

## **Appendix 2.4 B 1**

### **Task 2.4 B 1: Investigate chlorine tolerant thin film composite RO membranes**

**Submitted by:**

Project Development Group  
Orange County Water District  
10500 Ellis Avenue  
Fountain Valley 92728, California

**Submitted to:**

California Energy Commission  
Sacramento, California

January 2002

## **Legal Notice**

This report was prepared as a result of work sponsored by the California Energy Commission (Commission). It does not necessarily represent the views of the Commission, its employees, or the State of California. The Commission, the State of California, its employees, contractors and subcontractors make no warranty, express or implied, and assume no legal liability for the information in this report; nor does any party represent that the use of this information will not infringe upon privately owned rights. This report has not been approved or disapproved by the Commission nor has the Commission passed upon the accuracy or adequacy of the information in this report.

## **Acknowledgement**

This study would not have been possible without the support of the Board of Directors of the Orange County Water District. The authors gratefully acknowledge the Orange County Water District Water Resources & Technology Department and the Water Production Group for their assistance and technical insight.

## Table of Contents

Preface	vi
Executive summary	vii
Abstract	xi
1.0 Introduction	1
1.1 Background and Overview	
1.2 Project Objectives	
2.0 Project Approach	3
2.1 Membranes	
2.2 Computer Modeling	
2.3 Flat Sheet Membrane Test Unit	
3.0 Project Outcomes	8
3.1 Evaluation of CPTC1 membrane on lime clarified secondary municipal effluent	
3.2 Evaluation of CPTC2 membrane on lime clarified secondary municipal effluent	
3.3 Evaluation of CPTC2 membrane on media filtered secondary municipal effluent	
4.0 Conclusions and Recommendations	15
4.1 Conclusions	
4.2 Commercialization Potential	
4.3 Recommendations	
4.4 Benefits to California	
References	18
Glossary	20

## **List of Figures (in text)**

Figure 1 – TFC membrane degradation

Figure 2 – Rendering of a typical polyamide RO membrane

Figure 3 – Chemical composition of typical TMC/MPD polyamide membranes

Figure 4 – Chemical composition of a CPTC/MPD polyamide membrane

Figure 5 – Six possible stereoisomers of 1,2,3,4-cyclopentanetetracarboxylic acid chloride

Figure 6 – Plot of the steric energies exhibited by six stereoisomers of CPTC

Figure 7 – Flat sheet membrane test unit

Figure 8 – Illustration of a flatsheet RO membrane test cell

Figure 9 – Water Factory 21 and Green Acres Project treatment trains

Figure 10 – Normalized membrane performance of CPTC1 membranes

Figure 11 – Selected images of fouled membrane samples after 5000 hours of service

Figure 12 – Normalized membrane performance of CPTC2 membranes

Figure 13 – Selected images of fouled membrane samples after 4900 hours of operation

Figure 14 – Normalized membrane performance of CPTC26 membranes

## **List of Tables (in text)**

Table 1 – Initial performance of data of PA membranes prepared with CPTC acid chloride

Table 2 – Membrane performance data for the CPTC1 membrane series

Table 3 – Membrane performance data for the CPTC2 membrane series

Table 4 – Membrane performance data for the CPTC2 membrane series on Green Acres Project feed water

## Preface

The Public Interest Energy Research (PIER) Program supports public interest energy research and development that will help improve the quality of life in California by bringing environmentally safe, affordable and reliable energy services and products to the marketplace.

The PIER Program, managed by the California Energy Commission (Commission), annually awards up to \$62 million to conduct the most promising public interest energy research by partnering with Research, Development and Demonstration (RD&D) organizations including individuals, businesses, utilities and public or private research institutions.

Pier funding efforts are focused on the following six RD&D program areas:

- Building End-Use Energy Efficiency
- Industrial/Agricultural/Water End-Use Energy Efficiency
- Renewable Energy
- Environmentally-Preferred Advanced Generation
- Energy-Related Environmental Research
- Strategic Energy Research

What follows is the final report for Task 2.4 Salinity Removal Technologies, Sub-task: *Investigate chlorine tolerant thin film composite RO membranes*, conducted by the Orange County Water District. This report is entitled *Investigate chlorine tolerant thin film composite RO membranes*. This project contributes to the Energy-Related Environmental Research program.

For more information on the PIER Program, please visit the commission Web site at: <http://www.energy.ca.gov/research/index.html> or contact the Commission's publication Unit at 916-654-5200

## **Executive Summary**

As demand for water continues to grow in the western United States and other semi-arid regions throughout the world, developing safe and reliable water from non-traditional sources is becoming ever more attractive. The use of membrane separation processes has been shown to successfully treat a variety of challenging water types from seawater and brackish groundwater to industrial and process wastewaters. This project evaluated the performance of a newly developed reverse osmosis (RO) membrane for its ability to treat secondary municipal wastewater.

### **Background and Overview**

The development of the polyamide (PA) thin-film composite (TFC) reverse osmosis membrane has successfully enabled water producers to treat a variety of water sources to near distillation quality. Despite the high quality of the water produced by this process, TFC membranes are prone to both colloidal and biological fouling, which both serve to limit the effectiveness of this treatment process. In treating high biologically active wastewaters, membrane biological fouling (biofouling) is often times one of the most pronounced limitations. Numerous and costly pretreatment measures must be carried out in an effort to limit the onset of membrane biofouling. Chlorine and other disinfectants are commonly introduced into the feedwater to limit the occurrence of biological fouling. While this practice is generally effective, it can result in degradation of TFC membranes, which are susceptible to chemical attack by strong oxidizing agents such as chlorine. The development of a chemically tolerant, low-fouling TFC membrane would substantially reduce the cost associated with this advanced water treatment process.

### **Objective**

The performance of a chemically tolerant, low-fouling reverse osmosis (RO) membrane was evaluated at the Orange County Water District (OCWD) for its ability to treat clarified secondary municipal wastewater effluent. This RO membrane was previously

synthesized via an interfacial reaction between cyclopentanetetracarboxylic (CPTC) acid chloride, a tetrafunctional acid chloride, and the di-functional amine *m*-phenylenediamine (MPD). The supply of this membrane was limited since it is still in an adolescent stage of development. As a result, testing was conducted using flat sheets of membrane. Testing of the CPTC membrane was conducted using two different plant feedwaters produced at OCWD: Water Factory 21 and Green Acres Project (GAP). Membrane performance was compared to that of commercially available TFC membranes.

## **Project Approach**

### *Membranes*

Most commercial TFC membranes today are made by forming a thin-film layer (or a salt rejection barrier) on top of a polysulfone surface. The thin-film layer is formed by an interfacial reaction between trimesoyl chloride (TMC) and *m*-phenylenediamine (MPD). The CPTC membrane is also formed in a similar fashion with the exception that TMC is replaced with CPTC in the formation of the salt rejection barrier.

### *Computer Modeling*

An understanding of the chemical interactions associated with the formation of the thin-film rejection layer is critical in the development of a highly efficient TFC membrane. In this case, molecular modeling was employed to investigate the molecular properties and interactions of the CPTC molecule. The CPTC molecule exists in six unique forms, depending on the orientation of the acid chloride groups. More specifically, these forms are known as stereoisomers, which are molecules with the same bonding topology but vary in the spatial arrangement of the atoms. Molecular modeling exercises indicated that some forms of the CPTC were more stable than others based on their molecular atom orientations. With this, it is feasible that a more stable, chemically robust thin-film layer may be formed when using the more stable CPTC compound. This may explain the differences in membrane performance cited in the literature when different forms of CPTC were used.

