

Enhanced Transport Properties of Reverse Osmosis Membranes by Chemical Treatment

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SYNOPSIS

The performance of thin film composite (TFCL-LP[®]) membranes that were treated with hydrofluoric acid (HF) improved and their flux increased significantly without any loss in ion-rejection properties. In contrast, DESAL3 membranes do not show any significant change in transport properties after similar treatment with HF. We used scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS), and contact angle measurements to determine why this difference in behavior occurs. The difference in microstructure, as described by the interstitial void model, seems to be responsible for their behavior after being exposed to chemicals like HF. Therefore, we attempt to correlate transport properties with the microstructural changes (smoothing of membrane ridge-valley structure or no change in density of spherulites) observed. This method of treatment seems to be very effective in simultaneously enhancing the flux and rejection of reverse osmosis membranes which have a typical ridge and valley structure. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

Advanced thin film composite membranes now can tolerate wider pH ranges, higher temperatures, and harsher chemical environments. They also have improved water flux and solute rejection characteristics, compared to cellulose acetate (CA) membranes, which increases their potential for many new applications. In addition to traditional seawater and brackish water desalination processes, reverse osmosis (RO) membranes now are used for waste water treatment, production of ultrapure water, water softening, food processing, and many other applications. A comprehensive review of various applications of membrane processes, including reverse osmosis, can be found in several articles.¹⁻³ Most of the commercially available thin film composite membranes used in reverse osmosis are aromatic polyamides, and a small modification of the polymer chain by exposure to various chemicals may drastically change their behavior.⁴

The development of new applications of membrane systems is limited by the magnitude of the incremental improvements that have been achieved in their transport properties. After the development of the first thin film composite reverse osmosis membrane by Cadotte et al.,⁵ a major effort has been put into improving them. A wide body of literature exists on modifying the surfaces of microfiltration and ultrafiltration membranes. Various techniques that are used for this purpose include plasma treatment,⁶⁻¹¹ grafting,^{12,13} use of hydrophilizing agents, and protic acids.¹⁴⁻¹⁹ Numerous patents exist on the chemical treatment for either flux or rejection enhancement.²⁰⁻²⁶ Also, gas separation membranes have been treated with gaseous fluorine for increased selectivity and decreased flux.²⁷⁻³⁴

However, some work^{8,11,12,20,25} has also been directed toward reverse osmosis membranes. The improved properties were achieved either by increasing flux with a loss in rejection or vice versa. In some cases the reported enhancement in properties is not useful because the studies have dealt with polymers other than the commercially important aromatic polyamides.²⁰

Recently, we reported³⁵⁻³⁷ a technique to improve simultaneously and, in some cases, dramatically the

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flux and rejection of the commercially important aromatic polyamide-based thin film composite reverse osmosis membranes. Subsequent application of our surface modification technique to other commercially important membranes has shown varying degrees of flux and rejection improvements. An important feature of the membranes manufactured by the process described in Cadotte's⁵ patent is that they have a typical ridge and valley network of polymeric strands on the membrane skin. SW30HR³⁷ (from Filmtec) membranes, which are primarily based on Cadotte's patent, showed up to a sixfold increase in flux with an increase in rejection. After the chemical treatment, thinning of polymeric strands on the surface of the membrane was observed.

This article reports on the differences in behavior observed after such chemical treatment with HF of two of the most widely applied reverse osmosis membranes, DESAL3 (from Desalination Systems) and TFCL-LP (from UOP Fluid systems). According to the manufacturers, both of these membranes are aromatic polyamide based, and we expected them to show flux and rejection enhancement similar to the SW30HR.

Membranes were treated with hydrofluoric acid and then tested to determine the improvement obtained in their transport characteristics. These studies were motivated by the enhanced performance we observed when studying the ability of membranes to recycle pure hydrofluoric acid from spent microelectronic etching solutions.³⁵⁻³⁷

EXPERIMENTAL

Membranes

Two varieties of thin film composite reverse osmosis membranes were used here, including DESAL3 (manufactured and marked by Desalination Systems, Escondido, CA) and TFCL-LP (manufactured and marketed by UOP fluid systems). Most of the commercially available thin film composite reverse osmosis membranes are manufactured by interfacial polymerization.^{38,39} However, the composition of DESAL3 membrane has not been publicly revealed.

