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Polyamide Reverse Osmosis Membrane Fouling and Its Prevention: Oxidation-Resistant Membrane Development, Membrane Surface Smoothing and Enhanced Membrane Hydrophilicity

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13. ABSTRACT *(Maximum 200 words)*

The reverse-osmosis membrane of choice today is the polyamide thin-film composite membrane that is incorporated into the spiral-wound configuration. Although the membrane performance is excellent, major deficiencies remain 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 surface roughness, and high bacteria attachment counts on the membrane surface leading to biofouling. Development of an oxidation-resistant membrane is a preferred solution to control membrane fouling thereby increasing membrane life. The search for an oxidation-resistant polyamide membrane has been under investigation by a number of researchers for more than twenty-five years. This program pursues a new approach in that the amine and acid chloride for making the polyamide membrane are selected using molecular modeling on the basis of steric differences thereby optimizing the amide bond angles for greater strength. The focus was centered on identification of the acid chloride, acid chloride synthesis and purification and on the preparation, characterization and field testing of the resulting polyamide membranes on chlorinated feed streams. Also, polyamide membrane surface roughness and hydrophilicity were varied and controlled for bacterial attachment assays to determine biofouling tendencies.

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Details of the methodology used in this program are described in the text of this report. The program was a joint effort between Separation Systems Technology (SST), A. Murphy of the Bureau of Reclamation (BR) and H. Ridgway of the Orange County Water District (OCWD). The synthesis, isolation and purification of the *ctct*-CPTC acid chloride were conducted by A. Murphy (BR) and B. Murugaverl of the University of Denver (DU); the conversion of *cccc*-CPTC acid to *ctct*-CPTC acid was carried out by G. A. Hernandez of Instituto Tecnologico-Mexico (ITM) and NMR analysis was conducted at San Diego State University (SDSU) by R. Somanathan. Membrane development and optimization were conducted by S. W. Lin, C. Milstead, M. Patel, R. Riley and P. Su of SST. Membrane characterization was carried out by R. Bold, K. Ishida, T. Knoell, T. Cormack, H. Ridgway and J. Safarik, of OCWD. The long-term testing at the WQIC Yuma, AZ. was conducted by B. Corbett, M. Fabien, C. Moody and M. Norris.

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GLOSSARY

(Terms Are Shown Below As Used in Sections)

1. INTRODUCTION

PA	polyamide
TMC	trimesoyl chloride
MPD	m-phenylenediamine
cccc-	cis, cis, cis, cis
ctct-	cis, trans, cis, trans
CPTC	cyclopentanetetracarboxcylic acid or acid chloride
SST	Separation Systems Technology, Inc.
WQIC	Water Quality Improvement Center, Yuma AZ
OCWD	Orange County Water District
DU	University of Denver

2. CONCLUSIONS AND RECOMMENDATIONS

NMR	Nuclear Magnetic Resonance
GCMS	Gas Chromatograph Mass Spectrometry
FT-IR	Fourier Transform-Infrared
ATR/FT-IR	Attenuated Total Reflectance/Fourier Transform-Infrared
AFM	Atomic Force Microscopy

3. BACKGROUND AND TECHNICAL APPROACH

MD	Molecular Dynamics
PS	Polysulfone
CA	Cellulose Acetate
SPS	Sulfonated polysulfone
UC	Uranyl Cation
UA	Uranyl Acetate

4. SYNTHESIS AND PURIFICATION OF CIS, TRANS, CIS, TRANS-1, 2, 3, 4-CYCLOPENTANETETRACARBOXYLIC ACID CHLORIDE

DMF	Dimethylformamide
p-TSA	Para-toluenesulfonic Acid

6. LONG -TERM REVERSE OSMOSIS FIELD TESTING AT WQIC ON CHLORINATED BRACKISH WATER FEEDS

CRADA	Cooperative Research and Development Agreement
TCU	Test Cell Units

8. POLYAMIDE MEMBRANE SURFACE MORPHOLOGY

C-AFM	Contact AFM
NC-AFM	Non-Contact AFM
IC-AFM	Intermittent-AFM
RMS	Root Mean Square Roughness

9. ENHANCEMENT OF HYDROPHILICITY OF POLYAMIDE MEMBRANE SURFACE TO REDUCE BIOFOULING

UCB	Uranyl Cation Binding

1.0 INTRODUCTION

The reverse osmosis (RO) membrane of choice worldwide is the polyamide (PA) thin-film composite membrane developed by Cadotte (1980). The PA composite 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). Today, the membrane is commercially supplied by Dow-FilmTec, Koch-Fluid Systems, Osmonics-Desal, Tri-Sep, Nitto Denko-Hydranautics and Toray Industries in Japan. Although the membrane performance is excellent, major membrane deficiencies remain that contribute to fouling, reduced membrane life and higher operating costs. They are:

1. Lack of chemical stability to oxidants such as chlorine
2. High fouling rates due to surface roughness, and
3. High bacteria attachment counts on the membrane surface leading to biofouling.

There is 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 waste waters, 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 added costs and effectively nullifies disinfection on the membrane surface where it is needed. Development of a chlorine-resistant PA membrane is the ultimate solution to control biofouling, thereby increasing membrane life.

A primary objective of this work was to develop a PA membrane for RO desalination that is resistant to chlorine-disinfected feed waters and more resistant to biological fouling. The work of Ikeda and Tomaschke (1993) reported PA membranes made from MPD and three stereoisomers of 1,2,3,4-cyclopentanetetracarboxylic acid chlorides, namely *cccc*-CPTC acid chloride, *ctcc*-CPTC acid chloride and *ctct*-CPTC acid chloride. The said paper 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 acid chlorides were not cited.

U.S. Patent 5,254,261 was issued to Tomaschke and Ary on the aforementioned PA membrane chemistry prior to the publication. This patent was not cited in the publication of Ikeda and Tomaschke (1993) and there is no mention and/or claim in the patent of oxidation stability of the resultant PA membrane. However, Ikeda and Tomaschke cited in their publication that chlorine tolerance was the primary attribute of the membrane.

In recent years, membrane research at Separation Systems Technology (SST) focused on PA thin-film composite RO membranes. This work identified current membrane deficiencies, demonstrated cause and effect, developed methodologies for approaching the problems and determined pathways for solutions. One aspect of this work was to develop a methodology for the search for an oxidation resistant PA membrane. Toward this end molecular modeling was selected as the methodology to determine the optimal combination of amine and acid chloride monomers to enhance oxidation resistance.

The 1,2,3,4-CPTC acid chloride 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. As a result, Ridgway and SST molecular modeled the six isomers formed from the conversion of *cccc*-1,2,3,4-cyclopentanetetracarboxylic acid to acid chlorides. It was found that the bond angles and steric energies of the isomers were quite different and that *ctct*-CPTC acid chloride bond angles were least strained. These results, of course, assume 100% isomeric purity. To confirm long-term oxidative stability, high purity isomers were produced, membrane processing optimized, and the membranes were evaluated in long-term RO tests on brackish water at the Water Quality Improvement Center (WQIC) Yuma, AZ and on municipal waste water at the Orange County Water District (OCWD) for confirmation.

2.0 CONCLUSIONS AND RECOMMENDATIONS

The first PA thin-film composite membrane was commercialized in 1977 when it was placed into service in a large RO seawater desalination plant at Jeddah, Saudi Arabia. At that time it was recognized that the membrane was not tolerant to chlorine and the pre-treatment for the plant had to be arranged accordingly. The search for a chlorine-resistant PA membrane was begun some twenty-two years ago and has continued since.

This current program, while modest in funding and duration, possessed both depth and scope in pursuing a new approach; that is, to select the reactant pairs using molecular modeling for forming a PA membrane on the basis of steric differences. A major thrust of the program involved the synthesis, separation and purification of cis, trans, cis, trans-1,2,3,4-cyclohexanetetracarboxylic acid chloride from a mixture of six stereoisomers; analysis of the purified products were determined by C-13 NMR, H-NMR, P-31 NMR, GCMS, FT-IR and ATR/FT-IR spectrometry. Membranes were prepared from the purified isomer 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 (hydrophilicity), surface morphology by atomic force microscopy (AFM), and chemical and structural analysis by both FT-IR and ATR/FT-IR spectrometry. Chemical modifications of the membrane surface were made to reduce biofouling. Finally, an ambitious field RO test program was carried out with the optimized PA membranes using chlorinated feed waters at the WQIC, Yuma, AZ on surface waters and at the OCWD, Fountain Valley, CA on municipal waste water. The initial results of those long-term RO tests are very promising.

The success of this program can be attributed to the coordinated effort of the six participating teams involving several different disciplines. These include synthetic organic chemists, instrumental analysis specialists, microbiologists, membrane specialists, and field test engineers.

Recommendations:

* Membranes prepared from the *cccc* isomer of 1,2,3,4-CPTC acid chloride exhibited a much lower tolerance to chlorine in long-term field tests than the *ctct* isomer of 1,2,3,4-CPTC acid chloride. Thus, the importance of steric bond differences on chlorine stability of PA membranes was demonstrated. This finding is very important and justifies additional work with the *ctct*-CPTC acid chloride/MPD system.

New acid chloride/amine systems with potentially greater bond stability identified by molecular modeling.

* Toward the end of the program, the synthesis of *ctct*-CPTC acid chloride reached a purity level of 99+% (1% or less impurity). While this is relatively pure, higher levels are required to attain maximum chlorine tolerance; the presence of any amount of the five remaining isomers is expected to reduce long-term chlorine tolerance. Work must continue to produce *ctct*-CPTC acid chloride at a purity level of 99.9%.

* Long-term RO field testing was conducted at both WQIC and OCWD on chlorinated feed waters with PA membranes made from *ctct*-CPTC acid chloride (98% purity). Operational difficulties were encountered at WQIC that resulted in numerous shutdowns, one of which lasted several months. Nevertheless, a 1750-hr. (73 day) run was completed in which the membranes showed no change in transport properties; the surface water feed contained 1.5 mg/L free chlorine.

* A 4,900-hr. (204 day) run was completed at OCWD on a municipal waste feed that was fed 3 mg/L chlorine. Due to the high nitrogen levels in the waste water the chlorine was in the form of chloramines. As expected, membrane fouling occurred but with little or no loss in selectivity. It is recommended that field testing continue at WQIC with membranes made from high purity *ctct*-CPTC acid chloride, that is, 99+% and greater. Data from this test site is necessary for this program.

* All field testing on this program was carried out with 1 x 3 inch rectangular membrane test cells using O-ring seals. Consistent with past experiences, membrane damage was observed at the O-ring/membrane interface after each shutdown. Since shutdowns are inevitable, even under ideal conditions, it is difficult to obtain good long-term data. For this reason, it is recommended that the program be expanded to use spiral-wound elements as the test vehicle. This would require upscaling the *ctct*-CPTC acid chloride synthesis since larger amounts of material would be needed, contracting the production of PA membrane in the quantities required, and the assembly of a number of 2- x 12-inch spiral elements.

* Chlorine degradation of PA membranes may be the result of N-chlorination of the amide nitrogen followed by chlorine transfer to the aromatic ring of the MPD moiety (Singh and Glater, 1994). The steric configuration of a PA membrane made with *ctct*-CPTC acid chloride may hinder this reaction, thereby increasing chlorine

tolerance. The hindrance may or not be total, however. To gain more insight into this mechanism, it is recommended that a PA moiety of *ctct*-CPTC acid chloride/MPD be used to molecular model the potential reactions, that occur with chlorine at various pH levels. To complement this study, the moiety would be physically subjected to chlorine at the same pH levels and subsequently analyzed by NMR, GCMS and ATR/FT-IR. Similar experiments would be conducted with membrane swatches in a chlorinated RO feed and subsequently analyzed by ATR/FT-IR and/or x-ray photoelectron spectroscopy.

* A technique was developed to chemically modify the surface of the *ctct*-CPTC acid chloride PA membrane by reacting 3-amino-1-propanol with residual unreacted acid chloride groups remaining on the surface. This was done in an attempt to enhance the hydrophilicity of the surface to reduce biofouling. Due to the limitation of time and funding on this program, only one attempt was conducted. While the results were not conclusive, only one set of reaction parameters were evaluated. This promising method of tailoring a membrane surface, if successful, could have significant impact on reducing membrane fouling.

* A number of unique membrane characterization methods have been developed and used by the R&D team. For example, topographs of the surface morphology of the *ctct*-CPTC acid chloride membrane, as characterized by AFM, revealed folding of the PA layer that is believed to be responsible for poor performance. Additional work is required to eliminate PA film folding characteristics.

* A method was developed using ATR/IR spectrometry to determine the relative carboxylate density and thickness of the PA layer. It was shown that the thickness of the *ctct*-CPTC acid chloride PA layer is somewhat thinner than a standard TMC/MPD control. To improve physical membrane durability, it will be necessary to change and optimize the reaction parameters to develop a thicker *ctct*-CPTC acid chloride PA film.

* The sodium-ion transport of the *ctct*-CPTC acid chloride PA membrane, when compared to the TMC/MPD PA control membrane, is much greater at pH 4.5; at pH 6.5 and 9.0 the sodium-ion transport is similar. ATR/FT-IR was used to determine relative bulk charge density of the PA film while the uranyl cation analysis method was used to determine the surface charge of the membrane. It was found, by both methods, that the *ctct*-CPTC acid chloride PA membrane was less charged than the

control. Additional work is required to determine the mechanism for this behavior and how it may, or may not, relate to the surface charge.

It is recommended that the aforementioned work be continued, so that the R and D team, presently in place, can maintain the momentum that has been established. The technical composition of this team offers a unique opportunity for cooperative success.

3.0 BACKGROUND AND TECHNICAL APPROACH

RO plants have been operating with spiral-wound PA thin-film composite membrane elements to desalinate brackish water and seawater since 1977. Presently, spiral-wound PA elements are supplied worldwide by four major manufacturers. In the spiral configuration the PA membrane dominates market share.

ATR/FT-IR membrane surface analysis shows that all manufacturers use nominally the same aromatic PA membrane chemistry based on the interfacial reaction of MPD with TMC. Thus, the propensity for fouling is similar for all PA membranes. The major membrane deficiencies that contribute to fouling, reduced membrane life and higher operating costs [Elimelech (1994) and Ridgway (1991, 1996 and 1997)] are:

* Lack of chemical ***stability to oxidants*** such as chlorine,
* Enhanced fouling rates due to excessive ***surface roughness***, and
* High bacterial attachment counts on the ***hydrophobic membrane surface***.

There is 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 waste waters, surface waters and open seawater intakes where disinfection by chlorination is required to control growth of microorganisms on the membrane surface. 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 added costs and effectively nullifies disinfection on the membrane surface where it is needed. Development of a chlorine-resistant PA membrane is a preferred solution to control membrane fouling thereby increasing membrane life.

3.1 Membrane Oxidation Stability

Cadotte originally demonstrated the utility of interfacial polymerization with TMC and MPD in preparing PA membranes with good desalination properties. Presently, this is the membrane of choice worldwide. Sundet *et al* (1987) extended the aromatic/aromatic PA chemistry of Cadotte to aromatic/cycloaliphatic with 1,2,3,4-cyclohexanetricarbonyl chloride. Arthur *et al* (1988) disclosed in U.S. Patent 4,749,488 the preparation of membranes by interfacial polycondensation of 1,2,3,4-cyclopentanetetracarbonyl acid chloride (CPTC) with MPD. More recently Ikeda *et* al (1993) reported results in the literature similar to that of Arthur using 1,2,3,4-CPTC acid chloride with MPD. In addition, it was reported that the

chlorine tolerance of the membrane depended on which of the six stereospecific isomeric structures of 1,2,3,4-CPTC acid chloride was utilized. Membranes prepared with *cccc*-CPTC and *ctcc*-CPTC acid chloride reportedly deteriorated rapidly when operated in RO on a feed containing 1 mg/L chlorine for 50 and 150 hours, respectively. Membranes prepared with *ctct*-CPTC acid chloride, on the other hand, showed no deterioration after 1000 hours when operating at 214 psi applied pressure, 1500 mg/L NaCl, 1 mg/L chlorine and pH 6.5. This is a promising new approach to attaining a chlorine-resistant PA membrane. However, verification of this work is required since it is the only known reference on the subject.

The creation of a chlorine-resistant membrane has been under investigation by a number of researchers for more than twenty five years but without success. (Singh, Glater and Sundet) During these studies many different acid chlorides and amines were evaluated including 1,2,3,4-CPTC acid chloride. 1,2,3,4-CPTC has four reactive acid chloride groups that provide six possible geometric isomers. However, when the original studies were done, the steric configuration was not taken into consideration. Membranes had always been prepared from the isomer mixture of 1,2,3,4-CPTC acid chloride without isolation and purification of each isomer. It may be, for this reason, that chlorine resistance was never observed. The six stereoisomers of 1,2,3,4-CPTC acid chloride, derived by computer molecular modeling are depicted in Figure 3.0 (Ridgway, 1996).

To form a stable linkage between an amine and an acid chloride, the bond angles should be sterically optimized for maximum stability. Ridgway has determined the configuration for 1,2,3,4-CPTC using molecular modeling algorithms. Each CPTC isomer shown was geometrically optimized (at 300°K, 1 atm, no water) to <0.001 kcal/mole-A using the Polak-Ribiere algorithm via classical mechanics (MM+, HyperChem). Molecular Dynamics (MD) simulations showed that a stable (low-energy) geometric conformer was attained after about 110 psec for the *ctct* isomer of CPTC acid chloride whereas, attainment of a similarly low-energy conformer for the *cctt* isomer of CPTC was observed out to 340 psec. This suggests the *cctt*-CPTC acid chloride isomer bond angle was generally more strained than the *ctct*-CPTC acid chloride isomer bond angle. In each case, potential energy declined as the system approached more stable geometric configurations. A somewhat higher final potential energy value for the *cctt*-CPTC acid chloride isomer was consistent with its comparative instability. Thus, it is hypothesized that the PA membrane bond angle created by the reaction of *ctct*-CPTC acid chloride with MPD has greater stability than those created by the other five isomers of 1,2,3,4-CPTC acid chloride, and this could be responsible for the reported chlorine resistance.

3.2 Membrane Surface Roughness

Collaborative work between SST and Ridgway *et al* at the OCWD has shown that high levels of bacterial attachment occur on rough hydrophobic surfaces such as the fully aromatic PA membrane. Relatively low numbers of bacteria attach to smooth hydrophilic membranes such as cellulose acetate (CA). The PA membrane exhibits greater fouling rates than other types of membranes. The high level of surface roughness of PA membranes is partially responsible for fouling and has been well documented by SST and others by AFM. The low fouling characteristics exhibited by CA membranes are, in part, attributed to the smooth surface of the membrane that does not trap or hold suspended solids in most RO feedwaters. (Ridgway 1997). AFM photomicrographs presented in Figures 3.1 and 3.2 show the smooth surface of a CA membrane and the rough surface of a PA membrane made by the interfacial process with MPD and TMC. (It is realized that these two photomicrographs do not have the same vertical scale, however the difference in surface roughness is clearly illustrated.)

Previous work in this laboratory has shown that the mechanism responsible for surface roughness is not due to:

* Solvents - PA membranes produced with acid chloride dissolved in hexane, Isopar and Freon, have similar surface morphology.
* Crosslinking - both linear and crosslinked PA films show similar roughness.
* Post-treatment - processing following interfacial PA film formation.

Furthermore, it was shown in preliminary work that the surface roughness of the PA membrane could be modified without changing the RO transport properties, i.e. membrane flux and rejection. This surface modification is achieved by increasing the transfer rate of MPD from the aqueous phase into the acid chloride hydrocarbon phase by altering the composition of the aqueous phase.

3.3 Membrane Surface Hydrophilicity

Biological fouling of membrane surfaces is a well-known phenomenon and a serious problem encountered in PA membrane plants. The PA membrane exhibits greater fouling than other types of RO membranes. Studies by Ridgway, in the U.S., and Flemming (1996) in Germany, have indicated that RO microorganisms exhibit very different affinities for surfaces of different membrane polymers. This finding is encouraging since it 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 *et al* has 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 feedwater
- The nature of the bacterial cell surface

In these studies it was shown that the *mycobacterium sp.* are commonly present in pretreated municipal wastewaters used as RO feed. One isolate, *Mycobacterium* strain BT2-4, exhibited high attachment to the more hydrophobic PA membrane and low attachment to the more hydrophilic 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%. Polysulfone (PS) membranes are very hydrophobic and foul very rapidly. However, when the PS membrane is made more hydrophilic by incorporating sulfonated polysulfone (SPS) into the membrane matrix, bacterial attachment is greatly reduced. During this program a procedure was devised to increase the hydrophilic nature of the PA membrane surface by covalently bonding a hydrophilic moiety to the PA surface immediately after interfacial film formation. Details of this work are reported in Section 9.0.

3.4 Polyamide Membrane Characterization: Experimental Procedures

Surface properties of membranes affect the interaction of organic and inorganic colloidal substances on membrane surfaces in an aqueous media. Therefore, determination of membrane surface characteristics is critical to membrane fouling research. Surface characterizations are also important in selecting optimal pretreatment schemes and operating conditions for various membrane separation processes. Some surface properties used to

characterize separation membranes are roughness, hydrophilicity and surface charge. The knowledge of these surface properties provides essential information for understanding the mechanisms and details of fouling.

Variations of the TMC-MPD and *ctct*-CPTC acid chloride/MPD PA membranes, made during this program were characterized for biofouling potentials and chlorine resistance by Ridgway's Biotechnology Research Department at OCWD. The specific characterization methods are as follows:

3.4.1 Topological Characterization

The surface topology of dry and fully hydrated (submerged) PA membrane was determined by AFM (Park Scientific, Auto Probe CP-2). AFM imaging permits resolution and digital analysis of pore size distributions. Operation in the lateral force mode reveals possible chemical discontinuities in membrane surfaces, i.e., areas in which polymer components partition into "islands" having unique physio-chemical (and biofouling) properties. Chemical discontinuities may be related to heterogeneity in the adsorption of bacteria and organics. Especially, relevant is the quantification of membrane vertical topology and surface roughness, which can be correlated with organics and bacterial adsorption results. Pore size distributions were correlated with membrane flux and solute rejection as determined by SST.

3.4.2 Surface Energy

Relative hydrophilicity of new and modified PA membranes prepared by SST were compared to that of standard PA membranes. The surface hydrophobicities of polymer membranes is best determined by captive (air) bubble contact angle measurements (Prokop *et al*, 1996). The air-bubble contact angle, which unlike liquid drop methods, ensures membrane hydration during the determination. Bubble spreading indicates greater hydrophobicity and (in most cases) increased likelihood that bacteria and organics will adsorb. The hydrophobicities of cells and inanimate substrata influence the strength and kinetics of microbial adhesion and early biofouling (Rosenberg).

3.4.3 Surface Charge

While several parameters contribute to the fouling of polymer membranes, electrostatic interactions at the solid-liquid interface present one physicochemical factor generally recognized as contributing to the fouling process. Polymer separation membranes possess varying degrees of surface charge based on the amount and type of ionic species found at the membrane surface. Ionizable carboxyl groups form on the PA membrane surface from unreacted acid chloride that subsequently hydrolyze.

The relative membrane surface charge may be determined by quantifying the amount of uranyl cation (UC) binding. As first noted by Farrar *et al* (1951), a gravimetric method using uranyl acetate (UA) can be used to quantify the carboxylic acid groups in cellulose. The quantity of UC bound to the experimental membrane was determined by performing an attachment assay similar to one described by Ridgway *et al* (1991) that quantifies bacterial attachment in water separation membranes. A solution of UA (10mM: pH=5.0) was allowed to contact the membrane surface. After a 2-hr. contact time at room temperature (about 23°C), the membrane was rinsed in 18 megohm-cm deionized water and the quantity of bound UC determined by liquid scintillation counting.

Membrane surface charge, and its influence on bacteria and organic adsorption, is an important membrane property that must be considered when investigating the interactions occurred at the solid-liquid interface. A better understanding of these interactions is helpful in the development of a more efficient low fouling, high rejection polymer membrane.

3.4.4 Bacterial Adhesion

Bacterial attachment and subsequent biofouling of RO membranes results in a significant decline in their performance and cost-effectiveness. The successful and efficient operation of membrane systems requires that biofouling be minimized, thus resulting in higher water permeation and longer membrane life.

Bacterial attachment to PA membranes was quantified via a rapid laboratory bioassay in which radioactive labeled cells were contacted with the membrane surface for several hours (Ridgway, 1988 and 1991). Test bacteria included a hydrophobic *Mycobacterium* and hydrophilic *Flavobacterium* species previously isolated from membranes at OCWD. Bacterial adsorption estimates the inherent affinity cells for membranes and can be used to gauge the biofouling potential of membranes. Bacterial attachment to *ctct*-CPTC acid

chloride PA membranes was compared to that of standard PA, CA and PS membranes. A flow schematic of the adhesion assay is shown in Figure 3.3.

3.4.5 Oxidation Studies

Chemical stability of the *ctct*-CPTC acid chloride/MPD PA membrane to chlorine was determined by ATR/FT-IR spectroscopy. In addition, *ctct*-CPTC acid chloride/MPD PA membranes filmed onto internal reflectance elements (IREs) were exposed to chlorine to determine the kinetics of polymer oxidation. The latter effort was limited but this work is continuing.

3.5 Field Test Evaluations of Experimental Polyamide Membranes

PA membranes prepared from *ctct*-CPTC acid chloride and MPD were pilot tested at OCWD's WF21 using chlorinated secondary effluent. These tests were performed using membrane coupons provided by SST, each measuring three square inches, installed in a continuous flow membrane test apparatus. The water flux and solute rejections of the *ctct*-CPTC acid chloride/MPD PA membranes were compared to both TMC/MPD PA control membranes and standard commercial PA membranes. When the present run, still in operation, is terminated membrane coupons will be removed from the test apparatus and the amount of protein, carbohydrate, and bacteria will be determined. At that time the effects of chemical oxidants on membrane surfaces will be assessed by ATR/FT-IR following RO operation with chlorinated feedwaters. A portion of this work is being funded by the U. S. Army.

Similar testing has been conducted and is on-going on chlorinated surface waters at the WQIC in Yuma, AZ. This work is also funded by the U.S. Army.

3.6 Cost Benefits of an Oxidation-Resistant Polyamide Membrane

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. Leslie (1999) at 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, PA membrane, 5-yr membrane life and operation on secondary waste water feed. For an improved low-fouling PA membrane, the annual savings ($ / yr) attained by reducing membrane fouling to extend membrane life is as follows:

	5 Year Membrane Life Extended by (Hrs.)		
Membrane Fouling Reduction (%)	20 %	40%	100%
0	$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 PA membrane.

3.7 **Potential for Commercial Applicability**:

Membrane development at SST is conducted on a pilot level for rapid transfer to large-scale continuous processing. As a result, membrane improvements derived from this program can quickly move into production and the marketplace. These membrane improvements wound not add significant costs to membrane processing or to the final product. Membrane manufacturers can use their current PA membrane processing equipment with little, if any, modification.

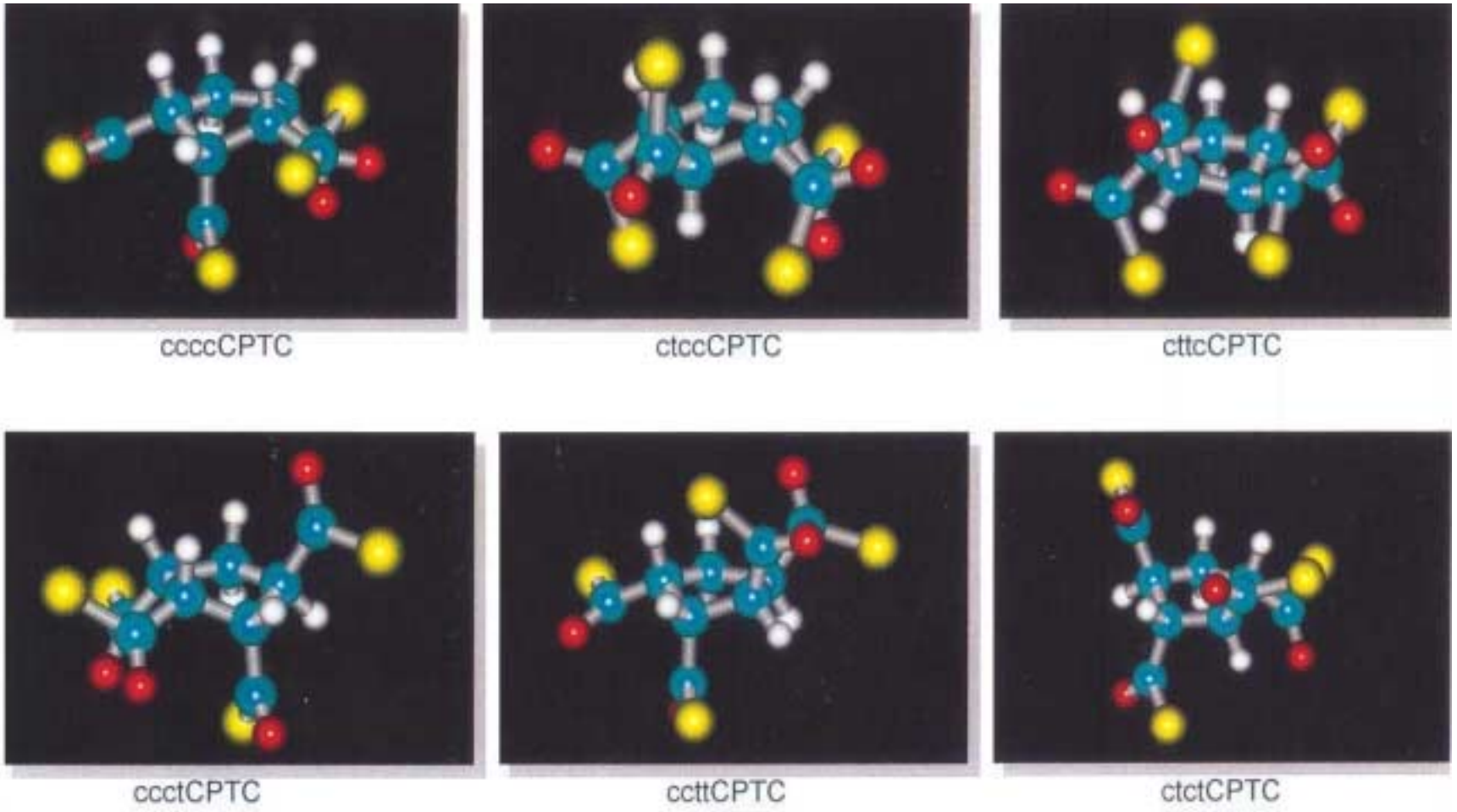

Figure 3.0 The six possible geometric isomers (stereoisomers) of 1,2,3,4 – cyclopentanetetracarboxylic acid chloride. Each isomer shown was geometry optimized to < 0.001 kcal/mol-A using Polak-Ribiere algorithm via classical mechanics (MM+, Hyperchem). Red atoms = oxygen; yellow atoms = chlorine; blue atoms + carbon; white atoms = hydrogen.