### *Flat Sheet Membrane Test Unit*

CPTC membrane performance was conducted using two flat sheet membrane test units (MTU), which were designed to simulate routine operating conditions. Each unit was composed of test cells, each capable of holding a flat sheet of membrane approximately 20cm<sup>2</sup>. The influent to each MTU was supplied from two OCWD treatment plants: Water Factory 21 (conventional pretreatment including a five-stage clarification process) and Green Acres Project (three-stage pretreatment process consisting of coagulation, mixed media filtration and chlorine disinfection).

### **Project Outcomes**

Membrane performance of the CPTC membrane was found to be equal, or superior to traditional commercial RO membranes operated simultaneously at OCWD. Solute rejection (water quality) was comparable while the total product water production (gal./ft<sup>2</sup>) was generally greater than the commercial membranes. The rate at which water production (or flux) declined (an indicator of membrane fouling) was also generally lower than the commercial membranes. In one trial, the CPTC membrane exhibited a dramatic difference in the rate of flux decline when compared to the commercial control. This observation suggests the CPTC membrane may have exhibited a moderate degree of fouling resistance.

### **Conclusions & Recommendations**

#### *Conclusions*

- The CPTC membrane used in this study consisted of a stable polymer system as determined by molecular modeling exercises.
- Performance of the CPTC membrane was equal, or superior to commercial TFC membranes.
- The CPTC membrane exhibited a degree of fouling resistivity based on performance models observed throughout the testing period.

### *Commercialization Potential*

- It has been successfully shown that membrane separation processes can successfully treat a variety of challenging water types. As a result the membrane industry is continually expanding as the demand for safe and reliable potable water continues to increase.
- Commercial TFC membranes in the marketplace lack chemical tolerance to such oxidants as chlorine. A chemically tolerant, low-fouling TFC membrane could quickly expand in the current membrane environment.

### *Recommendations*

- Since the CPTC membrane is still in its adolescence, more testing would be required to determine the practicability of this membrane as an alternative to conventional TFC membranes in treating high-fouling water and wastewater sources.
- Testing of the CPTC should be expanded using small spiral wound elements. This signifies the “next step” in membrane evaluation. Membranes used in this configuration, while more costly, will simulate those used in large treatment facilities.

### *Benefits to Southern California*

- Developing non-traditional water sources for potable purposes require advanced water treatment facilities, which ultimately include membrane processes. The use of highly efficient, low-fouling membranes would ultimately increase product water throughput while minimizing associated treatment costs.
- TFC polyamide membranes operate at lower operating pressures than cellulose acetate membranes, which translates into energy cost savings. Fouling resistant TFC membranes would further reduce energy costs since less biofilm would proliferate and load on the membrane surface, resulting in higher operating pressures and subsequently higher energy costs.

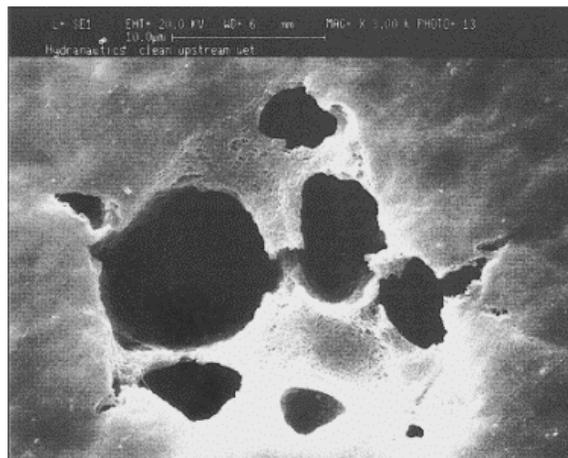
## Abstract

Reverse osmosis (RO) membranes are widely utilized throughout California and the nation to purify water for municipal and industrial applications ranging from wastewater reclamation and groundwater treatment to ultrapure water production for the semiconductor industry. Although RO membranes generally function well, they nevertheless are prone to biological fouling (biofouling), *i.e.*, the gradual build up of organic matter and microorganisms on their surfaces. Biofouling reduces the operational efficiency of RO membranes and increases system energy consumption and O&M costs. Chlorine is commonly used to slow the progression of RO membrane biofouling but can itself degrade the membranes if it is not used with special care. Thus, a need exists for a more chemically robust RO membrane that can better withstand the rigors of prolonged field operation under conditions where chlorine suppression of biofouling is practiced. A new chlorine resistant, low-fouling thin-film composite RO membrane was prepared from an interfacial reaction between cyclopentanetetracarbonyl chloride (CPTC), a tetrafunctional acid chloride, and the di-functional amine *m*-phenylenediamine (MPD). This membrane will be evaluated for its performance in treating high fouling secondary municipal wastewaters.

## 1.0 Introduction

### 1.1 Background and Overview

With recent advances in membrane treatment technologies, reverse osmosis (RO) has quickly developed into a mature and reliable technology utilized in a variety of water and wastewater applications. The development of the polyamide (PA) thin-film composite (TFC) membrane by Cadotte and coworkers (1980) has given the water treatment community a choice between two major membrane types: TFC and cellulose acetate (CA) membranes. While differences between the two membrane types exist and have been documented elsewhere (Byrne, 1995), the TFC membrane has largely displaced the CA membrane due to its superior operating performance (greater membrane water production (flux) at lower operating pressures) and improved product water quality. Despite these advancements, however, the occurrence of biotic and abiotic (colloidal) fouling continues to limit the efficient operation of membrane separation processes (Bharwada et al., 2000; Faibish et al., 1998; Ridgway, 1988; Ridgway and Flemming, 1996). In treating secondary municipal wastewater effluent, the occurrence of membrane biofouling is often times the most insidious forms of membrane fouling which can debilitate RO treatment systems. Membrane biological fouling results in a host of deleterious effects such as: (1) increased differential pressure, (2) reduced water production or flux, (3) deteriorated water quality due to solute loading on the membrane surface and (4) biodegradation of membrane polymer and element components such as polyurethane glue seals (Flemming et al., 1993, 1994). In an effort to slow the progression of biological fouling, various pretreatment measures are carried out such as lime clarification, pre-filtration (via microfiltration or ultrafiltration),



**Figure 1. TFC membrane degradation caused by free chlorine in the feedwater. Photo courtesy of Hydranautics.**

disinfection, etc. As part of common disinfection practices, chlorine and other oxidizing agents are routinely introduced in the RO feedwater to control membrane biological fouling. While this practice is generally effective, it can result in degradation to TFC membranes, which are susceptible to attack by strong oxidizing chemical agents. While most TFC membranes show limited tolerance to chlorine, membrane degradation may occur in as little as one week when exposed to 1 mg/L of free chlorine. Scanning electron microscopy imaging illustrates the effect of oxidation on a membrane thin-film due to chlorine exposure (Figure 1). Costly dechlorination measures such as activated carbon or chemical reducing agents must be added to the RO feedwater to eliminate this effect. Dechlorinating, however, essentially nullified disinfection on the membrane surface. Adding ammonia to a feed stream containing chlorine results in the formation of chloramines, which do not appreciably affect membrane performance. However, the bactericidal effectiveness of chloramines is significantly less than that produced by free available chlorine. It is estimated that 25-times as much chloramines are needed to produce the same germicidal efficiency as that of free chlorine (Dychdala, 1991). A chemically tolerant, low-fouling RO membrane would substantially reduce or possibly eliminate expensive pretreatment processes, frequent membrane cleanings, replacements and overall operations & maintenance costs.