The TFCL-LP membrane was introduced in 1987 for use as a chlorine-tolerant low-pressure membrane suitable for brackish water treatment. It is prepared by interfacial reaction of polyfunctional amine-reactive compounds, such as polyacyl halide, with a preformed aromatic poly amine containing at least three and preferably four aromatic nuclei.

The poly amine is derived from an aromatic polyacyl halide, but other poly halides, such as cyanuric chloride, phosphorus oxychloride, phosphonyl chlorides, thionyl chloride, and sulfuryl chloride, may be used.⁴⁰ This membrane, according to manufacturer's data on spiral wound units, has a nominal flux of 34 L/m²h at 200 psi with a salt rejection of 97%. The chlorine resistance is greater than 1000 ppm-h.⁴¹ The chemical formula of the membrane is given in Figure 1.⁴⁰

Chemical Treatments

Fresh sheets of DESAL3 and TFCL-LP were cut into circular sections of approximately 38.5 cm². These circular coupons were then soaked under controlled conditions of temperature in solutions of 15 wt % hydrofluoric acid (HF) in water for varying periods of time. The entire circular cut sections were wholly immersed without masking any face, since porous support does not play any role in determining the separation characteristics of the membranes. The membranes were taken out after various intervals of time and rinsed with deionized water, and then their performance in terms of pure water flux and salt (NaCl) rejection was measured.

Transport Measurements

A schematic of the single-cell, closed-loop recycle reverse osmosis apparatus used for measurement of flux and rejection is given in Figure 2. The pipings,

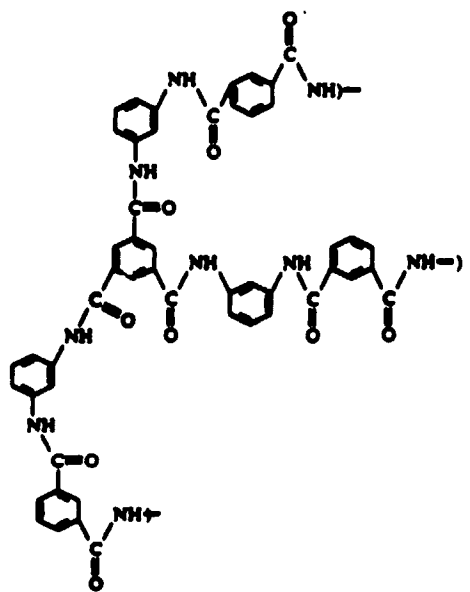


Figure 1 Chemical structure of TFCL-LP membranes.

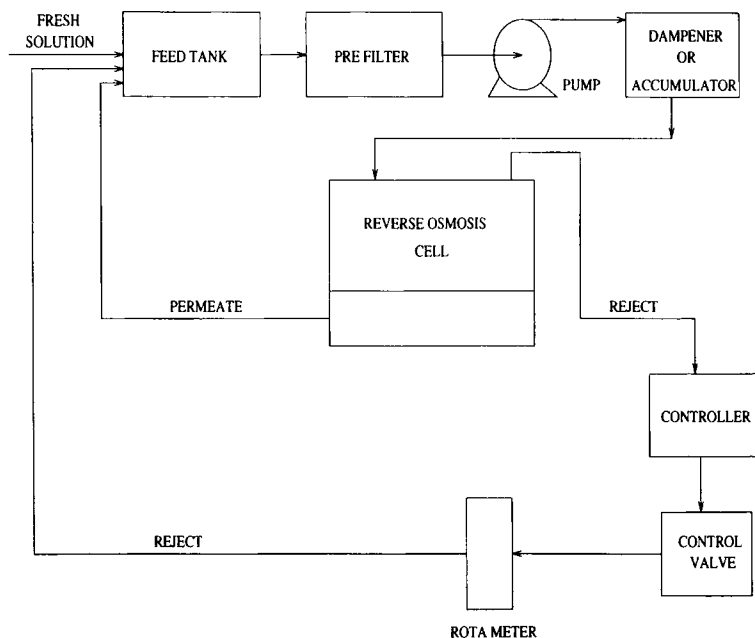


Figure 2 Schematic of experimental set-up used for transport measurements.

fittings, and cell were made of SS316. A diaphragm pump (PULSAFEEDER 7660) was used for recycling the salt solution (NaCl, 0.5 wt %) through the system. The experiments were conducted in the pressure range of 200–400 psi, and the temperature of the solution in the feed tank was maintained constant at 24°C. The conductivities of the feed, reject, and permeate samples were measured with a conductivity meter (COLE-PARMER).

