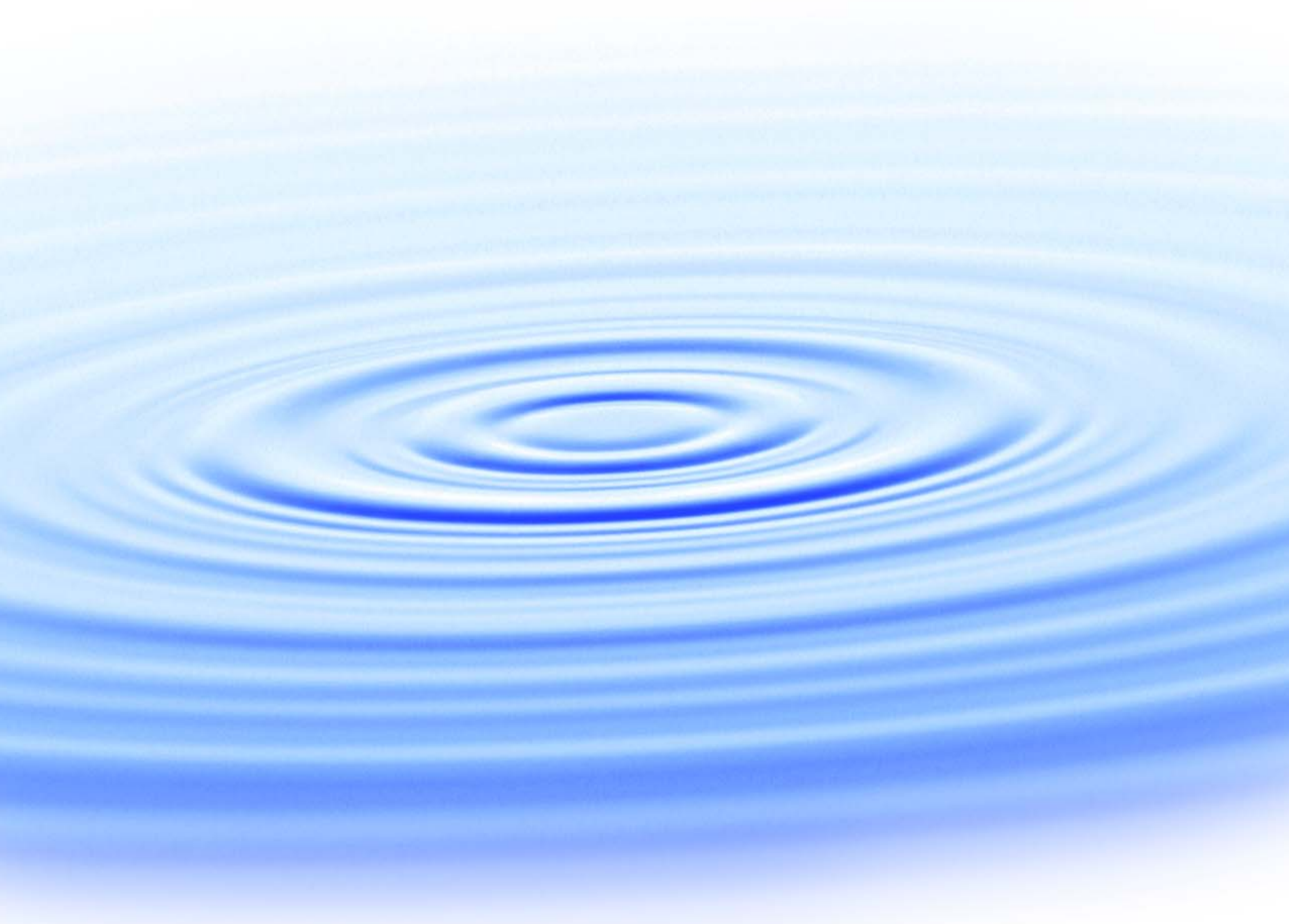
Maximizing Recovery of Recycled Water for Groundwater Recharge Employing an Integrated Membrane System



WateReuse Research Foundation

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About the WateReuse Research Foundation

The mission of the WateReuse Research Foundation is to conduct and promote applied research on the reclamation, recycling, reuse, and desalination of water. The Foundation's research advances the science of water reuse and supports communities across the United States and abroad in their efforts to create new sources of high quality water through reclamation, recycling, reuse, and desalination while protecting public health and the environment.

The Foundation sponsors research on all aspects of water reuse, including emerging chemical contaminants, microbiological agents, treatment technologies, salinity management and desalination, public perception and acceptance, economics, and marketing. The Foundation's research informs the public of the safety of reclaimed water and provides water professionals with the tools and knowledge to meet their commitment of increasing reliability and quality.

The Foundation's funding partners include the Bureau of Reclamation, the California State Water Resources Control Board, the California Energy Commission, and the California Department of Water Resources. Funding is also provided by the Foundation's Subscribers, water and wastewater agencies, and other interested organizations.

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Acronyms

CDPH	California Department of Public Health
CIP	clean-in-place
CSM	Colorado School of Mines
DOC	dissolved organic carbon
EDC	endocrine-disrupting compounds
EDS	energy-dispersive spectroscopy
EDTA	ethylenediaminetetraacetate
EEMs	excitation/emission matrices
EfOM	effluent organic matter
ESEM	environmental scanning electron microscopy
FE	field emission
FESEM/EDS	field emission scanning emission microscopy/EDS
GC/MS	gas chromatography/mass spectrometry
gfd	gallons per square foot per day
gph	gallons per hour
gpm	gallons per minute
kWh/kgal	kilowatt-hours per thousand gallons
IC	ion chromatograph
ICP-AES	inductively coupled plasma atomic emission spectrometry
IMS	integrated membrane system
LBWD	Long Beach Water Department
LBWRP	Long Beach Water Reclamation Plant
LC/MS/MS	liquid chromatography tandem mass spectrometry
LPRO	low-pressure reverse osmosis
LSI	Langelier Saturation Index
LVL	Leo J. Vander Lans Water Treatment Facility
MF	microfiltration
mg/L	milligrams per liter
mg-N/L	milligrams nitrogen per liter
MW	molecular weight
MWCO	molecular weight cutoff
MWD	Metropolitan Water District of Southern California
NF	nanofiltration
NDP	net driving pressure
ng/L	nanograms per liter
NOM	natural organic matter

PAC	Project Advisory Committee
PFBBr	pentafluorobenzyl bromide
PhACs	pharmaceutically active compounds
psig	pounds per square inch gauge
RAC	Research Advisory Committee
RO	reverse osmosis
SCADA	supervisory control and data acquisition
SCE	Southern California Edison
SEC	size exclusion chromatography
SFLUOR	specific fluorescence
SPE	solid phase extraction
SD	standard deviation
TCSF	temperature-corrected specific flux
TOC	total organic carbon
TN	total nitrogen
TT	Trusssell Technologies, Inc.
µs/cm	microsiemens per centimeter
VFD	variable-frequency drive
WBMWD	West Basin Municipal Water Districts
WRD	Water Replenishment District of Southern California

Foreword

The WateReuse Research Foundation, a nonprofit corporation, sponsors research that advances the science of water reclamation, recycling, reuse, and desalination. The Foundation funds projects that meet the water reuse and desalination research needs of water and wastewater agencies and the public. The goal of the Foundation's research is to ensure that water reuse and desalination projects provide high-quality water, protect the public health, and improve the environment.

An Operating Plan guides the Foundation's research program. Under the plan, a research agenda of high-priority topics is maintained. The agenda is developed in cooperation with the water reuse and desalination communities, including water professionals, academics, and Foundation subscribers. The Foundation's research focuses on a broad range of water reuse and desalination research topics, including

- Defining and addressing emerging contaminants
- Public perceptions of the benefits and risks of water reuse
- Management practices related to potable reuse
- Groundwater recharge and aquifer storage and recovery
- Evaluation and methods for managing salinity and desalination
- Economics and marketing of water reuse

The Operating Plan outlines the role of the Foundation's Research Advisory Committee (RAC), Project Advisory Committees (PACs), and Foundation staff. The RAC sets priorities, recommends projects for funding, and provides advice and recommendations on the Foundation's research agenda and other related efforts. A PAC is convened for each project and provides technical review and oversight. The Foundation's RAC and PACs consist of experts in their fields and provide the Foundation with independent review, which ensures the credibility of the Foundation's research results. The Foundation's project managers facilitate the efforts of the RAC and PACs and provide overall management of projects.

The Foundation's primary funding partners include the Bureau of Reclamation, the California State Water Resources Control Board, the California Energy Commission, Foundation Subscribers, water and wastewater agencies, and other interested organizations. The Foundation leverages its financial and intellectual capital through these partnerships and other funding relationships.

The Water Replenishment District of Southern California (WRD) uses recycled water for injection into three seawater intrusion barriers. The objectives of this tailored collaborative research are (a) to determine whether the Leo J. Vander Lans Water Treatment Facility's (LVL) integrated membrane system (IMS) can be operated at higher recovery and permeate flux without compromising product water quality, and (b) to investigate the opportunity for the treatment of primary reverse osmosis concentrate to further increase recovery of product water.

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This study would not have been possible without the insights, efforts, and dedication of many individuals and organizations. These include the members of the research team and PAC members; the WateReuse Research Foundation's project manager, Caroline Sherony; many key individuals at the participating utilities and related organizations; and support from the Long Beach Water Department (Robert Cheng and Gary Glasser).

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Executive Summary

The core mission of the Water Replenishment District of Southern California (WRD) is to replace the groundwater that is pumped out of wells by the 43 cities in the Central and West Coast Basins using storm, imported, and recycled waters. To ensure a safe supply of groundwater, the WRD also continually checks, tests, and monitors replenishment water and groundwater quality for compliance with applicable water standards.

The WRD uses recycled water for injection into three seawater intrusion barriers in the Central and West Coast Basins in the District. Currently, the Leo J. Vander Lans Water Treatment Facility (LVL) is the only seawater barrier production facility owned by the WRD, and the recycled water produced by the LVL represents the lowest unit cost of replenishment water for the WRD. Because of increasing water costs for injection at the barriers, the WRD is constantly looking for ways to minimize costs, such as reduction of pumping near the barriers, increasing recycled water to offset imported water, or banking water at lower seasonal rates. An increase in the recovery of product water at the LVL would therefore represent a significant part of the District's long-term plan to maximize beneficial reuse of recycled water.

The objectives of this Tailored Collaborative research are (a) to determine whether the LVL's integrated membrane system (IMS) can be operated at a higher recovery (>85%) and permeate flux without compromising product water quality, and (b) to investigate an opportunity for the treatment of primary reverse osmosis concentrate to further increase the recovery of product water. The study was conducted using bench- and pilot-scale facilities at the Colorado School of Mines (CSM) and the full-scale LVL operated under contract by the Long Beach Water Department (LBWD) for the WRD.

A literature survey was first conducted to identify previous experiences in operating IMS at an elevated flux and recovery and to explore foulants that can result in flux decline. The assembled literature review provided the guiding principles for the selection and optimization of recovery enhancement challenges at the LVL.

To test the fouling propensities of different membranes, bench-scale testing was also conducted on five promising nanofiltration (NF) membranes and one low-pressure reverse osmosis (LPRO) membrane, including ESPA2 (Hydranautics), NF-90, NF-270 (Dow/Filmtec), NF-4040 (Dow/Filmtec), TFC-S (Koch), and TFC-SR3 (Koch). These membranes were preselected because of their high flux at low pressure and their low fouling propensity. Two membranes were ultimately selected for piloting. The ESPA2 membrane served as the baseline membrane, as it is currently employed at the LVL, as well as other facilities utilizing integrated membrane systems for groundwater recharge. The other membrane selected was NF-270.

Pilot Testing

Pilot Testing of ESPA2 Membranes

A pilot skid loaded with ESPA2 membranes was operated for 100 h at a set point representing the current operational conditions of the full-scale train. Subsequently, the set point was altered to a higher flux at the same recovery, and the skid was operated for an additional 550 h. At the end of this test period, a clean-in-place (CIP) of the pilot skid was conducted. The ESPA2 was then operated for a total of approximately 2,200 h. During this time the performance of this membrane was evaluated at system recoveries of 83% (12 gallons per square foot per day (gfd) permeate flux), 85% (15 gfd), and 87% (15 gfd).

A membrane autopsy was performed on an ESPA2 membrane taken from the second stage of the pilot-scale testing unit after the second-stage permeate flow rate had decreased significantly.

Pilot Testing of NF-270 Membranes

The pilot skid was then loaded with NF-270 membranes, and the skid was operated for approximately 500 h at a permeate flux of 15 gfd and a recovery of 85%. Subsequently, the set point was altered to an 87% recovery, and the skid was operated for an additional 800 h.

Pilot Testing of RO Concentrate Using ESPA2

Treatment of primary RO concentrate with ESPA2 was conducted at 7 gfd and 50% recovery. An analysis was then performed to determine any operational issues associated with treating the concentrate using the ESPA2 membrane and the expected water quality. This analysis was performed using Hydranautics RO Projection Software.

Pilot Testing Results

Pilot Testing of ESPA2 Membranes

At a 15 gfd permeate flux and 85% recovery, ESPA2 remained relatively stable during the 500 h of pilot testing. At the same permeate flux, but 87% recovery, ESPA2 lost approximately 1.5% of permeability per day. Lower rejection values were observed during additional elevated flux and recovery experiments.

Pilot Testing of NF-270 Membranes

The NF-270 membrane exhibited minimal flux decline when operated at 15 gfd and 85% recovery. It maintained a specific flux two to three times higher than the existing ESPA 2 membrane. At 87% recovery and 15 gfd, the NF-270 membrane-specific flux decreased by approximately 0.5% per day, presumably because of scaling. The decline is significantly less than that observed for the ESPA2 membrane. NF-270 membrane provided no rejection of nitrate, however.

Pilot Testing of RO Concentrate Using ESPA2

The temperature-corrected specific flux (TCSF) decreased 20% from 0.075 to 0.060 gfd/psi over the operating period of 600 h. The net driving pressure (NDP) increase is attributed to inorganic scaling, primarily calcium carbonate. Moreover, to sustain a stable permeate flux of 7 gfd would require an increase in acid feed. Approximately 0.4 gallons per hour (gph) of sulfuric acid was dosed to maintain the operating pH at 6.3 during the study.

Economic Analysis

An economic analysis was performed to compare the costs of implementing eight potential alternatives at full scale. These include the following: (1) primary RO with 85% recovery and 9.9 gfd flux; (2) primary RO with 83% recovery and 12 gfd flux; (3) primary RO with 85% recovery and 15 gfd flux; (4) primary RO with 87% recovery and 15 gfd flux; (5) primary NF with 85% recovery and 15 gfd flux; (6) primary NF with 87% recovery and 15 gfd flux; (7) secondary RO with 50% recovery and 9.4 gfd flux, and (8) secondary NF with 50% recovery and 9.4 gfd flux. The following is a summary of findings based on the analysis.

1. The secondary membrane system (third-stage membrane train) has the highest dollar per acre-foot cost, but this estimate did not factor into the discharge cost. If there were a limited sewer capacity, the secondary membrane system option would provide an alternative for increasing recovery, thereby minimizing the concentrate discharge flow.

2. At 87% recovery, both RO and NF (primary RO-4 and primary NF-1) required acid injection for pH adjustment. Based on the acid dose required to maintain low pH in the feed water, the annual chemical cost was significantly higher than other operational conditions because of lower recovery and higher CIP frequency.

3. Based on the operational conditions tested, primary NF required lower power and chemical costs as a result of lower feed pressure and less frequent CIPs.

4. Additional, long-term tests may be needed to better define CIP frequency with and without the acid injection for pH adjustment, as the acid cost tends to outweigh the benefit of less frequent CIPs.

5. Without the sewer discharge limitations, primary NF alternatives tend to be the most cost-effective options among the configurations tested, given that the nitrate level is declining and that the total organic carbon (TOC) level is stable.

Conclusion and Recommendations

- NF-270 could enhance the production at the LVL, but with the current influent water characteristics, the finished water quality could meet the TOC but not the nitrate limit set by the California Department of Public Health (CDPH) for groundwater recharge.

- With no additional capacity allowed for discharge of plant waste at the LVL, an alternative to the treatment of RO concentrate that would increase the recovery of product water is recommended.

- The treatment of primary RO brine with ESPA 2 membrane at 7 gfd and 50% recovery could increase the overall plant recovery to over 92%. Acid feed to adjust the pH of the RO concentrate to 6.3 is required to mitigate the scaling tendency of the concentrate.

Chapter 1

Introduction

1.1 Background

The Water Replenishment District of Southern California (WRD) has instituted numerous projects and programs over the years in a continuing effort to effectively manage groundwater replenishment and groundwater quality in the Central and West Coast Basins. One of its goals is to meet its statutory responsibilities listed in the California Water Code, Sections 60220 through 60226, which stipulate that these projects and programs focus on activities that enhance the replenishment program, increase the reliability of the groundwater resources, improve and protect groundwater quality, and ensure that the groundwater supplies are suitable for beneficial use.

One of the key groundwater resources for the WRD is recycled water (reclaimed municipal wastewater.) The recycled water has primarily been used to replenish the groundwater basins by surface spreading and injection at seawater intrusion barriers. In view of the potential for drought conditions to strike California and uncertainty in the future availability of imported supplies, recycled water has become increasingly vital and essential as a replenishment source.

The WRD currently uses recycled water for injection into three seawater intrusion barriers in the Central and West Coast Basins in the District. It purchases water from the West Basin Municipal Water Districts' (WBMWD) West Basin Recycling Plant for injection at the West Coast Basin Barrier and from the city of Los Angeles's Terminal Island Treatment Plant for injection at the Dominguez Gap Barrier. Recycled water for the Alamitos Gap Barrier is supplied from the WRD's own Leo J. Vander Lans Water Treatment Facility (LVL), which provides the lowest unit cost of replenishment water for the WRD.

1.2 Overview

Because of the increasing costs of water for the barriers, the WRD is constantly evaluating alternatives to minimize costs, such as the reduction of pumping near the barriers, increased recycled water to offset imported water, or banking water at lower seasonal rates. One of the alternatives that the WRD is interested in is increasing the recovery at the LVL to produce more recycled water.

In a recent study funded by the Water Research Foundation and the WateReuse Research Foundation, a number of nanofiltration (NF) membranes were evaluated and tested for water recycling applications to replace conventional reverse-osmosis (RO) membranes while achieving similar product water qualities at lower operating pressures (Drewes et al., 2008). The findings of the study revealed that significant cost savings associated with lower feed pressure are limited to low-fouling, loose NF membranes. There is a potential for gaining additional benefits from NF membranes by operating at a higher permeate flux and higher overall system recoveries, given the high permeability of many NF membranes.

A significant operational issue associated with the implementation of the NF membrane technology for the reclamation of municipal wastewater is membrane fouling and subsequent flux decline (AWWA, 2005; Speth et al., 2000; Vrouwenvelder and van der Kooij, 2002; Wilf and Alt, 2000).

Besides the potential fouling and flux decline issues, previous research has demonstrated that although NF and LPRO membranes can achieve a high removal of total organic carbon (TOC), the rejection of inorganic monovalent ions such as ammonia and nitrate can be low, depending on the membrane (Bellona and Drewes, 2007; Lee and Lupetow, 2001; Van der Bruggen et al., 2001). Furthermore, incomplete rejection of various endocrine disrupters (synthetic and natural hormones), pharmaceutically active compounds (PhACs), disinfection by-products, and other organic compounds by RO, LPRO, and NF membranes has been reported by similar studies (Kimura et al., 2003; Kimura et al., 2004; Ng and Elimelech, 2004; Nghiem et al., 2004; Schäfer et al., 2003).

Most of these previous studies, however, have only been performed on bench-scale testing, using flat-sheet membrane units or dead-end filtration cells. Furthermore, these studies utilized deionized water spiked with target solutes, as well as virgin membrane specimens, neglecting water matrix effects and membrane property changes because of the fouling commonly observed in full-scale membrane applications.

To properly evaluate the rejection performance of NF and LPRO membranes representative of full-scale conditions, a more thorough investigation of rejection and recovery using pilot-scale is required.

1.3 Project Objectives

The main objective of the proposed study is to determine whether a multistage, high-pressure membrane process, such as the one used at the LVL, can be operated at higher recovery and permeate flux, resulting in lower overall operating costs, without compromising product water quality. For this specific water reuse application, it is hypothesized that new-generation NF and LPRO membranes could be operated at higher recovery and lower operating costs, while maintaining a product quality comparable to conventional RO membranes.

This study provides data on NF membrane treatment of recycled water, which are critical for acceptance by the regulatory authorities. If validated, it is expected that this mode of operation will allow savings in operations for utilities seeking to treat recycled water without stringent TDS removal requirements. It could also offer a proven, cost-effective option to existing facilities that use two-stage RO.

1.4 Project Approach

In order to further investigate the benefits of NF membrane treatment of recycled water based on the results of the previous studies, the focus of this study was to answer two questions:

- Which NF or LPRO membranes would be most suitable for replacing the RO membranes for the WRD's LVL operation?
- Would operation at the LVL and other recycling facilities, using the common low-pressure RO membrane ESPA 2 and the selected NF membrane at elevated fluxes and recoveries, be feasible?

The approach used in this report combines bench-top analysis of preselected NF and LPRO membranes and pilot-scale testing of the best membrane, which was selected based on the bench-top analysis.

Chapter 2

Literature Review

A brief literature review was conducted for the study to assess applications of the different types (i.e., high-pressure and low-pressure) of membranes. The following summarizes the findings from the literature review.

2.1 Current Applications

High-pressure membrane processes, such as RO and NF membranes, are becoming increasingly widespread in water treatment, industrial processes, and wastewater reclamation/reuse applications where high product water recovery is desired. (Bartels et al., 2004).

For groundwater injection projects in the United States that use reclaimed water, treatment using an integrated membrane system (IMS), such as microfiltration (MF) pretreatment followed by RO, is the industry standard (National Research Council, 2004). Facilities currently employing RO for water reclamation include the West Basin Water Recycling Facility (El Segundo, CA), Scottsdale Water Campus (Scottsdale, AZ), Leo J. Vander Lans Plant (Los Alamitos, CA), Terminal Island Treatment Plant (Long Beach, CA), Groundwater Replenishment System (Orange County, CA), and several installations in Singapore (NEWater) and Australia.

Although this IMS approach to reclaiming wastewater for groundwater recharge is becoming more widespread, numerous challenges exist, including selecting appropriate operating conditions, fouling and scaling, energy requirements, and the removal of organic contaminants of concern.

2.2 High-Pressure Membranes

Differences between thin film composite RO membranes, low-pressure RO membranes (LPRO), and NF membranes are subtle and often debatable. The nomenclature used to describe a particular membrane is often based on the application for which the membrane was designed. Membranes designed for applications in which monovalent, salt-free permeate is desired (i.e., seawater desalination and brackish water treatment) are most often termed seawater RO elements, brackish water RO elements, and/or low-pressure brackish water elements. These membranes hinder the diffusive transport of solutes through the membrane, are capable of rejecting >99% of monovalent salts, and will be termed RO membranes for this study (Zhao and Taylor, 2004; Zhao et al., 2005).

Low-pressure (<200 psi) RO membranes designed for high monovalent salt removal (>98%) and low-molecular-weight (MW) organic removal (<100 Dalton) are loosely termed LPRO membranes. Although it is debatable whether LPRO membranes have discrete pores or operate solely through diffusive transport limitations, it has been shown that solute removal involves a combination of steric and electric exclusion and is likely a combination of both diffusive and convective limitations (Košutić and Kunst, 2002; Ozaki and Li, 2002; Tsuru et al., 1991).

NF membranes span a wide range of properties and are indistinguishable from ULPRO membranes if they reject monovalent salts well, and indistinguishable from certain ultrafiltration (UF) membranes if they moderately reject low-MW organics (<300 Da) and divalent cations. Generally, NF membranes are considered to operate at lower pressures than ULPRO membranes (~100 psi), are considered to have pores in the 1-nm range (although this is debatable), efficiently remove divalent cations and most organic solutes, and pass monovalent salts and organics smaller than the membrane pore size (Bowen and Mukhtar, 1996; Nghiem et al., 2005; Schaep et al., 2001). It has been shown that NF membranes remove solutes through steric and electrostatic exclusion from pores (Bandini and Vezzani, 2003; Bowen and Mukhtar, 1996; Hagmeyer and Gimbel, 1998; Schaep et al., 2001).

2.3 Operating Conditions

The permeate flux of a membrane system (i.e., the amount of permeate throughput per membrane area) is an important parameter, because a system operating at low flux and 80–85% recovery requires more membrane area (and capital costs) than a system operating at higher flux. Because of the relatively high organic content of municipal wastewater effluent and to theoretically alleviate organic fouling, high-pressure membranes generally are operated at a flux between 8 and 12 gal-ft^{-2}-d^{-1} (Bartels et al., 2004; Drewes et al., 2008; Franks et al., 2007). The Hydranautics RO Projection Program, RO DESIGN, designates flux for RO membranes, treating tertiary treated wastewater effluent aggressively at 10 gfd, typically at 8 gfd, and conservatively at 7 gfd. Although the exact reason for this flux regime is unknown, past research has suggested the existence of a "critical flux," which is defined as the flux below which no fouling occurs (Vrouwenvelder et al., 2009). Past research has demonstrated that the initial flux has a dramatic effect on flux reduction because of fouling (Seidel and Elimelech, 2002; Tang et al., 2007); however, the majority of these studies have been performed at bench-scale using initial flux significantly higher than flux commonly used at pilot-scale (Tang et al., 2007). To our knowledge, there has been little work performed that evaluates the effect of permeate flux on pilot- and full-scale operations outside of the accepted permeate flux range (8 and 12 gal-ft^{-2}-d^{-1}).

The product water recovery of a membrane system is an important parameter that must be considered for several reasons. The lower the recovery, the higher the brine volume that must be disposed of, and currently, few options exist for a cost-effective reduction of high-pressure membrane application brine streams (Van der Bruggen et al., 2008). Most IMS applications reclaiming wastewater discharge the brine stream into the ocean or wastewater treatment plants. For systems returning brine to wastewater treatment plants, elevated salt and nutrient concentrations, anti-scalants, and cleaning chemicals can be a potential issue (Van der Bruggen et al., 2008). In addition, the feed-brine, cross-flow velocity within a membrane module has been reported to be an important factor controlling the rate of flux decline (Manttari et al., 1997; Tang et al., 2007). A cross-flow velocity that is too low results in increased concentration polarization and accumulation of foulants at the membrane surface (Seidel and Elimelech, 2002). Pilot- and full-scale systems operating at a high recovery have a reduced cross-flow velocity in the tail-end elements of each stage, which can potentially exacerbate fouling. Because membrane processes are a separation technology, an increase in the concentrations of sparingly soluble salts combined with an increasing recovery can reach levels above saturation, resulting in the formation of scale on the membrane surface (Shih et al., 2005).

2.4 Fouling, Scaling, and Membrane Cleaning

Membrane fouling and scaling present one of the greatest challenges to the application of an IMS for reclaiming municipal wastewater (AWWA, 2005; Wilf and Alt, 2000; Speth et al., 2000). As a result, considerable work has been performed on understanding the mechanisms of organic fouling, biofouling, and inorganic scaling.