## **1.2 Objective**

Several versions of an experimental TFC RO membrane, designed to withstand prolonged operation on chlorinated feedwaters while exhibiting low biological fouling propensities, were evaluated at the Orange County Water District (OCWD). The chemically tolerant, low-fouling membrane was prepared from an interfacial reaction between cyclopentanetetracarboxylic (CPTC) acid chloride and *m*-phenylenediamine (MPD). Membranes were evaluated using secondary municipal wastewater effluent provided by the Orange County Sanitation District, Fountain Valley, CA. Membranes were tested using different feedwaters produced by two treatment plants: Water Factory 21 and Green Acres Project (GAP). Membrane performance was compared to that of

traditional TFC membranes to assess the viability of this membrane as an alternative to TFC membranes currently found in the marketplace.

## 2.0 Project Approach

### 2.1 Membranes

Commercially available TFC polyamide membranes are made by forming a thin film layer via an interfacial reaction between trimesoyl chloride (TMC) and *m*-phenylenediamine (MPD). This film is formed on a polysulfone surface, which is prepared on a non-woven polyester support fabric (Figure 2). The chemical composition of a typical TFC membrane is illustrated in Figure 3.

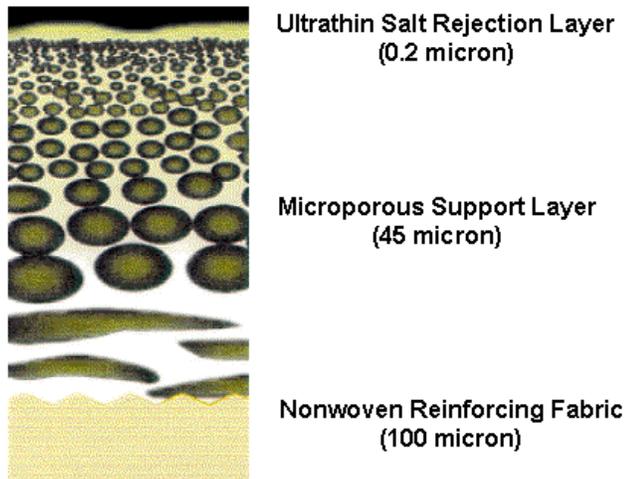


Figure 2. Rendering of a typical TFC polyamide RO membrane. Courtesy of Toray Industries, Inc.

The CPTC TFC membrane was prepared by Separation Systems Technology, Inc., San Diego, CA (SST). The membrane was created by an interfacial reaction of 1,2,3,4-cyclopentanetetracarboxylic (CPTC) acid chloride and *m*-phenylenediamine (MPD). The synthesis of the CPTC RO membrane was first reported in a U.S. Patent (#4,749,488, 1988), which outlined the preparation of

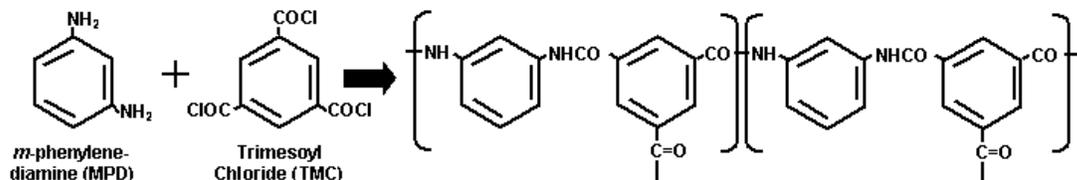


Figure 3. Chemical composition of a typical TMC/MPD polyamide membrane.

the CPTC membrane by an interfacial condensation reaction of 1,2,3,4-CPTC acid chloride with MPD (Figure 4). The 1,2,3,4-CPTC molecule has four reactive acid chloride groups that create six possible stereoisomers or geometric forms of the compound. In previous literature, Ikeda et al., (1993) reported that the chlorine tolerance of the CPTC membrane depended on which isomeric (or geometric) form was used during membrane synthesis. The results of this research demonstrated the importance of steric configurations (compound geometry) in the development of a stable, chlorine resistant TFC membrane.

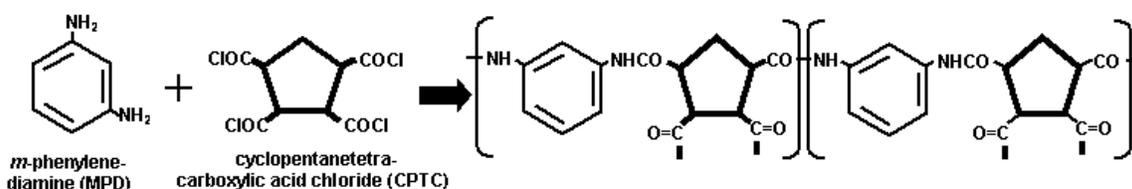


Figure 4. Chemical composition of a CPTC/MPD polyamide membrane.

To that end, SST focused on preparing the CPTC membrane using isolated and purified isomeric forms of the acid chloride. In this study, two sets of CPTC membranes were evaluated. The purity of the CPTC used in the first set (CPTC1) was 98% (determined by GC/MS). The purity of the CPTC acid chloride used in the second set (CPTC2) increased to greater than 99%. The initial performance data for these membranes are illustrated in Table 1.

**Table 1. Initial Performance Data of Polyamide Membrane Prepared with CPTC Acid Chloride.**

Acid Chloride Lot	Purity	Reverse Osmosis Performance	
		Water Flux (GFD)	Rejection (%)
<b>CPTC1</b>	<b>98%</b>	<b>19.2</b>	<b>98.6</b>
<b>CPTC2</b>	<b>99+%</b>	<b>11</b>	<b>99.3</b>

Test Conditions: 2000 mg/L NaCl feed; 225 psi applied pressure; 25°C; pH 6.9.

## 2.2 Computer Modeling

Computer molecular modeling was employed to gain an insight into the steric configurations of the CPTC molecule. Elucidating the molecular properties of the CPTC compound could validate the observations of Ikeda (1993) regarding the importance of steric configuration. Molecular models of the six possible stereoisomers of the CPTC