The membranes were taken out of the solutions at various times and rinsed with deionized water, and then the permeate flux and the rejection of salt were determined. The rejection was defined as

$$R = 1 - \frac{C_P}{C_R} \quad (1)$$

where C_P and C_R are average salt concentrations, respectively, of the permeate and the reject solutions as measured by the conductivity meter.

CHARACTERIZATION

Scanning Electron Microscopy

Scanning electron microscopic studies were performed on a Zeiss (Germany) CSM 950 computerized digital scanning system. The samples were coated with 100 Å of gold using a Denton Vacuum Desk II system. The samples were coated for 30 s under 50 mTorr pressure and 40 mA current.

X-ray Photoelectron Spectroscopy

X-ray photoelectron spectroscopy (XPS), also known as electron spectroscopy for chemical analysis (ESCA), was used to investigate the chemical composition of the membranes.⁴²

The XPS spectra in our work were obtained with a Perkin-Elmer 5500 multitechnique system using $MgK\alpha$ exciting radiation (1253.6 eV). Typically, the X-ray gun was operated at 15 kV and 14 mA and the sample chamber was evacuated to less than 10^{-10} Torr. The copper $2p_{3/2}$ level at 932.4 eV binding energy was used for calibration and had a full width half maximum (FWHM) of 1.17 ± 0.1 eV. The spectra were taken with the electron emission angle at 60° to give a sampling depth of approximately 50 Å. The analysis times were kept short to minimize radiation damage to the sample. The sensitivity factors used were carbon, 0.296; oxygen 0.711; fluorine 1.0; nitrogen 0.477; sulphur 0.666; calcium 1.833; they represented the average values provided by the manufacturer (Perkin-Elmer). The peak areas of the survey scan were used to determine the atomic concentration for the various elements with the help of a software program (ESCA version 4.0 and multitechnique version 2.0).

Contact Angle Measurements

Contact angle measurement is one of the most sensitive methods for obtaining surface wettability information.^{43,44} Octane/water (bulk liquid phase)/

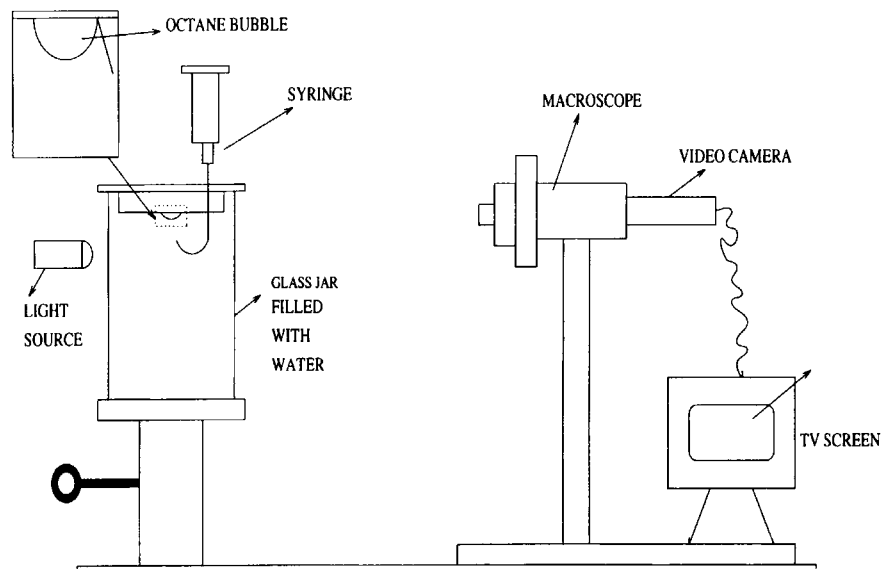


Figure 3 Schematic of experimental set-up used for contact angle measurements.