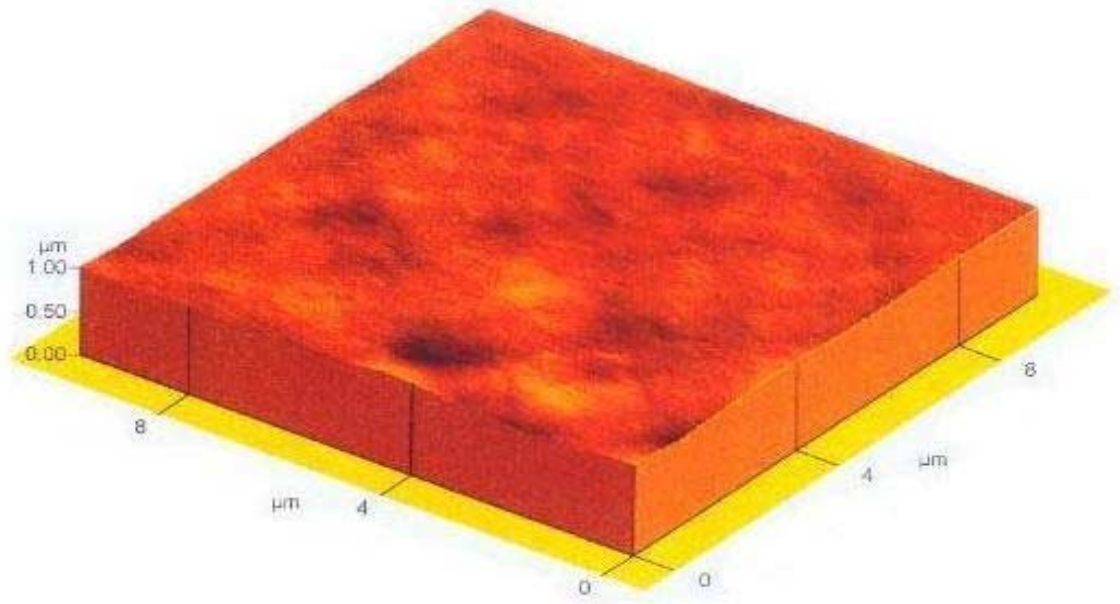

Figure 3.1 Three-D Atomic Force topograph of the desalination surface of a commercial cellulose acetate reverse osmosis membrane.

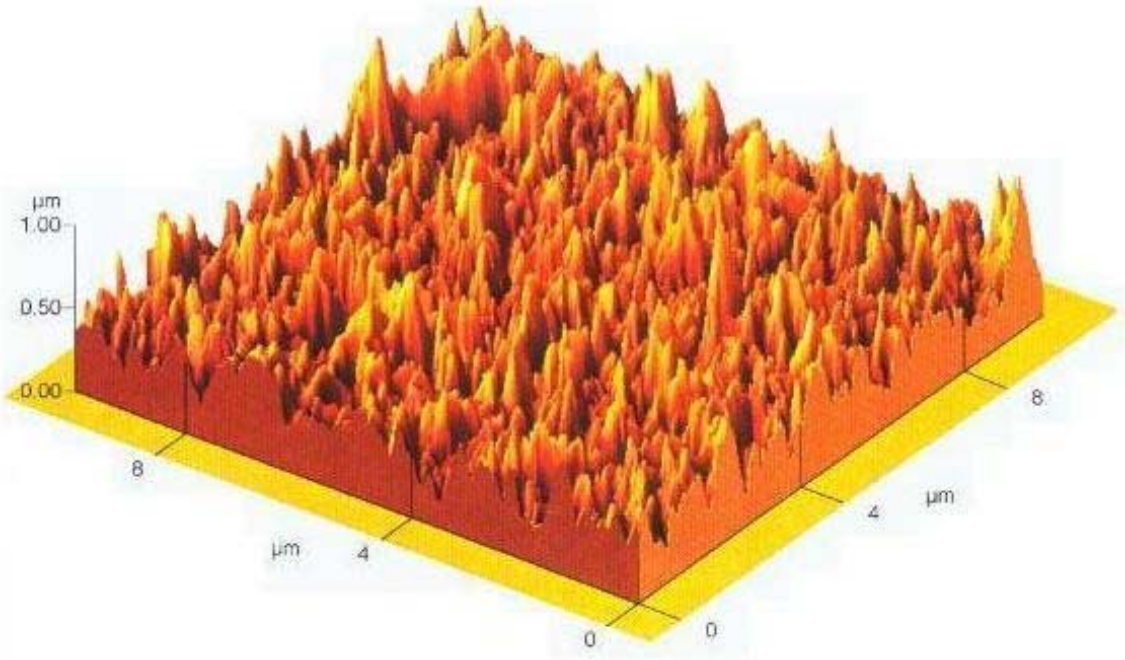

Figure 3.2 Three-D Atomic Force topograph of the desalination surface of a commercial polyamide (TMC / MPD) reverse osmosis membrane.

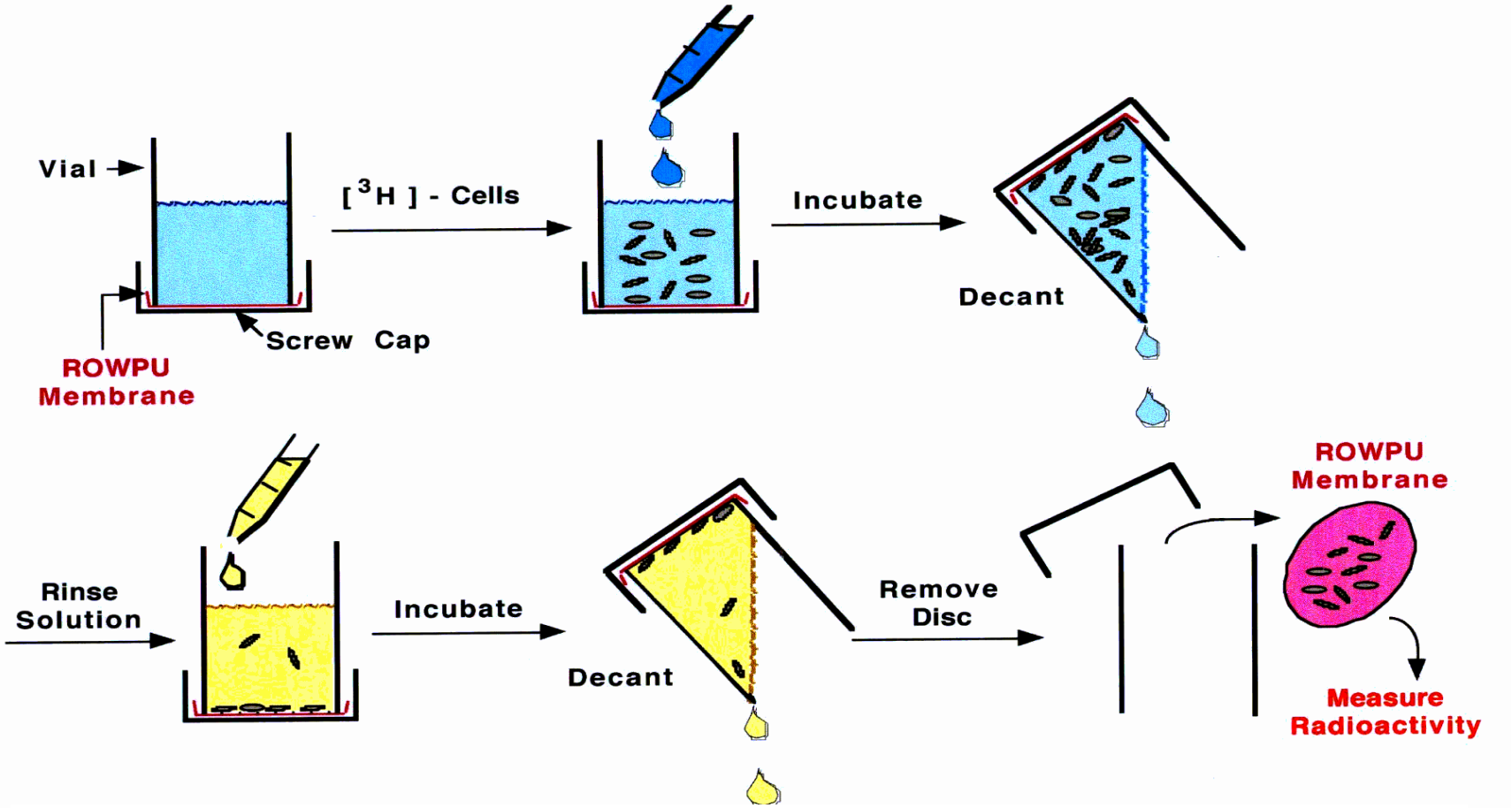

Figure 3.3 Flow schematic of rapid bacterial adhesion assay technique. Bacteria are uniformly radiolabeled by growing cells on labeled substrate (e.g., Triturated Amino Acids, 35S-Sulfate, etc.). Antimicrobial agents are added with cell suspension at the beginning of an assay, or later with the rinse solution. The number of adherent bacteria is quantified by measuring the amount of membrane bound radioactivity at the end of an experiment.

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4.0 SYNTHESIS AND PURIFICATION OF CIS, TRANS, CIS, TRANS-1,2,3,4-CYCLOPENTANETETRACARBOXYLIC ACID CHLORIDE

4.1 Background

Presently, PA membranes are made by interfacial polymerization of an acid chloride and an amine. The PA membranes used by industry are derived from TMC and MPD. The literature claims that PA membranes derived from one of six isomers of 1,2,3,4-cyclopentanetetracarboxylic acid chloride (1,2,3,4-CPTC acid chloride) and MPD possess superior chlorine tolerance (Ikeda *et al*). This has been attributed to sterics within the polymer, which supposedly hinders the attack of chlorine on the polymer. There are six different steric isomers of (1,2,3,4-CPTC acid chloride) (see Figure 3.0). The literature suggests that one of these isomers, the *cis, trans, cis, trans* (*ctct*) form, can be polymerized with MPD to produce a polymer that exhibits chlorine tolerance. Membranes made with the other isomers deteriorate rapidly.

Thus, to attain a chlorine-resistant PA membrane, it is necessary to obtain the *ctct*-CPTC acid chloride in high purity, i.e., greater than 99%. Since the material is not commercially available and a literature search did not identify a detailed preparative method, it was necessary to develop a synthetic route and procedures for purification and identification of the isomer. To improve the chances for success, two synthetic groups have been involved in the synthesis and purification of the isomer.

4.2 Experimental Program

The synthetic development of high purity *ctct*-CPTC acid chloride is a coordinated effort between Andy Murphy at BR, Dr. B. Murugaverl at DU, Dr. G. Hernandez at ITM and Dr. S. Lin, C. Milstead and Bob Riley at SST. The *ctct*-CPTC acid used in the program was synthesized at ITM under the direction of SST. Subsequently, the material was transferred to DU for conversion into *ctct*-CPTC acid chloride and purification by Andy Murphy and Dr. B. Murugaverl.

4.2.1 Thermal Conversion of *cccc*-1,2,3,4-Cyclopentanetetra-carboxylic Acid to *ctct*-1,2,3,4-Cyclopentanetetracarboxylic Acid

Experiment: Thermal conversion of *cccc*-CPTC acid to *ctct*-CPTC acid is carried out by heating an aqueous solution of the *cccc*-CPTC acid in a high pressure reactor at 200°C for 72 hours. This reaction yields approximately 80-85% of *ctct*-CPTC acid and other isomers. This step became the starting point for various studies yielding the final high purity acid chloride.

Advancement: A method using an aluminophosphate catalyst was found to provide similar conversion rates as the high-pressure method, but at substantially milder conditions; the conversion to the *ctct*-CPTC acid was achieved (actually somewhat better) at atmospheric pressures and below 100°C. This is valuable information which may be useful in the future. However, the immediate goal was to prepare high purity *ctct*-CPTC acid chloride at greater than 99% purity.

4.2.2 Conversion of *ctct*-CPTC Acid to *ctct*-CPTC Acid Chloride

Experiment: The "reasonably pure" *ctct*-CPTC acid from the thermal conversion step was converted to the corresponding acid chloride using PCl_5 as the chlorinating agent. Several attempts were made to isolate and purify the *ctct*-CPTC acid chloride from this product. Initially, problems were encountered during the conversion of the "reasonably pure" acid to its corresponding acid chloride, that is, incomplete conversion of all acid groups. After a number of trials, the product was determined to be "reasonably pure" based on H-1 NMR and C-13 NMR.

Advancement: When the phosphorous probe for the 400 MHz NMR became available, the above *ctct*-CPTC acid chloride samples were analyzed for phosphorous impurities; P-31 NMR data from the samples showed the presence of phosphorous species. It was noted that these samples developed a dark purple color. However, PA membranes made from this material exhibited good transport properties.

Alternate chlorinating agents including thionyl chloride and oxalyl chloride were also tried. With $SOCl_2$, complete conversion to the *ctct*-CPTC acid chloride was achieved using DMF or pyridine to catalyze the reaction. The results were encouraging but the acid chloride did not produce good membranes. Rather than invest additional time in pursuing this reaction, the decision was made to continue with PCl_5, a reagent that worked. Nevertheless,

this was useful information that can be used in the follow-on program. Reactions using oxalyl chloride as the chlorinating agent, where the reaction side products are HCl and CO_2, did not result in complete conversion of all of the acid groups. The advantage of this reaction was that residual phosphorous and sulfur compounds were not left behind.

4.2.3 Physical Methods Evaluated for Purification of *ctct*-CPTC Acid Chloride

Three physical methods were investigated to purify *ctct*-CPTC acid chloride. These methods included spinning band distillation, zone refining and falling film molecular distillation techniques.

Spinning Band Distillation: In theory an excess of 300 theoretical plates can be achieved in spinning band distillation making this a powerful technique to fractionate and purify liquids having small differences in boiling points. In principle, it should be possible to fractionate and purify the different acid chloride isomers of the CPTC. However, this was not the case; the compounds started to decompose before any distillation. The vacuum system was modified with a liquid nitrogen trap, a proportioning valve, controller and pressure transducer capable of controlling the spinning band pressures to below 20+/- 0.1 m torr. In spite of this effort, the compound still decomposed before distillation occurred.

Zone Refining: This is a well-established technique for obtaining high purity silicon wafers for microelectronics application. Zone refining appeared promising since *ctct*-CPTC acid chloride appeared to have a melting point within the capabilities of the technique. However, this proved not to be the case; the liquid-solid interface needed for this technique to work was not attained even after dry ice was used to lower the temperature of the cold zone.

4.2.4 Synthesis of *ctct*-CPTC Esters

Experiment: Attempts were made to produce high purity *ctct*-CPTC acid by an indirect method in which CPTC acid is converted to an ester. With this method the ester is purified and subsequently hydrolyzed to produce pure *ctct*-CPTC acid. Similarly, the corresponding propyl and benzyl esters were prepared from the impure acid. The boiling and melting points of the propyl ester were not in the range of either spinning band or zone refining techniques. The melting point of the benzyl ester was too low for zone refining. No attempt was made with spinning band because of the difficulty in attaining complete removal of benzyl alcohol.

Advancement: The molecular packing of the methyl ester, based on molecular geometry, is preferred to the corresponding propyl and benzyl esters. This gives the methyl ester a higher melting point which might fall within the realm of zone refining. The methyl ester of the *cccc*-CPTC acid was synthesized using p-toluenesulfonic acid (p-TSA) as a catalyst. The melting point was determined to be around 75°C, an ideal temperature range for zone refining. The product when subjected to zone refining, exhibited a very nice visual pattern (hot and cold zones) typical for this technique. The H-1 NMR of the zone refined sample showed some purification. This suggests that further purification of the *ctct*-CPTC acid is possible with this technique provided the starting *ctct*-CPTC acid is relatively pure (98-99%).

4.2.5 Removal of Phosphorous from Synthesized *ctct*-CPTC Acid Chloride Using Falling Film Distillation.

Experiment: The impure *ctct*-CPTC acid chloride made from PCl_5 was subjected to falling film molecular distillation to increase the purity of the product.

Advancement: Unlike spinning-band distillation, the results obtained with falling-film molecular distillation were encouraging. This technique not only showed that distillation of the *ctct*-CPTC acid chloride was feasible but it was found to remove residual phosphorous from the sample. This was confirmed by both P-31 NMR and elemental analysis. Unfortunately, the distillate still turned to a dark purple color during the distillation process. The change in color is not fully understood and no effort was made to investigate the cause of this effect. It is speculated that the color change is due to some phosphorous species. Four different heat transfer fluids and several mixtures were used in an attempt to improve the temperature conditions for the fractionation of the preferred CPTC acid chloride isomer. No measurable isomeric purification was observed with this technique except for the removal of phosphorous.

4.2.6 Purification of *ctct*-CPTC Acid by Physical Separation Techniques

Several other separation and purification techniques were evaluated in an effort to separate the CPTC acid isomers. If high purity *ctct*-CPTC acid can be isolated then the corresponding *ctct*-CPTC acid chloride could be made at a similar purity. Two different techniques, flash chromatography and selective extraction, were evaluated in an attempt to produce high purity *ctct*-CPTC acid.

Flash Chromatography: Preliminary HPLC data had indicated the possible separation of the components from the impure CPTC acid. Chromatographic separation of the mixed isomers was attempted in a preparative scale using flash chromatography on an octadecylsiloxane stationary phase using a methanol/phosphoric acid mixture as the eluent. This method was not only tedious, but the product recovered from this method showed more impurities than the starting compound.

Traditional Extraction/Crystallization: The impure *ctct*-CPTC acid was subjected to traditional extraction and recrystallization techniques using organic solvents, specifically, ethyl acetate, acetic acid and acetone. This method proved to be very effective in separating the *ctct*-CPTC acid from the other isomers. The separation required a number of steps, was time consuming and the yields were quite low. Nevertheless, product purity of greater than 99% was achieved routinely. The purity was confirmed by high resolution H-1 NMR and C-13 NMR. Further optimization of this process would be expected to improve yield.

4.2.7 Synthesis of *ctct*-CPTC Acid Chloride from High Purity *ctct*-CPTC Acid Using PCl_5

Experiment: Pure *ctct*-CPTC acid was transformed to its corresponding acid chloride using PCl_5 as the chlorinating agent. The product isolated from the reaction showed no sign of (not detectable) other isomeric impurities. This suggested that no isomerization had occurred during the synthesis, leaving the final product isomerically pure. This was confirmed using both H-1 NMR and C-13 NMR. The expected amounts of carbon, oxygen, hydrogen and chlorine were verified by elemental analysis. Phosphorous was detected in the *ctct*-CPTC acid chloride by both elemental analysis and P-31 NMR; later, the phosphorous was removed by falling film distillation.

Advancement: After some experimentation, it was found that the phosphorous could be removed by high vacuum overnight, thereby eliminating the need for falling film distillation. The phosphorous compounds that remain must all be volatile.

4.3 Conclusions and Recommendations

After a great deal of effort, the synthesis and purification of *ctct*-CPTC acid chloride at >99% purity was successful. It is anticipated, however, that higher purity material will be required to produce a chlorine-resistant PA membrane. Additional effort is also required to improve the yield, synthesis time, and the overall economics of the process. At this stage in the development, it is recommended that the separation and synthesis procedures be transferred to either SST and/or ITM to provide the quantities of acid chloride required to keep the program moving ahead. At the same time, research at DU and Reclamation should continue to improve the overall synthesis process.

5.0 OPTIMIZATION OF POLYAMIDE MEMBRANES MADE FROM *ctct*-CYCLOPENTANETETRACARBOXYLIC ACID CHLORIDE

5.1 Polyamide Membrane Formation Process

The standard commercial PA membrane dominating the RO desalination industry today is formed by a two-step process (Cadotte, 1980). This process, with only minor modification, was used throughout this program. First, the porous PS support membrane, upon which the thin PA membrane is formed, is prepared on a non-woven polyester support fabric by a knife-over-roll phase inversion process on a continuous casting machine. Soon after applying the PS-DMF solution onto the fabric (30 ft/min or greater), the membrane is immersed in water to remove the solvent and precipitate the PS, thereby forming the porous membrane structure. The process diagram for this process is given in Figure 5.0.

Subsequently, the finished PS membrane roll is transferred to a second machine where a fully aromatic PA desalination barrier is formed on the porous surface by an *in-situ* interfacial reaction between MPD and the acid chloride. Thus, the porous PS membrane becomes the foundation upon which the interfacial PA membrane is formed. The membrane is processed by first applying an aqueous MPD solution onto the finely porous surface of the PS membrane. Subsequently, the MPD-coated PS membrane is passed through a hydrocarbon solution containing either TMC or *ctct*-CPTC acid chloride; at the immiscible interface between the two solutions, a very thin PA film is formed. The chemistries of both the standard commercial PA membrane and the *ctct*-CPTC acid chloride PA membrane are shown in Figure 5.1. It should be noted that the TMC is aromatic while the *ctct*-CPTC acid chloride is aliphatic.

After the interfacial PA film is formed, the membrane passes through a series of leaching tanks to remove residual monomers before final drying. The MPD, entrained in the solid membrane phase, is particularly difficult to remove and if any residual remains it will oxidize, thereby discoloring the membrane. More importantly, the transport properties of the MPD laden PA membrane deteriorate with time and the membrane exhibits greater biofouling. Thus, it is imperative to utilize effective methods of removing MPD that are now well known. The process flow diagram for fabrication of the commercial PA membrane is shown in Figure 5.2. All *ctct*-CPTC acid chloride PA membranes prepared during this program were made by this general process. The more detailed steps for making the *ctct*-CPTC acid chloride PA membranes used in this study are shown in Figure 5.3.

5.2 *ctct*-CPTC Acid Chloride/MPD Membrane Development

A major portion of this program was spent evaluating the *ctct*-CPTC acid chloride samples received from DU for PA membrane preparation. Twelve synthesis lots were received throughout the program at regular intervals with each lot containing approximately six grams of material. About seventy (8- x 10-inch) membrane sheets were prepared from each sample lot. Throughout the program, 600 membrane sheets were made from 12 *ctct*-CPTC acid chloride synthesis lots.

Control PA membranes were made with TMC and MPD for each set of preparative conditions used for making the *ctct*-CPTC acid chloride / MPD membranes. As expected during this development period, the purity and reactivity varied between lots of *ctct*-CPTC acid chloride. Thus, it was necessary to vary, control and optimize the PA membrane preparative parameters for each individual synthetic lot of *ctct*-CPTC acid chloride in order to attain comparative water and salt transport data. The primary parameters that were varied and controlled included:

- PS membrane support characteristics such as fabric support, thickness, pore size, pore distribution and water permeability
- MPD concentration
- MPD pH
- Acid chloride concentration
- Reaction times
- Reaction phase additive, types and concentrations.
- Membrane post treatment leaching steps
  - Chemical type and concentration
  - Time and temperature
  - Sequence of the leaching steps
- Drying temperature and time

All membranes prepared from each lot of *ctct*-CPTC acid chloride along with control membranes prepared with TMC and MPD were evaluated side by side in laboratory reverse osmosis tests at 225 psi (1551 kPa) applied pressure, pH 6.5, 25°C with a 2000 mg/L sodium chloride feed solution. The transport properties of the *ctct*-CPTC acid chloride PA membranes were determined and compared with the controls. This information provided feedback required for optimizing membrane preparative parameters.

The transport properties of *ctct*-CPTC acid chloride PA membranes were optimized to equal or surpass those of the commercial control made with TMC and MPD. To achieve this objective it was necessary to make significant changes in the preparative parameters. A summary of the *ctct*-CPTC acid chloride synthesis lots, purity and PA membrane performance is given in Table 5.0.

Optimized *ctct*-CPTC acid chloride PA membranes were characterized as follows: surface topography by AFM, surface hydrophilicity by air bubble contact angle determinations, bacterial attachment, surface charge analysis, IR and ATR/FT-IR spectroscopic analysis. In addition, membranes were placed on long-term RO testing on a chlorinated surface water feed at WQIC Yuma, AZ and a chlorinated municipal waste water feed at OCWD Fountain Valley, CA. A summary of field testing for membranes made from different lots of *ctct*-CPTC acid chloride is shown in Table 5.1.

Table 5.0

Reverse Osmosis Performance of Polyamide Composite Membranes Prepared with *ctct*-Cyclopentanetetracarboxylic Acid Chloride

Brackish Water Test Conditions: 1551 kPa (225 psi) applied pressure, 2000 mg/L sodium chloride feed (4000 µmhos/cm^2), 25°C, pH 6.9, 0.9 gal/min (0.00200 ft^3/sec) feed flow

Date	Acid Chloride Synthesis Lot	Acid Chloride Purity (%)	Acid Chloride Color	Reverse Osmosis Performance Water Flux (GFD)	Reverse Osmosis Performance Rejection (%)
Nov 98	DU-1	~70	Dark purple/brown	15.6	98.6
Nov 98	DU-2	~70	Dark purple/brown	-	-
Nov 98	ITM All Cis	~98	Dark purple/brown	16.9	96.8
Feb 99	021599 SE-FF	~98	Clear pink	15.4	98.8
Feb 99	021799 SE	~98	Dark purple/brown	19.2	98.6
Mar 99	030399	~99	Dark purple/brown	20.3	99.2
Apr 99	041299**	99+*	Clean amber	13.9	98.1
Jun 99	061099	99+*	Dark purple/brown	22.3	99.2
Jun 99 (1,4 cis 2,3 trans isomer)	062199	99+*	Not soluble in solvent required to make membrane		
Jul 99	070899	99+*	Light color	13.0	99.0
Aug 99	081399	99+*	Dark purple/brown	14.0	99.2
Sep 99	092099S1	99+*	Clear Amber	11.0	99.3
Oct 99	100199S1	99+*	Dark purple/brown	15.6	99.0
		TMC Control Membrane		14.8	99.7
		FilmTec FT-30 Control Membrane		21.2	98.2

* Determined by GCMS SE = Selective extraction, FF = Falling-film molecular distillation, DU = University of Denver, ITM = Institute of Technology Mexico, TMC = Trimesoyl chloride, FT-30 = Dow-FilmTec polyamide membrane.

** Sample was stored in polypropylene vials, which may have contaminated sample.

Table 5.1

Reverse Osmosis Field Testing of Polyamide Thin-Film Composite Membranes Prepared from Different Synthetic Lots of *ctct* - Cyclopentanetetracarboxylic Acid Chloride

Acid Chloride		Reverse Osmosis Field Test Site				
Sample	Purity (%)	WQIC-Yuma			OCWD	Pt. Hueneme
		TCU 1 pH 4.1 / 1.5 ppm Cl 3 Cells Clearwell	TCU 2 pH 8 / 0.5 ppm Cl 9 Cells Potable	TCU pH 5.5 / 0.5 ppm Cl 9 Cells Potable	pH 8.5 / 3.0 ppm Cl 9 Cells Mun. waste water	pH 8.0/ 1.0 ppm Cl 3 Cells Seawater**
DU - 1	~70	x	x	-	-	-
ITM All Cis[(a)]	~98	-	x	-	-	-
0123999SE	~80	-	-	-	-	-
021599 SE-FF	~98	ab	x	-	a	-
021799 SE	~98	b	x	-	a	-
030399	~99	xa	x	a	-	-
041299	99+	-	-	-	-	-
061099	99+*	a	x	a	-	a
062199	99+* (1,2 cis 2,3 trans)	Not Soluble in solvent required to make membrane				
070899S1	99+*	-	-	-	-	-
081399S1	99+*	-	-	-	-	-
092099S2	99+*	-	-	-	-	-

[(a)] *cccc*-Cyclopentanetetracarboxylic acid chloride
x Test Terminated
a Currently in operation
b Run terminated after 1750 hours with no loss in membrane performance
- Not yet tested
* Determined by GCMS
Chlorine at OCWD converted to chloramines due to high nitrogen content in water; membranes have operated for > 4,000 hours with good performance
** Seawater testing conducted on U. S. Army contract

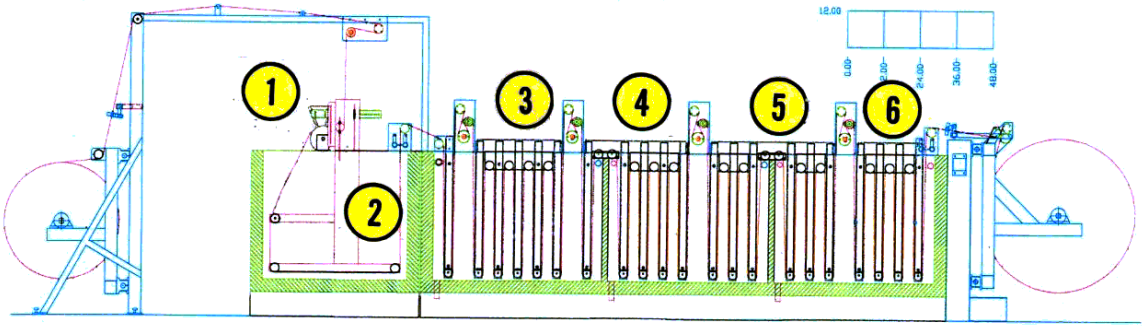

Figure 5.0 Process schematic of continuous casting machine producing porous polysulfone membrane support by phase inversion for polyamide thin-film composite membrane development. (1) Location of knife-over-roll casting assembly above non-woven casting fabric, (2) Aqueous phase inversion gelation tank (5ºC), and (3) (4) (5) Water rinse tanks for solvent removal (80ºC).