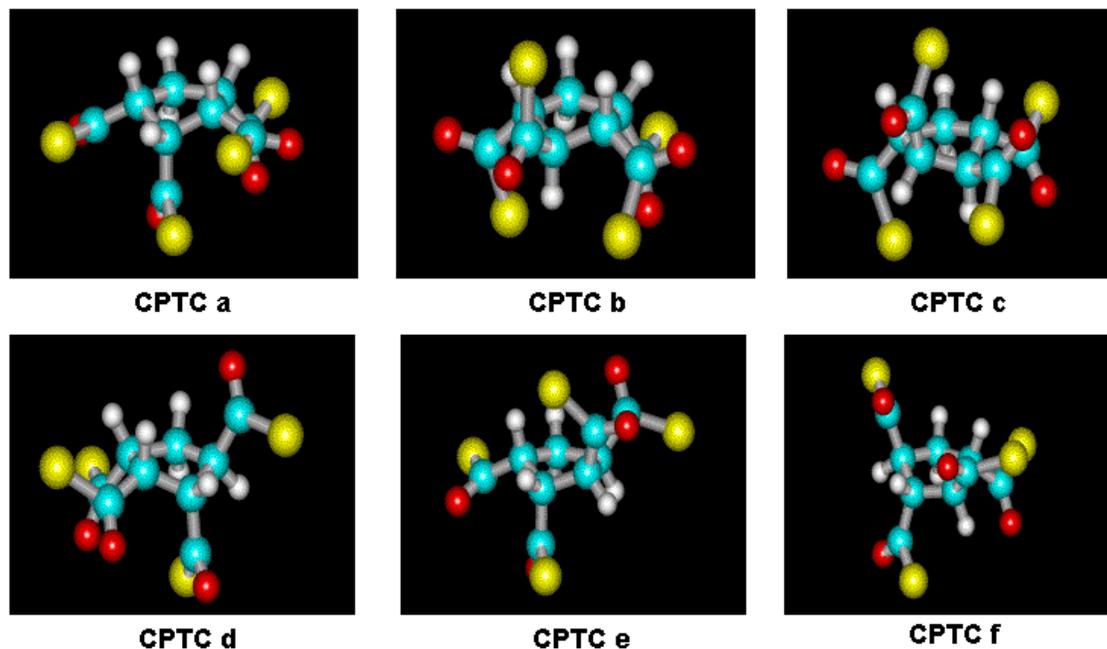


Figure 5. Six possible stereoisomers of 1,2,3,4 – cyclopentanetetracarboxylic acid chloride. Red atoms = oxygen; yellow atoms = chlorine; blue atoms = carbon; white atoms = hydrogen.

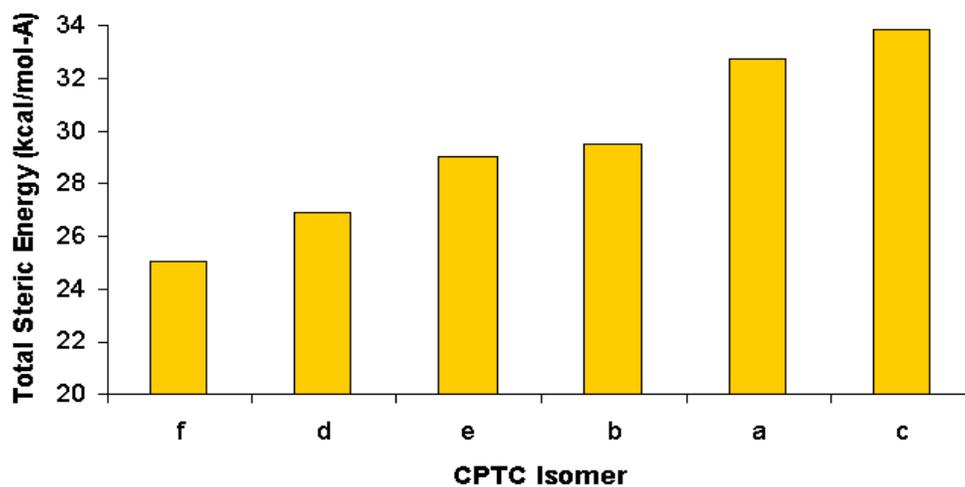
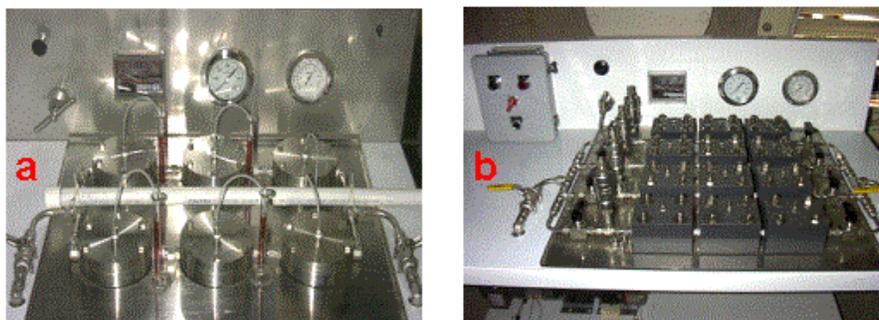


Figure 6. Plot of the steric energies exhibited by the six stereoisomers of CPTC. (PM3 semi-empirical force field; <0.1kcal/mol-A)

compound are illustrated in Figure 5. Each isomer was geometrically optimized to  $<0.001$  kcal/mole-Å using the Polak-Ribiere algorithm via classical mechanics (MM+, HyperChem, Gainesville, FL). Molecular dynamics simulations were then performed to determine which isomer exhibited the greatest stability (lowest energy) with the least amount of steric interference (Figure 6). The CPTCf acid chloride isomer exhibited the lowest, most stable geometric configuration. The increase in bond angle stability could feasibly aid in the formation of a stable bond between an amine and an acid chloride. The bond angles formed between the acid chloride and the MPD must be sterically optimized for maximum membrane stability. It is feasible that this stability may be responsible for the increase in chlorine resistance reported in the literature.

### 2.3 Flat Sheet Membrane Test Unit

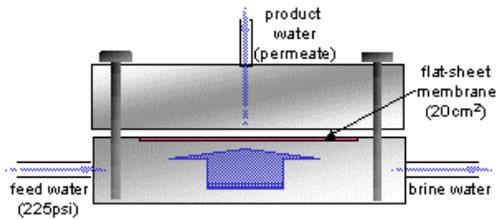
Membrane performance testing was conducted using two flat sheet membrane test units



**Figure 7. Flat sheet membrane test unit fed with Water Factory 21 RO Feed (a) and Green Acres Project Water (b).**

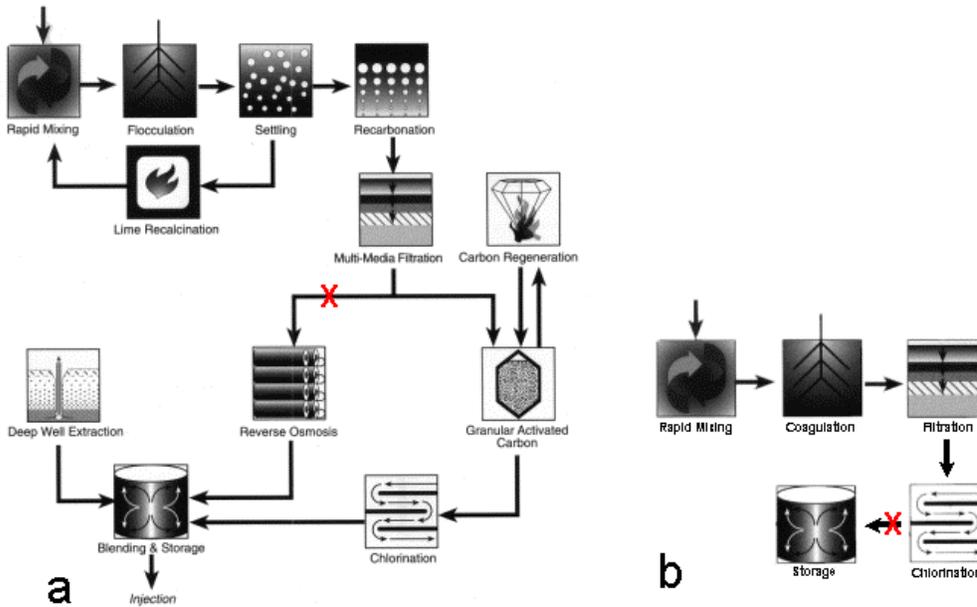
(MTU), designed to investigate membrane performance under simulated plant operating conditions (Figure 7). Each unit was designed to test  $20\text{cm}^2$  rectangular membrane samples. An individual flow cell used to hold an RO membrane is illustrated in Figure 8. Membranes were operated at a constant applied pressure of 225 psi and a flow rate of 1.0 gpm. Salt concentrations of the RO feed and product water were measured to determine membrane rejection using both a high and low level conductivity meter (Orion Research, Inc., Beverly, MA). On-line meters measured pH (Rosemount Analytical, Irvine, CA), turbidity (Hach Co., Loveland, CO) and chlorine concentrations (Wallace & Tiernan,

Inc., Vineland, NJ). Water permeation (flux), in gallons per square foot per day (GFD), was measured and the RO feed temperature recorded to normalize flux data to 25°C.