membrane⁴⁵ interfaces were used in our study, and we correlated contact angle measurements on heterogeneous membrane surfaces with wettability. Membranes were precleaned and allowed to soak in water for some time. Then octane/water/membrane interfaces were formed by immersing membranes in a glass observation cell containing octane-saturated water and releasing octane drops beneath the solid surface from a syringe. As octane has a lower density than water, the drops float upward, touch the solid surface, and form the interface. Contact angles on both sides of the bubble were recorded. The Zeiss macroscope with a video camera captured the image on a videotape, and the video picture was used to make still pictures

using Aldus eye software. The drop is magnified at least 200 times before the measuring the contact angle, and the whole assembly is depicted in Figure 3.

RESULTS

Transport Properties

Figures 4 and 5 show the effect of chemical treatment with 15% HF on the flux and rejection, respectively, of TFCL-LP membranes. Seven replications of each data point were obtained, and their arithmetic mean was plotted in the figures. The flux of this membrane

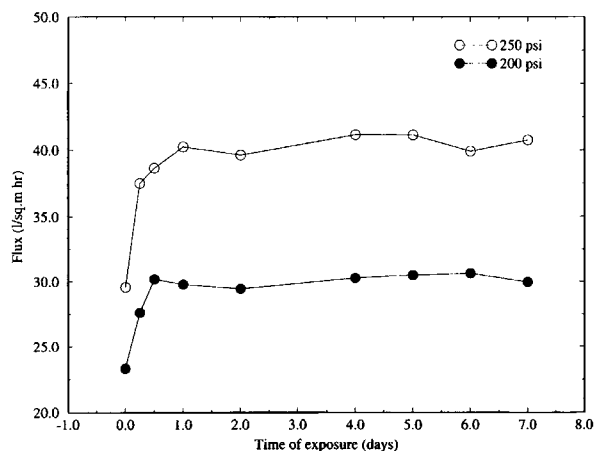


Figure 4 Flux of TFCL-LP membranes exposed to 15% HF for various periods of time.

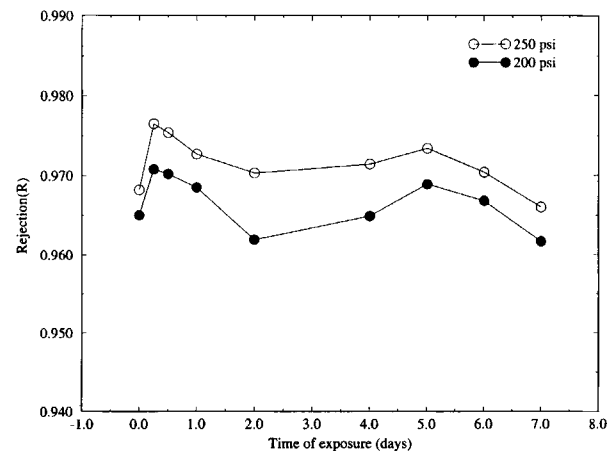


Figure 5 Rejection of TFCL-LP membranes exposed to 15% HF for various periods of time.

