Final Report

Task 2.5. Development of Salinity Reduction Technologies for Individual Source Waters

Subtask 2.5.2. Development of Salinity Reduction Technologies for Municipal Wastewater

Research & Development Group
Orange County Water District
10500 Ellis Avenue
Fountain Valley, CA 92728-8300

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Acknowledgement

Table of Contents

Preface

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What follows is the final report for Task 2.5. - Development of Salinity Reduction Technologies for Individual Source Waters, Subtask 2.5.2. Development of salinity Reduction Technologies for Municipal Wastewater, Contract No. 400-00-013, conducted by the Orange County Water District. This report is entitled "Development of salinity Reduction Technologies for Municipal Wastewater." This project contributes to the Energy-Related Environmental Research program.

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Executive Summary

Introduction

Since the development of the reverse osmosis (RO) membrane, membrane separation processes have been used to treat a variety of challenging water sources from seawater to municipal wastewater. The widespread use of the RO membrane resulted from the development of the modern polyamide (PA) membrane. The PA membrane is attractive because it produces high quality water at relatively low pressures, thus reducing overall RO treatment costs. Despite its many advantages, the PA membrane, like its predecessors, is prone to biological fouling, especially when treating municipal wastewater.

Disinfectants such as chlorine are typically used in wastewater treatment plants to maintain stable bacterial levels. This can pose a problem when operating PA membranes since they are susceptible to oxidation and degradation from exposure to both free chlorine and combined chlorine species. As a result, measures are typically taken to either remove the chlorine or transform it to a weaker, less aggressive form before the water reaches the RO treatment process. Membrane manufacturers maintain general exposure limits of 1,000ppm-hours for free chlorine and 100,000ppm-hours for combined chlorine, but detailed information is limited. Few simultaneous challenge studies have been conducted to evaluate a variety of commercial RO membranes for their tolerances to chlorine.

Objective

The objective of this project was to evaluate the sensitivity of RO membranes materials to chlorine using a RO test cell designed to simulate operations of manufactured RO membrane elements. Specific tasks undertaken to achieve this objective included:

- Design and construction of a small RO test cell to simulate operating conditions of a commercial spiral wound RO membrane element.

- Validation testing of the RO cell with a RO membrane element.
- Screening experiments to determine the sensitivity of commercial RO membrane materials to oxidizing agents such as chlorine.

Approach

A small RO test cell was designed and constructed to hydraulically simulate a full-scale membrane element. Operated under cross-flow conditions, the cell holds a flat sheet of membrane material and a feed spacer identical to one found in a membrane element. The RO test cell was evaluated in parallel testing with a RO membrane element to confirm that the cell could reasonably mimic the performance of a spiral element. Upon completion of testing (and validation of the RO cell), the same design was used to construct additional cells for the membrane oxidation tests. A small RO system was constructed and consisted of twelve test cells, each capable of operating independently. The system was designed to operate in a closed-loop configuration and therefore was equipped with a temperature control system to maintain a constant temperature.

Four commercial RO membranes were evaluated and represent those used at the various member agencies of the Desalination Research and Innovation Partnership (DRIP). The list of membranes included BW-30 (Dow FilmTec), ESPA-2 and LFC-1 (Hydranautics) and TFC-HR (Koch Membrane Systems). Membrane performance (defined as water flux and solute (salt) rejection) was evaluated upon operations with free chlorine and combined chlorine. Two species of free chlorine were used: hypochlorite (OCl^-) and hypochlorous acid ($HOCl$). Combined chlorine testing was conducted using monochloramines (NH_2Cl) in the presence and absence of iron (Fe^{+2}) to confirm whether or not a transition metal can influence the rate of membrane oxidation. Membrane tolerances in all trials were expressed in terms of ppm (concentration)-hours of exposure. Membranes were then examined to determine chemical and structural changes in the PA polymer material attributed to exposure to free and combined chlorine.

Results

RO Test Cell Validation

Results from duplicate, 1000-hour tests indicated that the RO cell and membrane element operated similarly. Specific biochemical analyses of the biological material (principally carbohydrates and proteins) present on both membranes revealed that the content and quantity were similar. Broader chemical analysis of the biological material indicated that the compositions were similar in both membranes as well. These observations, combined with similarities in the overall performance data, suggested that the internal operations of the RO cell and the membrane element were similar and therefore could be used to construct a larger system for the membrane oxidation testing.

Free Chlorine

All membranes tested under both species of free chlorine exhibited significant changes in performance. Changes in water transport were detected prior to changes in solute rejection. Since the oxidation capacity of HOCl is greater than OCl$^-$, changes in performance were experienced sooner when operated with HOCl. For example, ESPA-2 operated with HOCl exhibited a 20% change (from initial startup conditions) in water flux at 3,600ppm-hours vs. 8,958ppm-hous with OCl$^-$. In both trials, the TFC-HR exhibited the highest tolerance while LFC-1 exhibited the lowest. At the established exposure limit of 1000ppm-hours, no significant changes in water flux or solute rejection were experienced, thus confirming the accuracy of the limit. Membrane analyses indicated that chemical and structural changes had occurred as a result of exposure to OCl$^-$ and HOCl. Membranes became more hydrophilic upon exposure to both chlorine species. Chemical analysis of the membrane polymer material indicated that changes attributed to the addition of chlorine to the polymer material had occurred. Changes were more pronounced on the membranes operated with HOCl. Analysis of the membrane surface topography indicated that structural changes were subtle, with the exception of LFC-1, which experienced dramatic surface changes.

Combined Chlorine

Membranes operated in the presence of combined chlorine demonstrated fairly high chlorine tolerances when compared to operations with free chlorine. For example, the ESPA-2 membrane experienced a 20% change in water flux at 52,000ppm-hours when operated with NH_2Cl vs. 3,600ppm-hours with free chlorine (as HOCl). Changes in water transport were detected prior to changes in rejection for all membranes tested. Based on a 20% change in performance from initial startup conditions, BW-30 exhibited the highest tolerance (69,000ppm-hours (water flux) and 125,000ppm-hours (solute rejection)) while LFC-1 exhibited the lowest (8,000ppm-hours (water flux) and 108,000ppm-hours (solute rejection)). At the established tolerance limit of 100,000ppm-hours, significant changes in both water flux and solute rejection occurred in all membranes. BW-30 experienced a 62% increase in water flux (from initial startup conditions) while LFC-1 water flux increased by 147%. The tolerance limit for combined chlorine was not as accurate as the free chlorine limit. Membrane analyses indicated that both chemical and structural changes had occurred. Membranes became more hydrophilic as membrane became more polar as a result of chlorine exposure. Chemical analysis of the membrane polymer material indicated that changes attributed to the addition of chlorine to the polymer material had occurred.

Combined Chlorine plus Iron

Membranes operated in the presence of combined chlorine plus iron exhibited a more rapid change in performance vs. operating with combined chlorine alone. For example, a 20% change in ESPA-2 water flux was observed at 35,000ppm-hours with NH_2Cl plus iron vs. 52,000ppm-hours with NH_2Cl alone. The BW-30 membrane exhibited the highest tolerance (51,500ppm-hours (water flux) and 120,500ppm-hours (solute rejection)) while LFC-1 exhibited the lowest (5,000ppm-hours (water flux) and 79,000ppm-hours (solute rejection)). At the established tolerance limit of 100,000ppm-hours, significant changes in both water flux and solute rejection occurred in all membranes. BW-30 experienced a 120% increase in water flux (from initial startup conditions) while LFC-1 water flux increased by 374%. Changes in membrane structure and chemistry were the most pronounced of all the conditions tested. In particular, the membrane surface topography was clearly altered when iron was present in the system.

Distinct holes, present only under this set of testing conditions, were observed on the surfaces of all the membranes. This suggests that the iron precipitated onto the membrane surface where it caused a localized enhancement (i.e., catalysis) of membrane oxidation. This would account for the dramatic changes in membrane performance when compared to operations with combined chlorine alone.

Conclusions

A comparison of the membrane performance data suggest that the RO test cell can reasonably simulate the operations of a single RO membrane located in the lead position of a RO treatment system. Analyses of the material present on the membrane after two, 1000-tests indicated that the fouling material was consistent in terms of quantity and composition.

All membranes, regardless of manufacturer, were susceptible to oxidative degradation in varying degrees depending on the chlorine species: $HOCl > OCl^- > NH_2Cl+iron > NH_2Cl$. Changes in membrane water flux were experienced prior to changes in solute rejection for all chlorine species. It is apparent that membrane tolerance is highly dependent on the feed water composition, as seen through operations with combined chlorine plus iron. The membrane tolerance limit for free chlorine was more accurate than the limit for combined chlorine. In the presence combined chlorine and a transition metal such as iron, the discrepancy was even more pronounced.

Recommendations

Based on the findings presented, a small RO test system is an ideal means of conducting preliminary membrane evaluations prior to costly pilot and demonstration testing. While it is not intended to replace long-term pilot testing, it could provide valuable data useful in the design of any RO pilot or demonstration system and is therefore recommended. To agencies operating RO treatment systems, the use of small test cells to evaluate the susceptibility of membrane oxidation from chlorine in the presence of their own unique feed waters is an ideal application and is therefore highly recommended. Front-end

membrane elements (lead elements) are typically the most affected by the presence of chlorine. By virtue of the design and configuration, the RO test cell actually simulates operations of a lead element. In the presence of chlorine and iron (or other transition metals), enhanced membrane damage was observed, thus confirming what others have reported. In a membrane treatment facility, iron will typically convert to the insoluble ferric state (Fe^{+3}). As iron enters the RO system, it quickly drops out of solution onto the lead elements. Once on the membrane, enhanced localized oxidation around the iron particles occurs. The use of test cells is recommended if there are questions regarding a decline in RO lead element performance that may be attributed to operations in the presence of chlorine with or without transition metals.

As opposed to developing a chemically resistant RO membrane capable of continuous operations with various species of chlorine, industry has instead focused on the development of fouling resistant membranes principally through the use of existing polymer materials and the application of proprietary coatings. Given the cost and resources needed for development, the 'next-generation' RO membrane capable of withstanding chemical oxidation depends on the formation of an industry-wide consortium of membrane manufacturers and technologists. Through a collaborative effort, the development of a chemically tolerant, fouling resistant membrane would result in energy savings and overall cost savings associated with the treatment of municipal wastewater.

Benefit to California

The tools developed in this study and the means undertaken to conduct these analyses provides a framework that could be utilized by other water agencies faced with similar issues related to the use of RO membrane processes. The benefits associated with the PA membrane have resulted in agencies (including several DRIP members) throughout the state of California switching to, or considering the use of, RO treatment. The efficiency of high-performance PA membranes results in a less energy intensive process. Agencies adopting this technology to develop local and sustainable water supplies would reduce

their reliance on imported water. From a regional perspective, reducing the amount of imported water would equate to widespread energy savings.

Abstract

The treatment of municipal wastewater using advanced membrane processes such as reverse osmosis (RO) has gained in popularity due to the development of the polyamide (PA) membrane. This membrane is attractive because of the high water quality produced and the relatively low pressures required for operation. Despite its many advantages, the PA membrane is prone to biological fouling, especially when treating municipal wastewater. Disinfectants such as chlorine are typically used in wastewater treatment plants to maintain stable levels of bacterial activity. This can pose a problem when operating PA membranes since they are susceptible to oxidation and degradation from exposure to free chlorine and combined chlorine. The objective of this project was to evaluate the sensitivity of PA membranes materials to chlorine using RO test cells designed to simulate operations of manufactured membrane elements.

A series of four commercial RO membranes were evaluated using a small RO test cell designed to simulate operations of a spiral RO membrane element. Membranes selected represent those used at the various member agencies of the Desalination Research and Innovation Partnership and includes the BW-30 (Dow FilmTec), ESPA-2 and LFC-1 (Hydranautics), and TFC-HR (Koch Membrane Systems). Membrane performance (defined as water transport and solute (salt) rejection) was evaluated upon operations with free chlorine (as hypochlorite (OCl^-) and hypochlorous acid (HOCl)) and combined chlorine (as monochloramines (NH_2Cl)). Combined chlorine testing was conducted in the presence and absence of iron (as Fe^{+2}) to confirm whether or not a transition metal can influence the rate of membrane oxidation. Results indicated that all PA membranes, regardless of manufacturer, were susceptible to oxidative degradation in varying degrees depending on the chlorine species: $HOCl > OCl^- > NH_2Cl+iron > NH_2Cl$. RO membrane life and replacement may not be dictated solely by the incidence of irreversible fouling. Rather, consideration of PA membrane degradation resulting from long-term exposure to chlorine is warranted.

List of Figures

List of Tables

1.0 Introduction

Since the development of the reverse osmosis (RO) membrane by Loeb and Sourirajan in 1962, membrane separation processes have gained widespread acceptance for a variety of applications (Mcllvaine, 2004). Through advances in material science, high-pressure RO membranes are now capable of producing ultrapure water from the most challenging water sources. The use of RO for the treatment of municipal wastewater for potable reuse demonstrates the successful progression of this technology, in light of water quality levels that reflect increasing regulatory requirements. RO membranes are vulnerable to degradation when operated in conjunction with various chemical agents, including chlorine. This project will evaluate membrane chemical sensitivity through a series of challenge studies to validate manufacturers' exposure limits as well as to determine tolerance differences among different commercial RO membranes.

1.1 Background

The reclamation of municipal wastewater has been successfully conducted at the Orange County Water District (OCWD) since 1967. For over twenty-five years, OCWD used RO in conjunction with a five-stage chemical clarification process to treat secondary municipal wastewater. Chemical clarification prior to RO was employed to reduce high concentrations of both biological and colloidal material from impacting the RO. Recently, chemical clarification has given way to microfiltration (MF) – a process that uses microporous membranes to remove particles from the water prior to RO treatment. This process has been successfully demonstrated at OCWD and other locations (Henley, 2004; Mierzejewski et al., 2004; Pluim et al., 2003; Alexander et al., 2003; 2001; Viswanath et al., 2003; Dawes et al., 1999). When compared to conventional treatment, MF offers substantial space savings (using one sixth the space), reduced operations and maintenance cost, and most importantly, it provides a physical barrier to particulates larger than the nominal membrane pore size (typically in excess of 0.2-micron). Water quality produced by the MF is typically low in suspended solids and turbidity. It also exhibits a reduced fouling propensity (as indicated by low silt density index (SDI) values). This results in extended RO operations and a reduction in the frequency of

membrane cleanings. The use of membrane processes to treat municipal wastewater is a daunting task due to the biological and chemical nature of the source water. While the degree of RO biological fouling may be reduced, it has not been eliminated entirely. The impact of membrane biological fouling in all stages of the treatment process must be continually addressed to ensure overall cost-effectiveness of municipal wastewater reclamation.

1.2 Overview

The advent of the modern RO membrane can be attributed to the work of Cadotte and co-workers (1980). To be considered a viable treatment method, a membrane that produces highly purified water at relatively low pressures was needed. A membrane meeting these criteria was developed and is commonly referred to as the polyamide (PA) membrane. Due to its superior operating performance and product water quality, the PA membrane has become the membrane of choice for the advanced treatment of water and wastewater.

What has not changed over the years is the propensity for RO membranes to undergo fouling by either biological or colloidal materials (Bartels et al., 2004; Lee and Lee, 2004; Lewandowski and Beyenal, 2004; Koo et al., 2003; Bharwada et al., 2000; Faibish et al., 1998; Ridgway and Flemming, 1996; Saad, 1992; Ridgway, 1988). Membrane biological fouling (i.e., biofouling) results in a host of deleterious effects such as: (1) increased membrane differential pressure, (2) reduced water production, (3) deteriorated water quality and (4) biodegradation of membrane polymer and element components (Allred et al., 2005; Allred et al., 2004; Flemming et al., 1994, 1993). Manufacturers continually develop new polymer chemistries in an effort to enhance membrane performance. Recently, 'fouling resistant' membranes designed to limit biofouling, were introduced by a variety of manufacturers. The overall success of these products, however, has been mixed (Alexander et al., 2003). Membranes operated for the treatment of municipal wastewater are still prone to biological fouling.

Minimizing biological fouling is commonly achieved through periodic or continuous introduction of chlorine or other oxidizing agents into the feed water. This practice can pose significant problems when operating PA membranes since a major limitation is their sensitivity to oxidizing chemicals such as chlorine (Byrne, 2002; Glater et al., 1994; Jayarani et al., 2000; Kawaguchi and Tamura, 1984). Depending on the treatment configuration and source water, chlorine may be added prior to RO treatment for disinfection and later removed before reaching the RO. Chlorine can also be added at the plant influent to provide disinfection throughout the entire process, including the RO. This requires that the chlorine entering the RO be transformed to a weaker, less aggressive chlorine species. Since PA membranes are susceptible to permanent damage by chlorine, the challenge is to maintain bacterial stability in a chlorine-free (or near chlorine free) environment while maintaining optimal RO membrane performance.