For organic fouling, major influences on flux decline have been reported to be membrane properties (surface charge, hydrophobicity, roughness, and rejection), foulant characteristics and feed water solution chemistry (pH, ionic strength, and divalent cation concentration), hydrodynamic conditions of operation (permeate flux, recovery, and cross-flow velocity), feed-spacer characteristics, and pretreatment (Bartels et al., 2004; Li and Elimelech, 2004; Manttari et al., 1997; Seidel and Elimelech, 2002; Tang et al., 2007). High initial flux (increased drag force) and low cross-flow velocity (reduced shear force) have been reported to promote organic fouling (Manttari et al., 1997; Seidel and Elimelech, 2002). An increased divalent cation (e.g., calcium) concentration is theorized to bridge natural organic matter (NOM), resulting in a more compact fouling layer (Li and Elimelech, 2004). In addition, lower pH and increased ionic strength are thought to reduce electrostatic repulsion between NOM and the membrane, which can promote fouling (Tang et al., 2007). Past research on the influence of membrane properties on fouling has been less conclusive. For example, Peng et al. (2004) found that smoother membranes display a greater flux decline because of the formation of a dense fouling layer; however, Xu et al. (2010) reported that rough membranes displayed greater flux decline than less rough membranes. A recent fouling study performed at the pilot scale demonstrated that rough, hydrophobic membranes with high pure-water permeability were most affected by organic fouling, displaying rapid initial flux decline because of the adsorption of organic matter on the membrane surface (Xu et al., 2010). A good review of factors affecting organic fouling is given by Al-Amoudi and Lovitt (2007) and Goosen et al. (2005). Finally, the adhesion and growth of microorganisms on membrane surfaces (i.e., biofouling) can have a detrimental effect on membrane performance (Xu et al., 2010). For wastewater applications, biofouling is commonly controlled by forming chloramines (2–3 milligrams per liter (mg/L)), which polyamide membranes have a rather high tolerance to (Franks et al., 2007).

Similarly to organic fouling, feed-water composition, membrane characteristics, and hydrodynamic conditions influence membrane scaling (Shirazi et al., 2010). The formation of precipitates of sparingly soluble salts increases toward the tail end of a membrane system because of the increased concentration (function of recovery) and concentration polarization (function of cross-flow velocity and permeate flux; Shih et al., 2005). For wastewater reclamation, inorganic, species-forming scale often includes barium (sulfate), calcium (carbonate, phosphate, and sulfate), and silica (colloidal and aluminum silicate; Al-Amoudi and Lovitt, 2007; Chesters, 2009; Franks et al., 2007). Current practices to reduce scaling potential include pH adjustment (for calcium carbonate and phosphate), anti-scalant addition (for calcium carbonate, sulfate, and silica scales), and operational adjustments (reducing recovery; Al-Amoudi and Lovitt, 2007). Silica scaling can be difficult to control because of speciation and aggregation into colloidal particles and decreased solubility with decreased pH (Ning, 2002). Recent observations of calcium phosphate scaling in the presence of antiscalant suggests that colloidal calcium phosphate deposition presents a challenge for wastewater reclamation that uses an IMS (Ning and Troyer, 2007). Inorganic scaling is most often manifested as a drop in permeability in the later stages of a membrane system, followed by increased salt passage (Franks et al., 2007).

For many membrane applications, loss of permeability due to fouling and scaling is mitigated by cleaning. According to Li and Elimelech (2004), five cleaning agent categories are used in membrane applications: alkalines, acids, metal chelating agents, surfactants, and enzymes. For calcium carbonate, phosphate and sulfate scales, cleaning at a low pH (e.g., citric acid or hydrochloric acid) is an effective method for restoring permeate flux (Franks et al., 2007). Tailored colloidal and organic cleaning (and sometimes targeting biofouling) is often performed using combinations of alkaline cleaning solutions (e.g., NaOH), anionic surfactants (e.g., sodium dodecyl sulfate (SDS), sodium dodecyl benzyl sulfonate [SDDBS]), and chelating agents (sodium tripolyphosphate (STPP), sodium ethylenediaminetetraacetate [EDTA]) (Al-Amoudi and Lovitt, 2007). A good review of cleaning methods is given by Al-Amoudi and Lovitt (2007); however, it is worth noting that certain foulants and scalants can be very difficult to remove and initial permeability cannot always be restored.

2.5 Removal of Organic Contaminants

Research on the fate and occurrence of organic contaminants in wastewater effluents over the past 15 years has shown that many organic chemicals present in raw municipal sewage are incompletely removed by wastewater processes. Therefore, there is significant interest in the ability of RO and NF membranes to reject a wide variety of organic contaminants during water-reuse applications. Past research has demonstrated that organic removal by high-pressure membranes depends on solute properties (e.g., size, charge, hydrophobicity, and polarizabillity), membrane properties (e.g., MW cutoff [MWCO], pore size, and surface charge), solution chemistry (e.g., pH, ionic strength, and organic carbon), and operating conditions (e.g., flux, recovery, and cross-flow velocity; Bellona et al., 2004).

The rejection of uncharged organic compounds is largely dependent upon the size of a solute and the MWCO or the effective pore size of a membrane (Bellona et al., 2004). There have been many attempts to correlate rejection with different solute size descriptors, such as MW, molecular length, molecular width, and Stokes radius (Kiso et al., 2001; Van der Bruggen and Vandecasteele, 2002). Although some of these correlations have been successful, certain classes of solutes do not follow the expected trend of increasing rejection with increased size. For example, charged organic solutes are often well rejected by NF and RO membranes, regardless of size (Bellona et al., 2008). For charged solutes, three removal mechanisms are generally accepted: size exclusion, electrostatic (or Donnan) exclusion, and dielectric exclusion (Bowen et al., 2004; Timmer, 2001). For certain nonionic organic solutes, rejection is less than expected, based on size, and researchers have reported that certain compounds can adsorb to and partition through membrane materials (Kim et al., 2007; Nghiem et al., 2004; Williams et al., 1999). Although research has not, as of yet, isolated the main factors governing this phenomena, nonionic compounds with strong membrane interactions often have incomplete removal.

Bellona et al., (2008) investigated 12 commercially available RO and NF membranes for rejecting a wide variety of organic contaminants on a laboratory-scale testing unit that employed two spiral-wound 4040 membrane elements. One of the major findings was that nonionic organic contaminants are often incompletely removed, even by RO membranes, with more than 99% monovalent salt rejection. In addition, although RO and NF membranes operating at full scale at the West Basin Water Recycling Plant (WBWRP, El Segundo, CA) were observed to adequately reject negatively charged organic solutes, such as trichloroacetic acid, the removal of small nonionic MW organics such as N-nitrosodimethylamine and solutes with strong membrane affinity such as chloroform was marginal during pilot- and full-scale investigations. Other studies investigating organic contaminant removal at full-scale RO membrane applications have observed incomplete removal of PhACs (e.g., gemfibrozil, ibuprofen, sulfamethoxazole), personal care products (DEET and oxybenzone), plasticizers (bisphenol-A), and chlorinated flame retardants (2-trischloroethyl phosphate) (Snyder at al., 2007).

Chapter 3

Materials and Methods

3.1 Membranes Evaluated

Based on previous studies funded by the Water Research Foundation (formerly AwwaRF), five promising NF membranes and one LPRO membrane (Table 3.1) were targeted in this phase of the study, including ESPA2 (Hydranautics), NF-90, NF-270, and NF-4040 (Dow/Filmtec), and TFC-S and TFC-SR3 (Koch). These membranes were preselected because of their high flux at low pressure and their low fouling propensity. The ESPA2 membrane will serve as the baseline membrane, as it is currently employed at the LVL as well as other facilities utilizing IMSs for groundwater recharge (i.e., Orange County Water District, CA, and West Basin Municipal Water District, CA).

Table 3.1 Candidate Membrane Properties

Candidate Membrane	ESPA2	NF-90	NF-270	NF-4040	TFC-S	TFC-SR3
Classification	RO/ULPRO	NF	NF	NF	NF	NF
Manufacturer	Hydranautics	Dow/Filmtec	Dow/Filmtec	Dow/Filmtec	Koch	Koch
Material	Polyamide	Polyamide	Polyamide	Polypiperizine	Polyamide	Polyamide
NaCl Rejection (%)	99[a]	85–90[a]	>97[b]	>99[b]	99.25[b]	99.4[b]
MgSO4 Rejection (%)	99[a]	85–90[a]	>97[b]	>99[b]	99.25[b]	99.4[b]
Pure Water Specific Flux (gfd/psi)[c]	0.2	0.3		0.37	0.23	
MWCO (Da)[c]	<100	~100	~200	~200	~150	>300–400

Notes. [a & b] From manufacturer. [c] Computed during rejection experiments.
gfd = permeate flow (gallons per day) per area (ft^2).

3.2 Laboratory-Scale Membrane Testing Systems and Protocols

A laboratory testing protocol previously developed at the Colorado School of Mines (CSM) (Drewes et al., 2008) was implemented to screen the commercially available membranes presented in Table 3.1 with regard to performance criteria considered important for treating wastewater effluents. These performance criteria include fouling propensity, operational performance, and rejection performance.

3.2.1 Fouling Propensity and Rejection Performance

The fouling propensity of candidate membranes was evaluated utilizing a bench-scale flat-sheet SEPA (GE/Osmonics) test cell. Prior to the fouling experiments, feed water at the LVL was characterized in terms of water quality parameters relevant to membrane fouling, including, but not limited to, TOC, size-exclusion chromatography with dissolved organic carbon (DOC) detection, 3-D fluorescence spectroscopy to characterize the nature of DOC present in feed water, and major cations and anions. For fouling experiments, the wastewater effluent was filtered with a 0.2-µm filter, and the pH was adjusted to 6.5. Candidate membranes were fouled twice to ascertain repeatability. Each membrane was compacted with deionized water at a feed pressure of 150 pounds per square inch gauge (psig) operating for a period of 24 h. Subsequently, each membrane was fouled at a target flux of 12 gallons per square foot per day (gfd), operating for a period of 24 h.

During fouling propensity testing, feed and permeate samples were collected for water quality analysis, including TOC, dissolved metals, selected anions, and nitrate and ammonia. Water quality data were used to quantify the rejection performance of candidate membranes. Fouling tests were conducted in the laboratory at CSM; shipping enough LVL feed water for all fouling tests from California was difficult. Therefore, a surrogate source of wastewater from Colorado for LVL feed water was evaluated for the fouling propensity experiments.

For the water quality and fouling propensity comparison tests, approximately 100 liters of LVL feed water was shipped to CSM. Samples were also collected from the Denver Metro wastewater facility's North (nitrified/partially denitrified) and South (nonnitrified) treatment trains. A summary of key water quality parameters for these different wastewater effluents is presented in Table 3.2. Based on water quality, the Metro North and South samples were similar, with the biggest difference being the form of nitrogen present. Because LVL feed water is also partially denitrified, the Metro North effluent was selected as a surrogate source of wastewater for the bench-scale fouling propensity tests.

To evaluate the Metro North effluent as a surrogate for LVL feed water, replicate fouling propensity tests were performed with the NF-90 membrane using both water types; the results are summarized in Figure 3.1. For all fouling experiments, the NF-90 lost approximately 40% of the initial specific flux, and fouling curves were similar within 5%, at the termination of the experiments. Based on these results, the Metro North effluent was subsequently used in all flux decline experiments. In addition, previous research (Drewes et al., 2008) demonstrated similar results where the NF-90 displayed a relatively high specific flux decline that was due to fouling during fouling propensity tests caused by Effluent Organic Matter (EfOM) fouling. Further pilot-scale testing with the NF-90 showed that the NF-90 displayed a similar specific flux decline over a period of approximately 500 h. Because of the relatively high fouling propensity of the NF-90, it was not considered for further testing during this study.

Table 3.2 Comparison of Denver Metro Wastewater Effluent (North and South Plant) and LVL Feed Water Quality

Analyte (mg/L)	Metro	Metro	LVL	LVL
	South	North	Sample 1	Sample 2
Ca	49.2	46.1	50.4	50.3
Mg	10.8	11.5	10.8	10.8
Na	83.4	83.6	123.3	130.9
SiO2	13	11.1	24.8	27.2
Cl	73.2	83.8	158.8	96.8
NO3-N	0.3	10.3	6.7	4.7
NH3-N	14.9	0.5	0.7	0.6
SO4	120.9	110.6	116.1	93.6
K	10.2	13.8	11.8	13.9
TOC or DOC	9.8	8.8	5.8	6.1
UV-254 (m^{-1})	15.7	16.8	11	10.7
SUVA (L/mg-m)	1.6	1.91	1.9	1.75

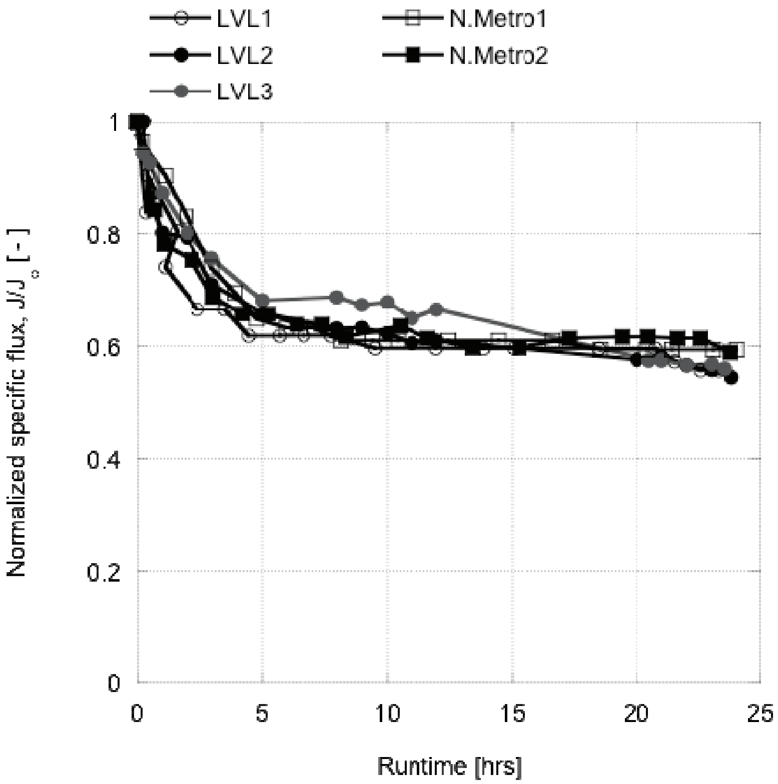

Figure 3.1 Normalized specific flux decline curve for the NF-90 membrane treating LVL feed water and Metro North effluent (constant permeate flux of 12 gfd).

3.2.2 Operation and Rejection Performance

The operation and rejection performance of the candidate membrane was evaluated utilizing a laboratory-scale membrane-testing unit consisting of two spiral-wound 4040 membrane elements in series (Figure 3.2). The unit has a supervisory control and data acquisition (SCADA) system that downloads operational data including system flow rates, pressure, conductivity, and temperature.

Figure 3.2 Laboratory-scale membrane system.

Actual candidate membrane operation and rejection experiments were performed at the LVL by diverting MF filtrate to the laboratory-scale testing unit. Rejection experiments were conducted at permeate fluxes of 12 and 18 gfd. Samples for water quality analysis were collected from the feed and permeate streams of the testing unit for each membrane at each permeate flux investigated. For each membrane, samples were collected for water quality, and the membrane system was allowed to run overnight to evaluate the initial flux decline caused by fouling.

3.3 Pilot-Scale Membrane Testing System

A pilot-scale membrane skid using spiral-wound 4040 membrane elements was used for membrane testing at the LVL. The pilot-scale system is a two-stage membrane unit that was designed to mimic a two-stage full-scale treatment system. The unit was built in a four-stage array configuration to minimize space, and consists of six pressure vessels, four in the first stage and two in the second stage. The pilot-scale unit requires 21 spiral-wound 4040 elements, with 14 elements in the first stage and 7 elements in the second stage. The system is equipped with a SCADA system; has a variable speed feed pump; and can be operated at different recoveries, feed-flow rates, and permeate flux. The pilot is equipped with a customized SCADA system to monitor and log flow rates, pressures, and selected water quality parameters online (e.g., pH, temperature, and conductance).

A picture of the pilot-scale unit installed at the LVL is provided in Figure 3.3. At the LVL, MF filtrate was diverted to the pilot-scale test unit from a 5,000 gallon buffer tank. Two separate membranes were evaluated at pilot-scale: the ESPA2 to demonstrate stable performance and the candidate NF membrane selected from laboratory-scale testing. For the ESPA2 membrane, testing was first conducted at a recovery of approximately 83% and a permeate flux of 12 gfd for 100 hours. This initial testing phase was to validate whether comparable performance of the ESPA2 membrane employed both at pilot- and full-scale is achievable. After this initial phase, the ESPA2 was evaluated at 85% and 87% recovery at a permeate flux of 15 gfd for 500 h each. Additional performance tests with the NF membranes were conducted with recovery set points of 85% and 87% for an operational run time of 500 h each.

Figure 3.3 Pilot-scale testing system at the LVL.

The overall goal of this study is to maximize the overall recovery of an IMS employed at the LVL or other facilities. For the pilot-scale testing portion of the study, we realized that running under conditions similar to the LVL RO train (i.e., a relatively low feed-flow rate, a relatively low permeate flux, and a high recovery) would not allow us to push recovery and operate within manufacturer-specified conditions, which would likely result in major operational issues. Based on typical membrane systems treating municipal wastewater effluents, it has been demonstrated that a system can operate under stable conditions with operational set points of a 10–12 gfd permeate flux and 80–85% recovery. However, these set points appear to have been selected somewhat arbitrarily, and there is little understanding of how far permeate flux and recovery can be pushed while stable operation is maintained. Therefore, for the pilot-scale portion of this study and with an LVL plant expansion in mind, an experimental matrix was developed to evaluate the effect of permeate flux and recovery on operation when utilizing RO and NF membranes. Evaluated operational set points are summarized in Table 3.3.

Table 3.3 Proposed Operational Set Points and Runtime for Testing of the ESPA2

Purpose	Set Point	Runtime (h)
Establish baseline	12 gfd, 83–84% recovery	100
Evaluate elevated permeate flux rate at current LVL recovery	15 gfd, 85% recovery	500
Evaluate elevated permeate flux rate at elevated recovery	15 gfd, 87% recovery	500

3.4 Sampling and Analysis

During these tests, samples were collected for TOC, ammonia, nitrate, and select trace organic chemicals. Flow and feed, as well as permeate quality data (pH and conductivity), were logged continuously through the SCADA system. Routine water samples were analyzed either by a Long Beach Water Department (LBWD) laboratory or by a certified commercial laboratory. Samples for trace organic chemicals were shipped via overnight courier to CSM. Selected endocrine-disrupting compounds (EDCs), pharmaceutical residues, and personal care products were analyzed to determine if the treatment configuration was sufficient to meet possible future regulations.

3.5 Analytical Methods

3.5.1 Membrane Autopsy Methods

3.5.1.1 Environmental Scanning Electron Microscopy

Membrane surface structure and morphology were analyzed by a Quanta 600 environmental scanning electron microscope (ESEM) (FEI Company, Hillsboro, OR). Membrane specimens were attached to a carbon tape on an aluminum holder and then coated with a thin layer of gold in a Hummer VI sputtering system (Technic Inc., Providence, RI). The plasma discharge current was 20 mA and the chamber vacuum was adjusted to 50-100 mtorr. Sputtering time was approximately 2 min. The coated membrane samples were examined using the ESEM at accelerating voltage 20–30 kV, spot size 2.0–2.5, and working distance 15 mm.

3.5.1.2 Energy-Dispersive Spectroscopy

Elemental composition of virgin and fouled membrane specimens was quantified by energy-dispersive spectroscopy (EDS) mounted in the ESEM. Prior to EDS analysis, the membrane specimens were coated with a thin carbon layer by a Denton DV-502 vacuum evaporator (Moorestown, NJ).

3.5.2 Bulk Water Quality Analysis

3.5.2.1 Alkalinity

Alkalinity was measured using a Hach (Loveland, CO) alkalinity kit. Each 100-mL sample was titrated with 1.6 N sulfuric acid to a pH of 4.6 using a Hach digital titrator (Model 16900-01).

3.5.2.2 Ammonia

Free ammonia was measured according to the Hach Nessler Method 8038, adapted from Standard Methods 4500-NH3 B & C.

3.5.2.3 Anions

Inorganic anions were quantified with a Dionex DS600 ion chromatograph (IC) (Sunnyvale, CA) using an AS14A column and an effluent with 6 mM sodium carbonate and a 1 mM sodium bicarbonate buffer, according to Standard Method 4110 B. The anions that were examined are fluoride, bromide, chloride, nitrate, phosphate, and sulfate.

3.5.2.4 Conductivity

Conductivity measurements were taken with a handheld Oakton pH/EC/DO meter (Model PCD650) following Standard Method 2510.

3.5.2.5 Dissolved Metals

A Perkin–Elmer Optima 3000 inductively coupled plasma atomic emission spectrometer (ICP-AES) (Norwalk, CT) was employed to determine the concentrations of inorganic cations (Standard Method 3125 B). This method measured a suite of 34 metals.

3.5.2.6 pH

The pH was measured using an Accumet (Fisher Scientific) bench-top pH meter (Fullerton, CA) (Standard Method 4500-H^+).

3.5.2.7 Total/Dissolved Organic Carbon

DOC was quantified using a Sievers 800 TOC analyzer with autosampler (GE/Ionics Instruments, Boulder, CO). TOC and DOC were also quantified using a Sievers 5310 TOC analyzer with autosampler (Ionics Instruments, Boulder, CO) according to Standard Method 5310 C. The samples were placed int 17-mL sample vials and acidified with phosphoric acid. Measurements of DOC were based on calibration with potassium hydrogen phthalate standards. For this study, all samples for TOC measurements were taken post-MF (0.2 µm), and with the assumption that TOC values can be considered DOC.

3.5.2.8 UV Absorbance

UV absorbance was analyzed using a Beckman UV/VIS spectrophotometer with a 1-cm quartz cell (Standard Method 5910 B). Samples were measured at wavelengths of 200–400 nm.

3.5.3 Organic Carbon Characterization

3.5.3.1 Fluorescence spectrometry

Fluorescence spectrometry excitation/emission matrices (EEMs) were developed using a Fluoromax 4 spectrofluorometer (HORIBA Jobin Yvon), blanked with Ultrapure Milli-Q water across an excitation spectrum of 240–450 nm and an emission spectrum of 290–580 nm. Samples were brought to room temperature prior to analysis. The blank was subtracted, and final matrices were further corrected with data from a space full spectrum UVA scan. EEMs were corrected and graphed using MatLab software. Fluorescence spectrometry can be used to distinguish humic-like organic matter from protein-like organic matter. The fluorescence of EfOM is caused by the presence of fluorophores that absorb photons, followed by excitation to a higher electronic energy state. The absorbed energy is released into the environment at a longer wavelength. Humic and fulvic acid-like intensities can be quantified at emission wavelengths of 420 and 440 nm and at excitation wavelengths of 330 and 240 nm, respectively. The specific fluorescence intensity is defined as the protein or humic fluorescence intensity (see wavelengths) divided by DOC. Last, differential EEM spectra can be used to assess the performance of treatment processes. SEC chromatograms for the LVL and Denver Metro treated effluent samples are presented in Figures 3.4 and 3.5. Although both samples are dominated by EfOM (humic-like and protein-like peaks), the LVL effluent samples exhibited less presence of protein.

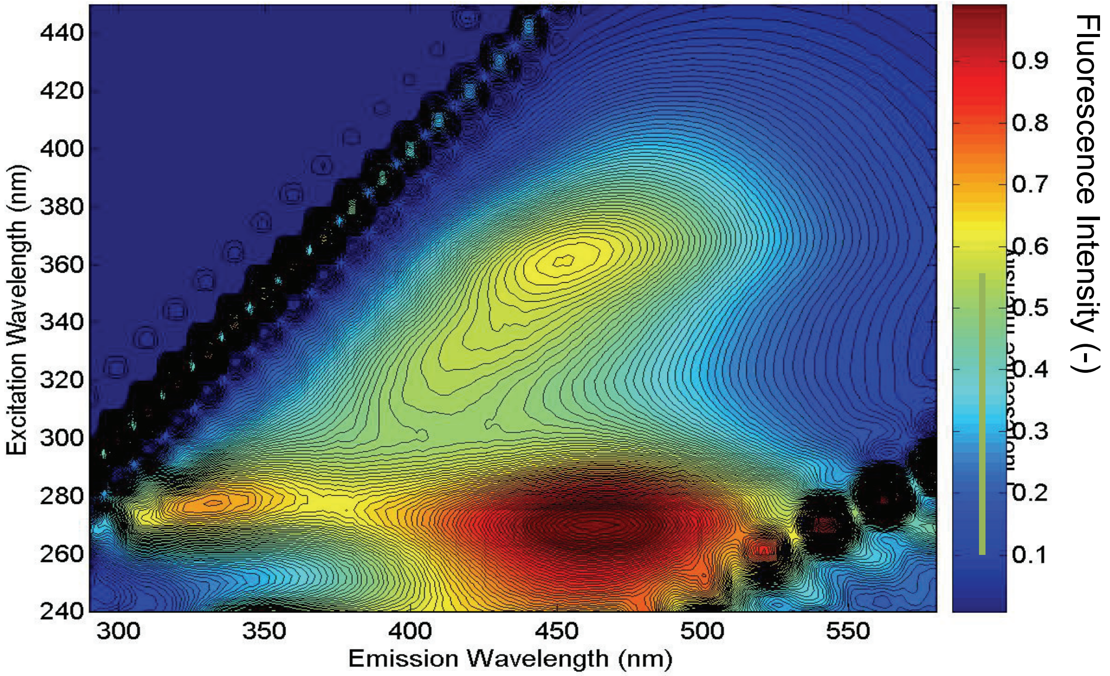

Figure 3.4 Results of fluorescence spectrometry for LVL water.