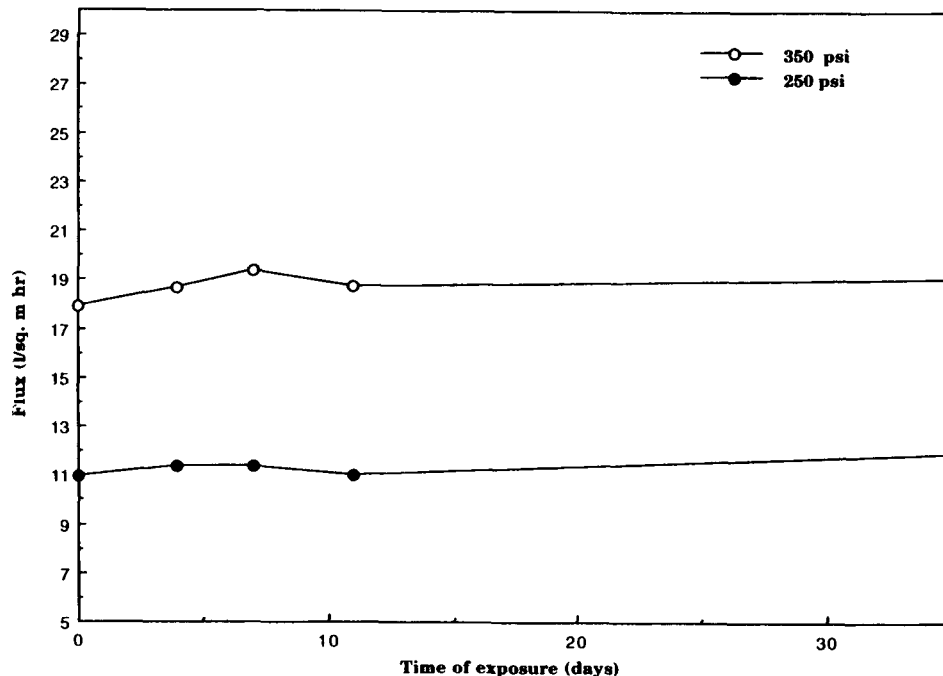


Figure 6 Flux of DESAL3 membranes exposed to 15% HF for various periods of time.

increases about 44% from 29 L/m²h to about 41 L/m²h at 250 psi and about 35% at 200 psi in one day and is not improved further even after 7 days of exposure. The rejection at 250 psi after one day in-

creases slightly from 96.5% to about 97.5% and changes very little beyond that time of exposure.

Figures 6 and 7 show that chemical treatment with HF on the flux and rejection of DESAL3 mem-

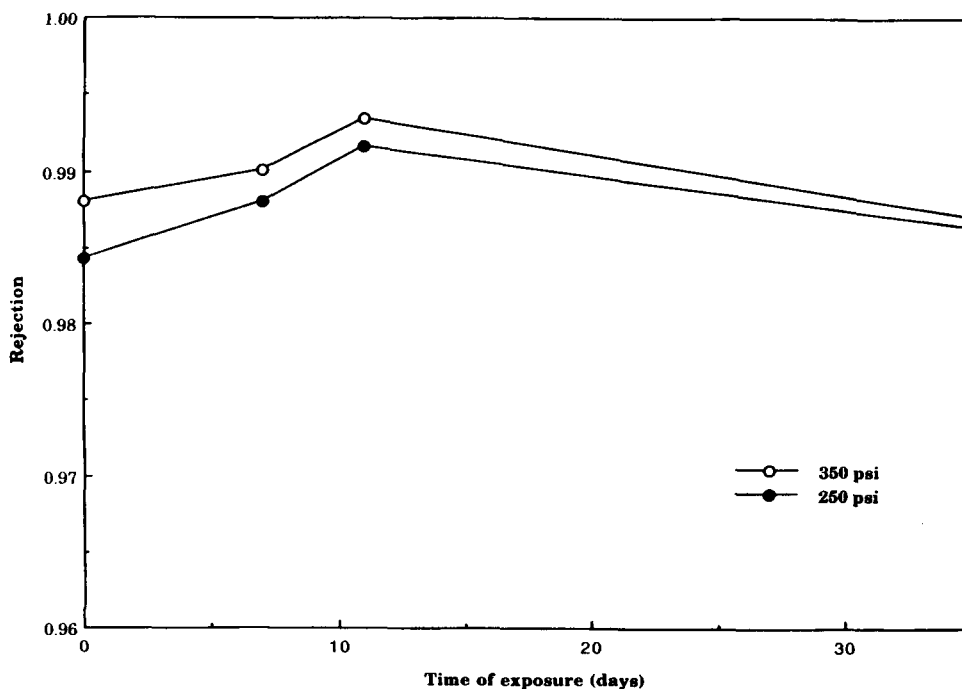


Figure 7 Rejection of DESAL3 membranes exposed to 15% HF for various periods of time.