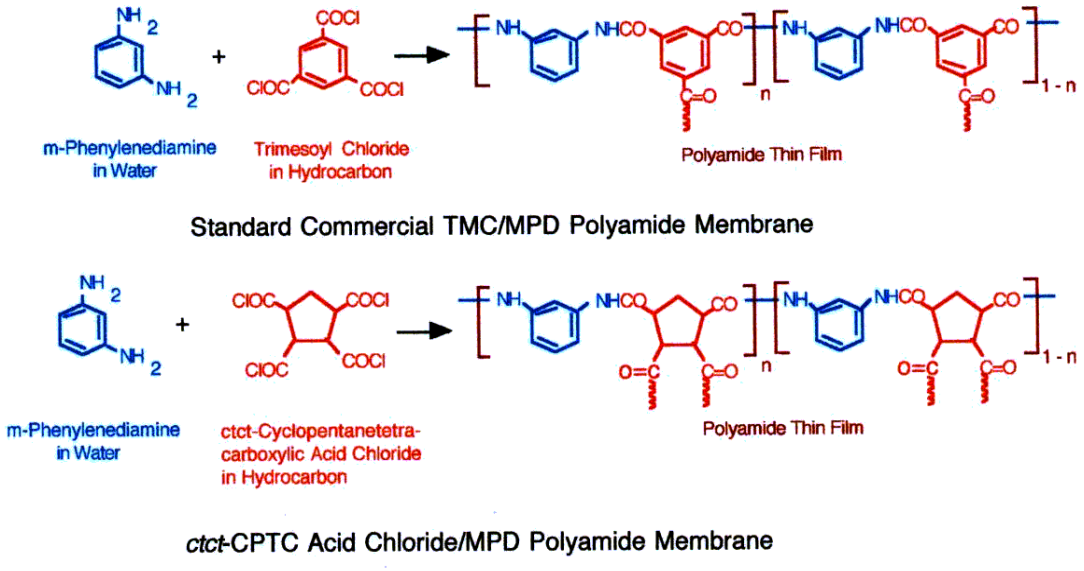

Figure 5.1 Polyamide membrane chemistries: Upper: Standard commercial PA membrane: TMC control. Lower: Projected chlorine tolerant PA membrane : *ctct*-CPTC acid chloride PA membrane.

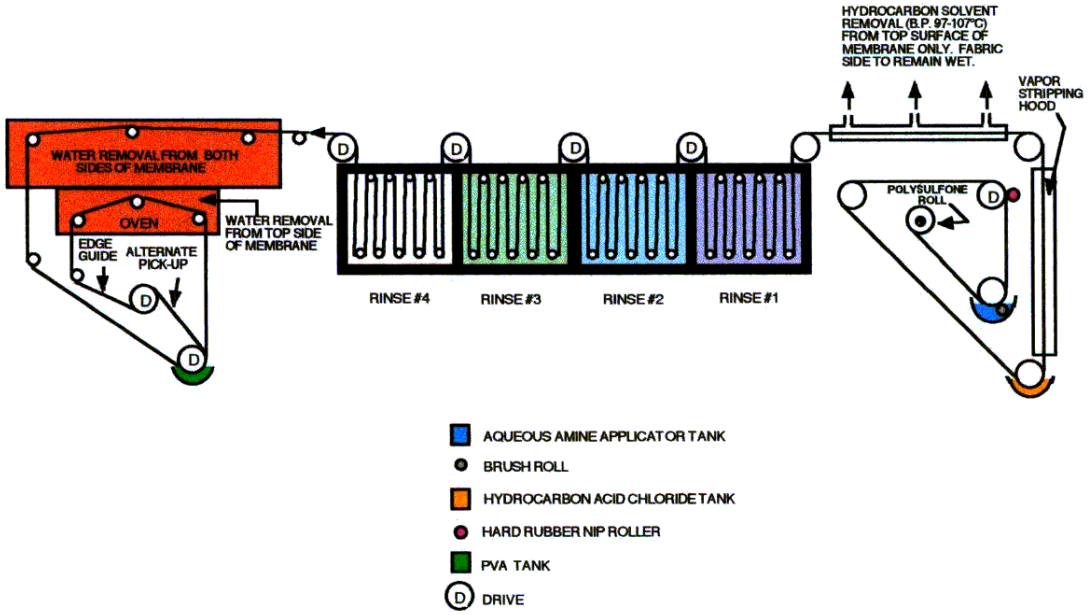

Figure 5.2 Interfacial polyamide thin-film coating machine

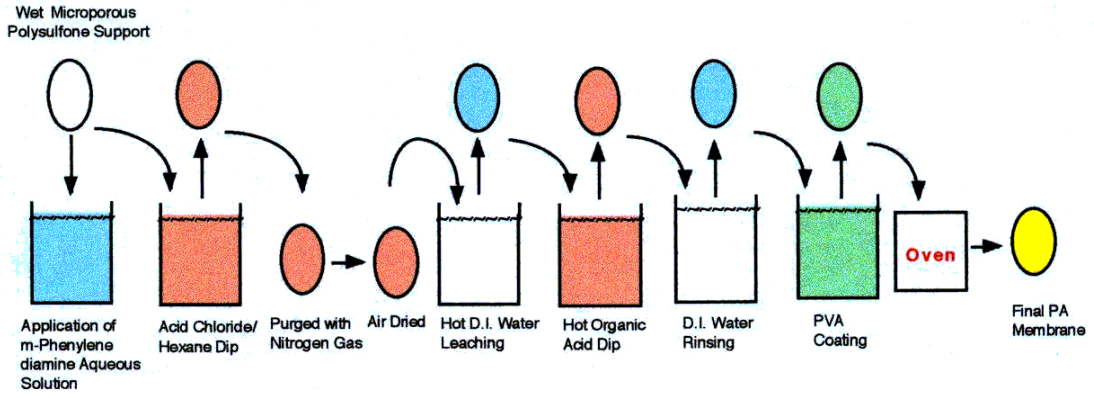

Figure 5.3 Process steps in preparation of *ctct*-CPTC polyamide membrane

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6.0 LONG-TERM REVERSE OSMOSIS FIELD TESTING OF POLYAMIDE MEMBRANES AT THE WATER QUALITY IMPROVEMENT CENTER YUMA, AZ ON CHLORINATED BRACKISH WATER FEEDS

Field testing of *ctct*-CPTC acid chloride PA membranes at the WQIC Yuma, AZ was initiated during the first quarter of this program with two test cell units (TCUs), each operating on a different feed water. Initially, each TCU operated with three 3-square inch (19.4 cm^2) test cells connected in series. Throughout the year the test cells were upgraded, and the number of cells was increased to nine in each TCU. Originally, TCU-2 was operated on the natural pH of the potable water feed. Midway through the program, an acid injection-pH control system was installed so that both systems could be pH controlled.

Testing at WQIC has been plagued with shutdowns, thereby limiting the amount of useful information that was anticipated. Both test cell units were shut down during May, June and August. TCU 1 was shut down to accommodate a research group from Los Alamos National Laboratory which had established a Cooperative Research and Development Agreement (CRADA) with WQIC, thereby establishing precedence over SST. To avoid such interruptions in the future, SST has now established a CRADA with WQIC which is funded by the U.S. Army. The CRADA assures future testing through December 31, 2000. More recently, the test units have been taken off line for the Bureau of Reclamation to do maintenance on the canals leading to the plant. The latter is expected to take several months.

6.1 Water Sources

Operating on two WQIC water sources enables evaluating the effects of different pH, varying chlorine levels and different feed compositions. The approximate compositions of the two waters are:

Test Unit	Water Source	TDS, mg/L	pH	Cl_2, mg/L
TCU-1	PS1 Clearwell	3,000	4.0	1.5
TCU-2	Potable water	350	8.0-8.5	0.5

6.2 Operating Pressures

Operating pressures were adjusted to maintain approximately equal and constant product water flow for each of the membranes. The product flow for each cell is approximately 1.0 mL/min or 18 gfd.

6.3 Membrane Locations

The initial and present test cell locations are shown in bold and ordinary type, respectively.

Test Unit	Water Source	Test cell designations			Installed
TCU-1	PS1 Clearwell	**1**	**2**	**3**	December 98
		4	**5**	**6**	April 99
		7	**8**	**9**	August 99
TCU-2	Potable water	**1**	**2**	**3**	December 98
		4	**5**	**6**	April 99
		7	**8**	**9**	August 99

6.4 Data Collecting and Reporting

The frequency of the manual data collection is once per shift. The raw data is telefaxed to Separation Systems daily where it is entered into Excel, standardized, evaluated and plotted.

Parameter	TCU Feed	TCU Reject	Product		
			Cells 1,2,3	Cells 4,5,6	Cells 7,8,9
Pressure, kPa	3xdaily	3xdaily	-	-	-
Temperature °C	3xdaily	3xdaily	-	-	-
pH	3xdaily	3xdaily	-	-	-
Cl_2 (free, mg/l)	3xdaily	3xdaily	Weekly	Weekly	Weekly
Cond., (uS/cm)	3xdaily	3xdaily	3xdaily	3xdaily	3xdaily
Flow (L/min)	-	3xdaily	-	-	-
Flow (g/min)	-	-	3xdaily	3xdaily	3xdaily

6.5 Test Results

6.5.1 *ctct*-CPTC Acid Chloride Based Polyamide Membranes

At the time TCU-1 was shut down to accommodate the Los Alamos Research Laboratory testing, a successful long-term test was in progress. The system was operating with PA membranes prepared with *ctct*-CPTC acid chloride synthesis lots 021599 SE-FF and 021799 SE which were both determined to have an isomeric purity of approximately 98%. Also included in the test were PA control membranes made with TMC by SST. Prior to shut-down, the membranes had accumulated 1760 hrs. (73 days) of continuous testing on clearwell feed containing 1.5 mg/L free chlorine at a feed pH of 4.0 - 4.24. The performance of all the membranes, shown in Figure 6.0, showed no signs of deterioration.

When the membranes were placed back on line, after three months off line in the test cells, the performance of the *ctct*-CPTC acid chloride membranes showed an abrupt loss in performance. The TMC control, was not affected. Nevertheless, the performance of the *ctct*-CPTC acid chloride membranes is very encouraging. Due to the abrupt loss of performance after shutdown, it is likely due to physical rather than chemical deterioration. In a parallel program it was shown by ATR/FT-IR that the PA film of the *ctct*-CPTC acid chloride membranes is somewhat thinner than that of the TMC control. In addition, the test system was operating at a low pH where the performance is less than optimal. In the future, both the thickness of the PA film and the pH of the feed will be increased to enhance membrane longevity.

The purity of *ctct*-CPTC acid chloride used to prepare these membranes was only 98%; the purity of the TMC used to prepare the control membranes, after double distillation, was ~99.9%. The synthesis of *ctct*-CPTC acid chloride has now progressed to the point where 99+% purity is obtained. However, variations between synthetic lots, as shown by membrane performance, still exist even at the higher *ctct*-CPTC acid chloride purity level. The need for very high purity *ctct*-CPTC acid chloride is inevitable.

6.5.2 *cccc*-CPTC Acid Chloride Based Polyamide Membranes

As with the *ctct*-CPTC acid chloride isomer described in Section 4.0, the *cccc*-CPTC acid chloride isomer was isolated from the mixture and purified to ~98% purity. The PA membranes prepared from the *cccc*-CPTC acid chloride (ITM-All Cis) were evaluated in two separate tests in TCU 2 at WQIC. The performance of the SST-137 membranes, tested with a 350 TDS feed, pH 8.0 - 8.5., 0.5 mg/L chlorine and 25°C, is shown in Figures 6.1 and 6.2. It is quite apparent that the oxidation resistance of the *cccc*-CPTC SST 137 membrane is very much less than for the SST-34-TMC control membrane. After only 75 hrs. of operation, the salt passage increased to an unacceptable level. Furthermore, PA membranes made from the *cccc*-CPTC acid chloride are much more susceptible to chlorine damage at 0.5 mg/L chlorine than the *ctct*-CPTC acid chloride membranes shown in Figure 6.0 operated at 1.5 mg/L.

The effect of isomeric purity of *ctct*-CPTC acid chloride becomes very apparent when the performances of the cccc-CPTC acid chloride membranes are compared with the *ctct*-CPTC acid chloride membranes. Even traces of other isomers in the *ctct*-CPTC acid chloride would be expected to be detrimental to long-term chlorine resistance. For this reason, the emphasis will continue to achieve 99.9% isomeric purity.

6.5.3 Test Cell Limitations - Recommendations

Long-term testing of membrane swatches in the 1 x 3-inch test cells at WQIC has proven difficult due to frequent shutdowns that have occurred. An increase in salt transport is typically observed after shutdown. Subsequent dyeing of the membranes indicates that the membranes are physically damaged at the O-ring/membrane interface. The area of O-ring contact with the membrane is quite large relative to the area of the membrane surface in the test cells. Thus, damage to the membrane can be quite significant.

It is recommended that new membranes be incorporated into small 2- x 12-inch spiral elements for future chlorine resistance testing. In the spiral configuration, there is no contact on the surface of the membrane as all seals are made on the back side of the membrane.

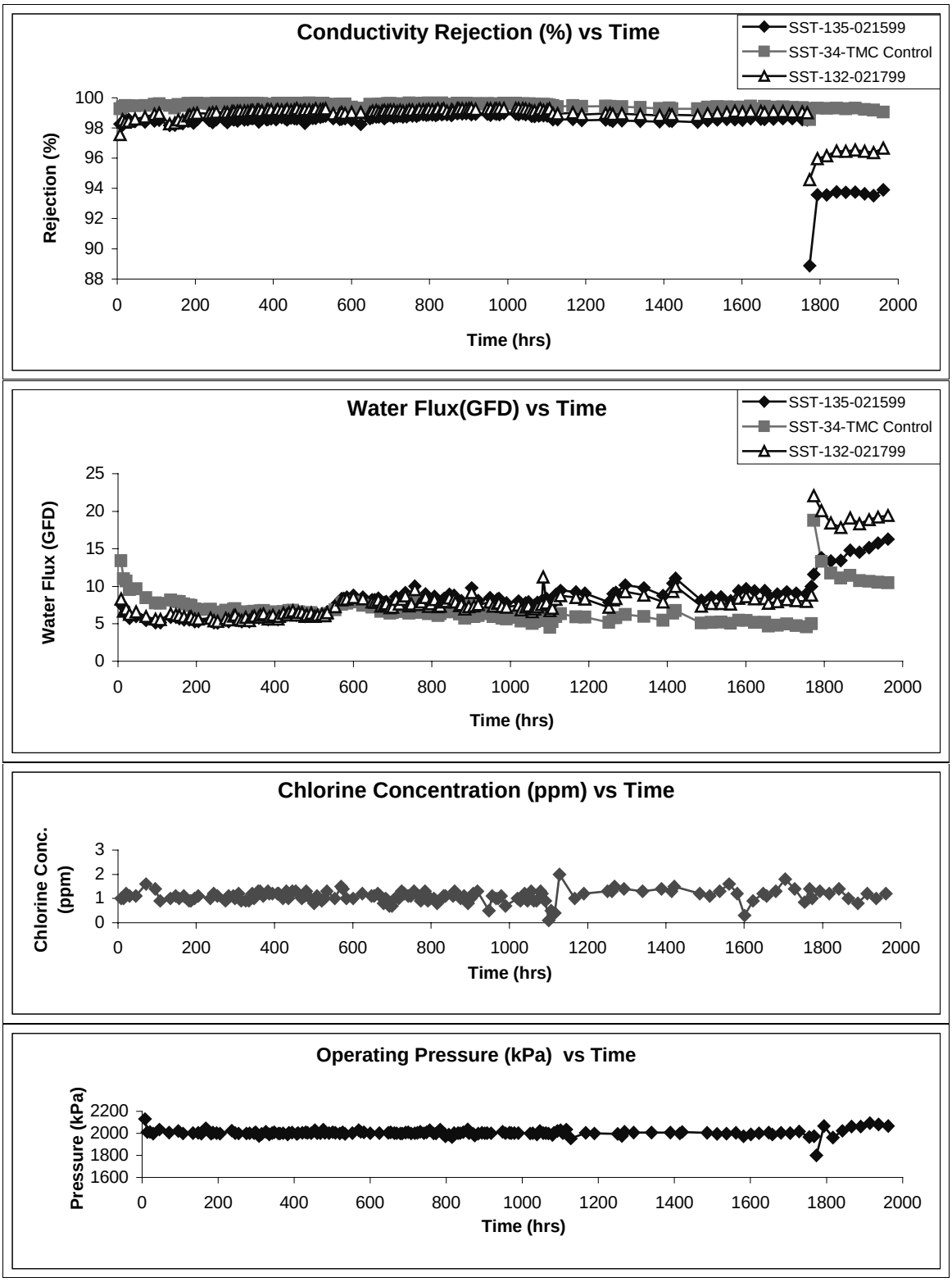
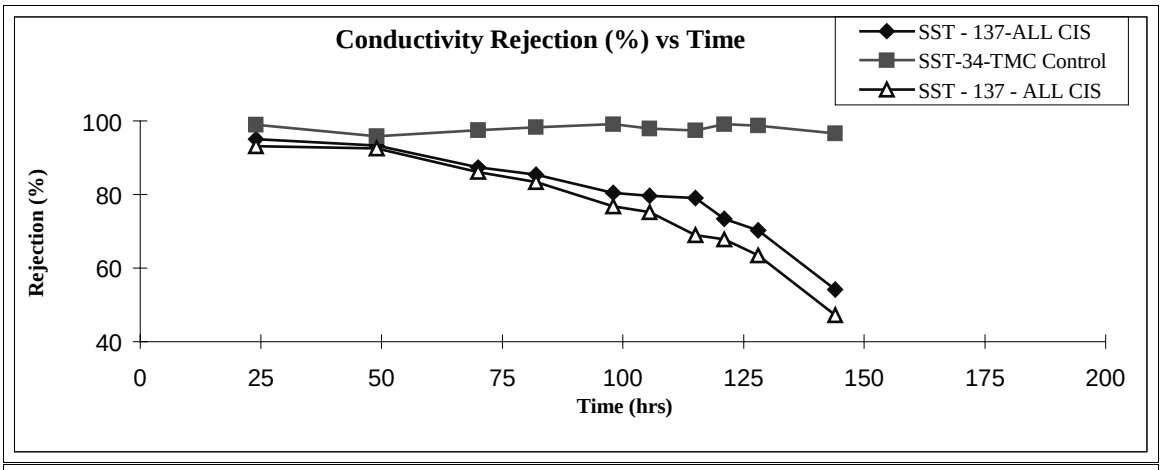
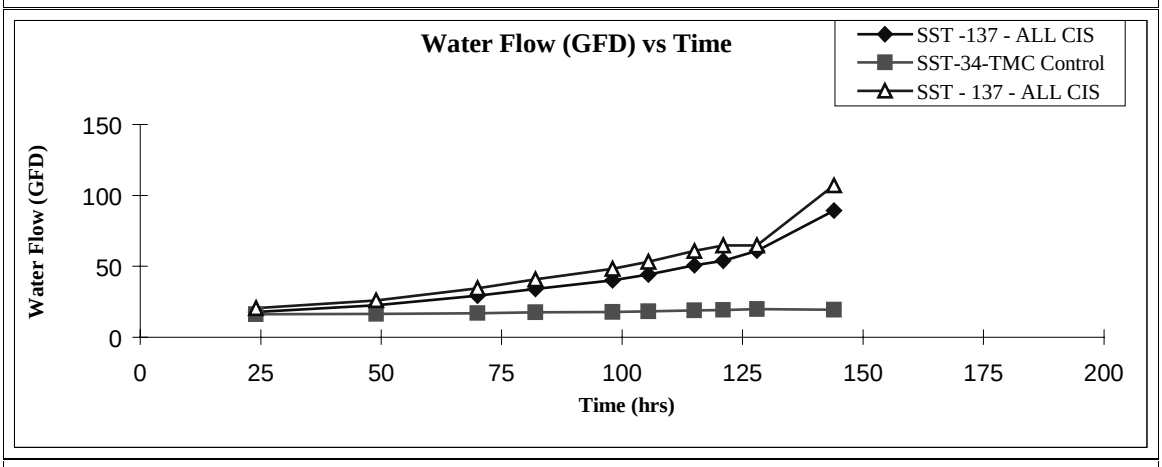
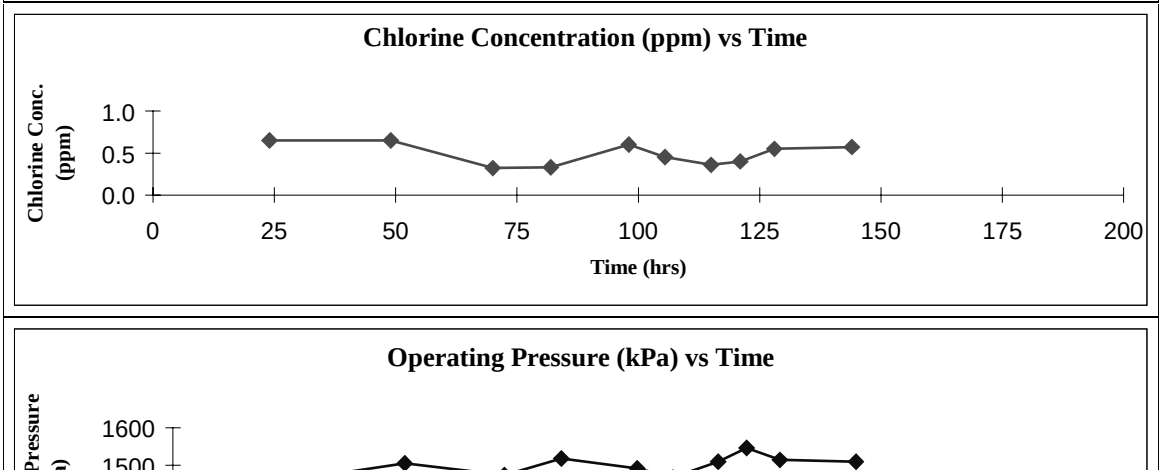


Figure 6.0 Reverse osmosis performance of ctct-CPTC acid chloride PA composite membranes in TCU 1 (Test 2) at WQIC-Yuma, AZ. Test conditions: Cells 1,2,3 clearwell feed, pH~4.0-4.25, (3/12/99 to 8/23/99)). System taken off line from 5/19/99 to 8/13/99







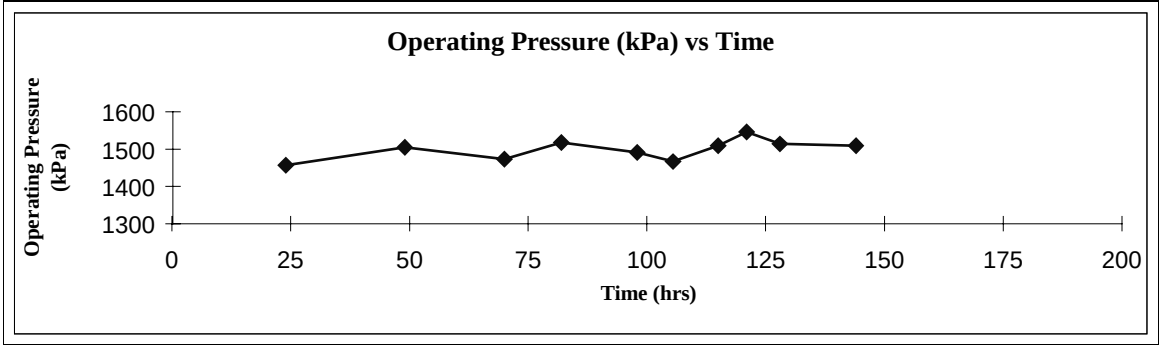


Figure 6.1 Reverse osmosis performance of *cccc*-CPTC acid chloride PA composite membranes in TCU 2 (Test 2) at WQIC-Yuma, AZ. Test conditions: Cell 1,2,3 potable feed, pH~8.0-8.5, 25ºC. (3/12/99 to 3/18/99)

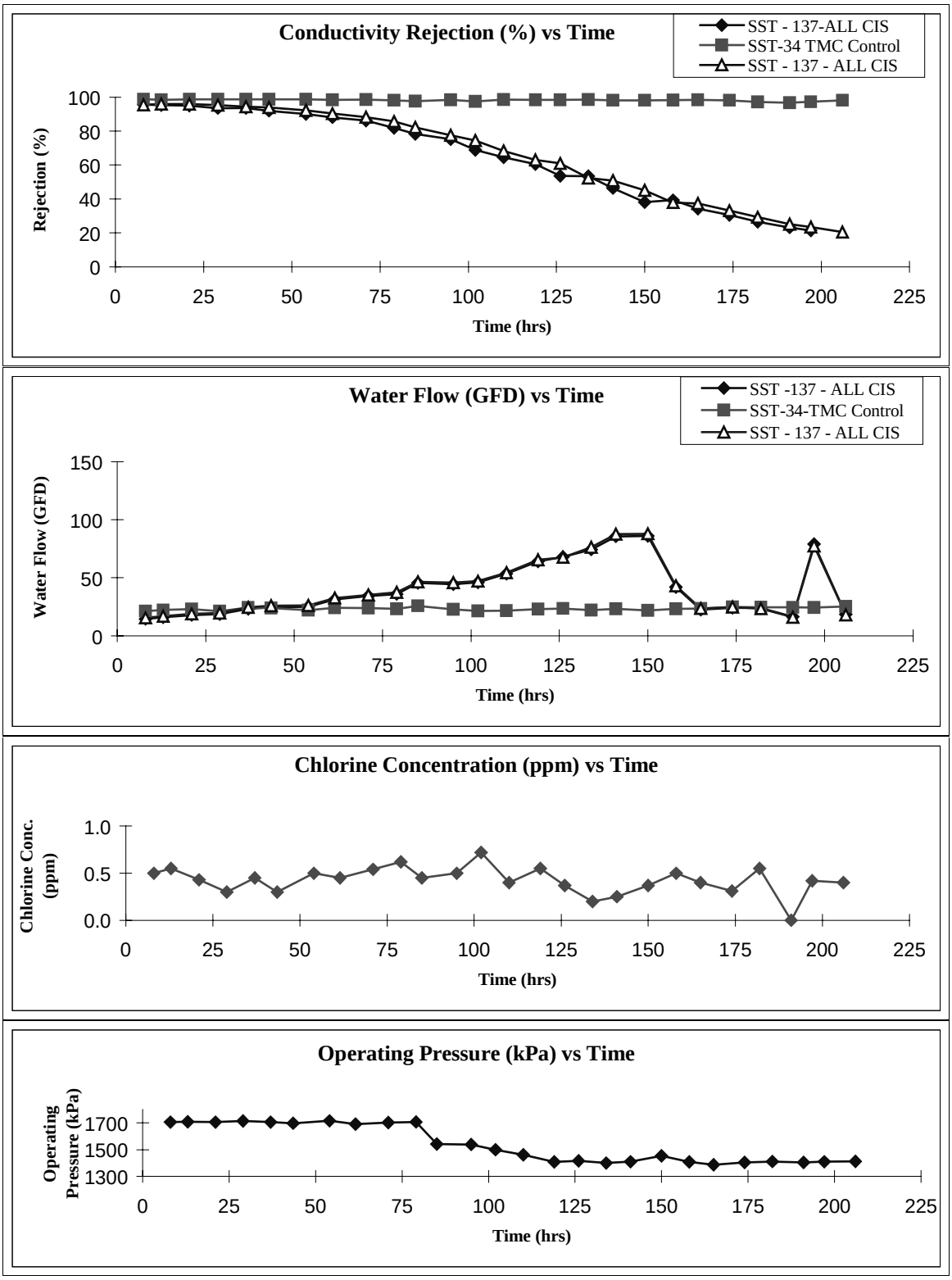


Figure 6.2 Reverse osmosis performance of *cccc*-CPTC acid chloride PA composite membranes in TCU 2 (Test 3) at WQIC-Yuma, AZ. Test conditions: Cell 1,2,3 potable feed, pH~8.0-8.5, 25C. (3/19/99 to 3/25/99)

7.0 LONG-TERM REVERSE OSMOSIS FIELD TESTING OF POLYAMIDE MEMBRANES AT THE ORANGE COUNTY WATER DISTRICT ON CHLORINATED MUNICIPAL WASTE WATER FEED

7.1 Long-Term Field Test Program

Field testing at OCWD on chlorinated municipal wastewater was funded, in part, by this contract. Field testing on chlorinated surface water and seawater was funded by a concurrent program at both WQIC Yuma AZ, and at The U. S. Naval Test Facility at Port Hueneme, CA, respectively. Field testing at the WQIC was funded through a CRADA contract with the Yuma Desalting Plant, Bureau of Reclamation.

7.2 Long-Term Reverse Osmosis Test Results at Orange County Water District

On April 1, 1999, OCWD began evaluating the performance of *ctct*-CPTC acid chloride PA composite membranes prepared from DU synthesis lots 021599 SE-FF and 021799 SE (See Table 5.1 in Section 5.0). The estimated isomeric purity of these samples was approximately 98%. Sample 021599 passed through falling-film distillation and was free of phosphorous. A FilmTec commercial control and an SST/TMC control membrane were evaluated simultaneously for comparative purposes. Codes for the membranes evaluated are as follows:

FT-30	=	Dow-FilmTec commercial PA membrane
SST/TMC	=	Separation Systems Technology PA control membrane made with trimesoyl acid chloride
BBCR-132	=	Separation Systems Technology PA membrane made with *ctct*-CPTC acid chloride 021799S1
BBCR-135	=	Separation Systems Technology PA membrane made with *ctct*-CPTC acid chloride 021599S1

The membranes are fed with conventionally pretreated secondary effluent from Water Factory 21 at OCWD. The pretreatment process includes chemical clarification, multimedia filtration, antiscalent, sulfuric acid and approximately 5 mg/L chlorine addition before water is passed through the RO system. The wastewater feed is high in nitrogenous materials. Thus, chlorine combines with these materials to form chloramines; the combined chlorine contacting the membrane ranges from 2 to 5 mg/L. Membranes are evaluated in 1 x 3 inch flat sheet test cells operated at 225 psi (1551 kPa) applied pressure at a flow rate of 1.9

gal/min (0.00423 ft^3/sec). Operating conditions are such that there have been only two supervised shutdowns throughout the entire 5000 hr. run (April 30, 1999 for 48 hr. and May 4, 1999 for 24 hr.). Permeate flow and conductivity measurements are taken daily (Monday - Friday). Data is normalized to 25°C using Dow-FilmTec temperature correction factor tables. Feedwater pH and total residual chlorine (TRC) concentrations are monitored on a regular basis. pH measurements are taken on a daily basis while TRC values are taken via an on-line meter every 15 sec. and the daily averages plotted. A more thorough ion rejection analysis was carried out after 1000 hrs. of operation. The water flux, conductivity rejection, chlorine concentration of the feed and feedwater pH are given in Figure 7.0 a-d. The ion rejection analysis of the permeate after 1000 hrs. (114 days) is given in Table 7.0.

As expected with a municipal wastewater feed, considerable fouling occurred on all of the membranes which were not cleaned during the run. In spite of the high fouling feed, PA membrane BBCR-132-021799S1 SE has clearly outperformed the other membranes, including the controls. It also exhibits the highest conductivity rejection. To date, the membranes appear to be very stable with 4-5 mg/L combined chlorine in the form of chloramines; this performance is encouraging.

