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## Assessment, Optimization, And Enhancement Of Ultrafiltration (uf) Membrane Processes In Potable Water Treatment

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ASSESSMENT, OPTIMIZATION, AND ENHANCEMENT OF ULTRAFILTRATION (UF)  
MEMBRANE PROCESSES IN POTABLE WATER TREATMENT

by

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B.S. University of Central Florida, 2009  
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A dissertation submitted in partial fulfillment of the requirements  
for the degree of Doctor of Engineering  
in the Department of Civil, Environmental, and Construction Engineering  
in the College of Engineering and Computer Science  
at the University of Central Florida  
Orlando, Florida

Spring Term  
2013

Major Professor: Steven. J. Duranceau

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## ABSTRACT

This dissertation reports on research related to ultrafiltration (UF) membranes in drinking water applications. A pilot-scale investigation identified seasonal surface water quality impacts on UF performance and resulted in the development of a dynamic chemically enhanced backwash protocol for fouling management. Subsequent analysis of UF process data revealed limitations with the use of specific flux, transmembrane pressure (TMP), and other normalization techniques for assessing UF process fouling. A new TMP balance approach is presented that identifies the pressure contribution of membrane fouling and structural changes, enables direct process performance comparisons at different operating fluxes, and distinguishes between physically and chemically unresolved fouling. In addition to the TMP balance, a five component optimization approach is presented for the systematic improvement of UF processes on the basis of TMP variations. Terms are defined for assessing process event performance, a new process utilization term is presented to benchmark UF productivity, and new measures for evaluating maintenance procedures are discussed. Using these tools, a correlation between process utilization and operating pressures was established and a sustainable process utilization of 93.5% was achieved.

UF process capabilities may be further enhanced by pre-coating media onto the membrane surface. Silicon dioxide ( $\text{SiO}_2$ ) and powdered activated carbon (PAC) are evaluated as pre-coating materials, and the applicability of the TMP balance for assessing pre-coated membrane performance is demonstrated. The first use of  $\text{SiO}_2$  as a support layer for PAC in a membrane pre-coating application is presented at the laboratory-scale.  $\text{SiO}_2$ -PAC pre-coatings successfully reduced physically unresolved fouling and enhanced UF membrane organics removal capabilities.

This dissertation is dedicated to my parents James and Anne, my brother Andrew, and my love  
Adriana. Their constant support has made this endeavor possible.

## **ACKNOWLEDGMENTS**

This work would not have been possible without the support provided by a number of individuals. Thank you to Dr. Steven Duranceau for providing the opportunity to conduct this research and contributing his time, knowledge, and experience. I would also like to thank my good friend Dr. Jayapregasham Tharamapalan for dedicating his time and effort to assist with research activities related to this dissertation. Thank you to Dr. David Cooper, Dr. Andrew Randall, and Dr. Christian Clausen for serving as committee members and donating their expertise to review this document. Additional thanks are offered to UCF research students Andrea Cumming, Nancy Holt, Nick Webber, Juan Rueda, Vito Trupiano, Genesis Rios, Shane Clark, David Yonge, and Yuming Fang who provided much appreciated assistance with laboratory tasks.

Thanks are in order for the municipalities and companies that assisted the UCF research team in this effort. The support offered by the Manatee County Utilities Department (Bradenton, FL), including Bruce MacLeod, Mark Simpson, Katherine Gilmore, Bill Kuederle, and others, greatly aided the research efforts. The support offered by the staff of the Alameda County Water District (Fremont, CA) and its Mission San Jose Water Treatment Plant is also noted and appreciated. Additional thanks are due to the team at Harn R/O Systems, Inc. (Venice, FL), including Julie Nemeth-Harn, James Harn, and Jonathan Harn. The contributions of Toyobo Co., Ltd. (Osaka, Japan), and Horizon Industries, Inc. (Las Vegas, NV) are duly noted and appreciated, as are the contributions of Microdyn Technologies, Inc (Raleigh, NC).

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## LIST OF ABBREVIATIONS

CEB – chemically enhanced backwash

CIP – clean-in-place

DOC – dissolved organic carbon

PAC – powdered activated carbon

PES – polyethersulfone

RP – residual pressure

SiO<sub>2</sub> – silicon dioxide

TCF – temperature correction factor

TCTMP – temperature corrected transmembrane pressure

TDS – total dissolved solids

TMP – transmembrane pressure

TOC – total organic carbon

TSS – total suspended solids

UF – ultrafiltration

VFD – variable frequency drive

WTP – water treatment plant



## **CHAPTER 1. GENERAL INTRODUCTION**

In March of 2010, the University of Central Florida began a two year ultrafiltration (UF) pilot test at the Lake Manatee Water Treatment Plant (WTP) in Manatee County, Florida. In September of that same year, UCF commenced a second UF pilot study at the Mission San Jose WTP in Fremont, California. The Lake Manatee and Mission San Jose WTPs were identified as excellent pilot test locations, because the facilities treated two distinctly different surface waters. The Lake Manatee WTP treats water from the Lake Manatee Reservoir with alum coagulation, flocculation, sedimentation, and periodic powdered activated carbon (PAC) dosing for seasonal taste and odor events. In contrast, the Mission San Jose WTP practices ferric chloride coagulation with up-flow solids contact clarifiers to treat water from the Sacramento delta.

UF technology offers significant possibilities for meeting anticipated water supply challenges in the coming years, and the pilot test projects provided an opportunity to evaluate concepts for the improvement of UF treatment capabilities. The research presented in this dissertation focuses on methods for improving the efficiency of UF processes, including the implementation of dynamic cleaning protocols, the provision of new tools for UF membrane performance evaluations, and the optimization of UF processes for improved filtrate production. In conjunction with the goal of improving UF process capabilities, a literature review was conducted to identify alternative applications for UF membranes in drinking water treatment. The pre-coating of UF membranes was identified as an emerging area of research offering the potential to both improve contaminant removal and reduce membrane fouling. Accordingly, laboratory scale experiments were performed to evaluate a new concept for the pre-coating of UF membranes.

## **CHAPTER 2. ASSESSING AND MAINTAINING MEMBRANE PERFORMANCE IN A POST-SEDIMENTATION ULTRAFILTRATION PROCESS**

The following information has been published in the peer-reviewed journal *Water Practice & Technology*:

Boyd, C. C., & Duranceau, S. J. (2012). Assessing and maintaining membrane performance in a post-sedimentation ultrafiltration process. *Water Practice & Technology*, 7(2). doi: 10.2166/wpt.2012.041

### 2.1. Abstract

A pilot test program was conducted to evaluate methods for maintaining the productivity of a hollow fiber ultrafiltration membrane operating at constant flux values of 49.2 and 62.3 gallons/ft<sup>2</sup>-day. The ultrafiltration pilot filtered settled water from a conventional surface water treatment plant in Florida. The testing assessed the impact of different chemical maintenance protocols on UF membrane performance. Seasonal variations in water quality necessitated changes in the type and combination of cleaning agents used to maintain membrane performance. Sodium hypochlorite, citric acid, and sodium hydroxide were used during pilot testing as the fouling characteristics of the water changed with time. Pilot results were used to develop alternative chemically enhanced backwash strategies that varied with seasonally-impacted changes in feed water quality. Citric acid, with a target pH of < 3, was found to be effective in August and September; whereas, a combination of citric acid and sodium hydroxide chemically enhanced backwashes successfully maintained performance between November, 2010 and May, 2011.

## 2.2. Introduction

Ultrafiltration (UF) is a membrane process that separates suspended solids from water streams, similar to conventional media filters. However, UF membrane filtration is also capable of effectively removing colloidal, microbiological, and particulate matter much smaller than conventional filters are capable of removing. UF membranes can consistently produce filtered water with turbidity values below 0.05 NTU (Duranceau & Taylor 2011). As a result, UF technology has gained acceptance within the drinking water community for use in treating surface water supplies in the production of drinking water. Because the quality of the source water treated by UF technology affects membrane performance, pilot studies are required to optimize membrane process operating parameters (American Water Works Association Research Foundation et al., 1996).

This document describes the results of a UF membrane pilot test conducted at the Lake Manatee Water Treatment Plant (WTP) in Manatee County, Florida. The pilot test was conducted to evaluate the performance of a hollow fiber UF membrane manufactured by Toyobo Co., Ltd. (Durasep UPF0860, Osaka, Japan) for producing drinking water from a difficult-to-treat, highly-organic, and variable Florida surface water supply. Membrane cleaning requirements were investigated to develop guidelines for chemical cleaning via chemically enhanced backwashes (CEBs). Surface water in Florida is known for being low in total hardness, microbially-active, warm, and highly organic in nature. These water quality characteristics represent significant daily challenges to conventional treatment plant operations.

The Lake Manatee WTP is owned and operated by the Manatee County Utilities Department (Bradenton, Florida) and treats surface water using a conventional treatment process that

includes alum coagulation, flocculation, sedimentation, media filtration, and disinfection. At the head of the treatment works, the utility doses powdered activated carbon (PAC) as needed for the removal of taste and odor compounds. Surface water then flows into rapid mix basins where alum and lime are added in varying amounts to facilitate coagulation. A polymer is then added during flocculation to promote the formation of a flocculant that will settle. Following sedimentation, water is dosed with additional lime for pH adjustment and a small dose of chlorine before flowing into filter beds to facilitate the removal of unsettled particles. Because the Lake Manatee WTP also treats a hard groundwater supply, filter bed effluent is blended with lime-softened groundwater before final disinfection with chloramines, corrosion prevention, and hydrofluorosilicic acid addition prior to distribution to its drinking water system (Manatee County Utilities Department, 2009).

### 2.3. Pilot Description and Methods

The UF pilot, designed by Harn R/O Systems, Inc. (Venice, Florida), incorporates one Toyobo Durasep UPF0860 hollow fiber UF membrane operated in an inside-out direct configuration. Toyobo's Durasep membrane fibers are composed of hydrophilic polyethersulfone (PES) blended with polyvinylpyrrolidone. The UF hollow fiber membrane has an outside fiber diameter of 1.3 mm (0.051 inches) and an inside fiber diameter of 0.8 mm (0.031 inches) with an average pore size diameter of 0.01  $\mu\text{m}$  offering 150,000 dalton cutoff. The pilot is automated and equipped with onboard pressure gauges and transmitters, feed and backwash pumps with variable frequency drives (VFDs), feed and filtrate turbidity meters, flow meters, a particle counter, two chemical feed systems, water sample taps, and an air compressor for pneumatic valve operation. Data is logged by the pilot at two minute intervals to facilitate data analysis and

pilot evaluation. A touch screen user interface allows for the configuration of pilot operating parameters and the monitoring of pilot status.