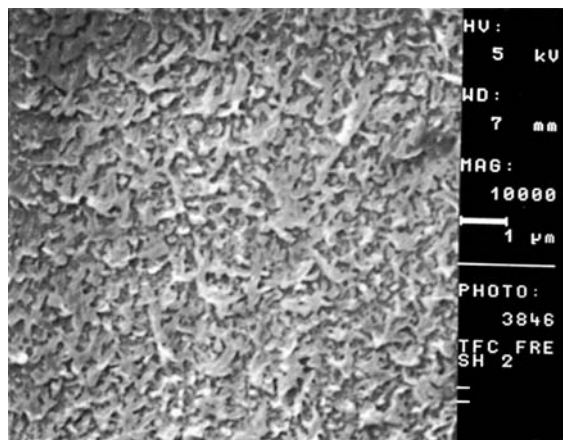


Figure 8 Scanning electron micrograph of fresh TFCL-LP membrane.

branes induces only minor changes in performance. Before treatment the flux of DESAL3 was significantly lower than that of TFCL-LP, and this difference increased substantially after exposure to HF. The permeability and rejection experiments were done with 0.5 wt % NaCl solutions. All the data points were determined by multiple replications, and the standard deviation of the observations was determined to be 5% for flux and 0.5% for rejection. Only a slight increase in flux and rejection which is not statistically significant is observed in the flux on exposure to these chemicals.

Surface Characterization

Scanning electron microscopic (SEM) studies were conducted with both DESAL3 and TFCL-LP membranes. Figure 8 shows the surface structure of

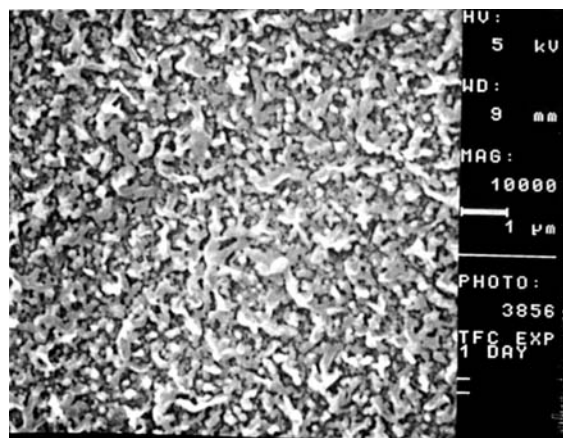


Figure 9 Scanning electron micrograph of TFCL-LP membrane exposed to 15% HF for 1 day.

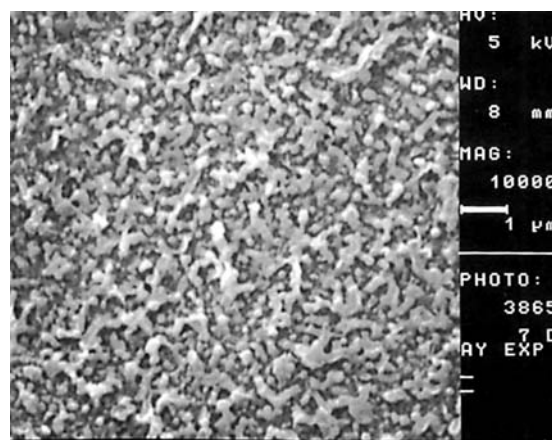


Figure 10 Scanning electron micrograph of TFCL-LP membrane exposed to 15% HF for 7 days.

TFCL-LP membrane prior to any chemical treatment to be ridges and valleys. In Figures 9 and 10 the density of the surface packing of the same membranes is seen to have decreased. This may be due to partial surface etching caused by HF. Figure 11 shows the morphology of fresh DESAL3 membrane, which has a typical globular structure. In Figure 12 we see that this membrane does not show any change in the morphology even after a long-term exposure to 15% HF.

The XPS spectra were obtained with Perkin-Elmer 5500 multitechnique system. Tables I and II show the atomic concentration values for TFCL-LP and DESAL3 membranes, respectively, before and after chemical treatment with 15% HF. The results indicate a small amount of fluorination on the surface of the membranes.

Contact angle measurements for TFCL-LP and DESAL3 membranes before and after the chemical

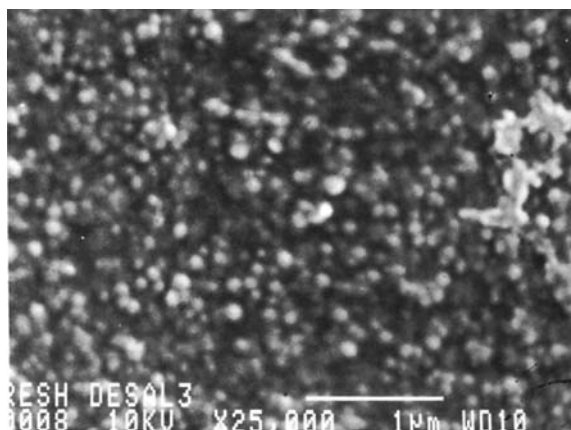


Figure 11 Scanning electron micrograph of fresh DESAL3 membrane.

