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Development of a New Chlorine And Biofouling Resistant Polyamide Membrane

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ABSTRACT

A new polyamide (PA) reverse osmosis (RO) composite membrane has been prepared, based on the reaction of highly purified *cis, trans, cis, trans* 1,2,3,4-cyclopentanetetracarboxylic acid chloride with *m*-phenylenediamine (MPD). The new membrane has demonstrated the ability to withstand high concentrations of chlorine in immersion tests without detrimental effects. The contact time was 30,000 mg/L-hr, or ~ 6.8 years of exposure at the 0.5 mg/L level. In long-term RO field tests using flat sheet membrane test cells with 0.5 mg/L chlorinated feed water the membranes showed slow deterioration particularly after system shutdowns (depressurizations). Nevertheless, the new membrane compared favorably with conventional PA membranes based on trimesoyl chloride and MPD. Degradation of the new PA composite membrane was not restricted to the PA desalination barrier. The chemical composition of the porous supporting membrane, delamination of the PA film from the support, and the presence of heavy metals in the feed have been shown to be contributing factors. Gradual degradation of PA membrane has not been ruled out. All PA composite membranes supported on porous polysulfone (PS) deteriorated more rapidly in immersion experiments compared to the same PA membranes supported on polyetherimide membranes. Ring chlorination of PS in the presence of chlorine may be a possible mechanism leading to PA composite membrane deterioration. Today, all commercial PA composite RO membranes are made with PS supporting membranes. Further development studies are required.

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Details of the methodology used in this program are described in the text of this report. Program management was a team effort between SST, BR, DU, WQIC and OCWD. The synthesis, isolation and purification of acid chloride monomers were conducted by A. Murphy and B. Murugaverl of BR and DU and the conversion of *cccc*-CPTC acid to *ctct*-CPTC acid was carried out by G.A. Hernandez of ITM. Membrane development and optimization were conducted by S. W. Lin, C.Milstead, I.Wiater-Protas and R.L. Riley of SST. Membrane characterization was carried out by K. Ishida, H.Ridgway and J Safarik of the OCWD. The long-term RO field testing at the WQIC was conducted by B.Corbett, M. Fabien, C. Moody and M. Norris.

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1.0 INTRODUCTION

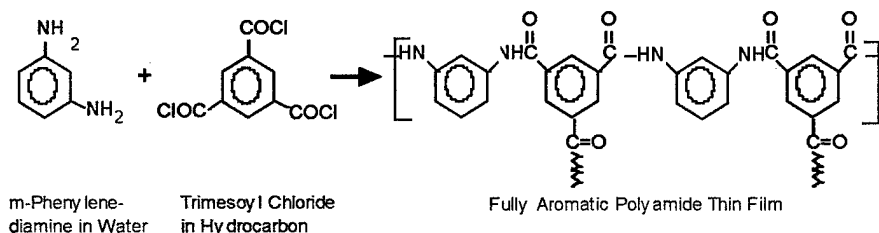
Reverse osmosis (RO) plants have been operating with polyamide (PA) spiral-wound thin-film composite membrane elements to desalinate brackish and seawater since 1977. The first PA RO membrane was commercialized at that time when it was placed in service in a large RO seawater desalination plant in Jeddah, Saudi Arabia.¹ It was soon recognized that the membrane was not tolerant to chlorine and the pre-treatment for the plant had to be adjusted accordingly. Thus, the search for a chlorine-resistant membrane was begun more than twenty years ago.

Mobile RO water purification units (ROWPU) have been used by the U.S. Armed Services with PA spiral-wound thin-film composite membrane elements for over a decade to produce potable water for field applications. Although technological advances have greatly enhanced the operation and performance of the spiral membrane elements, several deficiencies still exist that contribute to fouling, reduced membrane life and higher operating costs, they are:

- * Lack of chemical stability to oxidants such as chlorine
- * High fouling rates due to chemical and physical nature of the PA desalination barrier
- * High bacteria attachment counts on the membrane surface leading to biofouling.

Because of these deficiencies, large quantities of ROWPU membrane elements have to be transported to the field and frequently replaced. Thus, the logistics and maintenance time associated with purchasing, transporting, and replacing membrane elements are substantial. In addition, costly pre- and post-water treatment is required during the RO process to extend the life of the membrane.

Today, the RO membrane of choice worldwide is the PA thin-film composite membrane developed by Cadotte.² The PA membrane is made by forming a thin PA film on the finely porous surface of a polysulfone (PS) supporting membrane by an interfacial reaction between the reactant pair trimesoyl chloride (TMC) and *m*-phenylenediamine (MPD). The following equation illustrates the chemical formation of the PA desalination barrier.



Standard commercial TMC/MPD Polyamide Membrane

Currently the spiral membrane configuration dominates market share. Eight major manufacturers supply spiral-wound elements worldwide, they are: Dow/FilmTec, Koch/Fluid Systems, Osmonics/Desal, Tri-Sep, and Nitto Denko/Hydranautics in the U. S., Toray Industries in Japan, Projectos in Spain and Saehan Industries in Korea. ATR/IR membrane surface analysis shows that all manufacturers use nominally the same fully aromatic membrane chemistry based on the interfacial reaction of MPD with TMC.³

There is a great need to improve the stability of present state-of-the-art PA membranes to oxidizing agents. These improvements are critical for RO plants operating on wastewaters, surface waters and open seawater intakes where disinfection by chlorination is required to control growth of microorganisms (biofouling) on the surface of the membrane. These PA membranes are so susceptible to oxidation that dechlorination is required when chlorine is used as a disinfectant in the pretreatment. Dechlorination prior to the PA membrane creates additional costs and effectively nullifies disinfection on the membrane surface where it is needed. Development of a chlorine-resistant PA membrane would be a solution to control biofouling, thereby increasing membrane life.

The lifetime of RO elements is strongly influenced by membrane fouling and frequency of cleaning; that is, the greater the frequency of cleaning the shorter the membrane life. Leslie⁴ at Orange County Water District (OCWD) has estimated the annual savings that could be attained by reducing membrane fouling using the following assumptions: OCWD Water Factory 21 type RO plant, 6 mgd RO capacity, 5-yr membrane life and operation on secondary wastewater feed. For an improved low-fouling membrane, the annual savings (\$/yr) attained by reducing membrane fouling to extend membrane life is as follows:

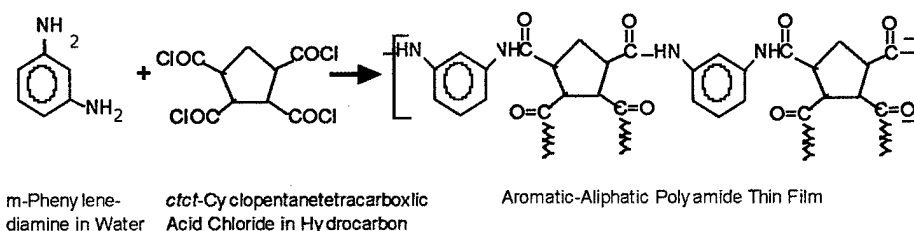
| Membrane Fouling Reduction (%) | 5 Year Membrane Life Extended by (Hrs.) | | |
|--------------------------------|---|-----------|-----------|
| | 20 % | 40% | 100% |
| 10 | \$36,000 | \$63,000 | \$108,000 |
| 25 | \$126,000 | \$153,000 | \$198,000 |
| 75 | \$306,000 | \$333,000 | \$378,000 |

The savings are quite apparent, emphasizing the benefit for a reduced fouling chlorine-resistant membrane

2.0 BACKGROUND AND PREVIOUS WORK

The work of Ikeda and Tomaschke⁵ reported PA membranes made from MPD and three stereoisomers of 1,2,3,4-cyclopentanetetracarboxylic acid chlorides (CPTC-AC), namely *cccc*-CPTC-AC, *ctcc*-CPTC-AC and *ctct*-CPTC-AC. They revealed that PA membrane made from the *ctct*-CPTC isomer showed greater tolerance to 1 mg/L chlorine in a 1000-hr RO test than did the *cccc*-CPTC or the *ctcc*-CPTC isomers. Chlorine tolerance of three to five years is the goal for a commercial membrane. Since the *ctct*-CPTC isomer must be isolated from a mixture of isomers, it could be expected that an isomeric purity of close to 100% would be required to attain maximum oxidation resistance. The methodology for selecting these acid chlorides, the percent conversion of the *cccc*-CPTC acid and finally the isomeric purity of the *ctct*-CPTC-ACs were not cited.

Unlike the fully aromatic TMC membrane, which is made from an aromatic acid chloride (TMC) and an aromatic amine (MPD), the CPTC membrane is made with an aliphatic acid chloride (CPTC) and an aromatic amine (MPD). The chemistry of formation of the thin PA film between CPTC and MPD is shown below.



CPTC Acid Chloride Polyamide Membrane

The 1,2,3,4-CPTC-AC with its six stereoisomers is a unique system for developing a methodology using molecular modeling, since each individual isomer from the six-isomer mixture show differences in oxidation tolerance. The six isomers formed from the conversion of *cccc*-1,2,3,4-cyclopentanetetracarboxylic acid to acid chlorides were modeled by Separation Systems Technology (SST). It was found that the bond angles and steric energies of the isomers were quite different and that *ctct*-CPTC-AC bond angles were least strained. These results, of course, assume 100% isomeric purity.

CPTC-AC will not significantly increase the price of the PA membrane. One gram of *ctct*-CPTC-AC will make 254 ft² of membrane. Assuming that CPTC is 8 times more expensive than TMC, a worst case scenario, the cost of an 8 x 40-in. spiral-wound element would increase in price by only 1.8 percent. (See Table 1.0)

Table 1.0

Membrane Costs Using TMC vs. CPTC-AC for Manufacture of 8 x 40-in Spiral-Wound Element

| Acid Chloride | Acid Chloride Concentrations | \$/g of Acid Chloride | g of /Acid Chloride | \$ Acid Chloride/Element | Cost % of Element (\$600 ea)* |
|---------------|------------------------------|-----------------------|---------------------|--------------------------|-------------------------------|
| TMC | | 0.84 | 1.59 | 1.34 | 0.2% |
| CPTC | 2 x TMC | 1.68 | 1.60 | 2.69 | 0.4% |
| CPTC | 4 x TMC | 3.36 | 1.60 | 5.38 | 0.9% |
| CPTC | 6 x TMC (worst case) | 6.72 | 1.60 | 10.75 | 1.8% |

* Estimated retail price of an 8 x 40-in element

2 mg PA film covers ~60 in²; CPTC = 45.6 wt-% of film; 1 g CPTC-AC makes 254.4 ft² of membrane; 1 g TMC makes 252.7 ft² of membrane.

A major thrust of the SST program involved the synthesis, separation and purification of *ctct*-CPTC-AC from a mixture of six stereoisomers; analysis of the purified products were determined by C-13 NMR, H-NMR, P-31 NMR, GCMS, IR and ATR/IR spectrometry. A synthesis procedure was developed to produce high purity *ctct*-CPTC-AC in 5 gram quantities. High purity was required

to attain optimum membrane transport properties and resistance to oxidation. To confirm long-term oxidative stability, PA membranes were prepared and the RO transport properties optimized for water flow, salt rejection and chlorine tolerance. The membranes were further characterized with respect to bacterial attachment (biofouling), surface charge, air bubble contact angle determinations (hydrophobicity), surface morphology (AFM and TEM) and chemical and structural analysis by EDX, IR and ATR/IR spectrometry. Chemical modification of the membrane surface was made to reduce biofouling. The membranes were evaluated in long-term RO tests on brackish water at the Water Quality Improvement Center (WQIC) Yuma, AZ, on municipal wastewater at the Orange County Water District (OCWD), Fountain Valley, CA and on seawater at the Naval Facility Engineering Service Center (NFESC) at Port Hueneme, CA. Some important observations³ from this work were drawn:

- *cccc*-CPTC membrane degrades very quickly compared to the *ctct*-CPTC membrane when tested on chlorinated feed water in RO field tests.
- *ctct*-CPTC membranes have demonstrated the ability to withstand high concentrations of NaOCl, without detrimental effects, in immersion tests when membranes were placed in full strength 3 wt-% (30,000 mg/L) NaOCl at pH 6.0 for 1 hr. The total membrane contact time with NaOCl was 30,000 mg/L-hr or the equivalent of 6.8 years of membrane exposure at the level of 0.5 mg/L. Field tests using membrane swatches, however, have showed deterioration in membrane transport properties after repeated shutdowns (See *Figure 1*). Transmission electron microscopy (TEM) studies of the membrane structure showed that the PA film has a tendency to delaminate from the PS support membrane after back pressure is applied to the membrane during RO depressurization (See *Figure 2*). Another possible explanation for decreased membrane performance is inflicted damage to the PA film at the "O"-ring membrane interface.
- Long-term RO field testing of CPTC membrane samples in 1 x 3 inch test cells at OCWD were quite successful. The CPTC membranes operated for more than 6 months in two independent RO tests on a chlorinated high-fouling municipal wastewater feed with little if any, increase in salt passage. Under these conditions, the CPTC membranes exhibited higher water fluxes, higher rejection and a lower degree of fouling than either TMC or FilmTec commercial membranes.
- We have observed metal-catalyzed degradation of all PA membrane types examined, including TMC, CPTC, and CHTrC-based membranes. Copper-II was apparently more effective than iron-II in terms of catalyzing the membrane oxidations. The actual mechanism of membrane chlorination remains unknown although several hypotheses have been postulated.
- Experiments recently performed at SST have demonstrated that free chlorine facilitates bromination of PA membranes. Therefore, it is believed that bromine addition reactions, not chlorination *per se*, are responsible for the observed degradation in membrane performance. Bromination and associated membrane degradation were only evaluated at pH <7.0. The exact mechanism of bromination and the associated membrane performance decline needs further investigation under a variety of operating parameters.

- In chlorination experiments where divalent metal cations such as iron and copper were absent, both water and salt transport decrease, suggesting that (i) the membrane structure is somehow physically altered, e.g., by "tightening" or some other related mechanism, or (ii) the hydrophobicity of the membrane was increased by the bromine addition leading to lower water and salt permeability.
- In parallel runs under actual field trials at the Bureau of Reclamation Water Quality Improvement Center (WQIC) at Yuma, AZ., CPTC and TMC membranes behaved differently. When run on chlorinated feed, the CPTC membrane performance declined after approximately 3000 hours of service, whereas the TMC membranes continued to operate well. More importantly, periodic system shutdowns appeared to accelerate the observed performance loss of the CPTC membranes (See figure on the following page). These data suggest that the CPTC membrane or its PS support has suffered some form of structural damage. Such damage could have occurred by (i) chlorination (bromination) of the PS or (ii) possibly by biodegradation of the CPTC rejection layer.

This program was based on work supported by the U. S. Army Research Office under Contract No. DAAD19-02-C-0031.