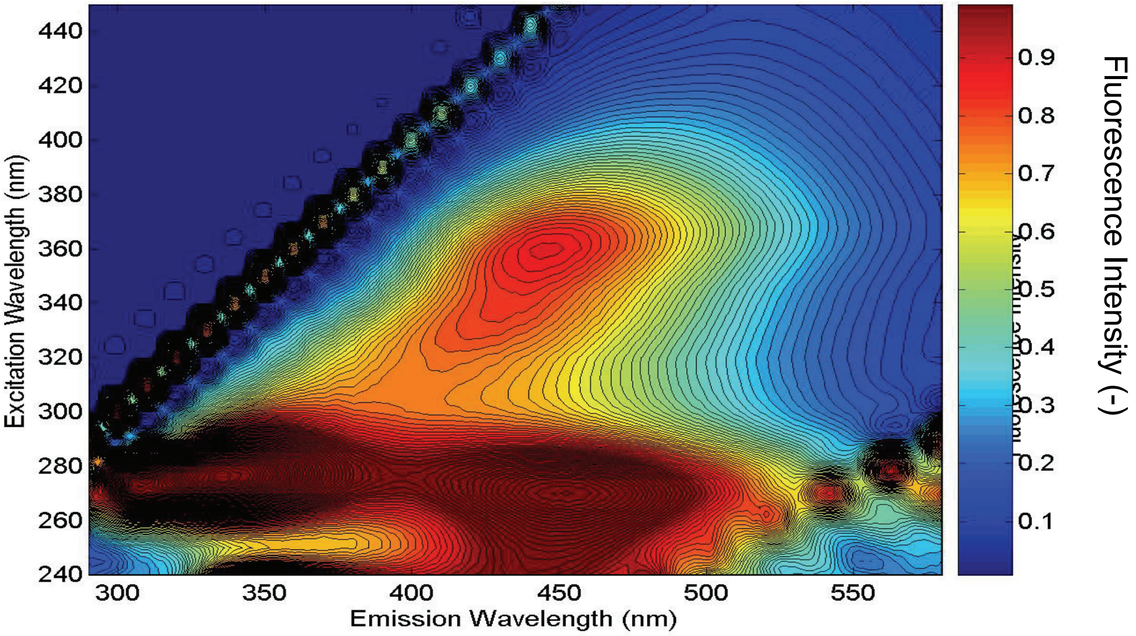

Figure 3.5 Results of fluorescence spectrometry for Metro North wastewater effluent.

Size exclusion chromatography (SEC) was carried out using paired UV (254-nm) and DOC detection, with an injection volume of 2 mL, an acid addition rate of 2 µL/min, and an oxidizer addition rate of 0.7 µL/min. Initially, samples were filtered, acidified with phosphoric acid (pH < 3), and sparged with nitrogen gas for 2 minutes, and the pH was readjusted with sodium hydroxide (pH~7) prior to analysis to remove interfering inorganic carbon fraction. SEC measures the MW distribution for a heterogeneous EfOM mixture. This system uses UV and DOC detection (Her et al., 2002). The EfOM present can differ in its MW and can range from a few hundred to a high of several thousands. SEC-DOC is used to reveal transformation/removal patterns of the entire EfOM, which consists of the following main fractions: polysaccharides (~30 min), humic substances (~ 45 min), and low-MW acids (~60 min). Based on the SEC chromatograms generated using LVL and Metro North wastewater effluent (Figures 3.6 and 3.7), the LVL exhibited smaller MW organic compounds relative to Metro wastewater, supporting the fluorescence spectroscopy results (Figures 3.4 and 3.5). The humic substances in the LVL effluent also seem to be more altered, suggesting a more extensively treated effluent quality.

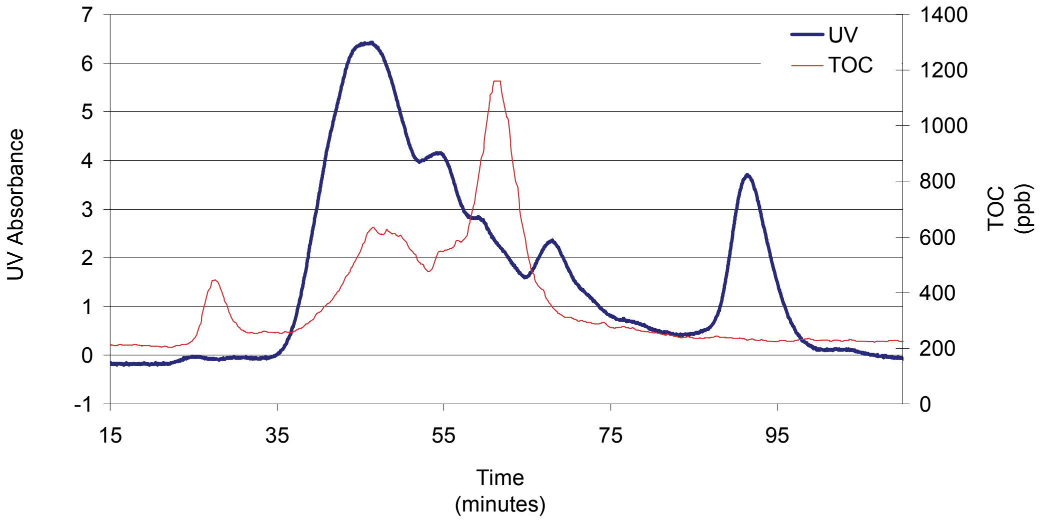

Figure 3.6 SEC chromatogram for LVL water.

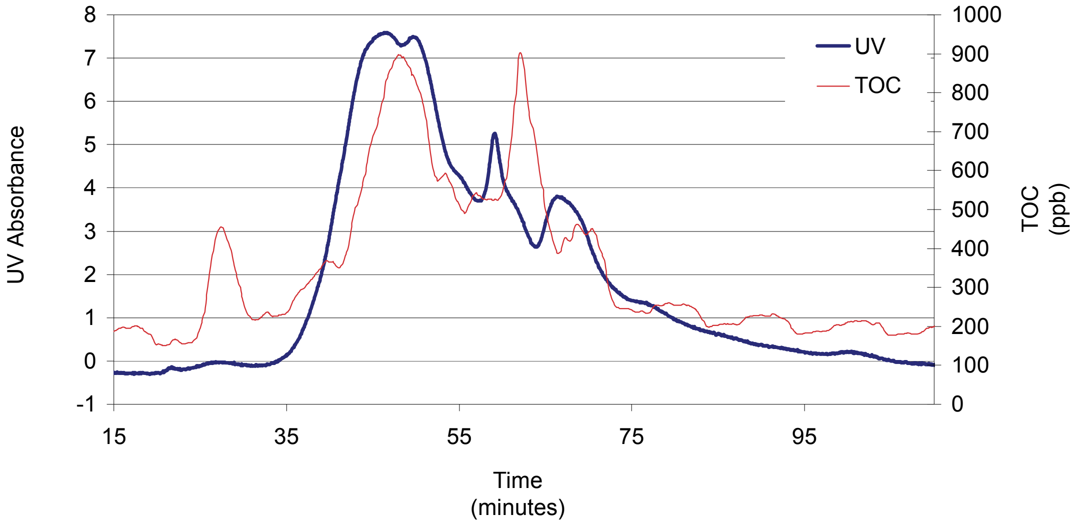

Figure 3.7 SEC chromatogram for Metro North wastewater effluent.

3.5.4 Trace Organic Contaminant Analysis

3.5.4.1 GC/MS Method

Gas chromatography/mass spectrometry (GC/MS) analysis was performed using a modified method from Reddersen and Heberer (2003). An Agilent Technologies (Palo Alto, CA) 6890 gas chromatograph with an Agilent 5973 quadrupole mass spectrometer was used for analysis. Prior to analysis by GC/MS, the samples were pretreated using solid phase extraction (SPE) followed by derivatization.

For SPE, the pH of a sample was adjusted to 2 with hydrochloric acid, and 10 mL of methanol added to each sample. As internal standards, deuterated ibuprofen and diclofenac and 2-(3-chlorophenoxy) propionic acid were added at a concentration of 100 nanograms per liter (ng/L) (100 µl of a 1 mg/L solution in methanol). SPE was performed using 1 g of reverse phase C-18 material as adsorbate (Bakerbond Polar Plus, Mallinckrodt-Baker, Phillipsburg, NJ). The samples were extracted through the C-18 cartridge on a PreSep 12-port manifold (Fisher Scientific International, Inc., Pittsburgh, PA) using an applied vacuum. The C-18 material was preconditioned with 5 mL of acetone, 10 ml of methanol, and 10 mL of pH 2 deionized water. The water sample was then passed through each column with a flow of 3–5 mL/min. One liter was extracted for permeate samples and 400 mL was extracted for feed water samples. The cartridges were dried overnight under a nitrogen stream.

The derivatization was performed the next day. The analytes were eluted from the cartridges with approximately 1.5 mL acetone into 2-mL autosampler vials. The eluate was dried under a gentle nitrogen stream and 100 µL of a pentafluorobenzyl bromide (PFBBr) solution (2% in toluene) was added as a derivatizing agent. As a catalyst, 4 µL of triethylamine was used. Then the sample vial was placed in a drying cabinet at 100 °C for 1 h. The residue was dried again and dissolved with 100 µL of toluene. The solution was then taken out of the vial and transferred into 200-µL glass inserts. The detection limits for the compounds analyzed by the GC/MS method are presented in Table 3.4.

Table 3.4 Analytical Detection Limit for GC/MS Method (when extracting 1 L during SPE)[a]

Compound	Detection Limit (ng/L)
Phenacetin	50
Salicylic acid	50
TCEP	50
TCPP	50
Clofibric acid	10
Ibuprofen	10
Mecoprop	10
Dichlorprop	10
Gemfibrozil	25
TDCPP	50
Naproxen	10
Fenofibrate	50
Ketoprofen	25
Diclofenac	10

[a] Detection limit determined through spike/recovery experiments using wastewater effluent

3.5.4.2 LC/MS/MS Method

Organic analysis by liquid chromatography tandem mass spectrometry (LC/MS/MS) was performed using an isotope dilution method that was modified from the one developed by the Southern Nevada Water Authority (Trenholm et al., 2006). Analysis was performed using an Agilent 1200 HPLC for injection and using chromatography coupled with an Applied Biosystems (USA) 3200 Q TRAP MS/MS system. Prior to analysis by LC/MS/MS, the samples were pretreated using SPE.

SPE was performed using Waters (Milford, MA) Oasis HLB cartridges. Isotope standards were obtained for all target analytes and spiked into water samples to achieve a 50 ng/L concentration prior to SPE. The detection limits for the compounds analyzed by the LC/MS/MS method are presented in Table 3.5.

Table 3.5 Calculated Detection Limit for LC/MS/MS Method (When Extracting 400 mL during SPE)[a]

Compound	Units (ng/L)
Acetaminophen	0.6
Atenolol	0.1
Atrazine	0.1
Caffeine	0.6
Carbamazepine	0.3
DEET	0.6
Diazepam	0.1
Dilantin	1.3
Fluoexetine	0.1
Hydrocodone	0.3
Meprobamate	0.1
Norfluoxetine	0.6
Primidone	0.3
Sulfamethoxazole	0.1
Trimethoprim	0.1
TCEP	0.3
TCPP	0.6
TDCPP	2.5
Bisphenol A	1.3
Diclofenac	0.6
Triclocarban	0.1
Ibuprofen	2.5
Ketoprofen	0.1
Naproxen	0.3
Propylparaben	0.1

[a] Detection limit determined by lowest standard concentration that passes the signal:noise limit (7:1)

Chapter 4

Historical and Current Plant Operation

4.1 Historical Plant Operation

As described earlier, the LVL treats disinfected tertiary effluent from the Long Beach Water Reclamation Plant (LBWRP) with MF, RO, and ultraviolet radiation to treat water, which is further blended with imported water from the Metropolitan Water District of Southern California (MWD) and subsequently injected into the Alamitos Seawater Barrier. Figure 4.1 shows the process flow diagram for the LVL.

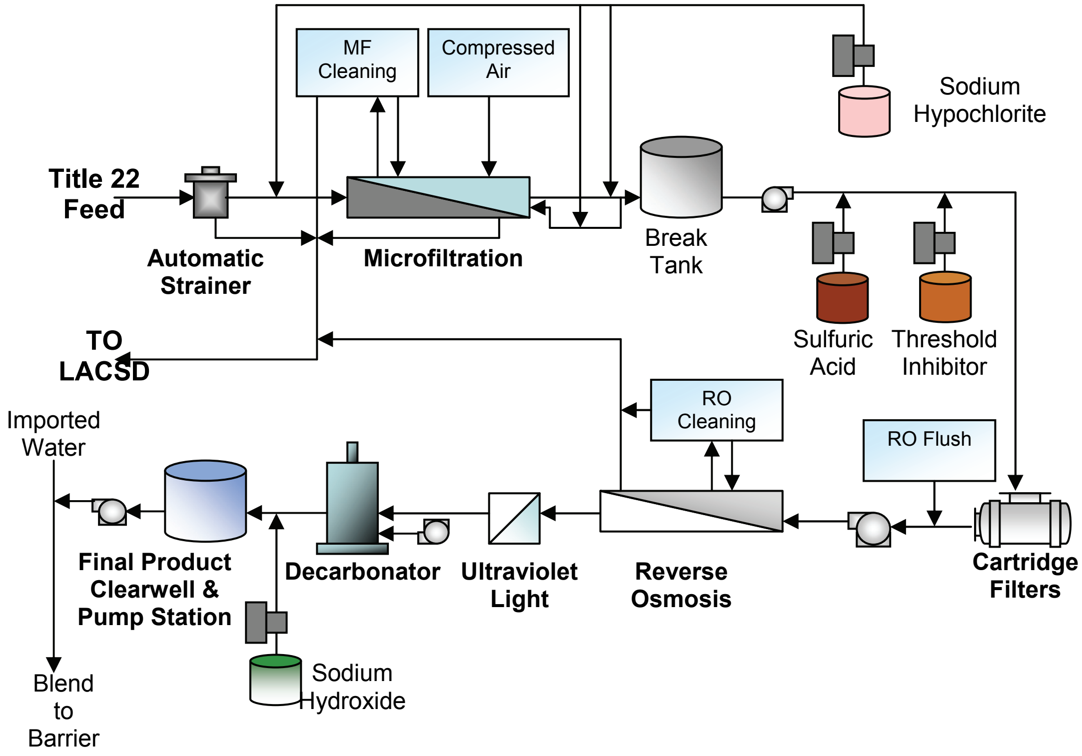

Figure 4.1 LVL advanced water treatment process flow diagram.

4.2 RO System at the LVL

The RO system at the LVL is configured as a two-stage array with 72 membrane vessels in the first stage and 36 vessels in the second stage. The system is designed to operate at a permeate flow rate of 2,080 gallons per minute (gpm), which results in a permeate flux of 10 gfd and 85% recovery based on a feed-flow rate of approximately 2450 gpm. The variable-frequency drive (VFD) on the high-pressure pump is currently at approximately 80% of its capacity. The RO facility also has a maximum discharge capacity of around 370 gpm.

Based on information from membrane manufacturers, the RO system at the LVL is operated at a fairly conservative permeate flux and a relatively high system recovery. In order to achieve this low permeate flux and high recovery, the feed-flow rate is kept relatively low. The flow into each first-stage vessel is approximately 34 gpm, which is at the low end of the acceptable spectrum for membrane operation, based on Hydranautics design criteria (maximum is 75 gpm, conservative is 60 gpm). Because of these operational set points, the concentrate flow rate leaving the final second-stage elements is low, resulting in a low cross-flow velocity. Therefore, based on the current configuration of the RO train at the LVL, increasing recovery would result in an unacceptable cross-flow velocity, which could negatively affect operation.

One way to increase the amount of water produced at the LVL would be to maintain an 85% recovery but increase the feed-flow rate and operate at a higher permeate flux and a higher cross-flow velocity. However, because the VFD is already operating at 80%, and the concentrate flow is near the discharge limit, there is little room to optimize the current facility without modifications to the RO train (e.g., reduced membrane area). Therefore, it appears that, in the current configuration, the only way to increase recovery would be to install an RO system on the brine stream or expand and retrofit the facility, for example, installing a higher-capacity pump.

The LVL was commissioned in the spring of 2003. The plant is designed to operate at a pH of 6.7, but historical water quality showed that the plant influent water's median pH was at about 7.2. The plant has always experienced frequent short-term and long-term shutdowns because of various operational and maintenance issues and fouling problems. The RO membranes experienced extensive fouling even after the plant capacity was reduced from 3 to 2.2 MGD (reduced recovery from 85% to 81%).

In 2008, Trussell Technologies, Inc. (TT, 2008) conducted a study to determine the most likely causes of membrane fouling. The study concluded that the primary cause of membrane fouling was the presence of excessive levels of dissolved aluminum in the reclaimed water being treated. The fouling was occurring primarily in the second stage, where aluminum reaches 20 to 100 times the solubility limit for fresh aluminum hydroxide. Besides this, the membrane autopsy also showed that the stage-two membranes were severely fouled with aluminosilicates. When aluminum hydroxide was above its solubility, an amorphous aluminum silicate would form, therefore creating the foulant that is seen on the second stage membranes. The study also concluded that the combined chloramine residual level in the water feeding to the RO at the LVL has often been below the recommended dose of 3 to 5 mg/L for biofilm control, which could have contributed to biofouling. Table 4.1 shows the LVL treatment plant historical feed-water-quality data taken from the TT (2008) report.

Table 4.1 LVL Treatment Plant Selected Feed Water Mineral Quality (Modified from 2008 TT Report)

Constituents	Units	2008 Results		
		Min	Max	Median
Aluminum, total	µg/L	130	170	150
Aluminum, dissolved	µg/L	100	120	120
Ammonia nitrogen	mg/L	0.76	1.6	0.91
Barium, total	µg/L	50	59	54
Bromide	µg/L	112	161	141
Calcium, dissolved	mg/L	56	60	58
Calcium, total	mg/L	51	61	58
Chloride	mg/L	130	140	140
DOC	mg/L	6.1	6.6	6.2
Fluoride	mg/L	0.73	0.78	0.75
Iron, total	mg/L	0.028	0.033	0.033
Manganese, total	mg/L	0.033	0.049	0.035
Nitrate	mg/L as N	3.9	6.4	5.2
Orthophosphate	mg/L as P	0.131	0.231	0.221
Reactive silica	mg/L as SiO_2	20	22	21
Silica	mg/L	21	23	23

4.3 Current Operation

To help minimize the potential for aluminosilicate fouling, the LBWRP switched from using alum- to ferric-based coagulant for its tertiary filtration operation in August 2008. The LVL also discontinued pH adjustment to help keep aluminum in solution. Because of the biofouling potential caused by the low combined chloramine residual in the RO feed, the plant has also stopped adding sodium bisulfate.

Table 4.2 shows a representative sample of the current feed water quality taken during this project.

Table 4.2 LVL Feed Quality after LBWRP Switch to Ferric

Constituents	Units	2009 Results		
		Min	Max	Average
Alkalinity	mg/L as CaCO3	200	244	220
Aluminum	µg/L	20	100	50
Barium	µg/L	30	50	40
Bromide	µg/L	0.04	0.15	0.09
Calcium	mg/L	45.44	6.27	50.91
Chloride	mg/L	25.3	146.2	104.26
Fluoride	mg/L	0.53	1.12	0.69
Iron, total	mg/L	0.02	0.07	0.04
Magnesium	mg/L	10	18.14	13.70
Manganese	mg/L	ND	0.07	0.03
Nitrate	mg/L	4.07	25.27	11.77
NO_3-N	mg/L	0.92	5.71	2.66
PO_4-P	mg/L	0.03	1.41	0.38
Potassium	mg/L	12.28	16.18	13.56
Silica	mg/L as SiO_2	8.79	11.72	10.10
Sodium	mg/L	120.67	154.87	130.29
Sulfate	mg/L	99.09	180.16	131.88
TOC	mg/L	6.27	8.29	7.27

ND = not detected.

Influent TOC concentration has remained relatively stable over the years (Figure 4.2). What is interesting to note is that there seems to be a decreasing trend in the nitrate level of the feed. This will be an important piece of data, as it might affect the recommendations of this study. Figure 4.3 illustrates the decreasing trend of the influent nitrate level.

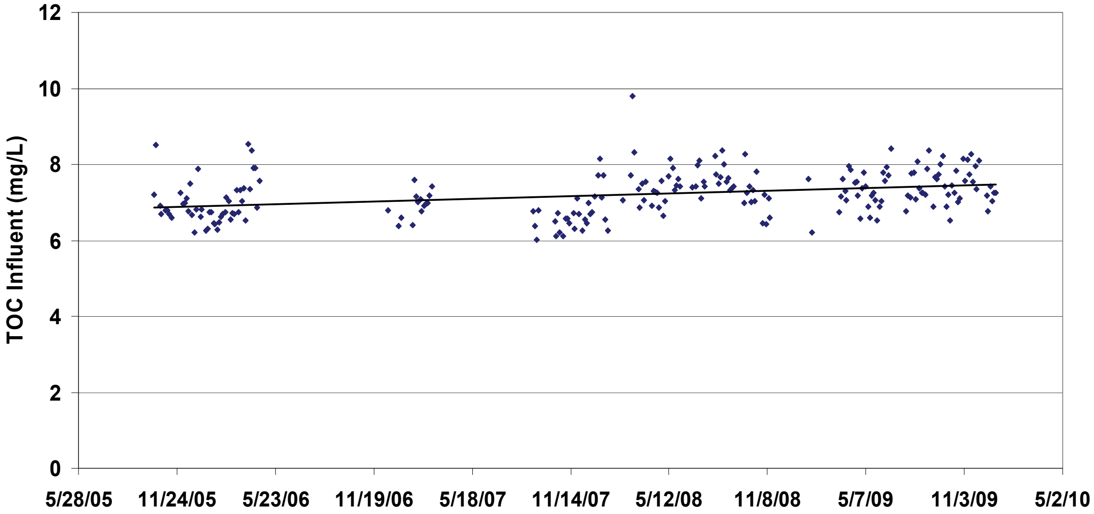

Figure 4.2 Historical trend of TOC level in the LVL influent.

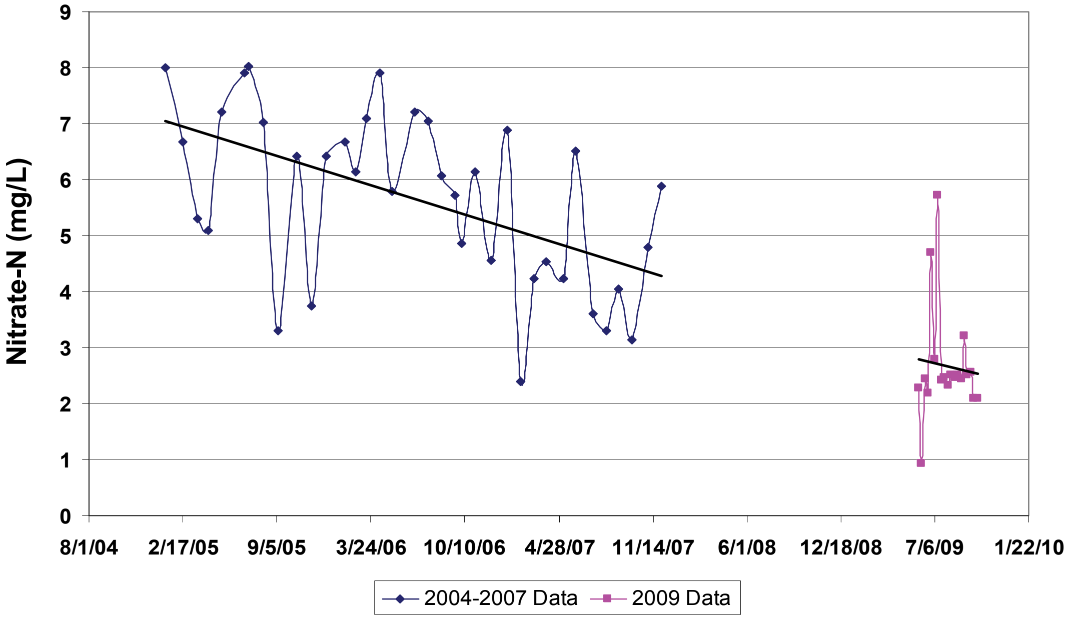

Figure 4.3 Decreasing trend of nitrate level in the LVL influent.

Chapter 5

Evaluating Membrane Performance at Higher Recovery and Flux

5.1 Selection of Suitable Membranes (Laboratory-Scale Selection)

Several candidate membranes were evaluated to select a membrane for pilot-scale testing at the LVL. Candidate membranes were evaluated by flux decline because of fouling, and operational and rejection performance. Results of this selection process are presented in the following sections.

5.1.1 Organic Fouling Propensity

A fouling test was developed to evaluate the propensity by which candidate membranes lose specific flux (or, alternatively, require increasing pressure to maintain a set permeate flow rate) as a result of EfOM fouling. Previous research has demonstrated that RO and NF membranes undergo varying degrees of specific flux decline, depending on membrane properties and feed water chemistry (Drewes et al., 2008). For this study, it was necessary to select low-fouling membranes, that is, a membrane that would retain its initial high permeability when treating wastewater effluent. Fouling propensity tests were performed with the ESPA2 and remaining candidate NF membranes (NF-4040, NF-270, TFC-S, and TFC-SR3) using Metro North effluent as a surrogate for LVL feed water (Figure 5.1). The NF-270 and TFC-SR3 membranes exhibited little specific flux decline because of fouling, whereas the ESPA2, NF, and TFC-S membranes exhibited approximately 20% specific flux decline due to EfOM fouling.

During fouling tests, feed and permeate samples were collected for water quality analysis, and subsequent rejection results are presented in Table 5.1. The main difference between the candidate membranes was the rejection of monovalent salts. The ESPA2, a low-pressure RO membrane, and the NF membrane TFC-S exhibited relatively high rejection of monovalent ions, whereas the NF-4040, NF-270, and TFC-SR3 membranes had approximately 50% rejection of sodium and potassium, and very low rejection of nitrate. Currently, the California Department of Public Health (CDPH) Draft Groundwater Recharge Requirements specify that plant effluent must not exceed 5 mg nitrogen per liter (mg-N/L) of total nitrogen (TN) and 0.5 mg/L of TOC, assuming a recycled water contribution of 100%. Based on the TOC and nitrate concentrations measured in LVL feed water (5.71 mg/L-N NO_3 and 8.29 mg/L TOC), a higher than 92% rejection of TOC would result in permeate concentrations of less than 0.5 mg/L, and a higher than 13% rejection of nitrate would result in permeate concentrations of less than 5 mg-N/L. Based on rejection values (Table 5.1), all of the candidate membranes would meet the TOC requirement; however, only the TFC-S membrane would meet the nitrate requirement at the nitrate concentration used.

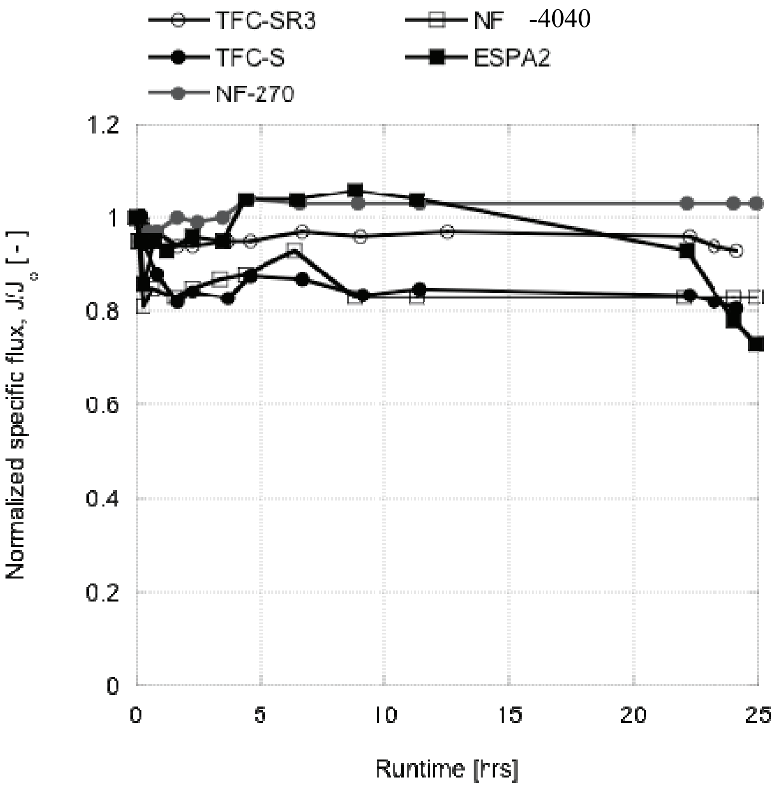

Figure 5.1 Normalized specific flux decline curve for the candidate NF membranes treating Metro North effluent (constant permeate flux of 12 gfd).