The feed water for the UF pilot is drawn from sedimentation basin effluent by siphon into a 200 gallon tank that serves as a feed water reservoir for the pilot. The filtrate stream is stored in a 1,000 gallon tank for use during backwash cycles. Two parallel strainers provide pretreatment of the feed water for removal of large diameter particles and debris. The photograph presented in Figure 2-1 provides several views of the UF pilot both before and after installation at the Lake Manatee WTP.

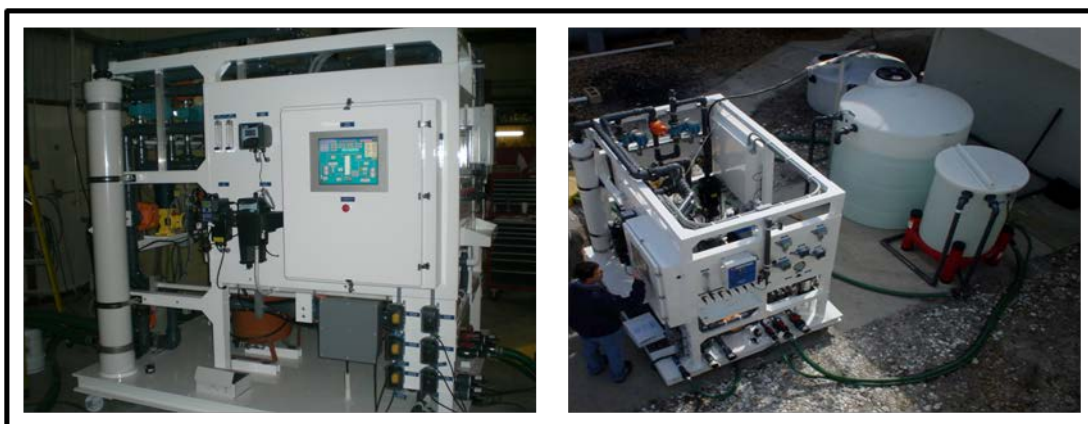


Figure 2-1 UF Pilot during Construction (left) and Installed at the Lake Manatee WTP (right)

During normal operation, the UF pilot cycles between forward filtration, backwash, and CEB operation modes in a user defined sequence. The pilot actively filters feed water during a forward filtration event producing a filtrate stream. Regular backwashes remove matter that has collected on the fiber surface. During backwashes, filtrate is first pumped through the feed side of the membrane and then through the filtrate side of the membrane at a flux three times greater than the forward filtration flux. At specified intervals, the pilot performs a CEB. During a CEB, a

chemical such as sodium hypochlorite or citric acid is injected into the backwash stream to remove a targeted foulant, allowed to soak on the membrane fibers, and then rinsed prior to the restart of forward filtration.

The pilot test plan required evaluation of UF membrane performance at different flux rates, backwash frequencies, and cleaning schedules to determine a suitable operating condition for the consistent production of filtrate with turbidity values below 0.1 NTU. This paper presents selected results from the pilot test at moderate and high filtration flux rates of 49.2 and 62.3 gallons/ft<sup>2</sup>-day. Table 2-1 provides a summary of the forward filtration and backwash operating parameters for each flux case. UF membrane performance was assessed by monitoring trends in specific flux and transmembrane pressure (TMP). The calculation of specific flux was carried out in accordance with guidelines in Water Treatment Principles and Design (MWH, 2005). Flux values were corrected to 20 °C using a generic temperature correction factor equation. Prior to graphing, a statistical analysis and hourly averaging of the data was performed.

Table 2-1 Summary of Pilot Test Operating Parameters

<b>Flux Case</b>	<b>Process</b>	<b>Water Flux (gal/ft<sup>2</sup>-day)</b>	<b>Water Flow (gal/min)</b>	<b>Duration (min)</b>
Moderate	Filtration	49.2	14.7	30.0
	Backwash	147.6	44.1	1.0
High	Filtration	62.3	18.6	30
	Backwash	186.9	55.8	1.0

#### 2.4. Results and Discussion

Successful membrane cleaning depends on foulant type, chemical type, contact time, flow rate, chemical concentration, and cleaning solution temperature (Zondervan & Roffel, 2007).

Although common cleaning chemicals include citric acid, sodium hypochlorite, and sodium hydroxide, the selection of cleaning agents is often a trial and error process (Strugholtz et al., 2005). Pilot testing is highly recommended to identify cleaning requirements for UF processes filtering surface waters. A significant amount of research has focused on understanding foulants and fouling mechanisms on membrane surfaces; however, Porcelli & Judd (2010) concluded that an understanding of chemical cleaning is not well developed and that there is significant room for further research in this area. The research presented herein focuses on the assessment of chemical protocols to maintain UF membrane performance.

Quantifying changes in water quality allows for the development of correlations between membrane performance and potential foulants. A typical pilot scale water quality monitoring plan includes the collection of pH, temperature, conductivity, total suspended solids (TSS), total dissolved solids (TDS), turbidity, alkalinity, total organic carbon (TOC), and dissolved organic carbon (DOC) data. For the treatment of settled surface water, as is the case at the Lake Manatee WTP, seasonal variations in water quality should be taken into account for the development of UF process operating protocols. Depending on the feed water quality being fed to the UF membrane, modifications may need to be made to operational parameters such as the backwash frequency, CEB frequency, or CEB chemical. Figure 2-2 graphically presents water quality data for both raw lake water and sedimentation basin effluent between August, 2010 and May, 2011. The figure demonstrates the influence that seasonal changes have on surface water quality.

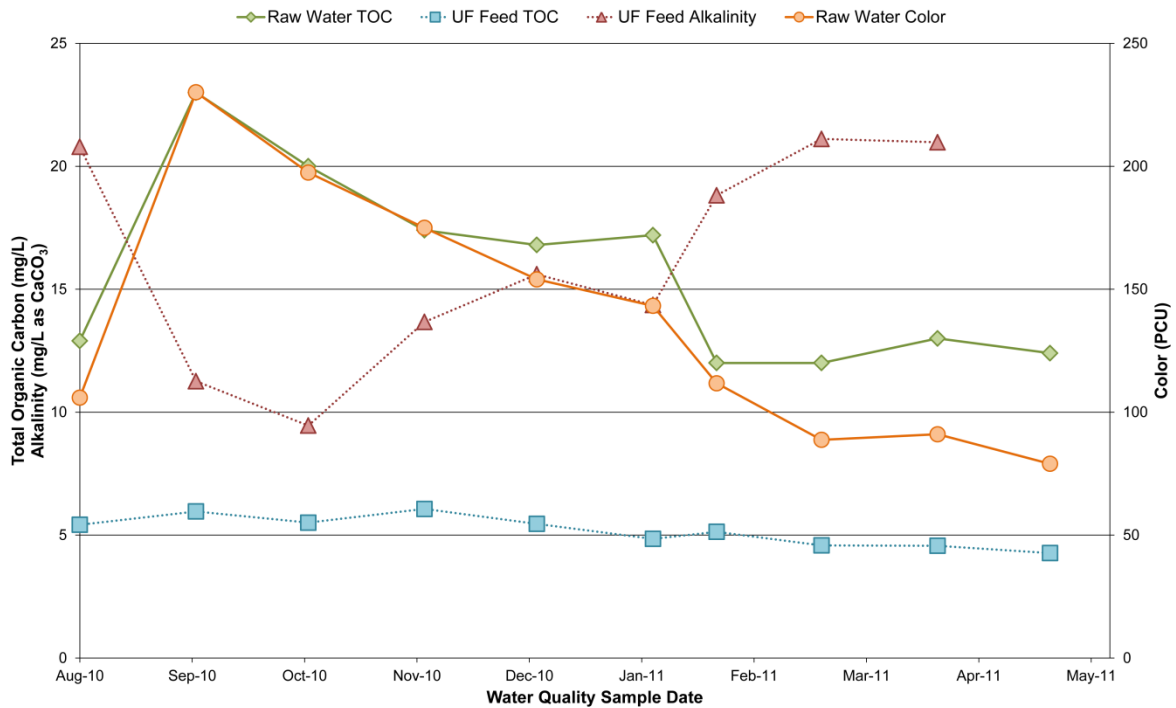


Figure 2-2 Water Quality Data (August, 2010 – May, 2011)

Variations in surface water quality during pilot testing required changes in CEB protocols to adapt to different fouling scenarios. Table 2-2 provides a summary of the CEB sequences used between August, 2010 and May, 2011. This table illustrates the complexity of identifying viable cleaning strategies for UF membranes in surface water applications. Sodium hypochlorite, citric acid, and sodium hydroxide cleaning agents were tested during pilot operations. Citric acid was found to be the most effective cleaning chemical from August through late September; whereas, a combination of citric acid and sodium hydroxide CEBs proved successful at maintaining membrane performance from November through May, 2011.

Figures 2-3 and 2-4 provide UF membrane performance and chemical maintenance data from August, 2010 through January, 2011. The UF pilot was operated at a constant flux of 49.2 gal/ft<sup>2</sup>-day during this period. Figure 2-3 presents the specific flux and TMP values recorded for the UF



pilot following a citric acid chemical cleaning-in-place (CIP) that was successful at removing a calcium foulant. The calcium foulant, which had deposited on the membrane surface during the first 80 days of UF pilot runtime, was most likely the result of lime addition in the sedimentation basin post mix. Regular citric acid CEBs were implemented in August and September with a target pH of < 3. The citric acid chemical maintenance protocol successfully maintained membrane performance at an average specific flux of 28.2 gal/ft<sup>2</sup>-day-psi.

Table 2-2 Summary of UF Pilot Test CEB Chemical Use

<b>Pilot Test Window</b>	<b>Flux</b>	<b>CEB Chemical(s)</b>	<b>Effective</b>
Aug. – Sept., 2010	49.2 gal/ft <sup>2</sup> -day	Citric Acid	Yes
Oct., 2010	49.2 gal/ft <sup>2</sup> -day	Citric Acid/Sodium Hypochlorite	No
Nov., 2010 – Jan., 2011	49.2 gal/ft <sup>2</sup> -day	Citric Acid/Sodium Hydroxide	Yes
Dec., 2010	49.2 gal/ft <sup>2</sup> -day	Citric Acid	No
Feb. - May, 2011	62.3 gal/ft <sup>2</sup> -day	Citric Acid/Sodium Hydroxide	Yes
Mar., 2011	62.3 gal/ft <sup>2</sup> -day	Sodium Hydroxide	No

Stable operation was observed with citric acid CEBs until the latter part of September, when citric acid alone proved insufficient to clean the UF membrane fibers. A combination of citric acid and sodium hypochlorite CEBs was attempted in October with a target sodium hypochlorite residual of 100 mg/L. However, membrane performance did not recover appreciably. Figure 2-3 depicts the decline in UF membrane performance observed in late September and October. During this period, the TMP increased to approximately 3.35 psi with a corresponding decrease in specific flux to 12.6 gal/ft<sup>2</sup>-day-psi.