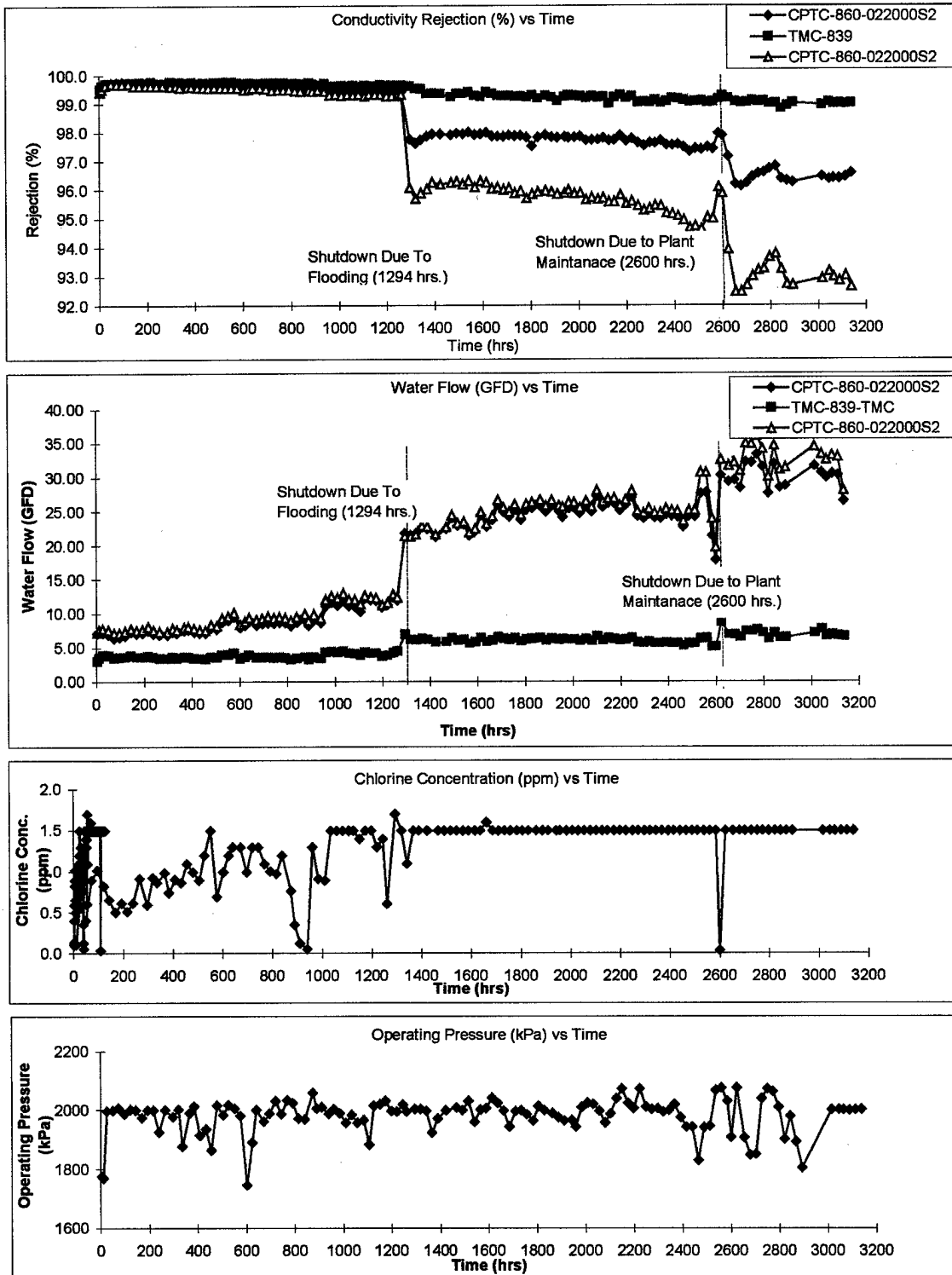
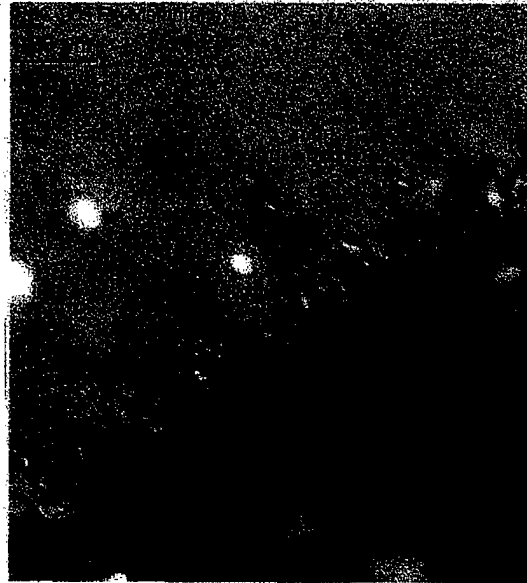
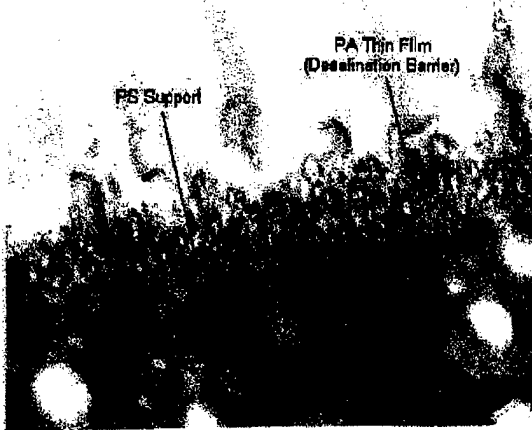


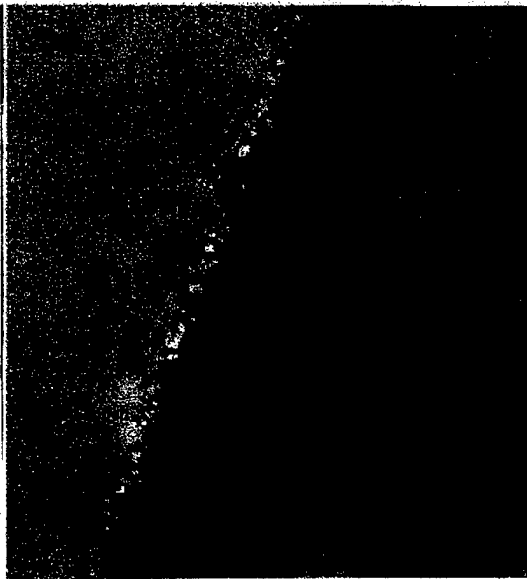
Figure 1. Performance of CPTC membranes in TCU-1 at WQIC. Test conditions: clearwell feed, pH 6.5, 25 °C.

Dow/FilmTec Seawater PA Membrane
0.30 μm



(A) FilmTec FT-30 PA Membrane (New)

(B) TMC PA Membrane (New)



(C) CPTC PA Membrane (New)

(D) CPTC PA Membrane after Repeated
RO Shutdowns

Figure 2. Transmission Electron Micrographs of cross-sections of the osmium stained PA barrier at the PA-PS interface of PA composite membranes.

3.0 PROGRAM OBJECTIVES

The overall objective of this program was to develop a *ctct*- CPTC membrane that is both chlorine and fouling resistant for use by DOD in ROWPUs and by private industry. The specific objectives of the program can be enumerated as follows:

- Improve the efficiency, yield and purity of the CPTC acid chloride synthesis by methods feasible for commercial scale-up.
- Investigate the bonding characteristics of the CPTC film to the support membrane substrate to improve adhesion. Improved adhesion will reduce and/or prevent delamination of the PA barrier from the membrane substrate during RO system shutdowns.
- Increase the hydrophilic nature of the CPTC membrane to reduce and/or eliminate biofouling.
- Evaluate the RO performance of the improved CPTC membrane on a chlorinated feed.

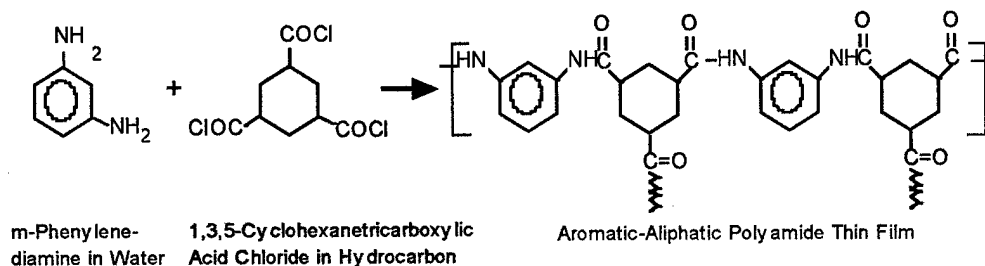
4.0 CHLORINE RESISTANT MEMBRANE DEVELOPMENT STUDIES

In the previous program CPTC was synthesized and the *ctct* isomer separated from a mixture of six isomers at a purity level of 99.5%. PA membranes made from the CPTC-MPD system were quite resistant to high concentrations of chlorine in static immersion tests. In our previous work it was found that the thin PA desalination barrier of the membrane had a tendency to delaminate from the supporting membrane structure during RO field tests after system shutdowns (depressurization). In this project the focus was to enhance adhesion of the PA layer to the supporting substrate membrane. This was done by:

- Making the porous supporting membranes from polymers other than polysulfone.
- Changing the structure of the porous substructure of the supporting membrane from a finely porous structure to an open columnar structure.
- Using porous substrates that are more hydrophilic and substrates that are charged.
- Crosslinking a portion of the MPD within the pores of the supporting membrane with glutaraldehyde just prior to PA film formation.
- Impregnating the pores of the supporting membrane with long chain segments of polyethyleneimine that extend into the PA layer by reacting with the CPTC acid chloride.
- Synthesizing and evaluating new acid chlorides that are similar to CPTC, namely, cyclohexanetriacid chloride (CHTrC).

4.1 Cyclohexanetriacid Chloride Synthesis and PA Membrane Formation

PA membranes were made with CPTC, TMC and cyclohexanetriacid chloride (CHTrC). The CHTrC was synthesized and purified to 99+% purity. The chemistry of the CHTrC PA thin-film composite membrane formation is shown in the following equation.



CHTrC Acid Chloride Polyamide Membrane

The RO performance of the CHTrC PA membranes was somewhat different that for CPTC and/or TMC PA composite membranes. The comparative RO performances of TMC 940, CHTrC 961, and CPTC 966 membranes are shown in Table 4; all of the membranes were prepared on a PEI porous supporting membrane and tested at 800 psi applied pressure on a 35,000 mg/L sodium chloride feed. The water flux exhibited by the CHTrC membrane is somewhat higher than for the other membranes while the salt rejection is lower.

4.2 Porous Supporting Membrane Preparation and Characterization

PA membranes were made from each of the acid chlorides and MPD on the porous surfaces of four types of porous supporting membranes namely, polysulfone (PS), polyetherimide (PEI), a blend of PS and polyvinylpyrrolidone (PVP), and a blend of PS and sulfonated PS (PS/SPEES/PES). The preparation parameters and characterization properties for the membranes are shown in Table 2.

4.3 Polyamide Composite Membrane Preparation and Performance

The preparation parameters used to prepare PA composite membranes from each of the supports and acid chlorides are shown in Table 3. The RO performances of the PA membrane in flat sheet test cells are shown in Table 4. Membranes of each type were selected from this group for long term testing on chlorinated feeds at the U. S. Bureau of Reclamation's Water Quality Improvement Center (WQIC) at Yuma, AZ.

Table 2

Polyamide Composite Supporting Membrane Preparation Parameters

| Supporting Membrane ID | Reinforcing Fabric ID | Membrane Casting Composition (wt-%) | Casting Knife Gap (mils) | Casting Speed (ft/min) | Solution Strike Through (Visual) | Membrane Thickness PS+Fabric (mils) | Membrane Thickness PS Only (mils) | Peel Strength | Pinholes | Membrane Surface Appearance (Visual) | Water Permeability (A-Value x 10 ⁻⁵) (g/cm ² sec-atm) |
|------------------------|-----------------------|--------------------------------------|--------------------------|------------------------|----------------------------------|-------------------------------------|-----------------------------------|---------------|----------|--------------------------------------|--|
| 218 | AWA 620 (3.5 mils) | 18.0 PEI 1.0 LiBr DMAC Solvent | 8.0 | 25 | Normal | 5.7 | 3.2 | Good | None | V. Smooth | 3848 |
| 220 | AWA 620 (3.5 mils) | 16.0 PS 3.0 SPS NMP Solvent | 6.0 | 20 | Normal | 7.0 | 4.0 | Good | None | V. Smooth | 3228 |
| 221 | AWA 620 (3.5 mils) | 16.0 PS 3.0 PVP NMP Solvent | 6.0 | 20 | Normal | 6.7 | 4.0 | Good | None | V. Smooth | 531 |
| 222 | AWA 16-1 (4.0 mils) | 16.5 PS 1.0 LiBr DMF Solvent | 7.0 | 30 | None | 6.2 | 3.0 | Moderate | Some | Smooth | 2882 |
| 223 | CRANE (4.5 mils) | 16.5 PS 1.0 LiBr DMF Solvent | 7.0 | 30 | None | 6.2 | 2.5 | Moderate | V. Few | Smooth | 1923 |

Casting solution temperature = 22°C

Gelation bath temperature = 20°C

Distance from casting knife to water immersion = 11 inches

Distance from casting knife to first roller = 20.5 inches

Note: Membrane processing variables / properties are somewhat dependent on casting machine design. Thus, some variation in membrane processing / properties can be expected between casting machines.

No hot water extraction

Angle of web entering gelation water = 65° C

Membrane cast on inside surface of fabric roll

Table 3
Polyamide Composite Membrane Preparation Parameters

| Composite Membrane ID | Supporting Membrane | | Interfacial Reaction Parameters | | Post-Treatment Steps | | | | | | |
|-----------------------|---------------------|---|--|---|--|--|-------------------------------------|--------------------------|--------------------------------------|--|--|
| | Identification | A-Value x 10 ⁻⁵ (g/cm ² -sec-atm) | Step 1 Solution A Solvent: water (wt-%) | Step 2 Solution B Solvent: hexane (wt-%) | Step 3 Water Rinse 80°C (5 min) | Step 4 5% Citric Acid Rinse 80°C (5 min) | Step 5 DI Water Rinse 25°C | Step 6 PVA Coating | Step 7 Drying 80°C (16 Min) | | |
| 940 | 218-2 PEI | 3848 | 4.0 % MPD 0.1% SLS 4% Acetone | 0.00236 M TMC | v | v | v | v | v | | |
| 945A | 220-2 PS/SPS | 3228 | 4.0 % MPD 0.1% SLS 4% Acetone | 0.00236 M TMC | v | v | v | v | v | | |
| 950A | 221 PS/PVP | 531 | 4.0% MPD 0.1% SLS 4% Acetone | 0.00236 M TMC | v | v | v | v | v | | |
| 951 | 223 PS | 1923 | 4.0% MPD 0.1% SLS 4% Acetone | 0.00236 M TMC | v | v | v | v | v | | |
| 958 | 221-3 PS/PVP | 531 | 4.0% MPD 0.1% SLS 4% Acetone | 0.00236 M TMC | - | v | v | v | v | | |
| 960 | 223 PS | 1923 | 4.0% MPD 0.1% SLS 4% Acetone | 0.00236 M TMC | - | v | v | v | v | | |
| 961 | 218 PEI | 3848 | 4.0% MPD 0.1% SLS 4% Acetone | 0.00236 M CHTrC | v | v | v | v | v | | |
| 966 | 218 PEI | 3848 | 4.0% MPD 0.1% SLS 4% Acetone | 0.00236 M CPTC | v | v | v | v | v | | |
| 969 | 220-2 PS/SPS | 3228 | 4.0% MPD 0.1% SLS 4% Acetone | 0.00236 M CPTC | v | v | v | v | v | | |

Table 3 (Continued)

| Composite Membrane ID | Supporting Membrane | | Interfacial Reaction Parameters | | Post-Treatment Steps | | | | | | |
|-----------------------|---------------------|---|--|---|--------------------------------|--|---------------------------|----------------|----------------------------|--|--|
| | Identification | A-Value x 10-5 (g/cm ² -sec-atm) | Step 1 | Step 2 | Step 3 | Step 4 | Step 5 | Step 6 | Step 7 | | |
| 973 | 221-3 PS/PVP | 531 | Solution A Solvent: water (wt-%) 4.0% MPD 0.1% SLS 4% Acetone | Solution B Solvent: hexane (wt-%) 0.00236 M CPTC | Water Rinse 80°C (5 min) | 5% Citric Acid Rinse 80°C (5 min) | DI Water Rinse 25°C | PVA Coating | Drying 80°C (16 Min) | | |
| 979 | 223 PS | 1923 | 4.0% MPD 0.1% SLS 4% Acetone | 0.00236 M CPTC | | | | | | | |
| 981 | 218-2 PEI | 3848 | * 5.0% GALD 4.0% MPD 0.1% SLS 4.0% Acetone | 0.00236 M CPTC | | | | | | | |
| 982 | 218-2 | 3848 | * 5% GALD 4.0% MPD 0.1% SLS 4.0% Acetone ** 5.0% GALD | 0.00236 M CPTC | | | | | | | |

PEI = Polyetherimide

PS = Polysulfone

SPS = Sulfonated polysulfone

PVP = Polyvinylpyrrolidone

MPD = m-phenylenediamine

SLS = Sodium Lauryl Sulfate

GALD = Glutaraldehyde

CPTC = Cyclopentanetetracarboxylic acid chloride

* Porous supporting membrane impregnated with 5% GALD solution prior to applying MPD solution

** Membrane flooded with 5% GALD solution after the deposition of MPD solution and before contact with CPTC solution

Table 4

Reverse Osmosis Performance of Polyamide Composite Membranes in Flat Sheet Test Cells

Test Conditions: 800 psi applied pressure, 35,000 mg/L sodium chloride feed, pH 6.3, 25°C, 0.9 gal/min feed flow, 1 x 3" rectangular test cell

| Composite Membrane Identification | Supporting Membrane ID (See Table 2) | Polyamide Thin Film ID (See Table 3) | Reverse Osmosis Performance | | | |
|-----------------------------------|--------------------------------------|--------------------------------------|-----------------------------|---------------------------|---------------------------|---------------------------|
| | | | FEED: | No Chlorine | Water Flux, gfd | Rejection, % |
| | | | No Chlorine | After Chlorine (3.5 mg/L) | After Chlorine (3.5 mg/L) | After Chlorine (3.5 mg/L) |
| 940 | 218-2 PEI | MPD / TMC | 22.9 | 12.1 | 99.5 | 99.9 |
| 945A | 220-2 PS / SPS | MPD / TMC | 16.0 | 10.7 | 99.58 | 99.86 |
| 950A | 221-3 PS / PVP | MPD / TMC | 17.7 | 17.8 | 22 | 20 |
| 951 | 223 PS | MPD / TMC | 34.6 | 31.9 | 19 | 19 |
| 958 | 221-3 PS / PVP | MPD / TMC | 8.1 | 5.5 | 99.89 | 99.69 |
| 960 | 223 PS | MPD / TMC | 18.8 | 14.0 | 99.30 | 99.86 |
| 961 | 218-2 PEI | MPD / CHTC | 26.1 | 20.7 | 95.9 | 98.4 |
| 966 | 218-2 PEI | MPD / CPTC | 17.0 | 6.7 | 97.8 | 99.77 |
| 969 | 220-2 PS/SPS | MPD / CPTC | 19.7 | 9.5 | 98.1 | 99.70 |
| 979 | 223 PS | MPD / CPTC | 23.1 | 21.7 | 98.7 | 99.47 |
| 981 | 218-2 PEI | MPD / CPTC | 7.2 | 3.0 | 98.4 | 99.6 |
| 982 | 218-2 PEI | MPD / CPTC | No Flow | - | - | - |

4.4 Atomic Force Microscopy

Atomic Force Micrographs (AFM's) of the porous surfaces of the supporting membranes were taken both before and after formation of the PA film. In addition, Scanning Electron Micrographs (SEM's) of the cross sections of the porous supporting membranes both before and after formation of the PA RO film were taken as well.

