Structure of Porous Cellulose Acetate Membranes and a Method for Improving Their Performance in Reverse Osmosis

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Synopsis

Experimental data support the hypothesis that the surface layer of the asymmetric Loeb-Sourirajan type porous cellulose acetate membranes has a heterogeneous microporous structure.   A general method is proposed for improving the performance of the above membranes in reverse osmosis, by which product rates are increased without decreasing solute separation.   The method consists in pumping pure water past the back side of the membrane under just enough pressure for a sufficiently prolonged period of time; after such pretreatment, the membrane is used in the reverse osmosis experiments in the normal manner with the surface layer facing the feed solution.   Back-pressure treatment at 400 psig for 85 hr on preshrunk and normally pressure-treated membranes increases the product rate by over 20% without decreasing solute separation in reverse osmosis experiments at 600 psig with the use of 0.5 wt-% NaCl–H$_2$O feed solutions; with a different sequence of back-pressure treatment, similar results have been obtained in reverse osmosis experiments at 1500 psig also.   The compaction effect of a normal membrane and that of a back pressure treated membrane are the same during continuous reverse osmosis operation under 600 psig; the effects of back-pressure treatment on a normal membrane and a compacted membrane are also the same.   The pure water permeability data obtained in cyclic experiments show that the smaller pores on the surface layer are opened more than the bigger ones during the back side operation.   The probable structural changes taking place in the film during back-pressure treatment are discussed.

INTRODUCTION

Since the development of the asymmetric Loeb-Sourirajan type porous cellulose acetate membranes[1] for reverse osmosis application, extensive investigations have been undertaken in different laboratories to study the characteristics of such membranes, to improve their performance, and/or to develop better membranes with particular reference to saline water conversion.   This work is part of such investigations.   The problem under consideration is to increase membrane permeability without decreasing solute separation under a given set of experimental conditions for saline water conversion and similar applications.

From the point of view of the preferential sorption-capillary flow mechanism for the reverse osmosis process,[2] which led to the development of the

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Loeb-Sourirajan type porous cellulose acetate membranes, several approaches to the above problem are possible: (1) the effective thickness of the membrane may be reduced; (2) the absolute number of pores of appropriate size on the microporous surface layer may be increased; (3) the rigidity of the overall porous structure of the membrane may be altered so that membrane compaction is less during continuous operation under pressure, and/or (4) the number, pore size, and pore size distribution on the microporous surface layer of a given membrane may be so altered that increased permeability results without decreasing solute separation. The above approaches are not mutually exclusive, but any proposed technique for membrane-preparation and/or membrane-treatment may emphasize one or more of the above approaches.

This work is concerned with the study of a method for improving the performance of a given Loeb-Sourirajan type porous cellulose acetate membrane for saline water conversion, by the approach (4) mentioned above.

EXPERIMENTAL DETAILS

Reagent grade sodium chloride, and three types of porous cellulose acetate membranes, designated here as CA-NRC-18, CA-NRC-25, and CA-NRC-47 type films, were used in this work. The film casting conditions for the three types of films used were as shown in Table I.

TABLE I

	CA-NRC-18	CA-NRC-25	CA-NRC-47
Casting solution composition, wt-%			
Cellulose acetate (acetyl content 39.8%)	17	22.2	25
Acetone	68	66.7	45
Magnesium perchlorate	1.5	1.1	—
Water	13.5	10.0	—
Formamide	—	—	30
Casting temperature, °C	−10	−10	room (~24)
Solvent evaporation time, min	4	4	<1
Duration of film-setting in cold water, hr	~1	~1	~1
Nominal film thickness, in.	0.003–0.006	0.003–0.006	0.003–0.006

Details of the above film-casting technique are available in the literature.[3-6] The apparatus and the experimental procedure have been reported.[6,7] Membranes shrunk under water at different temperatures were used to give different levels of solute separation at a given set of operating conditions.

The aqueous sodium chloride solution (feed) was pumped under pressure past the surface of the membrane held in a stainless steel pressure chamber provided with two separate outlet openings, one for the flow of the mem-

brane permeated solution, and the other for that of the concentrated effluent. A porous stainless steel plate, specified to have pores of average size equal to 5 μ, was mounted between the pump and the cell to act as a filter for dust particles which might otherwise clog the pores of the membrane surface. Unless otherwise stated, the experiments were of the short-run type, each lasting about 2 hr, and were carried out at the laboratory temperature; membranes were initially subjected to pure water pressures of 700 and 1700 psig, respectively for 1–2 hr for subsequent reverse osmosis operation at 600 and 1500 psig. This is referred as the normal pressure treatment. Aqueous sodium chloride feed solutions, 0.5M and 0.5 wt-%, were used for experiments involving operating pressures of 1500 and 600 psig, respectively. The reported product rates are those corrected to 25°C on the basis of the relative viscosity and density data for pure water. The feed rates were maintained at about 250 cc/min. In each experiment, the solute separation f, defined as

$$f = \frac{\text{molality of feed } (m_1) - \text{molality of product } (m_3)}{\text{molality of feed } (m_1)}$$

as well as the product rate [PR] and the pure water permeability [PWP] (in grams per hour per 7.6 cm² of effective film area) were determined at the preset operating conditions. In all cases, the terms "product" and "product rate" refer to the membrane-permeated solutions. The concentrations of the solute in the feed and product solutions were determined either by refractive index measurements using a precision Bausch and Lomb refractometer or by specific resistance measurements.

RESULTS AND DISCUSSION

Microporous Nature of Surface Layer in Reverse Osmosis Membrane

Some workers[8,9] consider that the surface layer in the reverse osmosis membrane must be nonporous in order to give high levels of solute separation. On the other hand, the preferential sorption–capillary flow mechanism[2] calls for a porous surface structure and requires a critical pore diameter on the membrane surface for maximum solute separation for any given membrane material–solution system; with reference to the Loeb-Sourirajan type porous cellulose acetate membranes, that the surface layer is microporous and heterogeneous, and that the transport of both the preferentially sorbed water and the bulk solution is through the capillary pores on the membrane surface at all levels of solute separation, are fundamental concepts of practical interest arising from the above mechanism.

With films giving near 100% solute separation, whether or not the surface layer remains porous is still an open question. In this connection the following experimental data are of interest.