Table 5.1 Rejection of Major Inorganic Solutes and TOC during Fouling Propensity Tests

Constituents	ESPA2	NF-4040	TFC-SR3	NF-270	TFC-S
Ca^{2+}	0.998	0.836	0.937	0.724	0.993
K^{+}	0.991	0.591	0.506	0.427	0.941
Mg^{2+}	1.000	0.879	0.974	0.834	0.995
Na^{+}	0.984	0.579	0.471	0.425	0.943
F^{-}	1.000	0.825	0.907	0.773	0.969
Cl^{-}	0.994	0.507	0.431	0.267	0.959
NO_3-N	0.976	0.019	0.068	-0.139	0.916
PO_4^{3-}	1.00	0.993	1.000	0.985	0.993
SO_4^{2-}	0.999	0.997	0.997	0.996	0.992
TOC	0.984	0.967	0.964	0.968	0.975

5.1.2 Operational Performance Comparison

The operational performance of the candidate membrane was evaluated utilizing a laboratory-scale membrane-testing unit consisting of two spiral-wound 4040 membrane elements in series. The unit has a SCADA system that downloads operational data, including system flow rates and pressures. Testing of the candidate membrane's operational and rejection performance was conducted at the LVL using MF effluent feed water for the full-scale RO system. The NF-4040 membrane was not considered for these tests, as it was found to perform similarly to the NF-270 membrane in terms of rejection performance, but fouled to a greater extent.

The candidate membranes (TFC-S, TFC-SR3, and NF-270) and benchmark membrane (ESPA2) were tested using a laboratory-scale membrane skid at the LVL treating LVL's MF effluent. Specific flux decline curves for the targeted membranes are presented in Figure 5.2. The ESPA2 and TFC-S membranes were operated at a permeate flux of approximately 14 gfd for 20 h. The ESPA2 membrane exhibited very little flux decline in the first 20 h of testing and operated at approximately 0.17 to 0.18 gfd/psi. Although the operational data are noisy in the first hour of operation; the TFC-S membrane exhibited approximately 10% flux decline in the first 4 h of testing, presumably because of organic fouling. The subsequent membrane tested, the NF-270, could not be operated in our testing system at a 14-gfd permeate flux because of its high permeability and so was operated at 16 gfd. Even with a high specific flux of 0.65 gfd/psi, the NF-270 membrane exhibited minimal flux decline in the first 20 hours of operation. The high specific flux of the NF-270 is the result of the required net driving pressure (NDP) being approximately 25 psi to achieve 16 gfd permeate flux. The TFC-SR3 membrane, which is considered a "loose" NF membrane, was found to operate at a higher NDP than the NF-270, which resulted in a specific flux of approximately 0.25 gfd/psi.

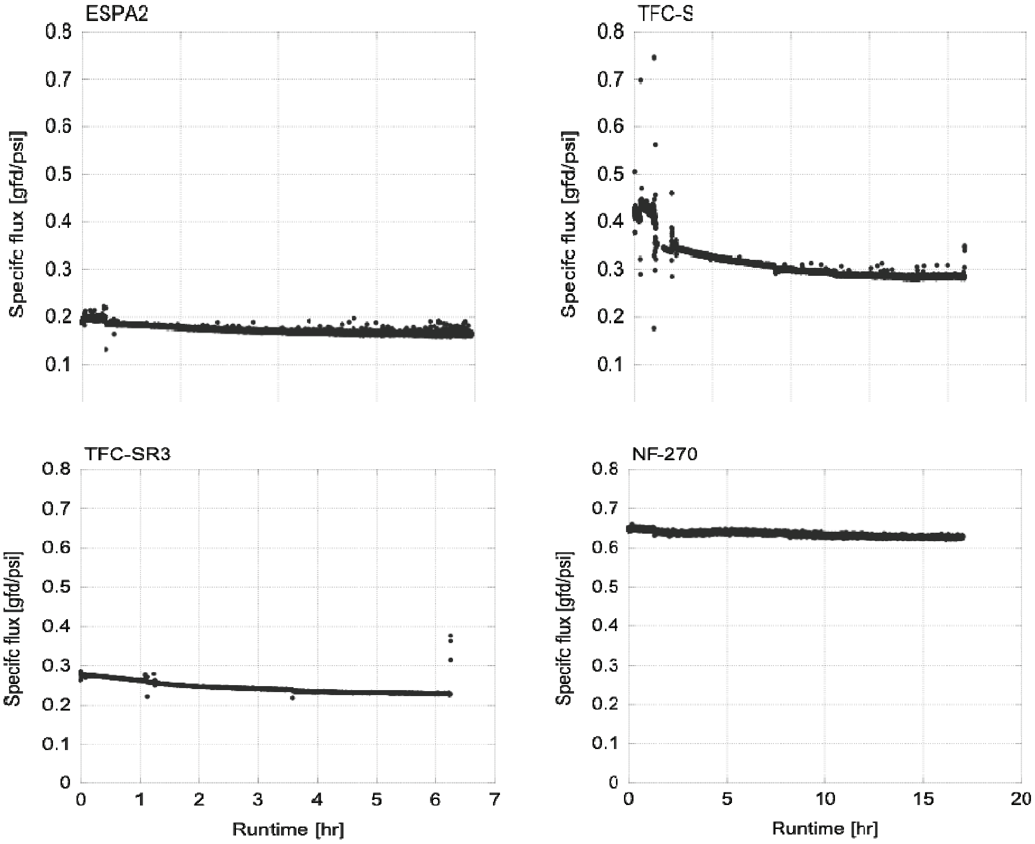

Figure 5.2 Specific flux decline curves for the ESPA2 at 14 gfd permeate flux (top left), TFC-S at 14 gfd (top right), TFC-SR3 at 16 gfd (bottom left), and NF-270 at 16 gfd (bottom right).

In summary, the ESPA2 membrane exhibited minimal fouling in the first 20 h of operation but required a relatively high NDP to produce 14 gfd of permeate flux. The TFC-S and TFC-SR3 membranes required less NDP but exhibited slightly more flux decline than the ESPA2 membrane because of fouling. The NF-270 membrane required very little NDP to achieve 16 gfd and exhibited very little flux decline in the first 20 h of operation at the LVL. The bench-scale fouling tests presented in Figure 5.1 yielded results somewhat similar to what was observed during the two-element testing at the LVL. During bench-scale flat-sheet testing, the order of membranes exhibiting the least amount of flux decline because of fouling was NF-270 (<0 % decline) > TFC-SR3 (~8%) > ESPA2 (~18%) > TFC-S (~20%). During two-stage spiral-wound element tests, the order was NF-270 (3%) > ESPA2 (12%) > TFC-SR3 (20%, only tested for ~7 hours) > TFC-S (33%). The biggest difference between bench scale and laboratory scale was the performance of the TFC-SR3 and TFC-S (i.e., fouled more at lab scale), which may be related to the conditions of testing at the LVL, as the recovery was higher at lab scale (~20%) than at bench scale (~1%).

5.1.3 Rejection Performance Comparison

In addition to operational considerations rejection performances of the candidate membranes was evaluated using the two-element, spiral-wound 4040 membrane testing unit. Samples for water quality parameters relevant to the treatment of wastewater effluents were monitored, including TOC, UV absorbance, TN, ammonia and nitrate, major cations and anions, conductivity, and selected trace organic contaminants. Rejection was evaluated at permeate fluxes of 12 and 18 gfd for the ESPA2 and the TFC-S membranes. Because of the high permeability of the NF-270 membrane, however, experiments could not be performed at 12 gfd, and for the TFC-SR3 and NF-270 membranes, experiments were conducted at 18 gfd only.

The rejection of TOC, nitrate, and conductivity by the candidate membranes is presented in Figure 5.3 at a permeate flux of 18 gfd. The ESPA2 and TFC-S membranes provided more than 80% rejection of TOC, nitrate and conductivity while the NF membranes TFC-SR3 and NF-270 had lower rejection for nitrate, and conductivity. Somewhat surprisingly, the NF-270 membrane exhibited only 84% rejection of TOC. A past study undertaken revealed that the NF-270 membrane could provide more than 90% rejection of TOC (Drewes et al., 2008). During testing, feed water nitrate concentrations were variable (0.92–5.71 mg-N/L); despite the low rejection of nitrate by the “loose” NF membranes (TFC-SR3 and NF-270), when testing of these membranes was conducted, feed water nitrate concentrations were low (~4 mg-N/L), which resulted in permeate concentrations of less than 5 mg-N/L, set as a limit for groundwater recharge applications by the CDPH.

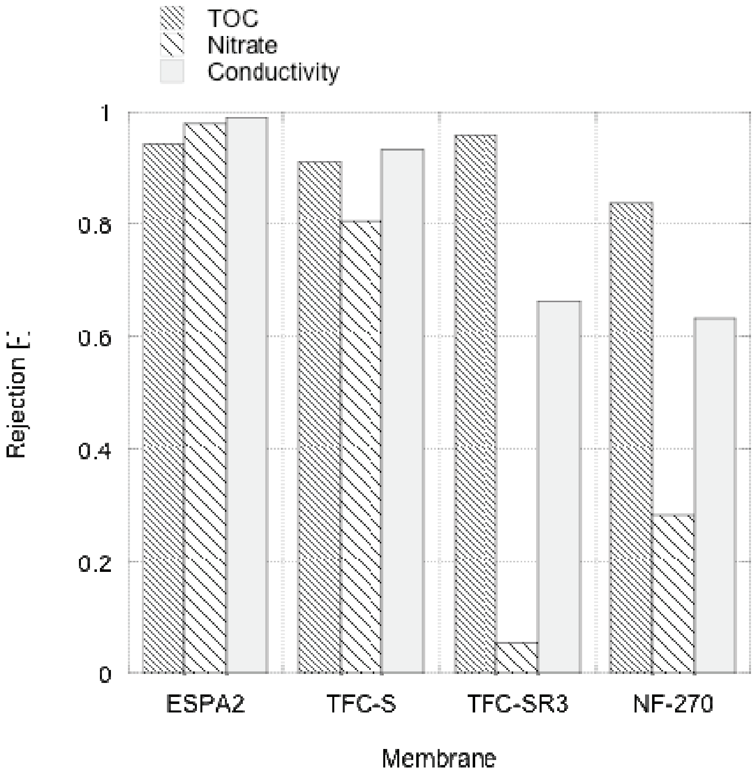

Figure 5.3 The rejection of TOC, nitrate, and conductivity by the candidate membranes at a permeate flux of 18 gfd.

The performance of the benchmark membrane (ESPA2) and candidate NF membranes (TFC-S, TFC-SR3, and NF-270) in rejecting trace organic contaminants was assessed at the LVL using the two, spiral-wound 4040 membrane testing units. For these experiments, chemical analysis was performed using the GC/MS method. Initially, rejection was to be assessed at two permeate fluxes (i.e., 12 and 18 gfd); however, the NF-270 and TFC-SR3 membranes could not be operated at the low-flux set point of 12 gfd because of their high permeability and therefore were tested only at 18 gfd. For each experiment, two feed samples (one each at the two fluxes, if possible) and two permeate samples (one at 12 gfd and one at 18 gfd, or replicates if experiments were performed only at 18 gfd) were collected. A summary of feed water contaminant concentrations detected and/or quantified in LVL feed water using the GC/MS method is presented in Table 5.2. The chlorinated flame retardants (i.e., TCEP, TCPP, and TDCPP) had the highest concentrations of the compounds that were quantified in the feed water. Similarly to past studies, PhACs (e.g., ibuprofen, gemfibrozil, ketoprofen, and diclofenac) were also quantified in LVL feed water.

Table 5.2 Contaminants Detected/Quantified in LVL Feed Water during Candidate Membrane Testing (5/22/2009 and 6/19/2009)

Compound	Average (*n* = 8) ng/L	SD ng/L
TCEP	809	282
TCPP	2188	687
Ibuprofen	26	6
Mecoprop	ND (6)-42	NA
Gemfibrozil	218	78
TDCPP	995	193
Naproxen	64	36
Ketoprofen	ND (6)-42	NA
Diclofenac	16	4

SD = standard deviation
ND = not detected (less than 3:1 signal to noise ratio)
NA = not applicable

A summary of the permeate sample concentrations of the detected and/or quantified trace organic contaminants is presented in Table 5.3. An increase in rejection is expected with an increase in permeate flux, but because the difference between the flux set points investigated was small (i.e., 12 and 18 gfd) and the error associated with the GC/MS method is significant, little difference in permeate concentration was observed between 12- and 18-gfd samples for the ESPA2 and TFC-S. Because no discernible difference was observed, results for these membranes were averaged. None of the compounds quantified in the feed water were detected or quantified in ESPA2 membrane permeate samples for either 12- or 18-gfd experiments. A few compounds were quantified in permeate samples collected during candidate NF membrane experiments, but at relatively low concentrations. The candidate NF membrane reduced feed water concentrations of negatively charged organic compounds (i.e., ibuprofen, mecoprop, gemfibrozil, ketoprofen, and diclofenac) below the quantification level. The candidate membranes, however, exhibited variable rejection for the nonionic flame retardants TCEP and TCPP. Concentrations of TCEP and TCPP were less than 100 ng/L in permeate samples taken for the TFC-S and NF-270 membranes.

Table 5.3. Trace Organic Contaminants in Permeate Samples

	Membrane			
	ESPA2[a] (*n* = 4)	TFC-S[a] (*n* = 2)	TFC-SR3[b] (*n* = 2)	NF-270[b] (*n* = 3)
Compound	**ng/L**	**ng/L**	**ng/L**	**ng/L**
TCEP	ND	53	145	79
TCPP	ND	79	24	48
Ibuprofen	ND	ND	ND	NQ
Mecoprop	ND	ND	ND	ND
Gemfibrozil	ND	23	ND	ND
TDCPP	ND	ND	ND	ND
Naproxen	ND	ND	ND	ND
Ketoprofen	ND	ND	ND	ND
Diclofenac	ND	NQ	NQ.	NQ

[a] ESPA2 and TFC-S membranes results are averaged values from 12- and 18-gfd experiments.
[b] TFC-SR3 and NF-270 membranes results are from 18-gfd experiments.
ND = not detected (<3:1 signal:noise).
NQ = not quantified (<11:1 signal:noise).

5.1.4 Membrane Selection for Pilot-Scale Testing

Based on the findings from the candidate membrane evaluation, the NF-270 membrane was selected for pilot-scale testing. The NF-270 membrane was selected because of its high specific flux and low fouling potential compared to the other membranes. Although NF-270 has lower rejection for nitrate, LVL feed water nitrate concentrations were below 5 mg/L during pilot testing and, thus, the poor rejection of the NF-270 membrane could potentially not be an issue.

5.2 Pilot-Scale Testing

5.2.1 ESPA2 Membrane Testing

The overall goal of this study is to maximize the overall recovery of an IMS employed at the LVL or other facilities. For the pilot-scale testing portion of the study, we realized that running under conditions similar to the LVL RO train (i.e., low feed-flow rate, low permeate flux, and high recovery) would not allow us to push recovery and operate within manufacturer-specified conditions, which would likely result in major operational issues. Based on past experience with membrane systems treating municipal wastewater effluents, we feel that it has been demonstrated that a system can operate under stable conditions with operational set points of a 10- to 12-gfd permeate flux and 80 to 85% recovery. However, these set points appear to have been selected somewhat arbitrarily, and there is little understanding of how far permeate flux and recovery can be pushed while stable operation is maintained. Therefore, for the pilot-scale portion of this study and with an LVL expansion in mind, an experimental matrix was developed to evaluate the effect of permeate flux and recovery on operation when the ESPA2 membrane was utilized.

As mentioned in Chapter 4, the full-scale system at the LVL had been off-line because second-stage aluminum silicate scaling issues, which had presumably been solved by replacing the second-stage membranes and switching to ferric coagulant at the wastewater treatment plant feeding the LVL (TT, 2008). Pilot-scale testing of the ESPA2 membrane was conducted to determine if the previous issues had been resolved and to determine the maximum system recovery and permeate flux that the ESPA2 membrane could be operated at without negatively impacting operation. To establish a baseline performance, the ESPA2 membrane was operated at 83 to 84% recovery and 12 gfd permeate flux for 100 h. Subsequently, the system was adjusted to 15 to 16 gfd permeate flux at a system recovery of 85%. The system was operated at this set point for approximately 550 h, after which the system set points were adjusted to 15 to 16 gfd and 87% recovery, followed by an additional 500 h of testing. Proposed operational set points are summarized in Table 5.4.

Table 5.4 Proposed Operational Set Points and Runtime for Testing of the ESPA2 Membrane

Purpose	Set Point	Runtime (hr)
Establish baseline	12 gfd, 83–84% recovery	100
Evaluate elevated permeate flux at current LVL recovery	15 gfd, 85% recovery	500
Evaluate elevated permeate flux at elevated recovery	15 gfd, 87% recovery	500

5.2.1.1 Baseline Conditions and 85% Recovery at 15 gfd

Figure 5.4 presents the temperature-corrected specific flux (TCSF) of the ESPA2 membrane from start-up until approximately 650 h of testing. The initial baseline conditions of a 12-gfd permeate flux and 83 to 84% recovery resulted in a stable specific flux value of 0.12 gfd/psi for approximately 100 h. After 100 h of operation, the system set points were adjusted to 15 gfd and 85% recovery, which was followed by a significant decrease in the specific flux over the subsequent 550 h of testing. Further analysis revealed that decrease in the specific flux was the result of severe fouling/scaling in the second stage, resulting in a shift of the total permeate flow into the first stage (Figure 5.5). Toward the end of the 550-h testing period at 15 gfd, very little permeate flow was produced by the second stage.

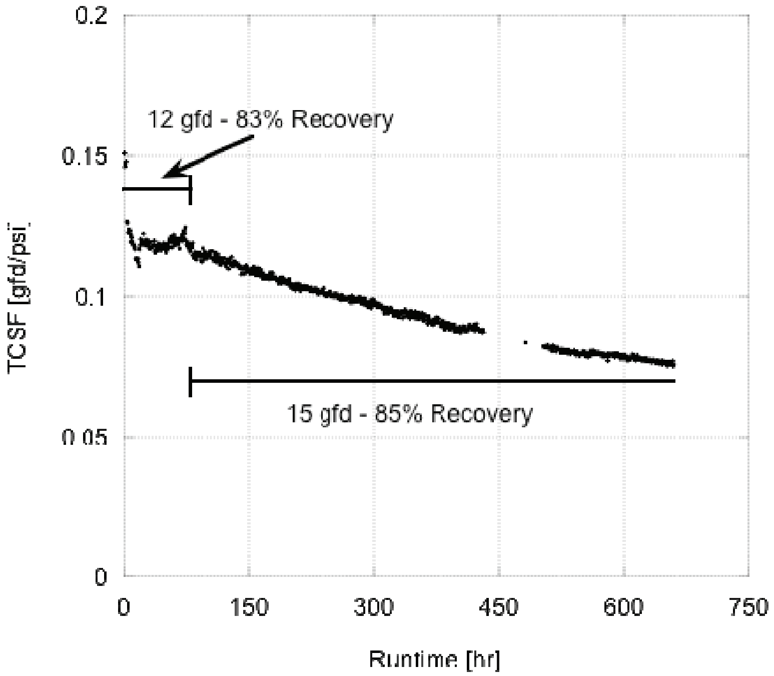

Figure 5.4 Temperature-corrected specific flux (gfd/psi) for the ESPA2 membrane prior to membrane cleaning. Membrane operated at a permeate flux of 12 gfd and system recovery of 83–84% for 100 h. During the final 500 h, the membrane was operated at a permeate flux of 15 gfd and a system recovery of 85%.

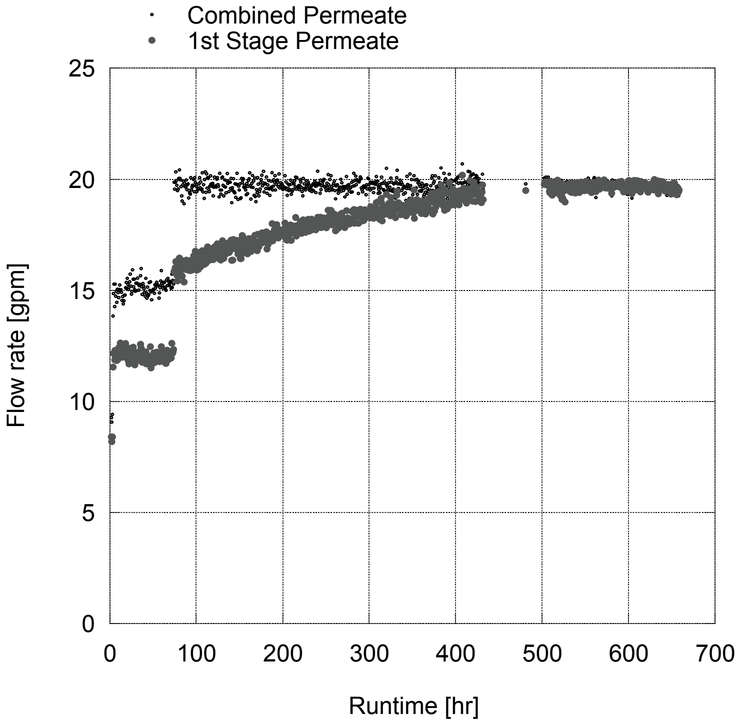

Figure 5.5 Total and first-stage permeate flow during testing. Membrane operated at a permeate flux of 12 gfd and system recovery of 83–84% for 100 h. During the subsequent 550 h, the membrane was operated at a permeate flux of 15 gfd and 85% system recovery.

5.2.1.2 Scaling and Membrane Cleaning Strategy

A membrane cleaning was performed to restore the permeate flow in the second stage. For the clean-in-place (CIP), a two-pronged approach was taken. The first was to remove organic foulants using a blend of sodium dodecylbenzene sulfonate (CalSoft-90) and EDTA at pH 11, and the second to remove inorganic scales using citric acid at pH 3-4. Cleaning was performed for each stage independently with circulation of the cleaning solutions for 60 min. The specific flux of the ESPA2 membrane after cleaning is presented in Figure 5.6. The cleaning strategy was effective in restoring the permeability of both the first and second stages and the specific flux of the system; however, the organic cleaning solution appeared to remove very little organic material from the membrane system. Subsequent cleanings were performed with citric acid only, which was found to be as effective as the two-pronged cleaning approach (Figure 5.6). This cleaning strategy, however, is expected to be successful only for removing inorganic scale with a higher solubility at a lower pH. A cleaning protocol was established where the pilot system was shut down, and citric acid was circulated throughout the second-stage for 1 h. The modified procedure took approximately 1.5 h to complete and resulted in the reestablishment of second-stage permeability.

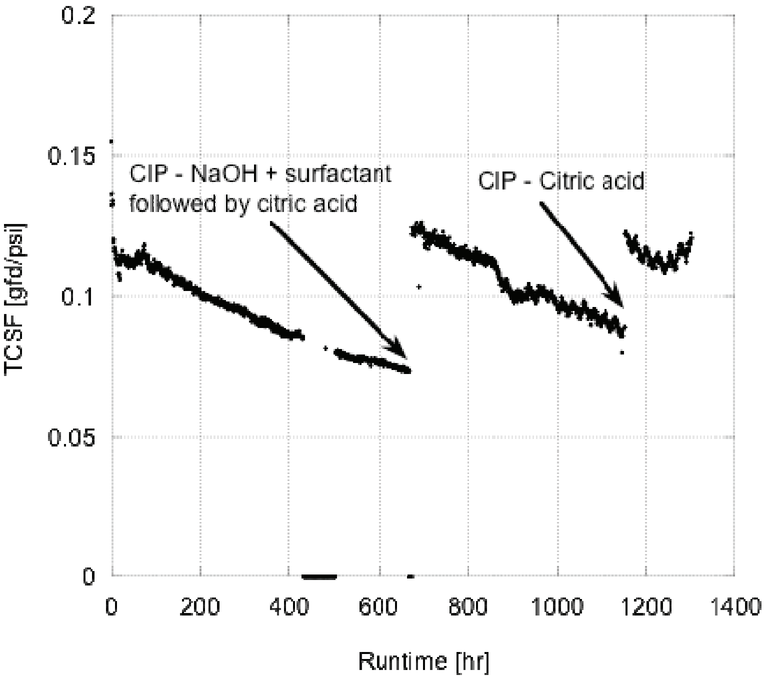

Figure 5.6 Temperature-corrected specific flux (gfd/psi) for the ESPA2 membrane prior to and after membrane cleaning.

This scaling issue has also been encountered during full-scale operation at the LVL. Figure 5.7 presents the specific flux of the ESPA2 membrane at full scale at the LVL since the second-stage membrane elements were replaced. The system has exhibited a decrease of approximately 20% in the specific flux since the second-stage elements were replaced. The facility also monitors the permeate flow rate from one vessel from both the first and second stage. The monitored first- and second-stage permeate flow rates since the last vessel was replaced are presented in Figure 5.8. Similarly to what was observed during pilot-scale testing, the permeability of the second stage has been decreasing faster than that in the first stage, especially over the last 600 h of operation. It is hypothesized that the pilot-scale second stage fouled much more quickly because of the elevated flux, which was 50% higher than at the full-scale facility.

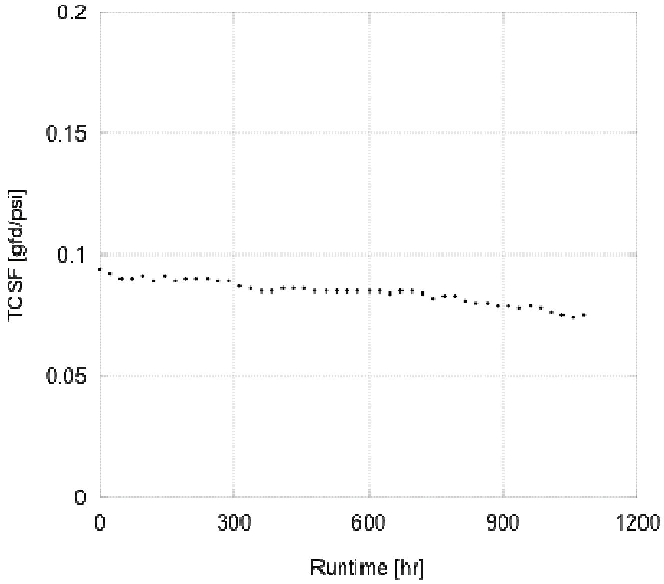

Figure 5.7 Full-scale specific flux for the ESPA2 membrane since the second-stage membranes were replaced.