1.3 Project Objective

The overall objective of this project was to evaluate the sensitivity of RO membrane materials to chlorine using a small RO test cell designed to simulate operations of a manufactured RO spiral wound element. Specific tasks undertaken to achieve this objective included the following:

- Construction of a small RO test cell designed to simulate conditions similar to commercial spiral wound RO membrane elements.
- Validation of the RO test cell.
- Screening experiments to determine the sensitivity of commercial RO membranes to oxidizing agents such as chlorine.

The development of a small RO test cell designed to hydraulically simulate a full-scale RO membrane element would allow for feasibility testing of RO treatment to meet specific water quality objectives for any application. It is not intended to entirely replace pilot or demonstration testing. Rather, this system would allow for economic evaluations of membrane treatment prior to the installation of costly demonstration or full-scale

treatment facilities. These test cells were utilized to evaluate the sensitivity of commercial RO membranes to degradation from exposure to various species of chlorine. Physical and chemical changes in the PA membrane were then evaluated by conducting a variety of laboratory analyses. Results will provide valuable insight and benefit facilities concerned about the addition of oxidizing chemicals to control fouling in their RO treatment processes.

1.4 Report Organization

The remainder of this report contains detailed information regarding the equipment and analytical procedures developed and utilized for the evaluation of RO membrane materials. This is followed by a presentation of the findings from these evaluations (Section 3.0). Section 4.0 provides an interpretation and discussion of the findings as well as recommendations for future investigations with respect to the issue of membrane tolerances in the presence of chemical disinfectants such as chlorine.

2.0 Project Approach

2.1 Polyamide RO Membranes

Five commercial RO membranes were used in the study and are presented in Table 1. This list differs from the proposed list outlined in the original test plan. The list was modified to represent membranes that were actually being used at the various member agencies of the Desalination Research and Innovation Partnership (DRIP). Each membrane was constructed of a thin film of polyamide cast onto a polysulfone support substrate. The thin film layer (i.e., separation layer) is formed by an interfacial reaction between trimesolyl chloride (TMC) and *m*-phenylenediamine (MPD) as outlined in Figure 1. It is this thin separation layer that is susceptible to degradation by chlorine through mechanisms that are incompletely understood (Byrne, 2002; Glater et al., 1994; Jayarani et al., 2000; Kawaguchi and Tamura, 1984; Glater et al., 1983). An image showing holes in the membrane separation layer due to chlorine exposure is presented in

Figure 2. Several mechanisms by which chlorine attacks the PA membrane (and the MPD ring) have been proposed (Gabelich et al., 2005; Glater et al., 1994; Kawaguchi and Tamura, 1984). A commonly cited mechanism, known as the 'Orton rearrangement,' involves the chlorination at the amide bond followed by "intramolecular rearrangement" whereby chlorine is introduced into the MPD ring (Figure 3). Other mechanisms suggest that chlorine addition may occur via direct chlorination of the MPD ring. While several mechanism(s) of membrane chlorination have been proposed, further investigation and discussion was beyond the scope of this study.

Membrane performance is typically characterized in terms of solute (salt) permeability and water permeability. Water permeate (i.e., water flux) is defined as the flow of permeate (Q_p) divided by the surface area of the membrane (S) as follows:

$$J_t = Q_p / S$$

where:

J_t = permeate flux at time t (gallons per ft^2-day)

Q_p = permeate flow (gallons per day)

S   = membrane surface area (ft^2)

The permeate flux (J_t) produced per unit driving pressure (NDP) is defined as the specific flux (J_s). Changes in specific flux will be monitored to determine the degree of damage resulting from membrane exposure to chlorine. The specific flux is defined as follows:

$$J_s = J_t / NDP$$

where:

J_s = specific flux (gallons per ft^2-day/psi)

J_t = permeate flux at time t (gallons per ft^2-day)

NDP   = net driving pressure

Solute (salt) rejection is a measure of how well a membrane rejects the passage of dissolved ions. Measurements of solute rejection are considered the standard for assessing a membrane's ionic rejection performance and will be used in this study. The removal of other contaminants, such as organic compounds, is of significant importance to the water treatment industry as well. However, specific analytical methods are typically required. For the purposes of this study, membrane rejection was measured in terms of ionic contaminant removal thorough field measurements of the specific conductance (conductivity).

Solute rejection is defined as follows:

$$\% \text{ Solute Rejection} = C_f - C_p / C_f \text{ x } 100$$

where:

C_f = feed water concentration of a specific constituent (ex. conductivity)

C_p = permeate concentration of a specific constituent (ex. conductivity)

Membranes exhibiting a high solute permeability generally exhibit a higher water permeability and visa versa. Irreversible membrane damage due to oxidation from chlorine is commonly expressed in terms of a decrease in solute rejection (i.e., increasing solute passage) and increasing water permeability. RO membranes are stated to have limited chlorine tolerances before measurable performance changes are observed. In the presence of free chlorine, PA membranes are estimated to withstand 1,000ppm-hours before experiencing a significant deterioration in performance (Byrne, 2002). For example, a membrane should exhibit changes in performance after operating for 200hours in the presence of 5.0mg/L chlorine. In the presence of combined chlorine, tolerances are estimated at 100,000ppm-hours (Fluid Systems, 2000). The rate of membrane degradation depends highly on the species of chlorine. Combined chlorine species generally have a lower oxidizing potential and are less effective oxidants than free chlorine (AWWA, 1973; White, 1972). Membrane tolerances also depend on the feed water composition. Previous investigations conducted at the Yuma Desalting Facility (Yuma, AZ) and more recently by the Metropolitan Water District of Southern

California (MWDSC) have shown that transition metals such as iron act as catalysts to increase the rate of membrane oxidation (Gabelich et al., 2005; Gabelich et al., 2002; Byrne, 2000). Demonstration testing conducted at OCWD using a variety of PA membranes found combined chlorine to be safe when operated in excess of 20,000ppm-hours (OCWD, 1997-2003). Despite these observations and other claims, membrane manufacturers maintain general tolerance guidelines, typically limiting continuous chlorine exposure to less than 0.1mg/L (Hydranautics, 2002; FilmTec, 1998). Detailed information regarding membrane exposure and behavior in the presence of chlorine are limited.

2.2 RO Membrane Test Cell

Membrane evaluations were conducted using cross-flow membrane cells designed and constructed by OCWD. The cells were each comprised of a flat sheet of membrane approximately 0.117-ft^2, a shim and feed spacer secured between two plates of 316-stainless steel (Figure 4). The shim, made of varying thicknesses of Teflon (typically 0.03-0.06-in), was used to set the flow channel height to match that of the feed spacer. The function of the feed spacer is to simulate actual flow characteristics in a spiral RO membrane element by creating turbulent flow dynamics across the surface to limit fouling and more importantly, the development of a concentration polarization layer. A permeate (product water) carrier consisting of porous 316-stainless steel (100 micron pore size) was engineered into the top plate of each cell. This not only directed permeate to the product collection tube (while minimizing hold-up volume due to the large pore sizes), but provided structural support for the flat sheet of membrane material.

2.2.1 Test Cell Evaluation

Prior to conducting the oxidation experiments, a single test cell was operated in parallel with a spiral RO membrane element using RO feed water from the full-scale treatment facility at OCWD. A series of two, 1000-hour evaluations were conducted to test the variability in membrane performance between the test cell and the spiral membrane element. Comparable performance would indicate that a membrane operated in the test

cell could reasonably mimic that of a spiral membrane element located in the lead position of an RO treatment train. A schematic of the single pass configuration is illustrated in Figure 5.

Identical spiral RO membranes (2.5-in diameter x 14-in length) were supplied by Applied Membranes, Vista, CA (Table 1. **Commercial RO Membranes used in the evaluations.**These membranes were cast and manufactured from the same batch/lot of polyamide material in an attempt to further reduce variability associated with the membrane material. Flat sheets of membrane and feed spacer were removed from a spiral RO and installed in the cell, while the other RO element was installed in a pressure vessel. Identical operating conditions of flux and cross-flow velocity were maintained in both systems. Performance was monitored daily over the course of the trials. Upon completion, membranes were removed and autopsied to determine differences in the fouling material between the two systems.

2.3 RO Test System

Upon validation of the RO test cell, the same design was used to construct additional cells for the membrane oxidation testing. A membrane test system was designed and constructed by OCWD and is illustrated in Figure 4 and Figure 6. The system consisted of 12 stainless steel cells connected by two high-pressure manifolds. Each cell was designed to operate independent of each other and can simulate a variety of hydraulic conditions. A stainless steel, multistage centrifugal pump (Grundfos Pumps Corporation, Olathe, KS) drew feed water from a 60gallon reservoir to maintain pulseless, cross-flow hydraulics across each membrane cell. A concentrate flow valve (316-stainless steel; Swagelok Company, Solon, OH) restricted flow exiting each cell to create the required backpressure and flow conditions needed to drive the RO process. The pressure was monitored by stainless steel pressure gauges (Noshok, Berea, OH). Since the test system was operated in a closed-loop configuration, a temperature control system (Lauda, Lauda-Konigshofen) was utilized to maintain a consistent temperature throughout the

duration of the tests.   The large number of cells allowed for testing of replicate membrane samples (n=3, 6, etc.) to reduce the incidence of experimental variability.

2.4 RO Membrane Oxidation Testing

2.4.1 Membrane Conditioning

The membranes outlined in Table 1 were installed in the RO test system and operated for 16-hours under low pressure/low water flux using deionized water prior to the start of testing. This conditioning step removes any unreacted monomers (e.g., trimesoyl chloride and *m*-phenylenediamine) from the membrane. Initial membrane performance was then conducted to ensure that the membranes were performing as specified before proceeding to the chlorination experiments. A solution of sodium chloride (1000mg/L) was made in the feed tank and each cell adjusted to a water flux (J_t) of 15 gallons per ft^2-day (gfd), a value typical of a lead RO element in a full-scale RO train. After several hours of operation, solute rejection was measured. Membranes exhibiting low solute removal were rejected and not included in further evaluation.

2.4.2 Membrane Oxidation Testing

Membranes were tested in the presence of free chlorine and combined chlorine. At the commencement of testing, the pressures required to produce a water flux of 15gfd in each test cell were recorded and held constant throughout the experiments. If membrane oxidation affected membrane permeability, water flux should increase irrespective of pressure and as a function chlorine exposure. Membrane water flux and solute rejection were monitored regularly throughout the experiments. Experiments were terminated once solute rejection and/or water flux changed by 20% compared to initial startup conditions.

2.4.2.1 Free Chlorine Testing

Depending on the operating pH of the feed water, free chlorine can exist predominantly as hypochlorous acid or hypochlorite ion (Figure 7). At pH levels greater than 8.5, chlorine exists almost exclusively as hypochlorite ion (OCl⁻), whereas at a low pH, chlorine exists primarily as hypochlorous acid (HOCl). The OCl⁻ species is stated to be nearly one-hundredth as effective as hypochlorous acid as an oxidant (White, 1972). Membranes were tested at a pH of 9.0 and 5.0 to represent testing in the presence of each chlorine species. A chlorine concentration of 500mg/L was made up and maintained throughout the experiments. The chlorine concentration was routinely monitored using portable chlorine test kits (Hach Company, Loveland, CO).

2.4.2.2 Combined Chlorine Testing

Combined chlorine testing was conducted in a similar fashion as described above. When combined with ammonia, chlorine will react to form various species of chloramines (monochloramines, dichloramines or trichloramines) depending on a host of conditions, including pH and temperature. Empirical laboratory trials were conducted to determine the conditions necessary to make a highly concentrated monochloramine solution in larger volumes to be used in the RO test system (Section 2.3). Monochloramines (NH_2Cl) were formed by combining ammonium chloride with sodium hypochlorite under controlled conditions determined in the laboratory. To ensure that principally monochloramines were produced, the pH was adjusted to 8.5 prior to formation as illustrated in Figure 7. The speed in which chloramines are formed is also dependant on temperature and pH, with the optimal pH being 8.3 (Faust and Aly, 1998; White, 1972). Given the potential for monochloramine degradation, the pH and temperature in the system were continually monitored and maintained (Peyrot et al., 1999). Monochloramine and free ammonia levels were monitored using field test kits (Hach Company, Loveland, CO). Since the oxidative potential of chloramines is significantly less than that of free chlorine, a high concentration (2,000mg/L) of monochloramines was used in this study. Initially, lower concentrations (5-10mg/L), representative of those used in the OCWD RO treatment facility, were proposed in the test plan. However, at a concentration of 5.0mg/L (and a membrane tolerance prediction of 100,000ppm-hours), a

decline in performance attributable to chlorine exposure could occur after 20,000 hours of operation. Therefore higher concentrations were needed if the study was to be conducted in a reasonable period of time.

2.4.2.3 Combined Chlorine/Catalyst Testing

Membrane testing in the presence of chloramines plus a catalyst was conducted and the results compared to operations under chloraminated conditions alone. Similar to the studies conducted by MWDSC, iron (as Fe(II)) was used as the test catalyst for this evaluation. A concentration of 0.10 mg/L (7.9×10^{-7}M) ferrous sulfate was selected to represent that used in previous MWDSC studies (Gabelich et al., 2005; Gabelich, 2004; Gabelich et al., 2004). In contrast to field trials, these experiments were conducted under controlled conditions where the only mechanism(s) acting to degrade the membrane are those associated with the chlorine and the iron. If iron is serving as a catalyst to increase the rate of membrane oxidation, the time elapsed before a deterioration in membrane performance is measured should be reduced.

2.5 Membrane Autopsy Analyses

Upon completion of testing, membranes were analyzed to determine the extent of surface and chemistry changes resulting from chlorine exposure. Changes in membrane chemistry were investigated using advanced spectroscopy techniques described in greater detail in Section 2.5.2 below. Atomic force microscopy (AFM) was employed to examine changes in the membrane surface topography attributed to oxidation and deterioration of the polyamide separation layer. Membrane hydrophobicity analyses using captive air bubble contact angle measurements were also conducted to examine changes in the membrane surface hydrophobicity. These latter methods are described in greater detail by Ridgway and co-workers (1999).

Membranes used in the RO cell validation trials (Section 2.2.1.) underwent additional testing to examine the degree and type of biological material present. As part of the normal protocol, three separate regions of the membrane surface were scraped and the

biofilms analyzed independently. This is done to reduce variability and ensure that a representative profile is obtained.

2.5.1 Biochemical Analyses

Two colorimetric assays were performed to determine the extent and type of biological material present on the membrane surface. The Lowry protein assay was employed to measure the protein content of the biofilm. This assay was run in conjunction with the total carbohydrate assay to measure the concentrations of sugars and related substances contained in the membrane biofilms. A detailed description of these techniques can be found elsewhere (Lowry et al., 1951). In both assays, biofilm was removed from three separate areas of the membrane. Results are typically expressed as a mass per unit area. The mass of biofilm collected from the membrane surface was also weighted to get a crude, wet-weight estimate of the overall quantity of biological material.

2.5.2 Spectroscopy Analyses

Attenuated total reflectance Fourier transform infrared (ATR/FTIR) spectrometry (Thermo Nicolet Instrument Corporation, Madison, WI) was used to determine the chemical structures of RO membranes and any changes attributed to membrane operations with chlorine. This technique was also utilized to chemically characterize the fouling layers (i.e., biofilms) on the membranes outlined in Section 2.2.1. Membrane pieces were cut from the elements upon completion of testing, dried and pressed in contact with the surface of an internal reflection element (IRE). Infrared (IR) radiation is focused on the end of the IRE and the light internally reflects down the length of the crystal. At each internal reflection, the IR radiation penetrates into the adjoining membrane. It is this physical phenomenon of light that enables one to obtain an infrared vibrational spectrum of the membrane and fouling layer. The sample single-beam spectrum is ratioed against a spectrum of the bare IRE and then converted to absorbance. Reference tables are then used to help identify the chemical structure of the membrane or

fouling layer. Digital subtraction of the reference membrane may be applied to aid in spectral interpretation. For the membranes used in the validation trials, principal component analysis (PCA) was employed as a data reduction technique to further extract information from the sample spectra. The PCA breaks apart the original spectral data into the most common spectral variations so that subtle differences can be magnified to reveal information regarding the composition of the fouling layer. The PCA reduces the spectra into mathematical spectra known as factors or principal components, which represent the most common variations in the data. A set of scaling coefficients (known as scores) for each factor can be calculated for each sample spectrum. Multiplying the scaling coefficients by the factors results a set of scores that represent the spectra as accurately as the initial responses at all wavelengths (Thermo Electron Corporation, 2005).