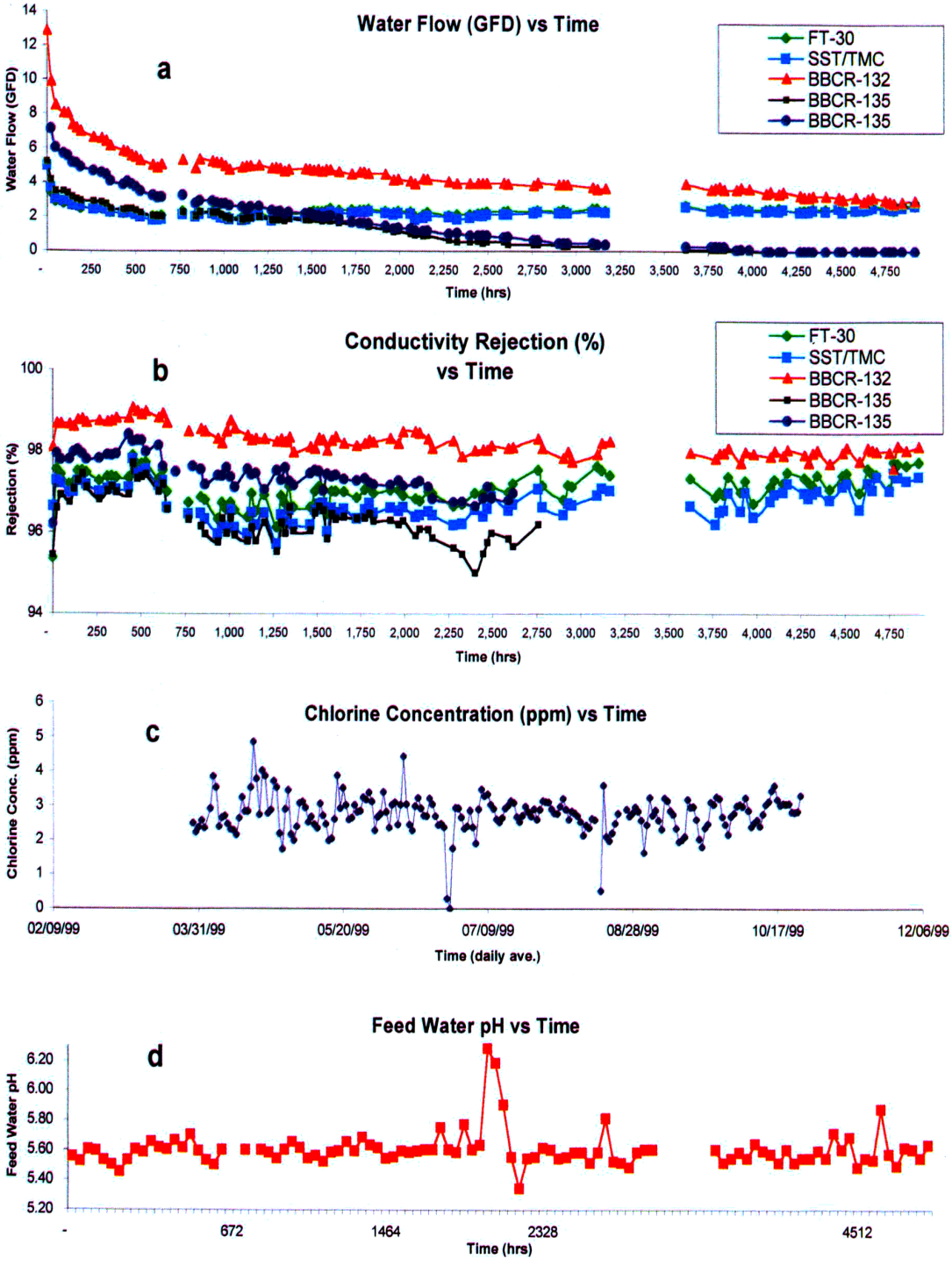


Figure 7.0 Reverse osmosis performance of polyamide membranes at OCWD. Permeate flow and conductivity measurements are shown in panels (a) and (b), respectively. Feed water parameters are represented in panels (c) and (d).

Table 7.0

Ion Rejection Data for SST Polyamide Membranes after 1000 Hours Reverse Osmosis Operation at OCWD on Municipal Waste Water Feed

Test Conditions: Municipal Waste Water Feed, 225 psi applied pressure, 1 gal/min feed flow rate, 2-4 mg/l chlorine (total residual chlorine)

	Ion Relection (%)											
Membrane	Na	K	MG	Ca	Totl. hd.	B	Cl	SO_4	Br	NO_3-N	NO_3-N	PO_4-P
FT-30	98.3	95.6	bdl	99.8	99.5+	bdl	98.4	99.4	bdl	bdl	73.9	bdl
SST / TMC	95.8	95.6	bdl	99.8	99.5+	bdl	98.4	99.5	bdl	bdl	73.9	bdl
SST 132 - 021799	99.3	96.5	bdl	99.6	99.5	bdl	96.5	99.5	bdl	bdl	bdl	bdl
SST 135 - 021599	95.9	95.6	bdl	99.9	99.5+	bdl	96.2	99.5	bdl	bdl	69.6	bdl
SST 135 - 021599	99.1	98.3	bdl	99.8	99.5+	bdl	98.4	99.5	bdl	bdl	bdl	bdl
Feed (mg/L)	183	13.5	0.6	80.5	203	0.24	202	385	<0.2	<0.4	0.46	<0.1

bdl = below detection limits
ICP = Inductively Coupled Plasma for Na , K, MG, Ca, B (Total detection limit = 0.1 mg/L)
Total hardness (Total detection limit = 1.0 mg/L)
IC = Ion Chromatography for Cl, SO_4, Br, NO_3-N, NO_3-N, and PO_4-P (Total detection limit = 0.5,0.5,0.5,0.2,0.4,0.1,and 0.1)

8.0 POLYAMIDE MEMBRANE SURFACE MORPHOLOGY

8.1 Membrane Surface Morphology

The microscale surface topography and pore geometries of polymer membranes can best be characterized and mapped using atomic force microscopy (AFM). This technique does not pretreat or alter the membrane surface, unlike other processes like scanning electron microscopy. The knowledge of surface morphology of PA membranes is essential for determining how well the synthesized CPTC acid chlorides form thin films relative to the trimesoyl chloride (TMC) and commercial FilmTec controls. Thus, it is possible to correlate surface morphology with transport properties. The knowledge of surface morphology is also essential for understanding the mechanisms of bacterial adhesion and biofilm formation.

AFM can examine the membrane surface in air dried as well as fully hydrated forms. AFM probes the membrane surface with a sharp tip, which is 2 microns long and 100 Å in diameter. The tip is located at a free end of a 100 to 200 µm long cantilever. A force between the tip and the membrane is an interatomic force called van der Waals force. A detector measures the tip deflection as the sample is scanned under the tip. A map of the surface topography is generated by the measured cantilever deflections. There are several modes in which the AFM may be operated, contact (C-AFM), non contact (NC-AFM) and intermittent or "tapping" mode (IC-AFM). The IC-AFM mode was selected which is very similar to NC-AFM. In IC-AFM the vibrating cantilever tip is drawn closer to the sample surface, and the tip just barely hits or "taps" the sample. IC-AFM is less likely to damage the membrane surface than C-AFM. It also eliminates lateral forces between the tip and the sample. It is also more effective than NC-AFM for imaging larger scan sizes that may include larger variations in topography.

AFM images were acquired at a scan rate of 1.0-2.0 kHz with an information density of 256 x 256 pixels. The root mean square roughness (RMS roughness) and mean surface height were calculated for each membrane using Park Scientific software provided with the CP AutoProbe. For a transect containing N data points, the RMS roughness is given by the standard deviation of the individual height measurements.

$$R_{rms} = \sqrt{\frac{\sum_{n-1}^{n} (z_n - \bar{z})^2}{N-1}}, \text{ where } \bar{z} = \text{mean z height}$$

The mean height is given by the average of the individual height determinations within the selected height profile.

$$\bar{z} = \frac{1}{N}\sum_{n-1}^{N} z_n, \text{ where } \bar{z} = \text{mean z height}$$

In Figures 8.0 and 8.1, three-dimensional (3-D) atomic force topographs of the surface of PA TMC control membranes 287 and 272 are shown. Figure 8.2 shows the 3-D topograph of the surface of PA membrane 275 made with *cccc*-CPTC acid chloride (all-cis). Figures 8.3 (TMC control) and 8.4 (*cccc*-CPTC acid chloride) show the two-dimensional surface of the same membranes. Visually, for the most part, the 3-D topographs are not as informative as the 2-D topographs. However, root mean square surface roughness and the mean height of surface elevations can be determined by AFM in the 3-D mode. Interestingly enough, neither of these determinations is greatly different for the three membranes. There is, however, a great difference in the membranes when a larger membrane area is viewed in 2-D, that is, when photo 0602G02B.HDF of TMC control membrane 272 in Figure 8.3 is compared with photo 0603G023.HDF of *cccc*-CPTC acid chloride membrane 275 in Figure 8.4. Membrane 275 made from the *cccc*-CPTC acid chloride shows the presence of many wrinkle or fold features in the thin film relative to control membrane 272. It is believed that this may be a factor responsible for the poor performance of PA membrane 275 made from the *cccc*-CPTC acid chloride isomer. This membrane showed lower than expected transport properties when evaluated in the laboratory in RO and when tested at the WQIC in Yuma, AZ on a 0.5 mg/L chlorinated feed. In the laboratory the membranes exhibited a water flux of 16-17 gfd and rejection of 96-97%; at WQIC the membranes started to fail after 50 hrs. of operation.

In Figures 8.5 and 8.6, 3-D atomic force topographs of the surface of PA membranes 315 and 283 prepared from *ctct*-CPTC acid chloride 041299 are shown; Figure 8.7 shows the 3-D topograph of the surface of PA membrane 333 made with *ctct*-CPTC acid chloride 061099. It should be noted that membranes prepared with *ctct*-CPTC acid chloride 041299 did not produce membranes that gave high transport properties. After synthesis, the acid chloride was stored in polypropylene vials under nitrogen to prevent any possible reaction with glass. It is believed that the acid chloride reacted with traces of catalyst that remained in the polypropylene, reducing its reactivity. The subsequent lot of acid chloride received from DU, *cccc*-CPTC acid chloride 061099, was again stored in glass vials. The RO properties of membrane 333 made from this synthesis lot were excellent, and the membranes are currently on test at WQIC in Yuma, AZ. The root mean square surface roughness and the mean height

of the surface elevations of these membranes were nominally the same as shown in Figure 8.8.

The 2-D atomic force topographs of membranes 315 and 333 are shown in Figures 8.9 and 8.10, respectively. When photos of the same magnification are compared, little if any raised features are observed. The strand like material seen in several of the topographies is believed to be polymer residuals left on the surface, even though the membranes were washed twice with hexane after the interfacial reaction to remove unreacted acid chloride. We would not expect to observe this material on the membrane surfaces if the membranes were made continuously on large scale. In a commercial process there is less movement of the hydrocarbon-acid chloride solution on the surface of the aqueous-MPD solution during the critical interfacial formation.

8.2 Characterization of Membrane Surfaces for Biofouling Potential

Bacterial attachment and subsequent biofouling of PA RO membranes results in a significant decline in their performance and cost-effectiveness. The successful and efficient operation of membrane systems requires that biofouling be minimized, thus resulting in higher water permeation and longer membrane life. In the development of a new PA membrane it is important to know early whether the membrane is susceptible to high levels of bacterial attachment and/or biofouling.

It is possible to evaluate the biological fouling propensities of both commercial and experimental polymer membranes inexpensively in the laboratory by performing a rapid bacterial adhesion assay. Test bacteria used in this assay include a hydrophobic Mycobacterium (BT12-100) and a hydrophilic Flavobacterium (PA-6) strain, each previously isolated from fouled membranes at the Orange County Water District's Water Factory 21, a 15 mgd advanced wastewater reclamation facility. In this assay, the test bacteria are initially grown in a sterile buffer solution containing radiolabled $Na^{235}SO_{4,}$ which serves to uniformly label (or tag) the bacteria for quantification purposes. A known quantity of this uniformly radiolabled cell suspension is allowed to contact the membrane surface in the absence of any applied pressures. As a result, the true inherent affinity of the bacteria for the membrane(s) in question is examined. After a set period of time, loosely or reversibly bound bacteria are removed from the membrane surface by two successive rinses. The membrane sample is then analyzed for irreversibly bound radioactive bacteria using a liquid scintillation counter. The quantity of "bound" bacteria was then compared to the amount in the stock cell suspension - termed "free" suspension. In this case, bacterial adhesion can be expressed as a ratio of the

bound bacteria/free bacteria (B/F). More detailed description may be found in the following references: (Ridgway, Isheda *et al*, 1999, Campbell, Srinivasan *et al*, 1999 and Knoell *et al*, 1999).

Three bacterial attachment assays were determined, as shown in Figures 8.11, 8.12 and 8.13, for the following membranes:

CA	Standard commercial blended cellulose acetate reverse osmosis membranes. (Yuma Desalting Plant type membrane)
O-PA	Old type commercial FilmTec PA membranes sold prior to 1998.
N-PA	New type commercial FilmTec PA membrane introduced in 1998.
SST-157	PA membrane made with DU *ctct*-CPTC acid chloride 021799S1. Acid chloride purity approximately 98%.
SST-158 SST-159	PA membrane made with DU *ctct*-CPTC acid chloride 021599S1. Acid chloride purity approximately 98%
SST-282	PA membranes 282 and 287 made with DU *ctct*-CPTC acid chloride 041299S1: Acid chloride purity approximately 99%. Sample stored in polypropylene vials believed to be contaminated. Transport properties of resulting membranes were low.
SST-287	PA control membrane made with trimesoyl chloride (TMC) Equivalent to FilmTec commercial PA membrane.

Some commercial PA membranes exhibit greater bacterial attachment than cellulose acetate membranes. This is apparent when one compares the values of commercial FilmTec membranes O-PA with N-PA in Figures 8.11, 8.12 and 8.13. Cellulose acetate membranes, on the other hand, exhibit low bacterial attachment. It is very encouraging to note that all of the SST membranes made with *ctct*-CPTC acid chlorides obtained from DU also show low bacterial attachment. This evaluation of membranes made from the higher purity acid

chlorides received from DU for bacterial attachment will continue as new samples are received.

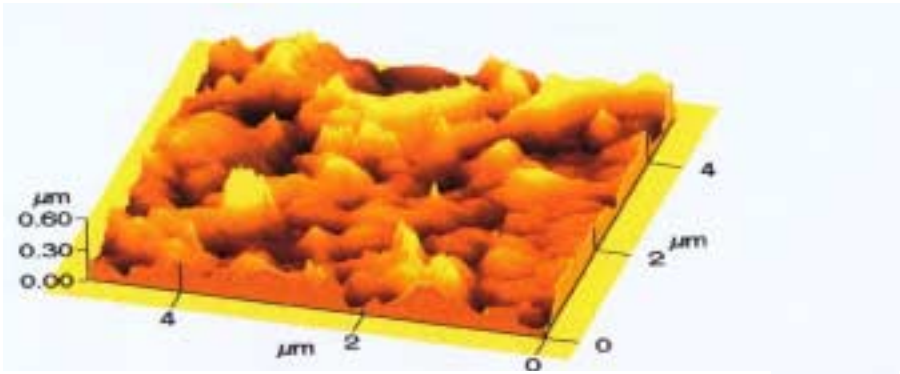


Figure 8.0 Three-D Atomic Force topograph of the top surface of polyamide membrane 287-TMC control. Concentration of TMC = 0.00236M. (0608G01B.HDF)

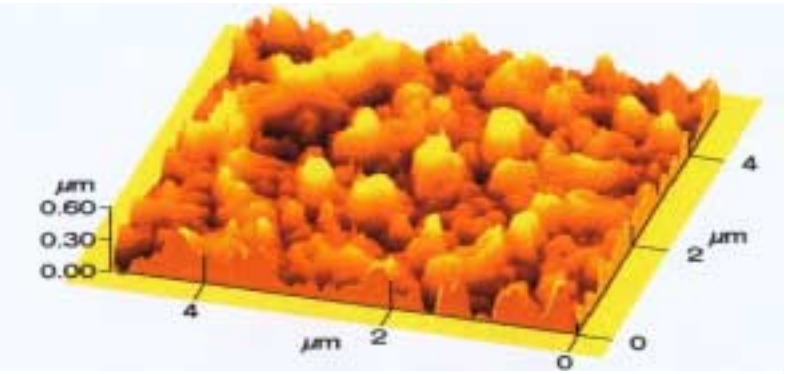


Figure 8.1 Three-D Atomic Force topograph of the top surface of polyamide membrane 272-TMC control. Concentration of TMC = 0.00236M. (0602S00B.HDF)

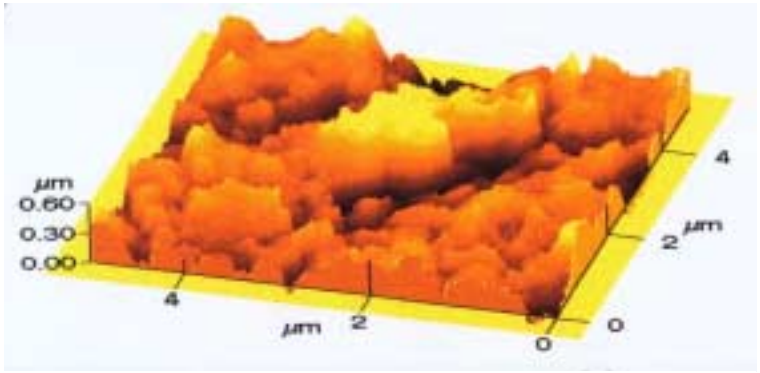


Figure 8.2 Three-D Atomic Force topograph of the top surface of polyamide membrane 275-All-Cis CPTC acid chloride. Concentration of acid chloride = 0.00236M. (060300F.HDF)

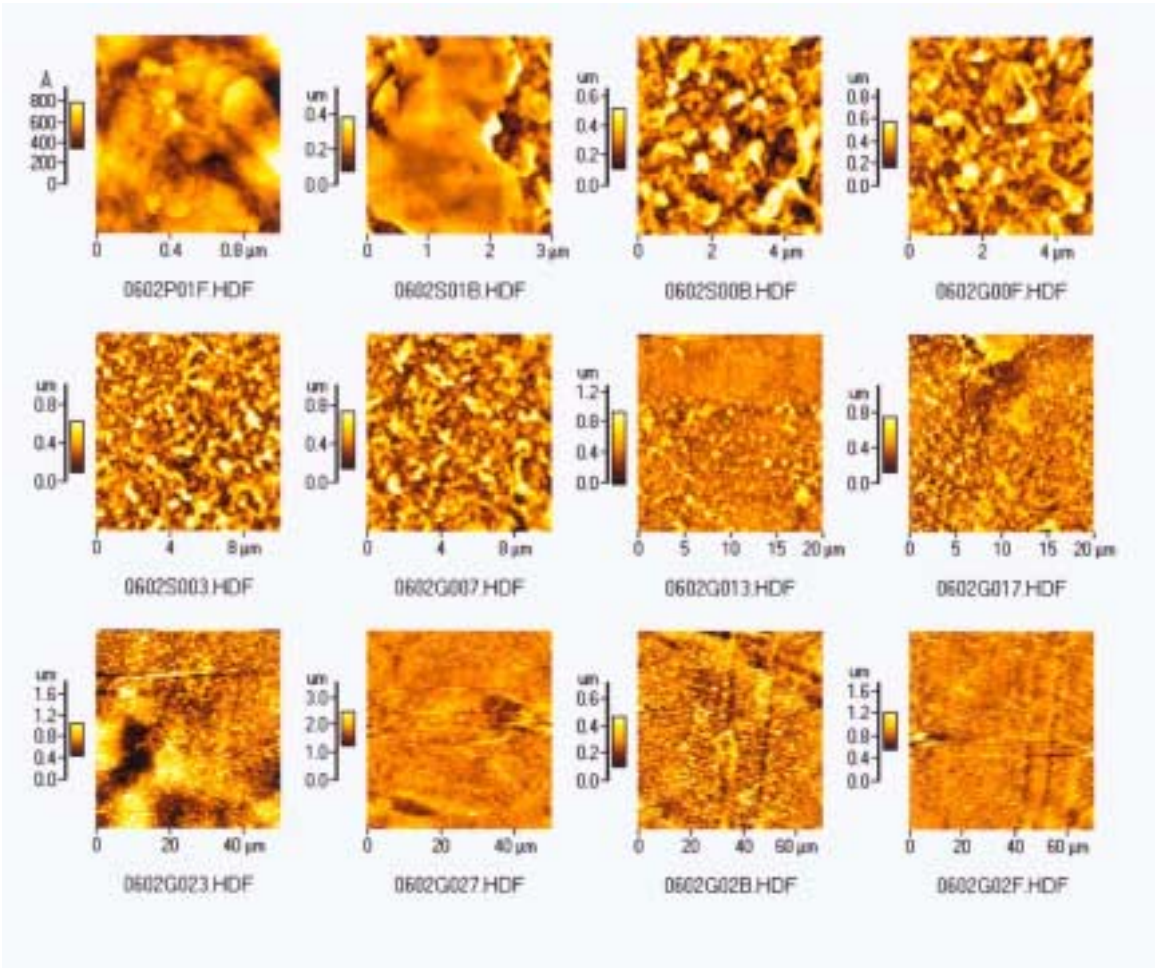


Figure 8.3 Two dimensional Atomic Force topographs of the surface of polyamide membrane 272-TMC control. Concentration of TMC = 0.00236 M. Figure 8.1 (3-D) corresponds to 0602S00B.HDF of this figure (2D).

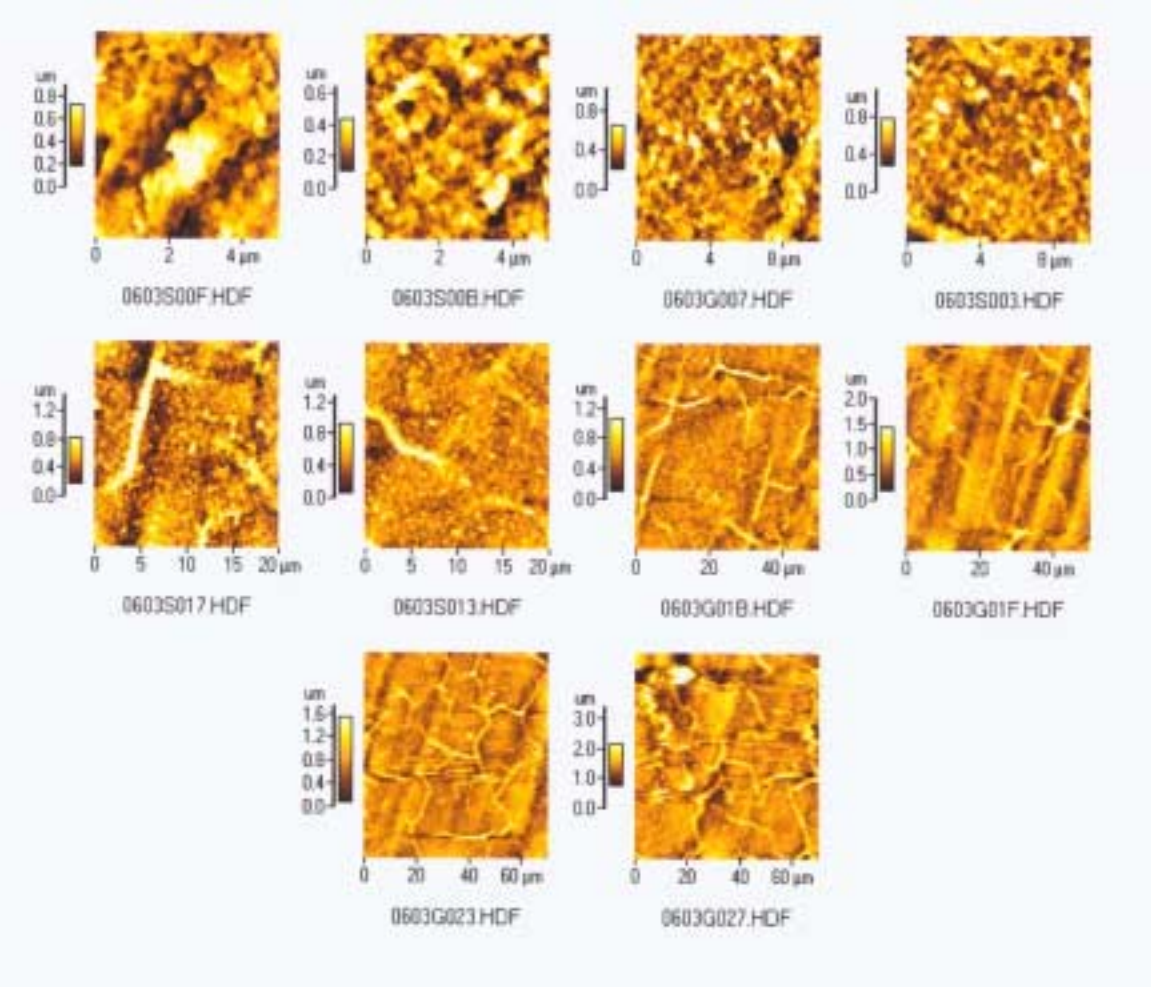


Figure 8.4 Two dimensional Atomic Force topographs of the surface of polyamide membrane 275-All Cis acid chloride. Concentration of All Cis CPTC acid Chloride = 0.00236 M. Figure 8.2 (3-D) corresponds to 0603S00F.HDF of this figure (2D).

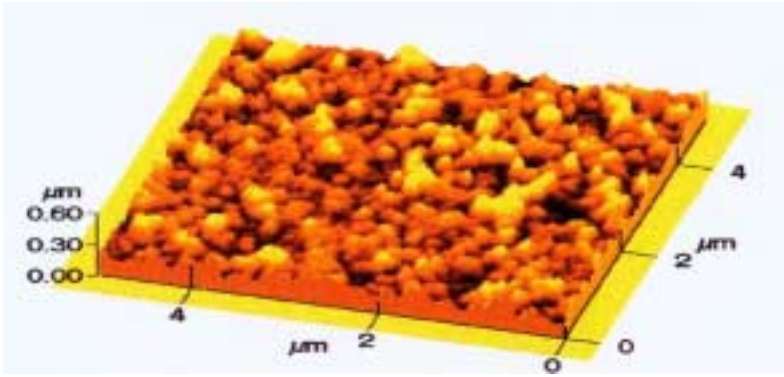


Figure 8.5 Three-D Atomic Force topograph of the top surface of polyamide membrane 315-*ctct*-CPTC acid chloride 041299. Concentration of acid chloride = 0.00236M (Freon solvent / hexane washed twice). (0629S013.HDF)

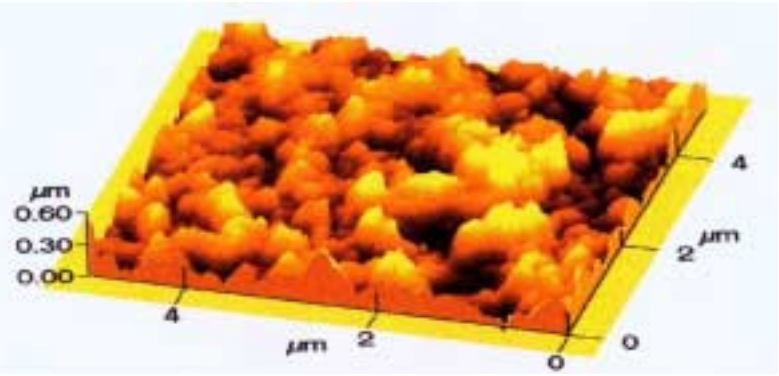


Figure 8.6 Three-D Atomic Force topograph of the top surface of polyamide membrane 283-ctct-CPTC acid chloride 041299. Concentration of acid chloride = 0.00236M (No hexane wash) (0604S00F.HDF)

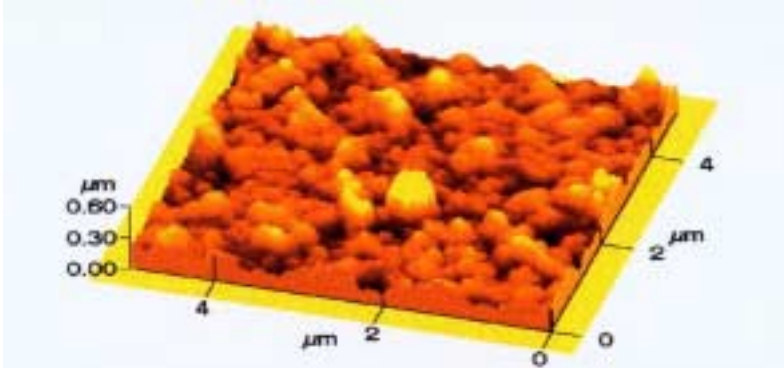


Figure 8.7 Three-D Atomic force topograph of the top surface of polyamide membrane 333-ctct-CPTC acid chloride 061099. Concentration of acid chloride = 0.00236M (Washed twice with hexane) (0629S013.HDF)

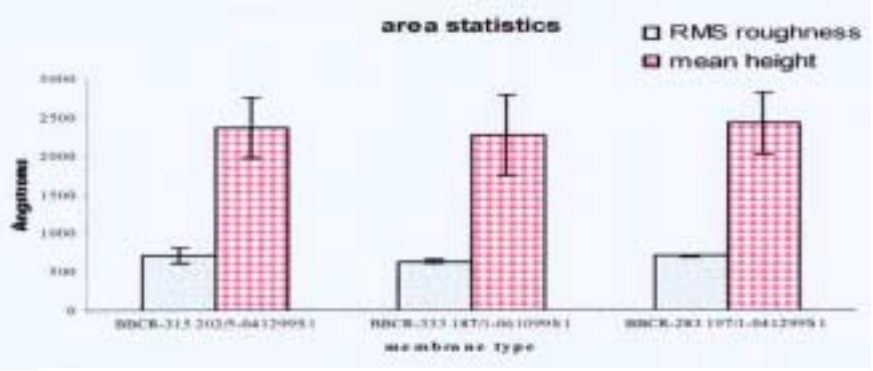


Figure 8.8 Root mean square surface roughness and the mean height of surface elevations on membranes 315 (Fig. 8.5), 283 (Fig. 8.6), and 333 (Fig. 8.7)

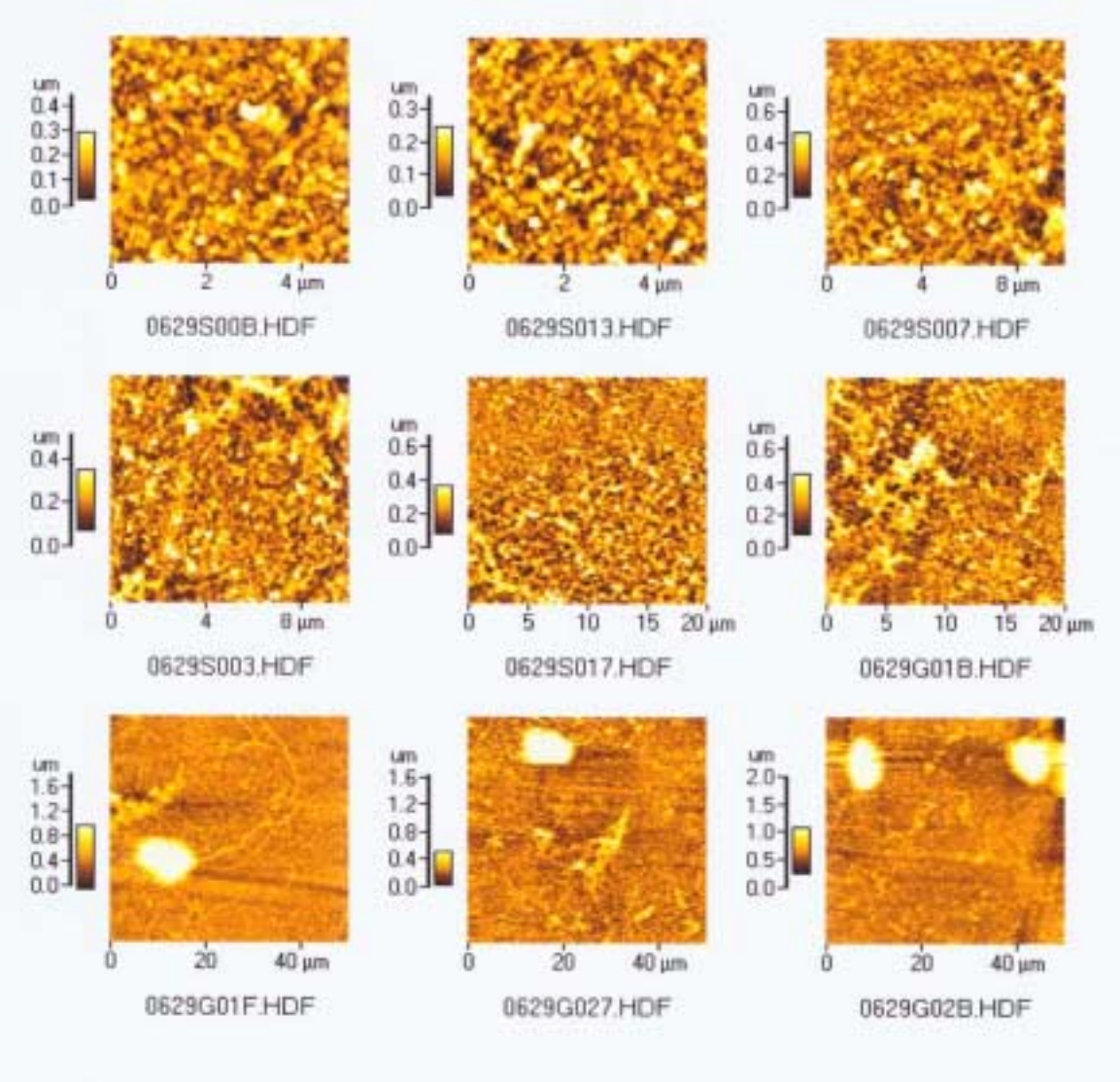


Figure 8.9 Two dimensional Atomic Force topographs of the surface of polyamide membrane 315-ctct-CPTC acid chloride 041299. Concentration of ctct-CPTC acid chloride = 0.00236 M. Figure 8.5 (3-D) corresponds to 0629S013.HDF of this figure (2D).