AFM's of the porous surfaces of the four supporting membranes are shown in *Figure 3*. AFM's of the desalination surfaces of the PA membranes formed on the respective porous supporting membranes are shown in *Figure 4*. The surface area statistics of the PA membranes are shown in *Figure 5*.

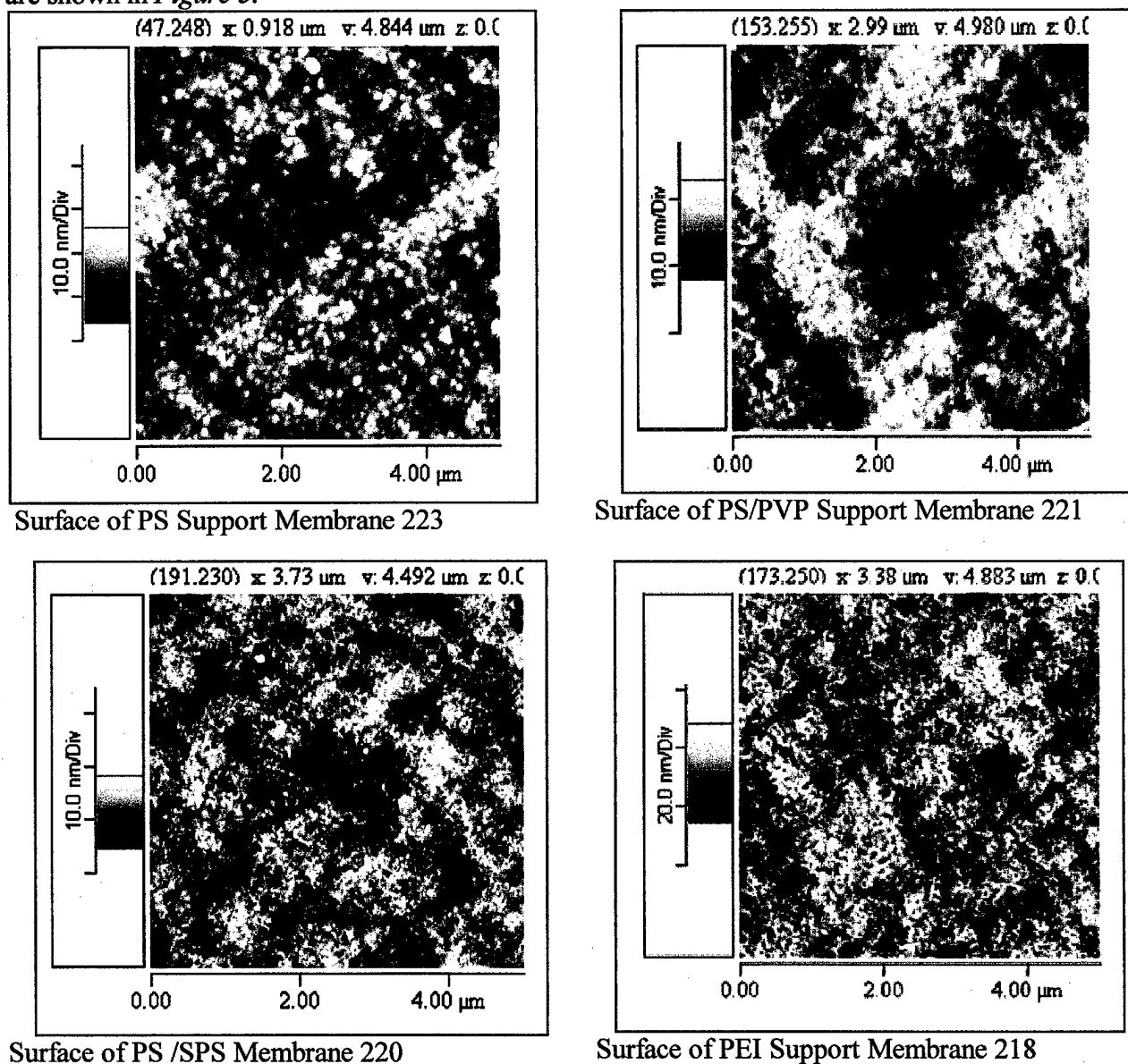
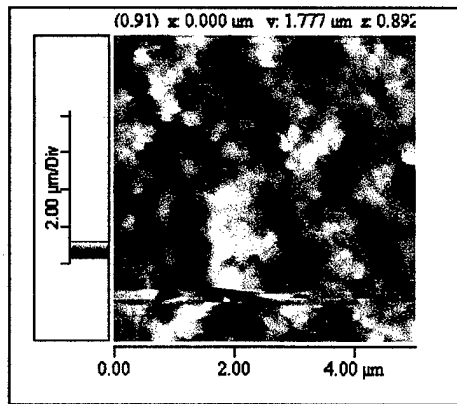
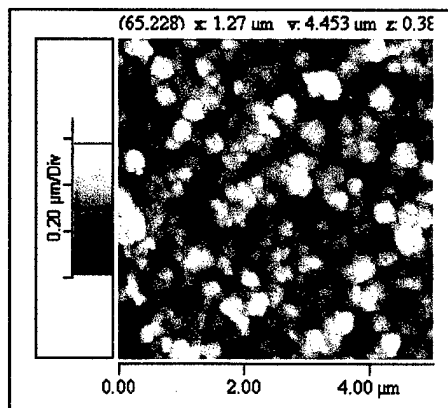


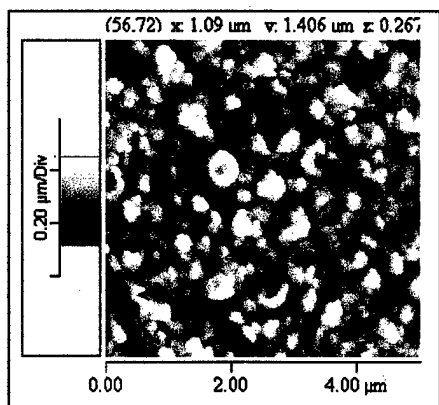
Figure 3. Atomic Force Micrographs of the porous surfaces of PS, PS/PVP, PS/SPEES/PES), and PEI support membranes.



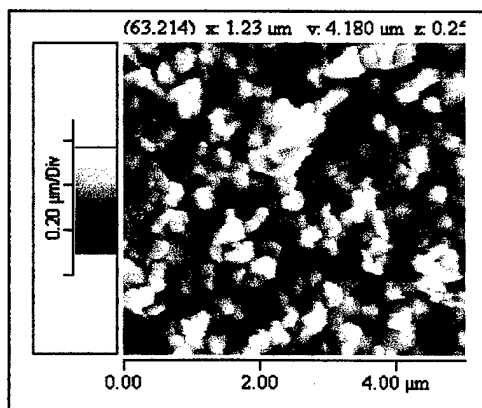
Surface of TMC- PA Membrane 954 supported on PS support membrane 223



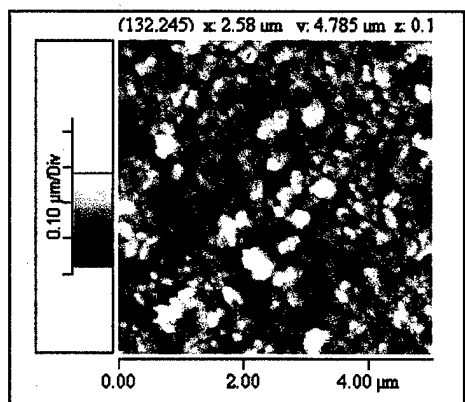
Surface of CPTC-PA Membrane 980 supported on PS support membrane 223



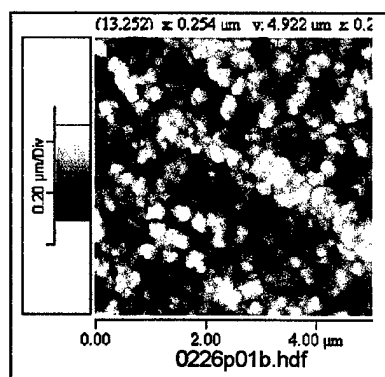
Surface of CPTC-PA membrane 968 supported on PEI support membrane 218



Surface of CPTC-PA membrane 972 supported on PS/SPS support membrane 220

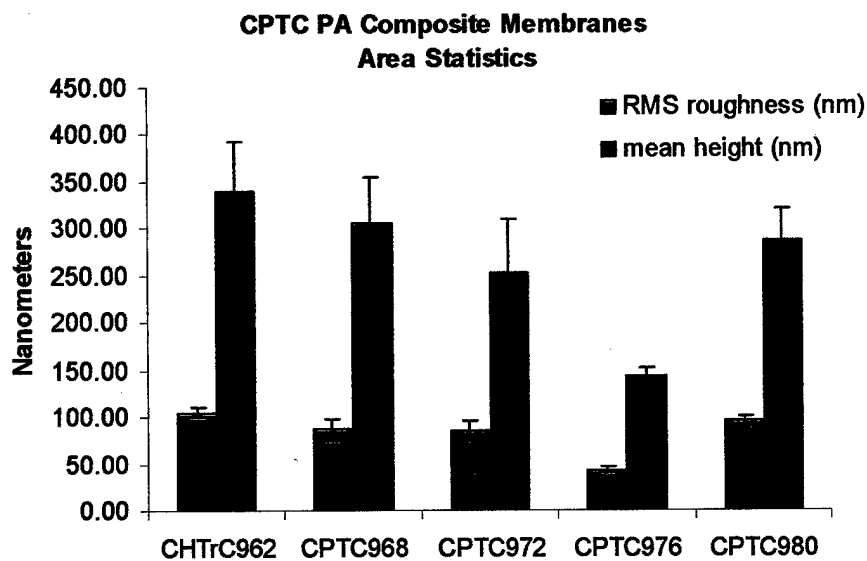


Surface of CPTC-PA membrane 676 supported on PS/PVS support membrane



Surface of CHTrC-PA membrane 962 supported on PEI support membrane 218

Figure 4. Atomic Force Micrographs of the desalination surface of TMC, CPTC and CHTrC membranes supported on the surfaces of PS, PS/PVP, PS/ SPEES/PES), and PEI support membranes.



| Membranes | RMS roughness (nm) | st dev | mean height (nm) | st dev |
|-----------|--------------------|--------|------------------|--------|
| CHTrC962 | 104.94 | 5.29 | 339.70 | 51.84 |
| CPTC968 | 86.88 | 12.08 | 304.73 | 49.96 |
| CPTC972 | 85.28 | 11.02 | 252.03 | 56.55 |
| CPTC976 | 43.40 | 3.11 | 142.20 | 9.59 |
| CPTC980 | 95.50 | 4.95 | 284.90 | 35.71 |

Figure 5. Surface area statistics determined from Atomic Force Micrographs of the PA desalination surfaces of CHTrC and CPTC-PA composite membranes (See Figure 4)

4.5 Scanning Electron Microscopy

SEM's were taken of the cross-sections, near the top surface, of the porous supporting membranes before and after formation of the PA layer to form the RO membrane. These are shown in Figures 6 through 17. The structures of the porous supporting membranes are quite different depending on the material of the membrane and the casting solvents from which they were prepared. The TMC-PA and CPTC-PA membranes shown in Figure 7 and 9 are supported on a PS membrane, which is standard for commercial ROWPU membranes. The PS membrane substrate has a very finely porous lacy like structure. All of the other membranes shown in Figures 10 through 17 have a very different column like substrate structure. In some membranes the columns are vertical and in others they are slanted. The latter is related to the speed of membrane casting. It was anticipated that bonding of the PA film to these types of substrates would be enhanced.