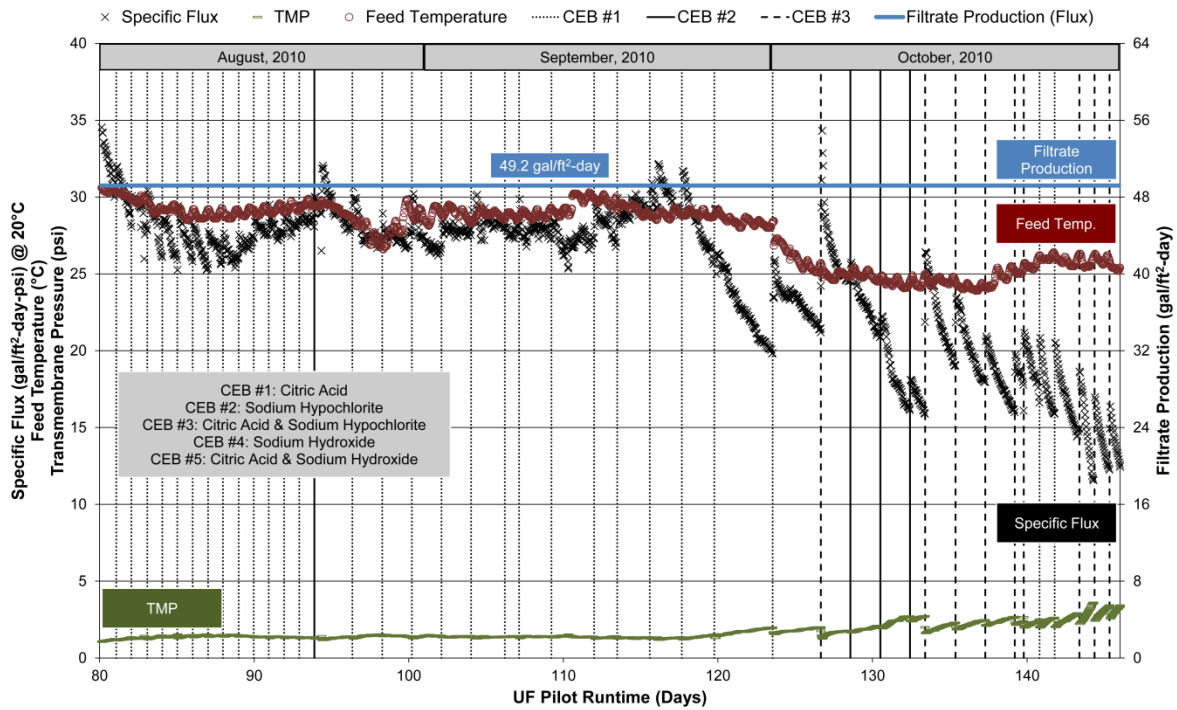


Figure 2-3 UF Pilot Performance Chart (August – October, 2010)

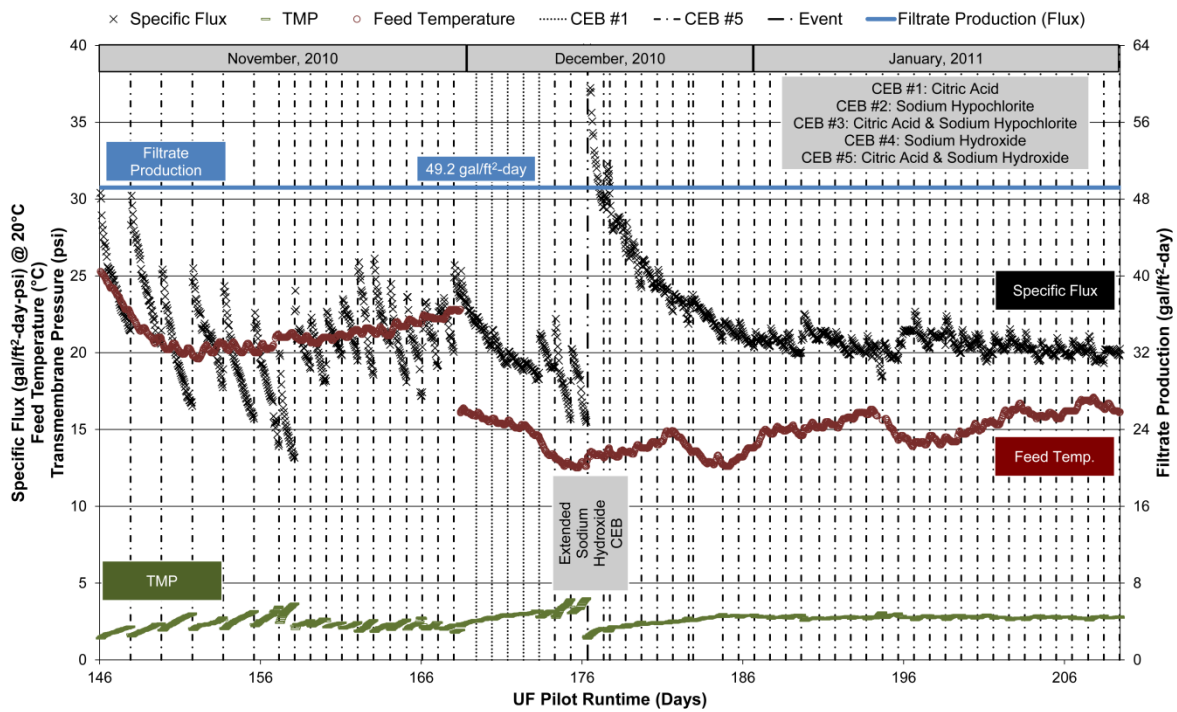


Figure 2-4 UF Pilot Performance Chart (November, 2010 – January, 2011)

In early November, the sodium hypochlorite cleaning solution was phased out in favor of sodium hydroxide to provide a high pH cleaning environment during chemically enhanced backwash cycles. The sodium hydroxide CEB step improved pilot performance as evidenced by the stabilization of specific flux trends in January. Figure 2-4 presents the performance chart for the UF pilot between November, 2010 and January, 2011. Average hourly TMP values ranged between approximately 1.39 and 3.99 psi with an average specific flux of 21.4 gal/ft<sup>2</sup>-day-psi. A CEB interval of once per two days was tested initially, but declines in specific flux prompted a change to a once per day citric acid and sodium hydroxide CEB sequence. The target pH for sodium hydroxide CEBs was 11. A citric acid only CEB sequence was tested briefly in December but proved ineffective at restoring membrane performance.

The high flux phase of the pilot test began in late January of 2011 at 62.3 gal/ft<sup>2</sup>-day. Increased fouling rates were anticipated at the higher operating flux, so the once per day CEB maintenance protocol was continued from the previous testing scenario. Figure 2-5 presents the 81 days of runtime recorded for the high flux case. For the majority of testing, the UF membrane was successfully maintained with a citric acid and sodium hydroxide CEB sequence at an average specific flux of 19.7 gal/ft<sup>2</sup>-day-psi. However, in the middle of March, a once per day sodium hydroxide CEB sequence was attempted to identify the contribution of sodium hydroxide to membrane cleaning. The sodium hydroxide CEB sequence failed to maintain pilot performance alone, and the citric acid and sodium hydroxide CEB sequence was resumed.

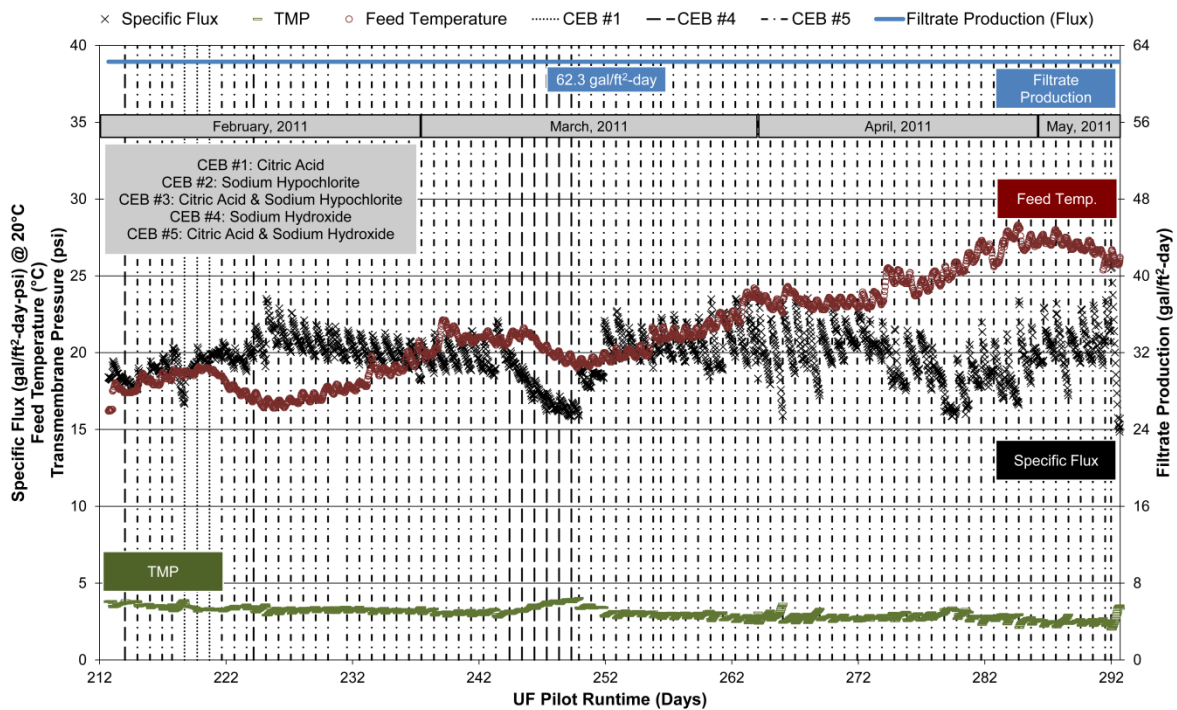


Figure 2-5 UF Pilot Performance Chart (February – May, 2011)

## 2.5. Conclusions

The operation of UF processes downstream of conventional coagulation, flocculation, and sedimentation basins poses challenges for maintaining membrane performance. The quality of water in contact with the membrane surface is a function of surface water characteristics and the performance of upstream unit operations and processes. Pilot test plans should include an investigation of the cleaning frequency, chemical type(s), and chemical concentration(s) required to maintain stable operation as water quality changes seasonally. Although it has been reported that municipalities do not require one year of pilot testing to demonstrate UF technology (American Water Works Association, 2005), this work demonstrates that a significant amount of pilot testing is required to identify the impact of seasonal water quality changes on UF membrane performance.