3.0 Project Outcomes

3.1 RO Test Cell Validation

As mentioned earlier, duplicate 1000-hour evaluations were conducted to test the variability in membrane performance between the RO cell and a spiral membrane element. The specific flux (Js; as defined earlier) and the solute rejection were recorded on a daily basis. Data for the first trial are presented in Figure 8. Comparison of the data suggests that the membrane operated in the RO test cell exhibited comparable behavior to that of the spiral membrane over the course of the 1400-hour trial. The fact that the two systems did not produce identical results was not surprising. Similar trends in membrane performance were deemed the critical issue when comparing the two systems. Nevertheless, statistical analyses (Statgraphics Plus, Manugistics, Inc., Rockville, MD) were performed to more closely examine the data. While there was no statistically significant difference between the specific flux data ($p>0.05$), there was a significant difference in the solute rejection data. Regression analyses were then employed to assign mathematical expressions to better describe the behavior and overall data trends. Both simple linear regression and non-linear regression analyses were conducted. Results of

these analyses produced a common equation (y=a+b*sqrt(X)) that described membrane performance in *both* the RO test cell and the spiral RO element. The relevance of these observations suggests that while the two systems may not produce identical results, their behaviors are comparable.

A second trial was conducted to confirm the findings of the first trial. Results from this trial are presented in Figure 9. A comparison of the data again indicated that the membrane operated in the RO test cell exhibited comparable behavior to that of the spiral membrane over the course of the 1100-hour trial. The fact that the two systems did not produce identical results was again not surprising. Statistic analyses indicated that there was a statistically significant difference (p<0.05) between the two data sets. However, regression analyses conducted independently on each data set produced the same mathematical expression ((y=1/(a+bx)), indicating the behavior was *similar* in both systems.

3.1.1 Membrane Autopsy Analyses

Membranes operated in the second trial were evaluated to determine if differences existed between the chemical and biological composition of the fouling material in the two systems. The RO test cell was designed to mimic the internal operating characteristics of a spiral membrane element.   Significant differences in the fouling profiles would suggest that the internal operating characteristics of the RO test cell and the spiral element were not similar.

3.1.1.1 Membrane Biochemical Analyses

Biological material was removed from the membranes as described in Section 2.5.1. Membrane autopsy data is presented in Figure 10. There were no differences in the content or concentration of biological material present on the two membranes. Statistical comparison of the data sets produced relatively high p-values for all measured parameters. There was no statistically significant difference in the data at the 95% confidence interval.

3.1.1.2 ATR/FTIR Analyses

ATR/FTIR spectra of the membranes removed from the test cell and the spiral element are presented in Figure 11. The fouling layers on both membranes appear virtually identical with respect to the chemical composition and relative quantity of adsorbed material. The foulants on both membranes were composed primarily of protein and carbohydrate material. The absorption band near 1057 cm^{-1} was indicative of carbohydrate material likely associated with the extracellular polymeric substances (EPS) produced by bacteria. Amide I and amide II bands indicative of proteins are visible near 1655 cm^{-1} and 1539 cm^{-1} on both membranes.

Principal component analysis (PCA) was performed to determine whether or not chemical differences in the biofilms existed between the spiral RO and the membrane removed from the RO test cell. A total of 36 spectra were collected – 18 for the spiral RO and 18 for the membrane operated in the test cell. A PCA plot of the two data sets is presented in Figure 12. If chemical differences existed, the data would cluster into distinct groups, each representing the spiral RO and the membrane flat sheet. The data appeared to be randomly scattered, absent of any discriminate clustering. The lack of clustering supports the notion that the internal operations of the RO test cell were similar to the spiral RO membrane.

3.2 RO Membrane Evaluations with Free Chlorine Species

3.2.1 RO Operations with Hypochlorite

Performance data for the membranes operated with free chlorine (principally as hypochlorite ion (OCl^-)) are presented in Figure 13. As mentioned earlier, membranes were defined as damaged when a 20% change in performance occurred relative to initial operating conditions. In the presence of OCl^-, the LFC-1 membrane exhibited a 20% increase in water flux after approximately 4,500ppm-hours of exposure (9 hours). The TFC-HR reached this point after 9,700ppm-hours (19.4 hours), while the BW-30 and

ESPA-2 membranes fell in between. In terms of solute rejection, both the BW-30 and ESPA-2 membranes experienced a 20% decrease at approximately 8,900ppm-hours (17.8 hours) and 11,000ppm-hours (22 hours) for LFC-1 and TFC-HR. In some instances, significant changes (i.e., 20%) in water flux did not coincide with changes in solute rejection (e.g., LFC-1). At 1,000ppm-hours (the point commonly defined as the free chlorine tolerance limit by the manufacturers), the LFC-1 membrane exhibited a 4% increase in water flux, while the other membranes exhibited no change. Changes in solute rejection at 1,000ppm-hours were less than 0.5% for all membranes.

3.2.2 RO Operation with Hypochlorous Acid

Performance data for the membranes operated with free chlorine (as hypochlorous acid (HOCl)) are presented in Figure 14. Membranes operated in HOCl exhibited different behavior kinetics than membranes operated with OCl^-. Membranes initially exhibited a loss in water flux, which was then followed by subtle increases in water flux and solute passage. In general, overall water flux increased in a linear fashion, as indicated by relatively high R-squared values. While membrane rejection behavior for TFC-HR and LFC-1 were similar to operations with OCl^-, rejection appeared to decline linearly in BW-30 and ESPA-2. As a stronger oxidant, it was not surprising to see a change in ESPA-2 water flux of 20% after only 3,600ppm-hours (7.2 hours) with HOCl vs. 8,900ppm-hours (17.8 hours) with OCl^-. A 20% change in ESPA-2 solute rejection was measured after 4,100ppm-hours (8.2 hours) vs. 8,900ppm-hours (17.8 hours) with (OCl^-). After 1,000ppm-hours of operation, water flux had decreased in all membranes, with BW-30 experiencing the largest drop of 11.7%. There was no measurable change in solute rejection in any membrane at 1000ppm-hour exposure to hypochlorous acid.

3.2.3 Chemical and Structural Alterations to the Polyamide Separation Layer

Membranes were analyzed to determine surface and chemical changes as a result of exposure to hypochlorite (OCl^-) and hypochlorous acid (HOCl) chlorine species. ATR/FTIR spectrometry was used to determine the chemical structures of the RO membranes and to examine any changes that may be attributed to operations with free

chlorine. ATR/FTIR spectra of the four membranes operated with different free chlorine species is presented in Figure 15. The vibrational structure of all the membranes changed significantly following exposure to both free chlorine species. The spectroscopic changes were more prominent at low pH (HOCl) than high pH (OCl$^-$). As noted in previous studies (Gabelich, et al., 2002), the C=C ring vibrations (1608, 1489, and 1448 cm^{-1}) dropped in intensity and the amide II N-H bending vibration (~1542 cm^{-1}) dropped in intensity, and shifted to lower frequency, or wavenumber. In most cases, the amide I carbonyl stretch (~1662 cm^{-1}) shifted to higher wavenumber in conjunction with the amide II shift. However, the amide I band did not shift in every case. Exposure to free chlorine at both low and high pH caused the carbonyl band (~1725 cm^{-1}) to increase in intensity. The amide II band shape and shift were notably different for membranes exposed to free chlorine at low pH as compared to high pH. At high pH (above 8.5), the amide II band significantly broadened, dropped in intensity and shifted slightly to a lower wavenumber. Under HOCl conditions, the amide II band shift to lower wavenumber was much greater, but the drop in intensity was not as great nor was the magnitude of the band broadening. One spectroscopic change was newly observed: After expose to HOCl, a vibrational band appeared at 1470 cm^{-1}. Assignment of this absorption band is not known at this time.

Membranes were also examined to determine if changes in hydrophobicity occurred as a result of exposure to free chlorine. Hydrophobicity data for membranes operated in the presence and absence of OCl$^-$ are presented in Figure 16. These data indicate that there was a statistically significant decrease in the contact angle in three of the four membranes exposed to OCl$^-$. The TFC-HR membrane experienced no significant change in contact angle. The other membranes became more hydrophilic (i.e., higher affinity for water) as a result of chlorine exposure. Membrane hydrophobicity was also affects when operated in the presence of HOCl (Figure 17). All membranes, with the exception of TFC-HR, experienced a decrease in the contact angle resulting in the membrane becoming more hydrophilic. The decrease was significant in all membranes except ESPA-2, despite exhibiting a decrease in contact angle.

Atomic force microscopy (AFM) was employed to assess surface changes in the polyamide separation layer resulting from exposure to chlorine. Since changes in the membrane surface chemistry were evident through both ATR/FTIR and hydrophobicity analyses, it was feasible that ensuing changes in the membrane surface topography would also be observed. Visual changes in surface structure were subtle in all membranes tested except LFC-1. Images of the LFC-1 membrane operated in the presence and absence of free chlorine are illustrated in Figure 18. Pronounced visual changes were observed when compared to the non-exposed control. The surface not only appeared smoother but as if material deposited on the membrane during operation. However, all tests were conducted under controlled conditions using particle-free solutions. The LFC-1 membrane was the only membrane to have additional anti-fouling coatings added during manufacturing. Since these observations were unique to LFC-1, it is possible that the dramatic changes were attributed to chlorine interacting directly with this surface coating material.

3.3 RO Membrane Evaluations with Combined Chlorine

3.3.1 RO Operations with Monochloramines

Performance data for the membranes operated with combined chlorine (principally as monochloramines (NH_2Cl)) are presented in Figure 19. Similar to the free chlorine trials, membranes were defined as damaged when a 20% change in performance occurred relative to initial conditions. All PA membranes demonstrated fairly high chlorine tolerances when compared to performance under free chlorine conditions. Since the oxidizing potential of combined chlorine is lower than free chlorine, it was not surprising that the membranes could withstand higher exposures. For example, ESPA-2 experienced a 20% change in water flux after 3,625ppm-hours of operation with HOCl vs. 52,000ppm-hours with NH_2Cl. Of the four membranes tested, LFC-1 exhibited a 20% change in performance the quickest (8,000ppm-hours for water flux and 105,000ppm-hours for solute rejection) followed by the TFC-HR membrane. BW-30 experienced the longest run time before a performance change of 20% was realized (69,000ppm-hours for water flux and 125,000ppm-hours for solute rejection). At

100,0000ppm-hours (the tolerance limit projected by the manufacturers for operations with combined chlorine), all membranes exhibited at least a 50% increase in water flux when compared to initial conditions. ESPA-2 water flux increased by 82%, while the LFC-1 water flux increased by 173%. The other membranes fell in between. Changes in solute rejection were less than 10% at 100,000ppm-hours for all membranes. BW-30 exhibited the smallest change (2.4%) while the LFC-1 experienced the largest at 9.0%.

3.3.2 RO Operations with Monochloramines plus Iron

Membranes were operated in the presence of combined chlorine (monochloramines) plus iron (as Fe(II)). Membrane water flux and solute rejection data for all membranes operated in the presence of NH_2Cl with and without iron are presented in Figure 20 and Figure 21, respectively. Membrane performance decline in the presence of iron exhibited similar behavior to membranes operated with combined chlorine alone and free chlorine, as OCl^-. Membrane performance declined more rapidly in the presence of NH_2Cl plus iron than in NH_2Cl alone. This was observed for all membranes tested. LFC-1 exhibited a 20% change in water flux the fastest (5,000ppm-hours) vs. BW-30, which reached the mark the slowest (51,500ppm-hours). For comparison to operations with chloramines alone, a 20% change in water flux for the LFC-1 and BW-30 membranes was reached at 8,000 and 69,000ppm-hours, respectively. A 20% change in solute rejection was observed for LFC-1 and TFC-HR at approximately 79,000ppm-hours. The ESPA-2 and BW-30 membranes exhibited a 20% change at 98,000 and 105,000ppm-hours, respectively. At the manufacturers tolerance limit of 100,000ppm-hours, percent changes in water flux (increase)/solute rejection (decrease) from initial startup conditions for the BW-30, ESPA-2, LFC-1 and TFC-HR membrane was 145/13, 181/21.2, 407/47.5 and 541/57.4%, respectively.

3.3.3 Chemical and Structural Alterations to the Polyamide Separation Layer

Membranes were analyzed to determine surface and chemical changes as a result of exposure to monochloramines and monochloramines plus iron. ATR/FTIR spectrometry

was used to determine the chemical structures of the RO membranes and any changes attributed to membrane operations with combined chlorine. ATR/FTIR spectra of the four membranes operated in the presence of NH_2Cl and NH_2Cl plus iron are illustrated in Figure 22. Membranes exposed to combined chlorine (with or without iron) did not exhibit significant changes in the spectral areas associated with the MPD ring of the PA membrane as was observed when operating with free chlorine. It is possible that chlorine attack (in the combined form) is limited to N-chlorination of the amide bond (step 2 in Figure 3). This would explain the changes in the amide I and amide II band intensities since these regions are associated with the amide bond of the PA membrane. The ratio of the band intensities appeared to drop slightly following exposure to both monochloramine treatments. The decrease in amide II band intensity indicates a loss of the N-H bending vibration. It is possible that changes in this ratio may signal the start of structural changes associated with the addition of chlorine to the MPD ring. However, the reason for this behavior is unknown as this time. Spectral changes in the membranes operated under chloraminated conditions in this study support what other investigators have observed in the field (Lozier, 2005, 2004).

Membranes were examined to determine if changes in hydrophobicity occurred as a result of chlorine exposure. Hydrophobicity data for membranes operated in the presence and absence of monochloramines and monochloramines plus iron are presented in Figure 23 and Figure 24, respectively. These data indicate a statistically significant decrease in the contact angle in all four membranes (including TFC-HR that previously exhibited no significant change in contact angle). The membranes became more hydrophilic (i.e., higher affinity for water) as a result of chlorine exposure. These data, combined with the observed chemical changes detected by ATR/FTIR, suggest that the membrane chemical structure is changing as a result of chlorine interaction or addition to the MPD ring, rendering the membrane more polar and electronegative.

AFM surface images of the four membranes operated in the presence of chloramines plus iron are presented in Figure 25. In all four membranes, distinct holes (highlighted in blue) were observed in the separation layer. The presence of these holes is likely

attributed to localized increases in oxidation associated with the deposition of insoluble iron (Fe (III)) acting as a catalyst to enhance the rate of membrane deterioration.

3.4 Effect of Operating Flux on Membrane Performance with Combined Chlorine

Membranes were operated at a water flux of 15gfd for both free chlorine and combined chlorine experiments. It was postulated that declines in membrane performance could be significantly influenced by the rate of water flux through the membrane. Membranes operated at a higher water flux may experience a faster deterioration than membranes operated at a lower water flux. To test this possibility, a trail was conducted whereby one of the four membranes (ESPA-2) was operated at varying water fluxes and the rate of performance decline measured. Membrane performance is presented in Figure 26. Replicate membrane samples were operated at four different water fluxes ranging from 2.54gfd to 30.4gfd. Regression analyses were conducted on all individual membrane data sets to define a single, common mathematical expression that could reasonably describe (i.e., high R-squared values) membrane behavior at each operating flux. The rate of change in performance (slope-as defined by the common mathematical expression) at each operating flux was established and compared to the slopes generated from operations at the other water fluxes. Results for both water flux and solute rejection are illustrated in Figure 27. Generally there were no significant differences in rate of change in water flux when operating at varying water fluxes. However, statistical analyses revealed a significant difference when membranes were operated at a water flux of 2.54gfd vs. 30.4gfd. The increase in the rate of change of water flux was hastened when operating at a lower water flux of 2.54gfd, contrary to what was postulated. Examination of the solute rejection data revealed that there was no significant difference in the rates (slopes) of solute decline when operating with a low (2.54gfd) or high (30.4gfd) water flux.

4.0 Project Conclusions and Recommendations

4.1 Conclusions

The overall objective of this project was to evaluate the sensitivity of polyamide RO membranes to various species of chlorine using a RO test cell. This required the design and construction of a small RO system capable of simulating operations of larger, spiral wound elements. This system could then be used to test a large number of membranes for their sensitivity to a host of oxidizing chemicals including chlorine.

The small RO test system was comprised of 12 test cells as described in Section 2.2. A comparison of membrane performance data for two, 1000-hour trials indicated that the test cell was effective in simulating operations of a larger, spiral wound element. As mentioned earlier, the fact that the two systems did not produce identical results was not surprising. Similar trends in the performance data were deemed the critical issue. Statistical analyses indicated that in both trials, similarities in the data from the spiral element and the RO test cell existed. As a further means of comparing the two systems, the biological material present on the surfaces of each membrane after shutdown were analyzed. If the RO test cell was operating as designed, similarities in the content and quantity of biological material should exist. Biochemical analyses indicated that there were no differences in the content or concentration of biological material present on the two membranes. ATR/FTIR analysis also confirmed that the chemical composition of the fouling material (and the relative quantity) appeared virtually identical. Further analyses of the data using PCA indicated that the chemical composition of the fouling layers on both membranes appeared identical. These findings, in conjunction with the membrane performance data, indicate that the RO test cell can reasonably simulate the operations of a single RO membrane located in the lead position of a RO treatment system.