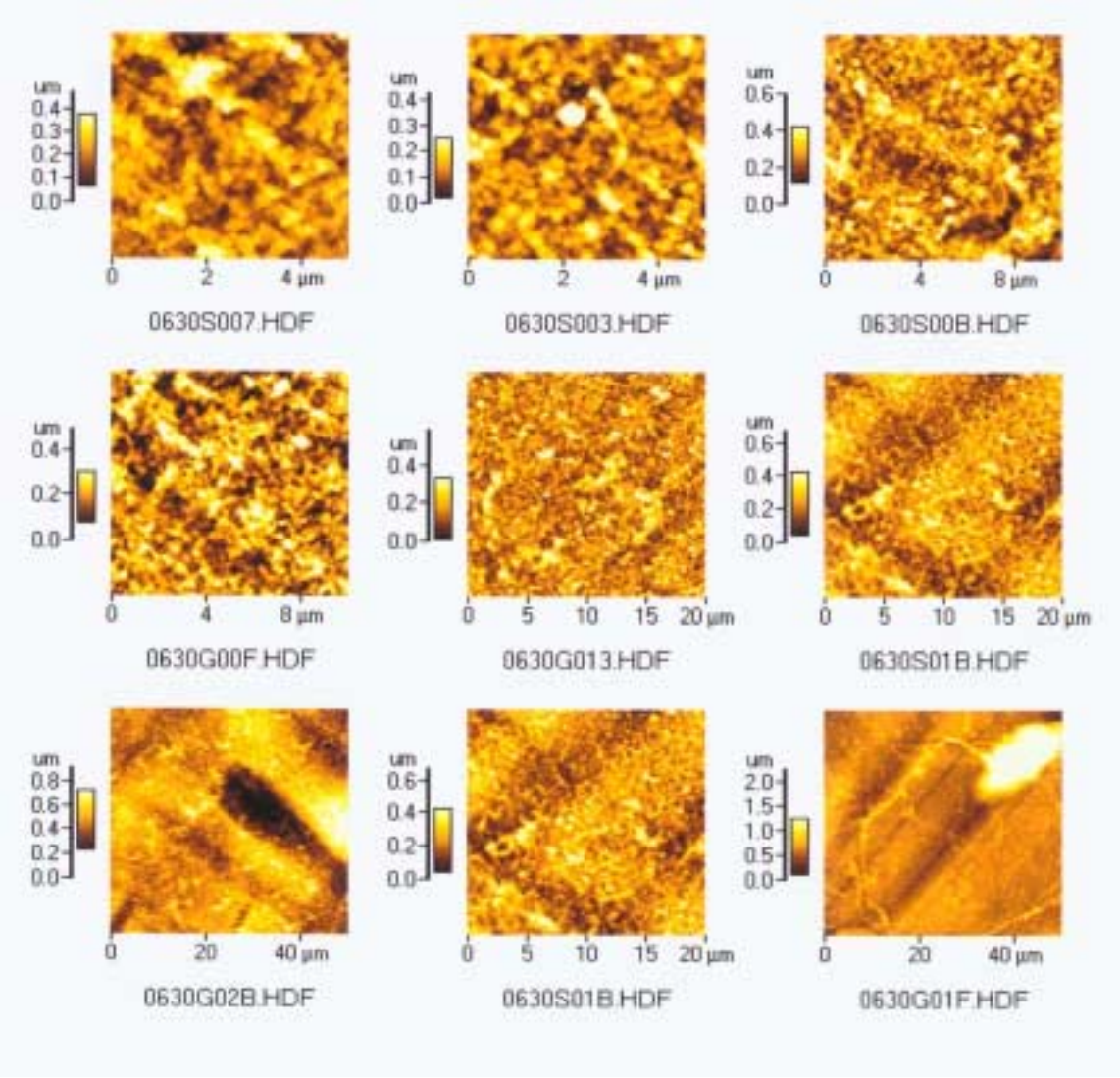


Figure 8.10 Two dimensional Atomic Force topographs of the surface of polyamide membrane 333-ctct-CPTC acid chloride 061099. Concentration of ctct-CPTC acid chloride = 0.00236 M. Figure 8.7 (3-D) corresponds to 0630S003.HDF of this figure (2D).

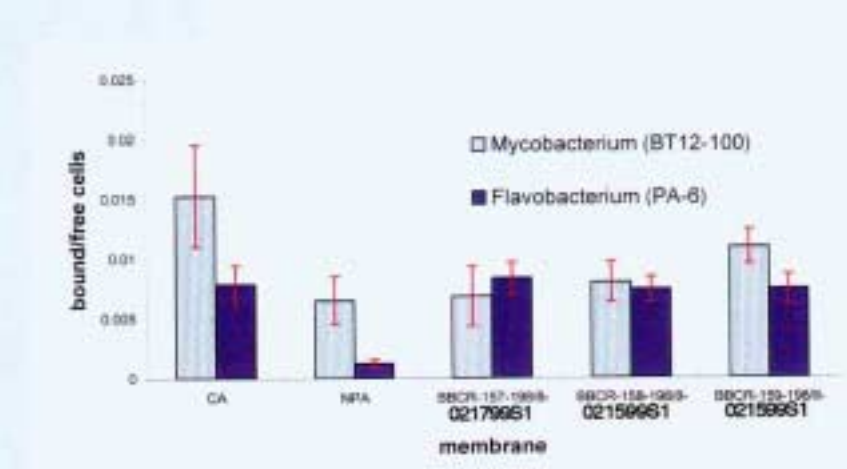


Figure 8.11 Bacterial attachment asay on BBCR-157-159 membranes (N=10).

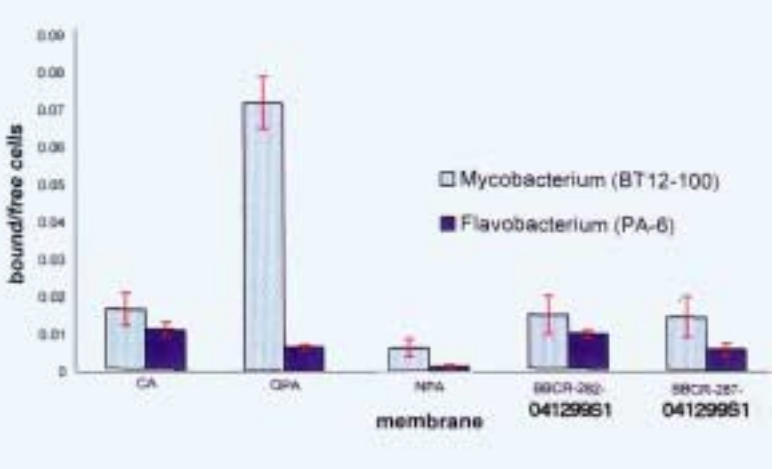


Figure 8.12 Bacterial attachment assay on BBCR-282 and BBCR-287 membranes (N=10)

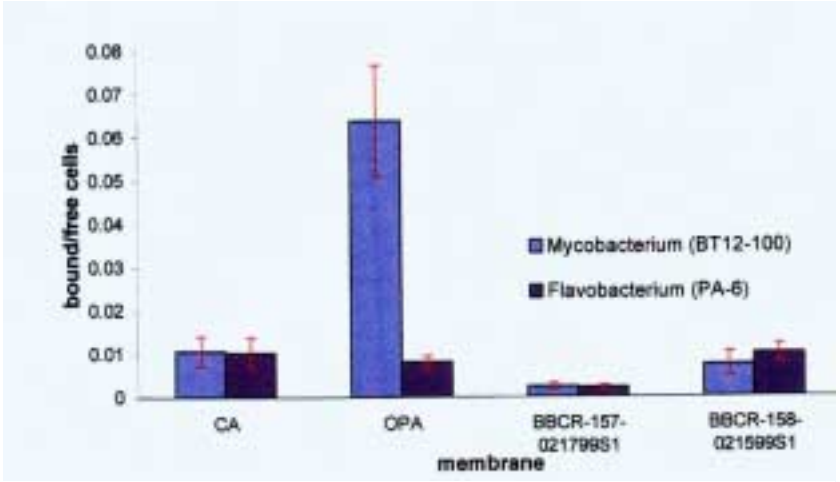


Figure 8.13 Bacterial attachment assay on BBCR-157 and BBCR-158 membranes (N=10).

9.0 ENCHANCEMENT OF HYDROPHILICITY ON POLYAMIDE MEMBRANE SURFACE TO REDUCE BIOFOULING

In an effort to reduce the membrane hydrophobicity, *ctct*-CPTC acid chloride membranes were modified by treatment with 3-amino-1-propanol. Acid chloride groups that do not react with MPD to form amide bonds are normally hydrolyzed to a carboxyl acid. Most of the carboxylic acid groups exist in the deprotonated carboxylate form, giving the membrane a net negative charge. The carboxylate content of the membrane can be reduced if the acid chloride is modified before it undergoes hydrolysis to form the carboxylic acid. Incorporation of an amino-propanol adduct at the polymer surface would effectively replace this negatively charged carboxylate group with a polar hydroxyl group. Modification of the polymer surface may enhance water transport across the membrane as well as reduce the potential for biological fouling.

9.1 Reaction of 3-Amino-1-Propanol with Reactive Acid Chloride Groups on the Surface of Polyamide Membranes

As described in Section 5, thin-film composite PA membranes are made by an interfacial polymerization reaction between an acid chloride (e.g. TMC or *ctct*-CPTC) and MPD. After the interfacial polymerization reaction has occurred, any unreacted acid chloride within the polymer can undergo further reaction with other chemical additives. Under the right conditions, the acid chloride can react with a hydroxylamine (e.g., 3-amino-1-propanol) to form a hydroxamic acid (Figure 9.1.1). The net result is the conversion or substitution of what normally would become a carboxylic acid into a hydroxyl or alcohol functional group.

The following procedure was used to modify the *ctct*-CPTC acid chloride membrane. After the initial polymerization reaction between acid chloride and MPD, excess *ctct*-CPTC was removed from the membrane and the surface immediately rinsed with hexane for 1 min. and discarded. This was followed by a second rinse of hexane for 1 min. Subsequently, the membrane surface was covered with a 2% solution of 3-amino-1-propanol in deionized water for 5 min. The membrane was dried under a stream of nitrogen for 2 min and then placed in a water bath at room temperature for 10 min. Finally, the membrane was dried at 80°C for 15 min before it was sent to OCWD for analysis. (See Figure 9.1.2).

9.2 Characterization of Membranes by ATR / IR Spectrometry

Membrane samples were analyzed by attenuated total reflectance infrared (ATR/ IR) spectrometry to confirm chemical structure. Small swatches of membrane ~1.5 x 0.375 inches were cut from full sheets. These swatches were pressed against each side of a zinc selenide (50 x 10 x 2 mm, 45°) internal reflection element. ATR / IR spectra of unmodified (BBCR-395-061099) and hydroxylamine modified (BBCR-393-061099) membranes are displayed in Figure 9.2.1. An expanded region of the spectrum between 4000 cm and 2000 cm is shown in the bottom of Figure 9.2.1. Significant changes in the O-H stretching region (~3300 cm) should appear if the propanol group is present at the surface of the membrane. The 3300 cm O-H stretching band should be more intense relative to amide I (1670 cm), amide II (1538 cm) and asymmetric and symmetric carboxylate bands when compared to the unmodified control membrane. There should also be a greater contribution to the aliphatic CH_2 stretching region just below 3000 cm, if 3-amino-1-propanol was incorporated into the membrane. These spectroscopic variations are not evident in the ATR/IR spectrum of the modified membrane. The relative band intensities of the two membranes look virtually identical.

Amide bonds are formed when MPD reacts with acid chloride. The amide bond is typified by the amide I band, which is primarily a C=O stretching mode (1670 cm), and the amide II vibrational band (1538 cm), which is primarily an N-H bending mode. Most of the carboxylic acid formed from the unreacted acid chloride exists as carboxylate. This is evident by the presence of symmetric and asymmetric carboxylate stretching bands at 1414 cm and 1608 cm and the lack of carbonyl band from the protonated acid. In theory, the more extensive the reaction between acid chloride and the amine groups of MPD, the greater the cross-linking, and the lower the carboxylate density. The relative carboxylate density ratios (1414 cm / 1670 cm and 1414 cm / 1538 cm) of the modified membrane were slightly greater than the ratios of the unmodified control (Figure 9.2.2). The surface modified *ctct*-CPTC acid chloride membrane should have a lower carboxylate ratio, as more free acid chloride groups are converted to aminopropanol groups, reducing the number of free carboxylate groups. The relative ratios of the carboxylate and amide bands of the modified membrane were all very similar to the control membrane.

Again, the IR spectra of the two membranes appeared to be virtually identical. Insufficient surface modification may have occurred to be detected by the ATR/IR spectroscopic technique. The IR spectra were analyzed further by difference spectroscopy. An unmodified *ctct*-CPTC acid chloride membrane was digitally subtracted from the 3-

amino-1-propanol modified membrane (Figure 9.2.3). There is nothing in the different spectra that indicates that a significant amount of surface modification has occurred. The vibrational bands near 1600 cm and 1500 cm are residual PS bands. The ATR / IR results do not support a conclusion that 3-amino-1-propanol is present on the surface of the membrane.

9.3 Surface Charge Characterization by Uranyl Cation Binding Analysis

A novel uranyl cation-binding (UCB) assay was employed to determine the relative surface charge of the *ctct*-CPTC acid chloride membranes currently under investigation. In this assay, the membrane surface charge (due to the presence of free carboxyl groups) is determined by quantifying the amount of uranyl cation bound to this functional group. To perform this assay, membrane disks were secured in plastic test tubes similar to that described for the rapid laboratory bioassay (see Section 9.5 below). A solution of 10 mM uranyl acetate (pH 5.0) was allowed to contact the membrane surface for a period of 2 hr. The disks were then removed, rinsed extensively in 18 megohm-cm deionized water and analyzed for bound uranyl cation by liquid scintillation counting. In this capacity, the relative membrane charge of the entire membrane (surface and any associated binding deep within the pore-like structures) can be determined. In some instances, however, it might be preferable to shorten the contact time in order to minimize binding within the polymer matrix. Shortening the contact time provides a more accurate reflection of the true binding capacity associated with the membrane surface. Surface binding capacity can be estimated by performing a UCB kinetics assay, where binding at T=0 min can be estimated by back extrapolation through the Y-axis.

A UCB kinetics assay was performed on a series of *ctct*-CPTC acid chloride membranes that were modified with 3-amino-1-propanol to enhance the hydrophilic nature of the membrane surface, thus rendering the membrane less susceptible to biological fouling. UCB data for these two membranes are presented in Figure 9.3.1. The 3-amino-1-propanol modified membrane (BBCR-393-061099) showed slightly less uranyl cation binding, consistent with the idea that less carboxylate groups were available as binding sites, due to substitution or replacement by 3-amino-1-propanol. However, this difference turned out to be insignificant upon further statistical analysis ($P>0.05$). (13) Therefore, the results of this characterization method indicate little or no surface modification of the *ctct*-CPTC acid chloride membrane has occurred.

9.4 Captive Bubble Contact Angle Measurements of Membrane Surface

The relative surface hydrophobicities of modified and unmodified *ctct*-CPTC acid chloride membranes were determined by captive (air) bubble contact angle measurements. An air bubble was introduced under the surface of membranes submerged in 18 megohm-cm deionized water with the active surface facing down. The bubble trapped under the surface of the membrane was imaged with a CCD camera and the tangent contact angle determined using CUE2 Series Image Analysis software. The lower the air bubble contact angle the more hydrophilic the surface. Air bubble contact angle measurements are displayed in Figure 9.4.1. Two modified and two unmodified control membranes were tested. One of the 3-amino-1-propanol modified membranes was more hydrophilic than the two *ctct*-CPTC acid chloride controls. It is difficult to determine before hand the exact extent modification would have on surface hydrophobicity. The alcohol functional group (along with the remaining carbonyl) adds polarity to the surface, increasing the hydrophilicity, and propylene adds a small amount of hydrophobic character to the membrane. The air bubble contact angle results are inconclusive, and more work needs to be done.

9.5 Characterization of Membrane Surfaces for Biofouling Potential

The biofouling potential of the *ctct*-CPTC acid chloride membranes were determined via a rapid laboratory bioassay. In this assay, uniformly radiolabeled (S^{35}) bacteria were allowed to contact the membrane surface in the absence of any applied pressure. As a result, the true inherent affinity of the bacteria for the membrane(s) in question is examined. Test bacteria include a hydrophobic *Mycobacterium* (BT12-100) and a hydrophilic *Flavobacterium* (PA-6) strain, each previously isolated from fouled RO membranes at OCWD. Three commercially available RO membranes were routinely included as controls to account for the possibility of inter-experiment variations. They consisted of a low pressure, non-post treated cellulose acetate (CA) membrane (Applied Membranes, Inc., San Marcos, CA) and a new (NPA) and old (OPA) version of a fully aromatic thin-film composite PA membrane (Dow-FilmTec FT-30, Midland, MI).

Bacterial attachment data for the 3-amino-1-propanol modified (BBCR-393-061099), unmodified control *ctct*-CPTC acid chloride membrane (BBCR-395-061099), and the standardized control membranes as shown in Figure 9.5.1. There was a significant reduction in mycobacterium and flavobacterium attachment ($P<0.05$) to both the modified and unmodified *ctct*-CPTC acid chloride membranes as compared to the commercial CA and OPA control membranes. There was also a significant reduction in flavobacterium attachment to the modified membrane as compared to the unmodified control, suggesting that the 3-amino-1-propanol treatment may have contributed to the observed decrease in bacterial attachment.

Unfortunately, this same trend was not observed for mycobacterium when attachment to the control was compared to attachment to the 3-amino-1-propanol modified membrane. It is clear by examining this data that further testing is needed to confirm these finding. It is nevertheless encouraging that the *ctct*-CPTC acid chloride membranes exhibit, in most cases, equal or lower affinity toward the *Flavobacterium* PA-6 and *Mycobacterium* BT12-100 isolates; thus suggesting a reduction in biofouling potential.

9.6 Reverse Osmosis Performance Testing

Performance testing was conducted for both the 3-amino-1-propanol modified *ctct*-CPTC acid chloride membrane (Lot # 092099S2) and the control membranes. The test conditions were as follows: 225 psi (1551 kPa) applied pressure, 2000 mg/l sodium chloride feed, 1.1 gal/min (0.00245 ft^3/sec) feed flow, pH 6.8 and 25°C. The performance of the two membranes was similar. The salt rejection of both the modified (BBCR-568) and control (BBCR-564) membrane was 99.1%. The permeate flow of the unmodified membrane was 7.5 gfd (3.54×10^{-6} m/sec). The permeate flow of the modified membrane was slightly higher at 7.7 gfd (3.630×10^{-6} m/sec).

9.7 Summary and Recommendations

Further experimentation is required to improve on the 3-amino-1-propanol surface modification. Some of the data, e.g., contact angle and uranyl cation binding data, suggest that 3-amino-1-propanol was incorporated on the membrane surface. Other data, i.e., the ATR/IR spectra, indicate no significant change in the surface chemistry. The relative carboxylate density ratios were opposite to what was expected. The surface modification did not affect the salt rejection, as both membranes had a measured rejection of 99.1%. However, the water flux of the modified membrane was slightly greater than the control.

Steps need to be taken to improve the efficiency of the 3-amino-1-propanol reaction. Some of the recommended changes are to (1) eliminate the second hexane rinse prior to aminopropanol addition, (2) increase the solubility/affinity of 3-amino-1-propanol for the organic hexane phase, (3) increase the concentration of the 3-amino-1-propanol, and (4) increase the contact time between the acid chloride and 3-amino-1-propanol.

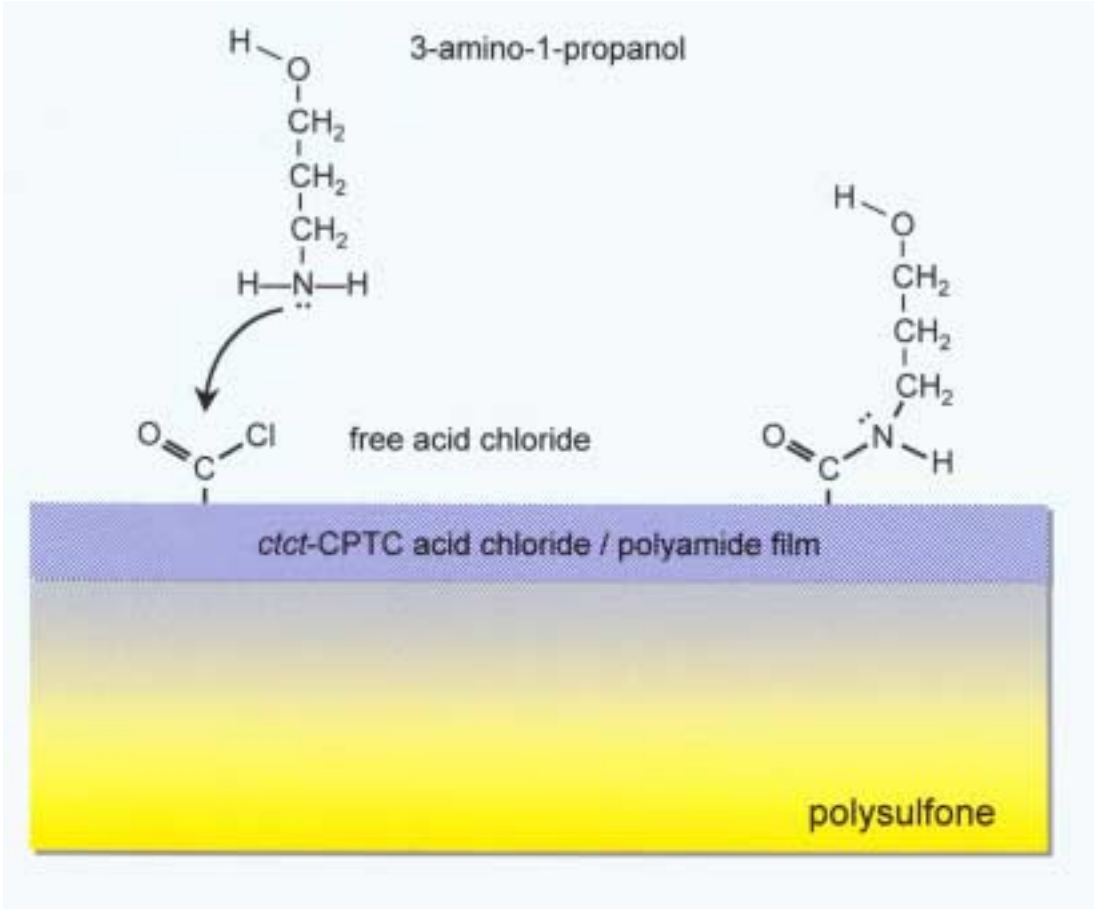


Figure 9.1.1 3-amino-1-propanol modification of *ctct*-CPTC acid chloride membrane.

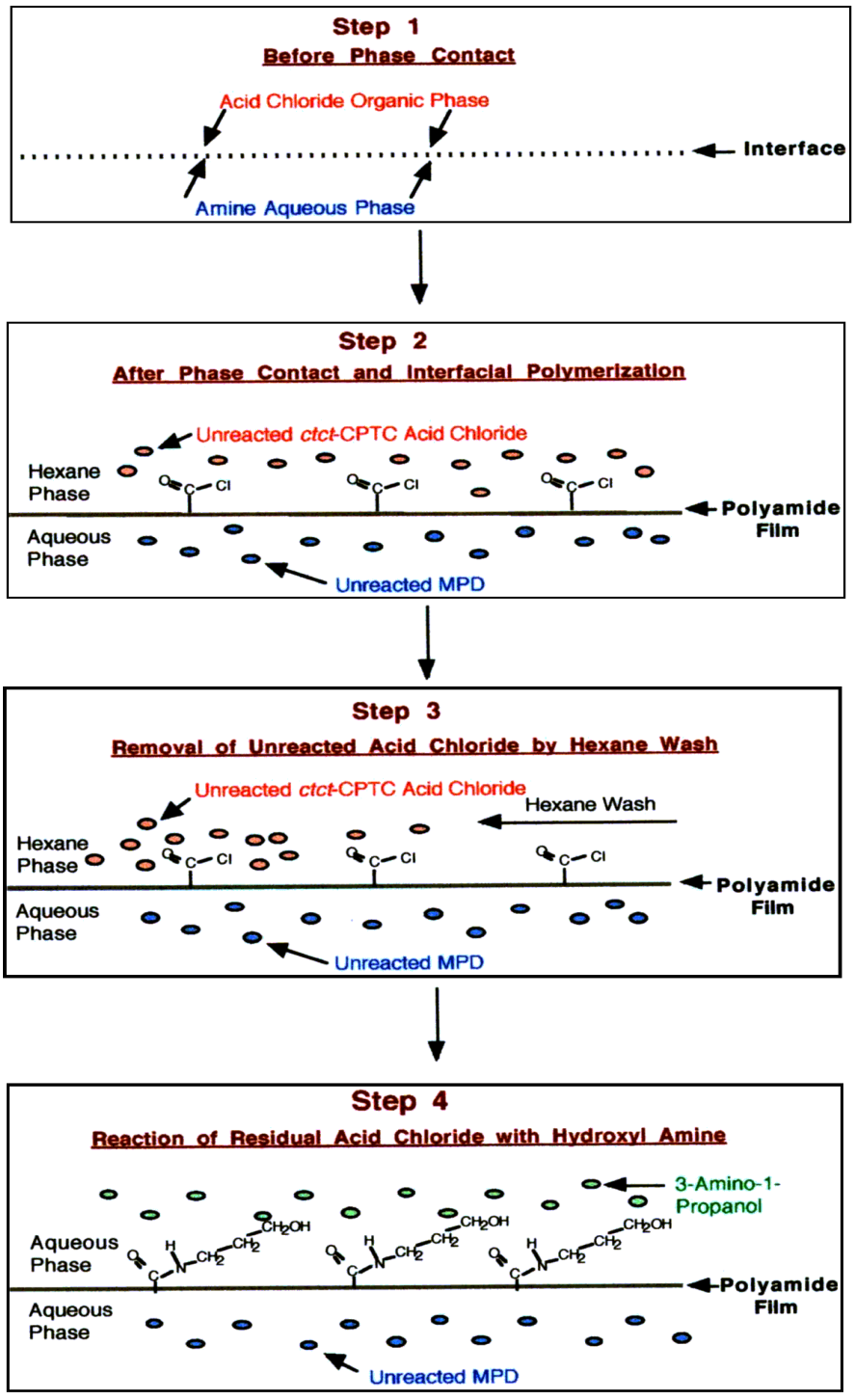


Figure 9.1.2 Procedure for 3-amino-1-proponal modification of *ctct*-CPTC acid chloride membrane.