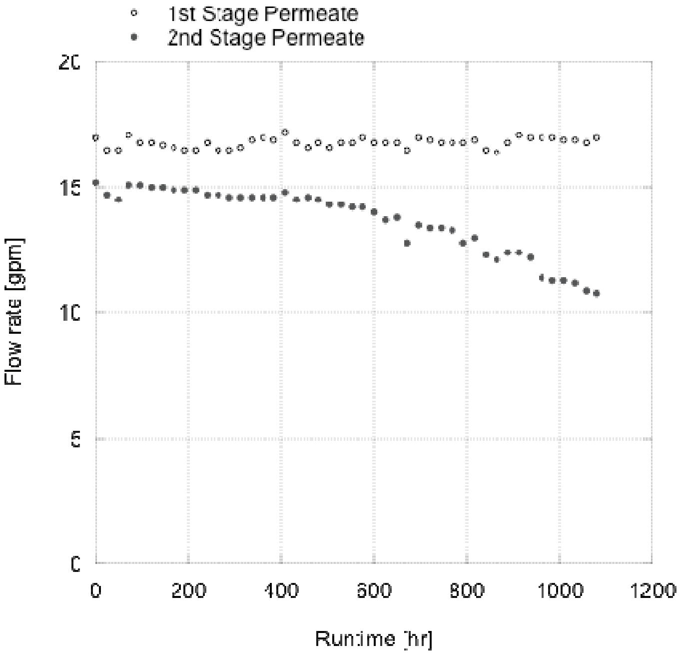

Figure 5.8 First- and second-stage permeate flow rates from vessels in the full-scale system.

During CIP events using citric acid, the solution was circulated through the system back to the CIP tank for approximately 1 h. During this time, a large number of gas bubbles were liberated, which were assumed to be CO_2 produced by the dissolution of $CaCO_3$. Citric acid is also an effective method for removing calcium phosphate scale, although based on water quality analysis, phosphate concentrations in LVL feed water are low (generally less than 1 mg/L). A sample of the CIP solution was collected prior to and after cleaning with citric acid. Analysis by ICP showed significant increases in calcium, sulfur, phosphorus, and silica during the CIP. Without pH adjustment, the Langelier Saturation Index (LSI) of the concentrate from the pilot-scale system was calculated to be 1.9, which indicates that deposition of $CaCO_3$ is favorable.

One ESPA2 membrane was removed from the second stage of the pilot-scale system (and was replaced with a new ESPA2 membrane) and shipped to CSM for membrane autopsy. The membrane was sacrificed and visually inspected, and the surface analyzed by ESEM, EDS, and field emission ESEM/EDS. During the visual inspection, no discoloration was observed; however, some very fine crystals could be observed. ESEM analysis showed a fairly homogenous scaling layer on the surface of the membrane with both amorphous and crystalline solids (Figure 5.9). Field emission ESEM/EDS analysis showed distinct peaks for calcium, phosphorus, carbon, oxygen, and magnesium. Small peaks were observed for sodium, silica, and sulfur.

Additional analysis with RO system design tools (from Hydranautics and Koch) indicated that calcite precipitation would be the major scalant. Additional analysis with speciation software (Visual MINTEQ) showed that calcite ($CaCO_3$) and hydroxyapatite ($Ca_5(PO_4)_3OH$) could potentially precipitate on the membrane surface. These minerals, however, are generally crystalline in nature, and much of the scale observed on the ESPA2 membrane was amorphous.

Although some researchers have observed amorphous or sludge-like calcium carbonate scale on membrane surfaces, the nature of the scale indicates a combination of calcium carbonate and amorphous calcium phosphate. Currently, the feed water at the LVL is not acidified, as previous research demonstrated that aluminum silicate fouling was exacerbated by adjusting the pH. With the aluminum problem currently under control, adjusting the pH along with the antiscalant would increase the solubility of both calcium carbonate and calcium phosphate and potentially address the scaling issue. Unfortunately, obtaining sulfuric acid took longer than expected and only a portion of ESPA2 membrane testing was performed with acidified feed water (see next section).

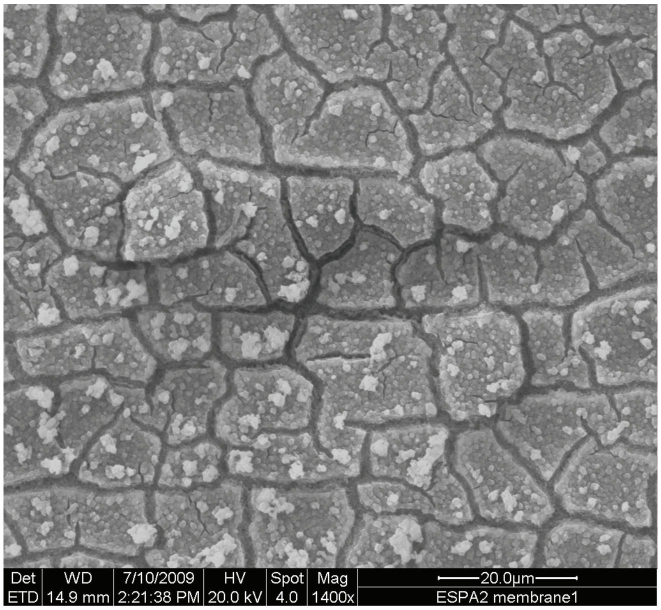

Figure 5.9 ESEM image of the sacrificed ESPA2 membrane (1400× magnification).

5.2.1.3 ESPA2 Testing at 85% Recovery and 15 gfd

Once the CIP strategy was developed, testing resumed with the ESPA2 membrane at 85% recovery and 15 gfd permeate flux. During the 500 h of testing at this set point, one CIP was performed (Figure 5.10) as a result of a decrease in the second-stage permeate flow rate and a subsequent increase in the first-stage permeate flow rate (Figure 5.11). Somewhat surprising, operation at this set point remained relatively stable over the last 350 h of testing (Figure 5.10), and no CIPs were performed. Before switching to the next set point, a citric acid CIP was performed on both the first and second stages of the membrane system.

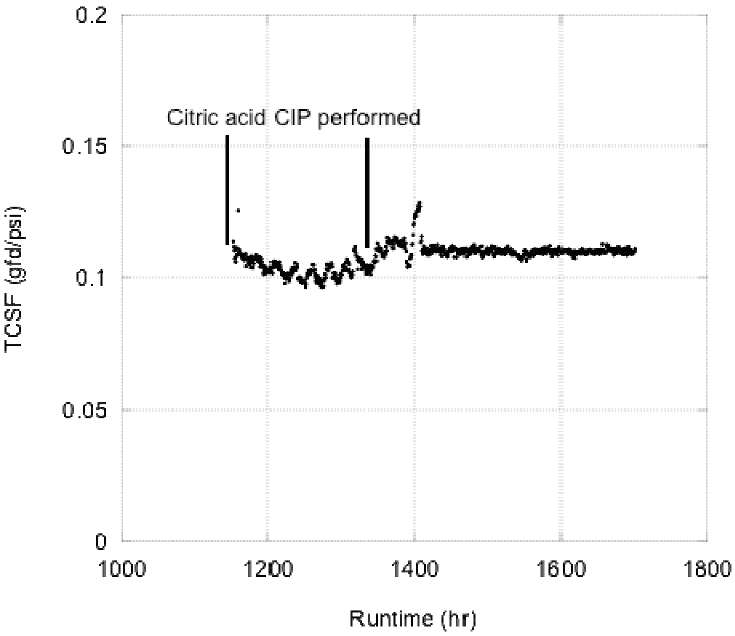

Figure 5.10 TCSF for the ESPA2 membrane at 15 gfd permeate flux and 85% recovery.

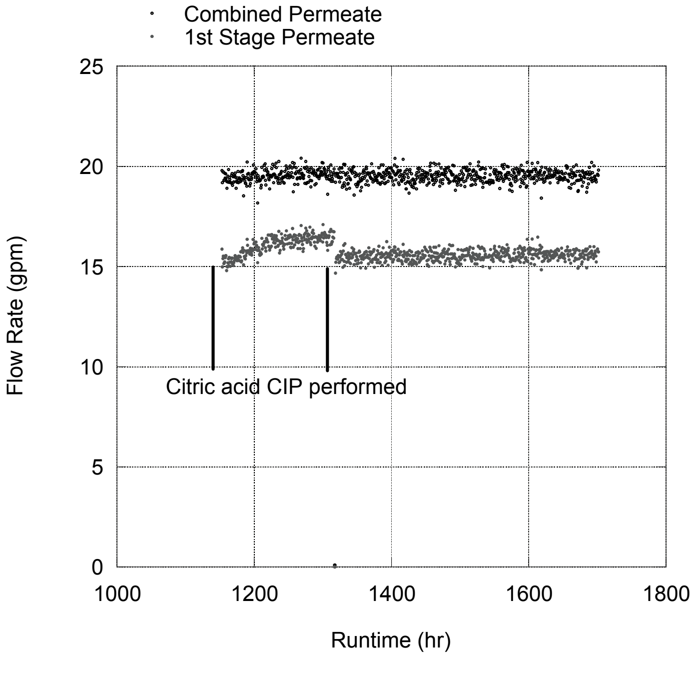

Figure 5.11 Combined permeate (black symbols) and first-stage permeate (gray symbols) flow rate versus runtime for the ESPA2 membrane at 15 gfd and 85% set point.

5.2.1.4 ESPA2 Testing at 87% recovery and 15 gfd

The specific flux during ESPA2 membrane testing at 15 gfd permeate flux and 87% system recovery is presented in Figure 5.12. During the first week of operation, the ESPA2 membrane lost approximately 1.5% of permeability per day, which is similar to the other operational set points tested. Prior to a CIP, the sulfuric acid dosing system was installed, and the feed-water pH was adjusted to 6.3. The acid adjustment resulted in the recovery of a portion of the second stage permeability (which had declined in the first 200 h of operation), resulting in an increase in the TCSF. At a pH of 6.3, the LSI was calculated to be 0.5. Although this period of testing was short, operation at a feed water pH of 6.3 continued for approximately 80 h, and the TCSF was relatively stable (Figure 5.12). Maintaining a pH of 6.3 required a relatively large volume of sulfuric acid, and to reduce the number of times the operator switched drums, the desired feed water pH was set to 6.8 at approximately 2000 h of runtime. The result was a steady decline in the TCSF until it was stabilized. The acid adjustment to a feed water pH of 6.3 appeared to have a positive effect on the performance of the ESPA2 membrane (Figure 5.13); however, because the flux stabilized after 2100 h and a period of decline, other factors besides pH may have contributed to the flux decline. Based on the constituents analyzed, the feed water quality during testing was relatively stable, and no one component of the feed water could be used to explain variations in observed flux decline.

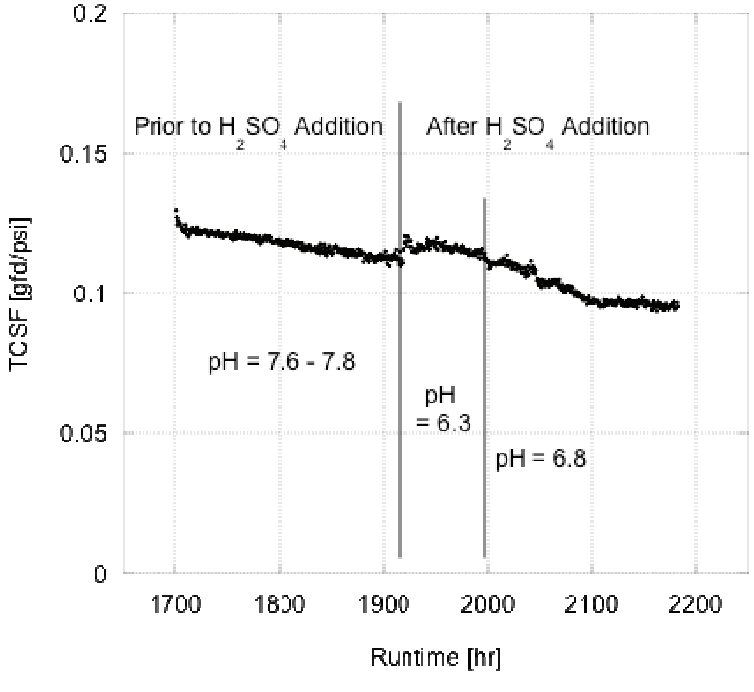

Figure 5.12 TCSF for the ESPA2 membrane at 15 gfd permeate flux and 87% recovery.

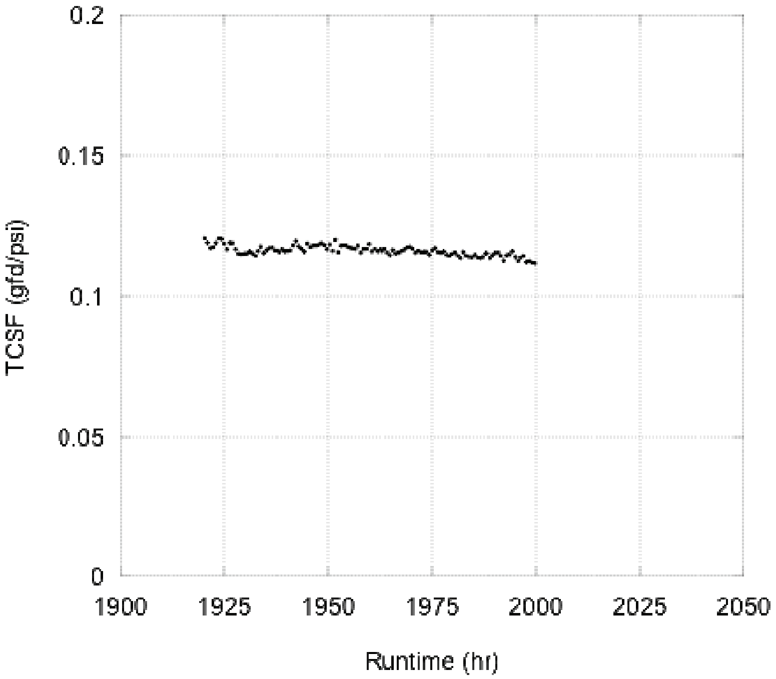

Figure 5.13 TCSF during ESPA2 membrane when the feed water pH was adjusted to 6.3.

5.2.1.5 Water Quality

Summarized TOC, nitrate, and conductivity results for ESPA2 membrane pilot-scale testing are presented in Table 5.5. During the initial phase of testing, the ESPA2 achieved good rejection of nitrate, TOC, and conductivity. Lower rejection values, however, were observed during elevated flux and recovery experiments. During periods of ESPA2 membrane operation, when the specific flux was low as a result of inorganic scaling, second-stage permeate conductivity, TOC, and nitrate concentrations were elevated, which lowered overall rejection. The adverse effect from scaling is assumed to be due to cake-enhanced concentration polarization.

Table 5.5 Summarized TOC, Nitrate, and Conductivity Results during ESPA2 Membrane Pilot-Scale Testing

Parameter	LVL Feed	Combined	Rejection
12 gfd 83%			
TOC (mg/L)	5.46 (0.67)	0.33 (0.07)	0.939
NO_3-N (mg/L)	2.3 (1.3)	0.06 (0.22)	0.887
Conductivity (mS/cm)	0.98 (0.03)	0.02 (0.001)	0.983
15 gfd 85 and 87%			
TOC (mg/L)	6.49 (0.24)	0.38 (0.12)	0.966
NO_3-N (mg/L)	3.00 (1.3)	0.32 (0.13)	0.893
Conductivity (mS/cm)	0.92 (0.03)	0.05 (0.002)	0.946

During pilot-scale testing of the ESPA2 membrane, samples were collected for trace organic contaminant analysis by GC/MS and LC/MS/MS. None of the compounds quantified in LVL feed water by the GC/MS method were detected in ESPA2 membrane permeate samples (Table 5.6). Samples were also collected and analyzed by LC/MS/MS. The results are presented in Table 5.7. Two of the compounds quantified in the feed water, atenolol and TCEP, were quantified in permeate samples.

Table 5.6 Trace Organic Contaminants in Permeate Samples during Pilot-Scale Testing of the ESPA2 Membrane[a]

Compound	5/22/09	6/19/09
TCEP	ND	ND
TCPP	ND	ND
Ibuprofen	ND	ND
Mecoprop	ND	ND
Gemfibrozil	ND	ND
TDCPP	ND	ND
Naproxen	ND	ND
Ketoprofen	ND	ND
Diclofenac	ND	ND

[a]Analysis was performed by the GC/MS method.
ND = not detected

Table 5.7 Trace Organic Contaminants in Permeate Samples during Pilot-Scale Testing of the ESPA2 Membrane (5/22/09)[a]

LC/MS/MS Compound	ESPA2 Average Feed (n ng/L	ESPA2 Average Perm (n = 2) ng/L
Diclofenac	3	ND
Triclosan	8	ND
Gemibrozil	180	ND
Ibuprofen	88	ND
Ketoprofen	20	ND
Naproxen	38	ND
Atenolol	854	48
Cabamazepine	191	ND
DEET	155	ND
Dilantin	191	ND
Fluoxetine	22	ND
Meprobamate	571	ND
Primidone	125	ND
Sulfamethoxazole	59	ND
TCEP	404	15
TCPP	1358	ND
TDCPP	1169	ND

[a]Analysis was performed by the LC/MS/MS method.
ND = not detected (< 8:1 signal:noise).

5.2.1.6 Conclusions from ESPA2 Testing

Pilot-scale testing at the LVL was conducted for a total of 2200 h. Significant second-stage inorganic scaling occurred, resulting in the need for several CIPs to restore second-stage permeability. Based on testing, the following can be concluded:

- During testing, both pilot- and full-scale systems had second-stage scaling issues. Based on pilot-scale testing, CIP with citric acid was an effective method for reversing the loss of permeability caused by scaling; however, little organic fouling was observed during pilot-scale testing, which may be more severe for other membrane applications treating wastewater.

- When CIPs were performed more frequently, operation at 85% recovery and 15 gfd permeate flux was relatively stable. The facility currently operates at a flux of 10 gfd, and therefore full-scale operation at 15 gfd would result in a 50% increase in permeate produced per day.

- Although the period of testing was short, operation at 87% recovery and 15 gfd was relatively stable when the feed water pH was adjusted to 6.3. Overall, however, operating at this set point resulted in an increase in 1.8 psi per day to maintain the permeate flow rate set point. It is worth noting that one potential issue of operating at 87% recovery with lowered feed water pH is silica scaling, which could result in increased second-stage flux decline.

- The feed pressure of the full-scale system currently increases between 1 to 3 psi per day, based on operational data from August 2009 until February 2010.

- The full-scale system is not currently pH-adjusted. Based on pilot-scale results, pH adjustment may help remedy the scaling issue and allow the facility to operate at a higher permeate flux and recovery.

- Current full-scale CIPs utilize separate NaOH and citric acid cleanings, which take approximately 4 days to complete. Based on pilot-scale results, organic fouling did not appear to be an issue, and citric acid alone was effective for restoring most, if not all, of the initial permeability of the membrane. The development of an efficient system for semi-regular citric acid cleaning could allow the system to operate at higher recovery.

5.2.2 NF-270 Membrane Testing

5.2.2.1 Operation

The NF-270 membrane TCSF curves generated during 85 and 87% recovery experiments are presented in Figures 5.14 and 5.15, respectively. Both experiments were conducted at a permeate flux of 15 gfd and a feed water pH of 6.3 (adjusted with concentrated sulfuric acid). In contrast to the ESPA2 membrane, no loss of permeability was observed during the 85% recovery experiments. In addition, the TCSF was approximately two to three times greater than the ESPA2 membrane due to the NF-270 membrane's low pressure requirements (approximately 70 psig to achieve 85% recovery at 15 gfd). At 87% recovery, a higher amount of flux decline was observed, approximately 0.5% per day, which is significantly lower than the flux decline rate observed for the ESPA2 membrane. CIPs with citric acid were performed at the termination of each experiment. The liberation of gas bubbles from the CIP tank was minimal during both CIPs, indicating that little calcium carbonate scale developed on the membrane during testing.

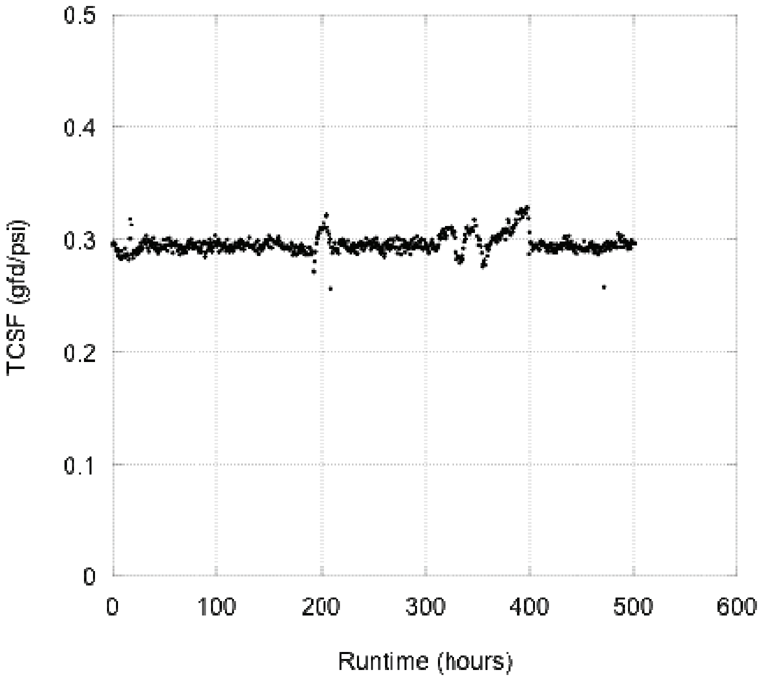

Figure 5.14 TCSF of the NF-270 membrane at 85% recovery and 15 gfd permeate flux experiments.

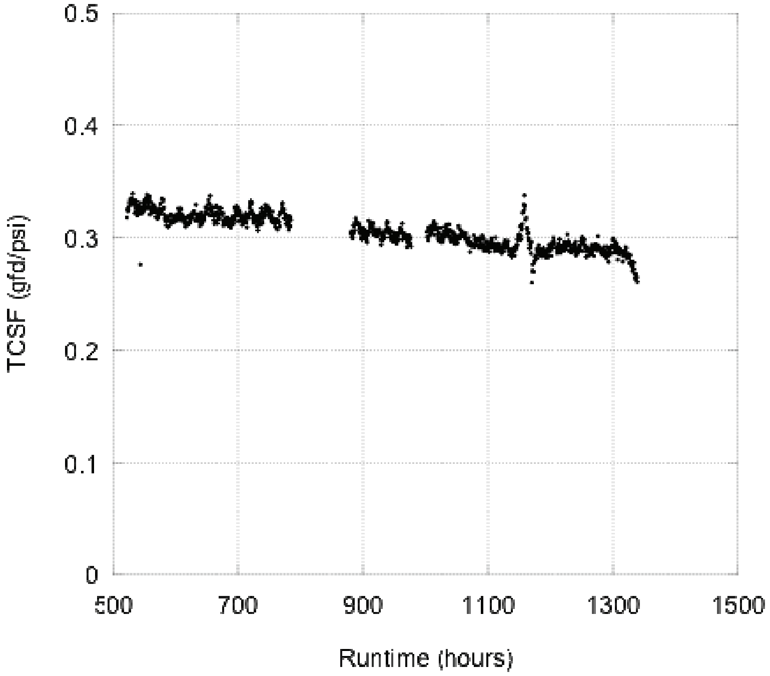

Figure 5.15 TCSF of the NF-270 membrane at 87% recovery and 15 gfd permeate flux experiments.

5.2.2.2 Water Quality

Summarized TOC, nitrate, and conductivity results for two sampling campaigns per operational set point during NF-270 membrane pilot-scale testing (at 24 h of operation and at 500 h of operation) are presented in Table 5.8. Although nitrate rejection was below zero, feed concentrations were less than 3 mg-N/L. A comparison of nitrogen data generated during this study versus historical sampling campaigns is presented in Table 5.9. Past nitrate concentrations were almost double the concentrations observed during this study. Permeate TOC concentrations for the sampling campaigns were slightly above the CDPH Draft Groundwater Recharge Regulation TOC limit of 0.5 mg/L, assuming a recycled water contribution of 100%.

Samples were also collected more frequently (a total of 18 samples) for feed and permeate TOC concentrations. The results for the NF-270 membrane are presented in Figure 5.16 as a box and whisker plot. Although these samples were taken over a range of operating conditions, permeate TOC concentrations were relatively consistent, with an average of 0.62 mg/L and 75% of samples having less than 0.7 mg/L. A similar figure for UV-254 absorbance measurements is presented in Figure 5.17. The majority of NF-270 membrane permeate samples had UV-254 less than 0.5 cm^{-1}. As a comparison, ESPA2 membrane UV-254 absorbance was less than 0.25 cm^{-1} for all samples collected and analyzed.

Table 5.8 Summarized TOC, Nitrate, and Conductivity Results during NF-270 Membrane Pilot-Scale Testing[a]

Parameter	LVL Feed Water	Combined Permeate	Rejection
	15 gfd 85%		
TOC (mg/L)	6.28	0.52	0.918
NO_3-N (mg/L)	2.66	2.87	-0.079
Conductivity (ms/cm)	0.98	0.57	0.418
	15 gfd 87%		
TOC (mg/L)	6.19	0.53	0.914
NO_3-N (mg/L)	2.3	2.46	-0.065
Conductivity (ms/cm)	0.96	0.62	0.360

[a]Average values, *n* = 2, taken at 24 and 500 h of operation.

Table 5.9 Summarized Nitrogen Data Generated during This Study and Historic Sampling Campaigns

	Feed (6/2–10/5)		Historic (2005–2007)	
	Average (mg-N/L)	SD (mg-N/L)	Average (mg-N/L)	SD (mg-
Nitrate	2.66	1.00	5.66	1.56
Ammonia	1.21	0.45	1.19	1.00
Organic-N	NA	NA	1.21	0.7

NA = not applicable

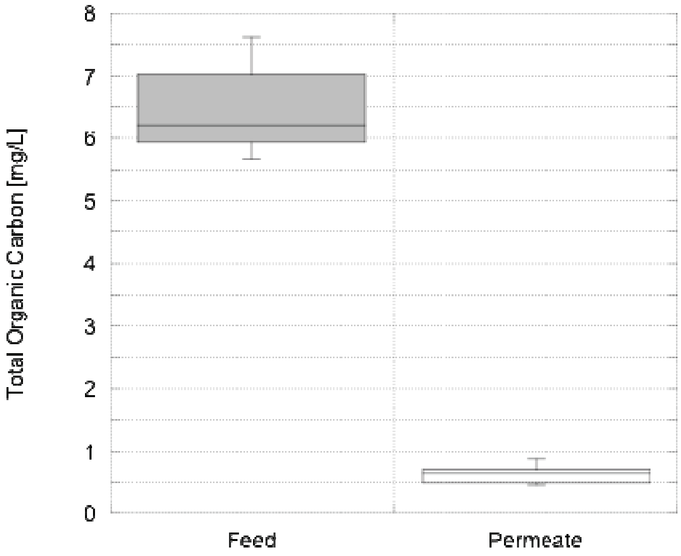

Figure 5.16 Box and whisker plot with feed and permeate TOC concentrations. (The box plot shows the maximum and minimum values and 25th, 50th, and 75th percentile concentrations, where *n* = 18.)