A series of four commercial PA membranes were evaluated for their chemical tolerances to various species of chlorine using the RO test system described earlier. Membranes evaluated in the presence of free chlorine (hypochlorite (OCl^-) and hypochlorous acid ($HOCl$)) generally exhibited significant increases (20% or more, as defined earlier) in

water flux prior to experiencing significant decreases in solute rejection. The LFC-1 membrane, treated with the anti-fouling coating, exhibited the quickest change in water flux of all the membranes tested under both free chlorine species. However, it also operated the longest before a significant change in solute transport was experienced. The chlorine appeared to enhance membrane water permeability before changes in solute rejection were observed. This observation is consistent with membrane hydrophobicity data that indicated an increase in hydrophilicity (i.e., higher affinity for water) upon exposure to free chlorine. However, the TFC-HR membrane exhibited no measurable change in hydrophobicity upon exposure to either chlorine species (Figure 16-17). A review of the operating data revealed that this membrane also operated the longest before a significant change in water flux was measured. These data suggest that the TFC-HR membrane was the most tolerant to operations in the presence of either free chlorine species. Changes in the chemical composition of all polyamide RO membranes had occurred due to exposure to free chlorine, however the changes did not lead to dramatic changes in TFC-HR membrane performance. At the manufacturer's tolerance limit of 1000ppm-hours, no significant changes in water flux or solute transport were observed for any of the four commercial membranes evaluated.

Membranes evaluated in the presence of combined chlorine (monochloramines (NH_2Cl)) demonstrated high tolerances when compared to operations under free chlorine conditions. Since the oxidizing potential of combined chlorine is lower than free chlorine, this finding was not surprising. Chlorine, in the combined form, enhanced water permeability in all membranes before changes in solute rejection were observed. This observation is consistent with membranes exposed to either form of chlorine (free or combined). All membranes (including the TFC-HR) became more hydrophilic, reflected in increases in the water permeabilities. The LFC-1 membrane exhibited the quickest change in water flux. It was also one of the longest operated before a significant change in solute transport was experienced. Based on the performance data, the oxidative sensitivity was fairly consistent in all the other membranes evaluated. At 100,0000ppm-hours (the reported tolerance limit), all membranes exhibited a significant increase in water flux, while only moderate changes in solute rejection were measured. Chemical

changes in the membrane separation layers had occurred, but were different than those observed when operated with free chlorine.

The rate of membrane degradation due to chlorine can depend on various feed water characteristics. The introduction of trace concentrations of iron (and other transition metals) has been linked to accelerated degradation of PA membranes operated in the presence of chloramines. The execution of controlled trials confirmed that changes in membrane performance occurred more rapidly in the presence of combined chlorine and iron than in the presence of chloramines alone. Its presence served to enhance the chemical degradation process. The degree of membrane sensitivity appeared to be uniformly influenced by the presence of added constituents such as iron. That is, the order in which the membranes demonstrated significant changes was similar in both the testing conditions.

A surprising finding was that the rate of change in membrane performance appears to be independent of operating flux. It was assumed that higher membrane throughput (water flux) would equate to enhanced degradation. This was not the case. Membranes operated at different water fluxes exhibited relatively similar rates of change in both water throughput and solute rejection. This suggests that the mechanism(s) of membrane degradation are occurring principally at the solid-water interface and not within the interstices of the membrane.

4.2 Recommendations

Based on the findings presented, a small RO test system is an ideal means of conducting preliminary evaluations prior to costly pilot and demonstration testing. While it is not intended to replace long-term pilot testing, it could provide valuable data useful in the design of any RO pilot or demonstration system. There have been many criticisms made regarding the use of small test systems (Reiss, 1997; Bergman, 1993). The fact that small membrane samples are typically used, variability in membrane material may result in unrepresentative performance that would have otherwise been masked in larger RO

elements. The issue of membrane sample variability becomes less of a factor as the number of testing replicates increases. The system utilized in this study contained multiple RO test cells in an effort to address the issue of sample variability. Generally speaking, the observed differences in membrane performance due to sample variability were negligible. The levels of variability were consistent with membrane elements operated in previous studies (data not shown). If considering the use of a small RO system for feasibility testing, it is highly recommended that multiple test cells be operated simultaneously to account for the possibility of membrane sample variability.

The use of small test cells to evaluate the susceptibility of membrane degradation from chlorine and other oxidizing agents is an ideal application of this technology and is therefore highly recommended. With the presence of these chemicals in RO feed water, front-end elements (lead elements) are typically the most affected. By virtue of the design and configuration, RO test cells actually simulate operations of a lead element. In the presence of chlorine and iron (or other transition metals), enhanced membrane damage was observed, thus confirming what others have reported as well. In a membrane treatment facility, iron will typically be converted to the insoluble ferric state (Fe^{+3}). As iron enters the RO system, it quickly drops out of solution onto the lead RO elements. Once on the membrane, enhanced localized oxidation around the iron particles occurs. The use of small RO test cells confirmed this, as small discrete holes were observed after membranes were operated with chlorine and iron (Figure 24). The use of test cells is also recommended if there are questions regarding a decline in RO lead element performance that may be attributed to operations in the presence of chlorine with or without transition metals.

The underlying fact is that regardless of the manufacturer, all polyamide membranes evaluated were susceptible to degradation in varying degrees from operations with free chlorine and combined chlorine. Previous research funded by the Commission (Contract #500-97-503) and conducted by OCWD, evaluated an RO membrane designed to withstand chemical degradation from operations with chlorine. Initially it was anticipated that this membrane would be included in this study. A review of the

economics associated with the production of this membrane, however, resulted in the cancellation of the initiative. The cost to produce the raw materials as well as the synthesis process itself proved too costly. The use of membrane processes would have been limited had it not been for the development of the modern polyamide membrane. Membrane technology is currently focused on the development of 'anti-fouling' surfaces in an attempt to limit the incidence of biological fouling. Evaluation of these products at OCWD indicated that they were ineffective in reducing fouling. As opposed to developing a chemically resistant RO membrane capable of continuous operations with high concentrations of chlorine, industry has instead focused on fouling resistant membranes. Given the cost and resources needed for membrane development, the 'next-generation' RO membrane depends on the formation of an industry-wide consortium of membrane manufacturers and technologists. Through a collaborative effort, the development of a chemically tolerant, fouling resistant membrane would result in energy savings and overall cost savings associated with the treatment of municipal wastewater.

4.3 Benefit to California

Imported water to the region of southern California has been instrumental to the growth and development of a thriving industrial and residential metropolis. As the demand for water has grown, so has the need for additional water imports. Water transfers from northern California via the State Water Project and from the Colorado River are continually subject to scrutiny by the indigenous regions that are also being pressured by increasing water demands. Meeting the regions future water demands depend highly on the development of local water supplies that are not only safe and reliable but sustainable as well.

The treatment of municipal wastewater for indirect potable reuse is gaining in popularity. The advanced treatment of municipal wastewater using membrane processes has allowed for the transformation of this supply into a viable resource. This is partly due to the development of the polyamide RO membrane, which has replaced the cellulose acetate membrane due to its high performance characteristics. For over twenty-five years,

OCWD used cellulose acetate membranes for the treatment of municipal wastewater. Realizing the benefits associated with the PA membrane, OCWD recently began operating of a 5 million-gallon-per-day (mgd) interim facility that uses high-performance PA membranes. It is also currently constructing a larger, 70mgd facility that will use the same membranes. The benefits of using PA membranes over cellulose acetate have resulted in agencies (including several DRIP members) throughout the state of California making the switch to these higher performing, less energy intensive products. Agencies that once thought the cost of wastewater treatment was prohibitive, are now considering it due in part to the savings associated with the use of high-performance PA membranes. The more agencies that begin pursuing wastewater treatment via membrane processes, the more questions will arise regarding the chemical sensitivity and vulnerability of the PA membrane. The tools developed in this study and the means undertaken to quantify the chemical sensitivity of PA membranes will greatly benefit agencies faced with the issue of membrane compatibility and treatment of their own unique source waters. As agencies embrace and adopt membrane technology, the dependence on imported water will be reduced. From a regional perspective, reducing the amount of imported water would equate to widespread savings in energy consumption.

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Glossary

AFM	atomic force microscopy
ATR/FTIR	Attenuated total reflectance Fourier transform infrared
BW-30	Dow FilmTec reverse osmosis membrane
DRIP	Desalination Research and Innovation Partnership
EPS	extracellular polymeric substances
ESPA-2	Hydranautics reverse osmosis membrane
Fe^{+2}	ferrous iron
Fe(II)	ferrous iron
Fe(III)	ferric iron
GFD	gallons per ft2-day
HOCl	hypochlorous acid
IN	inch
IR	infrared
IRE	internal reflection element
MF	microfiltration
MGD	million-gallon-per-day
mg/L	milligrams per liter
M	molar
MPD	*m*-phenylenediamine
MWDSC	Metropolitan Water District of Southern California
NH_2Cl	monochloramines
NDP	net driving pressure
OCl^-	hypochlorite
OCWD	Orange County Water District
PA	polyamide
PCA	principal component analysis
RO	reverse osmosis
SDI	silt density index
TMC	trimesolyl chloride
TFC-HR	Koch Membrane Systems reverse osmosis membrane
LFC-1	Hydranautics reverse osmosis membrane
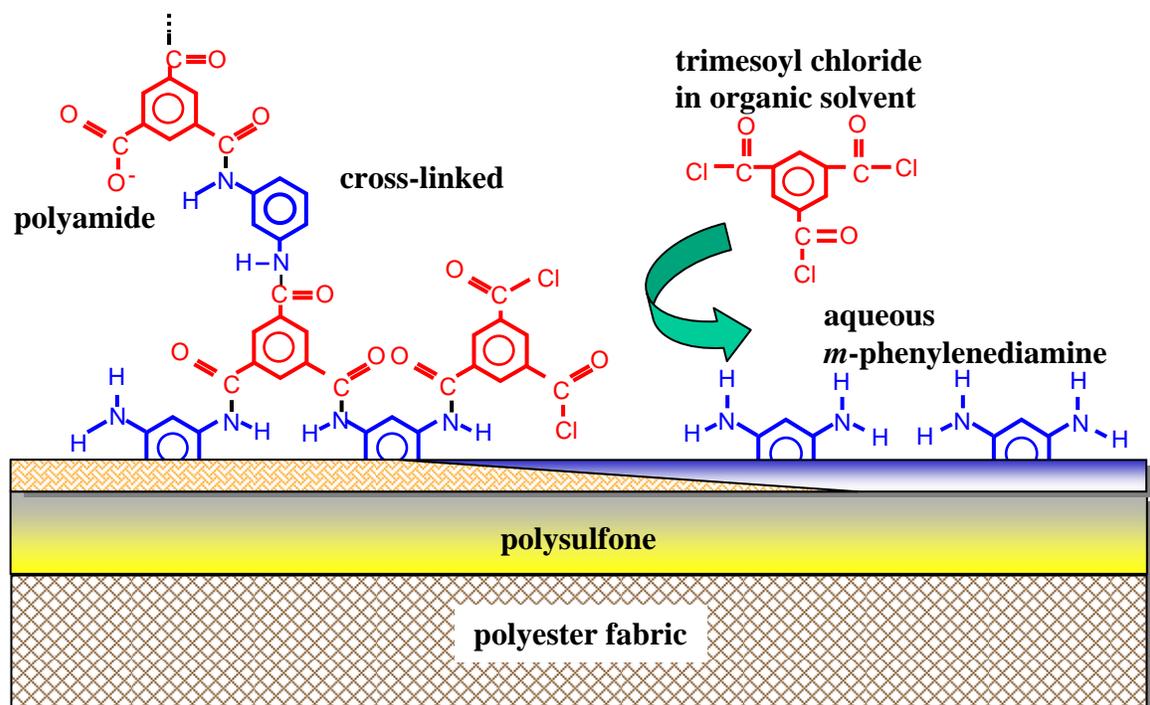
Figure 1. Polyamide membrane consisting of three layers: thin-film separation layer, polysulfone layer and the polyester fabric support. The thin film layer separation layer is created by an interfacial reaction between trimesoyl choride (red) and *m*-phenylenediamine (blue).
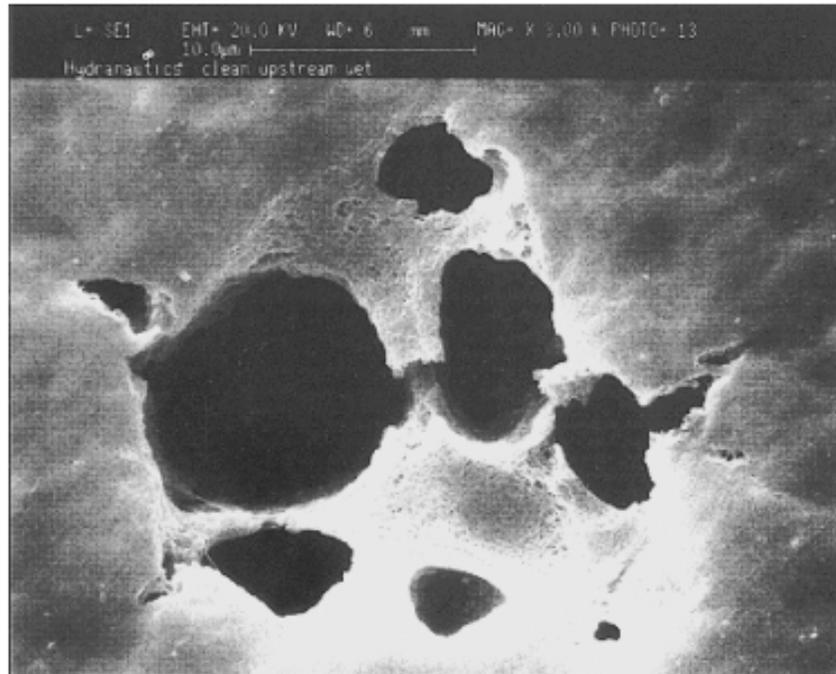
Figure 2. Scanning electron micrograph of a cellulose acetate membrane surface irreversibly damaged by chlorine exposure (courtesy of Hydranautics, Oceanside, CA).
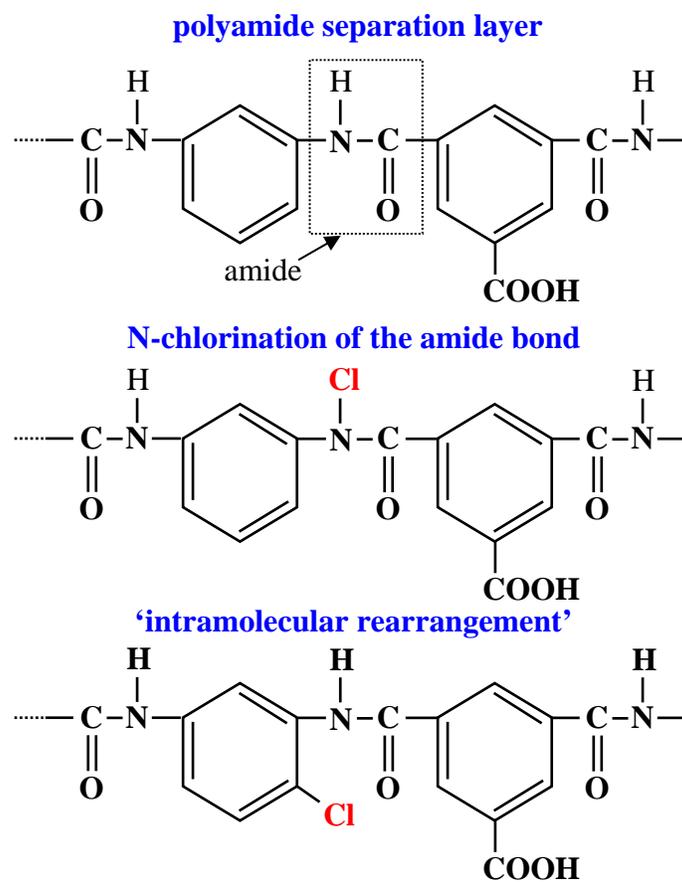
Figure 3. The proposed 'Orton rearrangement' whereby chlorine (red) is introduced into the MPD ring.
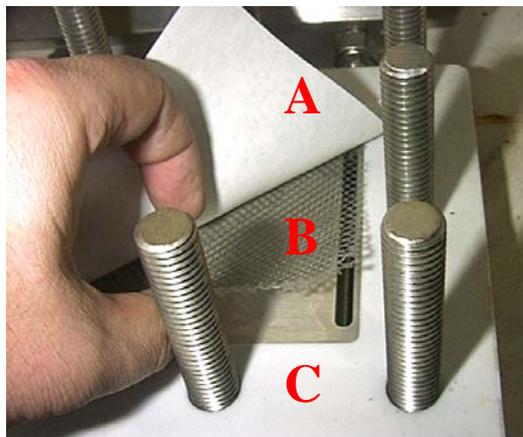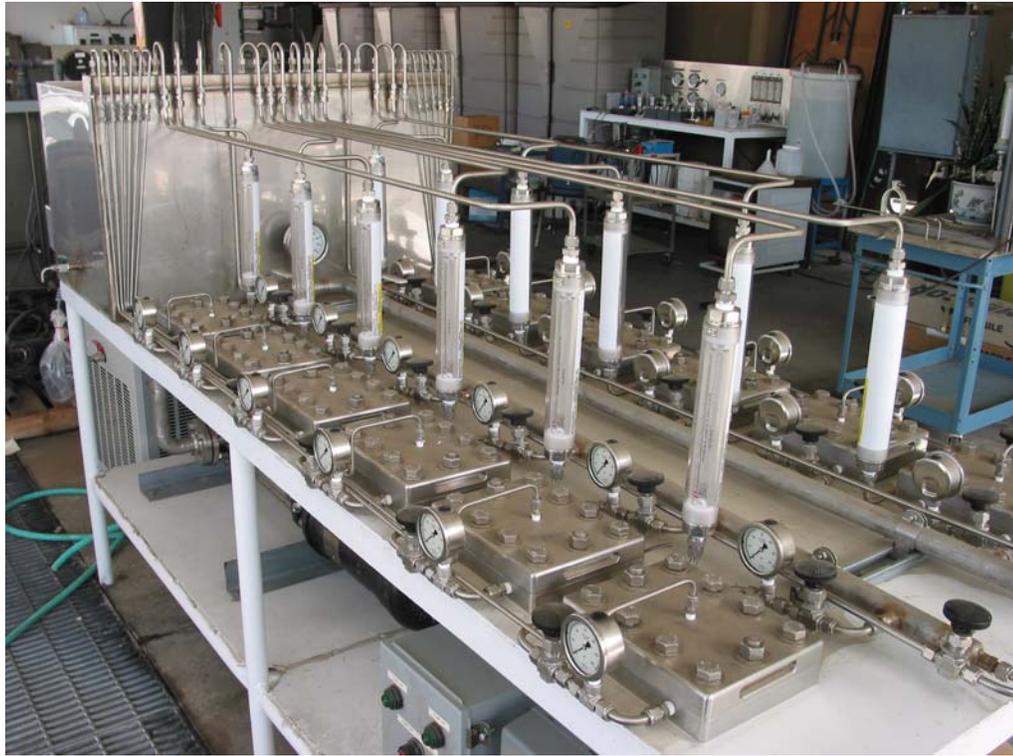
Figure 4. Image of the RO test system equipped with 12 RO test cells (above). Close-up image (below) of the test cell components including the membrane flat sheet (A), feed spacer (B) and the Teflon shim (C).
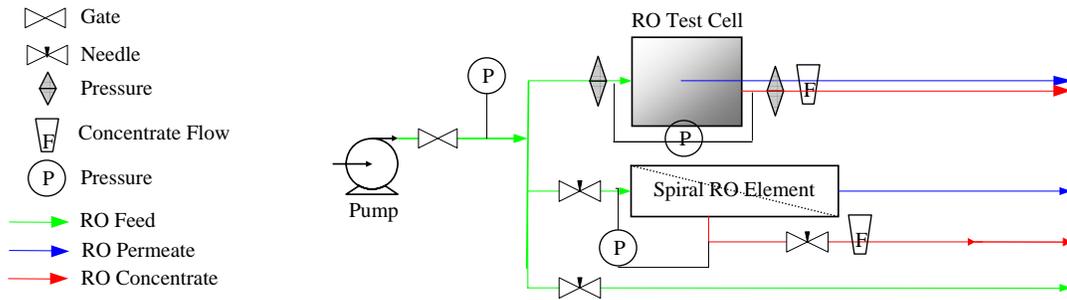
Figure 5. Schematic of the single pass configuration for evaluation of the RO test cell. This test platform was operated using RO feed water from the full-scale treatment facility.
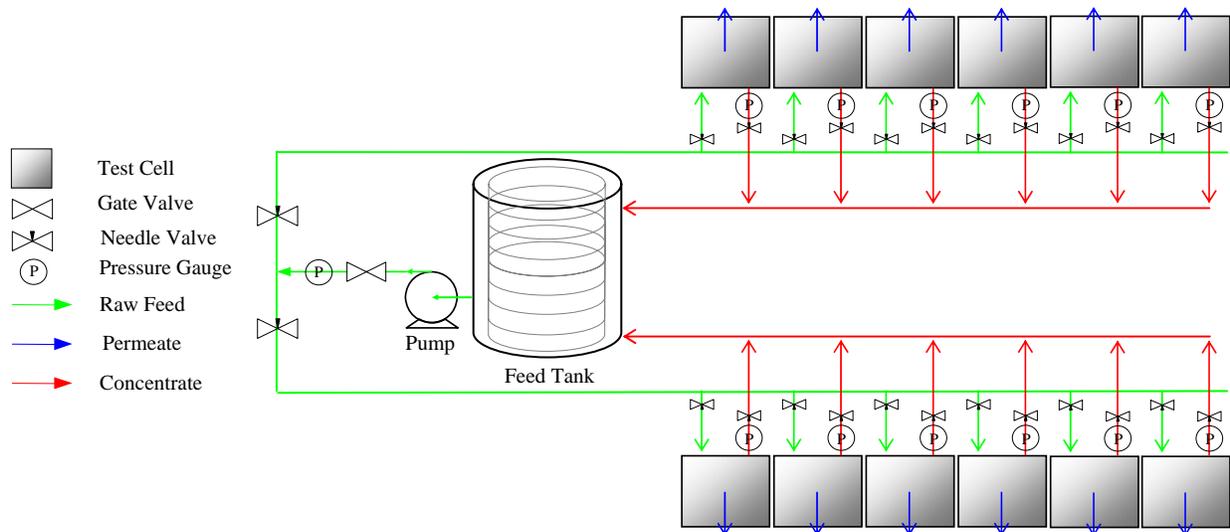
Figure 6. Schematic of the membrane test system designed and constructed by OCWD. The system contains twelve cells that can independently operate under varying conditions of flow and pressure.
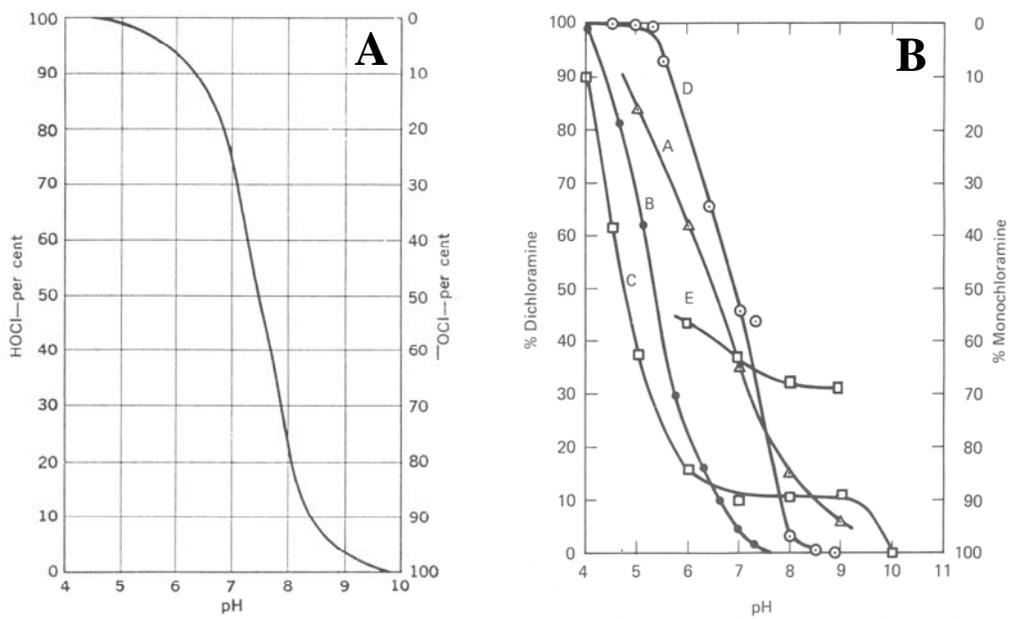
Figure 7. Relationship between HOCl, OCl⁻ and pH (AWWA, 1972) [A] and NH_2Cl, NH_2Cl_2 and pH (Handbook of Chlorination, 1972) [B].