In order to optimize UF process performance, cleaning protocols should be adaptable to changing water quality conditions. The CEB chemical or chemical combination that provides effective cleaning in the summer may be ineffective in the fall months. Customizing cleaning protocols for different water quality conditions may limit the unnecessary use of chemicals and improve UF process performance. Sodium hypochlorite, citric acid, and sodium hydroxide CEBs were used during pilot testing at the Lake Manatee WTP to varying degrees of success. Citric acid, with a target pH of  $< 3$ , was found to be effective in August and September; whereas, a combination of citric acid and sodium hydroxide CEBs successfully maintained performance between November, 2010 and May, 2011.

## 2.6. Acknowledgments

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## **CHAPTER 3. MEMBRANE FILTRATION PROCESS FOULING EVALUATION USING A NOVEL TRANSMEMBRANE PRESSURE (TMP) BALANCE APPROACH**

### 3.1. Abstract

The successful operation of membrane processes is dependent on the ability to quantitatively assess process performance on a continuous basis, because membrane fouling reduces process efficiency and results in increased operation and maintenance costs. A review of current methods for performance monitoring revealed limitations with the use of specific flux, transmembrane pressure (TMP) and other normalization techniques on ultrafiltration (UF) membrane processes. A new and alternative benchmark, termed the TMP balance, is presented to supplement existing membrane fouling evaluation approaches. The TMP balance defines process performance in terms of TMP changes relative to a reference condition in order to easily identify pressure variations associated with membrane fouling and morphology changes. TMP balance values may be used to distinguish between physically and chemically unresolvable resistance developments, assess operating pressure requirements, and compare process performance at different constant flux set-points. A demonstration of the TMP balance approach is provided using over 9000 hours of runtime data from two surface water UF pilots, and a comparison is made between the TMP balance and current fouling assessment methods.

Key Words: Balance, Fouling, Membrane, Performance, TMP

### 3.2. Introduction

Ultrafiltration (UF) membrane processes are separation processes that provide a physical barrier to aqueous particles (United States Environmental Protection Agency, 2005) and typically operate over a low pressure range of less than 1.03 bar (15 psi) (MWH, 2005). Membrane separation processes have a broad range of industrial and municipal applications including the filtration of water for potable use (Buckley & Hurt, 1996). A common role of UF membranes in water treatment is the filtration of surface water. Surface water sources contain a variety of contaminants harmful to human health, and membrane filtration may be incorporated into a multiple-barrier treatment approach to improve drinking water quality (Shannon et al., 2008).

Fouling is one of the major operating challenges for membrane processes, and the management of fouling is critical for maintaining sustainable water production. One important facet of fouling management is the monitoring of process performance. An investigation of the commonly used performance monitoring methods revealed limitations with the use of specific flux and other normalization techniques on low pressure membrane processes. Accordingly, there is a need for a new method to evaluate membrane performance. This paper reports on the development of the TMP balance approach, which defines process performance in terms of changes in TMP relative to a reference condition.

### 3.3. Background

#### 3.3.1. Operational Considerations for Membrane Filtration Processes

UF membranes may be operated using a constant pressure or constant flux approach in either a cross-flow or direct flow regime. During constant pressure operation, membrane fouling results



in flux decline; whereas, in constant flux processes, fouling manifests as increased operating pressure. The cross-flow mode of filtration involves the recycle of a percentage of the total feed flow, which creates shear forces along the fiber surface and reduces fouling (Wiesner & Chellam, 1992). Direct filtration is more commonly used, because the total feed flow is filtered through the membrane thereby increasing the efficiency of the process. For full-scale water treatment, constant flux operation with a direct flow regime is a common operating approach (Lee et al., 2008).

Fouling, whether organic, inorganic, colloidal, particulate, or biological, limits the operating efficiency of membrane filtration processes. Extensive research has been conducted on membrane fouling to elucidate the mechanisms by which fouling occurs (Lee et al., 2004; Kwon et al., 2005; Peiris et al., 2010; Gao et al., 2011), and the ability to manage membrane fouling determines the applicability of membrane filtration processes to specific water sources. Common approaches to fouling management include the incorporation of pretreatment processes and selection of operating set-points. Coagulation, pre-oxidation, adsorption, and ion exchange are possible pretreatment choices depending on the source water quality (Huang et al., 2009). The selection of operating flux and backwash frequency also play an important role in the fouling rates of polymeric membranes (Chen et al., 2003; Kim & DiGiano, 2006; Bacchin et al., 2006; Mosqueda-Jimenez et al., 2008). Regardless of the fouling management techniques employed, membrane fouling ultimately develops during the filtration of natural waters, and such fouling requires chemical removal (Yuan & Zydney, 2000; Katsoufidou et al., 2008). The chemical maintenance of membrane processes is conducted with either chemically enhanced backwashes (CEBs) or clean-in-place (CIP) procedures, and foulant removal is dependent on foulant type,

chemical selection, contact time, concentration, flow rate, and temperature (Strugholtz et al., 2005; Zondervan & Roffel, 2007; Porcelli & Judd, 2010). Cleaning chemicals may be categorized as either caustic, oxidant, acid, chelating, or surfactant type agents (Liu et al., 2006).

### 3.3.2. Common Approaches to Assessing Membrane Performance

In UF processes, a pressure (P) gradient develops across the porous membrane barrier during filtration. This pressure gradient, referred to as the transmembrane pressure (TMP), may be calculated by Equations 3-1 or 3-2 for direct or cross-flow operation, respectively. TMP values are influenced by the membrane material, fouling development, and water temperature. A temperature correction factor (TCF) may be utilized to account for the effects of water viscosity by normalizing to a standard temperature. For low pressure membrane filtration processes, the standard temperature is typically 20 °C. Manufacturers often develop membrane specific TCFs that account for both the influence of temperature on water viscosity and the membrane material (Duranceau & Taylor, 2011).

$$TMP = P_{feed} - P_{filtrate} \quad (3-1)$$

$$TMP = \frac{P_{feed} + P_{retentate}}{2} - P_{filtrate} \quad (3-2)$$

Where,

$P_{feed}$  is the UF feed pressure, bar (psi)

$P_{filtrate}$  is the UF filtrate pressure, bar (psi)

$P_{retentate}$  is the UF retentate pressure, bar (psi)

In constant flux operation, the process response to increased flow resistance is an increase in the TMP. Laboratory experiments often use TMP to investigate phenomena under controlled conditions at constant temperature (Liu et al., 2011; Zhang et al., 2012), and pilot scale investigations have employed TMP to evaluate process performance (Panglisch et al., 1998; Halpern et al., 2005; Neubrand et al., 2010). TMP values may also be temperature corrected to account for temperature variations in natural waters (United States Environmental Protection Agency, 2005; Oriol et al., 2012). In the absence of a membrane specific TCF, generic TCFs may be employed. Equation 3-3 utilizes a ratio of absolute viscosity values to calculate the temperature corrected TMP (TCTMP).

$$TCTMP_{20^{\circ}C} = TMP_T(TCF) = TMP_T \left( \frac{\mu_{20^{\circ}C}}{\mu_T} \right) \quad (3-3)$$

Where,

$TCTMP_{20^{\circ}C}$  is the TMP temperature corrected to 20°C, bar (psi)

$TMP_T$  is the TMP at temperature T, bar (psi)

$\mu_{20^{\circ}C}$  is the absolute viscosity at 20°C, cp (lb/ft-s)

$\mu_T$  is the absolute viscosity at temperature T, cp (lb/ft-s)

Membrane performance during constant pressure operation may be assessed by monitoring trends in the volumetric flux. Equation 3-4, which is a modified form of Darcy's law, calculates the clean water volumetric flux for a new membrane (American Water Works Association, 2005). Further modification to the flux equation may be made to incorporate the resistance contributions of membrane fouling mechanisms using the resistance-in-series model. A variety

of membrane related research utilizes the resistance-in-series approach to quantify membrane performance, such as membrane fouling and chemical cleaning studies (Cho et al., 2000; Zondervan & Roffel, 2007; Kimura et al., 2008). Equation 3-5 includes resistance terms for pore adsorption ( $R_a$ ), pore blocking ( $R_b$ ) and cake formation ( $R_c$ ). Flux values may also be corrected to a set of standard conditions (Howe & Clark, 2002; ASTM International, 2005) using Equation 3-6.

$$J_T = \frac{Q}{A} = \frac{TMP_T}{\mu(R_M)} \quad (3-4)$$

$$J_T = \frac{Q}{A} = \frac{TMP_T}{\mu(R_M + R_a + R_b + R_c)} \quad (3-5)$$

$$J_{20^\circ C} = \frac{(TMP_{20^\circ C})(TCF)}{(TMP_T)} (J_T) \quad (3-6)$$

Where,

$J$  is the volumetric flux,  $L/m^2$ -hr (gal/ft<sup>2</sup>-day)

$A$  is the membrane surface area, m<sup>2</sup> (ft<sup>2</sup>)

$R_M$  is the intrinsic membrane resistance, m<sup>-1</sup> (ft<sup>-1</sup>)

$R_a$  is the pore adsorption resistance, m<sup>-1</sup> (ft<sup>-1</sup>)

$R_b$  is the pore blocking resistance, m<sup>-1</sup> (ft<sup>-1</sup>)

$R_c$  is the cake formation resistance, m<sup>-1</sup> (ft<sup>-1</sup>)

$J_{20^\circ C}$  is the volumetric flux at standard temperature and pressure,  $L/m^2$ -hr (gal/ft<sup>2</sup>-day)

$J_T$  is the volumetric flux at temperature  $T$ ,  $L/m^2$ -hr (gal/ft<sup>2</sup>-day)

TMP<sub>20°C</sub> is the transmembrane pressure at the standard condition, bar (psi)

The specific flux ( $J_{SP}$ ), or membrane permeability, normalizes the flux for temperature and pressure as shown in Equation 3-7. Pilot-scale investigations typically utilize the specific flux to identify fouling associated with the treatment of natural waters (Crozes et al., 1997; Panglisch et al., 1997; Chellam et al., 1998), and calculation of the specific flux is commonly used for full-scale process performance assessments (American Water Works Association, 2005; MWH, 2005).

$$J_{SP} = \frac{(J_T)(TCF)}{TMP} \quad (3-7)$$

Where,

$J_{SP}$  = the specific flux, L/m<sup>2</sup>-hr-bar (gal/ft<sup>2</sup>-day-psi)

### 3.3.3. Limitations of Specific Flux and TMP

There are limitations with the use of specific flux and TMP for characterizing the performance of low pressure UF processes. Figure 3-1 presents the relationship between specific flux and TMP between 0.070 and 1.03 bar (1.00 and 15.0 psi), which is the typical operating TMP range for membrane filters (MWH, 2005). Specific flux values decrease exponentially with increasing TMP over this pressure range, and the non-linearity of the specific flux term means that small changes in TMP result in disproportionate changes to the specific flux. As a result, the specific flux exaggerates the extent of membrane fouling for low pressure processes.