When the shrinkage temperature is increased, solute separation increases,

and product rate decreases as illustrated in Figure 1, indicating that the size of the pores on the membrane surface becomes smaller during the process. On progressively increasing the shrinkage temperature, solute separation can be increased to levels >98 or 99%, and still good product rates can be obtained. On increasing the shrinkage temperature still further, the product rate does not remain constant (as one would expect if the membrane surface is nonporous), but it is reduced still further, indicating that the size of the pores on the membrane surface is getting still
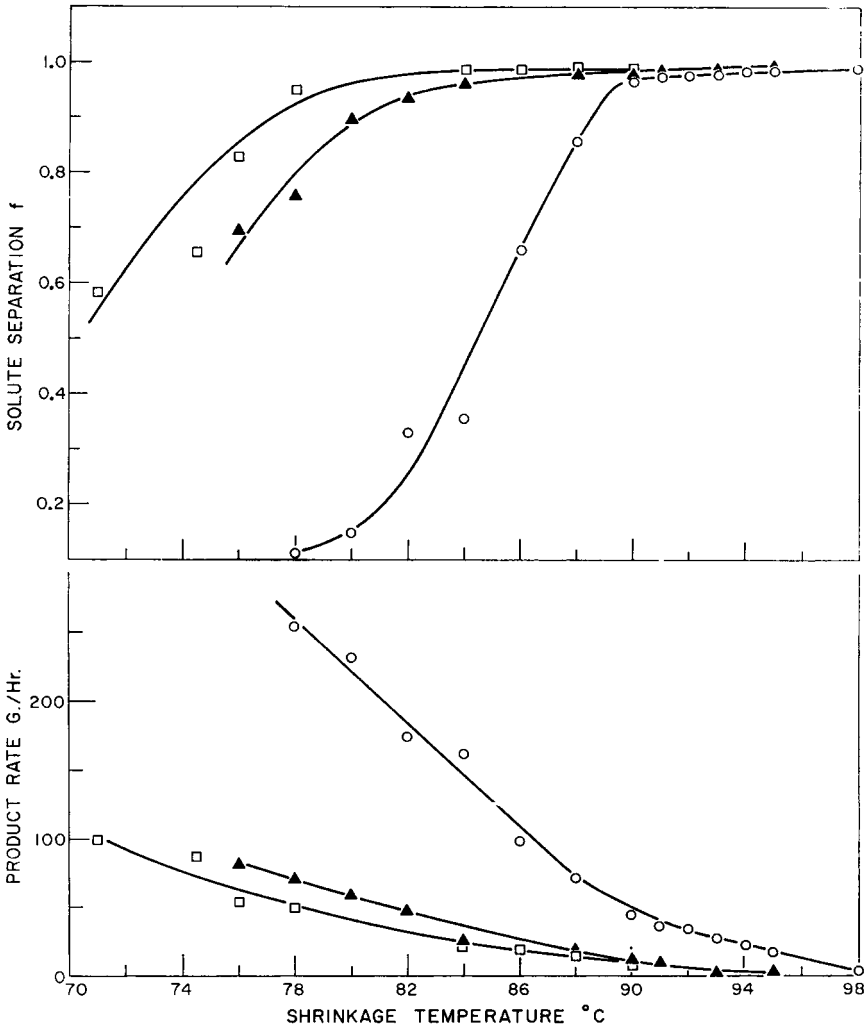

Fig. 1. Effect of shrinkage temperature on the performance of different porous cellulose acetate membranes. Film type, O CA-NRC-18, ▲ CA-NRC-47, ☐ CA-NRC-25; system, NaCl-H$_2$O; feed concentration, 0.5M; feed rate, 250 cc./min.; operating pressure, 1500 psig; film area, 7.6 cm^2.

further reduced. The above shrinkage temperature–product rate profile cannot be attributed to any steep increase in effective film thickness because the profile is different for films cast under different conditions and no abrupt changes in their mechanical properties are found in a wide range of temperature.[10]

The pure water permeability data for a set of four different films were obtained in the operating temperature range 6–36°C. With a $0.5M$ NaCl–H_2O feed solution at 1500 psig, films 23, 24, 25, and 26 gave solute separations of 28.2, 49.0, 68.9, and 97.1%, respectively. The pure water permeability constant A (in gram-mole H_2O per square centimeter-second-atmosphere) increased with increasing operating temperature, and A multiplied by the viscosity of water at the operating temperature remained constant for all the films tested. This is illustrated in Figure 2. The results indicate that fluid flow through each of the above films is essentially viscous, and the mechanism of fluid transport is the same for all the films tested.

The values of the pure water permeability constant A and the solute transport parameter $(D_{AM}/K\delta)$ (expressed in centimeter/second) for a number of films with respect to the system (NaCl–H_2O) have been determined by the Kimura-Sourirajan analysis;[11–13] the parameter $(D_{AM}/K\delta)$ plays the role of a mass transfer coefficient with respect to solute transport through the membrane, and hence it is treated as a single quantity for purposes of analysis. An increase in the value of A corresponds to an increase in the average pore size on the membrane surface. The films chosen covered a wide range of solute separation; for example, with respect to a $0.5M$ feed solution, films G1 and 12 gave 98.9 and 18.7% solute separations respectively; the other films gave intermediate levels of solute separation. A log-log plot of A versus $(D_{AM}/K\delta)$ is shown in Figure 3. The absence of any abrupt discontinuity in the A versus $(D_{AM}/K\delta)$ correlation shows that
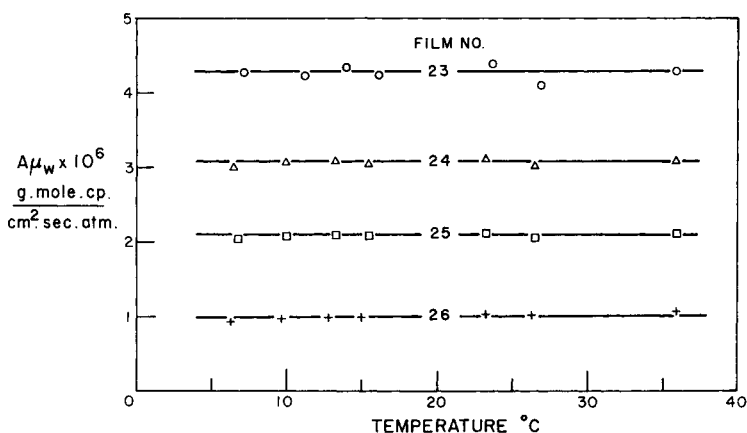