Specific Flux
Spiral vs. Test Cell
(gfd/psi)
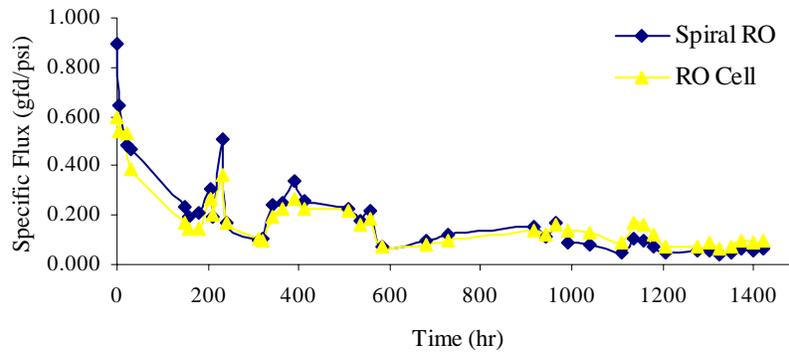
Solute Rejection
Spiral vs. Test Cell
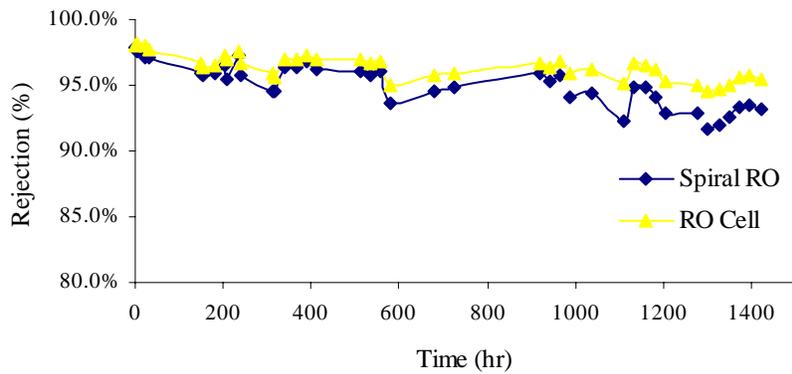
Figure 8. RO test cell validation trial #1, including specific flux (top) and solute rejection (bottom) data for the spiral RO and the RO test cell.

Specific Flux
Spiral vs. Test Cell
(gfd/psi)
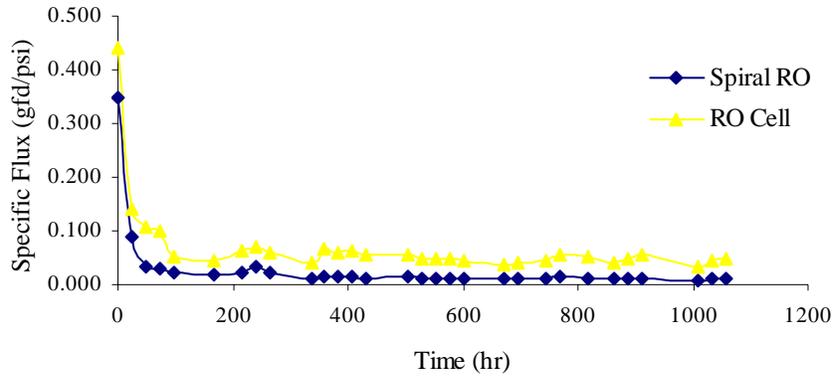
Solute Rejection
Spiral vs. Test Cell
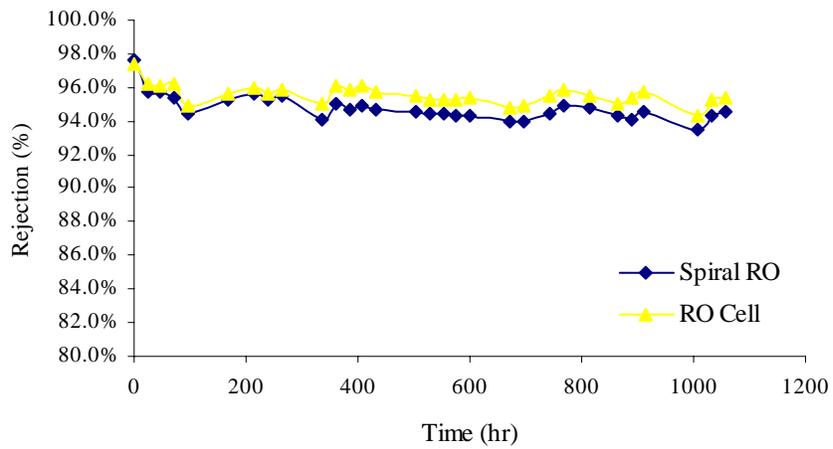
Figure 9. RO test cell validation trial #2, including specific flux (top) and solute rejection (bottom) data for the spiral RO and the RO test cell.
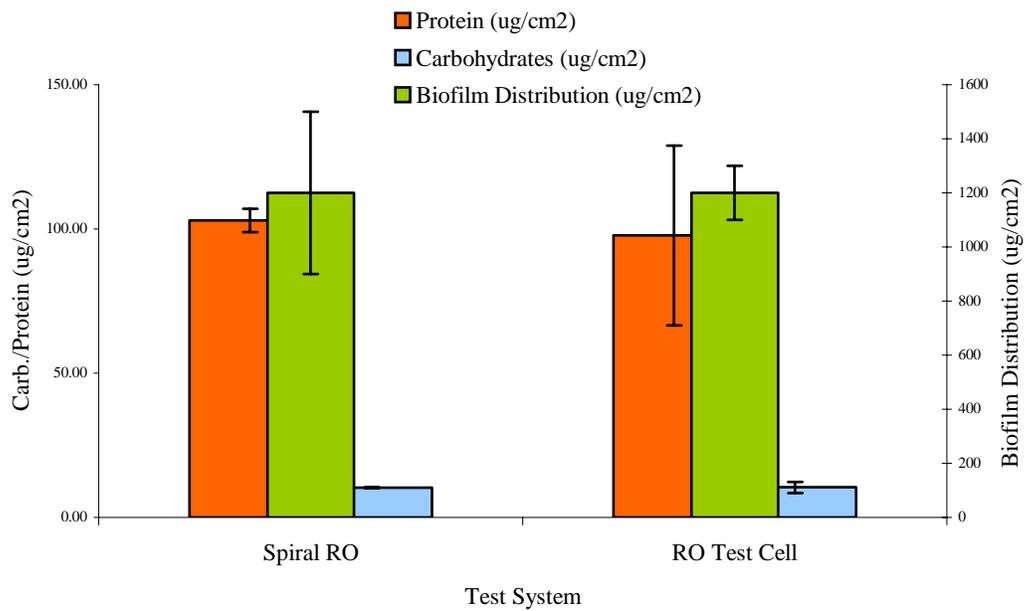
Figure 10. Membrane biofilm analyses including the concentrations of proteins, carbohydrates and total mass of biofilm present on the spiral RO and the membrane operated in the test cell.
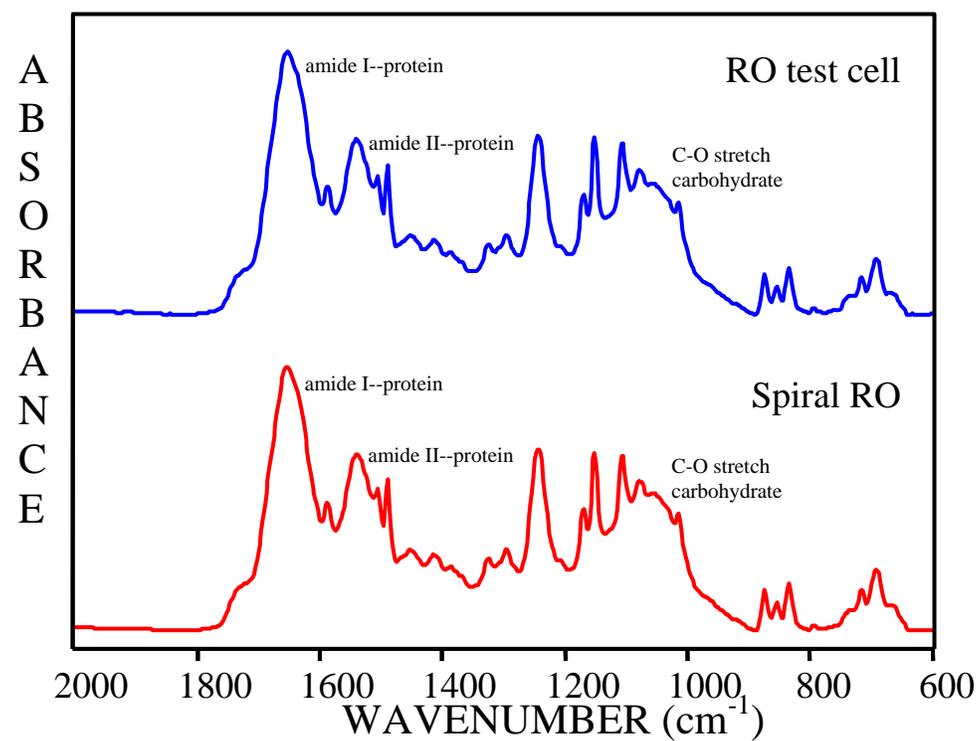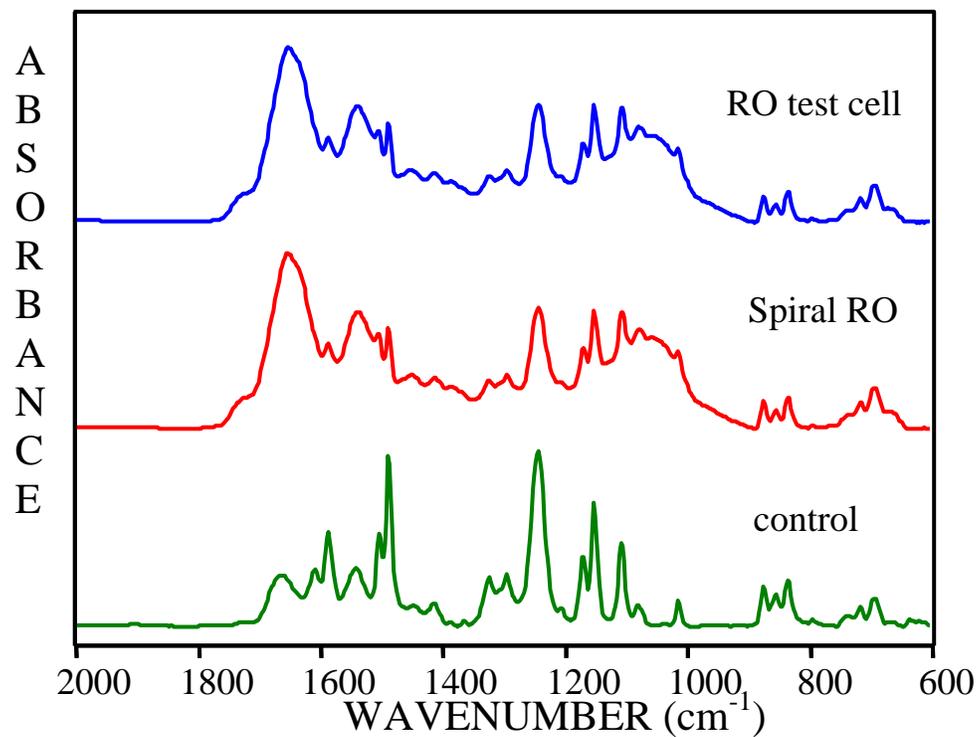
Figure 11. ATR/FTIR spectra of the membrane operated in the test cell (blue) and the spiral RO membrane (red). A non-operated control is illustrated in green. Major protein and carbohydrate bands are common in both membrane spectra.
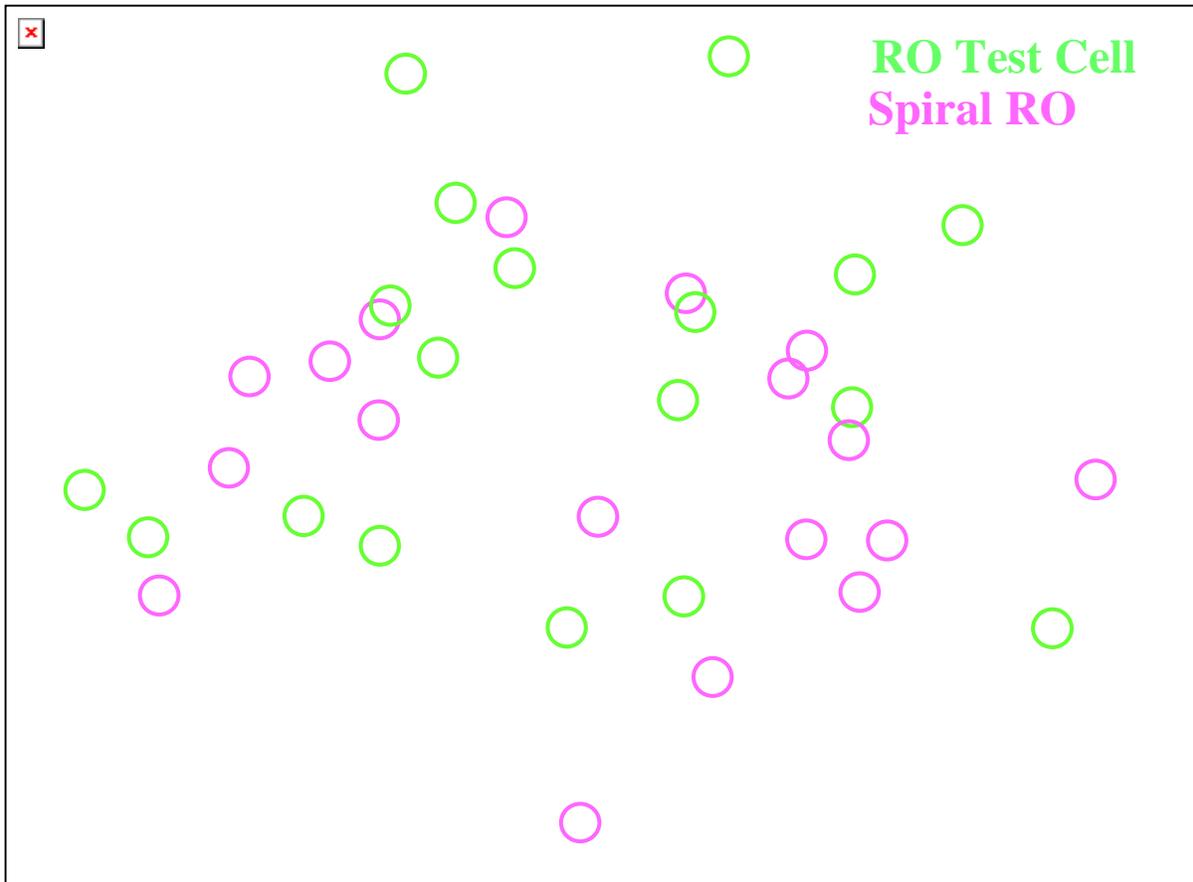
Figure 12. Principal components analyses of ATR/FTIR spectra of RO test cell (green) and the spiral RO (purple).