A variety of operating decisions are based on TMP. For example, TMP is often used to select backwash and cleaning intervals for fouling management, and TCTMP may be used to evaluate

long term process performance at a constant flux. However, TMP values have limited applicability for comparing fouling trends with constant flux processes at different flux set-points, because the magnitude of the TMP is influenced by both the volumetric flux and foulant deposition.

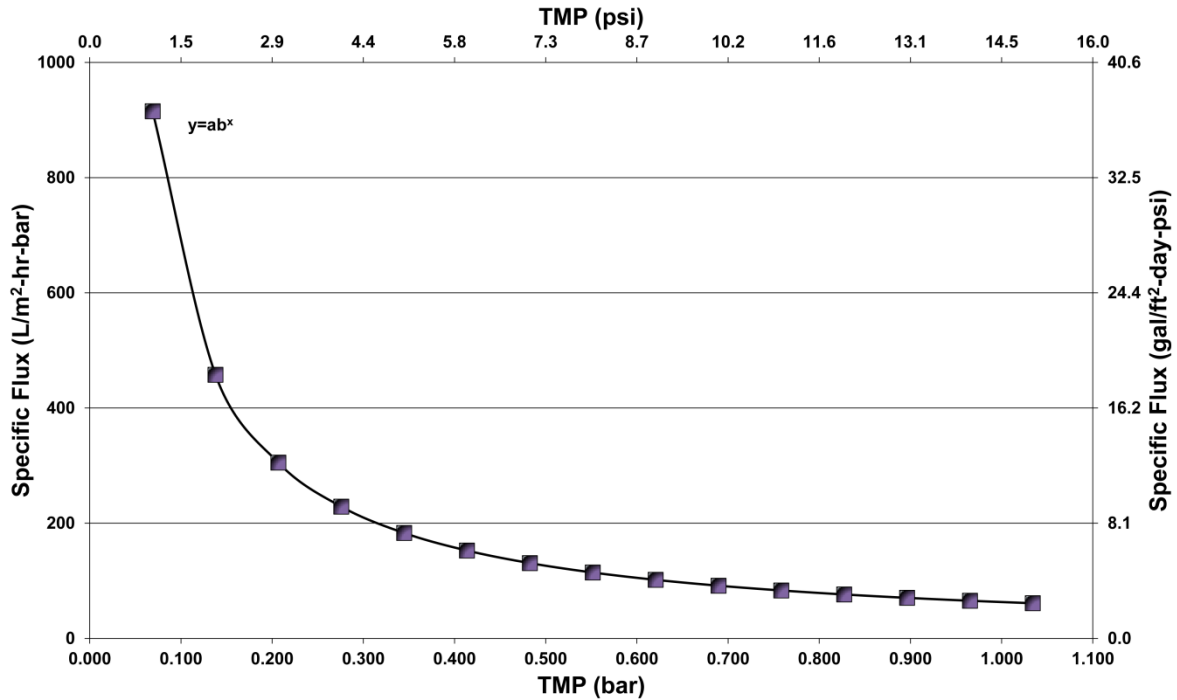


Figure 3-1 Relationship between Specific Flux and TMP

There are a variety of ways to present specific flux and TMP data. For example, specific flux and TMP values may be reported after a physical or chemical maintenance procedure (i.e. backwash or CEB) to assess the fouling condition of the membrane. However, this method of reporting does not indicate the magnitude of the historical performance change for the process unless compared to a reference value. Specific flux or TMP values may also be averaged over time, but this method of reporting only provides a measure of the central tendency of the data. Normalizing the specific flux or TMP by calculation of  $J_{SP}/J_{SP0}$  or  $TMP/TMP_0$ , where  $J_{SP0}$  and

TMP<sub>0</sub> are reference values, exaggerates the extent of membrane fouling. This observation is evidenced by a comparison between these ratios at low and high TMP values. For example, a TMP increase from 0.070 to 0.345 bar (1.00 to 5.00 psi) represents a 400% change in the TMP/TMP<sub>0</sub> ratio at a reference pressure of 0.070 bar (1.00 psi). However, a 0.345 bar (5.00 psi) increase from 5.52 to 5.86 bar (80.0 to 85.0) psi represents a 6.25% change in TMP/TMP<sub>0</sub> at a reference pressure of 5.52 bar (80.0 psi). Accordingly, it is apparent that the utility of existing evaluation techniques would be enhanced by the introduction of a new benchmark for assessing membrane performance.

### 3.4. Materials and Methods

#### 3.4.1. Pilot Test Plan

Pilot-scale UF tests were conducted at two surface water treatment plants (WTPs) in the United States to assess the treatability of settled surface water using hollow-fiber UF membranes. At each facility, a pilot unit was placed downstream of full-scale coagulation-flocculation-sedimentation pretreatment basins. One of the primary goals of the testing was to assess the impacts of changing water quality conditions on membrane filtration performance. Different flux values and chemical maintenance protocols were evaluated to identify sustainable operating configurations.

#### 3.4.2. Test Locations

##### 3.4.2.1. Lake Manatee WTP

The Lake Manatee WTP in Manatee County, Florida, which is operated by the Manatee County Utilities Department, was selected as the first pilot testing site. The facility practices alum

coagulation for the removal of organics from the Lake Manatee Reservoir. An organic polymer is added during flocculation to promote the formation of a settleable floc, and the settled water is pH adjusted with lime as needed. Additionally, a maintenance dose of chlorine is added in the post-mix to limit algae growth on the basin walls. During seasonal taste and odor events, powdered activated carbon is added to the raw water prior to coagulation.

#### 3.4.2.2. Mission San Jose WTP

The second pilot unit was located at the Alameda County Water District's (ACWD's) Mission San Jose WTP in Fremont, California. The Sacramento Delta serves as the primary feed water source for the Mission San Jose WTP, and water from nearby Lake Del Valle is periodically blended on an as needed basis. The facility practices ferric chloride coagulation using up-flow solids contact clarifiers. Raw water is pre-chloraminated prior to ferric chloride injection.

#### 3.4.3. Membrane Description

Pilot testing was conducted with Durasep UPF0860 inside-out hollow fiber UF membranes manufactured by Toyobo CO., Ltd. The hydrophilic Durasep membranes are composed of polyvinylpyrrolidone–modified polyethersulfone (PES) with an active surface area of 40 m<sup>2</sup> (430 ft<sup>2</sup>). The membrane fibers have an outside fiber diameter of 1.3 mm (0.051 in) and an inside fiber diameter of 0.8 mm (0.031 in) with an average pore diameter of 0.01 μm (3.94x10<sup>-7</sup> in) providing an approximate 150,000 dalton cutoff.

#### 3.4.4. UF Pilot Units

The Manatee County and ACWD UF pilot units were automated and each incorporated one membrane module. Feed and filtrate turbidity meters, pressure transmitters, and flow meters



were installed to record process data on both pilots. Feed and backwash pumps equipped with variable frequency drives supplied water to the units, and pneumatic valves controlled the direction of flow. Two chemical feed systems, consisting of separate chemical tanks and pumps, were installed on each pilot for chemical maintenance procedures.

#### 3.4.5. UF Pilot Operations

The pilot units were operated as constant flux processes in a direct filtration mode. In accordance with pilot test plans prepared for each location, the units cycled between filtration, backwash, and CEB events. Filtrate was collected in a tank to provide water for backwashes and CEBs. During backwashes, filtrate was first pumped out the bottom and then out the top of the module at a flux equal to three times the filtration flux. The CEB process involved an injection of chemical during a backwash, followed by a 10 minute soak, and concluding with a rinse. The CEB chemicals evaluated during testing included sodium hypochlorite, sodium hydroxide, and citric acid. In the event of a CIP, additional equipment was brought in to allow for the recirculation of cleaning chemicals.

#### 3.4.6. Method of Data Compilation

The UF pilot units recorded operating data at 2 minute intervals. For the purposes of the performance evaluations, pressure, temperature, and flow data were compiled and assigned runtime values. Data points beyond +/- 3 standard deviations from adjacent points were filtered out of the data set to account for measurements taken during transition periods. Transition periods were defined as the intervals of time between filtration, backwash, or CEB events when

data was logged prior to flux stabilization. The filtered data sets were then used for subsequent calculations.

### 3.5. Results and Discussion

#### 3.5.1. Development of the TMP Balance Equation

During the normal operation of membrane filtration processes, the resistance to flow is dynamic with respect to time, and the total resistance is determined by both the physical membrane material and the accumulation of foulants at the liquid-membrane interface. Since the TMP is a function of the total resistance, the condition of the membrane filters may be described by changes in the TCTMP. Based on this principle, a new approach, termed the TMP balance, was developed that utilizes TCTMP variations to quantify membrane fouling and structural changes related to filtration events, backwashes, CEBs, CIPs, and flux changes.