Fig. 2. Effect of operating temperature on pure water permeability. Film type, CA-NRC-18; operating pressure, 1500 psig; feed rate, 250 cc./min.
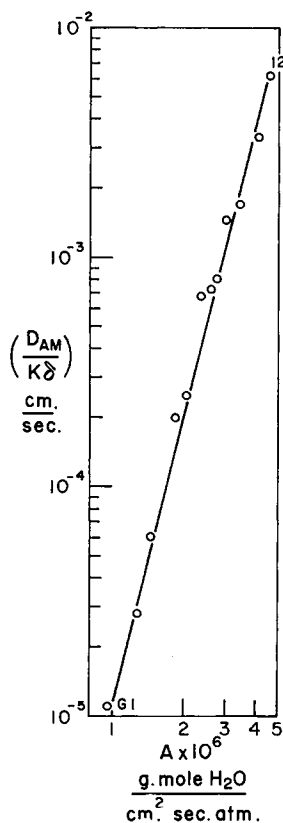
Fig. 3. Pure water permeability constant vs. solute transport parameter for sodium chloride.   Film type, CA-NRC-18; system, NaCl-H$_2$O; operating pressure, 1500 psig.

the mechanism of solute and solvent transport in film G1 is no different from that in film 12.

The foregoing experimental observations constitute sufficient basis to consider that the surface layer of the Loeb-Sourirajan type cellulose acetate membrane has a random heterogeneous microporous structure.   This basis is also supported by the theoretical work of Glueckauf[14] and Meares.[15]

Some Nomenclature

The steps involved in the film-casting technique, and the porous structure of the resulting asymmetric film are discussed in detail by Kesting et al.[16]   For the purpose of the following discussion, the following nomenclature is used.   The initial porous structure of the film before the temperature and pressure treatment is called the primary gel structure; the porous structure of the film after the temperature treatment is called the secondary gel structure; and the porous structure of the film after the normal pressure treatment is called the tertiary gel structure.

Method for Improving Membrane Performance

During the temperature treatment, those pores on the surface layer of the membrane, which were initially too big, become smaller—which is desirable—and those which were initially small enough become still smaller, which is not desirable from the point of view of overall membrane performance for a given application. If the latter pores could be opened up again, without opening the former ones too much, the product rate through the film can be increased without decreasing solute separation under a given set of operating conditions.

One possible technique for improving membrane performance based on the above approach is to force a fluid under pressure through the macropores on the back side of the film to enlarge the pores on the membrane surface advantageously.

Reverse osmosis experiments with the back side of the film in contact with the feed solution have been carried out first by Loeb and Sourirajan[17,18] and then by other workers.[19,20] The results are well known; under such experimental conditions, the product rate increases but solute separation decreases very much. For example, in a short-time run, with a NaCl (0.5 wt-%)–H_2O feed solution at 600 psig operating pressure, a particular CA-NRC-18 type film gave 90.2% solute separation and 47.4 g/hr of product rate when the surface layer of the film was in contact with the feed solution; when the experiment was repeated with the back side of the same film in contact with the feed solution, the product rate increased to 92.7 g/hr, and solute separation decreased to 3.5%. Similar results were obtained at the operating pressure of 1500 psig with the use of $0.5 M$ NaCl–H_2O feed solution. For example, a particular membrane which gave 98.4% solute separation and 26.3 g/hr product rate in a normal experiment gave 0.6% solute separation and 330.5 g/hr product rate when the experiment was carried out with the back side of the film facing seed solution. The above results are typical, and they simply show that during the reverse osmosis operation with the back side of the film in contact with the feed solution at 600 psig or more, the pores on the membrane surface layer open too much.

Therefore, even though the idea of trying to enlarge the surface pores by forcing a fluid under pressure from the back side of the membrane seems workable, it is obvious that the level of pressure applied for such purpose should not be too great. Consequently, any such workable back-pressure treatment in many cases may have to be a membrane pretreatment technique independent of the reverse osmosis experimental operation especially when the latter is at high pressures. Further, if any desirable changes in the structure of the surface layer can be brought about by a back pressure treatment, it is also desirable to make such changes permanent in the overall structure of the film material. The above considerations have led to the development of a general back pressure pretreatment method for improving the performance of Loeb-Sourirajan type porous cellulose acetate membranes for saline water conversion and other applications.

The method consists in pumping pure water past the back side of the film under just sufficient and necessary pressure for a sufficiently prolonged period of time; after such pretreatment, the membrane is used in the reverse osmosis experiment in the usual manner.

Performance of Back-Pressure-Treated Membranes

Reverse Osmosis Experiments at 600 psig
with 0.5 Wt-% NaCl in Aqueous Feed Solutions

Experimental Procedure. All membranes discussed in this part of the investigation were initially shrunk at different temperatures, and subsequently pressure treated in the usual manner at 700 psig for 1 hr. A set of at least two short-run reverse osmosis experiments were then carried out, after which they were subjected to a back pressure treatment. Unless otherwise stated, the back pressure treatment consisted of pumping pure water at the laboratory temperature past the back side of the film at 400 psig for 85 hr. The back-pressure-treated membranes were then used in the reverse osmosis experiments. All reverse osmosis experiments were carried out in the normal manner, i.e., with the surface layer of the membrane facing the feed solution.