Membrane Flux
Changes vs. Time

Membrane Solute Rejection
Changes vs. Time
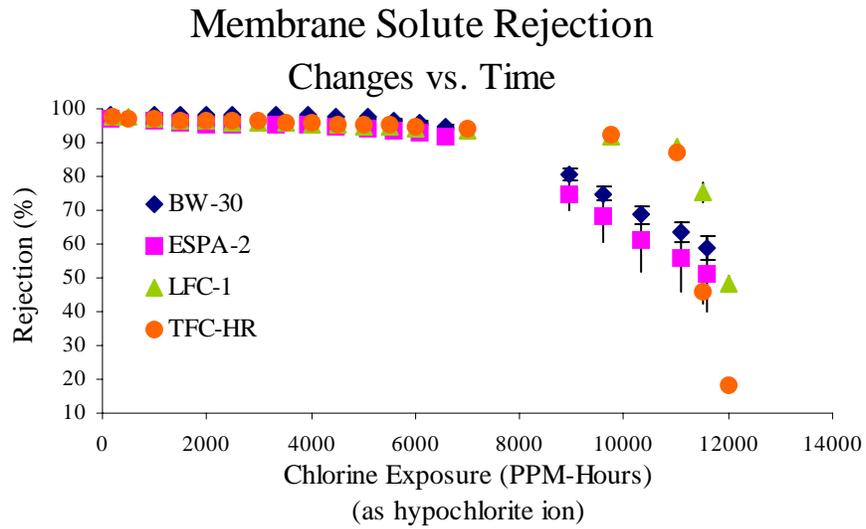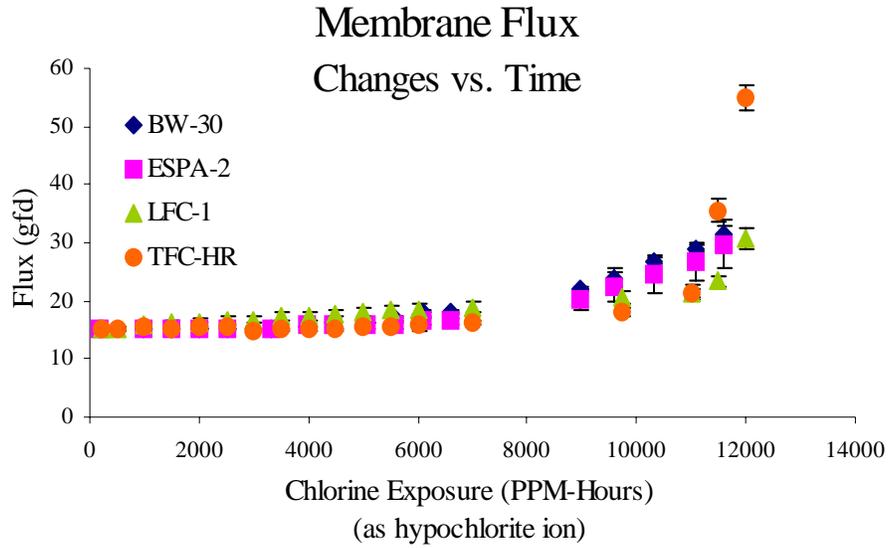
Figure 13. Membrane water flux (J_t) and solute rejection for membranes operated in the presence of free chlorine as hypochlorite ion (OCl⁻). N=3 per membrane type.
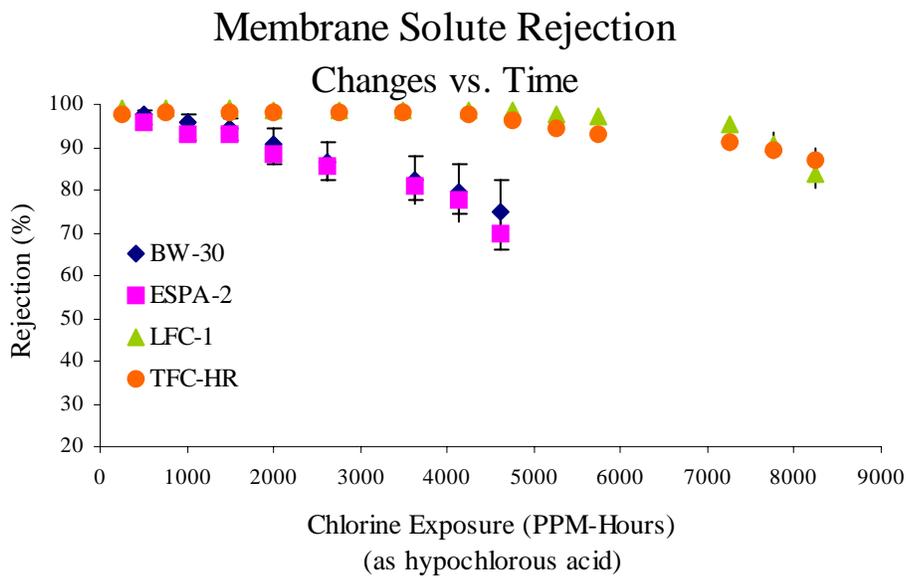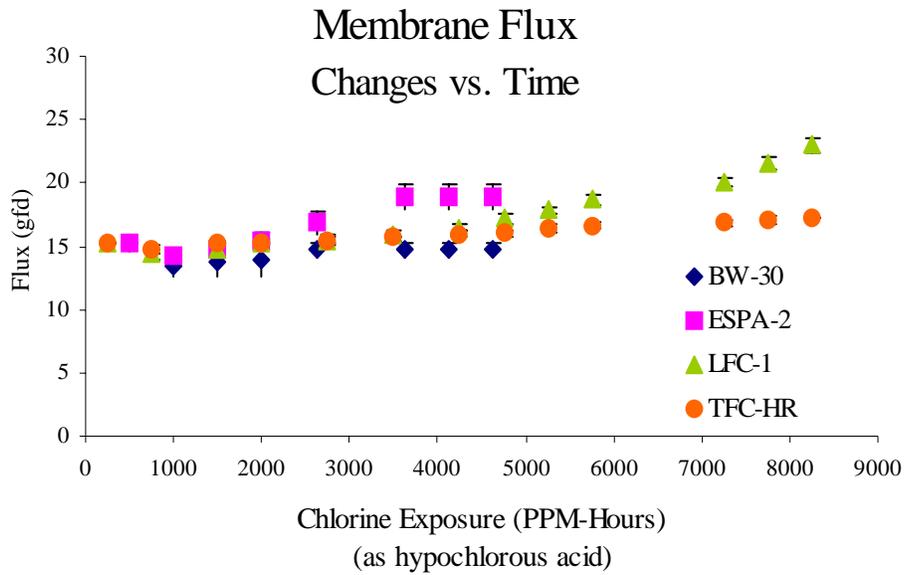
Figure 14. Membrane water flux (J_t) and solute rejection for membranes operated in the presence of free chlorine as hypochlorous acid (HOCl). N=3 per membrane type.
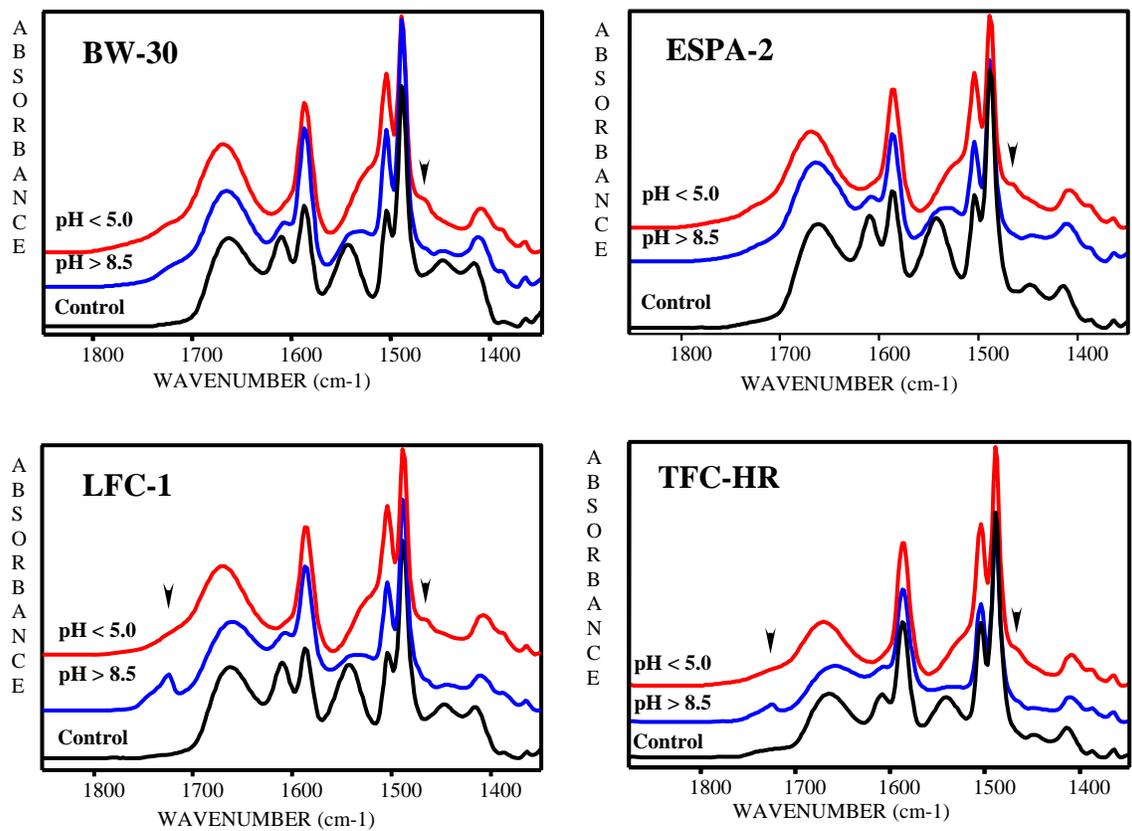
Figure 15. ATR/FTIR spectra of the four membranes operated with different free chlorine species: hypochlorite ion (blue), hypochlorous acid (red) and no chlorine (black).