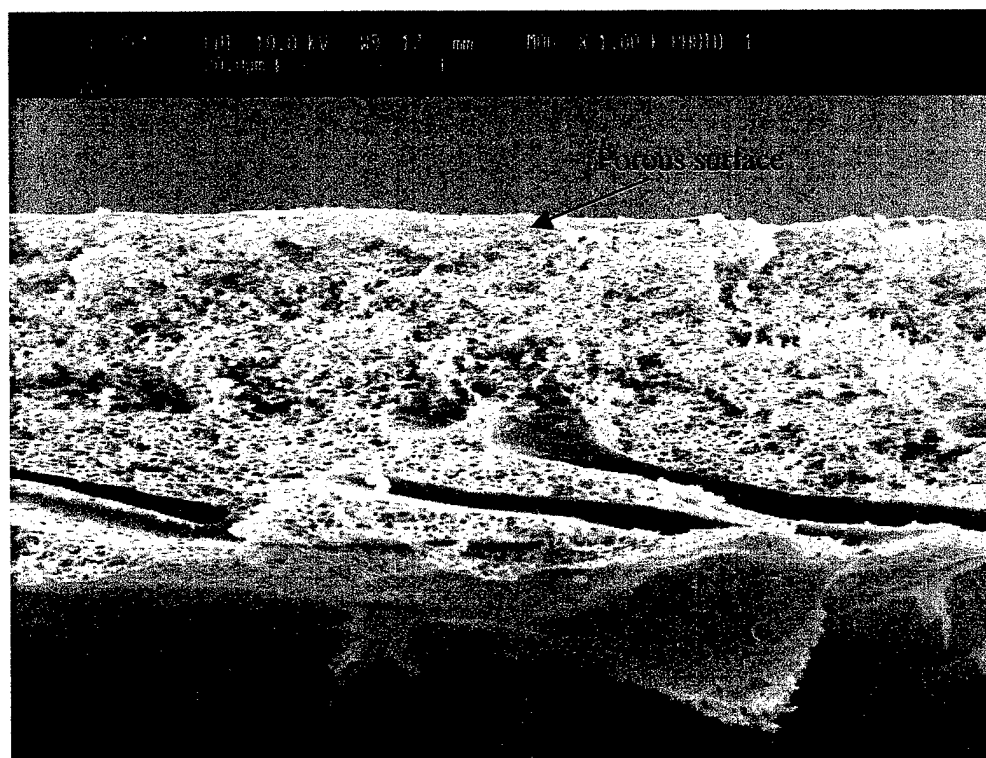


Figure 6. SEM of the cross-section of PS support membrane 223

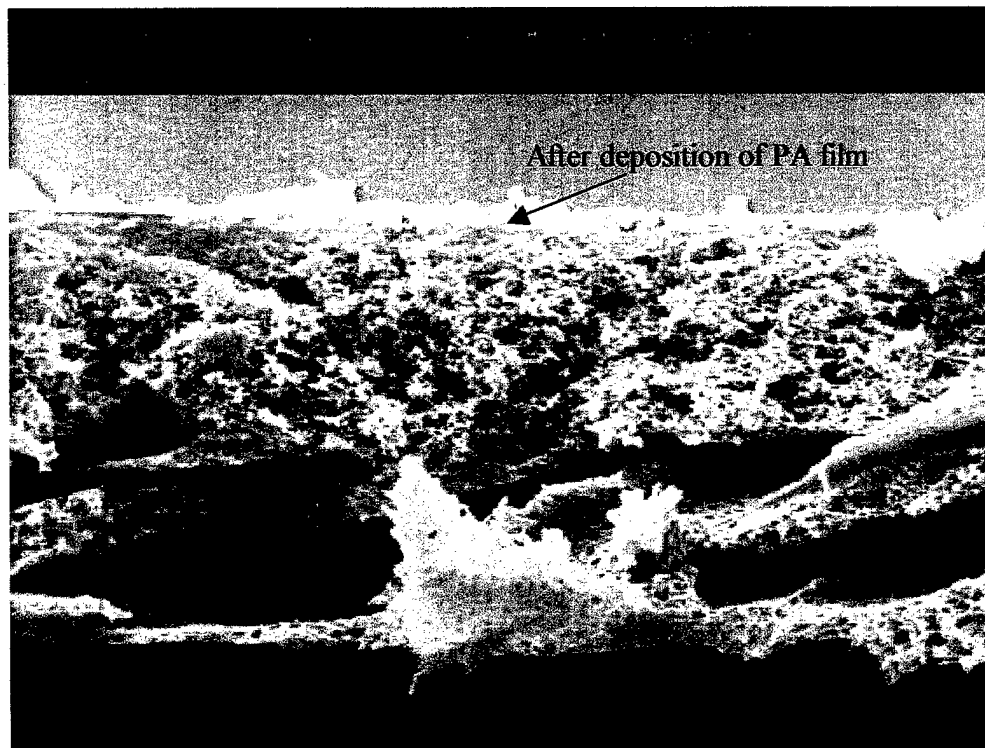


Figure 7. SEM of the cross-section of TMC-PA membrane 954 on the surface

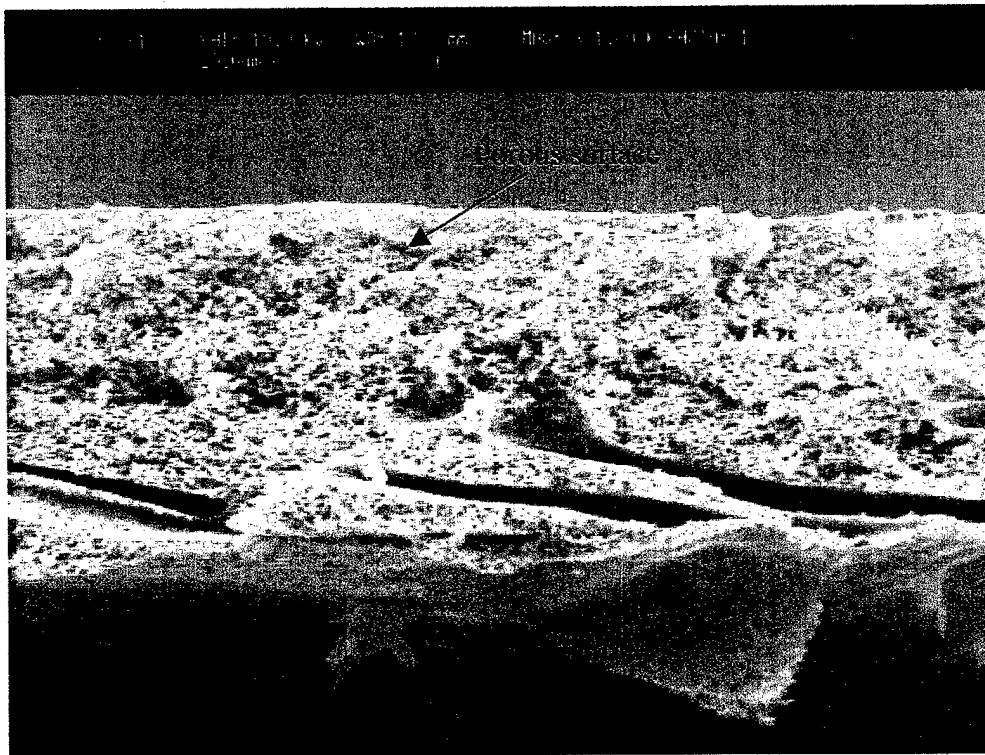


Figure 8. SEM of the cross-section of PS support membrane 223

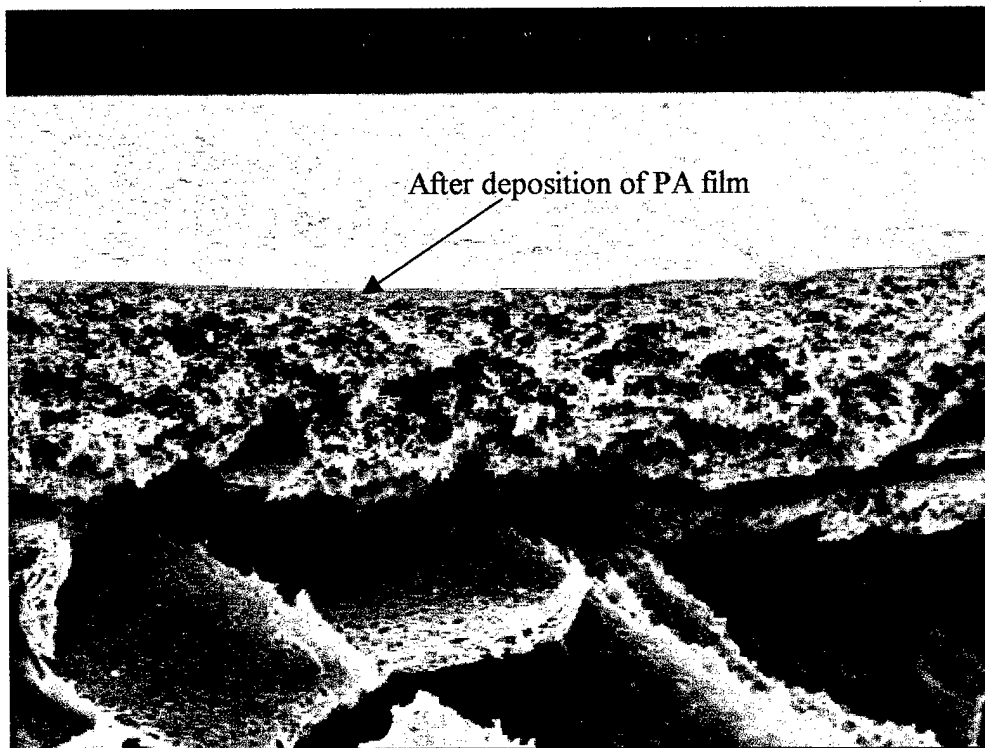


Figure 9. SEM of the cross-section of CPTC-PA membrane 980 on the surface of PS support membrane 223

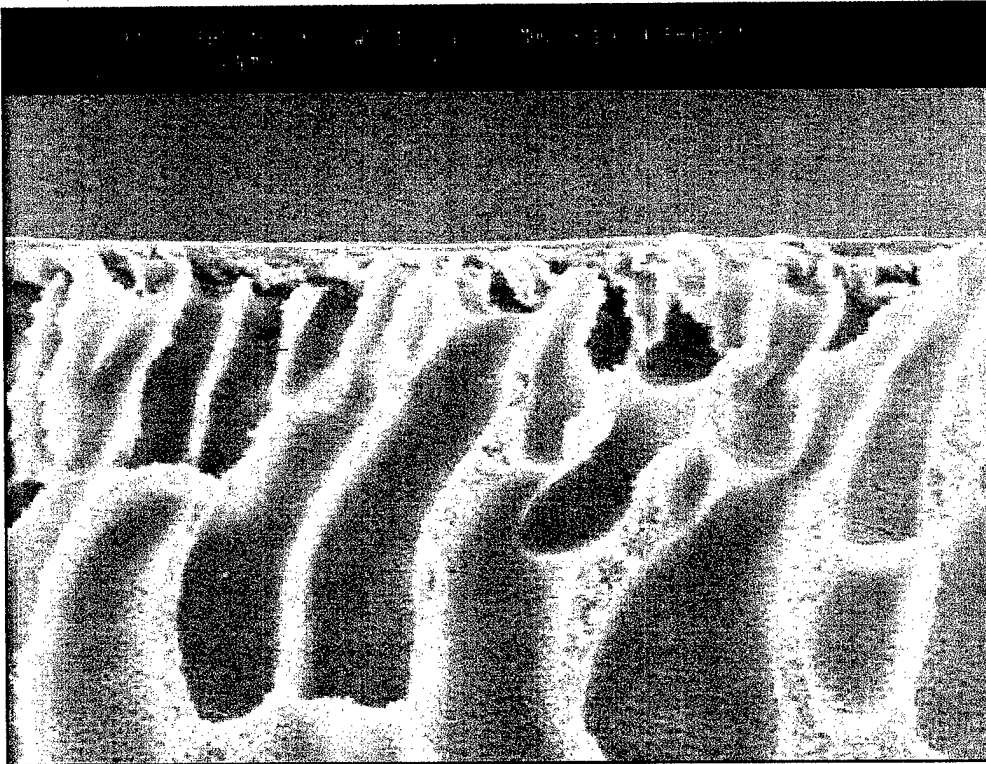


Figure 12. SEM of the cross-section of PS/PVP support membrane 221

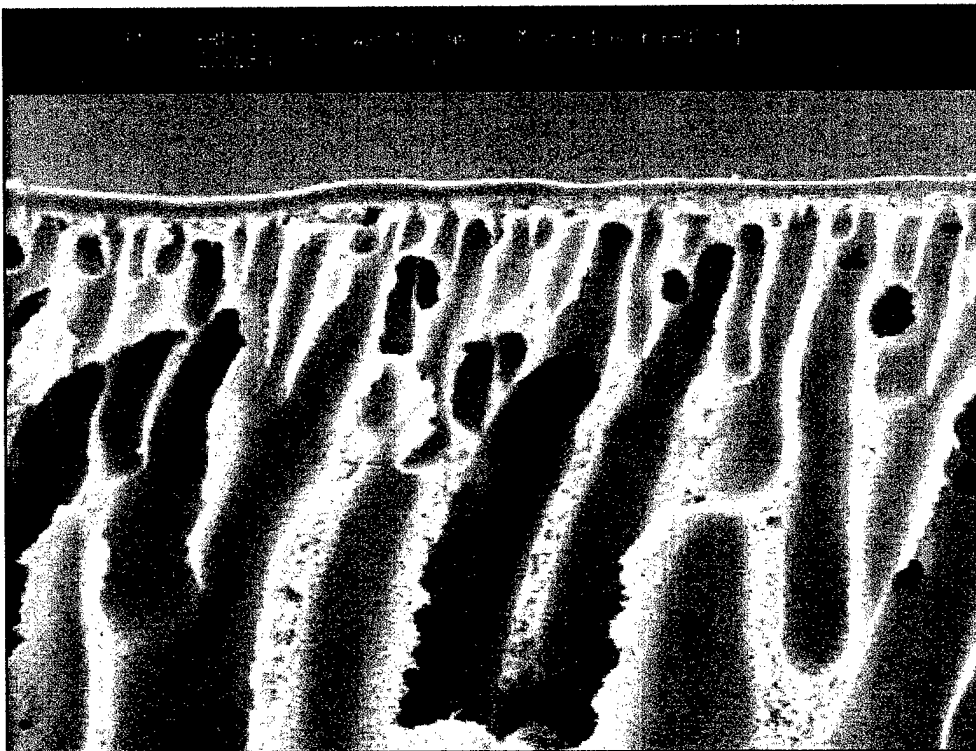


Figure 13. SEM of the cross-section of CPTC-PA membrane 976 on the surface of PS/PVP support membrane 221



Figure 14. SEM of the cross-section of PEI support membrane 218

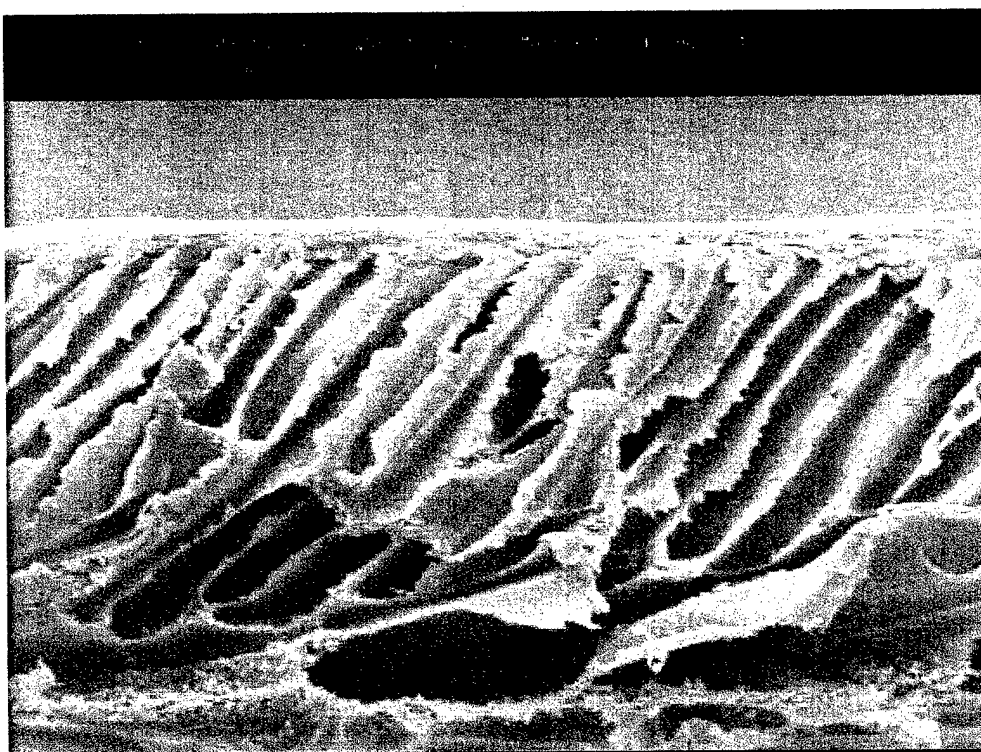


Figure 15. SEM of the cross-section of CPTC-PA membrane 968 on the surface of PEI support membrane 218

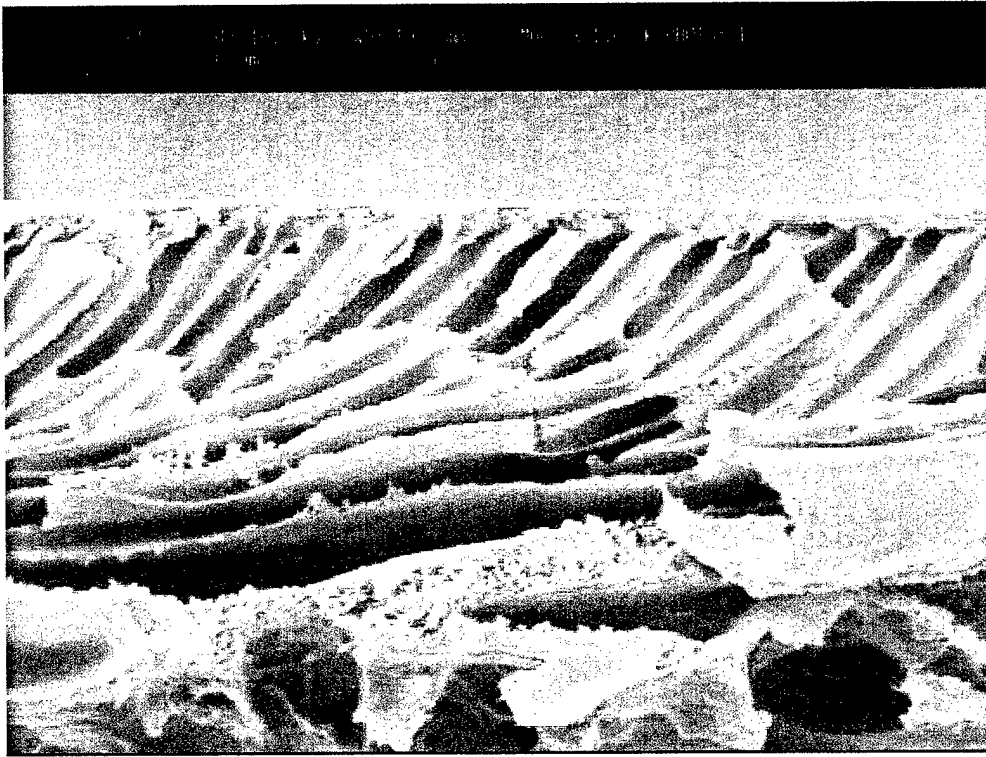


Figure 16. SEM of the cross-section of PEI support membrane 218

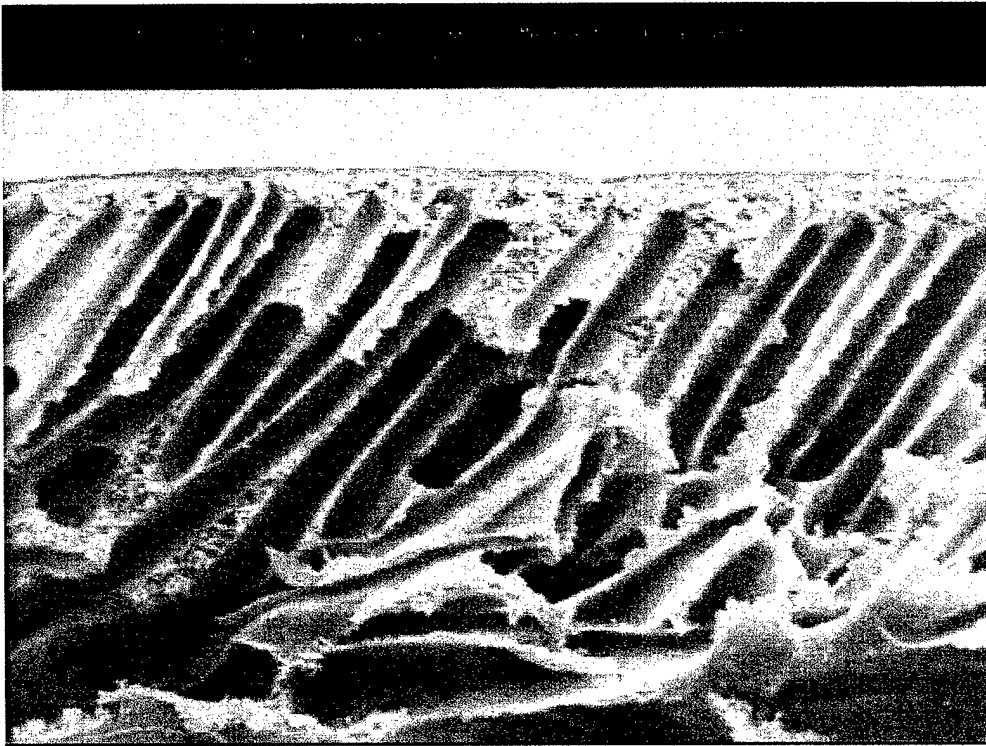


Figure 17. SEM of the cross-section of CHTrC-PA membrane 962 on the surface of PEI support membrane 218

4.6 Sodium Hypochlorite Membrane Immersion Test Results

PA RO composite membranes were prepared from TMC, CHTrC, and CPTC acid chlorides and MPD on the porous surfaces of PS, PEI and PS/SPEES/PES supporting membranes to determine their resistance to chlorine in high concentration sodium hypochlorite immersion tests.