Improvement in the Performance of Back-Pressure-Treated Membranes. In Figure 4, line *I* gives the product rate versus solute separation data for a set of five films, shrunk at different temperatures (covering a
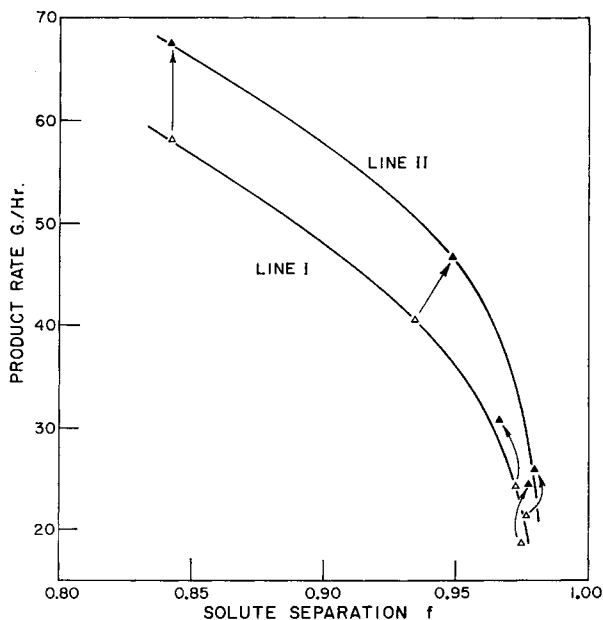

Fig. 4. Performance of back-pressure-treated membranes. Film type, CA-NRC-18; system, NaCl-H$_2$O; feed concentration, 0.5 wt. % NaCl; feed rate, 250 cc./min; operating pressure, 600 psig; film area, 7.6 cm^2.

solute separation range of 84–98%), without back pressure treatment, and line *II* gives the corresponding data for the same films with back pressure treatment. Line *II* is considerably above line *I*, and the arrows indicate the change in performance of the individual films tested. The results show that as a result of back pressure treatment the product rate increased by 15–30% and solute separation either remained the same or became better in all cases except one in which solute separation decreased by 0.6%. The above data illustrate the essential validity of the approach used in this work and the practical success of the back pressure treatment technique for improving membrane performance.

The data given in Table II illustrate both the improvement in the performance of the back pressure treated films, and the compaction effect on such films during continuous operation under 600 psig for 72 hr in reverse osmosis experiments. The results show that the structure of the surface layer in the back-pressure-treated membranes remains stable under the above experimental conditions; further, the reduction in product rate obtained due to membrane compaction during extended operation is no more than that obtained with films which were not subjected to back-pressure treatment. This means that the 15–30% increase in product rate (PR) obtained by back-pressure treatment is a net gain in the productivity of the CA-NRC-18 type films for saline water conversion and similar applications.

Figure 5 illustrates the effect of the duration of back pressure treatment on the change in the performance of the back pressure treated membranes. Three different sets of films were used in these experiments. Each set consisted of six films giving solute separations in the range 85–99%. Each set of these films was subjected to a back-pressure treatment at 400 psig for 50, 85, or 218 hr, and the changes in product rate and solute separation
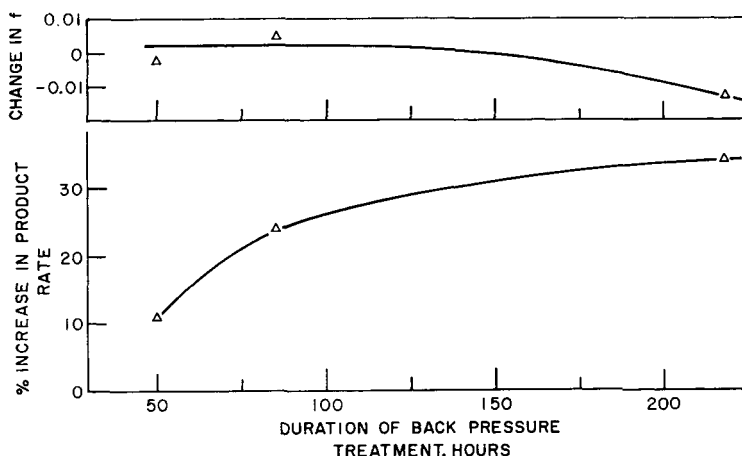

Fig. 5. Effect of duration of back-pressure treatment on membrane performance. Film type, CA-NRC-18; system, NaCl-H$_2$O; feed concentration, 0.5 wt. % NaCl; feed rate, 250 cc./min; operating pressure, 600 psig; back pressure, 400 psig.

TABLE II

Performance of Porous Cellulose Acetate Membranes Before and After Back-Pressure Treatment[a]

Film no.	Before treatment Start		Start			After back-pressure treatment at 400 psig for 85 hr					
						After 24 hr			After 72 hr		
	$(PR)_1$, g/hr	$f \times 10^2$	$(PR)_2$, g/hr	$f \times 10^2$	$\left[\dfrac{(PR)_2}{(PR)_1} - 1\right] \times 10^2$ [b]	$(PR)_3$, g/hr	$f \times 10^2$	$\dfrac{(PR)_3}{(PR)_2} \times 10^2$	$(PR)_4$, g/hr	$f \times 10^2$	$\dfrac{(PR)_4}{(PR)_2} \times 10^2$
33JK	18.7	97.5	24.5	97.8	31.0	21.1	98.0	86.1	20.4	98.1	83.2
37JK	21.4	97.7	25.9	98.0	21.0	22.8	98.1	88.0	22.1	98.1	85.3
45JK	24.3	97.3	30.5	96.6	25.6	27.3	96.9	89.5	26.6	96.9	87.3
47JK	40.7	93.5	46.9	94.9	15.3	41.5	95.1	88.5	41.3	94.7	88.2
49JK[c]	58.3	84.3	67.5	84.3	15.9	60.1	86.3	89.0	58.8	85.4	87.2

[a] Film type, CA-NRC-18; system, sodium chloride–water; feed concentration, 0.5 wt-% NaCl; feed rate, 250 cc/min; operating pressure, 600 psig; film area, 7.6 cm^2.

[b] Per cent increase in product rate by back-pressure treatment.

[c] With 0.25% NaCl in feed solution film 49 after back-pressure treatment gave 72.1 g/hr product rate and 84% solute separation.

were then determined in the regular reverse osmosis experiments at 600 psig. In all cases, the product rate increased significantly, and solute separation changed less than 1%. Figure 5 gives the average change obtained in the six films used in each set. The data showed that with a duration of 145 hours of back pressure treatment at 400 psig, the average increase in product rate was 30% with no change in solute separation in the reverse osmosis experiments at 600 psig.

With 85 hr back-pressure treatment at 400 psig, the average increase in product rate was 23% with a slight increase in solute separation. To be on the safer side, the duration of 85 hr was chosen for back-pressure treatment in most of the experiments reported here.