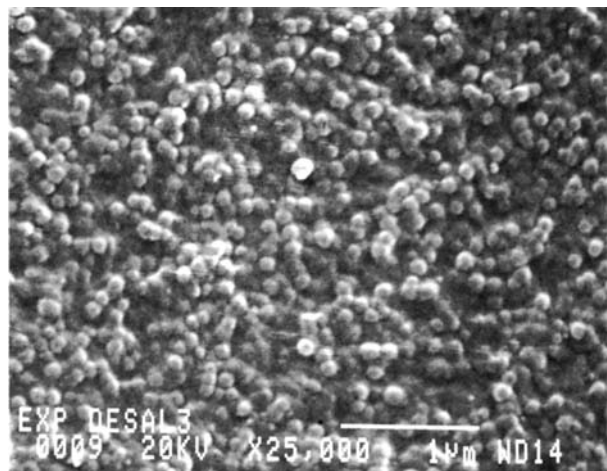


Figure 12 Scanning electron micrograph of DESAL3 membrane exposed to 15% HF for a long term (500 days).

treatment are given in Table III and show an increase, which suggests that an increase in hydrophilicity occurred.

DISCUSSION

Our XPS and contact angle studies indicate partial fluorination and an increase in hydrophilicity of both DESAL3 and TFCL-LP membranes. However, calcium is detected only on the DESAL3. In spite of partial surface fluorination and increased hydrophilicity of both membranes, a significant difference exists in the change in their performance after they have been exposed to chemicals like HF.

We propose the following explanation of this phenomenon based on our SEM studies, which show that the surface of DESAL3 membranes is packed with spherulites while TFCL-LP has a ridge and valley structure formed by strands of polymers. Ac-

cording to Sourirajan et al.,⁴⁶⁻⁵⁰ the macromolecules in phase inversion membranes usually are spherical, as in the case of DESAL3. Moreover, ionic salts like CaCl_2 and NaCl are added⁴⁸ as swelling agents in water (used as nonsolvent during the membrane fabrication process) to increase the flux through these membranes. Our XPS studies show the presence of calcium on the surface of DESAL3, which provides further evidence that it may be a phase inversion membrane.

Our explanation, however, relates to the microstructure of membranes regardless of how they are made. The flux and rejection for these membranes can be explained on the basis of the interstitial-void model proposed by Sourirajan et al.⁴⁶⁻⁵⁰ These authors assumed the presence of polymer aggregates with two types of pores (network and aggregate) on the surface of the membrane. Network pores originate from the spaces between polymer segments constituting polymer aggregates, and the aggregate pores arise from the interstitial spaces surrounding the polymer aggregates. Solute permeation takes place in the aggregate pores and solvent permeation in both the network and aggregate pores.⁴⁸ In order to obtain an increase in flux, an increase in both network and aggregate pores is required. But an increase in rejection corresponds to a decrease in the size and the number of aggregate pores. Our SEM studies show no changes in the microstructure (size and packing density of spheres) on the surface of DESAL3, and that is why we observe no change in its transport properties. The TFCL-LP membranes have a ridge-valley structure (typical of interfacially polymerized monomeric aromatic amines³⁹), as do the FT30 membranes that we used in our previous studies, in which we obtained up to an order of magnitude increase in flux with a significant improvement in ion rejection.³⁷ This less densely packed ridge and valley structure is more prone to attack

Table I Atomic Concentrations from the XPS Studies for Fresh and Exposed TFCL-LP Membranes (15% HF) for 1 and 7 Days Indicating Incorporation of Fluorine on Exposure to HF