The surfaces of the porous supporting membranes are shown in Figure 3; the surfaces of the porous supporting membranes after the formation of TMC, CHTrC and CPTC PA membranes are shown in Figure 4. The cross sections of the all of the aforementioned membranes are shown in Figures 6 through 16.

Accelerated chlorine resistant tests were conducted by immersing TMC, CHTrC and CPTC PA membranes in high concentration sodium hypochlorite solutions at pH 6 for 1-hr and subsequently evaluated in RO for any changes in transport properties. Immersion tests were conducted at two levels of sodium hypochlorite solutions, namely, 2,100 and 30,000 mg/L. After one hour immersion in sodium hypochlorite the transport properties of the PA membranes were evaluated in RO at 800 psi applied pressure, 35,000 mg/L sodium hypochlorite feed at pH 5.8. The results are shown in Tables 5 and 6.

The RO data for the membranes immersed in 2,100 mg/L sodium hypochlorite solution are summarized in Table 5. TMC membrane 951 and CPTC membrane 979 supported on the same lot of PS supporting membrane exhibited a substantial loss in rejection after immersion in sodium hypochlorite. Rejection before immersion in sodium hypochlorite is nominally 99.4%. This would seem to indicate that the PS support membrane may be subject to attack by the sodium hypochlorite solution. The same PA membrane, on the other hand, made on PEI supporting membrane showed no loss in salt rejection. As always observed, the water flux exhibited by the membranes was decreased substantially after contact with sodium hypochlorite.

The CHTrC membrane supported on PEI support membrane showed little or no loss in salt rejection while retaining high water flux. The rejection for this membrane before immersion in sodium hypochlorite is nominally 98%. It is not clear why the water flux of the CHTrC membrane is less affected by sodium hypochlorite than the water flux of the TMC or CPTC PA membranes on the same PEI support. This phenomenon deserves further study.

A second immersion study was conducted with TMC and CPTC PA membranes supported on PS/SPEES/PES and PEI membranes at a higher sodium hypochlorite concentration namely, 30,000 mg/L sodium hypochlorite for 1 hour at pH 6.0. The subsequent RO results, shown in Table 6, show that the TMC and CPTC membranes supported on PS/SPS membrane failed in RO testing after the immersion test. That is, the rejection was greatly diminished. The CPTC PA membrane supported on PEI membrane, on the other hand, showed no loss in salt rejection.

In summary, it appears that PS based supporting membranes (PS and PS/SPEES/PES) is being attacked upon immersion in sodium hypochlorite solutions thereby losing its ability to support either TMC or CPTC PA films without loss in salt rejection in RO testing. PEI supporting membrane does not appear to be affected by prolonged immersion in sodium hypochlorite. The

salt rejection of TMC, CPTC and CHTrC PA membranes supported on PEI membranes show no loss in salt rejection in RO tests after immersion in sodium hypochlorite. It should be noted that all commercial PA composite membranes are made with PS support membrane. One hypothesis is that the aromatic rings of the PS may be chlorinating thereby interfering with the bonding of the PA film to the surface of the PS and/or physically deteriorating the PS substrate thereby reducing its ability to support the PA film in RO. Further studies are recommended to resolve this problem.

Table 5

Reverse Osmosis Performance of Polyamide Composite Membranes in Flat Sheet Test Cells

Test Conditions: 800 psi applied pressure, 35,000 mg/L sodium chloride feed, pH 5.8, 25°C, 0.9 gal/min feed flow, 1 x 3" rectangular test cell

| Composite Membrane Identification | Supporting Membrane Identification (See Table 2) | Polyamide Thin-Film Identification (See Table 3,4) | Reverse Osmosis Performance | |
|-----------------------------------|---|---|-----------------------------|--------------|
| | | | Water Flux, gfd | Rejection, % |

Membranes Immersed in 2,100 mg/L Sodium Hypochlorite at pH 6.0 for 1 Hour Before Testing

| | | | | |
|-----|-----------------|-------------|------|-------|
| 951 | 223 PS | MPD / TMC | 49.6 | 17 |
| 951 | 223 PS | MPD / TMC | 58 | 12 |
| 941 | 218-2 PEI | MPD / TMC | 7.2 | 99.76 |
| 941 | 218-2 PEI | MPD / TMC | 6.5 | 99.26 |
| 961 | 218-2 PEI | MPD / CHTrC | 19.6 | 98.7 |
| 961 | 218-2 PEI | MPD / CHTrC | 16.2 | 98.4 |
| 969 | 220-2 PS/SPS | MPD / CPTC | 8.1 | 97.3 |
| 969 | 220-2 PS/SPS | MPD / CPTC | 6.3 | 99.34 |
| 966 | 218-2 PEI | MPD / CPTC | 4.2 | 99.43 |
| 966 | 218-2 PEI | MPD / CPTC | 4.2 | 99.43 |
| 979 | 223 PS | MPD / CPTC | 5.1 | 96.7 |
| 979 | 223 PS | MPD / CPTC | 9.0 | 91.3 |

Table 6

Reverse Osmosis Performance of Polyamide Composite Membranes in Flat Sheet Test Cells

Test Conditions: 800 psi applied pressure, 35,000 mg/L sodium chloride feed, pH 5.8, 25°C, 0.9 gal/min feed flow, 1 x 3" rectangular test cell

| Composite Membrane Identification | Supporting Membrane Identification (See Table 1) | Polyamide Thin-Film Identification (See Table 2) | Reverse Osmosis Performance | |
|-----------------------------------|--|--|-----------------------------|--------------|
| | | | Water Flux, gfd | Rejection, % |

| Membranes Immersed in 30,000 mg/L Sodium Hypochlorite at pH 6.0 for 1 Hour Before Testing | | | | |
|---|-----------------|------------|----------------|--------------|
| 945A | 220-2 PS/SPS | MPD / TMC | 14 | 24 |
| 945A | 220-2 PS/SPS | MPD / TMC | Very High Flow | No Rejection |
| 969 | 220-2 PS/SPS | MPD / CPTC | 20.1 | 22.2 |
| 969 | 220-2 PS/SPS | MPD / CPTC | 19.9 | 27 |
| 966 | 218-2 PEI | MPD / CPTC | 6.0 | 99.34 |
| 966 | 218-2 PEI | MPD / CPTC | 5.1 | 99.32 |

4.7 Impregnation of Porous Supporting Membrane During CPTC PA Membrane Preparation to Enhance PA Film Adhesion

In previous work it was found that the thin PA desalination barrier of the composite membrane had a tendency to delaminate from the supporting membrane structure during RO field tests after system shutdowns (depressurization). In addition to changing the polymer and porous nature of the porous supporting membrane, several process modifications were made in the interfacial formation of the PA film on the surface of the support membrane. Two methods for enhancing adhesion of the PA layer to the supporting membrane are described in this and the following Section 4.8.

CPTC PA composite membranes were made by impregnating the PEI porous supporting membrane with glutaraldehyde prior to applying MPD during the preparative process. (See Figure 18). Thus, glutaraldehyde within the pores and on the surface of the supporting membrane reacts to form a crosslinked network. Subsequently, the excess MPD on the surface is

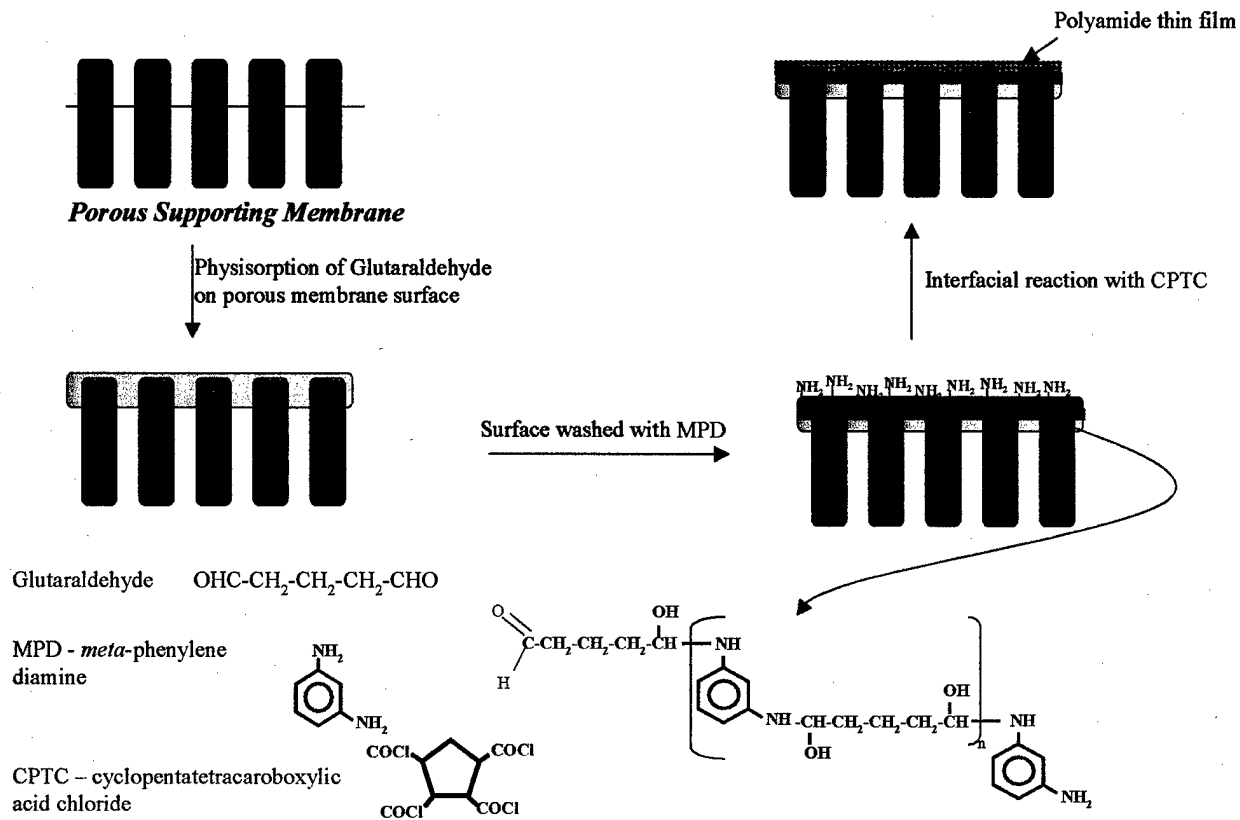


Figure 18. Mechanism for binding polyamide thin film to porous supporting membrane

reacted interfacially with CPTC to form the PA thin film. The initial RO transport properties of the membrane, as shown in Table 7, were good. These membranes were placed on test at the U.S. Department of Interior's WQIC at Yuma, AZ. for long-term pilot testing on chlorinated feeds along side CPTC and TMC controls. The results are shown in Section 4.11, *Figures 24 and 25.*

Table 7

Reverse Osmosis Performance of Polyamide Composite Membranes Modified with Glutaraldehyde in Flat Sheet Test Cells

Test Conditions: 800 psi applied pressure, 35,000 mg/L sodium chloride feed, pH 5.8, 25°C, 0.9 gal/min feed flow, 1 x 3" rectangular test cell

| Composite Membrane Identification | Supporting Membrane ID (See Table 1) | Polyamide Thin Film ID (See Table 2) | Reverse Osmosis Performance | | |
|--|--------------------------------------|--------------------------------------|------------------------------|---------------------------|---------------------------------------|
| | | | Water Flux, gfd | Rejection, % | |
| | | | FEED: No Chlorine (3.5 mg/L) | After Chlorine (3.5 mg/L) | No Chlorine After Chlorine (3.5 mg/L) |
| Control Membrane - No Glutaraldehyde | | | | | |
| 940 | 218-2 | MPD / TMC | 22.9 | 12.1 | 99.5 |
| 984 | 218-2 | MPD / TMC | 20.3 | 11.9 | 97.5 |
| Membrane Modified by Adding 0.1 wt-% Glutaraldehyde to the MPD Reactant Solution | | | | | |
| 983 | 218-2 | MPD / TMC | 17.3 | 11.1 | 98.5 |
| Membrane Modified by Adding 0.5 wt-% Glutaraldehyde to the MPD Reactant Solution | | | | | |
| 981 | 218-2 | MPD / TMC | 7.2 | 3.0 | 98.4 |
| Membrane Modified by Adding 5.0 wt-% Glutaraldehyde to the MPD Reactant Solution | | | | | |
| | | | | | 99.68 |

4.8 Preparation of CPTC PA Composite Membranes Supported on Polyethylenimine Washed Sulfonated Polysulfone Support

CPTC PA composite membranes were prepared on the surface of a blended PS supporting membrane that contained 3% SPEES/PES. SPEES/PES is a block copolymer of sulfonated polyetherethersulfone and polyethersulfone in which the charged sulfonate groups are uniformly dispersed. The amount of charge in the membrane can be controlled by the percentage of blend. The initial step in the formation of the CPTC PA composite membrane was to wash the surface of the negatively charged PS/SPEES/PES membrane with 50,000 MW polyethylenimine prior to applying MPD (See Figure 19). The polyethylenimine binds with the charged groups on the surface of the support membrane to serve as an attachment site for the PA film which is formed after washing the polyethylenimine bound surface of the support membrane with MPD and subsequently CPTC.

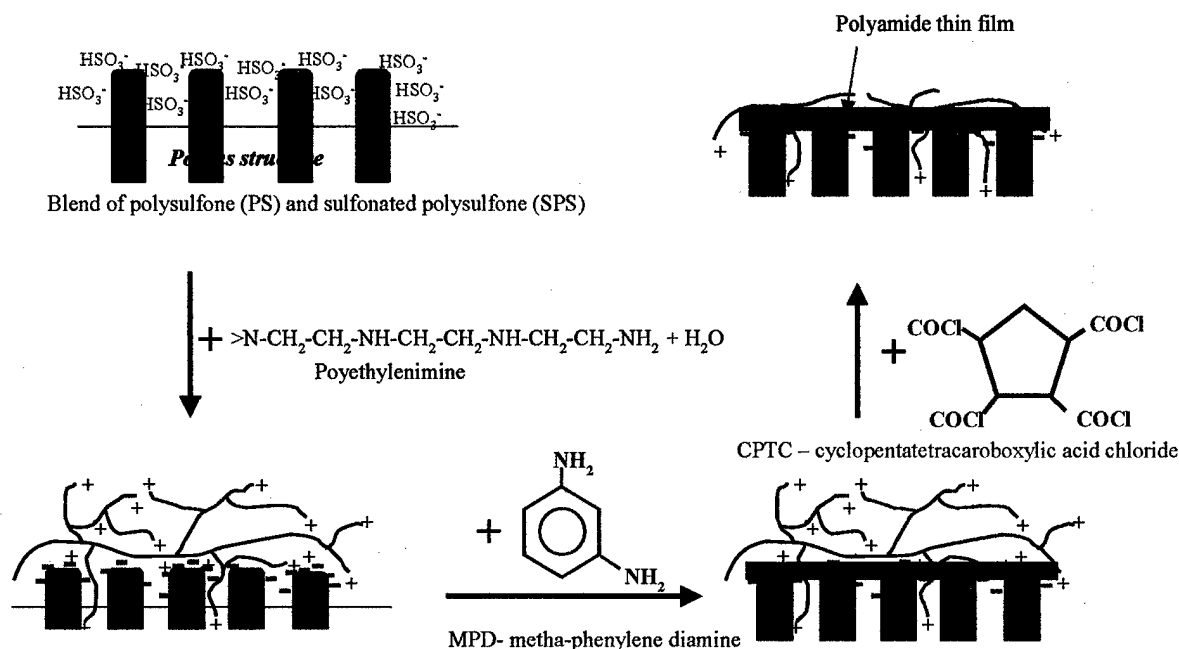


Figure 19. Mechanism for attachment of (MPD/CPTC) polyamide desalination barrier to surface of PS/SPEES/PES porous supporting membrane

The RO transport properties of the resulting membranes, shown in Table 8 were greatly reduced using this procedure. However, the concentration of polyethylenimine on the surface of the surface of the supporting membrane was not optimized. Additional work is required to minimize the concentration of polyethylenimine. This technique remains attractive.