Figure 6 illustrates the effect of the pressure used for back-pressure treatment. Here again the results shown are the average of six films used in each of the three different sets of experiments. The results show that the gain in product rate increased with increase in pressure used for back-pressure treatment, but pressures higher than 400 psig tend to decrease solute separation in the reverse osmosis experiments. Consequently a back-pressure treatment at 400 psig for 85 hr seems to give the maximum increase (~20–25%) in product rate with no decrease in solute separation in the reverse osmosis experiments at 600 psig. All the above results are

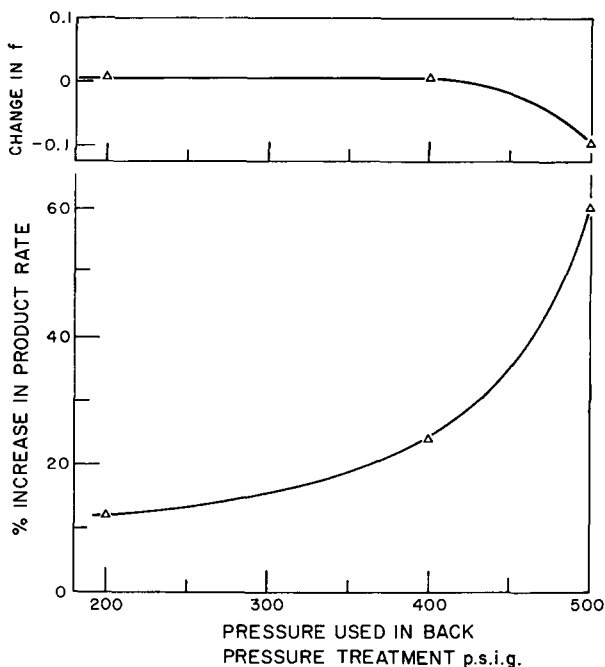Fig. 6. Effect of pressure used in back-pressure treatment on membrane performance. Film type, CA-NRC-18; system, NaCl-H$_2$O; feed concentration, 0.5 wt. % NaCl; feed rate, 250 cc./min; operating pressure, 600 psig; time of back pressure treatment, 85 hr.

with respect to CA-NRC-18 type films capable of giving more than 80% solute separation with respect to the system 0.5 wt-% NaCl–H₂O at 600 psig.

A set of experiments was carried out using water at $40 \pm 1°C$ for back-pressure treatment at 400 psig for 85 hr. The films subjected to the above treatment also gave 19–30% increase in product rate with no decrease in solute separation in the reverse osmosis experiments at 600 psig. Since similar results were obtained by using water at the laboratory temperature for back-pressure treatment, there seems no particular advantage in using water at higher temperatures for such purpose.

Figure 7 illustrates the effect of repeated back-pressure treatment at 400 psig for 85 hr on films subjected to continuous reverse osmosis experiments at 600 psig for over 30 hr. In this set of experiments, a long-time reverse osmosis run was conducted initially with the film in the usual manner. The experiment was then stopped, and the film was subjected to the first back-pressure treatment. A long-time reverse osmosis run was then conducted with the above film for another 30 hr. The experiment was stopped again, and the film was subjected to the second back-pressure treatment which was followed by another long-time reverse osmosis experiment. The experiment was stopped once again, and the film was subjected to the third back-pressure treatment followed by another long time
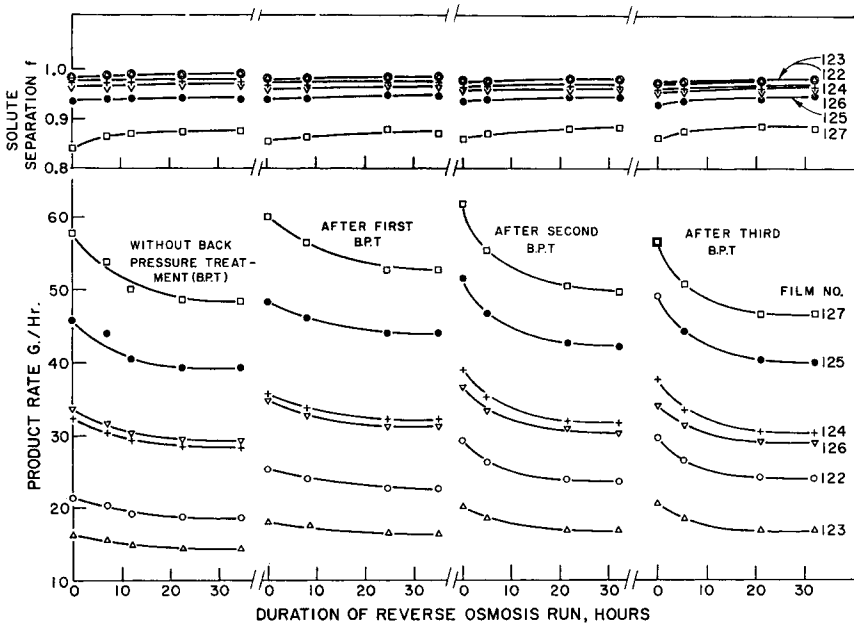

Fig. 7. Effect of repeated back-pressure treatment on membrane performance. Film type, CA-NRC-18; system, NaCl–H₂O; feed concentration, 0.5 wt. % NaCl; feed rate, 250 cc./min; operating pressure, 600 psig; film area. 7.6 cm².

reverse osmosis experiment.   The results of such tests carried out with six different films are plotted in Figure 7.

The results show that the back-pressure treatment technique for improving membrane performance works even when applied repeatedly. After the first treatment, however, the gain in product rate is partly off-set by an increase in membrane compaction.   Consequently, no more than two back-pressure treatments seems advisable for obtaining the most benefit out of the technique.