**Figure 8. Illustration of a flat sheet RO membrane test cell.**

Influent to each MTU was supplied with two distinct feedwaters: conventional pretreatment that included a five-stage clarification process (Water Factory 21; Figure 9a) and a three-stage pretreatment process consisting of coagulation, mixed media filtration and chlorine disinfection (Green Acres Project; Figure 9b).



**Figure 9. Water Factory 21 (a) and Green Acres Project (b) treatment train with corresponding MTU location (X).**

The latter water quality represented a more challenging water type for an RO membrane due to the limited number of treatment steps. The two water sources contained combined chlorine levels ranging from 1.0-3.0 mg/L (Water Factory 21) to 10.0-20.0 mg/L (Green Acres Project). Turbidities ranged from approximately 0.1 NTU (Water Factory 21) to 1.5 NTU (Green Acres Project). Once the membranes were installed, performance

parameters were monitored on a daily basis. The MTU's were connected directly to each facilities infrastructure and as a result were subject to both expected and unexpected shutdowns.

### 3.0 Project Outcomes

#### 3.1 Evaluation of CPTC1 membrane on lime clarified secondary municipal effluent

Membrane performance of the CPTC1 membrane operated on Water Factory 21 RO

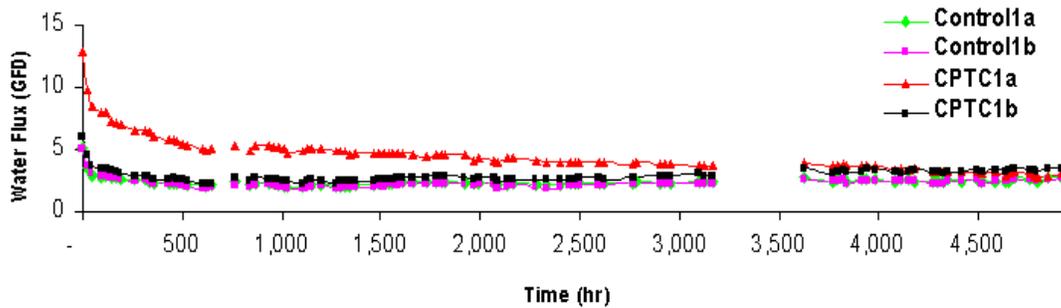


Figure 10. Normalized membrane performance of CPTC1 membranes with standard TFC polyamide controls evaluated on Water Factory 21 RO influent.

feedwater is illustrated in Figure 10. With the exception of an extended shutdown (400 hours) at the 3200 hour mark, testing proceeded uninterrupted for 5000 hours. Two standard TFC polyamide control membranes, supplied by Dow FilmTec (Midland, MI) and SST (San Diego, CA) and two CPTC experimental membranes (SST)

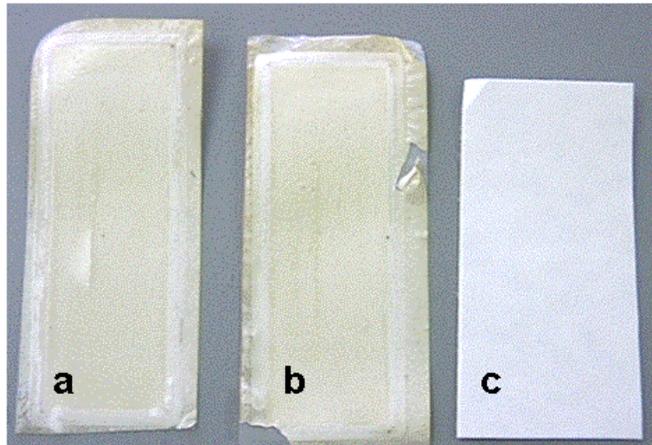


Figure 11. Selected images of fouled membrane samples after 5000 hours of operation on Water Factory 21 RO influent. Control membrane (a), CPTC membrane (b) and new, unfouled membrane (c) for comparative purposes.

were included in the experiment. Figure 11 illustrates sample images of fouled membrane samples removed from test cells after 5000 hours of operation. Water flux of

the CPTC1b membrane was the highest of the four membranes tested at 5000 hours, measuring 3.42GFD. Both CPTC1 membranes exhibited higher water flux than the Control1 membranes (Table 2). The observed membrane flux decline of all membranes can be considered biphasic, occurring in two distinct phases. This behavior was consistent with that of previous OCWD membrane tests using high biologically active feedwaters (data not shown). The initial flux decline was rapid, lasting approximately 600 hours. This point was selected based on changes observed in the overall membrane flux data. The rapid decline in flux was followed by a gradual flux decrease over time. Since a cleaning regimen was not incorporated in this experiment, it was not surprising that the initial flux followed logarithmic decay kinetics, suggesting that rapid accumulation of fouling material occurred on the membrane surface. During this period, the flux decay rate ( $R_1$ ) of the CPTC1a was greatest, declining at a rate of  $-1.24\text{hr}^{-1}$  (Table 2). However, this membrane did exhibit the greatest solute rejection (98.6%) and total water production ( $178\text{ gal/ft}^2$ ). The Control1b membrane, while maintaining a lower flux decay rate of  $-0.47\text{hr}^{-1}$ , had a lower solute rejection (96.6%) and a low total water production ( $66.9\text{ gal/ft}^2$ ). Following this rapid decline phase, the membrane flux stabilized, linearly declining at a slower pace. At this point, an equilibrium was established between the rate of foulant accumulation and the fluid shear at the membrane surface. The continual accumulation and sloughing of biological material (biofilm) from the membrane surface was also consistent with the observed biphasic flux decline. The sloughing of biological materials from the membrane surface is also more frequently witnessed in the treatment of nutrient-rich feedwaters such as municipal wastewaters (Characklis et al., 1990).

During this period from 600-5000 hours, membrane flux was observed to slightly increase, with the exception of the CPTC1a membrane, which decreased 44% during that period. However, this membrane did produce the highest quantity of water throughout

Table 2. Membrane performance data for the CPTC1 membrane series.