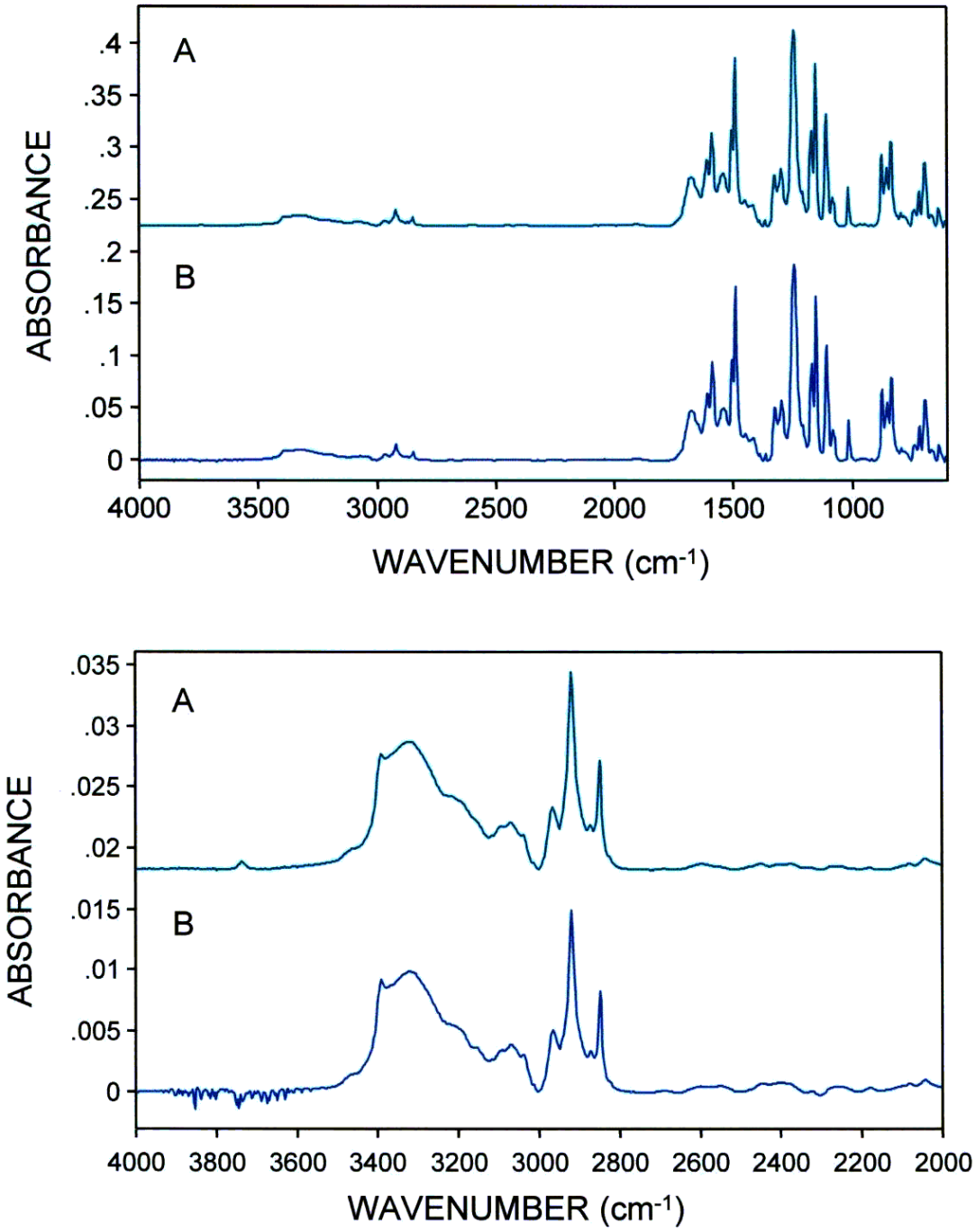


Figure 9.2.1 ATR/IR spectra of (A) unmodified and (B) 3-amino-1-proponal modified *ctct*-CPTC acid chloride membrane.

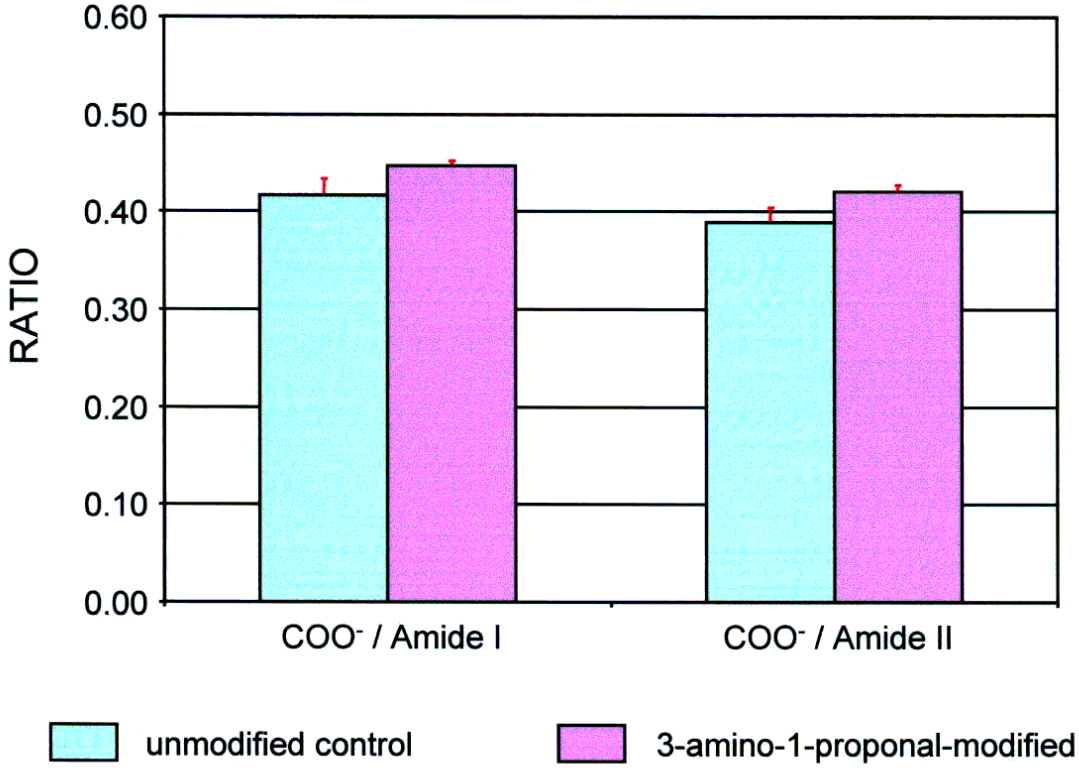


Figure 9.2.2 Effect of 3-amino-1-proponal modification on the relative carboxylate density. Average plus standard deviation based on the six pairs of membrane samples.

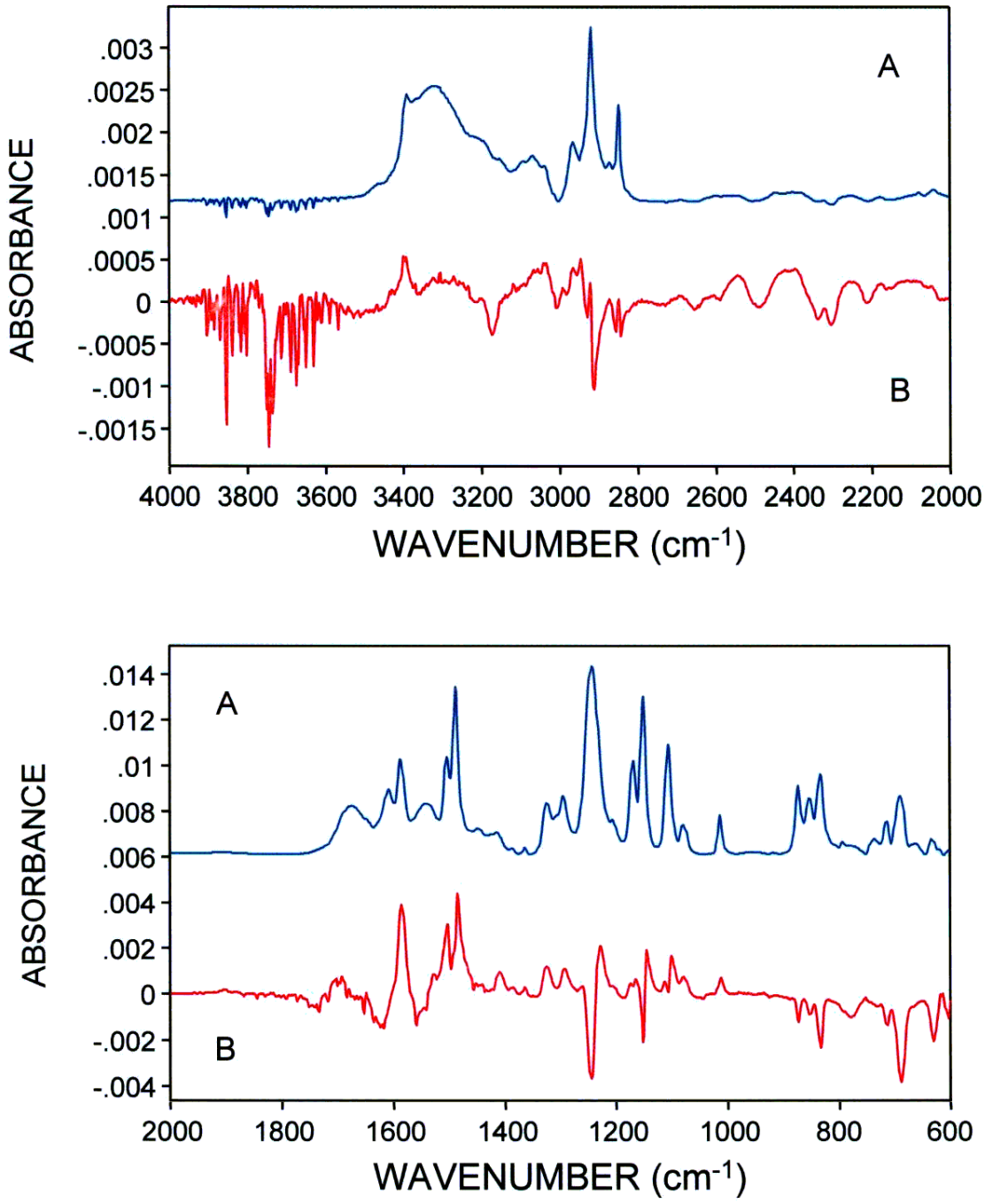


Figure 9.2.3 ATR/IR spectra of (A) 3-amino-1-proponal modified *ctct*-CPTC acid chloride membrane and (B) difference spectrum.

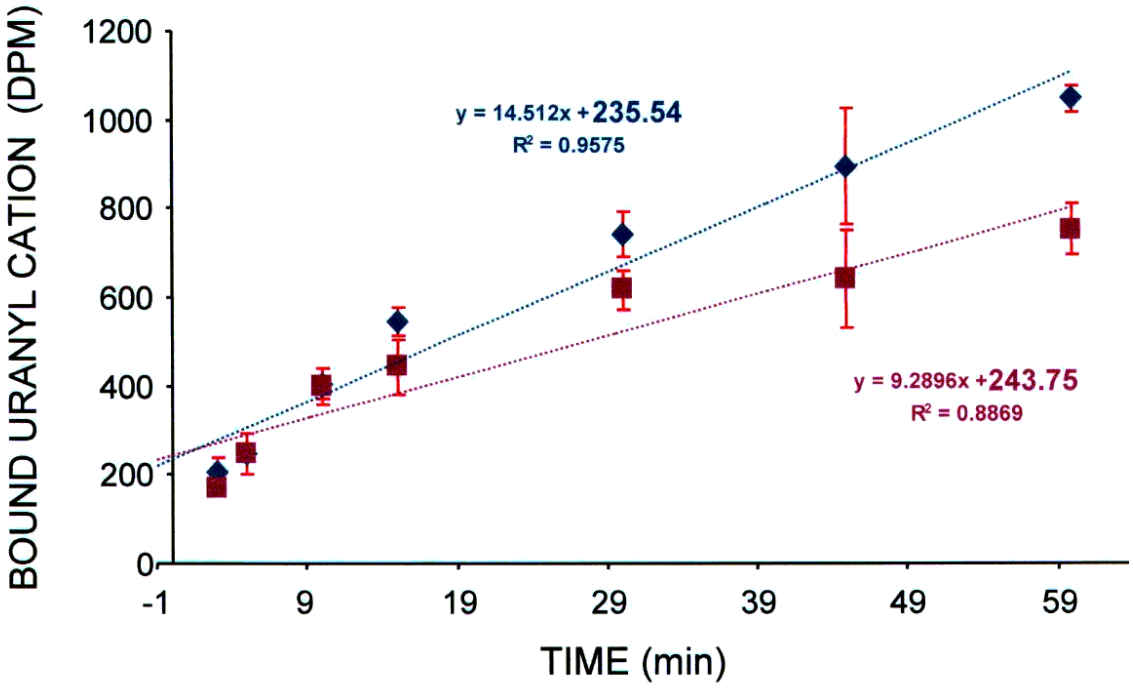


Figure 9.3.1 Uranyl cation binding kinetics of 3-amino-1-proponal modified (♦) and unmodified control (■) *ctct*-CPTC acid chloride membranes (N=3).

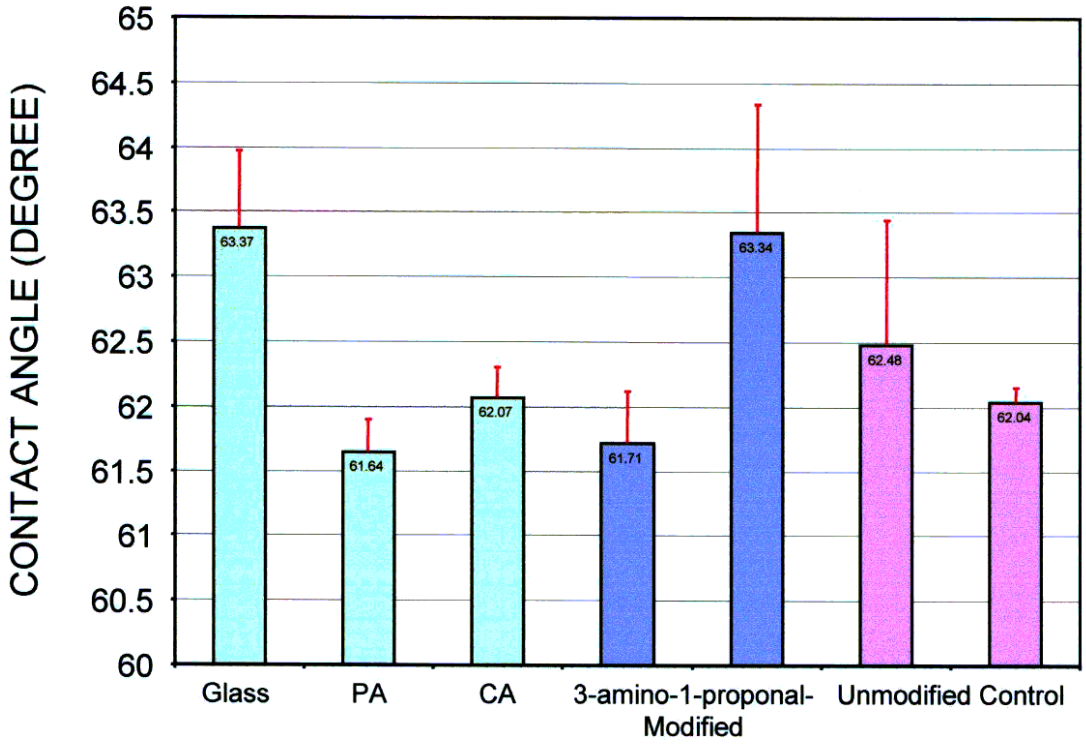


Figure 9.4.1 Captive air bubble contact angle measurements on glass, polyamide (PA) and cellulose acetate (CA) membrane control materials, and contact angle measurements of 3-amino-1-propanol modified and unmodified *ctct*-CPTC acid chloride membranes.

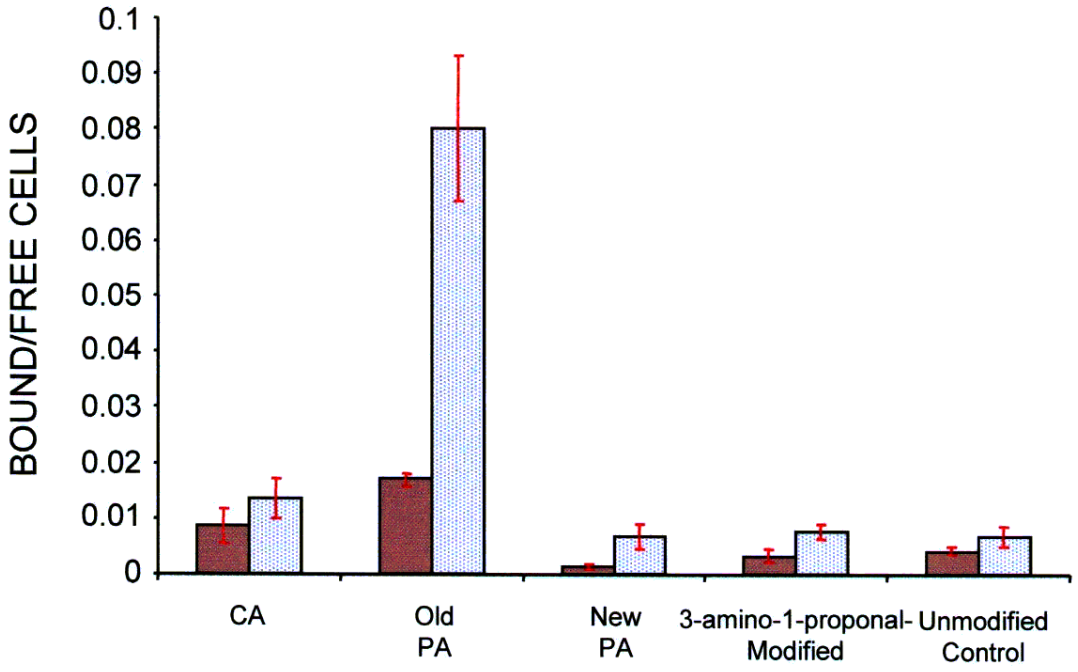


Figure 9.5.1 Flavobacterium PA-6 (■) and Mycobacterium BT12-100 (■) attachment to 3-amino-1-proponal modified (BBCR-393-061099) and unmodified control (BBCR-395-061099) *ctct*-CPTC acid chloride membranes (N=10).

REFERENCES

Arthur, S. D. *et al*, U. S. Patent No. 4,749,488 (1988).

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

Campbell, P., R. Srinivasan *et al, Quantitative Structure Activity relationship (QSAR) Analysis of Surfactants Influencing Attachment of a Mycobacterium Species to Cellulose Acetate and Aromatic Polyamide Reverse Osmosis Membranes,* Biotechnology and Bioengineering, **64**, 527-544 (1999).

Elimelech, X. Zhu, A. E. Childress, and S. Hong, *Role of Membrane Surface Morphology in Colloidal Fouling of Cellulose Acetate and Composite Aromatic Polyamide Reverse Osmosis Membranes*, Journal of Membrane Science, **127**, 101-109 (1997).

Farrar, J., S. M. Neale and G. R. Williamson, *A Gravimetric Estimation of The Carboxylic Acid Group in Cellulose*, Nature, **168**, 566 (1951).

Glater, J., Seung-Hong and M. Elimelech, *The Search for a Chlorine-Resistant Reverse Osmosis Membrane*, Desalination, **95**, (1994) 325-345

Ikeda, K. *et al, Novel Reverse Osmosis Composite Membranes,* Proceedings of the IDA and WPRC World Conference on Desalination and Water Treatment, November 3-6, 1993, Yokohama, Japan, Vol. 1, pp. 93-100.

Knoell, T *et al, Biofouling Potentials of Microporous Polysulfone Membranes Containing a Sulfonated Polyether-ethersulfone/Polyethersulfone Block Copolymer: Correlation of Membrane Surface Properties with Bacterial Attachment,* Journal of Membrane Science, **157**, 117-138 (1999).

Leslie, G., Orange County Water District, private communication (1999).

Prokop, R. M., O. I. del Rio, N. Niyakan and A. W. Neuman, *Interfacial Tension from the Height and Diameter of Sessile Drops and Captive Bubbles with an Arbitrary Contact Angle.* Can. J.Chem. Engineering, **74**, (1996).

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

Ridgway, H. F. and J. Safarik, *Biofouling of Reverse Osmosis Membranes,* in Biofouling and Biocorrosion in Industrial Water Systems, 81-111, H. C. Flemming and G.G. Geesey (Eds.), Springer-Verlah, New York (1991).

Ridgway, H. F. and H. C. Flemming, *Membrane Biofouling*, pp 6.1-6.62, In: Water Treatment Membrane Processes, J. Mallevialle, P. E. Odendaal, and M. R. Weisner (Eds.), McGraw-Hill Publishers, New York (1996)

Ridgway, H. F., *Molecular Modeling of Organics Adsorption to Synthetic Polymer Membranes*, Proc. International Membrane Science and Technology Conference, 12-14 November 1996, Sydney, Australia (1996).

Ridgway, H. F. *et al, Analysis of Bacterial Adhesion and Biofouling Membrane Separations Processes,* An Interim Progress Report to AWWA Research Foundation, Biotechnology Research Department, Orange County Water District, Fountain Valley, CA., March 1997.

Ridgway, H. F., K. Isheda *et al*, *Biofouling of Membranes: Membrane Preparation, Characterization, and Analysis of Bacterial Adhesion,* pp. 463-494. In Doyle, R. (Ed.), Methods in Enzymology: Biofilms, Academic Press, San Diego, CA (1999).

Rosenberg, M. and R. J. Doyle, Microbial Cell Surface Hydrophobicity: History, Measurement and Significance. (Ed.) Microbial Cell Surface Hydrophobicity, 1-38, American Society for Microbiology, Washington, D. C.

Singh, R., Characteristics of a Chlorine-Resistant Reverse Osmosis Membrane, Desalination, **95**, 27-37 (1994).

Sundet, S. A., S. D. Arthur, D. Campos, T. J. Eckman and R. G. Brown, Desalination, **64**, 259-269 (1987).

Tomaschke, J. E. and I. E. Ary, U. S. Patent No. 5,254,261 (1993).

APPENDIX 1 - DATA RECORD

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Table 7.0	Ion rejection data for SST polyamide membranes after 1000 hours Reverse osmosis operation at OCWD on municipal waste water feed.	44

Raw Data Corresponding to Figure 6.0

Date	Time	Elapsed Time (hrs)	Feed Pressure kPa	Feed Temp. C	Feed Conduct. (&S/cm)	Feed pH	Chlorine Conc. (ppm)	Product Conduct. #1 (&S/cm)	Product Conduct. #2 (&S/cm)	Product Conduct. #3 (&S/cm)	Salt Rejection #1 (%)	Salt Rejection #2 (%)	Salt Rejection #3 (%)	Total Sample Weight #1 (g)
3/10/99	2130	8.0	2130	19.6	3930	4.70	1.0	69	29	96	98.2	99.3	97.6	111.60
3/11/99	330	14.0	2012	19.3	3910	4.32	1.0	71	23	57	98.2	99.4	98.5	91.54
3/11/99	1100	20.5	2013	17.7	3820	4.28	1.2	53	20	62	98.6	99.5	98.4	79.08
3/11/99	2000	29.5	1998	18.4	3890	4.28	1.1	56	21	61	98.6	99.5	98.4	94.35
3/12/99	1230	46.0	2035	16.7	3740	3.96	1.1	59	20	53	98.4	99.5	98.6	83.76
3/13/99	1400	71.5	2008	17.6	3690	3.99	1.6	59	19	47	98.4	99.5	98,7	112.56
3/14/99	1400	95.5	2021	18.9	3920	4.11	1.4	60	17	43	98.5	99.6	98.9	119.15
3/15/99	230	108.0	2000	19.5	3900	4.36	0.9	58	16	40	98.5	99.6	99.0	83.32
3/16/99	430	134.0	2003	17.0	3860	3.73	1.0	71	20	67	98.2	99.5	98.3	112.16
3/16/99	1800	147.5	2005	17.6	3830	4.17	1.1	69	26	64	98.2	99.3	98.3	70.55
3/17/99	300	156.5	1997	17.7	3860	4.23	1.0	65	18	57	98.3	99.5	98.5	87.85
3/17/99	1430	168.0	2047	17.9	3940	4.16	1.1	67	21	59	98.3	99.5	98.5	164.20
3/18/99	400	181.5	1998	18.8	3000	4.24	0.9	61	15	47	98.4	99.6	98.8	94.12
3/18/99	900	186.5	2007	18'6	3900	4.24	0.9	59	15	45	98.5	99.6	98.8	95.45
3/18/99	1830	196.0	2003	20,1	4010	4.20	1.0	67	22	43	98.3	99.5	98.9	68.89
3/19/99	330	205.0	1998	20.2	4070	4.28	1.1	59	15	42	98.6	99.6	99.0	96.89
3/19/99	1030	236.0	2026	19.6	4040	4.15	1.0	61	16	42	98.5	99,6	99.0	77.51
3/19/99	1900	244.5	2003	21.1	4130	4.27	1.2	68	21	41	98.4	99.5	99.0	88.04
3/20/99	330	254.0	2000	21.5	4240	4.28	1.1	61	16	41	98.6	99.6	99.0	98.50
3/20/99	1000	274.5	2000	20.1	4110	4.21	0.9	60	15	40	98.5	99.6	99.0	80.87
3/20/99	1800	282.5	2002	21.3	4010	4.14	1.1	66	21	39	98.4	99.5	99.0	79.88
3/21/99	600	294.5	2002	19.7	4050	4.20	1.1	57	15	37	98.6	99.6	99.1	91.80
3/21/99	1000	298.5	2010	19.0	4080	4.18	1.0	60	16	38	98.5	99.6	99.1	78.89
3/21/99	1930	308.0	1975	20.7	4190	4.27	1.2	64	23	37	98.5	99.5	99.1	95.01
3/22/99	230	315.0	1995	21.2	4210	4.29	0.9	58	16	37	98.6	99.6	99.1	88.96
3/22/99	1330	326.0	2015	19.8	4120	4.25	0.9	60	16	37	98.5	99,6	99.1	180.98
3/22/99	2200	334.5	1991	21.3	4170	4.27	0.9	60	16	37	98.6	99.6	99.1	129.11
3/23/99	800	342.5	2003	20.5	4130	4.42	1.2	56	15	35	98.6	99.6	99.2	138.49
3/23/99	1100	347.5	2010	19.9	4050	4.23	1.0	56	15	34	98.6	99.6	99.2	87.43
3/23/99	2200	358.5	2000	20.8	4150	4.26	1.3	56	16	34	98.7	99.6	99.2	140.21
3/24/99	230	363.0	2000	20.1	4110	4.26	1.3	66	22	34	98.4	99.5	99,2	76.76
3/24/99	1030	371.0	2002	19.2	4040	4.18	1.1	57	16	35	98.6	99.6	99.1	83.47
3/24/99	2230	383.0	1991	21.0	4080	4.29	1.3	59	18	34	98.6	99.6	99.2	138.69
3/25/99	200	386.5	2005	21.0	4190	4.38	1.2	60	20	33	98.6	99.5	99.2	77.05
3/25/99	1000	394.5	2008	19.9	4200	4.42	1.2	59	18	34	98.6	99.6	99.2	80.32
3/25/99	2300	407.5	1995	21.2	4230	4.48	1.2	61	21	36	98.6	99.5	99.1	159.95
3/26/99	230	411.0	2003	20.9	4200	4.51	1.2	56	16	33	98.7	99.6	99.2	77.47
3/26/99	1300	421.5	2006	19.7	4090	4.13	1.0	54	15	34	98.7	99.6	99.2	121.43
3/26/99	2200	430.5	2010	20.2	4160	4.45	1.3	57	18	36	98.6	99.6	99.1	142.68
3/27/99	300	435.5	2005	19.8	4150	4.38	1.0	61	22	32	98.5	99.5	99.2	92.80
3/27/99	1300	445.5	2002	18.7	4150	4.20	1.3	56	15	35	98.7	99.6	99.2	113.64
3/27/99	2200	454.5	2030	20.8	4170	4.28	1.3	58	17	34	98.6	99.6	99.2	149.01
3/28/99	400	460.5	2002	20.3	4150	4.28	1.2	58	16	30	98.6	99.6	99.3	108.03
3/28/99	1300	469.5	2003	19.8	4200	4.10	1.0	56	16	35	98.7	99.6	99.2	132.20
3/28/99	2030	477.0	2033	21.6	4300	4.32	1.1	59	18	37	98.6	99.6	99.1	148.14
3/29/99	030	481.0	2005	21.7	4310	4.50	1.3	73	28	34	98.3	99.4	99.2	98.52

Raw Data Corresponding to Figure 6.0 (continued to the right from page 74)