Effect of Interruption and Release of Pressure during Long-Time Reverse Osmosis Experiments.   It is known[21] that interruption and release of pressure during long-time reverse osmosis experiments results in a temporary increase in product rate.   Figure 8 gives the results of a set of reverse osmosis experiments where the long time runs were interrupted for 2 to 3 days so that the results obtained could be compared with those given in Figure 7.   Figure 8 shows that the increase in product rate obtained by interruption and release of pressure in a long time continuous reverse osmosis experiment is only about 3–5%, and even that increase is temporary.   On the other hand, the increase in product rate obtained by back-pressure treatment is much higher ($\sim$20–25%), and the latter is a net increase in the productivity of the film as stated earlier.   This is understandable on the basis that the mechanism of product rate increase is different in the two cases.   In the former case, the increase is merely due to a
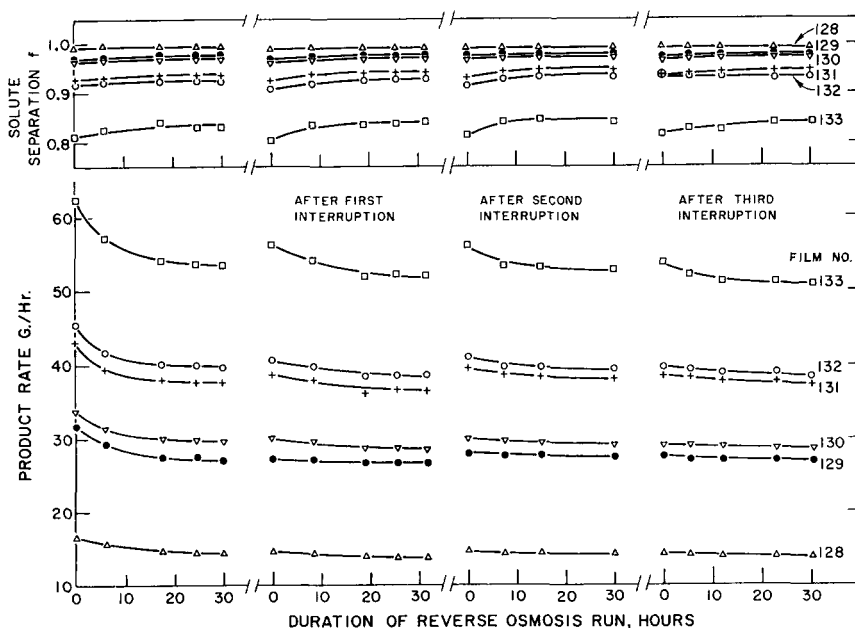

Fig. 8. Effect of interruption during continuous reverse osmosis operation on membrane performance. Film type, CA-NRC-18; system, NaCl-H_2O; feed concentration, 0.5 wt. % NaCl; feed rate, 250 cc./min; operating pressure, 600 psig; film area, 7.6 cm^2.

temporary release from membrane compaction; in the latter case, the increase is due to a change in the porous structure of the surface layer.

In summary, the back-pressure treatment at 400 psig for 85 hr offers a means of increasing the productivity of the Loeb-Sourirajan type porous cellulose acetate membranes by over 20% without decreasing solute separation in reverse osmosis experiments operating at 600 psig. Hence this technique is of practical importance in the application of reverse osmosis for brackish water conversion.

Reverse Osmosis Experiments at 1500 psig with 0.5 M NaCl–H₂O Feed Solutions

Experimental Procedure. All membranes discussed in this part of the investigation were initially shrunk at different temperatures. They were pressure-treated in the normal manner at 1700 psig for 1 hr. All reverse osmosis experiments were carried out with the surface layer of the membrane facing the feed solution.

Performance of Back-Pressure-Treated Membranes. Two sets of experiments were carried out to determine the effect of back pressure treatment on the performance of membranes in reverse osmosis experiments at 1500 psig.

In the first set of experiments, the back-pressure treatment was given to films which were initially subjected to the usual temperature and pressure treatment. Several pressures in the range 200–900 psig, and treatment periods in the range 65–150 hr were investigated for the back-pressure treatment. In all cases it was found that the performance of the back-pressure-treated film in the subsequent reverse osmosis experiment was either the same or worse (i.e., product rate increased and solute separation decreased) than its performance before back-pressure treatment.

In the second set of experiments, back-pressure treatment was given to films which were initially subjected to the usual temperature treatment but not the pressure treatment. The normal pressure treatment at 1700 psig with the surface layer of the film facing the feed water was given to the back-pressure-treated film. For the purpose of these experiments, three groups of films were used, each group consisting of five individual films. All the 15 films tested were cut from the same sheet of membrane subjected only to the temperature treatment. The five films used in each experiment were randomly chosen.

The usual reverse osmosis experiment was carried out with the first group of five films subjected to no back-pressure treatment. The second group of films was given a back-pressure treatment at 250 psig for 85 hr, after which the normal pressure treatment at 1700 psig was given. The third group of films was given a back-pressure treatment at 400 psig for 85 hr, after which the normal-pressure treatment at 1700 psig was given. A 24-hr continuous reverse osmosis test was given to the first and second group of films, and a short-run reverse osmosis test was given to the third group of films. The results of the tests are given in Table III.

TABLE III

Effect of Back-Pressure Treatment (BPT) of Preshrunk Membranes for Reverse Osmosis Service at 1500 psig[a]

Film group	Pressure used for BPT, psig	Reverse osmosis experimental data				Average values after 24 hr	
		Initial values			Average values	$\frac{(PR)}{(PR)_{initial}}$	Change $f \times 10^2$
		PWP, g/hr	PR, g/hr	$f \times 10^2$			
1	No BPT	75.0	50.0	97.7	PWP = 79.1	0.76	−0.6
		74.4	49.0	97.0	PR = 51.1		
		80.3	51.4	97.5	$f \times 10^2 = 96.7$		
		80.3	52.2	95.9			
		85.3	52.8	95.4			
2	250	87.6	57.3	97.6	PWP = 86.4	0.755	−0.3
	250	89.1	57.3	97.8	PR = 55.7		
	250	91.3	59.3	96.7	$f \times 10^2 = 97.4$		
	250	83.3	54.2	98.4			
	250	80.5	50.6	96.4			
3	400	90.1	58.5	96.8	PWP = 90.8	—	—
	400	89.8	58.0	96.7	PR = 58.2		
	400	88.7	57.6	96.9	$\times 10^2 = 96.6$		
	400	93.7	60.1	96.5			
	400	91.8	56.9	96.2			

[a] Film type, CA-NRC-18; system, sodium chloride–water; feed concentration, 0.5 M; feed rate, 250 cc./min; operating pressure, 1500 psig; film area, 7.6 cm.²; duration of back-pressure treatment, 85 hr.