Membrane ID	Logarithmic Kinetics Phase							Linear Kinetics Phase						
	$R_1$	$F_1$	$F_{600}$	Flux Change (%)	Rejection @ 600 hrs (%)	$r^2$	WaterProd. (gal/ft <sup>2</sup> )	$R_2$	$F_{600}$	$F_{6000}$	Flux Change (%)	Rejection @ 5000 hrs (%)	$r^2$	WaterProd. (gal/ft <sup>2</sup> )
Control 1a	-0.44	5.09	2.35	-54%	97.0%	0.974	67.5	1E-04	2.35	2.68	14%	97.7%	0.57	355
Control 1b	-0.47	4.98	2.15	-57%	96.6%	0.976	66.9	1E-04	2.15	2.68	24%	97.4%	0.67	338
CPTC1a	-1.24	12.8	5.32	-58%	98.6%	0.976	178	-5E-04	5.32	2.96	-44%	98.1%	0.94	600
CPTC1b	-0.59	6.05	2.76	-54%	97.0%	0.981	79.5	2E-04	2.76	3.42	24%	97.1%	0.82	431

$R_1$ : logarithmic kinetics rate constant defined by  $F=F_1e^{R_1t}$ ;  $R_1=hr^{-1}$

$R_2$ : linear kinetics rate constant defined by  $F=F_{600}RT$ ;  $R_2=gal/(24(ft^2hr^2))$

$F_1, F_{600}, F_{6000}$ : Flux at 1hr, 600hr and 5000hr, respectively

$r^2$ : correlation coefficient

the entire experiment (778 gal/ft<sup>2</sup>). The fact that this membrane produced the highest amount of product water while exhibiting the highest rate of flux decline in both phases is consistent with previous literature which suggests that higher flux rates lead to more rapid membrane fouling (Byrne, 1995). Initially it was suspected that the increase in flux might be associated with a deterioration in membrane integrity. However, solute rejection remained comparable throughout the duration of the experiment.

### 3.2 Evaluation of CPTC2 membrane on lime clarified secondary municipal effluent

Membrane performance of the CPTC2 membrane operated on Water Factory 21 RO influent is illustrated in Figure 12. A standard TFC polyamide control membrane (Dow FilmTec) and two CPTC2 experimental membranes (SST) were tested. Two unexpected

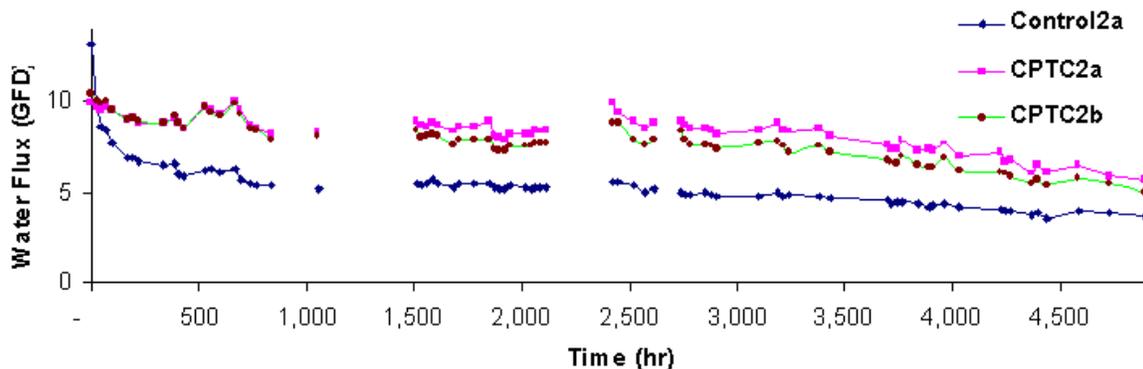


Figure 12. Normalized membrane performance of CPTC2 membranes with standard TFC polyamide control evaluated on Water Factory 21 RO influent

plant shutdowns were experienced over the course of the 4900 hour test: one lasting 670 hours and a second lasting 200 hours. Images of the fouled RO membranes are

represented in Figure 13. Water flux at the end of the experiment was highest in the CPTC2a (5.72GFD) and lowest in the control membrane (3.69GFD). Total water production by the CPTC2 membranes were higher than the control, producing an excess of 1100 gal/ft<sup>2</sup>, compared to approximately 800 gal/ft<sup>2</sup> for the control (Table 3). There was a slight decrease in membrane rejection between the control and the CPTC2 membranes, which might account for the variation in the total water production. Solute rejection for the Control2a membrane was 98.3%, compared to 97.5% and 97.1% for the CPTC2a and CPTC2b membranes, respectively (Table 3).

It again appeared that membrane flux decline was biphasic, occurring in two distinct phases (Figure 12). Like the previous membrane test, a cleaning regimen was not incorporated in the experiment so it was not surprising to observe the initial flux decline followed logarithmic decay kinetics ( $R_1$ ; Table 3). The initial, rapid flux decline lasted approximately 800 hours. Unlike

the strong logarithmic decay model ( $r^2 > 0.90$ ) of the CPTC1 membranes, a relatively weak model was demonstrated by the CPTC2 membranes ( $r^2 < 0.50$ ). The Control2a membrane, however, exhibited a high correlation ( $r^2 > 0.90$ ) similar to the Control1 membranes run during the first experiment. The weak logarithmic

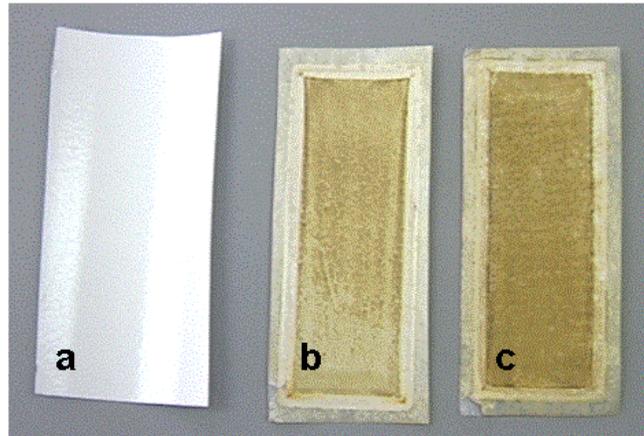


Figure 13. Selected images of fouled membrane samples after 4900 hours of operation on Water Factory 21 RO influent. Unfouled membrane (a) for comparative purposes, control membrane (b) and CPTC2 membrane (c).

kinetics model (and corresponding slower rate of flux decline ( $R_1$ ) from 1hr to 800hr) might suggest that the CPTC membrane may exhibit some level of fouling resistivity compared to the control. The fact that this trend was generally not observed in the CPTC1 test may pertain in part to the composition and isomeric purity of the CPTC acid chloride used during membrane synthesis (Table 1). However, further studies would need to be carried out to elucidate these observations. Nevertheless, it appears that the

initial rates of CPTC2 flux decline ( $R_1$ ) were generally slower than those of the CPTC1 membranes.