Table 8**Reverse Osmosis Performance of CPTC Polyamide Composite Membranes Supported On Polyethylenimine Washed Sulfonated Polysulfone* Support**

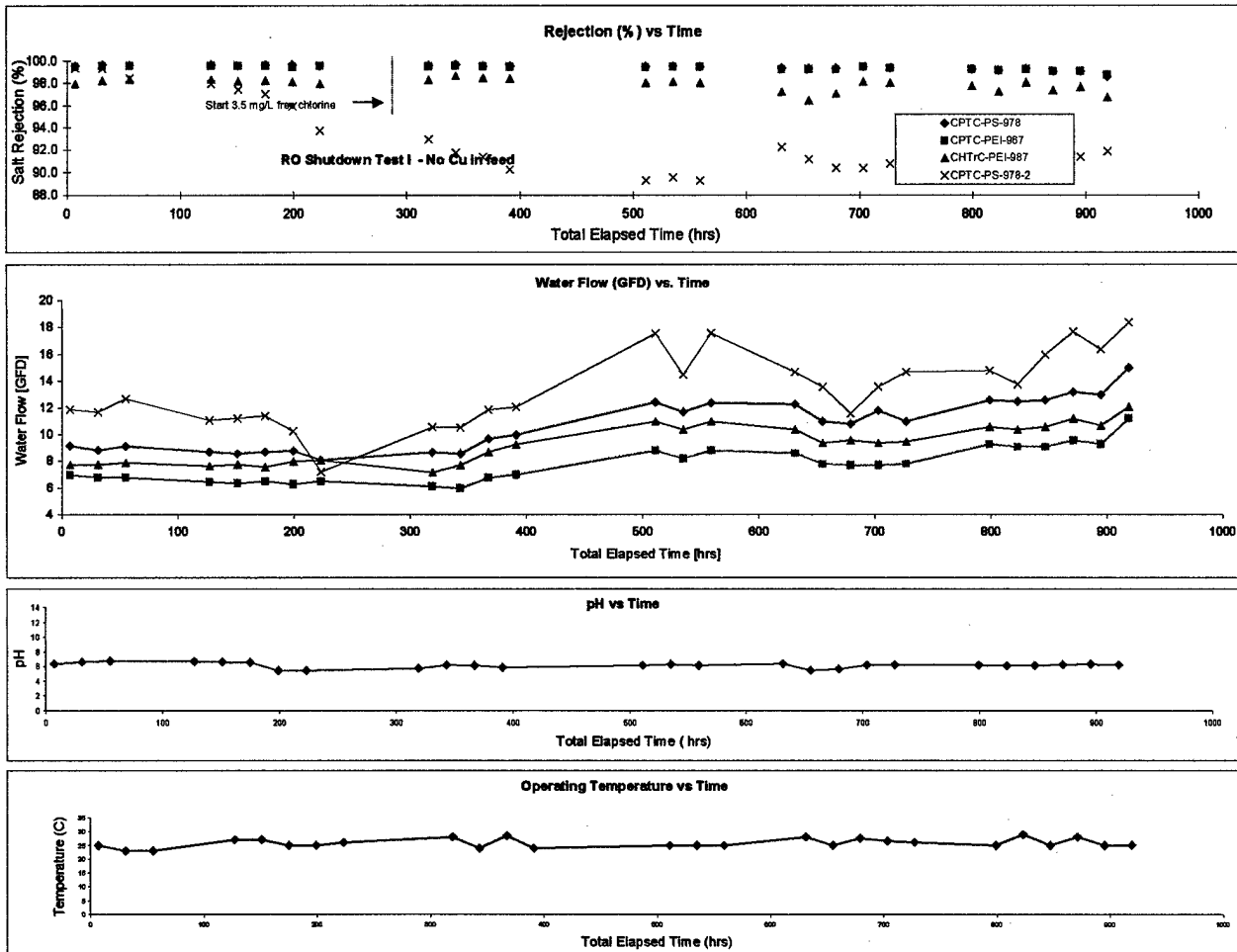
Test Conditions: 800 psi applied pressure, 35,000 sodium chloride feed, pH 6.56, 28.5C

| Composite Membrane Identification | Supporting Membrane* Identification | MPD / CPTC Molar Ratio | Elapsed Test Time (hrs) | Reverse Osmosis Performance | |
|---|-------------------------------------|------------------------|-------------------------|-----------------------------|---------------|
| | | | | Water Flux (gfd) | Rejection (%) |
| 1012 | 220-2 | 150:1 | 1 | 10.2 | 97.5 |
| 3.5 mg/L chlorine added to feed water after 1.5 hours | | | | | |
| 1012 | 220-3 | 150:1 | 3 | 3.9 | 99.36 |

* 3% SPEES/PEES + 16% Polysulfone (P 3500)

4.9 Programmed Reverse Osmosis Shutdown Testing in Laboratory Flat Sheet Membrane Test Cells

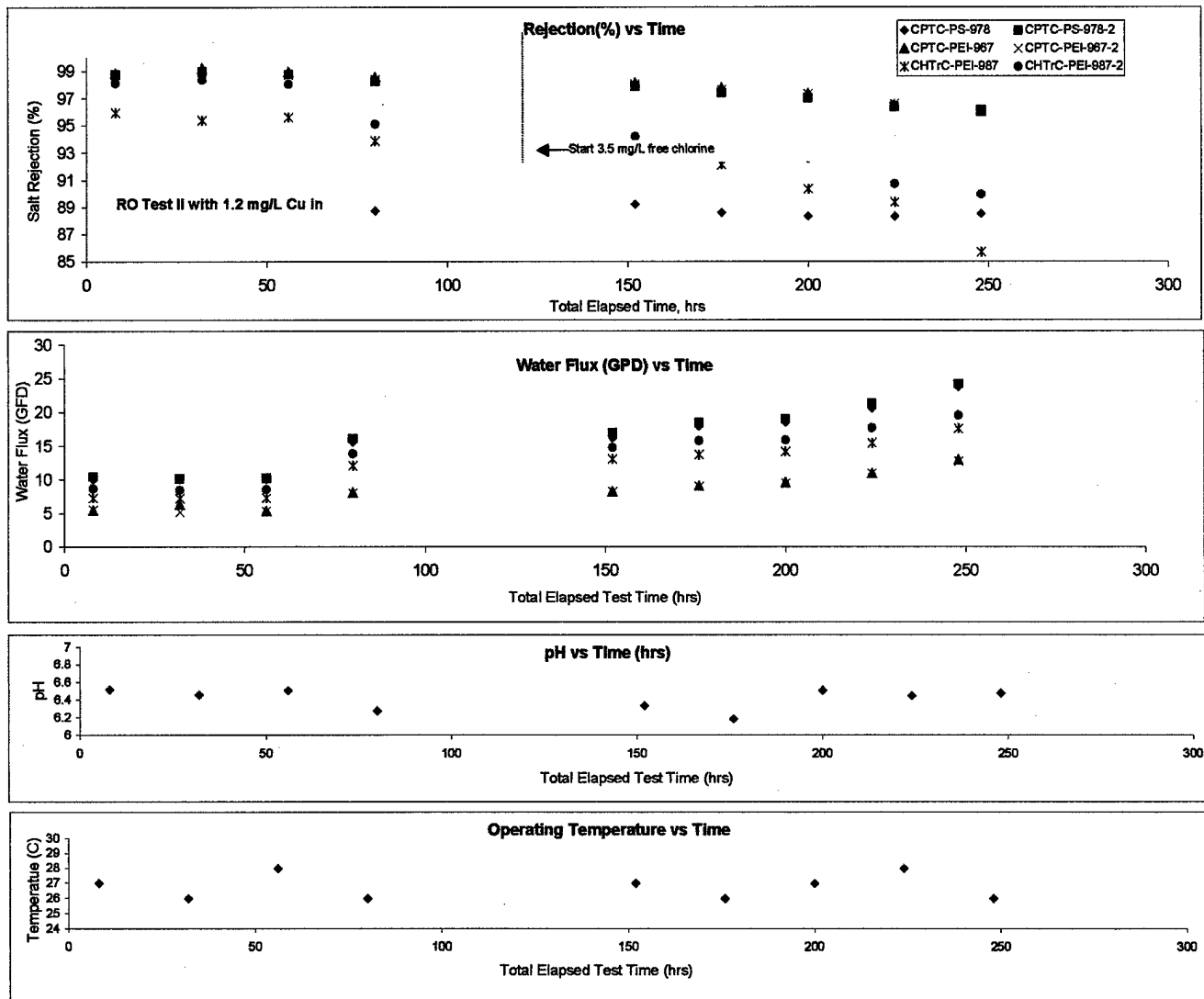
A programmed RO shutdown test was conducted to determine the cause and effect of CPTC PA membrane deterioration after depressurization. The later phenomenon has often been observed in pilot field-testing on chlorinated feeds at the WQIC at Yuma, AZ. At the WQIC test facility the membranes are tested in 1 x 3-inch membrane test cells using a rectangular Buna N "O"-ring seal at the PA membrane surface. Thus, a substantial membrane area is in contact with the "O"-ring. A visible impression is seen on the membrane at the "O"-ring interface after the membranes are removed from the test cells after long-term RO testing. When the membrane impressions are exposed to dye some uptake is observed. The dye uptake could be indicative of membrane damage. The laboratory shutdown test was designed to simulate the long-term RO testing at WQIC on chlorinated feed water but with a programmed shut-down schedule to induce and accelerate membrane damage. The test was conducted with six flat sheet membrane test cells, like those used at the WQIC, to evaluate three membrane types. The PA composite membranes evaluated were CPTC PA on a PS supporting membrane, CPTC PA on a PEI supporting membrane and a CHTrC PA membrane on a PEI supporting membrane. The test operated on 2000 mg/L sodium chloride feed, 200 psi applied pressure, 25 °C, and pH 6.4 with 3.5 mg/L free chlorine. The system was shut down each day after 8 hours of operation. Data was collected just prior to shut down. The test system was shut down a total of 26 times, 18 times after the addition of 3.5 mg/L free chlorine. The performance data is shown in *Figure 20*. Except for membrane CPTC-PS-978-2, the change in performance over this test period was not striking. There were no quantum increases in salt passage after any of the shutdowns. Some deterioration was observed but the test was not conclusive.



Test Conditions: 2,000 mg/L NaCl feed, 200 psi applied pressure, 1.0 gal/min feed flow, normalized to 25°C.

Figure 20. Effects of shutdowns on the long-term performance of CPTC-PS-978, CPTC-PEI-967 and CHTrC-PEI-987. RO system operated 8 hours daily: data collected after 8 hours of operation. Chlorine addition began after 223 hours of operation. No copper in feed water.

A second shutdown test was conducted under the same test conditions but with 1.2 mg/L Cu^{2+} present in the feed steam. The results, shown in Figure 21, show a dramatic increase in salt passage through the membranes with time. This test is indicative of the effect of heavy metals on the catalytic oxidation of PA membranes.



Test Conditions: 2,000 mg/L NaCl feed, 200 psi applied pressure, 1.0 gal/min feed flow, normalized to 25 C

Figure 21. Effects of shutdowns on long-term performance of CPTC-PS-978, CPTC-PEI-967 and CHTrC-PEI-987. RO system operated 8 hours daily: data collected after 8 hrs of operation. 3.5 mg/L chlorine addition began after 72 hours of operation. 1.2 mg/L Cu^{2+} in feed water at the end of the test.

4.10 Modification of Membrane Surface at “O”-Ring Membrane Interface to Minimize Potential Membrane Damage

It was demonstrated in flat sheet RO test cells that a fluorinated tape could be placed on the PA membrane surface at the “O”-ring membrane interface without affecting the transport properties of the membrane. The width of the tape exceeded the width of the “O”-ring so that any damage that may occur at the interface would be sealed. In this way, salt passage should not increase after RO shutdowns.

Near the end of this contract, TMC, CHTrC and CPTC PA membranes whose surfaces were prepared with the fluorinated tape were put on test at the WQIC at Yuma, AZ. to evaluate RO shutdown phenomenon on chlorinated feed water. The test is in progress at this time and is reported in section 4.11.

4.11 Long-Term Pilot Testing at U. S. Bureau of Reclamation's Water Quality Improvement Center (WQIC) at Yuma, AZ on Chlorinated Feed Waters

Long-term field testing of PA composite membranes on chlorinated feed water was begun at the WQIC two months into the program. Two RO test cell units were placed in operation. Each unit contained 9 flat sheet test cells connected in series with a membrane area of 19.4 cm²/cell. Both systems were equipped with an acid injection-pH control system to maintain constant pH. A 3-6 mg/L EDTA concentration was maintained in the feed streams to prevent iron fouling. Pressure was adjusted accordingly to maintain constant flow (about 1 ml/min) based on a permeate flow of a selected test cell (one in each system).

The long-term pilot testing with chlorinated feeds had several objectives: they were:

- To determine the long-term performance and durability of TMC, CPTC, gCPTC, and CHTrC PA composite membranes made on a PEI supporting membrane with. FilmTec PA control membranes that had been made on a PS supporting membrane. The hypothesis being that the PEI supporting membrane has a different chemistry and pore structure than PS that may enhance the bonding of the PA films to the support (See Section 4.5).
- Enhance the adhesion of the CPTC PA layer of the composite membrane to the supporting membrane to prevent damage to the membrane associated with RO shutdowns. Accordingly, CPTC PA were prepared that were supported on a glutaraldehyde washed PEI supporting membrane. The hypothesis being that the glutaraldehyde would crosslink with MPD within the pores and on the surface of the PEI support membrane to enhance the adhesion of CPTC PA film which was later formed on the crosslinked MPD surface. (See Section 4.8, *Figure 18*).
- Determine if membrane deterioration after shutdowns in long term RO tests is due to damage inflicted on the membrane at the O-ring membrane interface. In the most recent test, which remains in progress, fluorinated tape was placed on the surface of the PA surface of the membrane that contacts the O-ring during RO testing (See Section 4.10).

4.11.1 Test Cell Unit 1 (TCU-1) – Clearwell Feed with 1-1.5 mg/L Chlorine

The process flow diagram for TCU-1 is shown in *Figure 22*.

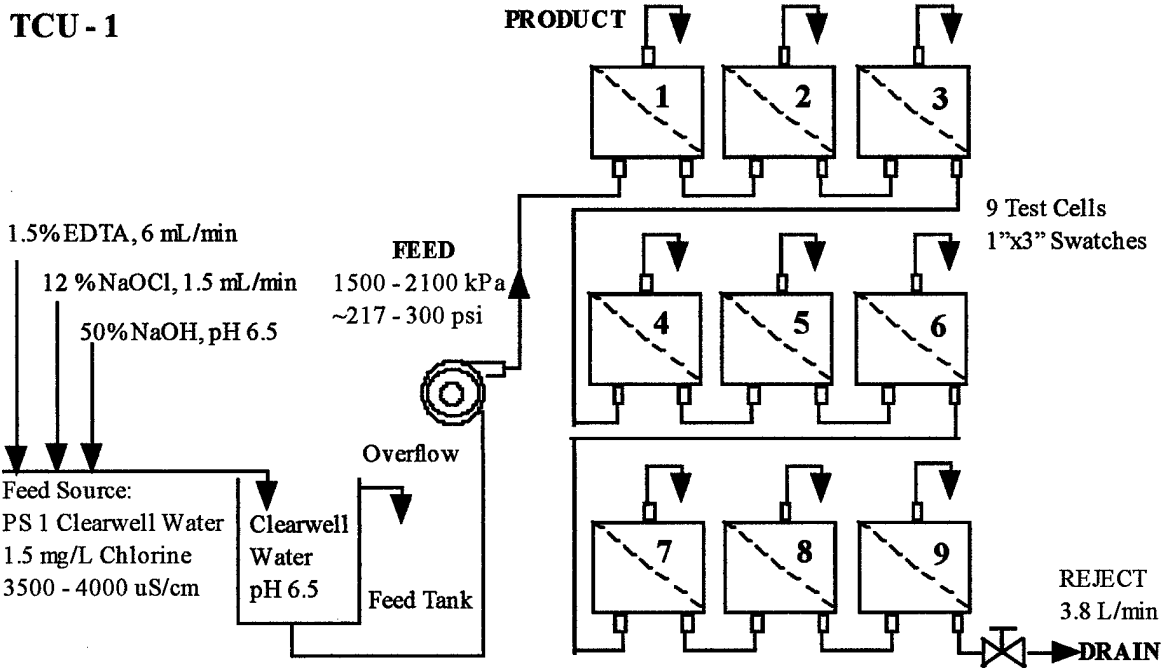


Figure 22. Process flow diagram. Swatch Test Cell Unit 1 (TCU-1) at U.S. Bureau of Reclamation Water Quality Improvement Center, Yuma, AZ.