Membrane Hydrophobicity
(Exposure to Hypochlorite Ion)
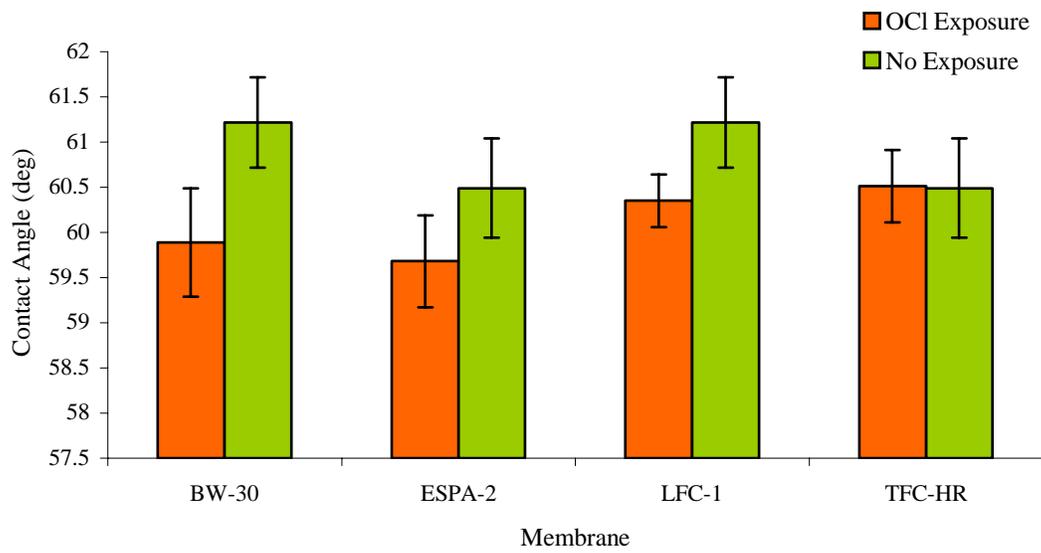
Figure 16. Membrane hydrophobicity data for exposure to (orange), and absent of (green) free chlorine as hypochlorite. N=15 for each membrane type.

Figure 17. Membrane hydrophobicity data for exposure to (orange), and absent of (green) free chlorine as hypochlorous acid. N=15 for each membrane type.
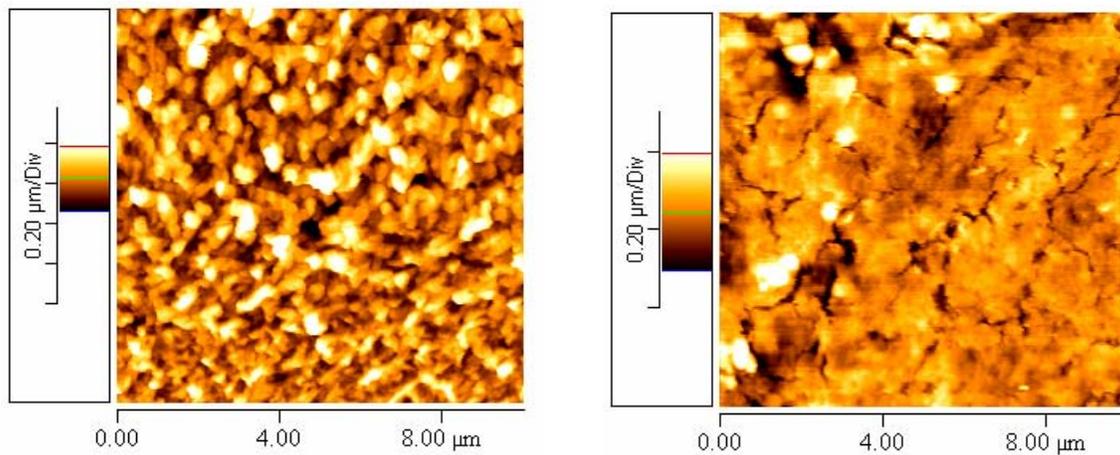
Figure 18. AFM images of the LFC-1 membrane operated in the presence (right) and absence of free chlorine (left).
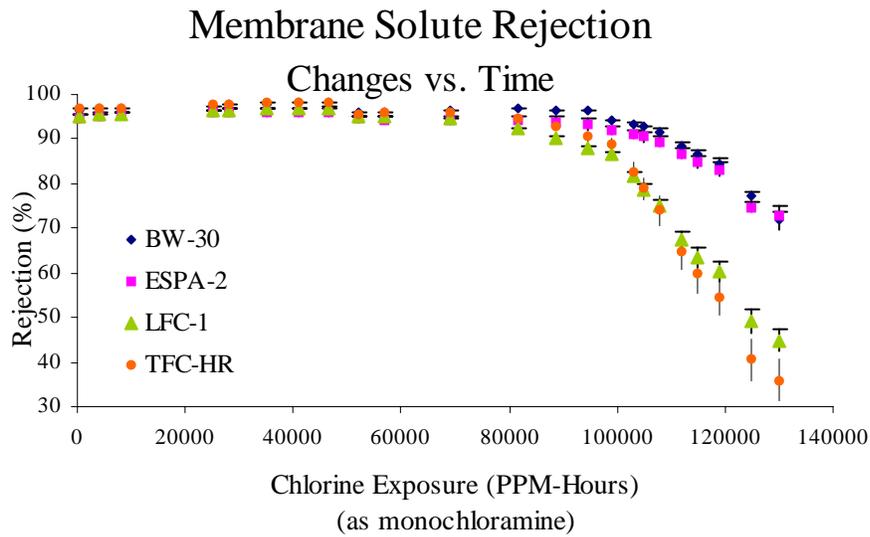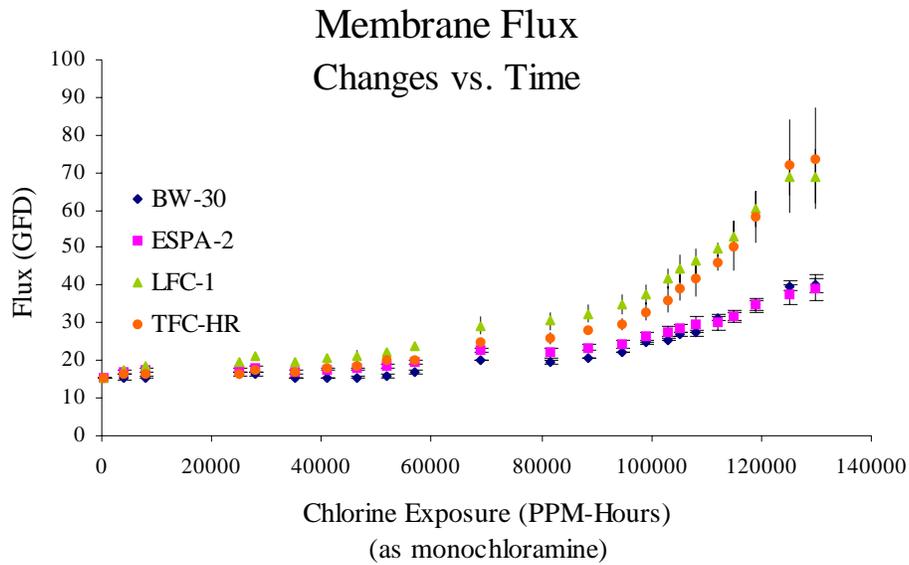
Figure 19. Membrane water flux (J_t) and solute rejection for membranes operated in the presence of combined chlorine (NH_2Cl). N=3 per membrane type.
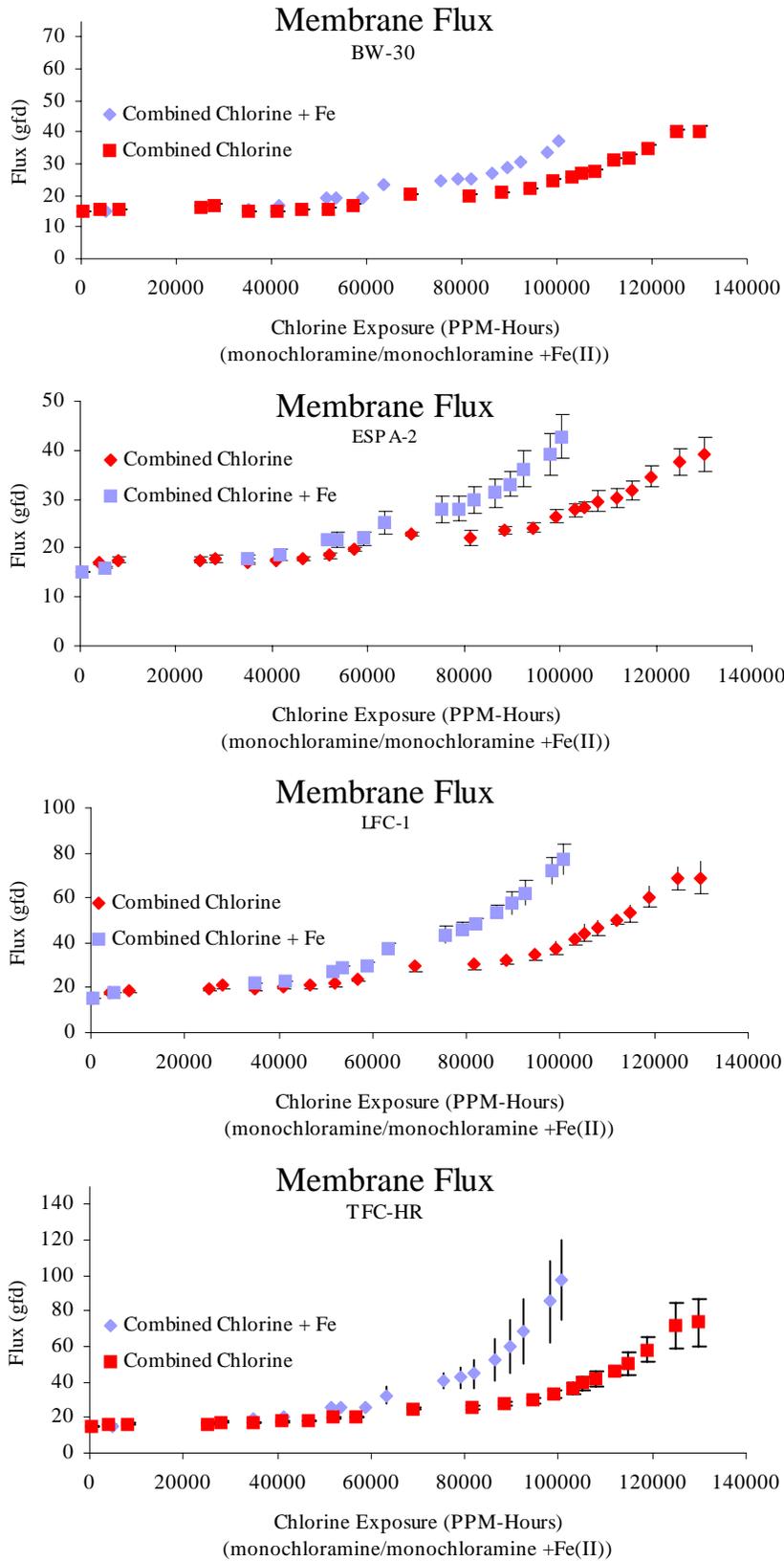
Figure 20. Membrane water flux (J_t) in the presence of combined chlorine (red) and combined chlorine with iron (blue). N=3 per membrane type.
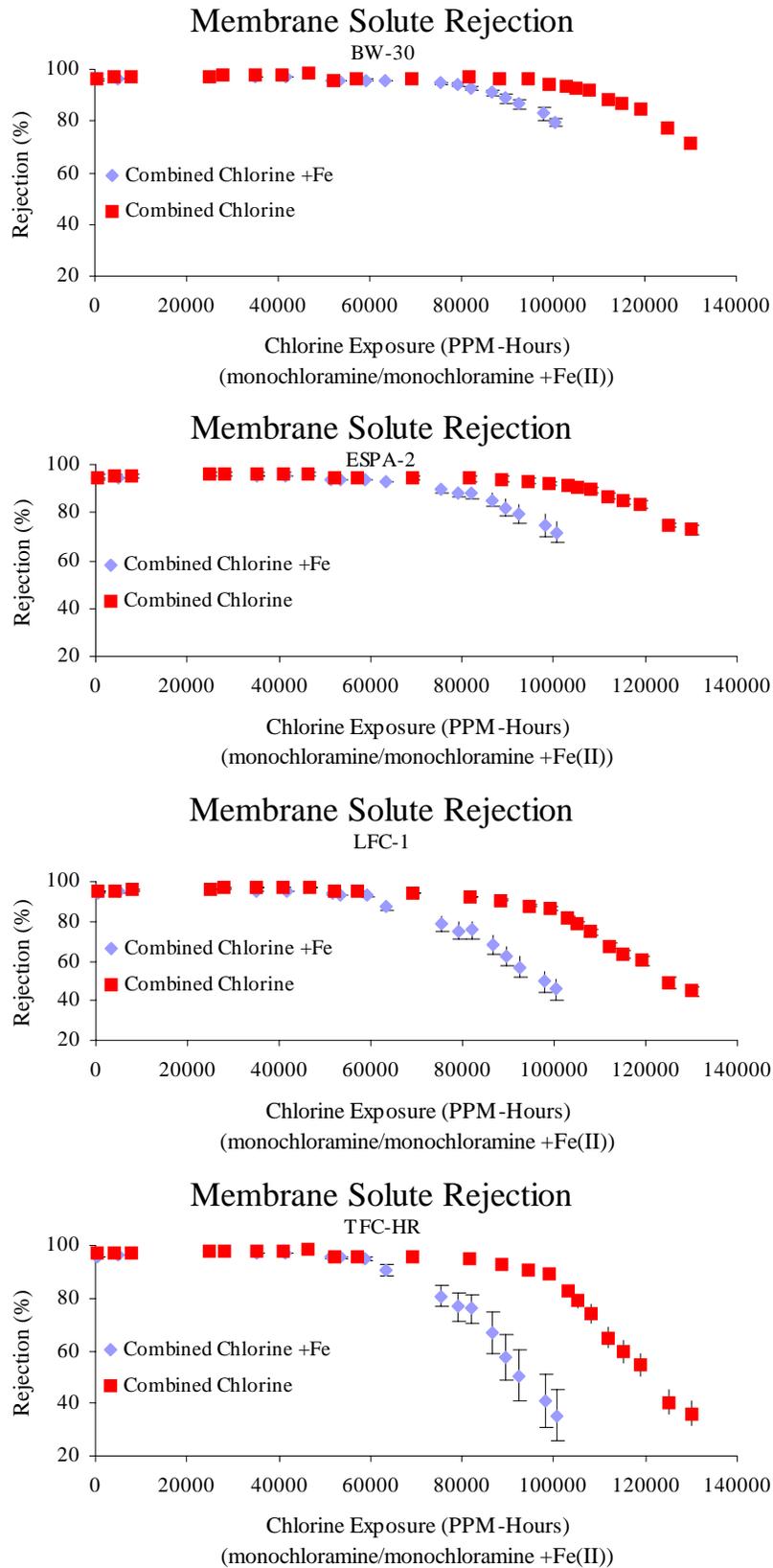
Figure 21. Membrane solute rejection in the presence of combined chlorine (red) and combined chlorine with iron (blue). N=3 per membrane type.
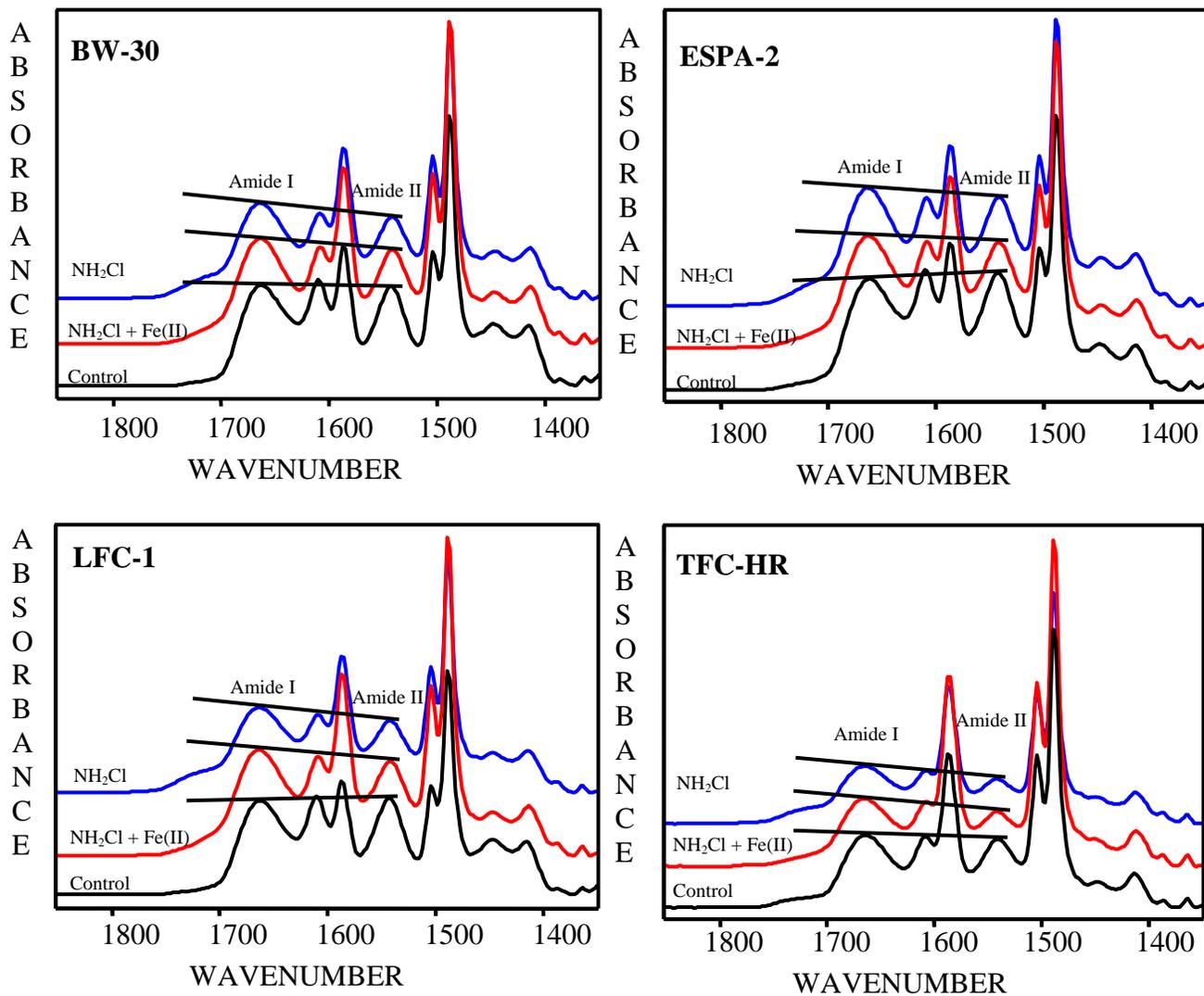
Figure 22. ATR/FTIR spectra of the four membranes operated in the presence of monochloramines (NH$_2$Cl; blue), monochloramines plus iron (red) and no chlorine (black).