The initial phase of rapid flux decline was again followed by a gradual decline in flux ( $R_2$ ), which exhibited a moderately strong correlation ( $r^2 > 0.50$ ) using linear kinetics from 1500 hours to 4900 hours (Table 3). The decline in membrane flux was greatest in the CPTC2 membranes, when compared to the control. At the same time, total water

**Table 3. Membrane performance data for the CPTC2 membrane series.**

Membrane ID	Logarithmic Kinetics Phase							Linear Kinetics Phase						
	$R_1$	$F_1$	$F_{800}$	Flux Change (%)	Rejection @ 600 hrs (%)	$r^2$	WaterProd. (gal/ft <sup>2</sup> )	$R_2$	$F_{1600}$	$F_{4900}$	Flux Change (%)	Rejection @ 4900 hrs (%)	$r^2$	WaterProd. (gal/ft <sup>2</sup> )
Control2a	-1.14	13.2	5.35	-59%	98.3%	0.98	230	-6E-04	5.51	3.69	-33%	98.3%	0.92	567
CPTC2a	-0.15	9.91	8.23	-17%	97.8%	0.22	320	-7E-04	8.91	5.72	-36%	97.5%	0.64	951
CPTC2b	-0.27	10.5	7.92	-24%	97.6%	0.46	320	-8E-04	8.38	4.98	-40%	97.1%	0.73	852

$R_1$ : logarithmic kinetics rate constant defined by  $F = F_1 e^{-R_1 t}$ ,  $R_1 = \text{hr}^{-1}$

$R_2$ : linear kinetics rate constant defined by  $F = F_{1600} - R_2 (t - 1600)$ ,  $R_2 = \text{gal}/(24(\text{ft}^2 \text{hr}^2))$

$F_1, F_{800}, F_{1600}, F_{4900}$ : Flux at 1hr, 800hr, 1500hr and 4900hr, respectively

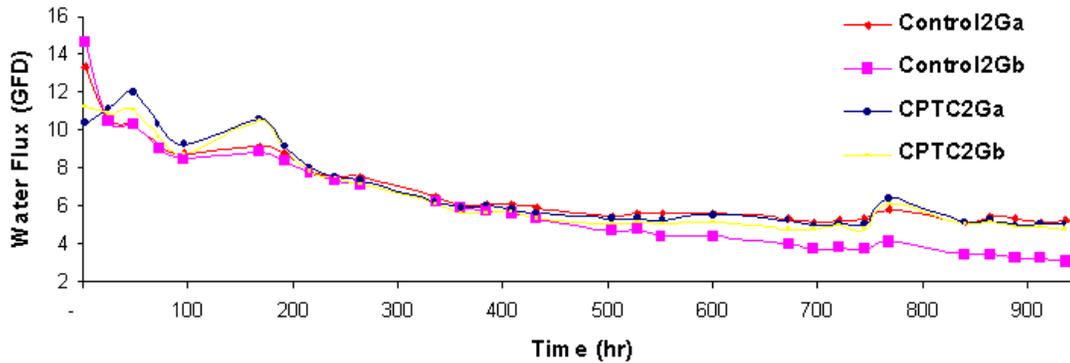
$r^2$ : correlation coefficient

production during this phase was greatest in the CPTC2 membranes, producing 951 gal/ft<sup>2</sup> and 852 gal/ft<sup>2</sup> for the CPTC2a and CPTC2b membranes, respectively. This behavior is again consistent with previous literature suggesting that higher flux rates lead to more rapid membrane fouling.

### 3.3 Evaluation of CPTC2 membrane on media filtered secondary municipal effluent

The CPTC2 membrane was also evaluated using GAP effluent (Figure 14). Two standard TFC polyamide control membranes (Dow FilmTec and Hydranautics, Oceanside, CA) and two CPTC2 experimental membranes (designated CPTC2G) were tested. The duration of this evaluation was shortened due to a shutdown of the GAP treatment plant. Since the shutdown lasted over 6 months, it was decided that testing should be terminated upon plant startup. This decision also coincided with an unexpected shutdown of the MTU. Design and mechanical problems associated with the influent pump required that a new pump system be installed. Since the MTU operates under high

pressure and relatively low flow-rate conditions (>200psi @ 1.0gpm), difficulties were experienced in obtaining a system that could meet these specifications. After an



**Figure 14. Normalized membrane performance of CPTC2G membranes with standard TFC polyamide controls evaluated on Green Acres Project effluent.**

extensive search, a new pump system was found (Tonkaflo 500SS Pump, Minnetonka, MN), design modifications were made, and the system was installed.

Membrane performance of the CPTC2G membranes essentially fell between that of the two control membranes. Water flux at the end of the experiment was highest in the Control2Ga membrane (5.22GFD) and lowest in the Control2Gb membrane (3.03gfd). Water flux of the CPTC2Ga and CPTC2Gb membranes was 5.01GFD and 4.80 GFD, respectively (Table 4). Total water production by the CPTC2G membranes also fell between the two control membranes, producing in excess of 200gal/ft<sup>2</sup>. Membrane rejection of the four membranes remained relatively constant throughout the entire experiment. The control membranes, however, exhibited higher solute rejections than the experimental membranes. Unlike the increase in water production (and corresponding decrease in rejection) demonstrated by the CPTC2a and CPTC2b membranes (Table 3), the Control2Ga membrane demonstrated high water production (253gal/ft<sup>2</sup>) and solute rejection (98.9%). The Control2Ga membrane was the exceptional performing membrane in this trial based on total water production and solute rejection.

Membrane flux decline of the Control2G membranes was biphasic, occurring in two distinct phases (Figure 14). The initial phase consisted of rapid flux decline that lasted approximately 500 hours. A relatively strong logarithmic decay model ( $r^2 > 0.75$ ) was calculated for the control membranes in the initial phase. The rate of flux decline ( $R_1$ ) within the control membranes was greatest in the Control2Gb membrane, which presumably led to a lower calculated flux at 500 hour and 936 hour ( $F_{500}$  and  $F_{936}$ , respectively). Unlike the biphasic flux decline demonstrated by the Control2G membranes, it was surprising to observe the CPTC2G membrane flux declined linearly in

**Table 4. Membrane performance data for the CPTC2 membrane series on GAP feedwater.**

Membrane ID	Logarithmic Kinetics Phase							Linear Kinetics Phase						
	$R_1$	$F_1$	$F_{500}$	Flux Change (%)	Rejection @ 500 hrs (%)	$r^2$	WaterProd. (gal/ft <sup>2</sup> )	$R_2$	$F_{500}$	$F_{936}$	Flux Change (%)	Rejection @ 936 hrs (%)	$r^2$	WaterProd. (gal/ft <sup>2</sup> )
Control2Ga	-1.29	13.4	5.42	-59.0%	98.9%	0.88	162	-9E-04	5.42	5.22	-3.7%	98.9%	0.49	90.8
Control2Gb	-1.55	14.7	4.66	-68.3%	98.9%	0.92	111	-4E-03	4.66	3.03	-35.0%	99.0%	0.92	65.6
CPTC2Ga								-7E-04	5.32	5.01	-5.6%	98.2%	0.39	87.7
CPTC2Gb								-8E-04	5.03	4.8	-4.6%	98.2%	0.18	84.1

Membrane ID	Linear Kinetics Phase						
	$R_{2a}$	$F_1$	$F_{500}$	Flux Change (%)	Rejection @ 500 hrs (%)	$r^2$	WaterProd. (gal/ft <sup>2</sup> )
CPTC2Ga	-0.01	10.4	5.32	-48.8%	98.2%	0.95	120
CPTC2Gb	-0.01	11.3	5.03	-55.5%	98.0%	0.95	127

$R_1$ : logarithmic kinetics rate constant defined by  $F = F_1 e^{R_1 t}$ ,  $R_1 = \text{hr}^{-1}$   
 $R_2$ : linear kinetics rate constant defined by  $F = F_{500} - R_2 T$ ,  $R_2 = \text{gal}/(24(\text{ft}^2 \text{hr}^2))$   
 $R_{2a}$ : linear kinetics rate constant defined by  $F = F_1 - R_{2a} T$ ,  $R_{2a} = \text{gal}/(24(\text{ft}^2 \text{hr}^2))$   
 $F_1, F_{500}, F_{936}$ : Flux at 1hr, 500hr, and 936hr, respectively  
 $r^2$ : correlation coefficient

both phases of the experiment. Flux decline kinetics ( $R_{2a}$ ) during the initial phase (1-500hrs) was strongly correlated ( $r^2 > 0.90$ ) using linear modeling. The fact that linear and not logarithmic kinetics were observed during this initial phase suggests that the impact of foulant loading on the membrane surface was not as severe as that on the Control2G membranes. Flux decline still occurred but the manner in which it declined may be associated with a lower propensity for biological fouling.