Element	Fresh Membrane		1-Day Exposed Membrane		7-Day Exposed Membrane	
	Atomic Concentration (%)	Element to Carbon Ratio	Atomic Concentration (%)	Element to Carbon Ratio	Atomic Concentration (%)	Element to Carbon Ratio
Carbon (C1s)	71.01	1	70.07	1	72.63	1
Oxygen (O1s)	16.53	0.233	16.88	0.241	16.78	0.231
Nitrogen (N1s)	12.47	0.176	12.27	0.175	8.69	0.120
Fluorine (F1s)	0	0	0.26	0.004	1.90	0.026

Table II Atomic Concentrations from the XPS Studies for Fresh and Exposed DESAL3 Membranes (15% HF) for 4 and 500 Days Indicating Incorporation of Fluorine on Exposure to HF

Element	Fresh Membrane		4-Day Exposed Membrane		500-Day Exposed Membrane	
	Atomic Concentration (%)	Element to Carbon Ratio	Atomic Concentration (%)	Element to Carbon Ratio	Atomic Concentration (%)	Element to Carbon Ratio
Carbon (C1s)	70.68	1	71.46	1	68.52	1
Oxygen (O1s)	19.41	0.275	18.78	0.263	19.10	0.278
Nitrogen (N1s)	8.33	0.118	8.46	0.1183	10.95	0.159
Fluorine (F1s)	0	0	0.74	0.011	1.25	0.018
Calcium (Ca2p)	0.27	0.004	0.56	0.008	0.23	0.003

by HF, which causes a thinning of the polymeric network (surface etching), as SEM photographs indicate. This increases the number of pores without causing any change in pore size distribution. Consequently, the flux increases without decreasing the rejection. Indeed, Mehdizadeh et al.^{51,52} predicted the flux and rejection characteristics of FT-30 membranes using a modified-surface-force-pore-flow model assuming a uniform pore size distribution. Similarly, we expect a uniform pore size distribution in the TFCL-LP membranes, and the increase in the number of pores causes an increase in the flux. We do not observe any loss in rejection because it is governed by the size of pores, which does not change on treatment.

The permeation of salt is given by

$$P = \frac{J_s}{J_v C_b} \quad (2)$$

where J_s is the salt flux, J_v is the solvent (water) flux, and C_b is the bulk feed side solution concentration. By increasing the number of pores, we increase the value of J_v without significantly changing J_s , and this decreases the salt permeation and increases rejection. Based on the experimentally ob-

served flux and rejection the ratio of J_{ve} , the flux of exposed membrane, and J_{vu} , the solvent flux of unexposed membrane is 1.44. Also, the value of J_{se}/J_{su} is 1.03, where J_{se} and J_{su} are the solute flux of exposed and unexposed membrane, respectively.

Therefore, increasing the number of pores by surface etching increases both the solvent and solute flux. But the relative increase in flux of solvent is greater than solute and the rejection increases for TFCL-LP membranes.

As we have seen, very different responses were observed for the two membranes on treatment with HF. Thus, this article shows that simultaneous and large improvements in flux and rejection are possible for most varieties of commercially important thin film composite reverse osmosis membranes (based on Cadotte's patent), but the treatment may be ineffective for certain membranes having different microstructure and surface features.

Simultaneous increase in flux and rejection of TFCL-LP has substantial economic implications. It indicates that smaller, less expensive, more energy efficient units may be used to process a given amount of feed. Furthermore, the behavior of DESAL3 suggests that the surface microstruc-

Table III The Contact Angles of Fresh and Exposed (15% HF) Membranes

TFCL-LP Membrane		DESAL3 Membrane	
Time of Exposure (days)	Contact Angle (degrees)	Time of Exposure (days)	Contact Angle (degrees)
0	129.5 ± 2	0	133 ± 2
0.25	143 ± 2	80	142 ± 2
1	146 ± 2		

ture plays a very important role in controlling the stability and transport properties of RO membranes.

CONCLUSIONS

Because of differences in microstructure, TFCL-LP shows a significant increase in flux and rejection while DESAL3 shows no change on treatment with HF. Treatment of TFCL-LP membranes with HF causes an increase in hydrophilicity and fluorination and probably increases the number of pores. This approach seems to be most effective for improving flux and rejection of interfacially synthesized aromatic polyamide membranes with typical ridge-valley structure. However, such a treatment procedure may be ineffective with membranes like DESAL3, which have a surface that is close packed with spheres.

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