- **Test Conditions:** Operating pressure 2150-1150 kPa (adjusted to maintain constant permeate flow), operating feed temperature 17-32 C, clearwell feed conductivity (3800 uS/cm), free chlorine 0.0-1.8 mg/L, pH≈6.8-7.0, 6 mg/L EDTA.
- **Membranes:** Nine 1 x 3" membrane swatches operated in series in TCU-1. With the exception of the FilmTecTMC PA control membrane, all of the membranes were made by SST from TMC, CPTC and CHTrC on a PEI microporous support membrane. All commercial PA membranes including the FilmTec TMC control are made on PS microporous supporting membrane.
- **RO Performance of PA Membranes inTCU-1:** See *Figure 23*
- **System Operation:** An interruption in the feed source was encountered after 97 hours into the test. As a result, the unit was secured for nearly one month. After 750 hours of operation the chlorine analyzer failed at which time a large chlorine spike occurred. The concentration was not known.

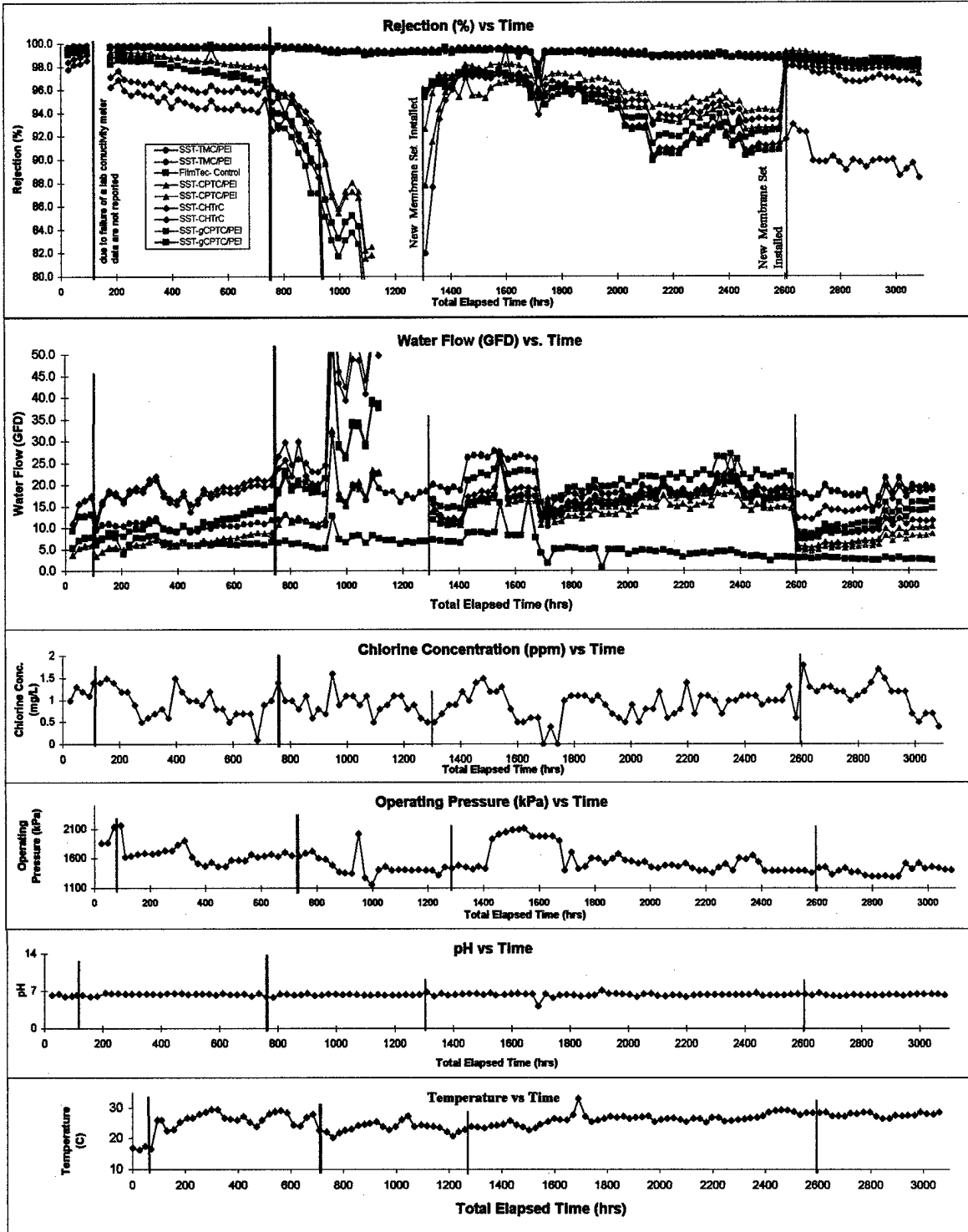


Figure23. RO performance of PA membranes in TCU-1 at WQIC at Yuma, AZ.

Clearwell feed, data normalized to 25 °C

Unit was secured for almost one month afetr 95 hours of continious operation

After 750 h of operation swatch unit recived a large chlorine spike due to failure of the chlorine analyzer

After 1300 h of operation new membranes in swatch cells 4-9 were installed

- **System Shutdowns:** There was one system shutdown after 95 hours into the run.
- **Membrane Fouling:** Throughout the run the FilmTec TMC commercial membranes fouled at a greater rate than the SST PA membranes even though the initial permeate water flux of the FilmTec TMC membrane was lower.

Oxidation Resistance: Membrane deterioration is observed by an increase in salt passage or a decrease in salt rejection. Throughout the 3000 hour test little, if any, change in salt passage was observed for TMC membranes prepared by SST or FilmTec. All CPTC membranes, however, showed deterioration after the initial shutdown which accelerated after the chlorine spike. The first replacement set of CPTC membranes also showed slow deterioration in salt rejection over a 1200 hour period. The second replacement set of CPTC membranes are currently on line and have been operating steadily for approximately 450 hours.

- **Membrane Replacement:** Membranes were replaced twice during the 3000 hour test. The first replacement of six CPTC membranes was installed after 1300 hours of operation due to a chlorine spike after the chlorine analyzer failed. The system was not shut down for the membrane replacement. The order in which membranes were replaced is as follows:

| | | |
|--------|---------------|--------------|
| Cell 1 | TMC/PEI-940 | Not replaced |
| Cell 2 | TMC/PEI-940 | Not replaced |
| Cell 3 | FilmTec TMC | Not replaced |
| Cell 4 | CPTC/PEI-967 | Replaced |
| Cell 5 | CPTC/PEI-967 | Replaced |
| Cell 6 | CHTrC/PEI-961 | Replaced |
| Cell 7 | CHTrC/PEI-961 | Replaced |
| Cell 8 | gCPTC/PEI-983 | Replaced |
| Cell 9 | gCPTC/PEI-983 | Replaced |

A second replacement of CPTC membranes was made after 2580 hours of operation at which time seven membranes were replaced without shutting down the system. The new CPTC replacement membranes were prepared with a strip of fluorinated tape on the PA surface upon which the "O"-ring of the test cells rests. This currently ongoing test is being conducted to determine if the decrease in salt rejection that is observed following system depressurizations is due to physical damage at the "O"-ring/membrane interface. (See Section 4.10)

The order in which membranes were replaced is as follows:

| | | |
|--------|-------------|--------------|
| Cell 1 | TMC/PEI-940 | Not replaced |
| Cell 2 | TMC/PEI-940 | Not replaced |

| | | |
|--------|---------------|--------------|
| Cell 3 | FilmTec TMC | Not replaced |
| Cell 4 | CPTC/PEI-967 | Replaced |
| Cell 5 | CPTC/PEI-967 | Replaced |
| Cell 6 | CHTrC/PEI-961 | Replaced |
| Cell 7 | CHTrC/PEI-961 | Replaced |
| Cell 8 | gCPTC/PEI-983 | Replaced |
| Cell 9 | gCPTC/PEI-983 | Replaced |

- Future Plans:** The current test will continue with the new set of replacement membranes for 1000 hours (~42 days) during which time the salt passage will be followed to determine if membrane deterioration is taking place. If the membranes are stable during this period a series of programmed plant shutdowns will be started to determine if the cause of membrane deterioration is being observed is due to damage of the membrane at the "O"-ring / membrane interface.

4.11.2 Test Cell Unit 2 (TCU-2) – Potable Feed Water with 0.5 mg/L Chlorine

The process flow diagram for TCU-2 is shown in *Figure 24*

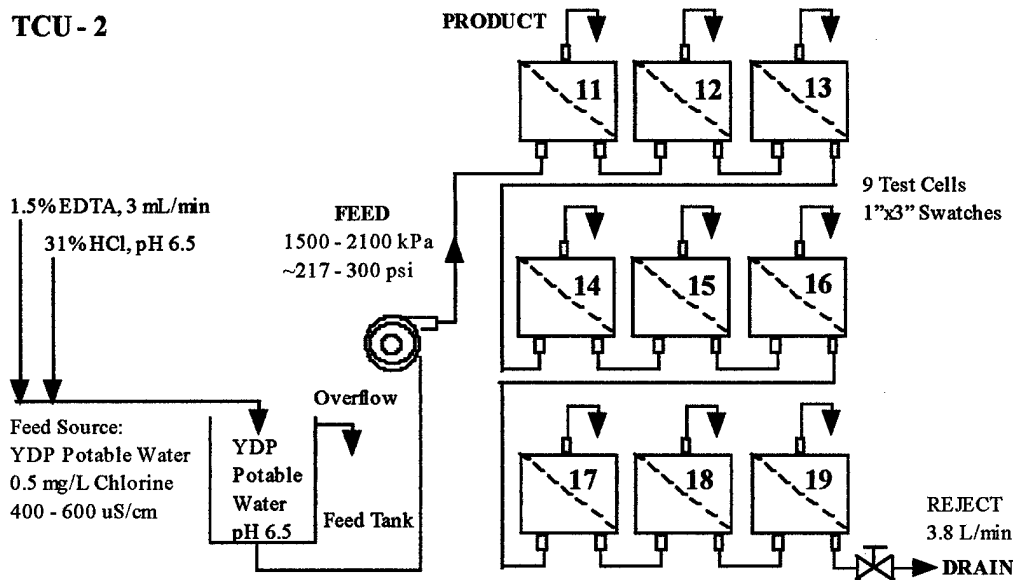


Figure 24. Process flow diagram. Swatch Test Cell Unit 2 (TCU-2) at U.S. Bureau of Reclamation Water Quality Improvement Center, Yuma, AZ.

- Test Conditions:** Operating pressure 2400-1300 kPa (adjusted to maintain constant permeate flow), operating feed temperature 17-37 C, potable water feed conductivity (400-800 uS/cm), free chlorine 0.1- 0.9 mg/L, pH= 6.0-7.0, 3 mg/L EDTA

- **Membranes:** Nine 1 x 3" membrane swatches operated in series in TCU-2. With the exception of the FilmTec TMC PA control membrane, all of the membranes were made by SST from TMC, CPTC and CHTrC on a PEI microporous support membrane. All commercial PA membranes including the FilmTec TMC control are made on PS microporous supporting membrane.
- **RO Performance of PA Membranes in TCU-2:** See *Figure 25*
- **System Operation:** Problems with the reject control valve were encountered during the first 1650 hours of the test which contributed high scatter in the water flux data. After the reject control valve was replaced the water flow data was quite uniform.
- **System Shutdowns:** Six system shutdowns were experienced throughout the 3800 hour test at approximately 250, 425, 850, 1610, 1900 and 3275 hours. No deterioration in membrane performance (salt rejection) was observed after four shutdowns during the initial 1900 hours (79 days) of testing. Except for the FilmTec TMC membrane the water flux exhibited by the all of the membranes was stable.
- **Membrane Fouling:** Unlike FilmTec commercial PA membranes, membranes prepared by SST from TMC, CPTC and CHTrC showed no signs of decreased water flow (fouling) after 3200 hours (133 days) of operation. The permeate flows of the latter membranes were kept constant by adjusting (reducing) the applied pressure throughout the test. After 3200 hours of continuous operation the permeate flow of the FilmTec PA membrane control had decreased from approximately 16 GFD to essentially no flow. It should also be noted that the temperature of the feed water increased during this period increased from 18 to 36 °C.
- **Oxidation Resistance:** Membrane deterioration due to chlorine oxidation is first observed by an increase in salt passage or a decrease in salt rejection. After 1640 hours of operation and after five shutdowns there was no significant change in salt rejection for any of the membranes. Between 1640 and 3300 hours of operation and after the fifth shutdown some increase in salt passage was observed for the FilmTec TMC control membrane, a CPTC membrane and a CHTrC membrane. It is not clear at this time if the increase in salt passage is due to chlorine attack of the PA film or due to inflicted damage on the membrane by the "O"-ring after the last shutdown.
- **Membrane Replacement:** After 3300 hours of operation seven membranes were replaced, without shutting down the system, with new samples having a strip of fluorinated tape on the PA surface upon which the "O"-ring of the test cells rests. This test is being conducted to determine if the decrease in salt rejection that is observed following system depressurizations is due to physical damage at the "O"-ring/membrane interface. (See Section 4.10)

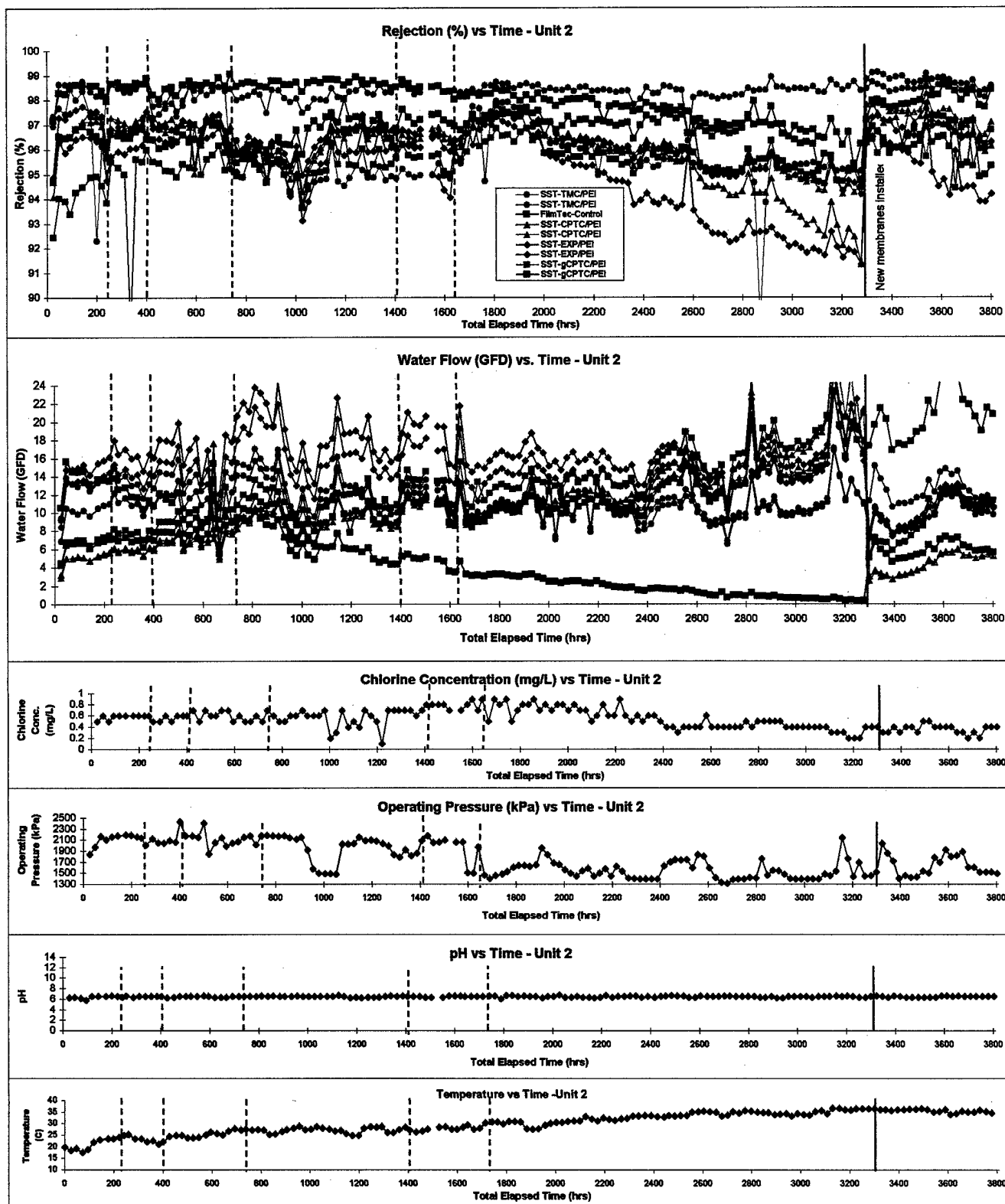


Figure 25. RO performance of PA membrane in TCU-2 at WQIC in Yuma, AZ.