A moderate decline in membrane flux was exhibited in the second phase of the experiment (500-936 hours). With the exception of the Control2Gb membrane, which exhibited a high correlation ( $r^2 > 0.90$ ) using linear kinetics ( $R_2$ ) and a large decline in flux (35%), all the membranes demonstrated weak linear kinetics correlations ( $r^2 < 0.50$ ). The

somewhat inconsistent flux data generated during this phase may have been associated with a deteriorating MTU pump system, which eventually failed and needed to be replaced. Further testing would need to be conducted to verify these preliminary observations and those pertaining to the linear decay kinetics demonstrated by the CPTC2G membranes in the initial testing phase.

## **4.0 Conclusions & Recommendations**

### **4.1 Conclusions**

- Molecular modeling confirmed the existence of a relationship between membrane stability and bond angle steric optimization in membrane synthesis. The CPTC membrane tested in this study was sterically (geometrically) optimized to create a stable polymer membrane.
- Long-term performance of the CPTC membrane was equal, or superior to traditional commercial membranes. While still in its adolescent, the CPTC membrane looks promising as a membrane that could successfully treat high fouling water sources without compromising membrane integrity and performance due to fouling and chemical degradation.
- The CPTC membrane appeared to exhibit moderate fouling resistance based on flux decline kinetics modeled in both the linear and logarithmic phase. Continued testing would need to be conducted to confirm these preliminary findings.

### **4.2 Commercialization Potential**

- Membrane treatment technologies are continually expanding as locations within the United States and around the world are witnessing substantial population growth rates and corresponding increases in water demand. This is particularly evident when noting the expansion of the membrane technology market, which is estimated to have increased from \$363 million in 1987 to more than \$1 billion in 1997 (Roger, 1998).

- Commercial TFC polyamide RO membranes in the marketplace lack the chemical stability to oxidants such as chlorine. A chemically tolerant CPTC TFC membrane could quickly expand in the marketplace since most treatment facilities already operate TFC polyamide membranes.

### **4.3 Recommendations**

- The successful development and widespread implementation of a new polymer membrane is a timely process. Since the CPTC/MPD membrane is still in its adolescence, more testing would be required to determine the practicability of this membrane as an alternative to conventional TFC membranes in treating high fouling water and wastewater sources.
- Current evaluations have been conducted using flat-sheets of membrane, housed in membrane test cells (Figure 8). Cleaning regimen's were not incorporated in these tests so to evaluate the inherent fouling tendencies without the interference of biocides or other cleaning agents. While the results of this initial stage of testing was encouraging, expansion of the testing program should be carried out using small spiral wound elements (2"DI x12"L), the next step in membrane evaluation. Membranes used in this configuration, while more costly, will simulate those used in large treatment plants.

### **4.4 Benefits to Southern California**

- As the population of continues to increase in Southern California (and other areas in the California), water agencies will have to address the issue of increasing water demand. In Orange County, the population is estimated to increase to more than 3 million in the next 20 years. Reliable, safe and cost-effective sources of potable water must be developed to sustain population growth in Southern California. Developing non-traditional water sources for potable purposes require advanced water treatment facilities, which ultimately include membrane

- processes. The use of highly efficient, low fouling membranes would ultimately increase product water throughput while minimizing associated treatment costs.
- TFC polyamide membranes operate at lower operating pressures than cellulose acetate membranes, which can translate into significant energy savings of 30% to 40%. Using a lower pressure TFC membrane that exhibits fouling resistance would further reduce energy costs as well. Less biofilm proliferation and accumulation on the membrane surface would result in lower operating pressures and subsequently lower energy costs. An increase in feed pressure of 25psi due to membrane biofouling is estimated to result in an increase of \$7000 (500gpm, 75% pump efficiency) at \$0.10/KWH (Dow Chemical, 1999). Minimizing the occurrence of membrane biofouling through the use lower fouling, more efficient TFC membranes could ultimately result in significant energy savings for the California water producer already faced with looming power concerns.

## References

Bharwada, U.J., Summerfield, J.M., Coker, S.D., Marsh, T.A.R., (2000). "Membranes: Strategies for Combating Biofouling in Membrane Systems." *Ultrapure Water*, 17:7: 40-45.

Byrne, W., (1995). *Reverse Osmosis: A Practical Guide for Industrial Users*, Tall Oaks Publishing Inc., Colorado.

Cadotte, J.E., Peterson, R.J., Larson, R.E., Erickson, E.E., (1980). *Desalination*, 32, 25-31.

Characklis, W.G. and Marshall, K.C., (1990). *Biofilms*, John Wiley & Sons, Inc., New York.

Dychdala, G.R., (1991). "Chlorine and Chlorine Compounds." In S. Block (Ed.), *Disinfection, sterilization, and preservation* (fourth ed.), Lea & Febiger, Philadelphia and London.

Dow Chemical, (1999). "FilmTec Fouling Resistant Membrane Elements-Winning The Battle Against Biofilm Formation." Technical Paper.

Faibish, R.S., Elimelech, M., Cohen, Y., (1998). "Effect of Interparticle Electrostatic Double Layer Interactions on Permeate Flux Decline in Crossflow Membrane Filtration of Colloidal Suspensions: An Experimental Investigation." *J. of Colloid and Interface Science*, 204, 77-86.

Flemming, H-C., Shaule, G., McDonogh, R. (1993). "How do performance parameters respond to initial biofilm formation on separation membranes?" *Vom Vasser*, 80, 177-186.

Flemming, H-C., Shaule, G., McDonogh, R., Ridgway, H.F. (1994). "Effects and extent of biofilm accumulation in membrane systems." In Geesey, Lewandowski, Flemming (Ed.), *Biofouling and biocorrosion in industrial water systems*, CRC Press, Boca Raton, Fl.

Ikeda, K., et al., (1993). "Novel Reverse Osmosis Composite Membranes." Proc. IDA and WPRC World Conference on Desalination and Water Treatment., Yokohama, Japan.

Ridgway, H.F., (1988). "Microbial Adhesion and Biofouling of Reverse Osmosis Membranes." In B. Parekh (Ed.), *Reverse Osmosis Technology: Application for High-Purity Water Production*, Marcel Dekker, Inc., New York and Basel.

Ridgway, H.F. and Flemming, H-C., (1996). "Membrane Biofouling." In J. Mallevalle, P.E. Odendaal, and M.R. Wiesner (Ed.), *Water Treatment Membrane Processes*, McGraw-Hill, New York.

Rogers, R., (1998). *Chemical Engineering News*, 74(34), 38-39.

## **Glossary**

RO – Reverse osmosis

PA – Polyamide

TFC – Thin film composite

CA – Cellulose acetate

CPTC – Cyclopentanetetracarboxylic

MPD – m – phenylenediamine

GAP – Green Acres Project

TMC – Trimesoyl chloride

MTU – Membrane test unit

GFD – Gallons per square foot per day

SST – Separation Systems Technology, Inc.