The results show that back-pressure treatment of the preshrunk membranes before normal-pressure treatment does increase product rate by an average amount of 10–15% without any significant change in solute separation in reverse osmosis experiments at 1500 psig. The compaction effect for the back-pressure-treated films is no different from that for films without any back-pressure treatment. Therefore, the increase in product rate obtained by back-pressure treatment is a net gain in productivity of the films under conditions of continuous operation. Back-pressure treatment at 400 psig gives results better than those obtained with the same treatment at 250 psig; the optimum pressure for such treatment for films meant for reverse osmosis operation at 1500 psig has however not been investigated. The above results are sufficient to show that back-pressure treatment of preshrunk membranes improves their performance for reverse osmosis operation at 1500 psig.

Effect of Pressure on Pure Water Permeability through Each Side of the Membrane during Cyclic Operations

The object of these experiments is to obtain some insight into the possible changes taking place in the overall structure of the film during back-pressure treatment. The experiments consisted in determining the pure water permeability (PWP) of the film as a function of increasing or decreasing pressure using alternately the surface layer side of the film and the back side of the film to face the feed water under pressure. Two sets of films were used, one for operating pressures up to 600 psig, and the other for operating pressures up to 1500 psig. All the films were initially shrunk at different temperatures, and then pressure-treated in the normal manner at 700 and 1700 psig, respectively. During the experiments the PWP data were taken at each operating pressure after the film had been under that pressure for at least 10 min. Operating pressures were changed from one to the next without stopping the run. The run was stopped only when the side of the film facing the feed water, was changed. The experimental data obtained are plotted in Figures 9 and 10 for two typical films in each operating pressure range. The data on the top-right side of each plot are for the surface-layer side operation, and those on the bottom-left side of each plot are for the back-side operation. The numbers I, II, III etc. represent the sequence of the cyclic operations, and the arrows indicate the direction of pressure change in each operation.

Similar experiments have been reported by Banks and Sharples.[9] In the extent of work, object of the experiments, and the details of observation, this work is different from that of Banks and Sharples.

PWP Data for Operating Pressures up to 600 psig

The films whose data are plotted in Figure 9a and 9b were preshrunk at 91 °C and 85 °C, respectively, and both were pressure-treated in the normal manner at 700 psig. The films gave solute separations of 98.4% and 73.0%
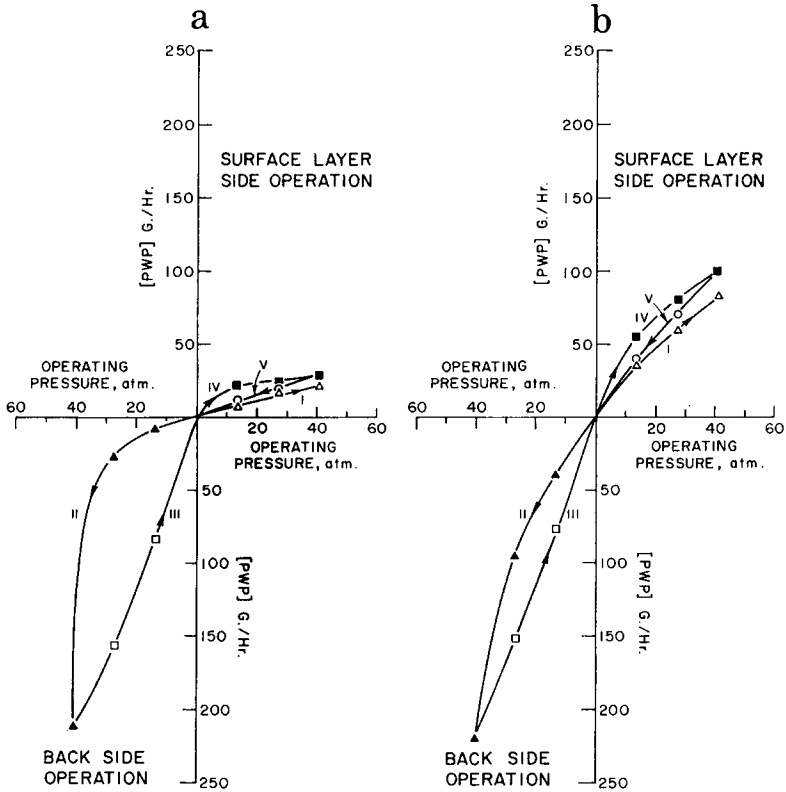
Fig. 9. Effect of pressure on pure water permeability through each side of the membrane during cyciic operations up to 600 psig. Film type, CA-NRC-18; film area, 7.6 cm².
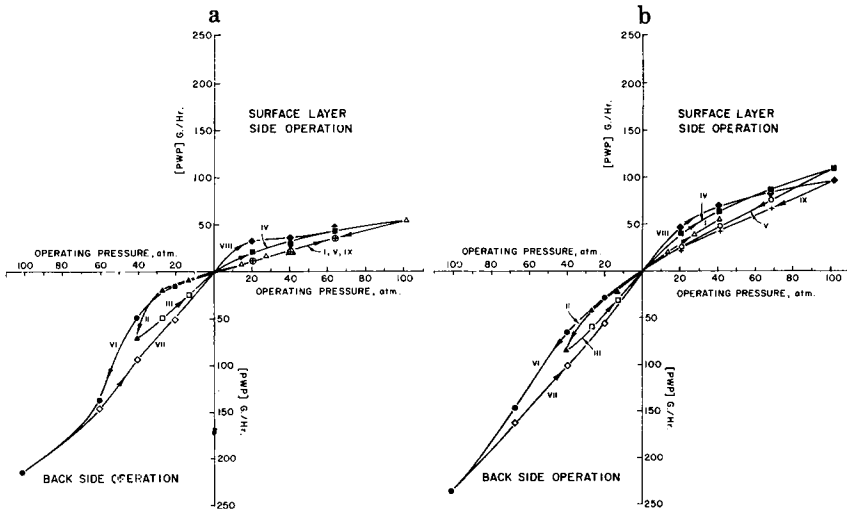

Fig. 10. Effect of pressure on pure water permeability through each side of the membrane during cyclic operations up to 1500 psig. Film type, CA-NRC-18; film area, 7.6 cm².

respectively with 0.5 wt-% NaCl–H₂O feed solutions. Referring to Figure 9a, the following observations can be made with respect to changes in the average pore size on the surface layer of the film during each of the five operations indicated in the cycle.