Potable water feed, data normalized to 25 C.

----- unit was shut down (after 225 hours, 395 h, 730 h, 1400 h, 1635 h)

After 3300 h of operation new membranes in swatch cells (except 1 and 9) were installed

The order in which membranes were replaced is as follows:

| | | |
|---------|---------------|--------------|
| Cell 11 | TMC/PEI-940 | Replaced |
| Cell 12 | TMC/PEI-940 | Not replaced |
| Cell 13 | FilmTec TMC | Replaced |
| Cell 14 | CPTC/PEI-967 | Replaced |
| Cell 15 | CPTC/PEI-967 | Replaced |
| Cell 16 | CHTrC/PEI-961 | Replaced |
| Cell 17 | CHTrC/PEI-961 | Replaced |
| Cell 18 | gCPTC/PEI-983 | Replaced |
| Cell 19 | gCPTC/PEI-983 | Not replaced |

- **Future Plans:** The current test will continue with the new set of replacement membranes for 1000 hours (~42 days) during which time the salt passage will be followed to determine if membrane deterioration is taking place. If the membranes are stable during this period a series of programmed plant shutdowns will be started to determine the cause of membrane deterioration is due to damage of the membrane at the "O"-ring / membrane interface.

5.0 FOULING RESISTANT PA COMPOSITE MEMBRANE DEVELOPMENT

Biological fouling of membrane surfaces is a well-known phenomenon and a serious problem encountered in membrane plants. The PA membrane exhibits greater fouling than other types of RO membranes, particularly commercial PA membranes. Studies by Ridgway, in the U.S., and Flemming, in Germany⁶, have indicated that microorganisms exhibit very different affinities for surfaces of different membrane polymers. This suggests that membrane surface chemistry and structure play an important role in the bacterial adhesion process. Thus, membranes having special anti-fouling properties can be designed and manufactured. Ridgway et⁷. al. have shown that the attachment of bacteria to a membrane surface is dependent upon such variables as:

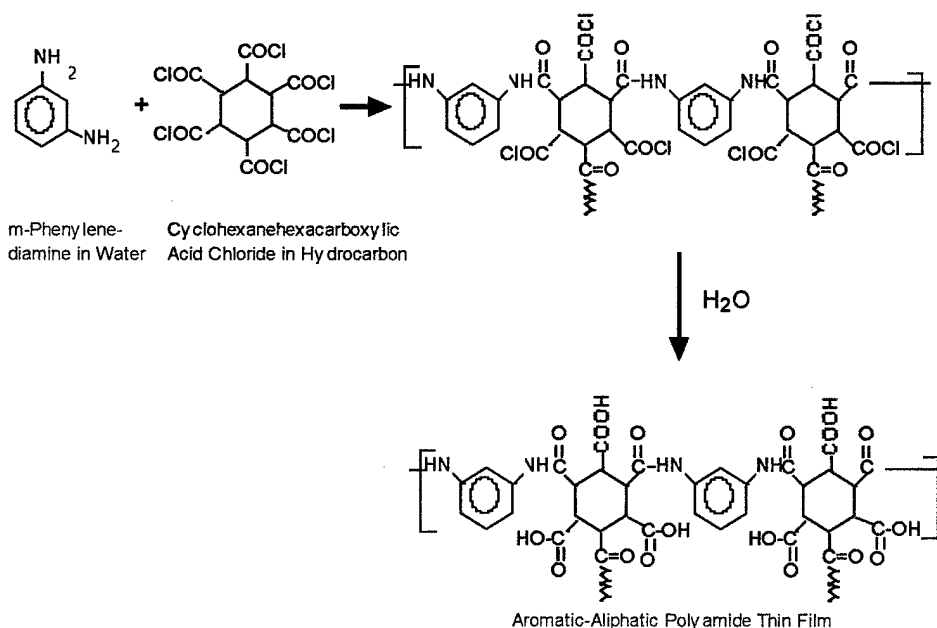
- The hydrophilic/hydrophobic nature of the membrane surface
- Membrane charge, surface roughness and available surface area
- The ionic composition and nutrient composition of the feed water
- The nature of the bacterial cell surface

In these studies, it was shown that the *Mycobacterium* sp. strain is commonly present in pretreated municipal wastewaters used in RO feed. One isolated *Mycobacterium* strain BT2-4, exhibited high attachment to the more hydrophobic PA membrane and low attachment to the more hydrophilic cellulose acetate (CA) membrane. Hydrophilic polymers exhibit greater water uptake than hydrophobic polymers. The highly cross-linked structure of the PA membrane has an intrinsic water content of ~ 5% while CA has an intrinsic water content of ~ 14%. PS membranes are very hydrophobic and foul very rapidly. However, when the PS membrane is

made more hydrophilic by incorporating sulfonated polysulfone into the membrane matrix, bacterial attachment is greatly reduced. During a parallel program, a procedure was devised to increase the hydrophilic surface immediately after interfacial formation.

5.1 Synthesis of Cyclohexanehexa Acid Chloride (CHHC) and the Preparation of CHHC PA Composite Membranes

The hydrophilicity of the PA film can be increased by incorporating a more hydrophilic monomer into the PA structure. Toward this end, cyclohexanehexa acid chloride (CHHC) was synthesized and purified for reaction with MPD. CHHC has a six member aliphatic ring substituted with six acid chlorides. CHHC is soluble in hexane at the concentration commonly used with TMC and CPTC. It has been shown by modeling that only three of the acid chlorides react with MPD. That is, in the 1,3,5 positions just as with TMC. The reaction for forming the PA is shown by the following equation.



CHHC Acid Chloride Polyamide Membrane

The unreacted and remaining acid chlorides of CHHC after forming the PA film hydrolyze to carboxyl groups. The carboxylic groups are charged and hydrophilic. In this way the hydrophilicity of the PA film can be greatly increased. In beaker experiments a strong PA film was formed at the aqueous MPD – hexane CHHC interface. However, the transport properties of the CHHC PA composite membranes were disappointing. The observed water flux was high but with correspondingly high salt passage. Nevertheless, this is a promising approach and requires further optimization. The RO performance of the membranes is given in Table 9.

Table 9

Reverse Osmosis Performance of CHHC Polyamide Composite Membranes

Test Conditions: 800 psi applied pressure, 35,000 sodium chloride feed, pH 6.35, 30.5 °C

| Composite Membrane Identification | Supporting Membrane Identification | MPD/ CHHC Molar Ratio | CHHC Molar Concentration (M) | Reverse Osmosis Performance | |
|-----------------------------------|------------------------------------|-----------------------|------------------------------|-----------------------------|---------------|
| | | | | Water Flux (gfd) | Rejection (%) |
| 1020 | PEI 218 | 150:1 | 0.00236 | 38.8 | 37 |
| 1024 | PEI 218 | 75:1 | 0.00472 | 34.7 | 78 |
| 1025 | PEI 218 | 30:1* | 0.0118 | 45.5 | 70 |

CHHC = cyclohexanhexacarboxylic acid chloride

* Limit of CHHC solubility in hexane

5.2 Attachment of Glycidol to the Surface of CPTC PA Composite Membranes to Increase Surface Hydrophilicity

The surface hydrophilicity of the CPTC PA membrane can be increased by covalently attaching hydrophilic groups to the PA film during formation as shown in Figure 26. After the interfacial

Attachment of Glycidol to Polyamide Membrane Surface

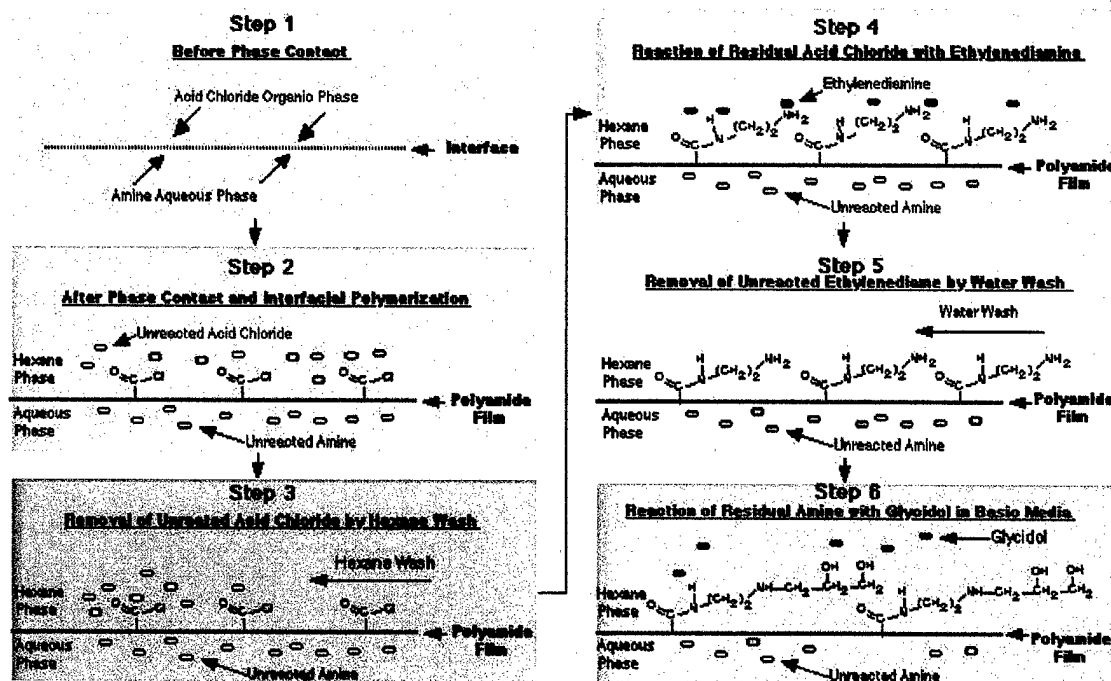


Figure 26. Process steps for reacting residual acid chloride sites on polyamide film surface with ethylenediamine and subsequently glycidol.

reaction of CPTC with MPD is complete, and before further processing, the PA layer that is formed is rich in unreacted acid chloride groups. At this stage in the process, the surface is washed with hexane (Step 3) to remove any excess acid chloride that has not reacted with MPD. Subsequently (Step 4), the surface is washed with an aqueous solution of ethylenediamine. Ethylenediamine reacts with the acid chloride groups thereby introducing free primary amine groups to the surface of the PA film. After washing away the excess and unreacted amine (Step 4), the free amine groups are reacted with glycidol (Step 6) to add hydroxyl groups to the PA surface thereby increasing hydrophilicity.

The RO performance of the glycidol modified CPTC membrane is shown in Table 10. Unexpectedly, the water flux was only half that of the unmodified controls. Like all CPTC PA composite membranes, the salt passage decreased significantly after sodium hypochlorite was added to the feed. Since the water flow of the modified CPTC PA membrane was low, the membrane were not evaluated for fouling in long term pilot testing on municipal waste water feed at OCWD. Additional work should be conducted on this system to optimize the glycidol reaction with the PA membrane surface.

Table 10

**Reverse Osmosis Performance of CPTC Polyamide Membranes
Modified with Glycidol on PA Surface**

Test Conditions: 800 psi applied pressure, 35,000 mg/L sodium chloride feed, pH 6.4, 30.5 °C

| Membrane Identification Composite/ Porous Support | Ethylenediamine Wash See Step 5, Fig 23 | Glycidol Wash See Step 6, Fig 23 | Reverse Osmosis Performance | |
|--|--|-------------------------------------|-----------------------------|---------------|
| | | | Water Flux (gfd) | Rejection (%) |
| 989/ PEI 218-2 | None | 10% glycidol in DI water | 12.1 | 98.0 |
| | | | 5.2* | 99.66* |
| 990/ PEI 218-2 | None | 10% glycidol in DI water | 12.8 | 97.0 |
| | | | 5.4* | 99.63* |
| 995/ PEI 218-2 | 10% ethylenediamine in DI water | 10% glycidol in DI water | 5.0 | 96.6 |
| | | | 3.7* | 99.32* |

* 1 hour after the addition of 1.5 mg/L sodium hypochlorite to the feed.

6.0 SUMMARY AND CONCLUSIONS

Cyclopentanetetracarboxylic acid chloride (CPTC), cyclohexanetricarboxylic acid chloride (CHTrC) and cycloheptanetricarboxylic acid chloride (CHHC) were synthesized, purified and reacted interfacially with m-phenylenediamine (MPD) on the porous surfaces of polysulfone (PS), polysulfone / sulfonated polysulfone (PS / SPEES/PES) and polyetherimide (PEI) supporting membranes to process PA composite RO membranes. The performances of these membranes were compared with those of PA composite membrane formed interfacially between trimesoyl chloride (TMC) and MPD on the same and differing porous supporting membranes.

SEMs of the cross sections of PS, PS / SPEES/PES and PEI porous supporting membranes show that the substructures of the membranes are quite different.

RO tests have shown that the salt transport properties of TMC, CPTC and CHTrC PA membranes, when supported on PEI supports, do not deteriorate after prolonged immersion in strong solutions of sodium hypochlorite at pH 6.0. Under the same conditions, the same PA membranes supported on either PS or PS / SPEES/PES) deteriorate significantly. It is hypothesized that the aromatic rings of the PS support membrane may become chlorinated thereby compromising the ability of the membrane to support the PA film. More work is required to determine if the PS supporting membrane is a major cause of chlorine attack on the PA membrane. PS is the supporting membrane upon which all commercial PA composite membranes are made.

It was demonstrated during long term RO field tests on chlorinated feed waters at the WQIC in Yuma, AZ. that:

- Commercial FilmTec TMC membranes foul very rapidly when compared with SST TMC membranes. The latter showed little, if any, loss in flow over several thousand hours of operation.
- CPTC PA membranes, when compared to TMC PA membranes, exhibit a greater tendency to deteriorate (increased salt transport) after plant shutdowns and / or chlorine spikes. The cause of greater deterioration may be due to membrane damage at the 'O' ring - membrane interface. Further studies are required to determine the mechanism.
- The stability of TMC PA membranes is similar whether supported on PEI or PS porous support membrane.
- When Cu^{+2} is added to a chlorinated RO feed at pH 6.5, the deterioration of both CPTC and TMC PA membranes is very rapid. Salt passage doubles after a few hundred hours, a result of heavy metal catalyzed chlorine oxidation. Thus, all mechanism studies must be conducted in the absence of heavy metals.

Several methods were examined to improve bonding of the CPTC PA film to the porous supporting membrane and to attach hydrophilic moieties to the surface of PA film to reduce fouling. Each of these methods are quite promising but require further studies.

Considerable progress was made during the program in the development of a PA RO membrane for use in the military's mobile reverse osmosis purification units (ROWPU's) that is both oxidation (chlorine) resistant and low fouling. Further work is required to meet these objectives. To attain these goals it is recommended that the following studies be continued:

- *Monomer Synthesis and Design:* Design, synthesis, and characterization of novel multifunctional amine and acid chloride monomers (including CPTC derivatives) possessing hydrophilic substitutions designed to block potential chlorinating (bromination) sites. Molecular simulations should be used to help delineate the range of substituted monomers to be synthesized and tested.
- *Monomer Modeling and Chlorination Simulation:* Use molecular modeling to study the synthesized amides. There may be several iterations of molecular modeling-synthesis until the most hopeful candidates are found for actual membrane production.
- *Polysulfone Support Membrane Chlorination:* Additional studies should be conducted to improve the understanding of factors controlling the stability of interactions between the PA thin films and the PS support layer. Several new approaches should be studied for improving the adhesion between the permselective PA thin film and the PS support. Chlorination of the PS support may be a possible mechanism for PA film failure. Modification of the PS support and/or alternative support materials should be considered if this mechanism is confirmed.
- *Biofouling:* Modify PA membrane surface to make it less attractive (adhesive) and/or biocidal to bacteria, primarily by increasing the surface wettability and reducing charge.
- *PA Membrane Development:* Convert newly designed and synthesized amine and/or acid chloride monomers into PA membranes that exhibit competitive transport properties, low fouling and oxidation (chlorine) resistant.
- *CPTC PA Membrane Durability:* Determine the cause and solution for membrane degradation associated with RO system shutdowns after long-term RO field testing on chlorinated feeds.
- *Membrane Biodegradation:* Distinguish between chemical attack from chlorination (bromination) reactions and biological attack on the CPTC PA membrane.

7.0 REFERENCES

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