Total Sample Weight #2 (g)	Total Sample Weight #3 (g)	Product Flow #1 (g)	Product Flow #2 (g)	Product Flow #3 (g)	Time (min)	Product Flow Rate # 1 (g/min)	Product Flow Rate # 2 (g/min)	Product Flow Rate # 3 (g/min)	Temp. Control Factor (TCF)	TCF* Constant	Product Flux GFD #1	Product Flux GFD #2	Product Flux GFD #3
162.90	117.70	66.9	118.2	73.3	240	0.28	0.49	0.31	1.240	21.97	7.59	13.41	8.32
115.79	87.43	46.9	71.0	43.0	180	0.26	0.39	0.24	1.255	22.24	7.26	11.01	6,67
101.86	81.65	34.4	57.1	37.3	170	0.20	0.34	0.22	1.340	23.74	6.44	10.69	6.97
127.58	98.72	49.7	82.8	54.3	260	0.19	0.32	0.21	1.302	23.07	5.74	9.57	6.28
107.95	87.36	39.1	83.2	43.0	226	0.17	0.28	0.19	1.397	24.75	5.98	9.67	6.58
150.45	118.97	67.9	105.7	74.6	400	0.17	0.26	0.19	1.345	23.83	5.44	8.47	5.98
156.92	125.41	74.5	112.2	81.0	416	0.18	0.27	0.19	1.275	22.59	5.16	7.77	5.61
102.56	86.06	38.6	57.8	41.7	206	0.19	0.28	0.20	1.245	22.06	5.15	7.71	5.56
138 54	116.85	67.5	93.8	72.5	387	0.17	0.24	0.19	1.379	24.44	5.87	8.17	6.31
79.87	71.70	25.9	35.1	27.3	141	0.18	0.25	0.19	1.345	23.83	5.88	7.98	6.21
104.78	90.52	43.2	60.0	46.1	240	0.18	0.25	0.19	1.340	23.74	5.72	7.96	6.12
209.09	172.58	119.5	164.3	128.2	674	0.18	0.24	0.19	1.329	23.55	5.55	7.63	5.95
111.63	96.73	49.4	66.9	52.3	260	0.19	0.26	0.20	1.281	22.70	5.53	7.48	5.85
111.99	97.91	50.8	67.2	53.5	267	0.19	0.25	0.20	1.291	22.88	5.61	7.44	5.92
76.52	69.96	24.2	31.8	25.6	120	0.20	0.26	0.21	1.219	21.60	5.31	6.97	5.61
112.13	99.20	52.2	67.4	54.8	255	0.20	0.26	0.21	1.214	21.51	5.35	6.90	5.61
86.25	78.70	32.8	41.5	34.3	163	0.20	0.25	0.21	1.240	21.97	5.95	6.94	5.74
100.05	89.72	43.4	55. 3	45.3	205	0.21	0.27	0.22	1.172	20.77	5.15	6.57	5.38
112.01	100.34	53.8	67.3	56.0	245	0.22	0.27	0.23	1.148	20.34	5.13	6.41	5.33
89.50	81.98	36.2	44.8	37.6	173	0.21	0.26	0.22	1.219	21.60	5.51	6.81	5.72
87.68	81.17	35.2	42.9	36.8	158	0.22	0.27	0.23	1.157	20.50	5.28	6.45	5.52
101.15	93.37	47.1	56.4	49.0	220	0.21	0.26	0.22	1.235	21.88	5.79	6.93	6.02
85.28	79.88	34.2	40.5	35.5	165	0.21	0.25	0.22	1.270	22.50	5.92	7.02	6.15
104.34	96.46	50.3	59.6	52.1	232	0.22	0.26	0.22	1.187	21.03	5.42	6.41	5.60
96.71	90.09	44.3	52.0	45.7	200	0.22	0.26	0.23	1.161	20.57	5.29	6.21	5.46
202.55	85.05	136.3	157.8	140.7	643	0.21	0.25	0.22	1.230	21.80	5.68	6.58	5.86
142.18	131.32	84.4	97.4	86.9	380	0.22	0.26	0.23	1.157	20.50	5.27	6.08	5.43
152.31	140.48	93.8	107.6	96.1	415	0.23	0.26	0.23	1.198	21.23	5.75	6.59	5.89
92.99	87.93	42.7	48.2	43.5	192	0.22	0.25	0.23	1.225	21.71	5.92	6.68	6.03
151.65	141.72	95.5	106.9	97.3	418	0.23	0.26	0.23	1.193	21.14	5.76	6.45	5.87
80.52	77.19	32.1	35.8	32.8	140	0.23	0.26	0.23	1.219	21.60	6.03	6.73	6.17
87.06	83.87	38.8	42.3	39.5	176	0.22	0.24	0.22	1.260	22.33	6.20	6.76	6.31
147.46	139.51	94.0	102.7	95.1	411	0.23	0.25	0.23	1.172	20.77	5.57	6.08	5.63
80.22	77.17	32.4	35.5	32.8	135	0.24	0.26	0.24	1.172	20.77	5.83	6.40	5.91
83.10	80.27	35.6	38.4	35.9	155	0.23	0.25	0.23	1.225	21.71	6.11	6.58	6.16
169.00	160.53	115.3	124.3	116.1	494	0.23	0.25	0.24	1.161	20.57	5.57	8.01	5.62
79.77	77.19	32.8	35.0	32.8	135	0.24	0.26	0.24	1.177	20.86	5.96	6,37	5.96
124.17	121.53	76.7	79.4	77.1	325	0.24	0.24	0.24	1.235	21.88	6.38	6.60	6.41
147.22	142.77	98.0	102.5	98.4	414	0.24	0.25	0.24	1.214	21.51	6.18	6.48	6.21
94.97	92.51	48.1	50.2	48.1	202	0.24	0.25	0.24	1.240	21.97	6.49	6.77	6.49
114.43	113.29	69.0	69.7	68.9	300	0.23	0.23	0.23	1.286	22.79	6.74	6.61	6.73
150.95	148.44	104.3	106.2	104.1	426	0.24	0.25	0.24	1.193	21.14	6.18	6.29	6.16
108.55	107.46	63.3	63.8	63.1	250	0.25	0.26	0.25	1.208	21.41	6.55	6.60	6.52
131.66	131.66	87.5	86.9	87.3	360	0.24	0.24	0.24	1.230	21.80	6.52	6.47	6.50
148.03	147.24	103.5	103.3	102.9	399	0.26	0.25	0.26	1.144	20.27	6.01	6.00	5.98
98.58	96.92	53.8	53.8	52.5	195	0.28	0.28	0.27	1.139	20.18	6.35	6.35	6.19

Raw Data Corresponding to Figure 6.0 (continued down from page 74)

3/29/99	1130	492.0	2003	20.5	3990	4.40	1.0	53	14	32	98.7	99.6	99.2	197.85
3/29/99	1900	501.5	2011	22.3	3990	4.33	0.8	54	18	34	98.6	99.6	99.1	89.32
3/30/99	200	508.5	2005	22.1	4210	4.46	1.1	57	26	31	98.6	99.4	99.3	89.56
3/30/99	1330	520.0	2000	21.1	4120	4.13	0.9	53	15	32	98.7	99.6	99.2	139.28
3/30/99	2100	527.5	2012	22.3	4190	4.41	1.0	52	15	32	98.8	99.6	99.2	80.31
3/31/99	300	533.5	1996	21.1	4170	4.53	1.3	50	19	31	98.8	99.5	99.3	110.04
3/31/99	2300	553.5	2003	19.6	4120	4.18	1.0	57	18	44	98.6	99.6	98.9	77.43
4/1/99	530	570.0	2029	17.3	4070	4.24	1.5	58	18	43	98.6	99.6	98.9	134.05
4/1/99	1000	575.0	2013	16.0	3960	4.59	1.4	56	17	39	98.6	99.6	99.0	63.27
4/1/99	1830	583.5	2010	16.1	4020	4.07	1.0	56	17	42	98.6	99.6	99.0	80.58
4/2/99	1135	600.5	2002	15.5	3950	4.22	1.0	59	25	39	98.5	99.4	99.0	96.56
4/3/99	1100	624.0	2004	17.0	3920	4.00	1.2	69	27	38	98.2	99.3	99.0	78.18
4/4/99	1030	647.5	2006	16.4	3930	4.21	1.1	54	17	39	98.6	99.6	99.0	90.39
4/5199	500	654.0	2010	17.6	4040	4.55	1.1	53	19	36	98.7	99.5	99.1	128.96
4/5/99	1430	663.5	2003	17.7	4100	3.91	1.2	52	20	35	98.7	99.5	99.1	171.87
4/5/99	2100	670.0	2001	19.5	4150	4.23	1.1	53	18	39	98.7	99.6	99.1	144.92
4/6/99	600	679.0	2000	19.3	4120	4.50	0.8	50	17	36	98.8	99.6	99.1	144.66
4/6/99	1100	684.0	1999	19.1	4030	4.15	1.0	56	21	34	98.6	99.5	99.2	97.47
4/6/99	2000	693.0	2007	20.6	4070	4.24	0.7	49	16	35	98.8	99.6	99.1	133.11
4/7/99	300	700.0	2011	20.6	4130	4.41	0.7	49	16	34	98.8	99.6	99.2	112.20
4/7/99	1100	708.0	2000	18.8	4100	3.97	1.0	54	18	34	98.7	99.6	99.2	105.45
4/7/99	2000	717.0	2002	19.3	4080	4.06	1.0	51	18	37	98.8	99.6	99.1	130.49
4/8/99	330	724.5	2005	18.0	3940	4.34	1.3	48	16	33	98.8	99.6	99.2	111.86
4/8/99	1000	732.0	2015	17.1	3950	4.05	1.2	50	19	35	98.7	99.5	99.1	83.00
4/8/99	1930	741.5	2001	19.3	3900	4.49	1.1	49	17	35	98.7	99.6	99.1	143.99
4/9/99	200	748.0	2010	19.6	4010	4.48	1.1	46	14	32	98.9	99.7	99.2	79.98
4/9/99	1030	756.5	2030	17.2	3910	4.26	1.3	47	15	32	98.8	99.6	99.2	83.98
4/9/99	2100	767.0	2000	19.5	4090	4.30	1.1	50	18	36	98.8	99.6	99.1	148.85
4/10/99	330	773.5	2000	19.2	4100	4.35	0.9	47	17	32	98.9	99.6	99.2	115.72
4/10/99	1400	784.0	2036	17.6	4070	4.07	1.3	46	15	33	98.9	99.6	99.2	157.06
4/10/99	2130	791.5	1996	19.7	4130	4.44	0.9	48	16	34	98.8	99.6	99.2	147.96
4/11/99	400	798.0	1973	19.4	4050	4.49	1.0	45	14	31	98.9	99.7	99.2	108.26
4/11/99	1300	807.0	1990	18.8	4090	4.10	1.0	47	16	33	98.9	99.6	99.2	159.40
4/11/99	2130	815.5	1966	21.0	4200	4.26	0.8	49	18	35	99.8	99.6	99.2	158.04
4/12/99	300	821.0	2004	21.0	4210	4.53	0.9	46	15	31	96.9	99.6	99.3	105.19
4/12/99	1330	831.5	2004	19.8	4050	4.34	1.1	45	14	32	98.9	99.7	99.2	142.98
4/12/99	1830	836.5	2002	19.7	4050	4.25	1.1	43	18	30	98.9	99.6	99.3	93.09
4/13/99	230	844.5	2012	18.8	3990	4.18		45	24	36	98.9	99.4	99.1	95.37
4/13/99	1430	856.5	2037	18.5	4090	4.25	1.1	48	18	33	98.8	99.6	99.2	213.78
4/13/99	1900	880.0	2001	20.4	4150	4.30	1.3	45	24	36	98.9	99.4	99.1	94.37
4/14/99	600	871.0	1995	20.9	4180	4.52	1.1	44	15	31	98.9	99.6	99.3	160.92
4/14/99	1000	875.0	1981	20.6	4190	4.15	1.0	42	15	31	99.0	99.6	99.3	95.49
4/14/99	1900	884.0	1998	22.8	4200	4.25	1.1	45	20	31	98.9	99.5	99.3	111.25
4/15/99	500	894.0	2006	22.4	3960	4.35	0.8	42	15	30	98.9	99.6	99.2	173.62
4/15/99	1230	901.5	2001	20.4	4060	4.35	1.0	40	19	29	99.0	99.5	99.3	136.69
4/15/99	1830	907.5	2004	21.7	4110	4.14	1.2	46	18	30	98.9	99.6	99.3	177.71
4/16/99	500	918.0	2002	21.3	4050	4.28	1.3	44	16	31	98.9	99.6	99.2	168.52
4/16/99	1100	948.0	2015	20.3	4040	4.39	0.5	44	16	30	98.9	99.6	99.3	99.38

Raw Data Corresponding to Figure 6.0 (continued down from page 75)

143.05	169.93	134.8	98.3	125.5	360	0.37	0.27	0.35	1.082	19.17	7.77	5.66	7.23
108.83	126.44	88.1	64.1	82.1	246	0.36	0.26	0.33	1.126	19.95	8.05	5.85	7.49
103.01	119.11	80.5	58.3	74.7	210	0.38	0.28	0.36	1.044	18.50	7.40	5.36	6.87
150.72	182.23	148.3	106.0	137.8	380	0.39	0.28	0.36	1.061	18.80	7.78	5.56	7.24
161.85	196.31	163.2	117.1	151.9	427	0.38	0.27	0.36	1.082	19.17	7.93	5.69	7.38
153.55	187.11	153.8	108.8	142.7	374	0.41	0.29	0.38	0.988	17.51	7.11	5.03	6.60
145.98	177.14	142.7	101.2	132.8	360	0.40	0.28	0.37	1.032	18.29	7.48	5.31	6.96
113.56	136.45	99.4	88.8	92.1	260	0.38	0.26	0.35	1.075	19.05	7.82	5.42	7.25
154.78	190.54	156.5	110.0	146.2	400	0.39	0.28	0.37	1.080	19.14	8.08	5.69	7.55
91.26	140.80	65.5	46.5	96.4	167	0.39	0.28	0.58	1.048	18.57	7.63	5.42	11.24
96.53	112.93	73.7	51.8	68.5	204	0.36	0.25	0.34	1.144	20.27	8.38	5.89	7.79
134.06	178.44	145.7	89.3	134.1	392	0.37	0.23	0.34	1.057	18.73	7.3a	4.51	6.77
84.87	98.31	58.0	40.1	53.9	154	0.38	0.26	0.35	1.069	18.94	7.63	5.28	7.09
95.10	114.35	75.4	50.4	70.0	201	0.38	0.25	0.35	1.157	20.50	8.90	5.94	8.26
142.71	179.35	145.8	98.0	135.0	347	0.42	0.28	0.39	1.126	19.95	9.44	6.34	8.74
141.02	182.37	149.9	96.3	138.0	420	0.36	0.23	0.33	1.208	21.41	9.23	5.93	8.50
130.37	165.07	131.7	85.6	120.7	360	0 37	0.24	0.34	1.182	20.95	9.06	5.89	8.30
86.40	102.01	63.0	41.7	57.6	150	0 42	0 28	0.38	1.028	18.22	7.87	5.20	7.19
127.91	161.76	129.2	83.2	117.4	340	0.38	0 24	0.35	1.157	20.50	9.01	5.80	8.19
107.68	134.76	99.1	62.9	90.4	248	0.40	0.25	0.36	1.139	20.18	9.19	5.83	8.38
92.84	115.74	78.3	48.1	71.4	220	0.36	0.22	0.32	1.270	22.50	10.18	6.25	9.27
84.55	103.18	65.1	39.8	58.8	168	0.39	0.24	0.35	1.193	21.14	9.78	5.97	8.83
115.69	146.63	113.2	70.9	102.2	270	0.42	0.26	0.38	1.086	19.24	8.76	5.49	7.91
114.53	146.16	113.6	69.8	101.8	290	0.39	0.24	0.35	1.225	21.71	10.41	6.40	9.33
82.28	99.65	61.5	37.5	55.3	164	0.38	0.23	0.34	1.291	22.88	11.08	6.75	9.95
132. 57	171.03	139.9	87.8	126.6	320	0.44	0.27	0.40	1.024	18.15	8.12	5.10	7.35
162.23	218.08	193.3	117.5	73.7	420	0.46	0.28	0.41	1.024	18.15	8.55	5.20	7.68
145.65	193.22	166.7	100.9	148.8	360	0.46	0.28	0.41	1.024	18.15	8.60	5.21	7.68
147.69	199.71	164.4	102.9	155.3	375	0.44	0.27	0.41	1.020	18.07	8.08	5.06	7.64
81.76	101.29	63.5	37.0	56.9	133	0.48	0.28	0.43	1.053	18.66	9.38	5.47	8.41
128.92	178.76	149.4	84.2	132.4	320	0.47	0.26	0.41	1.082	19.17	9.68	5.46	8.58
71.63	87.64	48.6	26.9	43.3	102	0.48	0.26	0.42	1.053	18.66	9.37	5.18	8.33
88.36	114.73	79.1	43.6	70.3	165	0.48	0.26	0.43	1.053	18.66	9.41	5.19	8.38
99.32	133.88	101.0	54.6	89.5	199	0.51	0.27	0.45	0.984	17.44	8.71	4.70	7.72
102.95	140.79	108.7	58.2	96.4	220	0.49	0.26	0.44	1.012	17.93	8.97	4.80	7.95
106.60	146.32	115.0	61.9	101.9	238	0.48	0.26	0.43	1.040	18.43	9.26	4.98	8.21
116.22	165.64	138.8	71.5	121.3	262	0.52	0.27	0.46	0.992	17.58	9.10	4.76	8.07
157.89	240.85	222.1	113.1	196.5	416	0.53	0.27	0.47	0.976	17.29	9.01	4.59	7.97
99.67	141.10	109.2	54.9	96.7	213	0.51	0.26	0.45	1.048	18.57	9.98	5.02	8.84
198.06	195.93	153.2	153.3	151.5	600	0.26	0.26	0.25	1.198	21.23	6.49	6.50	6.42
88.52	88.22	44.6	43.6	43.8	160	0.28	0.27	0.27	1.112	19.70	6.11	5.99	6.00
88.95	88.70	44.9	44.2	44.3	160	0.28	0.28	0.28	1.120	19.85	6.23	6.14	6.16
135.62	137.46	94.6	90.9	93.1	360	0.26	0.25	0.26	1.166	20.66	6.33	6.08	6.23
79.23	79.19	35.6	34.5	34.8	125	0.28	0.28	0.28	1.112	19.70	6.24	6.04	6.10
107.83	108.50	65.4	63.1	64.1	239	0.27	0.26	0.27	1.166	20.66	6.59	6.36	6.46
74.86	76.43	32.7	30.1	32.0	120	0.27	0.25	0.27	1.240	21.97	7.43	6.64	7.27
126.04	132.06	89.4	81.3	87.7	352	0.25	0.23	0.25	1.362	24.13	8.34	7.59	8.19
82.24	82.66	18.6	17.5	18.3	81	0.23	0.22	0.23	1.437	25.46	8.39	7.90	8.25

Raw Data Corresponding to Figure 6.0 (continued down from page 76)

4/16/99	1900	956.0	2001	22.0	4070	4.26	1.1	47	23	30	98.8	99.4	99.3	108.22
4/17/99	530	966.5	2006	21.7	4010	4.26	1.0	42	16	30	99.0	99.6	99.3	177.71
4/17/99	1000	971.0	2004	21.0	3940	4.20	1.0	43	17	29	98.9	99.6	99.3	93.34
4/17/99	1800	979.0	2004	22.7	4090	4.18	1.1	46	21	29	98.9	99.5	99.3	98.08
4/18/99	500	990.0	2003	23.0	4310	4.34	0.7	44	16	31	99.0	99.6	99.3	179.53
4/18/99	1200	1021.0	2000	22.0	4300	4.50	1.0	46	16	31	98.9	99.6	99.3	132.78
4/18/99	1900	1028.0	2001	24.0	4230	4.32	0 9	48	20	30	98.9	99.5	99.3	125.17
4/19/99	600	1039.0	1992	23.5	4250	4.30	1.2	45	17	31	98.9	99.6	99.3	192.97
4/19/99	1300	1046.0	2021	23.0	4130	4.79	0.9	46	18	31	98.9	99.6	99.2	207.86
4/19/99	2230	1055.5	2003	25.3	4390	4.16	1.3	47	18	34	98.9	99.6	99.2	198.46
4/20/99	500	1062.0	2004	24.2	4210	4.30	0.9	52	18	38	98.8	99.6	99.1	187.39
4/20/99	1200	1069.0	2000	23.1	4350	4.01	0.9	54	19	38	98.8	99.6	99.1	144.04
4/20/99	2230	1079.5	1986	24.8	4430	4.38	1.3	54	21	37	98.8	99.5	99.2	201.15
4/21/99	230	1083.5	2005	23.8	4380	4.50	1.2	50	24	32	98.9	99.5	99.3	110.14
4/21/99	1100	1092.0	2021	21.6	4200	4.52	0.9	50	18	35	98.8	99.6	99 2	118.40
4/21/99	2000	1101.0	2030	23.6	4230	4.63	0.1	51	19	34	98.8	99.6	99.2	190.38
4/22/99	200	1107.0	2001	23.2	4220	4.54	0.5	51	21	31	98.8	99.5	99.3	102.73
4/22/99	1100	1116.0	2035	21.3	4225	4.22	0.4	61	22	44	98.6	99.5	99.0	120.11
4/22/99	2300	1128.0	1953	22.0	4200	4.42	2.0	61	25	45	98.5	99.4	98.9	190.44
4/24/99	1400	1167.0	2005	20.3	4190	4.26	1.0	60	22	42	98.6	99.5	99.0	194.61
4/25/99	1300	1190.0	2000	20.8	4200	4.39	1.2	63	24	47	98.5	99.4	98.9	176.40
4/28/99	200	1251.0	1995	24.3	4310	4.56	1.3	63	24	45	98.5	99.4	99.0	107.71
4/28/99	1300	1262.0	1975	21.3	4190	4.61	1.3	61	24	43	98.5	99.4	99.0	173.89
4/28/99	2000	1269.0	2015	21.7	4190	4.26	1.5	65	26	46	98.4	99.4	98.9	143.78
4/29/99	2000	1293.0	2007	19.0	4010	4.10	1.4	61	24	43	98.5	99.4	98.9	123.03
4/31/99	1900	1340.0	2007	20 6	4150	4.02	1.3	64	27	46	98.5	99.3	98.9	109.82
5/2/99	2000	1389.0	2007	22 9	4260	4.17	1.4	68	31	50	98.4	99.3	98.8	157.89
5/3/99	2130	1414.5	2000	20.0	4120	4.19	1.3	63	28	45	98.5	99.3	98.9	158.25
5/4/99	400	1421.0	2013	18.6	4060	4.28	1.5	63	30	46	98.4	99.3	98.9	106.20
5/6/99	2130	1486.5	2005	24.4	4330	4.35	1.2	70	32	51	98.4	99.3	98.8	184.55
5/7/99	2230	1512.0	1996	25.3	4350	4.20	1.1	66	27	46	98.5	99.4	98.9	238.01
5/8/99	2100	1537.0	1998	25.3	4340	4.40	1.3	64	26	44	98.5	99.4	99.0	211.39
5/9/99	2130	1561.5	2005	24.5	4250	4.37	1.6	61	26	42	98.6	99.4	99.0	209.11
5/10/99	1800	1582.0	1973	23.8	4140	4.25	1.2	60	26	37	98.6	99.4	99.1	108.18
5/11/99	1300	1601.0	1991	23.0	4240	4.05	0.3	63	27	40	98.5	99.4	99.1	194.08
5/12/99	1030	1622.5	2002	23.7	4290	4.22	0.9	59	24	39	98.6	99.4	99.1	93.33
5/13/99	1215	1648.5	2007	23.7	4310	4.36	1.2	61	32	39	98.6	99.3	99.1	123.75
5/14/99	2100	1657.5	1989	25.4	4320	4.15	1.1	62	25	42	98 6	99.4	99.0	145.69
5/15/99	2000	1680.5	2006	24.7	4300	4.25	1.3	61	27	40	98.6	99.4	99.1	153.41
5/16/99	1945	1704.5	2004	24.0	4270	4.32	1.8	59	26	39	98.6	99.4	99.1	159.68
5/17/99	2000	1728.5	2017	25.2	4180	4.24	1.4	58	27	39	98.6	99.4	99.1	181.45
5/18/99	2210	1754.5	1967	26.1	4170	4.23	0.85	60	28	39	98.6	99.3	99.1	286.80
5/19/99	1100	1767.5	1973	23.8	4030	4.30	1.4	59	29	40	98.5	99.3	99.0	153.92

Raw Data Corresponding to Figure 6.0 (continued down from page 77)

77.21	79.32	35.9	32.5	34.9	153	0.23	0.21	0.23	1.432	25.38	8.52	7.71	8.30
91.27	94.58	51.9	46.5	50.2	225	0.23	0.21	0.22	1.468	26.01	8.80	7.90	8.52
73.94	77.05	33.5	29.2	32.7	132	0.25	0.22	0.25	1.379	24.44	8.55	7.45	8.34
84.91	88.30	45.7	40.2	43.9	180	0.25	0.22	0.24	1.351	23.94	8.21	7.22	7.89
119.89	125.32	84.3	75.1	80.9	330	0.26	0.23	0.25	1.345	23.83	6.19	7.30	7.86
155.45	167.61	127.2	110.7	123.2	480	0.26	0.23	0.26	1.340	23.74	6.43	7.34	8.17
131.85	140.71	100.2	86.9	96.3	360	0.28	0.24	0.27	1.245	22.06	7.65	6.63	7.35
132.16	140.58	100.0	87.4	96.2	356	0.28	0.25	0.27	1.255	22.24	7.84	6.85	7.54
90.06	95.11	52.8	45.3	50.7	188	0.28	0.24	0.27	1.265	22.42	7.98	6.84	7.65
121.03	129.27	88.4	76.3	84.9	300	0.29	0.25	0.28	1.193	21.14	7.43	6.41	7.14
102.73	108.93	67.5	58.0	64.5	225	0.30	0.26	0.29	1.193	21.14	7.57	6.50	7.23
94.66	102.55	60.8	49.9	58.2	205	0.30	0.24	0.28	1.281	22.70	8.62	7.08	8.25
115.73	126.40	85.8	71.0	82.0	300	0.29	0.24	0.27	1.255	22.24	7.98	6.60	7.63
100.78	108.43	67.2	56.0	64.0	241	0.28	0.23	0.27	1.323	23.44	8.64	7.21	8.24
75.74	80.89	38.3	31.0	38.5	140	0.27	0.22	0.26	1.373	24.33	9.14	7.39	8.71
127.52	139.32	99.3	82.8	94.9	380	0.28	0.23	0.26	1.255	22.24	7.70	6.42	7.36
74.74	78.07	35.3	30.0	33.7	120	0.29	0.25	0.28	1.240	21.97	8.01	6.81	7.65
77.02	81.82	39.3	32.3	37.4	130	0.30	0.25	0.29	1.368	24.24	10.02	6.23	9.55
130.32	143.19	104.2	85.6	98.8	360	0.29	0.24	0.27	1.245	22.08	7.95	6.53	7.54
103.12	111.65	71.0	58.4	67.3	240	0.30	0.24	0.28	1.260	22.33	8.33	6.84	7.88
134.00	151.15	112.4	89.3	106.8	402	0.28	0.22	0.27	1.345	23.83	8.96	7.12	8.51
128.91	141.85	103.3	84.2	97.5	360	0.29	0.23	0.27	1.235	21.88	7.75	6.32	7.32
97.03	104.26	63.6	52.3	59.9	216	0.29	0.24	0.28	1.250	22.15	8.15	6.70	7.67
134.53	153.23	114.7	89.8	108.8	385	0.30	0.23	0.28	1.281	22.70	8.86	6.78	8.22
134.64	151.95	113.4	89.9	107.6	360	0.31	0.25	0.30	1.172	20.77	7.66	6.08	7.27
94.10	101.60	60.5	49.4	57.2	190	0.32	0.26	0.30	1.172	20.77	7.75	6.32	7.33
121.89	137.21	98.3	76.9	92.8	319	0.31	0.24	0.29	1.240	21.97	8.40	6.57	7.93
83.05	90.12	48.4	38.3	45.7	155	0.31	0.25	0.30	1.235	21.88	8.44	6.68	7.97
84.26	92.20	50.7	39.5	47.8	165	0.31	0.24	0.29	1.281	22.70	8.93	6.96	8.43
173.69	203.85	169.1	126.9	159.5	573	0.30	0.23	0.28	1.297	22.98	8.80	6.71	8.30
83.97	91.46	49.7	39.2	47.1	153	0.32	0.26	0.31	1.203	21.32	8.33	6.57	7.89
137.17	153.38	116.2	92.4	109.0	360	0.32	0.26	0.30	1.177	20.86	7.93	6.30	7.43
85.09	92.10	50.8	40.3	47.7	159	0.32	0.25	0.30	1.193	21.14	8.06	6.40	7.57
96.44	107.14	66.6	51.7	62.8	190	0.35	0.27	0.33	1.091	19.33	7.39	5.74	6.97
143.76	165.35	128.9	99.0	121.0	360	0.36	0.28	0.34	1.107	19.62	7.78	5.97	7.30
114.83	130.65	92.0	70.1	86.3	241	0.38	0.29	0.36	1.203	21.32	9.79	7.46	9.18
91.54	102.45	62.1	46.8	58.1	181	0.34	0.26	0.32	1.139	20.18	7.88	5.94	7.37
137.88	159.98	123.8	93.1	115.6	360	0.34	0.26	0.32	1.152	20.41	8.09	6.08	7.55
85.62	95.46	54.7	40.9	51.1	167	0.33	0.24	0.31	1.208	21.41	8.47	6.33	7.91
92.28	103.27	63.5	47.5	58.9	180	0.35	0.26	0.33	1.126	19.95	7.93	5.93	7.35
143.10	168.39	133.0	98.4	124.0	370	0.36	0.27	0.34	1.139	20.18	8.26	6.11	7.70
80.38	89.62	48.7	35.6	45.2	140	0.35	0.25	0.32	1.166	20.66	8.37	6.13	7.78
83.97	94.21	53.4	39.2	49.8	145	0.37	0.27	0.34	1.095	19.40	7.82	5.75	7.30

Raw Data Corresponding to Figure 6.0 (Continued down from pages 78 and 79)

Date	Time	Elapsed Time (hrs)	Feed Pressure kPa	Feed Temp. C	Feed Conduct. (&S/cm)	Feed pH	Chlorine Conc. (ppm)	Product Conduct. #7 (&S/cm)	Product Conduct. #8 (&S/cm)	Product Conduct. #9 (&S/cm)	Salt Rejection #7 (%)	Salt Rejection #8 (%)	Salt Rejection #9 (%)	Total Sample Weight #7 (g)
3/12/99	1200	24.0	1457	22.3	795	8.40	0.70	39	8	54	95.1	99.0	93.2	113.30
3/13/99	1300	49.0	1505	22.7	826	8.40	0.65	55	34	62	93.3	95.9	92.5	233.62
3/14/99	1400	70.0	1473	23.4	801	8.24	0.32	101	20	111	87.4	97.5	86.1	171.96
3/15/99	200	82.0	1518	23.3	787	8.04	0.33	115	13	131	85.4	98.3	83.4	262.73
3/15/99	1800	98.0	1491	24.0	785	8.14	0.60	153	7	182	80.5	99.1	76.8	231.81
3/16/99	130	105.5	1467	22.9	782	8.25	0.45	159	16	194	79.7	98.0	75.2	262.82
3/16/29	1200	115.0	1509	22.4	792	8.21	0.36	166	20	246	79.0	97.5	68.9	291.62
3/16/99	1800	121.0	1546	23.3	807	8.40	0.40	215	7	260	73.4	99.1	67.8	283.70
3/17/99	100	128.0	1514	22.1	834	8.41	0.55	248	10	305	70.3	98.8	63.4	293.99
3/18/99	1700	144.0	1509	23.7	814	8.45	0.57	373	27	430	54.2	96.7	47.2	294.90

