, Contract 14-01-0001-2205, Report 1319-F, Aerojet-General Corporation, January 1970.

7. R. L. Riley, U. Merten, and J. O. Gardner, *Desalination*, **1**, 30 (1966).

8. K. D. Vos, F. O. Burris, Jr., and R. L. Riley, *J. Appl. Polym. Sci.*, **10**, 825 (1966).

9. K. D. Vos, A. P. Hatcher, and U. Merten, *Ind. Eng. Chem., Prod. Res. Develop.*, **5**, 211 (1966).

10. R. L. Riley, H. K. Lonsdale, C. R. Lyons, and U. Merten, *J. Appl. Polym. Sci.*, **11**, 2143 (1967).

11. H. K. Lonsdale, R. L. Riley, C. E. Milstead, L. D. LaGrange, A. S. Douglas, and S. B. Sachs, *Research on Improved Reverse Osmosis Membranes*, Final Report to Office of Saline Water, U.S. Department of the Interior, Contract 14-01-0001-1778, Gulf General Atomic, April 1970.

12. V. G. Levich, *Physicochemical Hydrodynamics*, Prentice Hall, Englewood Cliffs, New Jersey, 1967.

13. W. J. Elford, *Proc. Roy. Soc.*, **B106,** 216 (1930).

14. J. D. Ferry, *Chem. Rev.*, **18,** 373 (1936).

15. R. F. Zsigmondy, R., *Z. Angew. Chem.*, **30,** 398 (1926).

16. *Instrumentation for Desalination*, Bulletin B-31-2M, The Foxboro Company, Foxboro, Massachusetts, 1967.

17. R. C. Weast and S. M. Selby, Eds. *Handbook of Chemistry and Physics*, 46th ed., Chemical Rubber Co., Cleveland, 1965–66, pp. D-127 and D-155.