Membrane Hydrophobicity
(Exposure to Monochloramines)
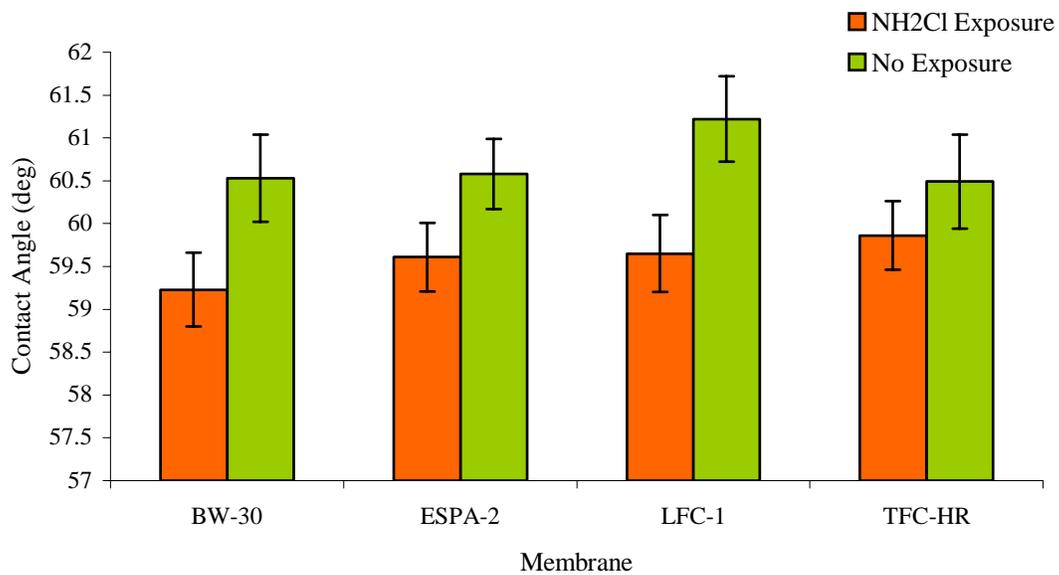
Figure 23. Membrane hydrophobicity data for exposure to (orange), and absent of (green) combined chlorine in the form of monochloramines (NH_2Cl). N=15 for each membrane type.

Membrane Hydrophobicity
(Exposure to Monochloramines+Iron)
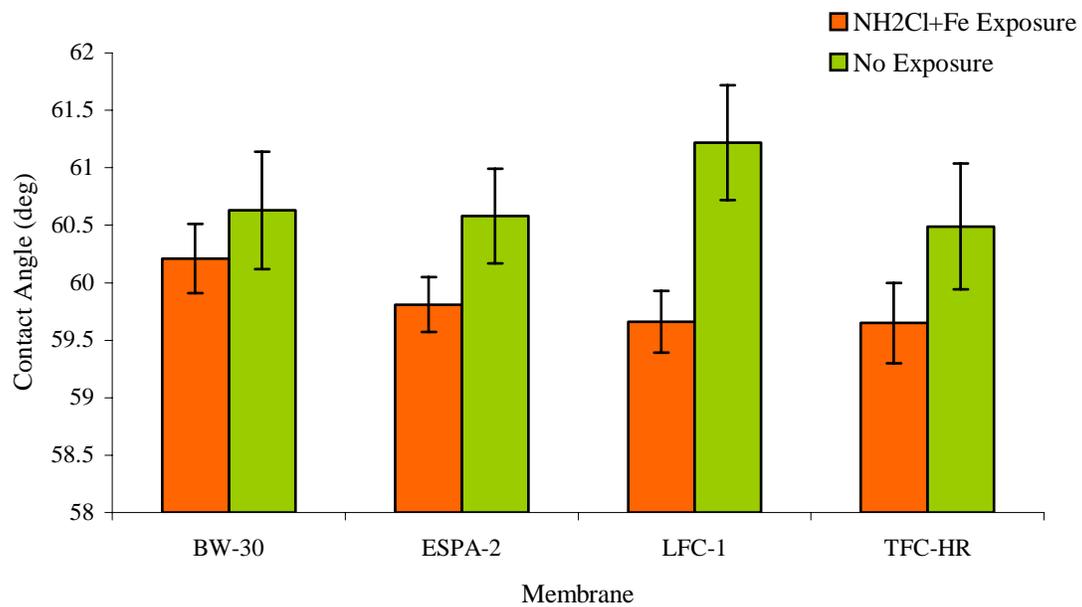
Figure 24. Membrane hydrophobicity data for exposure to (orange), and absent of (green) monochloramines (NH_2Cl) + iron (Fe^{+2}). N=15 for each membrane type.
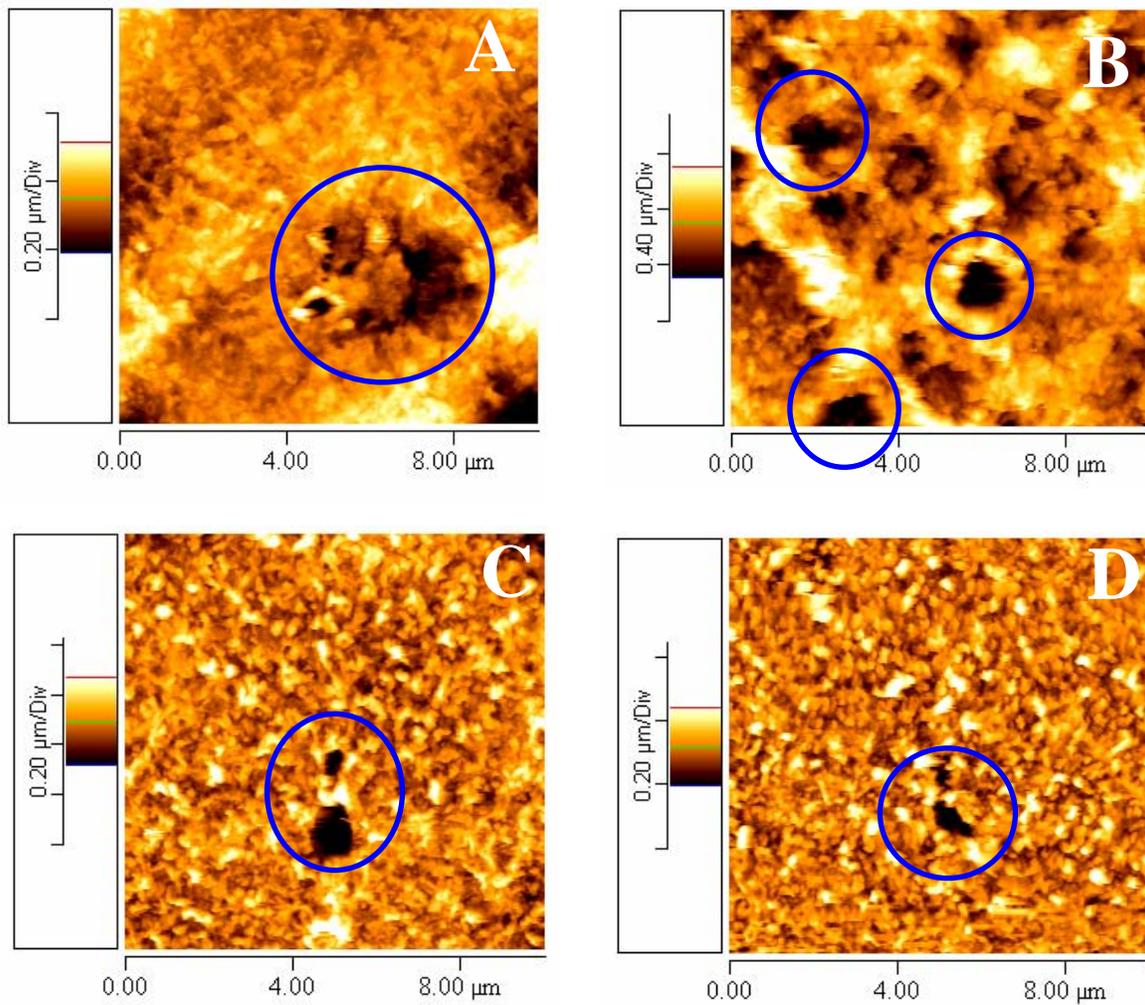
Figure 25. AFM images of the PA membranes operated in the presence of NH$_2$Cl plus iron: (A) BW-30, (B) ESPA-2, (C) LFC-1, (D) TFC-HR. Note the presence of distinct holes (outlined in blue) present in the PA separation layer.
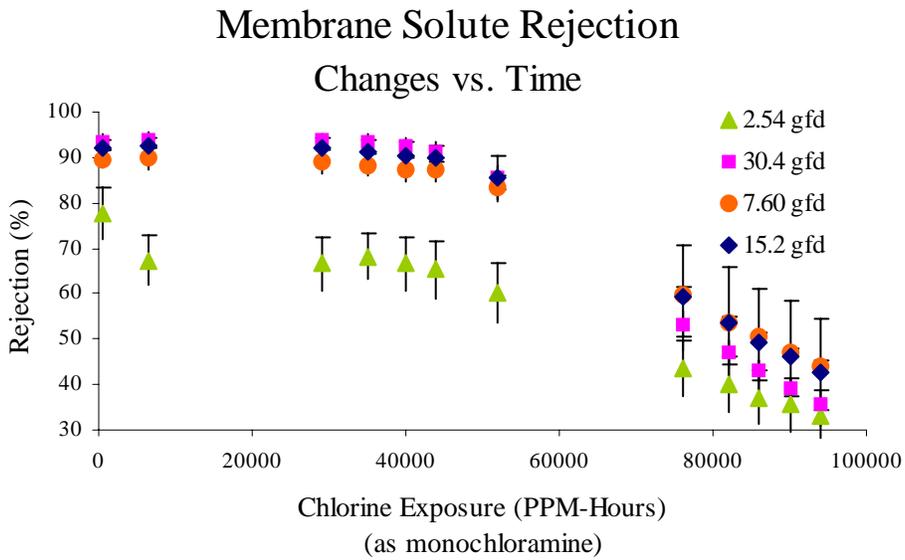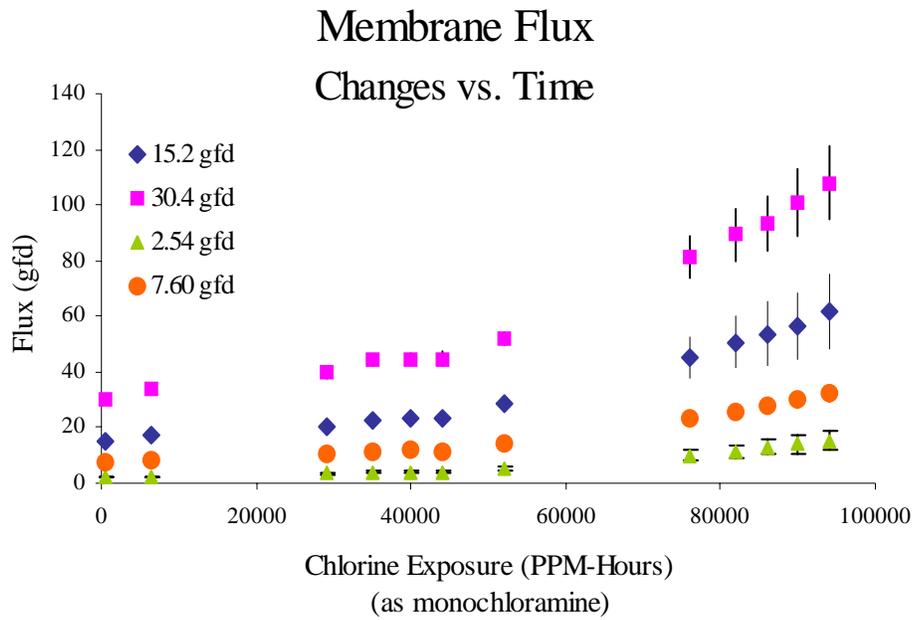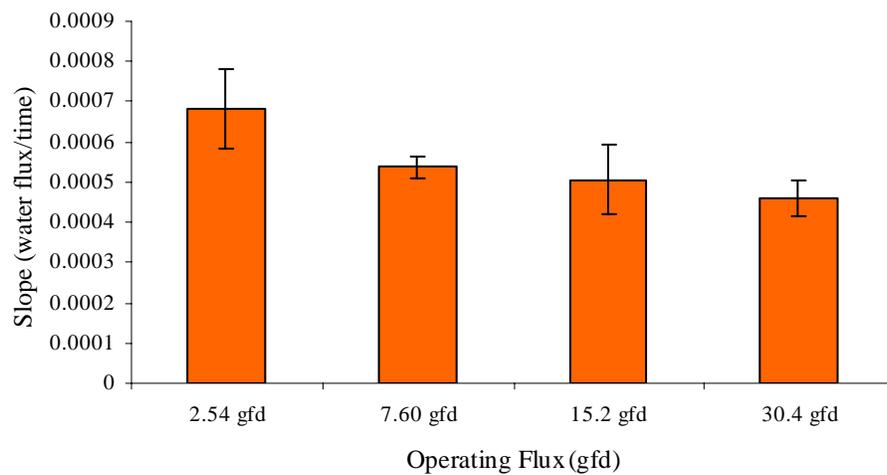
Figure 26. Membrane water flux (J_t) and solute rejection for membranes operated in the presence of combined chlorine (NH_2Cl) at various water flux rates from 2.54gfd to 30.4gfd. N=3 per membrane type.

Water Flux Rate Changes vs. Operating Flux

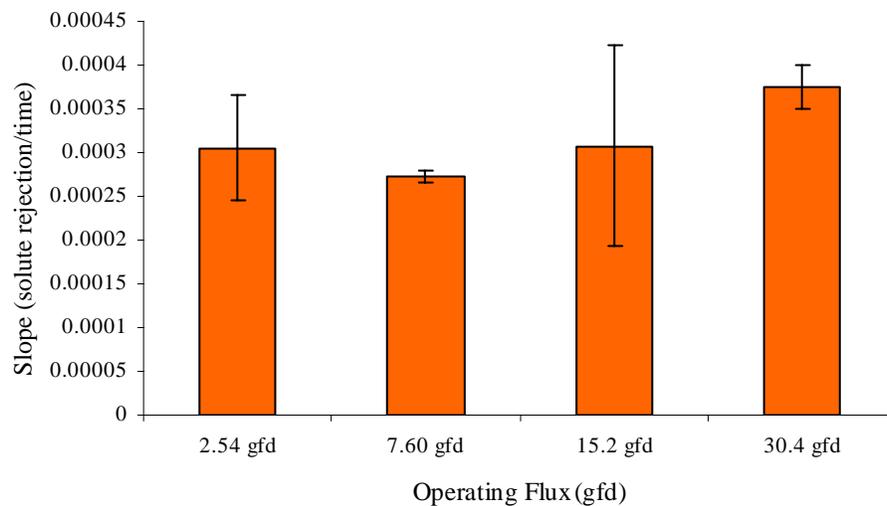**Solute Rejection Rate Changes vs. Operating Flux**

Figure 27. Differences in the rates (slopes) of water flux and solute rejection changes in the presence of monochloramines at four operating water fluxes. N=3 per operating flux.

Table 1. Commercial RO Membranes used in the evaluations.

Membrane	Manufacturer	Type	Material
BW-30	Dow FilmTec, Midland, MI	RO	polyamide
ESPA-2	Hydranautics, Oceanside, CA	RO	polyamide
LFC-1	Hydranautics, Oceanside, CA	RO	polyamide
TFC-HR	KMS, Wilmington, MA	RO	polyamide
AM-MT	Applied Membranes, Vista, CA	RO	polyamide