Total Sample Weight #8 (g)	Total Sample Weight #9 (g)	Product Flow #7 (g)	Product Flow #8 (g)	Product Flow #9 (g)	Time (min)	Product Flow Rate #7 (g/min)	Product Flow Rate #8 (g/min)	Product Flow Rate #9 (g/min)	Temp. Control Factor (TCF)	TCF* Constant	Product Flux GFD #7	Product Flux GFD #8	Product Flux GFD #9
106.90	123.80	68.6	62.6	79.2	55	0.81	0.74	0.93	1.112	19.70	17.73	16.13	20.42
183.33	264.33	189.1	139.0	220.0	180	1.05	0.77	1.22	1.095	19.40	22.32	16.41	25.97
118.53	195.16	127.4	74.2	150.8	88	1.45	0.84	1.71	1.065	18.87	29.10	16.95	34.45
157.21	306.32	218.2	112.9	262.0	130	1.68	0.87	2.02	1.069	18.94	33.99	17.58	40.81
126.87	269.00	187.1	82.6	224.7	90	2.08	0.92	2.50	1.044	18.50	40.15	17.71	48.21
134.00	306.89	218.3	89.7	282.6	103	2.12	0.87	2.55	1.086	19.24	44.29	18.20	53.27
136.50	341.47	247.1	92.2	297.1	106	2.33	0.87	2.80	1.107	19.62	50.62	18.88	60.87
129.30	332.25	239.2	85.0	287.9	90	2.66	0.94	3.20	1.069	18.94	53.81	19.12	64.78
125.25	309.04	249.5	80.9	264.7	91	2.74	0.89	2.91	1.120	19.85	60.93	19.77	64.66
98.50	344.10	250.4	54.2	299.8	55	4.55	0.99	5.45	1.053	18.66	89.44	19.36	107.09

Raw Data Corresponding to Figure 6.2

Date	Time	Elapsed Time (hrs)	Feed Pressure kPa	Feed Temp. C	Feed Conduct. µS/cm	Feed pH	Chlorine Conc. (ppm)	Product Conduct. #7 µS/cm	Product Conduct. #8 µS/cm	Product Conduct. #9 µS/cm	Salt Rejection #7 %	Salt Rejection #8 %	Salt Rejection #9 %	Total Sample Weight #7 (g)
3/19/99	2000	8	1705	25.3	832	8.50	0.50	33	10	38	96.0	98.8	95.4	171.50
3/20/99	100	13	1708	24.5	860	8.50	0.55	38	13	34	95.6	98.5	96.0	123.15
3/20/99	900	21	1705	23.5	866	8.48	0.43	40	11	35	95.4	98.7	96.0	126.20
3/20/99	1700	29	1713	26.1	901	8.37	0.30	45	12	42	95.0	98.7	95.3	238.01
3/21/99	100	37	1706	23.8	893	8.44	0.45	58	12	49	93.5	98.7	94.5	165.61
3/21/99	730	43.5	1697	24.0	896	8.37	0.30	56	12	54	93.8	98.7	94.0	260.33
3/21/99	1800	54	1715	26.1	887	8.48	0.50	71	11	69	92.0	98.8	92.2	273.80
3/22/99	135	61.5	1691	24.5	891	8.31	0.45	88	14	86	90.1	98.4	90.3	252.13
3/22/99	1100	71	1702	24.2	857	8.36	0.54	102	12	101	88.1	98.6	88.2	295.20
3/22/99	1900	79	1707	26.0	867	8.43	0.62	120	16	124	86.2	98.2	85.7	290.99
3/23/99	100	85	1542	24.8	872	8.36	0.45	158	20	155	81.9	97.7	82.2	276.42
3/23/99	1100	95	1538	24.1	852	8.42	0.50	185	13	191	78.3	98.5	77.6	283.94
3/23/99	1800	102	1500	25.4	873	8.45	0.72	216	21	223	75.3	97.6	74.5	309.97
3/24/99	200	110	1462	24.7	878	8.45	0.40	273	13	278	68.9	98.5	68.3	310.02
3/24/99	1100	119	1408	24.3	910	8.39	0.55	322	14	336	64.6	98.5	63.1	212.66
3/24/99	1800	126	1416	25.8	935	8.33	0.37	369	15	365	60.5	98.4	61.0	346.12
3/25/99	200	134	1400	24.7	949	8.36	0.20	440	14	452	53.6	98.5	52.4	291.35
3/25/99	900	141	1410	23.9	946	8.35	0.25	440	17	466	53.5	98.2	50.7	302.74
3/25/99	1800	150	1453	25.3	943	8.36	0.37	506	17	518	46.3	98.2	45.1	268.90
3/26/99	200	158	1408	24.4	869	8.32	0.50	538	14	540	38.1	98.4	37.9	258.02
3/26/99	900	165	1387	24.0	913	8.44	0.40	554	14	572	39.3	98.5	37.3	179.40
3/26/99	1800	174	1404	24.9	953	8.33	0.31	626	17	637	34.3	98.2	33.2	174.72
3/27/99	200	182	1411	24.0	880	8.30	0.55	611	25	623	30.6	97.2	29.2	225.45
3/27/99	1100	191	1404	24.4	868	8.39	0.40	638	28	650	26.5	96.8	25.1	167.97
3/27/99	1700	197	1410	25.1	872	8.25	0.42	670	24	667	23.2	97.2	23.5	305.93
3/28/99	200	208	1413	24.1	951	8.40	0.40	748	17	756	21.3	98.2	20.5	181.42

Raw Data Corresponding to Figure 6.2 (continued to the right from page 81)

Total Sample Weight #8 (g)	Total Sample Weight #9 (g)	Product Flow #7 (g)	Product Flow #8 (g)	Product Flow #9 (g)	Time (min)	Product Flow Rate #7 (g/min)	Product Flow Rate #8 (g/min)	Product Flow Rate #9 (g/min)	Temp. Control Factor (TCF)	TCF* Constant	Product Flux GFD #7	Product Flux GFD #8	Product Flux GFD #9
228.90	178.70	126.2	184.1	133.6	150	0.84	1.23	0.89	0.988	17.51	14.56	21.23	15.40
152.97	127.47	77.9	108.2	82.4	90	0.87	1.20	0.92	1.020	18.07	15.95	22.16	16.87
148.28	129.80	80.9	103.5	84.7	90	0.90	1.15	0.94	1.061	18.80	17.93	22.94	18.77
265.67	248.29	192.7	220.9	203.2	170	1.13	1.30	1.20	0.962	17.05	18.59	21.31	19.60
171.06	171.65	120.3	126.3	126.5	101	1.19	1.25	1.25	1.048	18.57	23.18	24.34	24.38
253.39	273.13	215.0	208.6	228.0	169	1.27	1.23	1.35	1.044	18.50	24.57	23.84	26.06
246.47	284.67	228.5	201.7	239.6	150	1.52	1.34	1.60	0.962	17.05	24.98	22.05	26.19
204.64	260.15	206.8	159.9	215.0	122	1.70	1.31	1.76	1.020	18.07	31.25	24.16	32.49
220.14	302.99	249.9	175.4	257.9	138	1.81	1.27	1.87	1.032	18.29	34.18	23.98	35.27
203.14	300.79	245.7	158.4	255.7	112	2.19	1.41	2.28	0.962	17.05	35.97	23.19	37.43
175.34	281.73	231.1	130.6	236.6	105	2.20	1.24	2.25	1.080	19.14	45.49	25.70	46.58
166.70	290.39	238.8	121.9	245.3	102	2.34	1.20	2.40	1.036	18.36	44.50	22.73	45.73
168.24	317.12	264.7	123.5	272.0	99	2.67	1.25	2.75	0.984	17.44	45.87	21.40	47.14
152.43	315.23	264.7	107.7	270.1	90	2.94	1.20	3.00	1.012	17.93	53.38	21.71	54.47
104.96	216.44	167.4	60.2	171.3	49	3.42	1.23	3.50	1.028	18.22	63.96	23.00	65.47
149.05	344.19	300.8	104.3	299.1	63	3.62	1.26	3.60	1.028	18.22	67.87	23.53	67.48
117.61	290.98	246.1	72.8	251.9	60	4.10	1.21	4.20	1.012	17.93	74.42	22.03	76.18
114.23	307.77	257.4	69.5	262.7	58	4.44	1.20	4.53	1.044	18.50	85.73	23.13	87.46
101.40	273.86	223.6	56.6	228.7	45	4.97	1.26	5.08	0.988	17.51	85.95	21.77	87.92
161.99	263.05	212.7	117.2	218.4	94	2.26	1.25	2.32	1.024	18.15	42.05	23.17	43.17
185.25	184.79	134.1	140.5	139.7	115	1.17	1.22	1.21	1.044	18.50	22.52	23.59	23.46
178.21	179.11	129.4	133.4	134.0	103	1.26	1.30	1.30	1.040	18.43	24.08	24.83	24.93
230.90	221.50	180.2	186.1	176.4	146	1.23	1.27	1.21	1.044	18.50	23.83	24.62	23.33
229.71	164.97	122.7	184.9	119.9	140	0.88	1.32	0.86	1.024	18.15	16.28	24.55	15.91
125.06	300.46	260.6	80.3	255.3	58	4.49	1.38	4.40	0.996	17.65	78.99	24.33	77.39
231.01	178.68	136.1	186.2	133.6	140	0.97	1.33	0.95	1.036	18.36	18.49	25.30	18.14

Raw Data Corresponding to Figure 7.0

Time	pH	Temp. C	Feed (µS/cm)	FT-30 (µS/cm)	FT-30 Flux norm.25C	FT-30 GFD norm.	FT-30 Reject (%)	SST/TMC (µS/cm)	SST/TMC Flux norm.25C	SST/TMC GFD Norm.	SST/TMC Reject (%)	BBRC-132 (µS/cm)	BBRC-132 Flux norm.25C	BBRC-132 GFD norm.	BBRC-132 Reject (%)	BBRC-135 (µS/cm)	BBRC-135 Flux norm.25C	BBRC-135 GFD norm.	BBRC-135 Reject (%)
0	5.55	24.9	1746	80.7	0.481	5.09	95.4	58.7	0.471	4.99	96.6	33.5	1.214	12.84	98.1	79.8	0.491	5.20	95.4
24	5.52	22.7	1654	40.5	0.325	3.43	97.6	45.0	0.346	3.66	97.3	22.2	0.931	9.84	98.7	56.5	0.390	4.12	96.6
48	5.60	23.5	1640	42.2	0.274	2.90	97.4	45.8	0.284	3.01	97.2	22.2	0.800	8.46	98.6	50.7	0.326	3.45	96.9
96	5.59	23.5	1449	40.8	0.263	2.78	97.2	43.9	0.274	2.90	97.0	19.7	0.758	8.02	98.6	47.5	0.326	3.45	96.7
120	5.53	22.4	1500	41.8	0.273	2.89	97.2	45.0	0.273	2.89	97.0	21.3	0.754	7.98	96.6	44.3	0.317	3.35	97.0
144	5.50	23.2	1603	40.0	0.255	2.70	97.5	43.8	0.255	2.70	97.3	20.0	0.692	7.31	98.8	43.9	0.298	3.15	97.3
168	5.45	23.5	1602	39.7	0.253	2.67	97.5	43.7	0.253	2.67	97.3	19.6	0.674	7.13	98.8	41.4	0.284	3.01	97.4
192	5.53	24.2	1657	41.8	0.236	2.50	97.5	46.9	0.247	2.61	97.2	21.9	0.658	6.96	98.7	48.3	0.278	2.94	97.1
264	5.60	23.4	1512	41.2	0.243	2.57	97.3	45.4	0.232	2.46	97.0	19.3	0.623	6.59	98.7	48.5	0.275	2.90	96.8
312	5.58	24.1	1668	43.8	0.237	2.51	97.4	48.9	0.237	2.51	97.1	21.6	0.619	6.54	98.7	50.2	0.268	2.84	97.0
336	5.65	26.2	1675	43.8	0.230	2.44	97.4	48.5	0.230	2.44	97.1	21.3	0.605	6.40	98.7	48.4	0.259	2.74	97.1
360	5.61	28.0	1644	43.5	0.217	2.29	97.4	48.5	0.217	2.29	97.0	19.8	0.579	6.12	98.8	49.7	0.235	2.49	97.0
432	5.60	27.5	1448	38.4	0.211	2.24	97.3	41.9	0.211	2.24	97.1	17.4	0.551	5.83	98.8	44.6	0.230	2.43	96.9
456	5.66	26.8	1727	36.2	0.216	2.29	97.9	37.9	0.216	2.29	97.8	16.4	0.546	5.77	99.1	39.9	0.235	2.49	97.7
480	5.61	25.8	1819	42.2	0.214	2.26	97.7	46.5	0.214	2.26	97.4	18.9	0.525	5.56	99.0	48.9	0.234	2.47	97.3
504	5.70	24.5	1743	40.4	0.214	2.26	97.7	43.5	0.203	2.15	97.5	19.5	0.519	5.49	98.9	46.1	0.224	2.37	97.4
528	5.59	24.9	1680	38.2	0.201	2.12	97.7	41.1	0.191	2.02	97.6	17.5	0.502	5.30	99.0	43.6	0.211	2.23	97.4
600	5.53	25.9	1463	39.2	0.194	2.05	97.3	41.7	0.175	1.85	97.1	17.5	0.475	5.03	98.8	43.9	0.194	2.05	97.0
624	5.50	26.2	1584	39.1	0.192	2.03	97.5	43.1	0.173	1.83	97.3	17.3	0.461	4.87	98.9	44.7	0.192	2.03	97.2
648	5.60	25.1	1619	48.5	0.199	2.11	97.0	54.9	0.179	1.90	96.6	21.6	0.479	5.06	98.7	55.9	0.189	2.00	96.5
672																			
696																			
768	5.60	26.0	1435	46.8	0.222	2.35	96.7	50.9	0.203	2.15	96.5	21.9	0.503	5.32	98.5	53.1	0.213	2.25	96.3
792																			
840	5.60	27.8	1532	48.0	0.200	2.12	96.9	54.1	0.191	2.02	96.5	22.6	0.455	4.81	98.5	59.0	0.191	2.02	96.1
864	5.58	27.0	1488	47.6	0.215	2.27	96.8	54.5	0.206	2.18	96.3	22.7	0.505	5.34	98.5	60.2	0.215	2.27	96.0
936	5.54	26.5	1248	45.7	0.219	2.31	96.3	50.3	0.209	2.21	96.0	21.3	0.495	5.23	98.3	53.0	0.209	2.21	95.8
960	5.60	27.5	1481	48.4	0.221	2.33	96.7	56.9	0.202	2.14	96.2	26.9	0.487	5.15	98.2	54.3	0.211	2.24	96.3
984	5.65	27.1	1558	53.5	0.196	2.07	96.6	60.7	0.186	1.97	96.1	23.8	0.485	5.13	98.5	62.9	0.196	2.07	96.0
1008	5.61	25.8	1570	51.3	0.185	1.96	96.7	54.0	0.185	1.96	96.6	19.9	0.467	4.94	98.7	57.3	0.185	1.96	96.4
1032	5.54	27.1	1541	53.1	0.186	1.97	96.6	59.7	0.177	1.87	96.1	22.6	0.447	4.73	98.5	62.9	0.177	1.87	95.9
1104	5.56	28.1	1336	48.3	0.189	2.00	96.4	53.8	0.171	1.81	96.0	21.8	0.460	4.86	98.4	56.4	0.171	1.81	95.8

Raw Data Corresponding to Figure 7.0 (continued down from page 83)

				FT-30				SST/TMC				BBRC-132				BBRC-135			
Time	pH	Temp. C	Feed (µS)	(µS/cm)	Flux norm.2 5C	GFD norm.	Reject (%)	(µS/cm)	Flux norm.2 5C	GFD norm.	Reject (%)	(µS/cm)	Flux norm.2 5C	GFD norm.	Reject (%)	(µS/cm)	Flux norm.2 5C	GFD norm.	Reject (%)
1128	5.52	27.1	1565	47.5	0.1957	2.0700	96.965	54.9	0.1771	1.8729	96.49	27.2	0.4660	4.9287	98.262	61.0	0.1771	1.8729	96.10
1152	5.58	26.9	1543	53.7	0.2064	2.1826	96.520	58.8	0.1876	1.9842	96.19	26.3	0.4690	4.9604	98.296	65.0	0.1782	1.8849	95.79
1200	5.59	25.5	1505	46.3	0.2064	2.1833	96.924	52.9	0.1966	2.0793	96.49	25.8	0.4718	4.9904	98.286	56.7	0.1868	1.9754	96.23
1272	5.65	28.4	1363	52.7	0.1873	1.9812	96.134	58.3	0.1695	1.7925	95.72	24.2	0.4549	4.8115	96.225	61.0	0.1695	1.7925	95.52
1296	5.59	27.0	1510	46.8	0.1870	1.9778	96.901	53.8	0.1777	1.8789	96.44	26.0	0.4582	4.8456	98.278	57.1	0.1683	1.7800	96.22
1320	5.68	27.9	1526	50.2	0.1905	2.0145	96.710	56.9	0.1905	2.0145	96.27	27.2	0.4535	4.7965	98.218	61.5	0.1723	1.8227	95.97
1344	5.63	27.8	1512	43.2	0.1911	2.0212	97.143	52.0	0.1911	2.0212	96.56	25.4	0.4368	4.6198	98.320	51.3	0.1638	1.7324	96.61
1368	5.61	27.1	1522	51.3	0.2050	2.1686	96.629	57.9	0.1864	1.9715	96.20	31.1	0.4474	4.7315	97.957	60.5	0.1771	1.8729	96.02
1464	5.54	26.9	1321	44.6	0.2064	2.1826	96.624	50.3	0.1876	1.9842	96.19	25.2	0.4502	4.7620	98.092	52.4	0.1688	1.7857	96.03
1488	5.55	27.0	1560	46.5	0.2151	2.2745	97.019	53.7	0.1964	2.0767	96.56	30.5	0.4488	4.7467	98.045	55.0	0.1683	1.7800	96.47
1512	5.59	26.1	1530	44.0	0.2215	2.3426	97.124	50.4	0.1926	2.0370	96.71	26.0	0.4430	4.6852	98.301	51.8	0.1733	1.8333	96.61
1536	5.58	26.5	1477	43.4	0.2187	2.3134	97.062	48.4	0.2092	2.2128	96.72	25.8	0.4470	4.7274	98.253	51.4	0.1712	1.8105	96.52
1560	5.59	27.7	1344	47.6	0.2191	2.3175	96.458	53.5	0.2100	2.2210	96.02	26.9	0.4382	4.6351	97.999	56.0	0.1643	1.7381	95.83
1584	5.60	27.1	1520	45.3	0.2237	2.3658	97.020	51.7	0.1957	2.0700	96.60	26.6	0.4474	4.7315	98.250	54.1	0.1678	1.7743	96.44
1608	5.60	27.9	1540	46.0	0.2358	2.4942	97.013	54.0	0.2177	2.3023	96.49	25.7	0.4444	4.7005	98.331	56.7	0.1633	1.7267	96.32
1656	5.75	27.9	1540	46.1	0.2268	2.3982	97.006	52.6	0.2086	2.2064	96.58	28.0	0.4354	4.6046	98.182	56.0	0.1542	1.6308	96.36
1728	5.60	28.8	1367	42.9	0.2288	2.4199	96.862	49.9	0.2112	2.2338	96.35	25.7	0.4224	4.4675	98.120	50.2	0.1496	1.5822	96.33
1776	5.58	28.0	1531	45.0	0.2260	2.3903	97.061	52.6	0.2170	2.2947	96.56	27.9	0.4339	4.5894	98.178	56.0	0.1537	1.6254	96.34
1800	5.77	28.0	1602	45.2	0.2260	2.3903	97.179	52.5	0.2170	2.2947	96.72	28.0	0.4339	4.5894	96.252	57.0	0.1446	1.5298	96.44
1824	5.60	28.6	1561	47.3	0.2304	2.4364	96.970	55.0	0.2215	2.3427	96.48	27.9	0.4253	4.4980	98.213	58.2	0.1329	1.4056	96.27
1920	5.63	27.5	1552	45.7	0.2206	2.3328	97.055	52.6	0.2114	2.2356	96.61	26.3	0.4227	4.4711	98.305	57.6	0.1195	1.2636	96.29
1968	6.28	28.5	1547	45.6	0.2134	2.2566	97.052	53.5	0.2045	2.1626	96.54	28.2	0.3912	4.1371	98.177	59.0	0.1067	1.1283	96.19
1992	6.18	27.5	1421	43.8	0.2206	2.3328	96.918	48.0	0.2114	2.2356	96.62	21.7	0.3952	4.1795	98.473	52.8	0.1103	1.1664	96.28
2064	5.90	29.0	1475	46.7	0.2185	2.3110	96.834	53.3	0.2098	2.2185	96.39	22.6	0.3846	4.0673	98.468	60.1	0.0961	1.0168	95.93
2088	5.55	28.9	1513	48.7	0.1936	2.0476	96.781	54.0	0.1760	1.8615	96.43	23.6	0.3696	3.9091	98.440	59.4	0.0880	0.9307	96.07
2136	5.34	27.3	1581	47.1	0.2035	2.1523	97.021	54.9	0.1850	1.9567	96.53	27.1	0.3978	4.2068	98.286	62.1	0.0833	0.8805	96.07
2160	5.54	26.9	1550	47.0	0.2157	2.2818	96.968	55.3	0.1970	2.0834	96.43	30.2	0.3940	4.1667	98.052	64.0	0.0844	0.8929	95.87
2280	5.55	29.2	1438	48.1	0.1999	2.1139	96.655	54.8	0.1912	2.0220	96.19	25.2	0.3824	4.0440	98.248	63.0	0.0608	0.6434	95.62
2328	5.61	30.2	1458	48.0	0.2030	2.1475	96.708	55.0	0.1777	1.8790	96.23	31.3	0.3722	3.9370	97.853	66.2	0.0508	0.5369	95.46
2400	5.60	30.2	1281	38.8	0.2030	2.1475	96.971	43.9	0.1861	1.9685	96.57	25.6	0.3722	3.9370	98.002	64.0	0.0508	0.5369	95.00
2448	5.54	29.3	1339	40.5	0.2078	2.1982	96.975	48.1	0.1992	2.1066	96.41	26.5	0.3724	3.9385	98.021	60.6	0.0520	0.5496	95.47
2472	5.55	29.9	1405	41.8	0.2123	2.2449	97.025	47.9	0.1953	2.0653	96.59	27.9	0.3736	3.9510	96.014	59.6	0.0425	0.4490	95.76
2496	5.58	30.2	1422	41.0	0.2200	2.3264	97.117	44.1	0.2030	2.1475	96.90	26.7	0.3722	3.9370	98.122	57.2	0.0508	0.5369	95.98
2592	5.58	30.3	1473	44.2	0.2200	2.3264	96.999	50.9	0.2030	2.1475	96.54	28.6	0.3722	3.9370	98.058	61.2	0.0508	0.5369	95.85

Raw Data Corresponding to Figure 7.0 (continued down from page 84)

				FT-30				SST/TMC				BBCR-132				BBCR-135			
Time	pH	Temp. C	Feed (µS/cm)	(µS/cm)	Flux nor25 C	GFD norm.	Reject (%)	(µS/cm)	Flux nor25 C	GFD norm.	Reject (%)	(µS/cm)	Flux nor25 C	GFD norm.	Reject (%)	(µS/cm)	Flux nor25 C	GFD norm.	Reject (%)
2616	5.51	29.7	1512	42.2	0.2220	2.3484	97.209	50.0	0.2050	2.1678	96.69	29.1	0.3672	3.8839	98.075	65.8	0.0342	0.3613	95.65
2760	5.58	28.8	1427	35.0	0.2200	2.3268	97.547	41.7	0.2112	2.2330	97.08	24.4	0.3608	3.8160	98.290	54.4	0.0352	0.3723	96.19
2784	5.81	29.1	1551	44.2	0.2267	2.3979	97.150	52.4	0.2180	2.3057	96.62	30.2	0.3750	3.9658	98.053	*	0.0349	0.3689	*
2904	5.52	29.9	1279	40.8	0.2207	2.3347	96.810	45.6	0.2123	2.2449	96.43	28.0	0.3651	3.8612	97.811	*	0.0340	0.3592	*
2928	5.51	29.9	1426	40.5	0.2292	2.4245	97.160	46.8	0.2123	2.2449	96.72	29.0	0.3651	3.8612	97.966	*	0.0255	0.2694	*
2952	5.48	30.0	1437	41.2	0.2200	2.3264	97.133	47.8	0.2115	2.2369	96.67	32.7	0.3638	3.8475	97.724	*	0.0254	0.2684	*
3096	5.58	29.0	1439	34.1	0.2360	2.4958	97.630	44.3	0.2185	2.3110	96.92	30.0	0.3496	3.6976	97.915	*	0.0262	0.2773	*
3120	5.60	29.1	1489	36.7	0.2354	2.4901	97.535	43.5	0.2180	2.3057	97.08	27.0	0.3401	3.5969	98.187	*	0.0262	0.2767	*
3168	5.60	29.5	1453	37.7	0.2236	2.3649	97.405	43.2	0.2150	2.2740	97.03	25.8	0.3440	3.6383	98.224	*	0.0258	0.2729	*
																*			*
																*			*
																*			*
																*			*
																*			*
																*			*
																*			*
3624	5.60	28.8	1489	39.8	0.2552	2.6991	97.327	49.9	0.2464	2.6061	96.65	30.6	0.3696	3.9091	97.945	*	0.0088	0.0931	*
3768	5.51	28.9	1334	41.7	0.2272	2.4034	96.874	50.7	0.2272	2.4034	96.20	29.3	0.3409	3.6051	97.804	*	0,0087	0.0924	*
3792	5.54	30.0	1528	45.9	0.2369	2.5054	96.996	53.4	0.2284	2.4159	96.51	31.5	0.3469	3.6686	97.938	*	0.0085	0.0895	*
3816	5.58	30.4	1670	51.3	0.2453	2.5948	96.928	57.7	0.2369	2.5054	96.54	34.6	0.3553	3.7581	97.928	*	0.0085	0.0895	*
3840	5.54	28.9	1617	42.4	0.2360	2.4958	97.378	48.9	0.2185	2.3110	96.98	31.4	0.3409	3.6051	98.058	*	0.0087	0.0924	*
3912	5.64	29.8	1346	40.4	0.2386	2.5231	96.999	46.7	0.2300	2.4330	96.53	31.0	0.3408	3.6045	97.697	*	0.0085	0.0901	*
3936	5.59	28.2	1496	40.8	0.2425	2.5644	97.273	45.2	0.2335	2.4694	96.98	30.4	0.3502	3.7041	97.968	*	0	0	*
3984	5.57	27.8	1637	53.7	0.2366	2.5024	96.720	59.3	0.2275	2.4062	96.38	34.0	0.3458	3.6574	97.923	*	0	0	*
4080	5.51	29.3	1253	36.0	0.2338	2.4730	97.127	40.4	0.2252	2.3814	96.78	26.9	0.3204	3.3889	97.853	*	0	0	*
4104	5.60	27.7	1439	38.7	0.2374	2.5107	97.311	44.0	0.2283	2.4141	96.94	28.9	0.3287	3.4763	97.992	*	0	0	*
4152	5.51	29.5	1489	41.4	0.2408	2.5468	97.220	44.8	0.2236	2.3649	96.99	31.6	0.3182	3.3655	97.878	*	0	0	*
4176	5.54	29.4	1383	34.7	0.2330	2.4644	97.491	38.6	0.2330	2.4644	97.21	27.4	0.3279	3.4685	98.019	*	0	0	*
4272	5.54	29.0	1447	38.3	0.2272	2.4034	97.353	43.8	0.2185	2.3110	96.97	30.4	0.3059	3.2354	97.899	*	0	0	*
4296	5.59	30.1	1450	39.8	0.2284	2.4159	97.255	45.7	0.2200	2.3264	96.85	33.2	0.2961	3.1317	97.710	*	0	0	*
4320	5.54	30.2	1476	41.9	0.2287	2.4187	97.161	44.9	0.2202	2.3292	96.96	30.3	0.2965	3.1354	97.947	*	0	0	*
4344	5.71	30.1	1562	40.4	0.2369	2.5054	97.414	46.4	0.2284	2.4159	97.03	31.1	0.3046	3.2212	98.009	*	0	0	*
4416	5.60	28.2	1297	37.9	0.2335	2.4694	97.078	41.4	0.2245	2.3744	96.81	30.0	0.3053	3.2292	97.687	*	0	0	*
4488	5.68	31.2	1673	43.2	0.2383	2.5202	97.418	47.8	0.2383	2.5202	97.14	34.2	0.2979	3.1502	97.956	*	0	0	*
4512	5.48	30.0	1605	40.6	0.2284	2.4159	97.47	44.6	0.2200	2.3264	97.22	30.8	0.2876	3.0422	98.081	*	0	0	*
4584	5.54	30.5	1427	43.1	0.2292	2.4245	96.96	48.9	0.2292	2.4245	96.57	32.2	0.2972	3.1428	97.744	*	0	0	*
4632	5.53	29.6	1703	41.3	0.2314	2.4473	97.575	47.3	0.2314	2.4473	97.22	32.9	0.2742	2.9005	98.068	*	0	0	*
4656	5.87	29.0	1795	45.5	0.2360	2.4958	97.465	53.0	0.2360	2.4958	97.05	35.7	0.2884	3.0505	98.011	*	0	0	*
4680	5.57	28.1	1667	42.8	0.2523	2.6682	97.433	43.7	0.2433	2.5730	97.38	33.8	0.2973	3.1447	97.972	*	0	0	*
4752	5.49	28.9	1484	43.2	0.2464	2.6061	97.089	44.1	0.2376	2.5130	97.03	30.3	0.2816	2.9783	97.958	*	0	0	*
4776	5.61	28.9	1612	36.4	0.2376	2.5130	97.742	40.7	0.2376	2.5130	97.48	39.0	0.2728	2.8853	97.581	*	0	0	*
4800	5.60	29.7	1622	37.3	0.2306	2.4387	97.7	42.7	0.2306	2.4387	97.37	30.6	0.2647	2.8000	96.113	*	0	0	*
4848	5.54	26.9	1667	39.2	0.2533	2.6786	97.648	45.5	0.2439	2.5794	97.27	33.4	0.2720	2.8770	97.996	*	0	0	*
4920	5.63	29.0	1699	38.6	0.2535	2.6807	97.728	44.6	0.2535	2.6807	97.37	32.2	0.2797	2.9580	98.105	*	0	0	*