In order to assign meaning to the TMP balance, presented as Equation 3-8, it is necessary to correlate TMP balance values with the operating history of the process. Accordingly, the factors that influence the TMP balance are organized into operating sequences ( $J$ ), cycles ( $K$ ), and periods ( $L$ ), as illustrated in Figure 3-2. An operating sequence consists of consecutive filtration and backwash events; whereas, an operating cycle is comprised of a series of sequences culminating in a CEB. Operating periods conclude with a CIP event and generally consist of many operating cycles. Further classification of TMP balance data may be made according to the flux case ( $M$ ) if the flux set-point is changed during operation. This nomenclature allows for TMP balance values to be chronologically organized according to process events. For example,

TMP balance<sub>2,1,1,1,1</sub> represents the TMP balance subsequent to two TMP measurements during the first sequence, cycle, period, and flux case of operation.

$$TMP\ Balance_{ijklm} = \Delta Reference + \left( \sum_{m=1}^M \sum_{l=1}^{L_m} \sum_{k=1}^{K_{lm}} \sum_{j=1}^{J_{klm}} \sum_{i=1}^{n_{jklm}} (TCTMP_{i+1,jklm} - TCTMP_{ijklm}) \right) + \sum_{m=1}^M \Delta Flux_m \quad (3-8)$$

Where,

Subscript *i* refers to the TCTMP value

Subscript *j* refers to the sequence number

Subscript *k* refers to the cycle number

Subscript *l* refers to the period number

Subscript *m* refers to the flux case number

An important step in the calculation of the TMP balance is to select the reference condition. A reference pressure may be chosen based on the criteria of the evaluator and should generally coincide with the TCTMP value for an acclimated process near optimum performance. The TCTMP for a clean membrane is a good reference condition; however, in the absence of a clean membrane, the startup condition or a condition of acceptable performance may be used. If the first value in a data set is not the reference pressure, the  $\Delta Reference$  term must be calculated to account for the difference between the starting value and the reference pressure. This is done so that a zero TMP balance represents the resistance observed at the reference condition. Equation 3-9 may be used to convert the reference pressure to a TMP balance value by subtracting reference pressure from the initial TCTMP reading in a data set.

$$\Delta Reference = TCTMP_{ijklm} - TCTMP_{Reference} \quad (3-9)$$

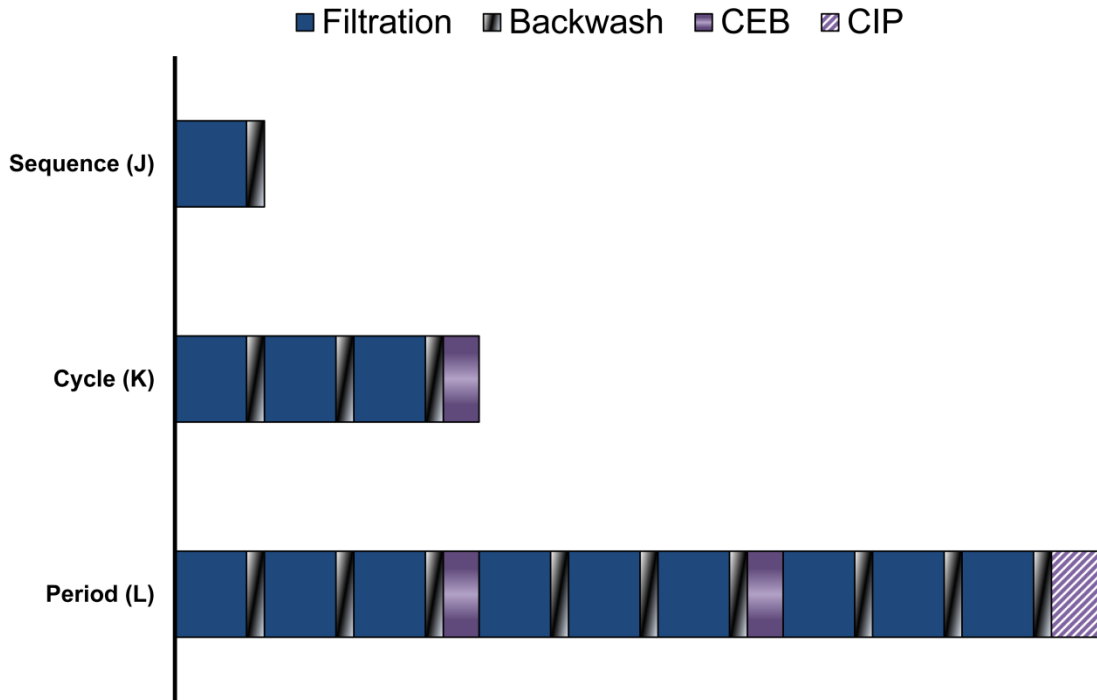


Figure 3-2 Distinction between Operating Sequences, Cycles, and Periods

The operating flux case for a constant flux process may be varied as needed to meet water demand requirements or minimize membrane fouling, and the corresponding pressure change that results is a function of the total resistance to flow. Research has indicated that the relationship between flux and TMP is not linear in the presence of certain foulants (Lin et al., 2005); however, a linear relationship exists between flux and TMP for an unfouled membrane filtering clean water (Yeh & Wu, 1997; Chellam et al., 1998; Cheryan, 1998). A manipulation of the resistance-in-series model, as presented in Equation 3-10, demonstrates that the TMP is a summation of the factors contributing to flow resistance. An additional term,  $\Delta R_m$ , has been added to the equation to account for changes in the physical structure of the membrane over

time. Physical changes to the membrane have been shown to result from chemical cleaning (Gitis et al., 2006; Arkhangelsky et al., 2007).

$$TMP = J\mu(R_M) + J\mu(R_a) + J\mu(R_b) + J\mu(R_c) + J\mu(\Delta R_M) \quad (3-10)$$

Where,

$\Delta R_M$  is the change in the intrinsic membrane resistance,  $m^{-1}$  ( $ft^{-1}$ )

Since the purpose of the TMP balance is to determine the pressure contribution of membrane fouling and structural deterioration, it is necessary to exclude the TMP change associated with the hydraulic resistance of the unaltered membrane material. This is accomplished by calculation of the  $\Delta Flux$  term, as presented in Equation 3-11, where the slope term is that of a line describing the relationship between flux and TMP. The incorporation of the  $\Delta Flux$  term, which should be calculated for each individual membrane process, allows for the process performance to be compared at different operating flux values. For full-scale processes, practical limitations often preclude the possibility of establishing the flux-TMP relationship for new membranes with clean water, and an approximation may be made during start-up or following a membrane cleaning.

$$\Delta Flux_M = slope(Flux_m - Flux_{m+1}) \quad (3-11)$$

### 3.5.2. Example TMP Balance Calculation

An example TMP balance calculation is presented in Equations 3-12 and 3-13 for a new constant flux membrane filtration process, where  $TCTMP_{1,1,1,1,1} = 0.100$  bar (1.45 psi),  $TCTMP_{2,1,1,1,1} = 0.107$  bar (1.55 psi), and  $TCTMP_{1,2,1,1,1} = 0.103$  bar (1.50 psi). For the purposes of the example,  $TCTMP_{1,1,1,1,1}$  has been selected as the reference pressure. Accordingly, the  $\Delta Reference$  term calculated using Equation 3-9 is equal to zero. The  $\Delta Flux$  term, defined in Equation 3-11, is also

equal to zero, because a change in the operating flux set-point has not been made. Thus, the TMP balance at the start of the second sequence (i.e. after one backwash) is + 0.003 bar (+0.05 psi).

$$TMP\ Balance_{1,2,1,1,1} = \Delta Reference + \left( \sum_{m=1}^1 \sum_{l=1}^1 \sum_{k=1}^1 \sum_{j=1}^1 \sum_{i=1}^1 [(TCTMP_{2,1,1,1,1} - TCTMP_{1,1,1,1,1}) + (TCTMP_{1,2,1,1,1} - TCTMP_{2,1,1,1,1})] \right) + \sum_{m=1}^1 \Delta Flux_1 \quad (3-12)$$

$$\therefore TMP\ Balance_{1,2,1,1,1} = 0 + [(0.107 - 0.100) + (0.103 - 0.107)] + 0 = +0.003\ bar\ (+0.05\ psi) \quad (3-13)$$

### 3.5.3. Interpreting the TMP Balance

TMP balance values are either greater than, equal to, or less than zero, because the TMP balance reflects the change in resistance relative to the reference condition. The magnitude of the TMP balance quantifies the resistance change in units of pressure, and the sign denotes position relative to a zero TMP balance. TMP balance values greater than zero indicate an increase in the resistance to flow relative to the reference pressure; whereas, TMP balance values of less than zero indicate decreased resistance to flow. Negative values may occur if the selected reference condition does not represent a clean membrane. A summary of TMP balance interpretations is provided in Table 3-1.

Table 3-1 Interpretation of TMP Balance Values

<b>TMP Balance</b>	<b>Interpretation</b>
> 0	Increased flow resistance relative to the reference pressure
0	No change in flow resistance relative to the reference pressure
< 0	Decreased flow resistance relative to the reference pressure

#### 3.5.4. Monitoring Performance Using the TMP Balance Method

Monitoring membrane performance is critical for the successful design and operation of membrane filtration processes. For example, capital construction costs are determined in part by the selection of a sustainable operating flux, because the design flux influences membrane surface area and pump sizing requirements. Operating decisions, such as the frequency of backwashes and chemical maintenance procedures, are dictated by the fouling condition of the membranes. These decisions, in turn, influence operating costs relative to the consumption of energy, backwash water, and cleaning chemicals. The TMP balance provides a tool for quantifying and easily interpreting process performance to aid in the design and operation of membrane filters. Performance monitoring should involve quantification of the four items defined in Table 3-2 and graphically illustrated in Figure 3-3.

Reporting the operating, post-backwash, post-CEB, and post-CIP TMP balance values isolates the pressure contributions associated with membrane fouling and morphology changes. Operating TMP balance values are recorded during filtration and quantify the pressures required to maintain constant flux production. Accordingly, the operating TMP balance may be used to select an appropriate backwash frequency for the process. After successive filtration events, resistance develops on the membrane surface that is not removed by routine backwashing (Yamamura et al., 2007). The post-backwash TMP balance quantifies the pressure contribution associated with physically unresolved resistance changes and indicates the need for chemical maintenance. CEB or CIP procedures are used to chemically clean membranes and may be assessed using post-CEB and post-CIP TMP balance values. Monitoring the post-CEB or post-

CIP TMP balance provides information on the effectiveness of selected chemicals and cleaning protocols, as well as the deterioration of the membranes over time.