Operation I (surface-layer-side operation). Since PWP is essentially proportional to operating pressure, no change in pore size is indicated.

Operation II (back-side operation). Up to an operating pressure of about 14 atm, there seems no change in pore size; at higher operating pressures, PWP increases disproportionately with pressure, indicating widening and/or opening and redistribution of surface pores.

Operation III (back-side operation). Since PWP versus operating pressure is mostly a straight line in this decreasing pressure sequence, the pore size obtained at the end of Operation II seems to be maintained.

Operation IV (surface-layer-side operation). When the operating pressure is increased the surface pores, which were widened and/or opened during operation II, seem to shrink rapidly. However, at the highest operating pressure of 40.8 atm, the average pore size on the surface layer is significantly higher than that prevailing during operation I.

Operation V (surface-layer-side operation). During this sequence of decreasing operating pressure, PWP versus pressure graph is a straight line, indicating that the increase in average pore size observed at the end of operation IV is still maintained.

Referring to Figure 9b, the changes in the average pore size on the surface layer of the film during the above sequence of five operations is similar to those given above.

The data for both the above films indicate that the back-side operation with a film subjected to an initial pressure treatment at only 700 psig in the normal manner, ultimately results in a permanent increase in the average pore size on the surface layer in subsequent surface layer side experiments at 600 psig. Six films preshrunk at different temperatures were tested in the above cycle of operations, and the results obtained were similar in all cases.

Further, with respect to the first film (Fig. 9a) whose initial average pore size was smaller, the PWP changed from 21 to 212 g/hr at 40.8 atm pressure by changing the operation from surface layer side to back side of film; this represented a change of over 10-fold. But with respect to the second film (Fig. 9b) whose initial average pore size was bigger than that of the first one, the corresponding change in PWP was from 83 to 219 g/hr, representing a change of only about 2.6-fold. These data indicate that the back side operation widens and/or opens the smaller pores preferentially.

PWP Data for Operating Pressures up to 1500 psig

The films whose data are plotted in Figure 10a and 10b were preshrunk at 91°C and 86°C, respectively, and both were pressure treated in the normal manner at 1700 psig. The films gave solute separations of 98.9% and 90.0%, respectively with 0.5M NaCl–H₂O feed solutions. The data

given in Figures 10a and 10b are similar to those given in Figures 9a and 9b with one important difference. The back-side operation with a film initially subjected to a normal pressure treatment at 1700 psig ultimately results in either no change or a decrease in the average pore size on the surface layer (or probably a slight increase in effective film thickness in subsequent experiments at 1500 psig. These results are in agreement with those obtained in reverse osmosis experiments with back-pressure-treated membranes.

Further with respect to the first film (Fig. 10a), the PWP increased about 4-fold in back-side operation compared to surface-layer side operation at 1500 psig; the corresponding change with respect to the second film (Fig. 10b) was only about 2-fold. These data again indicate that the back-side operation widens and/or opens the smaller pores more than the larger ones.

Probable Structural Changes in the Film During Back-Pressure Treatment

The Loeb-Sourirajan type porous cellulose acetate membrane has an asymmetric and amorphous structure with extensive physical crosslinks in the membrane structure. The initial temperature and pressure treatments create additional crosslinks which contribute to the rigidity of the surface layer.

During the back-side operation under pressure, the pores on the surface layer are widened and/or opened; such change in pore size is more with respect to smaller pores than with respect to larger ones. This is clearly shown by the data in Figures 9 and 10, and this property is made use of in back-pressure treatment.

Further, back-pressure treatment brings about significant viscoelastic deformations in the macromolecular structure of the surface layer. The extent of such deformation depends of course on the secondary and tertiary gel structure existing in the membrane prior to back-pressure treatment. Due to such deformation, the polymer flows, and the macromolecules change their spatial distribution including a rearrangement of the physical crosslinks. The most probable distribution of end-to-end distances of polymer segments obtained finally is time-dependent. Due to the long duration involved in back-pressure treatment, the creep recovery is reduced, and a degree of permanent deformation is set in the membrane structure.

Since all the membranes tested were made by the same method (and hence presumably had the same primary gel structure), the permanent deformation caused by back-pressure treatment depends upon the secondary and tertiary gel structure.

The results obtained with back-pressure-treated membranes initially pressure-treated at 700 and 1700 psig, respectively, show that the former ones were more susceptible to such deformation than the latter ones which were probably too rigid to change by such treatment. Hence, in the latter

case, back-pressure treatment had to be done to change the secondary gel structure prior to normal pressure treatment.

The increase in product rate obtained (with no change in solute separation) by back-pressure treatment of a normal membrane, (initially temperature- and pressure-treated in the normal manner), subjected only to short-time reverse osmosis experiment is proportionately about the same as that obtained by such treatment of the same membrane which has been subjected to a continuous 30-hr reverse osmosis experiment. This means that the improvement in performance obtained with a normal membrane is about the same as that obtained with a compacted membrane, as a result of back-pressure treatment. Further, the compaction effect on a normal membrane is essentially the same as that on a back-pressure-treated membrane during continuous long-time experiments. These observations indicate that the deformations induced in the spongy macroporous mass of the film underneath the surface layer during back-pressure treatment have no significant effect on the product rate and solute separation characteristics of the film. Consequently, the deformation brought about in the surface layer by back-pressure treatment seems to control the improvement obtained in membrane performance.

In the normal long-time experiments the creep phenomenon seems responsible for closing pores and reducing product rate. By back-pressure treatment, the same phenomenon is made use of to obtain a wider pore size distribution and improve membrane performance.

The compaction effect of the membrane increases with repeated back-pressure treatment. This indicates some irreversible weakening of the membrane structure on such treatment similar to that observed by Haward.[22]

CONCLUSIONS

The back-pressure treatment technique offers a general method of improving the performance of asymmetric membranes in the reverse osmosis process. It can be used to change either the secondary or tertiary gel structure of the membrane. The duration, and pressure employed for back-pressure treatment may be chosen to suit particular applications and the nature of the membrane structure prior to such treatment. The success of the back-pressure treatment technique for improving the performance of the Loeb-Sourirajan type porous cellulose acetate membranes in reverse osmosis is yet another experimental evidence for the heterogeneous and microporous structure of their surface layer.

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