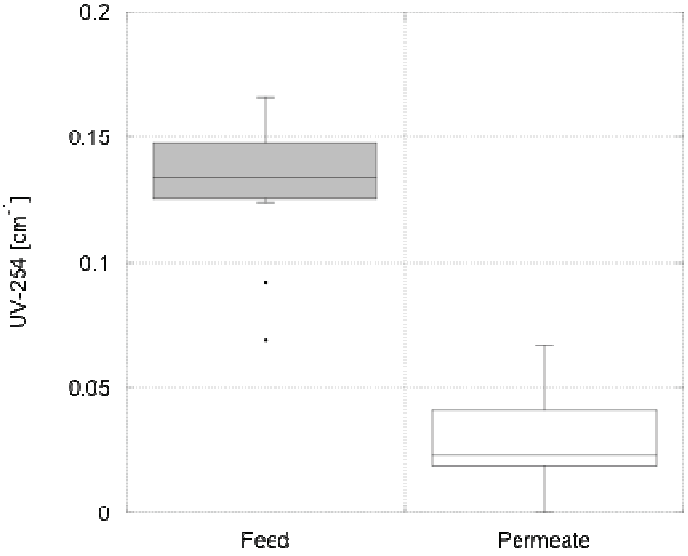

Figure 5.17 Box and whisker plot with feed and permeate UV-254 absorbance. (The box plot shows the maximum and minimum values and 25th, 50th, and 75th percentile concentrations, where *n* = 11.)

Trace organic contaminant results obtained during pilot-scale testing of the NF-270 membrane are presented in Table 5.10. Feed and permeate samples were collected for both 85 and 87% recovery experiments. Compared with the ESPA2 membrane, a few more compounds were detected/quantified in permeate samples. Atenolol and TCEP were found to have the lowest rejection; however, most compounds quantified in the LVL feed water were rejected at more than 90% by the NF-270 membrane. In addition, the difference in recovery appeared to have a small effect on rejection as 85% recovery conditions marginally improved rejection over 87% recovery conditions.

Table 5.10 Trace Organic Contaminants in Permeate Samples during Pilot-Scale Testing of the NF-270 Membrane[a]

Compound	87% Rec. Feed 1	85% Rec. Feed 2	87% Rec. Perm 1	85% Rec. Perm 2	87% Rej 1	85% Rej 2
Diclofenac	8	8	nd	nd	ND	ND
Triclosan	13	45	nd	4	ND	0.91
Gemibrozil	108	242	nd	nd	ND	ND
Ibuprofen	48	49	4	4	0.917	0.918
Ketoprofen	20	26	nd	nd	ND	ND
Naproxen	11	25	nd	nd	ND	ND
Atenolol	474	981	183	231	0.614	0.765
Cabamazepine	270	345	44	30	0.837	0.913
DEET	156	371	28	64	0.821	0.828
Dilantin	205	169	26	18	0.873	0.894
Fluoxetine	37	36	2	1	0.946	0.972
Meprobamate	900	906	92	84	0.898	0.907
Primidone	167	171	7	6	0.958	0.965
Sulfamethoxazole	124	305	3	4	0.976	0.987
TCEP	688	806	196	213	0.715	0.736
TCPP	NA	NA	NA	NA	NA	NA
TDCPP	NA	NA	NA	NA	NA	NA

[a] Samples collected on 9/9/2009 for 85% and 9/10/2009 for 87% recovery conditions, and the analysis was performed by the LC/MS/MS method.
nd = not detected (< 8:1 signal:noise).
NA = method not developed for these compounds at time of the study.
ND = could not be determined because of permeate non-detect.

5.2.2.3 Conclusions from NF-270 Testing

Pilot-scale testing at the LVL was conducted for a total of 1100 h. Based on testing, the following can be concluded:

- The NF-270 membrane exhibited minimal flux decline when operating at 85% recovery and 15 gfd and maintained a specific flux two to three times higher than the ESPA2 membrane.
- At 87% recovery and 15 gfd, the specific flux decreased by approximately 0.5% per day, presumably due to scaling. This decline is significantly less than that observed for the ESPA2 membrane.
- The NF-270 membrane provided no rejection of nitrate; however, nitrate in the feed water was significantly lower than the CDPH requirement of 5 mg-N/L.
- The NF-270 membrane achieved more than 90% rejection of TOC; however, concentrations were approximately 0.6 mg/L on the average.
- More trace organic contaminants were quantified in the NF-270 membrane permeate samples versus ESPA2 membrane permeate samples, but concentrations were relatively low, generally less than 100 ng/L.

5.3 Water Quality Comparison between the ESPA2 and NF-270 Membranes

A summary of the major bulk constituent concentrations in LVL feed water is presented in Table 5.11. As previously discussed, the NF-270 membrane operated at a much higher specific flux than the ESPA2 membrane, requiring less than half of the feed pressure to achieve 15 gfd permeate flux. These savings in pressure and energy are partially due to the low rejection of dissolved ions compared with the ESPA2 membrane (Figures 5.18 and 5.19). Although nitrate was not removed by the NF-270 membrane, feed water concentrations were well below the 5 mg-N/L Draft CDPH Water Reuse Guideline. Permeate TOC concentrations, however, were generally between 0.5 and 0.6 mg/L, equating to approximately 90% TOC rejection by the NF-270 membrane.

Table 5.11 Major Bulk Constituents in LVL Feed Water (from four sampling campaigns with replicate for each campaign) during Pilot-Scale Testing

Constituent	Average	SD
Conductivity (us/cm)	1023.2	96.4
UV-254 (cm^{-1})	0.13	0.01
DOC	6.4	0.9
NO_3-N	2.66	1.0
Alkalinity (as $CaCO_3$)	216.0	21.0
Chloride	123.1	15.6
Calcium	54.2	9.4
Magnesium	14.5	4.0
Phosphate	0.4	0.4
Sodium	136.3	16.1
Silica	10.7	1.4

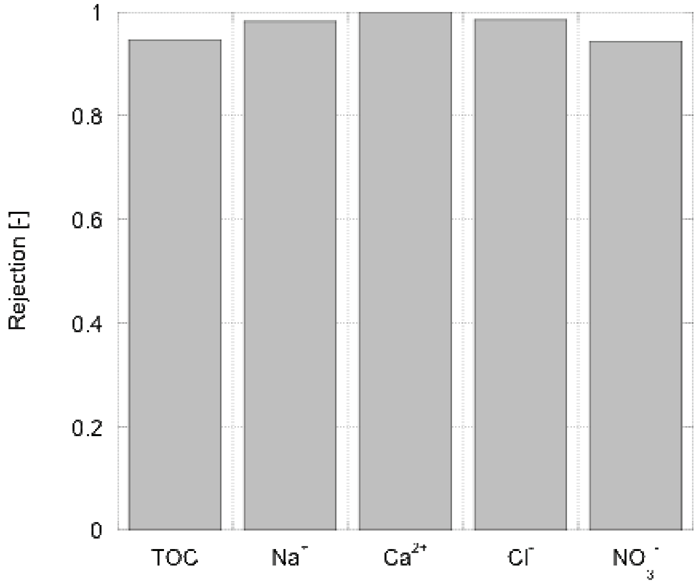

Figure 5.18 Rejection of bulk constituents by the ESPA2 membrane (85% recovery and 15 gfd permeate flux).

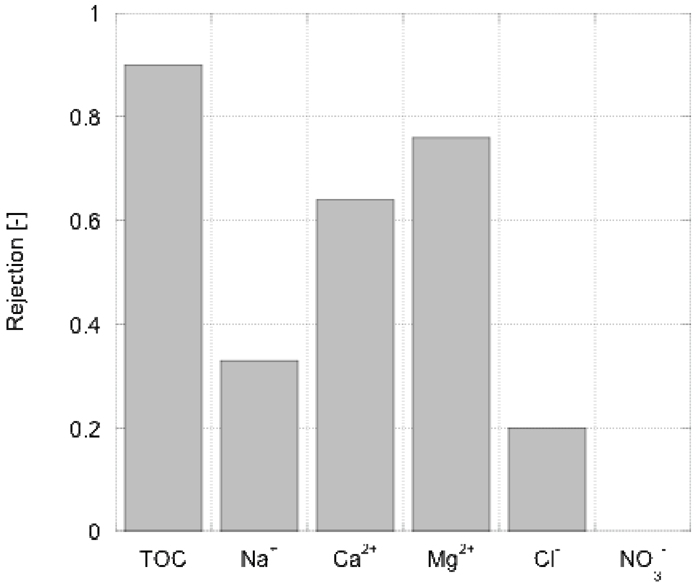

Figure 5.19 Rejection of bulk constituents by the NF-270 membrane (85% recovery and 15 gfd permeate flux).

Chapter 6

Recovery Enhancement through Treatment of Primary Brine

6.1 Desk-Top Brine Management Study

A bench-top analysis was initiated to examine the feasibility of further brine treatment with an additional membrane system. The following details are the preliminary findings of the exercise. The analysis was performed using the RO and NF design software from Hydranautics (IMS Design) and Dow/Filmtec (ROSA) and LVL feed water quality data.

6.1.1 Secondary RO with Final Effluent Blending

One possible scenario for reducing the brine volume would be to use a secondary membrane system to treat the brine from the primary membrane system. Such a scenario would not require that the primary system's recovery and permeate flux be elevated in order to produce less brine.

Using IMS Design, LVL feed water quality, and the current configuration and operating conditions of the LVL, the brine water quality was calculated (Table 6.1). The brine concentrations of constituents presented in Table 6.1 were then input into the IMS Design membrane simulation software (using the ESPA2 membrane) and the ROSA software (using the NF-270 membrane), using a one-stage membrane system to evaluate the feasibility of further membrane treatment. The system was designed to handle 370 gpm of brine from the primary membrane system and was modeled at 50% recovery. Such a system would result in an overall recovery of 92.5% at the LVL. Both programs can be used to model the rejection of inorganic ions; however, neither has an input for TOC, and thus the rejection of TOC was estimated from pilot-scale testing results.

Two scenarios were considered: one where the NF-270 membrane was the primary RO and one where the ESPA2 membrane was the primary RO (Figure 6.1). For the ESPA2 membrane primary system, two simulations were run where the NF-270 or the ESPA2 membrane was installed in the secondary system. For the NF-270 membrane primary system, only the ESPA2 membrane was considered for the secondary system. Mass balance calculations were performed to calculate the final concentration of constituents after the primary RO permeate (at a flow rate of 2080 gpm) was blended with the permeate from the additional brine treatment system (at 50% recovery, treating 367 gpm of brine would result in a permeate flow rate of 183.5 gpm), using both the ESPA2 and NF-270 membranes for further brine treatment.

Both brine treatment membrane simulations recommended that the pH of the feed water (in this case, brine from the primary RO) be adjusted at least below 6.5 to avoid calcium carbonate scaling (in addition to dosing the appropriate antiscalant). Barium sulfate saturation, however, was higher than the membrane manufacturer's specifications for both membranes, which could be an issue, although barium sulfate scaling was not observed during pilot-scale testing.

Table 6.1 Feed (Measured) and Brine (Simulated with IMS Design) Concentrations[a]

Constituent	**Feed Concentration (mg/L)**	**ESPA2 Brine Concentration (mg/L)**	**NF-270 Brine Concentration (mg/L)**
Sodium	165	1067.1	414.8
Calcium	67	443.8	280.3
Magnesium	15	99.4	69.1
Potassium	16	102.7	40.9
Ammonia	1.2	7.7	3.03
Barium	0.1	0.66	0.4
Strontium	0.7	4.64	2.9
Carbonate	0.7	4.7	6.75
Bicarbonate	294.1	1902	762
Sulfate	160	1062	1023.2
Chloride	115.4	756.4	155.75
Fluoride	0.8	5.2	0.62
Nitrate[b]	25	147.1	18.7
Silicon dioxide	8	52.5	12.1
TDS	883.8	5656	2790.4
TOC[c]	6.4	40.5	**39.5**
pH[d]	7.6	8.4	7.81

[a] Simulation performed at 85% recovery with the ESPA2 and NF-270 membranes using a membrane system mimicking the full-scale system.

[b] Nitrate value selected to represent the LVL historic average (2004–2007).

[c] TOC brine concentration estimated by assuming ROC rejection of 0.94 for ESPA2 and 0.916 for NF-270 (observed during pilot-scale experiments).

[d] pH does not have units and was unaltered for the simulation.

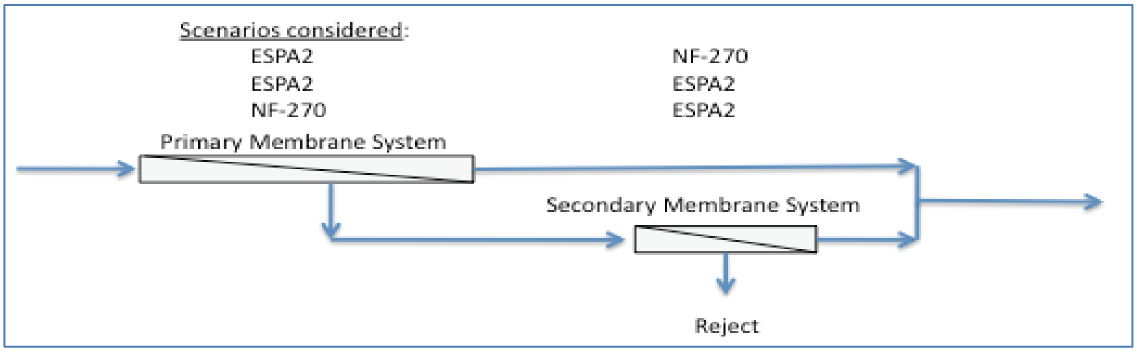

Figure 6.1 Schematic showing secondary membrane system.

6.1.1.1 ESPA2 Primary Membrane System

A comparison of membrane performance and permeate water quality is presented in Table 6.2. The NF-270 membrane offers advantages because of its low fouling and scaling properties and low feed pressure and energy requirement compared to the ESPA2 membrane but only provides partial rejection of ions. Because of the high rejection provided by the ESPA2 membrane for most constituents, blending the primary RO permeate with ESPA2 brine treatment would have a marginal impact on the water quality of the final blended permeate, with the exception of TOC, which was equal to the CDPH limit (Table 6.2). Because of the low rejection of ions by the NF-270 membrane, however, TDS in the final blend of primary RO permeate and NF-270 membrane permeate would increase by one order of magnitude over the current primary RO TDS concentration. In addition, by blending NF-270 membrane permeate, plant effluent TOC concentrations would be higher than the CDPH Draft Groundwater Recharge Regulation (0.5 mg/L, assuming a recycled water contribution of 100%, Table 6.3). The final effluent concentrations, however, would depend on the TOC and nitrate concentrations in LVL feed water.

Table 6.2 Operational Parameters, Permeate Water Quality, and Scaling Parameter Data Generated by Membrane Simulations for Brine Treatment[a]

	ESPA2	NF-270
Operational Parameters		
Feed pressure (psi)	135.4	41.6
Flux (gfd)	9.4	9.44
Permeate Water Quality (mg/L)		
Sodium	28.9	603.3
Calcium	2.5	120.8
Magnesium	0.6	22.03
Potassium	3.5	57.2
Ammonia	0.3	4.3
Barium	0.01	0.3
Strontium	0.02	1.2
Carbonate	0	0.1
Bicarbonate	35.5	639.9
Sulfate	8.8	43
Chloride	14.9	763.2
Fluoride	0.2	4.8
Nitrate[b]	20.9	163.8
Nitrate (mg-N/L)	4.72	36.99
Silicon dioxide	0.9	42.9
TDS	117.1	2466.7
pH	4.9	6.1
TOC[c]	2.43	3.48
Scaling Parameters for Concentrate		
LSI (%)	1	0.8
BaSO4 sat. (%)	19072	14903

[a] Simulation performed on a one-stage system (10 vessels, 7-8040 elements each), and operated at 50% recovery, 370 gpm feed-flow rate.

[b] Nitrate value selected to represent the LVL historic average.

[c] Estimated, based on TOC rejection observed during pilot study.

Table 6.3 Water Quality for the ESPA2 Membrane Primary RO System Blended with Permeate of Secondary ESPA2 and NF-270 Membranes for Brine Treatment

Constituent	Primary RO Perm (mg/L)	Blended with ESPA2 Perm (mg/L)	Blended with NF-270 Brine Perm (mg/L)
Sodium	4.37	6.36	52.94
Calcium	0.37	0.54	10.14
Magnesium	0.08	0.12	1.86
Potassium	0.53	0.77	5.13
Ammonia	0.03	0.05	0.38
Barium	0.001	0.00	0.03
Strontium	0.004	0.01	0.10
Carbonate	0.001	0.00	0.01
Bicarbonate	6.7	9.04	58.05
Sulfate	0.53	1.20	3.97
Chloride	1.53	2.61	63.29
Fluoride	0.02	0.03	0.41
Nitrate[a]	3.81	5.20	16.78
Nitrate (mg-N/L)	0.86	1.17	3.79
Silicon dioxide	0.1	0.16	3.57
TDS	18.4	26.41	216.93
TOC[b]	0.38	0.55	0.64

[a] Nitrate value selected to represent the LVL historic average (2004–2007).
[b] Estimated, based on TOC rejection observed during pilot study.

6.1.1.2 NF-270 Primary Membrane System

A simulation was performed to determine the final effluent quality when the primary NF-270 membrane system's permeate was blended with the secondary ESPA2 membrane system. This scenario was evaluated because of the operational advantages of the NF-270 membrane versus the ESPA2 membrane observed during pilot-scale testing, that is, a high specific flux and no specific flux decline because of fouling or scaling. The simulated ESPA2 secondary membrane system's permeate water quality, when treating NF-270 brine (water quality provided in Table 6.1), is presented in Table 6.4. The final blended effluent water quality is presented in Table 6.5. Because of the poor rejection of nitrate, the final effluent would have TN concentrations higher than 5 mg-N/L. The nitrate concentration used for LVL feed water was based on a historical average from 2004 to 2007, which was approximately twice as high as the concentration observed during pilot-scale evaluations. The final effluent TOC is also elevated over the CDPH limit.

Table 6.4 Operational Parameters, Permeate Water Quality, and Scaling Parameter Data Generated by Membrane Simulations for ESPA2 Membrane Brine Treatment[a]

Operational Parameters	
Feed pressure (psi)	99.4
Flux (gfd)	9.4
Permeate Water Quality (mg/L)	
Sodium	7.8
Calcium	1.1
Magnesium	0.3
Potassium	0.96
Ammonia	0.07
Barium	0.002
Strontium	0.02
Carbonate	0
Bicarbonate	12.6
Sulfate	5.9
Chloride	2.8
Fluoride	0.02
Nitrate[b]	2.4
Nitrate (mg-N/L)	0.54
Silicon dioxide	0.16
TDS	34.2
pH	4.9
TOC[c]	2.37
Scaling Parameters for Concentrate	
LSI (%)	0.43
BaSO4 sat. (%)	13692

[a] Simulation performed on a one-stage system, 10 vessels, 7-8040 elements each, and operated at 50% recovery, 370 gpm feed-flow rate.

[b] Based on elevated LVL feed concentration.

[c] Estimated, based on TOC rejection observed during pilot study.

Table 6.5 Permeate Water Quality for the NF-270 Primary RO System and Final Effluent after Blending with Secondary ESPA2 Permeate (Water Quality in Table 6.4)

Constituent	Primary NF-270 Brine Perm (mg/L)	Blended with ESPA2 Perm (mg/L)
Sodium	120.9	111.73
Calcium	29.4	27.11
Magnesium	5.46	5.04
Potassium	11.6	10.74
Ammonia	0.88	0.81
Barium	0.06	0.06
Strontium	0.32	0.30
Carbonate	0.46	0.42
Bicarbonate	210.52	194.47
Sulfate	7.63	7.49
Chloride	123.32	113.55
Fluoride	0.83	0.76
Nitrate[a]	26.1	24.18
Nitrate (mg-N/L)	5.89	5.46
Silicon dioxide	7.27	9.45
TDS	544.72	500.96
TOC[b]	0.55	0.70

[a] Nitrate value selected to represent the LVL historic average (2004–2007)
[b] Estimated, based on TOC rejection observed during pilot study.

6.1.1.3 Conclusions

A summary of the feed pressure requirements from the simulation scenarios is presented in Table 6.6. Using the previous scenarios, the recovery of the LVL would be approximately 92.5%, which would allow doubling the facility's capacity while meeting the brine discharge requirement. This recovery set point would be achieved by blending the permeate of the primary membrane system with the secondary brine treatment system. All scenarios analyzed would have plant effluent TOC concentrations marginally above the CDPH limit of 0.5 mg/L, assuming a recycled water contribution of 100%. Using the ESPA2 membrane as the primary system and either the NF-270 or ESPA2 membrane as the secondary system would yield TN (ammonia + nitrate) concentration of less than 5 mg/L. From a simulated pressure and specific cost standpoint, the ESPA2/NF-270 membranes would be preferable (Table 6.6).

Table 6.6 Summary of Pressure Requirements and Specific Costs

Primary/Secondary	Feed Pressure (psi)	Specific Energy (kWh/kgal)
ESPA2/ESPA2	96.2/135.4	1.06/2.64
ESPA2/NF-270	96.2/41.6	1.06/0.76
NF-270/ESPA2	48.5/99.4	0.52/1.94

6.1.2 Returning the Secondary System's Permeate to the Head of the Plant

An additional secondary brine treatment membrane system was evaluated where the permeate of the secondary membrane system was routed to the head of the primary RO system. Two scenarios were analyzed, one with the ESPA2 membrane as the primary membrane and the NF-270 membrane as the secondary membrane, and the other with the NF-270 membrane as the primary membrane and the ESPA2 membrane as the secondary membrane (Figure 6.2). The primary membrane system was identical to the current LVL system (operated at 85% recovery), and the secondary system was identical to the system described in Section 6.1.1 (operated at 50% recovery). For these simulations, an iterative approach was taken, where the initial feed water quality was the LA County WRP effluent and through subsequent iterations it became a blend of LA County effluent and permeate from the secondary system. The iteration was stopped when the blended feed water quality was within 1% of the blended feed water quality from the previous iteration.

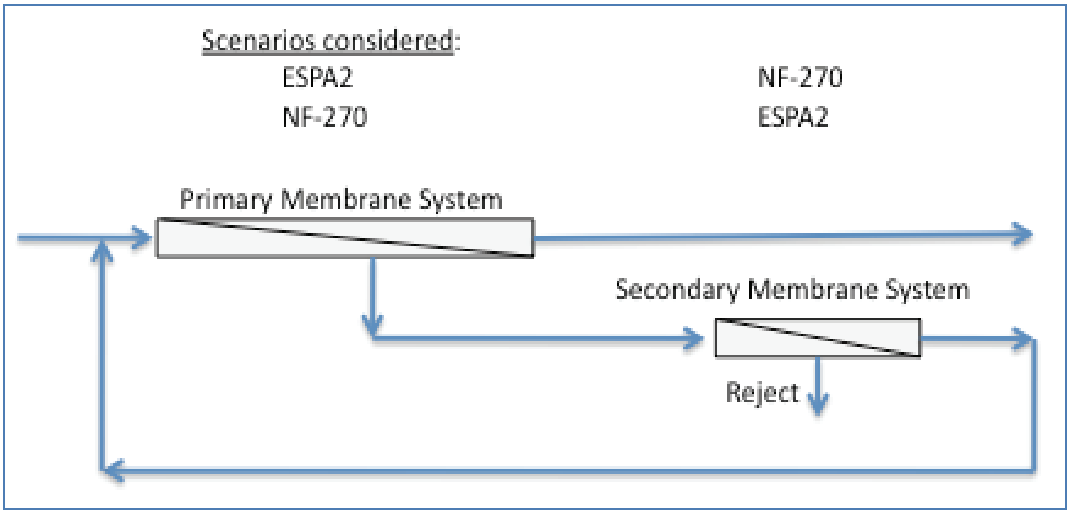

Figure 6.2 Schematic showing simulations that were run.

6.1.2.1 ESPA2 membrane as primary membrane and NF-270 membrane as secondary membrane

The water quality data generated through simulations are presented in Table 6.7. For this scenario, the pH of the primary RO system was adjusted to pH 6.3 using sulfuric acid. Because of the relatively high TOC rejection of both membranes, the final plant effluent TOC concentration for this scenario would be less than than in either permeate blending scenario presented earlier (Section 6.1.1). This option may be preferable to other secondary treatment options, as the NF-270 membrane is a low-energy and low-fouling membrane. However, the secondary membrane could also be the ESPA2 membrane, which would result in even lower TOC and nitrate concentrations in the plant effluent. However, implementing the ESPA2 membrane as secondary membrane will likely raise second-stage scaling issues.

Table 6.7 Primary ESPA2 Membrane and Secondary NF-270 Membrane System's Water Quality

Constituent	Primary System Feed[a] (mg/L)	Primary ESPA2 Brine Concentration (mg/L)	Plant Effluent Concentration (mg/L)	Secondary NF-270 Perm (mg/L)
Sodium	204.46	1327.90	6.25	777.50
Calcium	71.63	474.70	0.46	138.95
Magnesium	15.64	103.40	0.10	25.02
Potassium	19.71	127.10	0.75	73.33
Ammonia	1.49	9.70	0.06	5.67
Barium	0.11	0.66	0.00	0.28
Strontium	0.75	4.64	0.01	1.28
Carbonate	0.69	0.10	0.00	0.54
Bicarbonate	312.71	1004.00	5.83	527.30
Sulfate	152.77	1844.40	1.47	46.55
Chloride	177.16	1160.30	3.72	1102.40
Fluoride	1.16	7.70	0.05	6.89
Nitrate	38.65	225.10	5.68	244.57
Nitrate (mg-N/L)	8.73	50.83	1.28	55.23
Silicon dioxide	11.15	73.50	0.21	61.61
TDS	1021.90	6363.30	24.60	3011.84
TOC	6.1978	39.16	0.4	3.29
pH[b]	6.3	7.10	5.00	6.91

[a]After blending with secondary NF-270 permeate.

[b]Feed water pH of the primary RO adjusted to 6.3 in all simulations.

6.1.2.2 NF-270 As Primary Membrane and ESPA2 as Secondary Membrane

An alternate to the previous scenario would be to have the NF-270 membrane as the primary membrane and the ESPA2 membrane as the secondary membrane. Because the nitrate rejection of the NF-270 is poor, the final plant effluent would have TN concentrations above the CDPH limit. The advantage of this scenario is the low-pressure and low-fouling properties of the NF-270 membrane, the resulting energy savings, and infrequent cleaning requirements as compared to the ESPA2 membrane. In addition, because of the medium rejection of calcium, the scaling potential of the brine would be less, which may improve the operation of the secondary RO-ESPA2 system. Based on preliminary analysis, this scenario would only meet the CDPH requirements if the preliminary NF-270 membrane system was operated at lower recovery and the secondary system treated a larger brine volume operating at a recovery higher than 50%.