Table 3-2 Definition of the Key Performance Monitoring TMP Balance Values

Performance Indicator	Definition
Operating TMP balance	Quantifies the TMP balance during filtrate production
Post-backwash TMP balance	Quantifies the TMP that is unresolved by physical backwashing
Post-CEB TMP balance	Quantifies the TMP that is unresolved by the selected CEB protocol
Post-CIP TMP balance	Quantifies the TMP that is unresolved by the selected CIP protocol

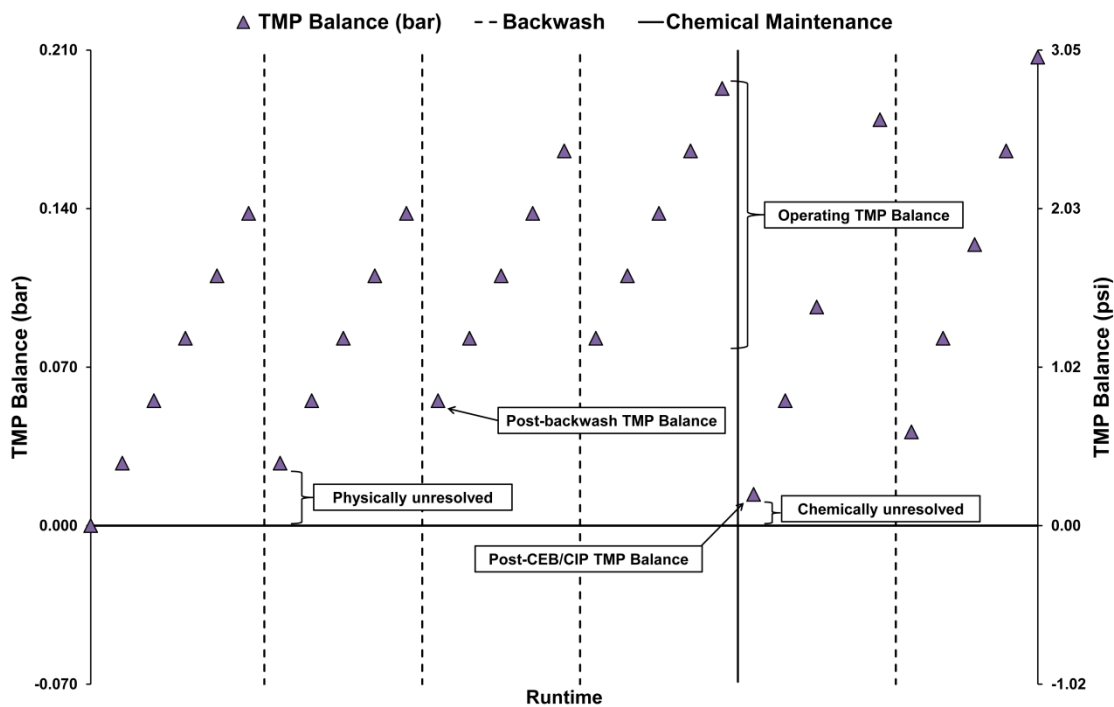


Figure 3-3 Graphical Description of the Key Performance Monitoring TMP Balance Values



### 3.5.5. Pilot-Scale Application of the TMP Balance Method

Data from the Mission San Jose and Lake Manatee WTP UF pilot tests have been compiled and analyzed to demonstrate the usefulness of the TMP balance approach in assessing the performance of membrane filtration processes. Collectively, more than 9,000 hours of runtime data have been selected to assess the operating, post-backwash, post-CEB, and post-CIP TMP balance levels observed during testing. The results of the analyses are discussed along with comparisons to specific flux and TCTMP performance monitoring methods. Prior to the TMP balance analysis, an experiment was performed to calculate the  $\Delta\text{Flux}$  term for the Durasep UPF0860 membrane over a flux range of 34.0 to 119 L/m<sup>2</sup>-hr (20.0 to 70.0 gal/ft<sup>2</sup>-day). The test was conducted following a chemical cleaning during a period of minimal membrane fouling development. Using linear regression, the slope of a line describing TMP versus flux was found to be 0.042 with an R<sup>2</sup> of 0.99 using 11 data points. This slope was utilized in Equation 3-11 to calculate the  $\Delta\text{Flux}$  term for the UF pilots.

#### 3.5.5.1. Mission San Jose WTP UF Pilot

The UF pilot located at the Mission San Jose WTP operated for approximately 2200 hours with the 40 m<sup>2</sup> (430 ft<sup>2</sup>) Durasep UPF0860 membrane. An initial flux of 68.6 L/m<sup>2</sup>-hr (40.5 gal/ft<sup>2</sup>-day) was selected to gather preliminary data and then increased to 83.0 L/m<sup>2</sup>-hr (48.9 gal/ft<sup>2</sup>-day) after 130 runtime hours. The backwash frequency during testing ranged between 30 to 45 minutes, with a typical backwash event consisting of a flow reversal out the bottom and then top end of the module, followed by a forward flush. A conservative CEB interval of once per day was chosen to resolve anticipated membrane fouling, and two different pretreatment configurations were used during testing as part of the pilot test plan. Scheduled maintenance at

the Mission San Jose WTP resulted in approximately two months of downtime after 250 runtime hours.

#### 3.5.5.1.1. Evaluation of Pilot Performance with the TMP Balance Approach

The Mission San Jose UF pilot test provides a performance comparison between two different pretreatment configurations. A uniform CEB protocol was used during testing to minimize the number of performance influencing variables, and the results show a significant difference between the two pretreatment approaches. In Figure 3-4, post-backwash and post-CEB TMP balance values are used to monitor the development of unresolved resistance changes over time. The CEB protocol had limited effect during the first pretreatment scenario, as demonstrated by the proximity of the post-CEB and post-backwash TMP balance values. Daily CEBs had a greater impact under the second pretreatment configuration; however, physically and chemically unresolved pressure development increased markedly. This is evidenced by a comparison between the magnitudes of the TMP balances observed during the two pretreatment approaches. A gradual increase in the post-CEB TMP balance from 0.000 bar (0.00 psi) to +0.029 bar (+0.42 psi) occurred under the first pretreatment configuration, but a sharp increase to +0.076 bar (+1.10 psi) was observed shortly after the pretreatment transition.

While the post-backwash and post-CEB TMP balance calculations track the development of unresolved resistance changes, the operating TMP balance defines the pressures required to produce water at a constant flux. Figure 3-5 presents the frequency distribution of operating TMP balance values for the two pretreatment scenarios. The data indicates a low mass loading on the UF membrane with the first pretreatment scenario, because the pilot operated between a TMP balance of 0.000 bar and +0.034 bar (0.00 psi and +0.50 psi) for 77% of the runtime. In

contrast, the predominant operating TMP balance range for the second pretreatment scenario was between +0.103 bar and +0.172 bar (+1.50 psi and +2.50 psi). The second pretreatment scenario, therefore, requires a higher operating cost in terms of cleaning frequency and energy consumption.

#### 3.5.5.1.2. Comparison of Performance with Specific Flux Trends

Specific flux data are presented per cycle, i.e. following a CEB, in Figure 3-6. During the first 1800 runtime hours, the specific flux decreased by 156 L/m<sup>2</sup>-hr-bar (6.33 gal/ft<sup>2</sup>-day-psi). This decline represents a 22.6% reduction in the magnitude of the specific flux term; whereas, the TMP balance value for chemically unresolved resistance only increased by +0.029 bar (+0.42 psi) over the same time interval. An additional decrease in the specific flux of 140 L/m<sup>2</sup>-hr-bar (5.67 gal/ft<sup>2</sup>-day-psi) was observed during the second pretreatment scenario, resulting in a total specific flux decline of 45.3% during pilot testing. In comparison, the final post-CEB TMP balance value was +0.085 bar (+1.24 psi), which is well within the operating pressure range of the Durasep UPF0860 membrane. Therefore, the specific flux exaggerates the extent of membrane fouling due to the non-linearity of the specific flux calculation for low pressure membrane processes.