6.1.2.3 Conclusion

A summary of the feed pressure requirements from the simulation scenarios is presented in Table 6.8. By utilizing the ESPA2 membrane as the primary membrane and the NF-270 membrane as the secondary membrane and recycling the NF-270 membrane permeate to the head of the plant, the TOC and TN CDPH requirements could be met. Similar results would be obtained using the ESPA2 membrane as the primary and secondary membranes. Based on pilot-scale testing, the NF-270 membrane would be preferred as the secondary membrane, as it does not scale or foul to the extent of the ESPA2 and operates at lower pressure and energy.

Table 6.8 Summary of Pressure Requirements and Specific Costs

Primary/Secondary	Feed Pressure (psi)	Specific Energy (kWh/kgal)
ESPA2/NF-270	111.4/45.4	1.2/1.25
NF-270/ESPA2	48.5/99.2	0.52/1.86

6.2 Preliminary Experimentation with Secondary RO

Testing was conducted with the laboratory-scale two-element testing system to determine the viability of treating the RO brine to increase the overall system recovery. The ESPA2 membrane was utilized because of its high rejection of various constituents and relatively low fouling potential. The two-element membrane system was operated at a conservative permeate flux of 10 gfd and in “internal recycle mode” to simulate a higher system recovery of approximately 50%. The system was operated for approximately 27 h, with samples taken for water quality analysis.

The specific flux of the ESPA2 membrane during brine treatment is presented in Figure 6.3. During the testing, the specific flux remained relatively constant, exhibiting a decline of approximately 10% in the first hour of testing and remaining constant throughout the remaining portion of the experiment. The specific flux was presumably lower for brine treatment compared to testing on LVL feed water as a result of increased osmotic pressure. Feed water and permeate concentration and rejection values for TOC, nitrate, and conductivity are presented in Figure 6.4. Even with elevated TOC and nitrate concentrations, ESPA2 membrane permeate concentrations for TOC and nitrate were below 0.5 mg/L and 5 mg-N/L, respectively.

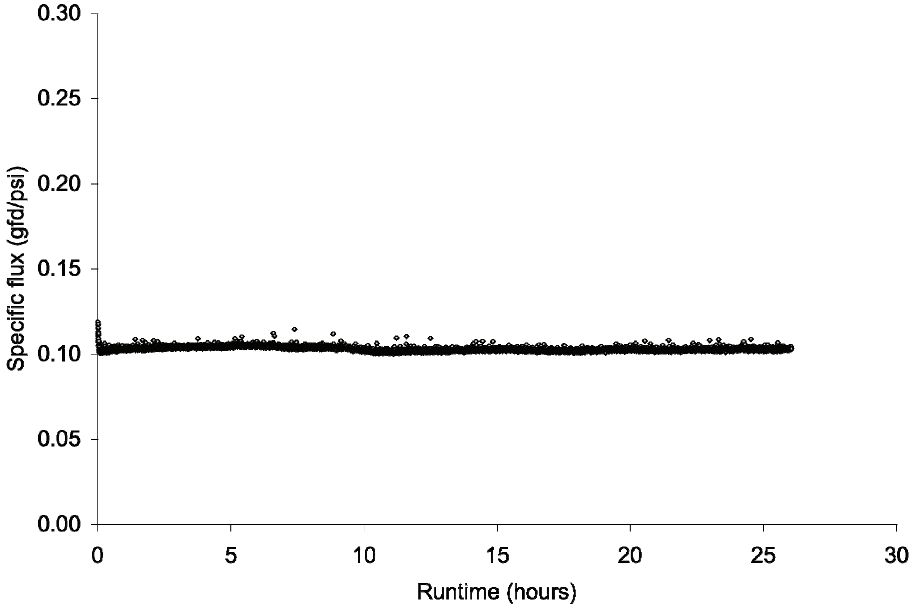

Figure 6.3 Specific flux decline curve for the ESPA2 during brine treatment operated at a permeate flux of 10 gfd and 50% recovery.

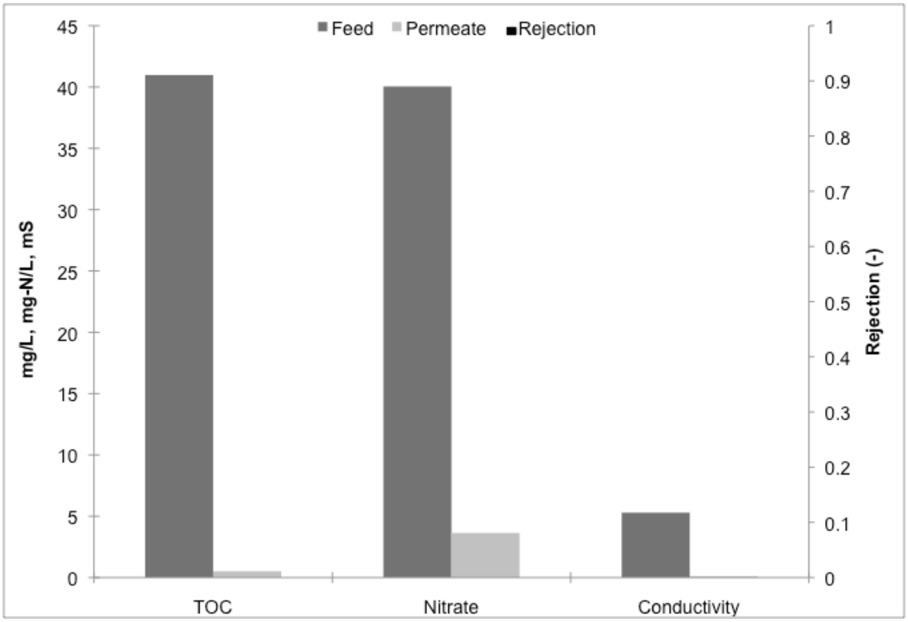

Figure 6.4 TOC, nitrate, and conductivity feed water; permeate concentrations; and calculated rejection.

6.3 Pilot-Scale Testing with Secondary RO

6.3.1 Introduction and Testing Conditions

This phase of the study was designed to explore the viability of primary RO concentrate treatment using a secondary RO treatment unit to increase the overall water recovery of a water recycling facility. A pilot-scale membrane unit with a capacity of 24 gpm was fed with RO concentrate generated at the LVL.

This study investigated operational conditions that are suitable to sustain flux and characterize the product water with regard to removal of bulk parameters (i.e., TOC and nitrogen) and trace organic chemicals.

Concentrate from the RO train at LVL was diverted and used as the feed to the pilot-scale test unit. ESPA2 membranes that were previously employed in pilot-scale testing at the LVL were used. The feed water was adjusted to pH 6.3 using sulfuric acid (93%). Although hydrochloric acid was preferred over sulfuric acid to lower the scaling potential of the feed water, particularly for barium sulfate scale, practical concerns led to the use of sulfuric acid. No additional scale inhibitor was dosed, as it was expected that the residue in the primary RO brine was sufficient to avoid scale formation. The scale inhibitor is tailored to mitigate calcium carbonate, barium sulfate, and silica scales.

The pilot skid was operated at a recovery of approximately 50%, a feed flow of 18 gpm, and a permeate flux of 7 gfd for approximately 600 h. The specific flux was monitored over time.

During these tests, samples were collected for TOC, nutrients (ammonia and nitrate), cations, anions, and select trace organic compounds. Operational parameters (e.g., flow, pressure), feed pH, and feed and permeate conductivity data were logged every 30 s by the SCADA system. Routine water samples (e.g., pH and conductivity) were collected and analyzed once a week from feed water and combined permeate by LBWD staff. Additional samples for Tier 1 parameters (TOC, nitrate, nitrite, and ammonia) and the Tier 2 parameter (ICP analysis) were collected once a week from feed water and combined permeate by LBWD staff and shipped and analyzed by the CSM laboratory. Samples for trace organic compounds (Tier 3) were collected twice by CSM personnel from the feed water (primary RO concentrate) and combined permeate at the beginning (after start-up) and at the end of the pilot study and analyzed by LC/MS/MS.

6.3.2 Operation

Pilot-scale testing commenced on October 25, 2009 and was terminated on November 22, 2009. The TCFS during ESPA2 membrane testing is presented in Figure 6.5. The feed pressure was approximately 120 psi at start-up and was approximately 150 psi when testing was terminated. Specific flux decline followed a relatively linear trend, with approximately 1.2 psi increase in pressure per day, to maintain a constant flux (7 gfd), which is similar to the pressure increase observed for full scale (1–3.5 psi per day). The observed increase in the NDP required to achieve 50% recovery was presumably due to inorganic scaling, likely calcium carbonate, which was observed during previous pilot-scale tests and full-scale operation for the primary RO. As a result of inorganic scaling, the second stage of the pilot permeate flux decreased significantly. To achieve a feed water pH of 6.3, approximately 0.4 gph of concentrated sulfuric acid was dosed during testing.

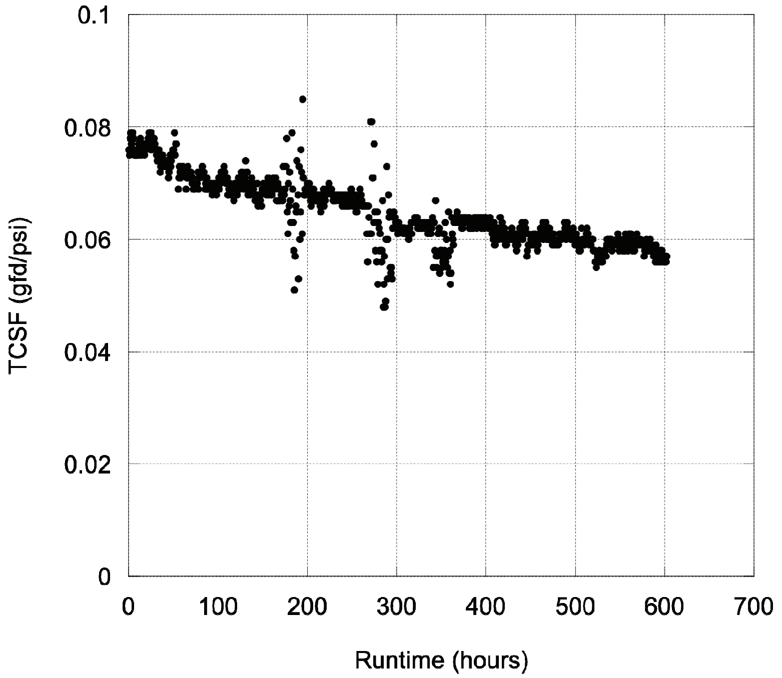

Figure 6.5 Temperature-corrected specific (normalized to 25°C) flux for the ESPA2 membrane pilot-scale test run using primary RO concentrate for feed water. Operated at 50% recovery, 18 gpm feed-flow rate, and an average permeate flux of 7 gfd.

6.3.3 Water Quality

Bulk constituent water quality for the feed water (i.e., concentrate of primary RO) and combined permeate is presented in Table 6.9. High rejection (higher than 90%) was obtained for most constituents measured in the feed water, with the exception of boron and fluoride. Nitrate rejection was approximately 88%, which resulted in combined permeate concentrations of 1.1 mg-N/L. Sulfate feed water concentrations were elevated as a result of dosing of sulfuric acid.

Feed and combined permeate trace organic contaminant data for organic compounds detected in the pilot feed water are presented in Table 6.10. Relatively high concentrations were observed for atenolol, carbamazepine, meprobamate, TCEP, TCPP, and TDCPP in the feed water. Rejection for all compounds detected in the feed water was higher than 90%.

Table 6.9 Bulk Water Quality (Data from Five Weekly Sampling Campaigns)

	Concentrate (Pilot Feed)	SD	Combined Permeate	SD	Rejection
Constituents			**mg/L**		**%**
DOC	38.77	2.58	0.77	0.20	98.0
TOC	39.61	2.20	0.63	0.227	98.4
Al^{3+}	0.12	0.01	BDL	BDL	NA
B	0.54	0.05	0.43	0.08	20.2
Ba^{+}	0.31	0.06	0.00	0.007	98.4
Ca^{2+}	351	49.24	0.66	0.11	99.8
Fe^{-}	0.21	0.02	0.01	0.003	96.3
K^{+}	79.41	5.81	4.07	0.58	94.9
Mg^{2+}	88.12	25.44	0.10	0.045	99.9
Mn	0.13	0.03	BDL	BDL	NA
Na^{+}	733	28.55	37.54	4.54	94.9
Si	49.02	3.01	1.56	0.15	96.8
F^{-}	3.20	0.10	0.65	0.12	79.7
Cl^{-}	678	36.68	18.76	4.05	97.2
Br^{-}	0.19	0.05	BDL	BDL	NA
NO_3^{-}	91.20	45.95	11.08	4.89	87.9
NO_3-N	20.59	10.38	2.50	1.10	87.9
PO_4^{3-}	1.46	0.47	BDL	BDL	NA
SO_4^{2-}	1468	167	1.60	0.46	99.9

Note. BDL = below detection limit; NA = not applicable.

Table 6.10 Beginning Feed and Combined Permeate Trace Organic Contaminant Data for Two Sampling Campaigns

Compound	Feed (ng/L)	Combined Permeate (ng/L)	Feed (ng/L)	Combined Permeate (ng/L)	Rejection	
	11/2/09		11/22/09		11/2/09	11/22/09
Atenolol	5180	32	7320	29	0.994	0.996
Atrazine	30.2	BDL	38.6	BDL	NA	NA
Caffeine	46	BDL	36	BDL	NA	NA
Cabamazepine	1548	4	1414	2	0.997	0.999
DEET	610	4	1070	3	0.994	0.997
Diazepam	19	BDL	16	BDL	NA	NA
Dilantin	960	3	684	2	0.997	0.997
Fluoxetine	161	1	174	0.31	0.995	0.998
Hydrocodone	17	BDL	34	BDL	NA	NA
Meprobamate	5100	10	5360	6	0.998	0.999
Primidone	986	2	924	1	0.998	0.999
Sulfamethoxazole	452	2	862	3	0.997	0.997
Trimethoprim	99	1	216	1	0.995	0.995
TCEP	3800	22	3820	10	0.994	0.997
TCPP	13280	47	18340	18	0.996	0.999
TDCPP	12220	3	16660	8	1.000	1.000
Triclosan	18	2	50	2	0.915	0.957
Gemibrozil	762	2	2520	2	0.997	0.999
Triclocarban	338	18	428	42	0.946	0.902
Ibuprofen	105	4	114	3	0.962	0.972
Naproxen	66	2	96	3	0.968	0.972

Note. BDL = below detection limit; NA = not applicable.

6.3.4 Conclusions

Based on pilot-scale testing using the primary RO brine as feed water, the following can be concluded:

- Treatment of primary RO brine with the ESPA2 membrane at 50% recovery resulted in an initial TCSF of 0.075 gfd/psi. Operation under these conditions could increase the overall plant water recovery to over 92%.
- Over the operating time of 600 h, the TCSF decreased by 20% to approximately 0.06 gfd/psi. To maintain a constant permeate flux of 7 gfd required an increase in feed pressure of approximately 1.2 psi per day of operation. The increase in required NDP was presumably due to inorganic scaling. Based on previous studies, this scale comprises calcium carbonate predominantly. Previous CIP cycles with citric acid demonstrated that the scale is reversible.
- Mitigation of inorganic scaling was attempted by decreasing the feed pH to 6.3, which requires a rather high addition of acid to the feed stream. For a plant generating 1 MGD

of RO brine with the same water chemistry, 370 gal/day of acid would be consumed to maintain a pH of 6.3.

- Rejection of key constituents was in excess of 90%, resulting in TOC concentrations of 0.63 mg/L and nitrate of less than 2.5 mg N/L. Rejection of select unregulated compounds also exceeded 90%. Blending the permeate with the full-scale permeate would achieve compliance with current CDPH regulations.

Chapter 7

Economic Assessment of the Alternatives

7.1 Economic Basis and Assumptions

The focus of this section is on comparing the costs of implementing different approaches at full scale. The following is a list of the assumptions and basis used for the economic evaluations for the different approaches:

1. SCE charges the WRD at different tier rates based on usage. For the purpose of this study, the average power cost for the past 6 months was calculated to be $0.15 per kWh and was used in the economical analysis.

2. The chemical costs used for the analysis were provided by the WRD and were based on the current quotes from the different vendors. Table 7.1 lists the unit cost of each chemical.

3. The different approaches may have some effect on the upstream and downstream processes, such as on UV dose and chlorine demand, but these were beyond the scope of the project, and therefore were not included in the economic analysis.

4. The plant would operate 24 h a day and 365 days a week, except for scheduled CIP cleaning, maintenance work, and any down times due to mechanical problems.

5. Plant utilization was calculated based on the detailed operational records from August 2009 to January 2010, conducted while the pilot plant was running. The average utilization rate from this period is 89%. Table 7.2 and Figure 7.1 illustrate the shutdowns due to maintenance and CIP during this period.

Table 7.1 List of Chemical Costs Based on Current Quotes for the WRD

Chemical	Cost ($)	Unit
Antiscalant-threshold inhibitor (Pretreat Plus)	9.76	per gal
Caustic soda	42.25	per lb
Citric acid	1.18	per lb
Sulfuric acid	4.90	per gal

Table 7.2 Utilization Rate Calculation

Month	CIP Shutdown (days)	Unplanned Shutdown (days)	Total Shutdown (days)	Utilization Rate (%)
Aug-09	0	1	1	97
Sep-09	4.5	3	7.5	75
Oct-09	0	2.09	2.09	93
Nov-09	0	0	0	100
Dec-09	4	5.5	9.5	69
Jan-10	0	0.4	0.4	99
Average Utilization Rate				*89*

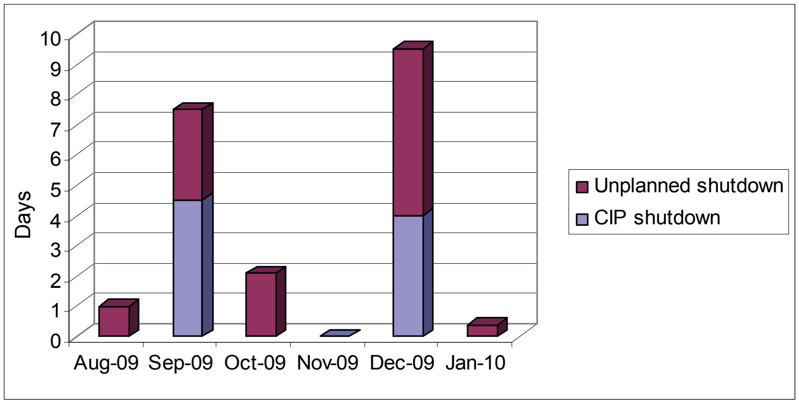

Figure 7.1 Comparison of total number of off-line days during pilot study.

7.2 Operational Basis

As discussed in Chapters 5 and 6, there were various scenarios investigated for maximizing recovery of recycled water for groundwater recharge. Economic analysis was performed for the following alternatives: (1) baseline, primary RO, (2) optimized, primary RO at higher recoveries and fluxes, (3) primary NF, and (4) secondary RO (or a third-stage RO).

7.2.1 Baseline Case—Primary RO

The current operational condition will be used as the base case to compare the other approaches. As mentioned earlier, the LVL is currently operating at 85% recovery with 2080 gpm of product water at a 10-gfd flux. The water quality from the LBWRP also requires the plant to inject 3 ppm of threshold inhibitor before feeding to the RO system. As shown in Table 7.2, the CIP runs every 60 to 80 days and takes approximately 4 days to complete.

7.2.2 Optimized Primary RO at Higher Recoveries and Fluxes

As indicated in Chapter 4, the primary RO can be operated at higher recoveries and fluxes with the addition of acid or perhaps with more frequent CIPs annually. Two cases for using primary RO at higher recoveries and fluxes will be discussed: 85% recovery and 15 gfd flux, and 87% recovery and 15 gfd flux. For the economic analysis, the first case will be evaluated assuming more frequent CIPs and the second, assuming acid injection.

7.2.3 Primary NF

The model NF membrane used for testing (NF-270) does not effectively reject nitrate under the operating conditions tested. However, as illustrated in Figure 4.3, the plant influent nitrate level has been decreasing at a steady rate since 2004. Thus, the NF option summarizes the cost of replacing current RO elements with NF elements and running NF as a primary membrane at 85% recovery at 15 gfd. As with the previous alternative, it is assumed that the addition of acid is required to operate the NF plant at 87% recovery at 15 gfd. It is also assumed that the required CIP frequencies will be half of those required for the RO membranes.

7.2.4 Secondary RO

The concentrate from the full-scale RO was used to test the secondary RO (or third-stage RO) in an effort to further increase the overall recovery. Unlike the two alternatives mentioned previously(i.e., optimized primary RO and primary NF), the secondary RO requires new capital equipment (i.e., a new RO train with 10 vessels). The recovery of this stage used is 50% for an overall plant recovery of 92%. Additional chemicals, such as sulfuric acid, are required to run the secondary RO, and depending on the conditions, additional treatment may be needed for the feed water to the secondary RO system.

Table 7.3 summarizes the conditions for each membrane train discussed earlier. Based on the historical record, a typical CIP takes about 4 days at the LVL. The total down days per year are a summation of CIP days per year and the maintenance down days per year (based on the 6 months' data provided by the WRD). The utilization rates estimated are similar to the average 89% observed during the pilot run. It should be noted that the feed rate is higher for any alternatives with higher recoveries and higher fluxes.

Table 7.3 Summary of the Conditions for the Alternatives

No.	Conditions	Feed (gpm)	Recovery (%)	Flux (gfd)	No. CIP/Year	Total Down Days/Year	Utilization Rate (%)	AF/Year
1	Primary RO	2447	85	9.9	6	48	87	2908
2	Primary RO	3036	83	12	6	48	87	3524
3	Primary RO	3706	85	15	8	56	85	4294
4	Primary RO[a]	3620	87	15	8	56	85	4293
5	Primary NF	3706	85	15	6	36	90	4571
6	Primary NF[a]	3620	87	15	3	36	90	4679
7	Secondary RO[a]	370	50	9.4	6	48	87	3167
8	Secondary NF[a]	370	50	9.4	6	48	87	3167

[a] Operated with acid addition to adjust pH to 6.3.

7.3 Capital Costs

In the review of the different alternatives shown in Table 7.3, the cases involving NF and the addition of a secondary treatment train will incur capital costs. There won’t be any capital costs for Alternatives 1 to 4, as shown in Table 7.3; however, for Alternatives 5 and 6, new NF elements will need to be purchased and the costs will be associated as capital costs incur. For Alternatives 7 and 8, the capital costs include equipment and new membrane costs.

The 8-in. RO element cost is about \$550, and the cost for an 8-in. NF element is about \$700. The exact quote may be different depending on the terms, but these numbers were used for the capital cost estimates. The cost for the NF element is based on a scenario where all 756 RO elements currently installed in the RO train are changed to NF. For the secondary RO, an estimate of \$1/gallon was used to estimate an equipment cost of \$530,000 for a 370-gpm system. An additional 50% was added for installation, engineering, site support, and so on. The number of RO elements needed for the secondary RO is 70 for 10 vessels, as summarized in Table 7.4. For the annualized capital costs, a 5% interest rate with an estimated life of 5 years for the membrane and 20 years for equipment was used.

Table 7.4 Capital Cost Comparison for the Alternatives

Alt. No.[a]	Conditions	Items	Equipment ($K)	Element No.	Installation Cost ($K)	Total Cost ($K)	Annualized Cost ($K)
1–4	Primary RO	RO Element	NA	756	NA	—	—
5–6	Primary NF	NF Element	NA	756		529	122.2
7	Secondary RO[a]	Equip.	530		265	795	63.8
		RO Element		70		38.5	8.9
		Total					72.7
8	Secondary NF[a]	Equip.	345		173	518	41.5
		NF Element		70		49	11.3
		Total					52.8

[a] Alt. No. matches No. in Table 7.3

7.4 Power Consumption and Costs

For each alternative, two sets of numbers are provided for power consumption. The first cost is related to pumping to provide the pressure required to feed the water to the membrane systems. The second cost is the electricity cost associated with CIP, including the heater, pump, and flush pump. As anticipated, the bulk of the electrical cost is associated with pumping. The NF option provides a lower electrical cost because a lower pumping pressure and less frequent CIP are required. For all scenarios, the feed pump, the CIP heaters, and the pumps were assumed to operate under the conditions described in Table 7.5

Table 7.5 Equipment Operation Conditions and Assumptions

Conditions	Equipment	Units	Cycles/ CIP	Duration/Cycle
Normal operation	Feed pump	1	1	24
CIP	CIP heater	4	2	4
	CIP pump	1	6	4
	Flush pump	1	9	0.25

Table 7.6 shows the power costs for all the alternatives. As described earlier, the NF alternatives have the lowest power costs, as they require the lowest pumping and fewer CIP cycles.

Table 7.6 Power Cost Comparison for the Alternatives

Train	Conditions	Equipment	kW each	kW/cycle	Cost per Day or CIP	Annual Cost
Primary RO-1	Normal operation	Feed pump	202	4855	$ 728	$ 231,236
	CIP 6 times annually	CIP heater	175	5600	$ 840	$ 5,040
		CIP pump	100	2400	$ 360	$ 2,160
		Flush pump	30	67.5	$ 10	$ 61
	Total					**$ 238,497**
Primary RO-2	Normal operation	Feed pump	293	7032	$ 1,055	$ 334,948
	CIP 6 times annually	CIP heater	175	5600	$ 840	$ 5,040
		CIP pump	100	2400	$ 360	$ 2,160
		Flush pump	30	67.5	$ 10	$ 61
	Total					**$ 342,209**
Primary RO-3	Normal operation	Feed pump	434	10405	$ 1,561	$ 495,601
	CIP 8 times annually	CIP heater	175	5600	$ 840	$ 6,720
		CIP pump	100	2400	$ 360	$ 2,880
		Flush pump	30	67.5	$ 10	$ 81
	Total					**$ 505,282**
Primary RO-4	Normal operation	Feed pump	424	10165.2	$ 1,525	$ 484,194
	CIP 8 times annually	CIP heater	175	5600	$ 840	$ 6,720
		CIP pump	100	2400	$ 360	$ 2,880
		Flush pump	30	67.5	$ 10	$ 81
	Total					**$ 493,875**
Primary NF-1	Normal operation	Feed pump	244	5864.74	$ 880	$ 288,985
	CIP 3 times annually	CIP heater	175	5600	$ 840	$ 2,520
		CIP pump	100	2400	$ 360	$ 1,080
		Flush pump	30	67.5	$ 10	$ 30
	Total					**$ 292,615**
Primary NF-2	Normal operation	Feed pump	236	5670	$ 850	$ 279,374
	CIP 3 times annually	CIP heater	175	5600	$ 840	$ 2,520
		CIP pump	100	2400	$ 360	$ 1,080
		Flush pump	30	67.5	$ 10	$ 30
	Total					**$ 283,004**
Secondary RO	Normal operation	Feed pump	42.7	1025	$ 154	$ 48,825
	CIP 6 times annually	CIP heater	175	5600	$ 840	$ 5,040
		CIP pump	100	2400	$ 360	$ 2,160
		Flush pump	30	67.5	$ 10	$ 61
	Total					**$ 56,339**
Secondary NF	Normal operation	Feed pump	22.8	546	$ 82	$ 26,025
	CIP 6 times annually	CIP heater	175	5600	$ 840	$ 5,040
		CIP pump	100	2400	$ 360	$ 2,160
		Flush pump	30	67.5	$ 10	$ 61
	Total					**$ 34,635**

7.5 Chemical Costs

As with power cost estimates, chemical costs are divided into two categories. For normal plant operation, antiscalant at 3 ppm is required. The plant has used sulfuric acid in the past, but this cost is not included for the primary RO, as it has not been used in the current operation. Because the feed water does not contain alum since the wastewater treatment plant operation has changed, acid addition can be considered as one option to increase overall recovery and operation flux. For higher recovery and flux alternatives, it was assumed that acid injection was required.

Because of the poor water quality of the primary concentrate, acid injection is also a necessity in operating the secondary RO. The chemical cost for each CIP is related to the total number of elements to be cleaned, and the annual cost is estimated based on the number of annual cleanings required.

Table 7.7 shows the chemical unit costs, which were based on manufacturer current quotes for the WRD's operation.

Table 7.7 Chemical Unit Costs

Conditions	Chemicals	Unit Cost per Lb	Unit Cost per Gal
Normal Operation	Antiscalant	NA	$9.76
	Sulfuric acid	$0.32	$4.90
CIP	Citric acid	$1.18	NA
	Caustic soda	$42.25	NA

Table 7.8 shows the total costs per CIP and the annual chemical costs for each alternative. As shown, the primary NF-1 alternative results in the lowest chemical costs; however, all alternatives that require the use of sulfuric acid result in a much higher annual chemical cost. Although the use of sulfuric acid might keep the CIP cycles to a minimum requirement, it may not be a cost-effective way to operate the plant.

Table 7.8 Chemical Cost Comparison for the Alternatives

Train	Conditions	Chemicals	Dose (lb)	Dose (gph)	Total Cost per CIP ($)	Annual Cost ($)
Primary RO-1	Normal operation	Antiscalant		0.4405		37,658
		Sulfuric acid		NA		
	CIP 6 times annually	Citric acid	1960		2,313	13,877
		Caustic soda	235		9,929	59,573
	Total					**111,108**
Primary RO-2	Normal operation	Antiscalant		0.53		45,184
		Sulfuric acid		NA		
	CIP 6 times annually	Citric acid	1960		2,313	13,877
		Caustic soda	235		9,929	59,573
	Total					**118,633**
Primary RO-3	Normal operation	Antiscalant		0.53		45,184
		Sulfuric acid		NA		
	CIP 8 times annually	Citric acid	1960		2,313	18,502
		Caustic soda	235		9,929	79,430
	Total					**143,116**
Primary RO-4	Normal operation	Antiscalant		0.67		57,034
		Sulfuric acid				540,842
	CIP 8 times annually	Citric acid	1960		2,313	18,502
		Caustic soda	235		9,929	79,430
	Total					**695,809**
Primary NF-1	Normal operation	Antiscalant		0.67		57,034
		Sulfuric acid		12.6		-
	CIP 3 times annually	Citric acid	1960		2,313	6,938
		Caustic soda	235		9,929	29,786
	Total					**93,758**
Primary NF-2	Normal operation	Antiscalant		0.67		57,034
		Sulfuric acid		12.6		540,842
	CIP 3 times annually	Citric acid	1960		2,313	6,938
		Caustic soda	235		9,929	29,786
	Total					**634,601**
Secondary RO	Normal operation	Antiscalant		0.067		5,694
		Sulfuric acid		10		428,890
	CIP 6 times annually	Citric acid	180		212	1,274
		Caustic soda	22		930	5,577
	Total					**441,435**
Secondary NF	Normal operation	Antiscalant		0.067		5,694
		Sulfuric acid		10		428,890
	CIP 6 times annually	Citric acid	180		212	1,274
		Caustic soda	22		930	5,577
	Total					**$ 441,435**

NA = not applicable

7.6 Summary

Table 7.9 shows an overall comparison among the different alternatives evaluated for this study. These include the total annualized cost, including the power and chemical cost, and, based on the annual acre-feet of water produced, a cost per acre-ft was estimated. The following summarizes the results of this economic analysis. For the capital cost estimates, an interest rate of 5% was used with an estimated life of 5 years for the membrane and 20 years for the equipment, including items such as the vessels and the pumps.

1. The secondary membrane system (third-stage membrane train) has the highest dollar per acre-foot cost, but this estimate did not factor in the discharge cost. If there is a limited sewer capacity, the secondary membrane system option would provide an alternative that would increase recovery and thus minimize the concentrate discharge flow.

2. At 87% recovery, both RO and NF (primary RO-4 and primary NF-1) required acid injection for pH adjustment. Based on the acid dose required to maintain a low pH in the feed water, the annual chemical cost was significantly higher than under other operational conditions with a lower recovery without acid injection but probably a higher CIP frequency.

3. Based on the operational conditions tested, primary NF required lower power and a lower chemical cost because of a reduced requirement for feed pressure and a less frequent CIP, respectively.

4. Additional, long-term tests may be needed to better define CIP frequency with and without acid injection for pH adjustment, as the acid cost seems to outweigh the benefit of a less frequent CIP.

5. The projections shown in the following are for full-scale operation, based on the pilot data under representative conditions. Note that the higher flux conditions are based on the assumption that additional water sources are available beyond the current capacity.

6. Without the sewer discharge limitations, primary NF alternatives seem to be the most cost-effective options among the configurations tested, assuming that nitrate level is declining and that TOC level is stable.

Table 7.9 Overall Economic Comparisons for the Alternatives

No	Conditions	Production (AF)	Recovery (%)	Utilization Rate (%)	Annualized Capital Cost ($)	Annual Electricity Cost ($)	Annual Chemical Cost ($)	Total Annual Cost ($)	Total Annual Cost ($/AF)
1	Primary RO-1	2908	85	87	—	238,500	111,110	349,600	120
2	Primary RO-2	3524	83	87	—	342,210	118,630	460,840	131
3	Primary RO-3[a]	4294	85	85	—	5,280	143,120	648,400	151
4	Primary RO-4[a]	4293	87	85	—	493,880	695,810	1,189,680	277
5	Primary NF-1	4571	85	90	122,232	292,620	93,760	477,830	111
6	Primary NF-2[a]	4571	87	90	122,232	283,000	634,600	1,009,060	227
7	Primary RO-1 + Secondary RO[a]	3165	92.5	87	72,685	294,580	441,435	808,960	256
8	Primary RO-1 + Secondary NF[a]	3165	91.5	87	52,843	273,130	441,435	767,410	242

[a] Operated with an acid injection to adjust the pH to 6.3.

Chapter 8

Conclusions and Recommendations

8.1 Conclusions

Based on the findings from the modeling, pilot testing, and economic analysis, the following conclusions are made.

8.1.1 Operations Analysis

1. One possibility for increasing the amount of water produced at the LVL would be to maintain an 85% recovery but increase the feed-flow rate and operate at a higher permeate flux and a higher cross-flow velocity. However, because the VFD is already operating at 80% and the concentrate flow is near the discharge limit, the only way to increase recovery would be to install a secondary RO system or a higher-capacity pump.

2. Four membranes were tested at bench and pilot scale. The order of membranes exhibiting the least amount of flux decline because of fouling was NF-270 (<0% decline) > TFC-SR3 (~8% decline) > ESPA2 (~18% decline) > TFC-S (~20% decline) during bench-scale flat sheet testing. On the other hand, the order of membranes with the least amount of flux decline because of fouling was NF-270 (3%) > ESPA2 (12%) > TFC-SR3 (20% but only tested for ~ 7 h) > TFC-S (33%) during two-stage, spiral-wound element tests.

3. The ESPA2 membrane exhibited minimal fouling in the first 20 h of pilot operation but required a relatively high NDP to produce 14 gfd of permeate flux. The TFC-S and TFC-SR3 membranes require less NDP but exhibited slightly more flux decline than the ESPA2 membrane because of fouling. The NF-270 membrane required very little NDP to achieve 16 gfd and exhibited very little flux decline in the first 20 h of operation at the LVL.

4. Feed water nitrate concentrations were variable despite the low rejection of nitrate by the loose NF membranes (TFC-SR3 and NF-270). When membranes were tested, feed water nitrate concentrations were low (~4 mg-N/L), which resulted in permeate concentrations of less than the 5 mg/L-N/L limit set by the CDPH for groundwater recharge applications. The NF-270 membrane achieved a higher than 90% rejection of TOC; however, concentrations were approximately 0.6 mg/L on average.

5. For the ESPA2 membrane, all trace organic compounds monitored (TCEP, TCPP, ibuprofen, mecoprop, gemfibrozil, TDCPP, naproxen, ketoprofen, and diclofenac) were below the quantification level, with the exception of salicylic acid. For other membranes (TFC-S, TFC-SR3, and NF-270), the rejections for trace organic compounds were 15 to 43% for salicylic acid, 6 to 18% for TCEP, and 1 to 4% for TCPP compared with the feed water concentration.

6. For the CIP, a blend of sodium dodecylbenzene sulfonate (CalSoft-90) and EDTA with a pH of 11, and citric acid at a pH of 3–4, were used. The organic cleaning solution

appeared to remove very little organic material from the membrane system. Therefore, subsequent cleanings were performed with citric acid only, which was found to be effective.

7. Simulations using RO system design tools (Hydranautics and Koch) indicated that calcite precipitation would be the major scalant. Additional analysis with speciation software (Visual MINTEQ) showed that calcite ($CaCO_3$) and hydroxyapatite ($Ca_5(PO_4)_3OH$) could potentially precipitate on the membrane surface. These minerals are generally crystalline in nature, but much of the scale observed on the ESPA2 membrane was amorphous.

8. The acid adjustment of the feed water to a pH of 6.3 appeared to have a positive effect on the performance of the ESPA2 membrane, but maintaining a low pH required a relatively large volume of sulfuric acid. For a plant to generate 1 MGD of RO brine with the same water chemistry, 370 gal/day of acid would need to be consumed to maintain a pH of 6.3.

9. For the ESPA 2, as long as the CIPs were performed more frequently, operation at 85% recovery and 15 gfd permeate flux was relatively stable. Full-scale operation at this set point would result in a 50% increase in permeate produced per day. Operation at 87% recovery and 15 gfd was relatively stable when the feed water pH was adjusted to 6.3. Overall, however, operating at this set point resulted in an increase of 1.8 psi per day to maintain the permeate flow rate set point.

10. The feed pressure of the full-scale system currently increases between 1 and3 psi per day, based on operational data from 8/2009 to 2/2010. The full-scale system is not currently pH-adjusted. Based on pilot-scale results, pH adjustment may help remedy the scaling issue and allow the facility to operate at a higher permeate flux and recovery.

11. The NF-270 membrane exhibited minimal flux decline when operating at 85% recovery and 15 gfd and maintained a specific flux two to three times higher than the ESPA2 membrane. At 87% recovery and 15 gfd, the specific flux decreased by approximately 0.5% per day, presumably because of scaling. This decline is significantly less than that observed for the ESPA2 membrane.

12. More trace organic contaminants were quantified in the NF-270 membrane permeate samples versus ESPA2 membrane permeate samples, but concentrations were relatively low and generally less than 100 ng/L.

13. Treatment of primary RO brine with the ESPA2 membrane at 50% resulted in an initial TCSF of 0.075 gfd/psi. Operation under these conditions could increase the overall plant water recovery to over 92%.

14. Over the operating time of 600 h, the TCSF decreased by 20% to approximately 0.06 gfd/psi. Maintaining a constant permeate flux of 7 gfd required an increase in feed pressure of approximately 1.2 psi per day of operation. The increase in required NDP was presumably due to inorganic scaling. Based on previous studies, this scale predominantly comprises calcium carbonate. Previous CIP cycles with citric acid demonstrated that the scale is reversible.

15. Rejection of key constituents was in excess of 90%, resulting in TOC concentrations of 0.63 mg/L and nitrate of less than 2.5 mg N/L. Rejection of select unregulated

compounds also exceeded 90%. Blending the permeate with the full-scale permeate would achieve compliance with current CDPH regulations.

8.1.2 Economic Analysis

1. The secondary membrane system (third-stage membrane train) has the highest dollar per acre-foot cost, but this estimate did not factor in the discharge cost. If there is a limited sewer capacity, the secondary membrane system option would provide an alternative for increasing recovery and would thus minimize the concentrate discharge flow.

2. At 87% recovery, both RO and NF (primary RO-4 and primary NF-1) required acid injection for pH adjustment. Based on the acid dose required to maintain a low pH in the feed water, the annual chemical cost was significantly higher than for other operational conditions with a lower recovery without acid injection but probably a higher CIP frequency.

3. Based on the operational conditions tested, primary NF required less electricity and lower chemical cost because of less required feed pressure and less frequent CIP, respectively.

4. Additional, long-term tests may be needed to better define CIP frequency with and without acid injection for pH adjustment, as the acid cost seems to outweigh the benefit of a less frequent CIP.

5. Without sewer discharge limitations, primary NF alternatives seem to be the most cost-effective options among the configurations tested, where nitrate level is declining and TOC level is stable.

8.2 Recommendations

1. Current full-scale CIPs utilize separate NaOH and citric acid cleanings, which take approximately 4 days to complete. Based on pilot-scale results, organic fouling did not appear to be an issue and citric acid alone was effective for restoring most, if not all, of the initial permeability of the membrane. The development of an efficient system for semiregular citric acid cleanings could allow the system to operate at higher recoveries without caustic cleaning.

2. Based on full-scale and pilot-scale data, pH adjustments help with scaling issues. However, the cost of continuous acid injection is significantly higher than the cost of an additional CIP. If the CIP can be done using citric acid without caustic soda, as recommended, then an additional CIP will still result in lower chemical costs than continuous pH adjustment in the feed water.

3. The economic analysis performed in Chapter 7 did not factor in the cost of discharging the RO concentrate, because this cost is site-specific. At the LVL, there is no additional capacity for discharging the waste concentrate from the membrane system. Thus, although the total annual cost of water produced in $/AF is the highest among the alternatives considered, the alternatives using a secondary membrane system are the only option for plant expansion. Additional economic analysis including concentrate discharge is thus recommended for specific evaluation depending on site conditions.

4. Although they were not tested as part of the field demonstration, some configurations using the hybrid system modeled in Chapter 6 may be able to address the low nitrate rejection by NF membranes. Integration of NF with RO can increase recovery and reduce energy cost without compromising the finished water quality. Additional modeling and field demonstration are recommended to assess the benefits and applicability of such hybrid membrane systems using both NF and RO.

References

Al-Amoudi, A.; Lovitt, R. W. Fouling strategies and the cleaning system of NF membranes and factors affecting cleaning efficiency. *J. Membr. Sci.* **2007**, *303*, 4–28.

American Public Health Association (APHA). *Standard Methods for the Examination of Water and Wastewater*, 21st ed. American Public Health Association, American Water Works Association, Water Environment Federation: Washington, DC, 2005.

American Waterworks Association (AWWA), Membrane Technology Research Committee. Recent advances and research needs in membrane fouling. Committee Report. *J. Am. Water Works Assoc.* **2005**, *97*, 79–89.

Bandini, S.; Vezzani, D. Nanofiltration modeling: The role for dielectric exclusion in membrane characterization. *Chem. Eng. Sci.*, **2003**, *58*, 3303–3326.

Bartels, C.; Franks, R.; Furukawa, R.; Murkute, P.; Papukchiev, U. Integrated Membrane System for Low Fouling RO Desalting of Municipal Wastewater. California Energy Commission Report. Hydranautics website. http://www.membranes.com, 2004.

Bellona, C.; Drewes, J. E.; Oelker, G.; Luna, J.; Filteau, G.; Amy, G. Comparing nanofiltration and reverse osmosis for drinking water augmentation. *J. Am. Water Works Assoc.* **2008**, *100,* 102–116.

Bellona, C.; Drewes, J. E. Viability of a low pressure nanofilter in treating recycled water for water reuse applications. A pilot-scale study. *Water Res*. **2007**, *41*, 3948–3958.

Bellona, C.; Drewes, J.; Xu, P.; Amy, G. Factors affecting the rejection of organic solutes during NF/RO treatment. A literature review. *Water Res*. **2004**, *38*, 2795–2809.

Bowen, W. R.; Cassey, B.; Jones, P.; Oatley, D. L. Modelling the performance of membrane nanofiltration—Application to an industrially relevant separation, *J. Membr. Sci*. **2004**, *242*, 211–220

Bowen, W. R.; Mukhtar, H. Characterization and prediction of separation performance of nanofiltration membranes. *J. Membr. Sci*. **1996**, *112*, 263–274.

Chesters, S. P. Innovations in the inhibition and cleaning of reverse osmosis membrane scaling and fouling. *Desalination* **2009**, *238*, 22–29.

Drewes, J. E.; Bellona, C.; Xu, P.; Amy, G.; Filteau, G.; Oelker, G. *Comparing Nanofiltration to Reverse Osmosis for Treating Recycled Water;* AwwaRF Project #3012 Final Report, 2008.

Franks, R.; Bartels, C. R.; Andes, K.; Patel, M. Implementing energy saving RO technology in large scale wastewater treatment plants. In *Proceedings of the IDA World Congress*-Maspalomas, Gran Canaria, Spain, October 21–26, 2007.

Goosen, M. F. A.; Sablani, S. S.; Al-Hinai, H.; Al-Obeidani, S.; Jackson, D. Fouling of reverse osmosis and ultrafiltration membranes: A critical review. *Sep. Sci. Technol.* **2005**, *39*, 2261–2297.

Hagmeyer G.; Gimbel, R. Modeling the salt rejection of nanofiltration membranes for ternary ion mixtures and for single salts at different pH values. *Desalination* **1998**, *117*, 247–256.

Her, N.; Amy, G.; Foss, D.; Cho, J.; Yoon, Y.; Kosenka, P. Optimization of method for detecting and characterizing NOM by HPLC-size exclusion chromatography with UV and on-line DOC detection. *Environ. Sci.Technol*. **2002**, *36,* 1069–1076.

Kim, T-U.; Drewes, J. E.; Summers, R.S.; Amy, G.L. Solute transport model for trace organic neutral and charged compounds through nanofiltration and reverse osmosis membranes. *Water Res*. **2007,** *41*, 3977–3988.

Kimura, K.; Amy, G.; Drewes, J. E.; Heberer, T.; Kim, T-U; Watanabe, Y. Rejection of organic micropollutants (disinfection byproducts, endocrine disrupting compounds, and pharmaceutically active compounds) by NF/RO membranes. *J. Membr. Sci*. **2003**, *227*, 113–121.

Kimura, K.; Toshima, S.; Amy, G.; Watanabe, Y. Rejection of neutral endocrine disrupting compounds (EDCs) and pharmaceutically active compounds (PhACs) by RO membranes. *J. Membr. Sci.* **2004**, *245*, 71–78.

Kiso, Y.; Sugiura, Y.; Kitao, T.; Nishimura, K. Effects of hydrophobicity and molecular size on rejection of aromatic pesticides with nanofiltration membranes. *J. Membr. Sci*. **2001**, *192*, 1–10.

Košutić, K.; Kunst, B. Removal of organics from aqueous solutions by commercial RO and NF membranes of characterized porosities. *Desalination* **2002**, *142*, 47–56.

Lee, S.; Lueptow, R. M. Membrane rejection of nitrogen compounds. *Environ. Sci. Technol.* **2001**, *35*, 3008–3018.

Li, Q.; Elimelech, M. Organic fouling and chemical cleaning of nanofiltration membranes: Measurement and mechanisms. *Environ. Sci. Technol*. **2004**, *38*, 4683–4693.

Manttari, M.; Nuortila-Jokinen, J.; Nystrom, M. Influence of filtration conditions on the performance of NF membranes in the filtration of paper mill total effluent. *J. Membr. Sci*. **1997**, *137*, 187–199.

Ng, H. Y. ; Elimelech, M. Influence of colloidal fouling on rejection of trace organic contaminants by reverse osmosis. *J. Membr. Sci.* **2004**, *244*, 215–226.

Nghiem, L. D.; Schäfer, A. I.; Elimelech, M. Removal of natural hormones by nanofiltration membranes: measurement, modeling, and mechanisms. *Environ. Sci. Technol*. **2004**, *38*, 1888–1896.

Nghiem, L. D.; Schäfer A. I.; Elimelech, M. Pharmaceutical retention mechanisms by nanofiltration membranes. *Environ. Sci. Technol*. **2005**, *39* (19), 7698–7705.

Ning, R. Y. Discussion of silica speciation, fouling, control and maximum reduction. *Desalination* **2002**, *151*, 67–73.

Ning, R. Y.; Troyer, T. L. Colloidal fouling of RO membranes following MF/UF in the reclamation of municipal wastewater. *Desalination* **2007**, *208*, 232–237.

National Research Council. *Review of the Desalination and Water Purification Technology Roadmap*, The National Academies Press: Washington, DC, 2004.

Ozaki, H.; H. Li. Rejection of organic compounds by ultra-low pressure reverse osmosis membrane. *Water Res*. **2002**, *36* (1), 123–130.

Peng, W.; Escobar, I. C.; White, D. B. Effects of water chemistries and properties of membrane on the performance and fouling: A model development study. *J. Membr. Sci.* **2004**, *236*, 33–46.

Reddersen, K.; Heberer, T. Multi-compound methods for the detection of pharmaceutical residues in various waters applying solid phase extraction (SPE) and gas chromatography with mass spectrometric (GC-MS) detection. *J. Sep, Sci.* **2003**, *26,*1443–1450.

Schaep, J.; Vandecasteele, C.; Mohammad, A. W.; Bowen, W. R. Modelling the retention of ionic components for different nanofiltration membranes. *Sep. Purif. Technol.* **2001**, *22–23*, 169–179.

Schäfer, A. I.; Nghiem, L. D.; Waite, T. D. Removal of natural hormone estrone for aqueous solutions using nanofiltration and reverse osmosis. *Environ. Sci. Technol*. **2003**, *37*, 182–188.

Seidel, A.; Elimelech, M. Coupling between chemical and physical interactions in natural organic matter (NOM) fouling of nanofiltration membranes: Implications for fouling control. *J. Membr. Sci*. **2002**, *203*, 245–255.

Shih, W-Y.; Rahardianto, A.; Lee, R-W.; Cohen, Y. Morphometric characterization of calcium sulfate dihydrate (gypsum) scale on reverse osmosis membranes. *J. Membr. Sci.* **2005**, *252*, 253–263.

Shirazi, S.; Lin, C-J.; Chen, D. Inorganic fouling of pressure-driven membrane processes—A critical review. *Desalination* **2010**, *250*, 236–248.

Snyder, S.; Adham, S.; Redding, A. M.; Cannon, F. S.; DeCarolis, J.; Oppenheimer, J.; Wert, E. C.; Yoon., Y. Role of membranes and activated carbon in the removal of endocrine disruptors and pharmaceuticals. *Desalination* **2007**, *202*, 156–181.

Speth , T. F.; Gusses, A. M.; Summers, R. S. Evaluation of nanofiltration pretreatments for flux loss control. *Desalination* **2000**, *130*, 31–44.

Tang, C. Y.; Kwon, Y-N.; Leckie, J. O. Fouling of reverse osmosis and nanofiltration membranes by humic acid—Effects of solution composition and hydrodynamic conditions. *J. Membr. Sci*. **2007**, *290*, 86–94.

Timmer, J. M. K. Properties of Nanofiltration Membranes, Model Development, and Industrial Application. Ph.D. Thesis, Technische Universiteit Eindhoven, The Netherlands, 2001, ISBN No. 90-386-2872-2.

Trenholm, R. A.; Vanderford, B. J.; Holady, J. C.; Rexing, D. J.; Snyder, S. Broad range analysis of endocrine disruptors and pharmaceuticals using gas chromatography and liquid chromatography tandem mass spectrometry. *Chemosphere* **2006**, *65*, 1990–1998.

Trussell Technologies, Inc. *Condition and Performance Assessment of Leo J. Vander Lans Water Treatment Facility*, Technical Memorandum—1, prepared for Water Replenishment District of Southern California, April 28, 2008.

Tsuru, T.; Nakao, S-I.; Kimura, S. Calculation of ion rejection by extended Nernst–Planck equation with charged reverse osmosis membranes for single and mixed electrolyte solutions. *J. Chem. Eng. Jpn.* **1991**, *24* (4), 511–517.

Van der Bruggen, B.; Manttari, M.; Nystrom, M. Drawbacks of applying nanofiltration and how to avoid them: A review. *Sep. Purif. Technol.* **2008**, *63*, 251–263.

Van der Bruggen, B.; Everaert, K.; Wilms, D.; Vandecasteele, C. Application of nanofiltration for removal of pesticides, nitrate and hardness from ground water: Rejection properties and economic evaluation. *J. Membr. Sci*. **2001**, *193*, 239–248.

Van der Bruggen, B.; Vandecasteele, C. Flux decline during nanofiltration of organic components in aqueous solution. *Environ. Sci. Technol*. **2002**, *35*, 3535–3540.

Vrouwenvelder, J. S.; van Passen, J. A. M.; van Agtmaal, J. M. C.; van Loosdrecht, M. C. M.; Kruitof, J. C. A critical flux to avoid biofouling of spiral-wound nanofiltration and reverse osmosis membranes: Fact or fiction? *J. Membr. Sci*. **2009**, *326*, 36–44.

Vrouwenvelder, J. S.; van der Kooij, D. Diagnosis of fouling problems of NF and RO membrane installations by a quick scan. *Desalination* **2002**, *153*, 121–124.

Wilf, M.; Alt, S. Application of low fouling RO membrane elements for reclamation of municipal wastewater. *Desalination* **2000**, *132*, 11–19.

Williams, M. E., Hestekin, J. A., Smothers, C. N., & Bhattacharyya. Separation of organic pollutants by reverse osmosis and nanofiltration membranes: Mathematical models and experimental verification. *Ind. Eng. Chem. Res*. **1999**, *38*, 3683–3695.

Xu, P.; Bellona, C.; Drewes, J. E. Fouling of nanofiltration and reverse osmosis membranes during municipal wastewater reclamation: Membrane autopsy results from pilot-scale investigations. *J. Membr. Sci*. **2010**, *353*, 111–121.

Zhao, Y.; Taylor, J., Hong, S. Combined influence of membrane surface properties and feed water qualities on RO/NF mass transfer, a pilot study. *Water Res*. **2005**, *39*, 1233–1244.

Zhao, Y.; Taylor, J. S. Modeling membrane performance over time. *J. Am. Water* **2004**, *96*, 90–97.

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