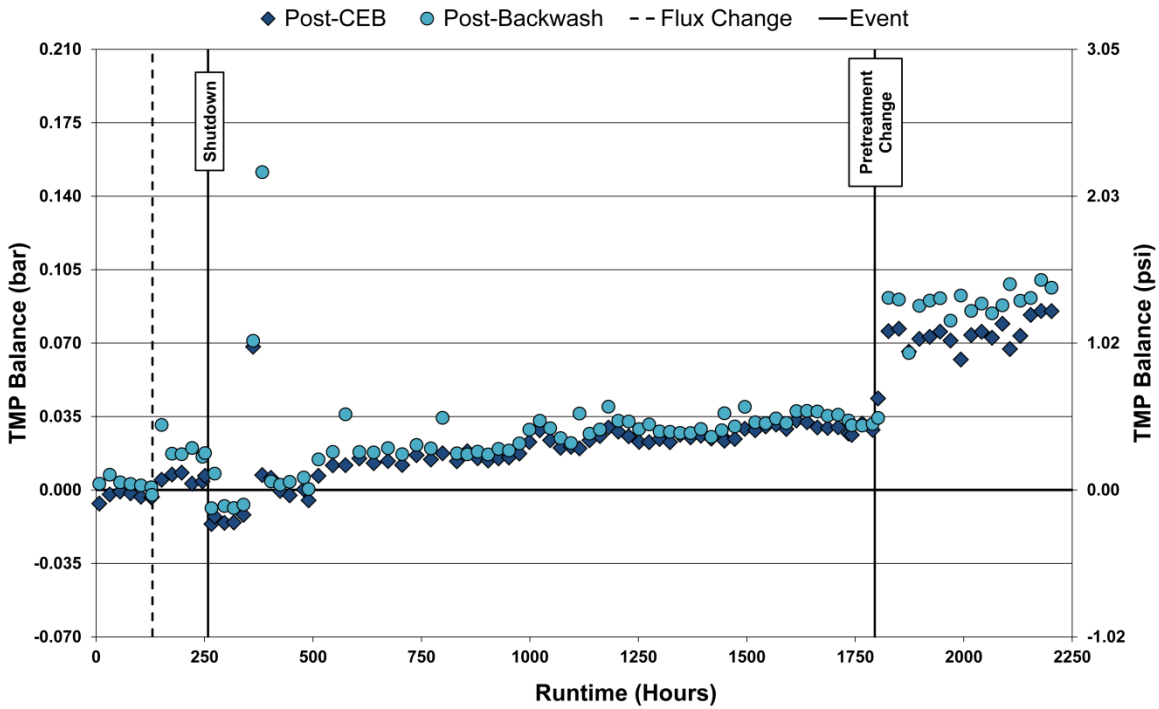


Figure 3-4 Mission San Jose WTP UF Pilot – TMP Balance Results

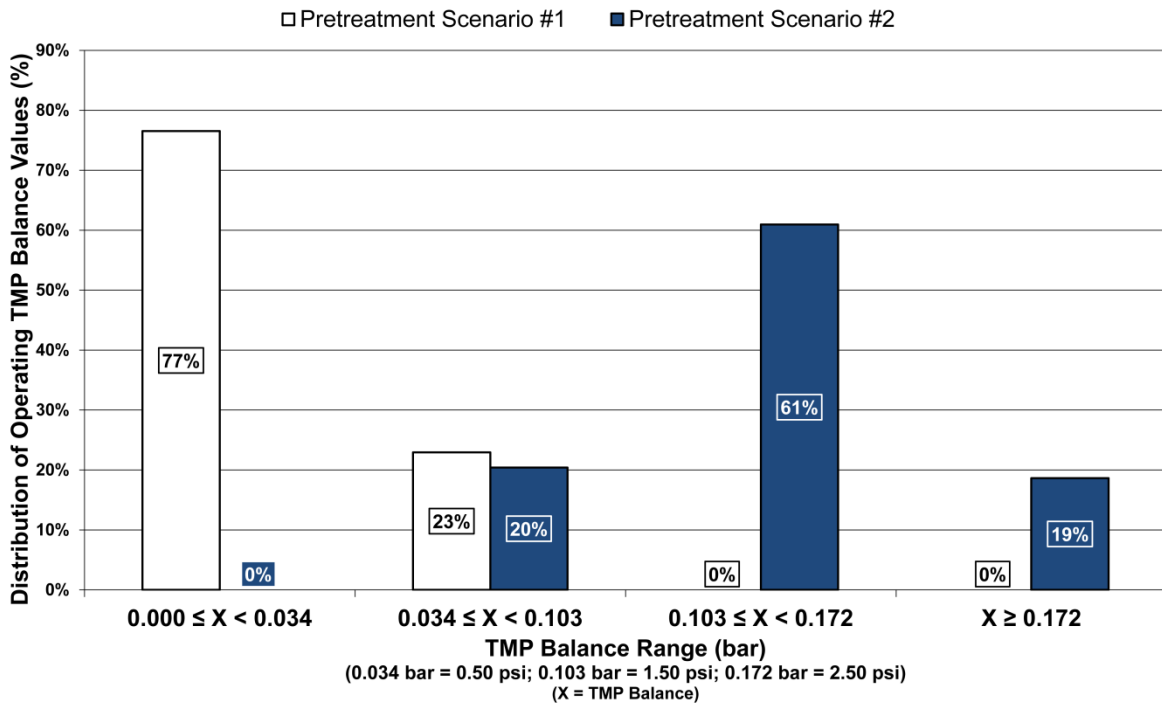


Figure 3-5 Mission San Jose WTP UF Pilot – Distribution of Operating TMP Balance Values

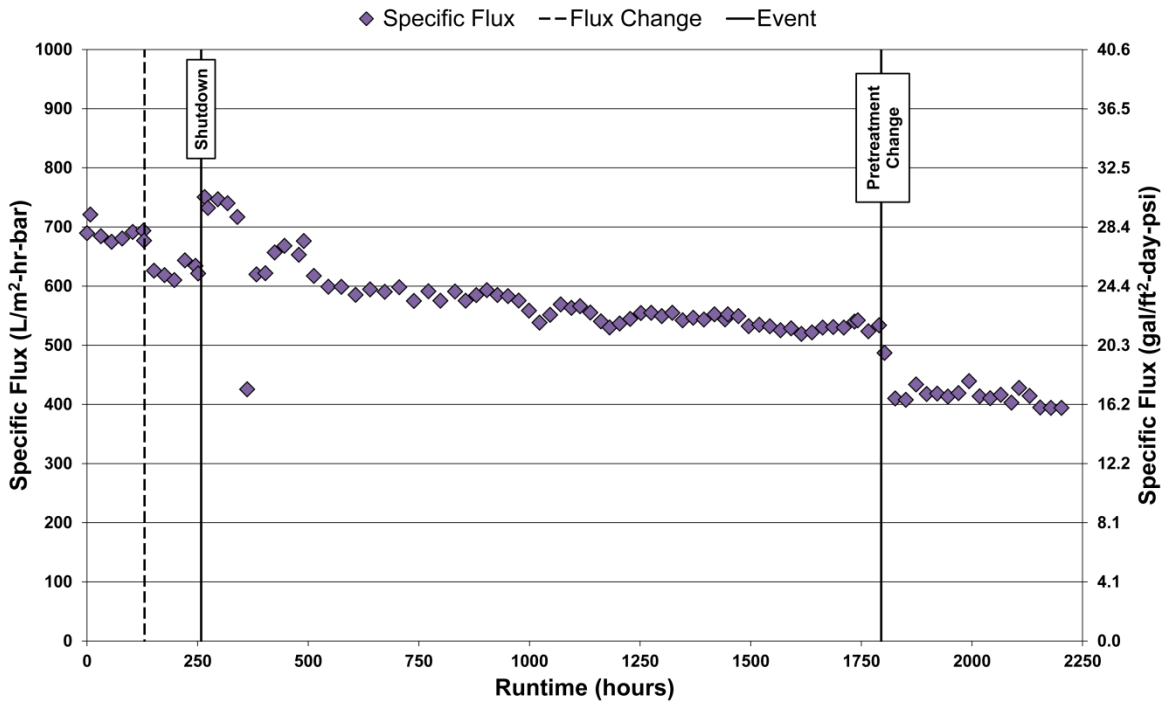


Figure 3-6 Mission San Jose WTP UF Pilot - Specific Flux per Cycle

### 3.5.5.2. Lake Manatee WTP UF Pilot

The Lake Manatee WTP UF pilot was operated for over 7000 runtime hours at three flux cases with values of 63.0, 84.2, and 106 L/m<sup>2</sup>-hr (37.1, 49.6, and 62.3 gal/ft<sup>2</sup>-day) to identify a suitable flux range for sustainable performance. The backwash frequency and duration remained constant for each of the three flux cases in order to reduce the number of variables contributing to performance changes. A consistent CEB interval of once per day was also maintained with the exception of several short duration tests where different CEB intervals were evaluated. CEB chemical selection varied in response to different types of fouling conditions that resulted from seasonal changes in water quality and pretreatment performance (Boyd & Duranceau, 2012). Three CIPs were performed during testing to either resolve major membrane fouling or evaluate chemical effectiveness.

### 3.5.5.2.1. Evaluation of Pilot Performance with the TMP Balance Approach

The post-CEB and post-backwash TMP balance results for the Lake Manatee UF pilot are presented in Figure 3-7. Transitions between the three flux cases are denoted on the figure. Performance during the first flux case was characterized by a stable TMP balance with negligible variations between the TMP balance measures. Sodium hypochlorite was used during the once per day CEB procedure, and the post-CEB TMP balance ranged between -0.013 and +0.013 bar (-0.18 and +0.18 psi) over the approximately 900 hours of Case 1 testing. These results demonstrate that the UF pilot could operate with low fouling rates at a constant flux of 63.0 L/m<sup>2</sup>-hr (37.1 gal/ft<sup>2</sup>-day).

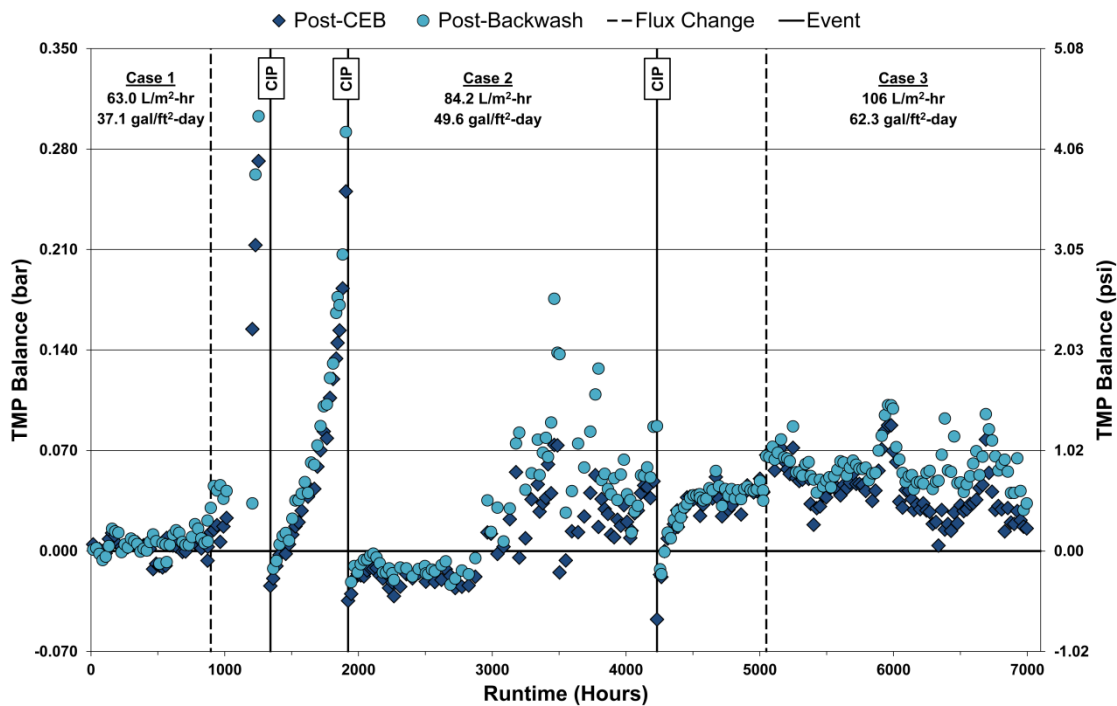


Figure 3-7 Manatee County UF Pilot - TMP Balance Results

Case 2 began with approximately 100 hours of stable performance before a rapid rise in pressure suspended operations at a post-CEB TMP balance of +0.492 bar (+7.13 psi). This increase in the post-CEB TMP balance demonstrates that the fouling development was not resolvable with sodium hypochlorite CEBs. An analysis of the feed water revealed a significant loading of a predominantly calcium carbonate foulant onto the UF membrane that was subsequently resolved with a citric acid CIP. Unfortunately, an instrumentation error caused a loss of data during the first calcium carbonate fouling event, so the fouling scenario was repeated a second time to gather additional information and allow time for the installation of a citric acid CEB system. Following completion of a second citric acid CIP, the post-CEB TMP balance stabilized between values of -0.035 and -0.012 bar (-0.50 and -0.17 psi) for approximately 1000 hours of runtime. At runtime hour 3000, another fouling event occurred that yielded post-CEB and post-backwash TMP balance values as high as +0.074 bar (+1.07 psi) and +0.176 bar (+2.55 psi), respectively. Sodium hydroxide CEBs were implemented around runtime hour 3500 to resolve the pressure development, and a subsequent sodium hydroxide CIP resulted in stable performance by the conclusion of Case 2 testing with a post-CEB TMP balance value of +0.041 bar (+0.59 psi).

As shown in Figure 3-7, negative TMP balance values were observed following the Case 2 CIPs. These negative values are the result of the selected reference condition, which was chosen from data collected during the Case 1 evaluation. Prior to the start of Case 1, a series of tests were performed to verify proper pilot equipment functioning. These tests allowed for the development of additional flow resistance beyond the intrinsic resistance of the membrane. The citric acid and sodium hydroxide CIPs during Case 2 reduced the flow resistance below the Case 1 reference pressure and resulted in the calculation of negative TMP balance values.

The Case 3 flux of  $106 \text{ L/m}^2\text{-hr}$  ( $62.3 \text{ gal/ft}^2\text{-day}$ ) was selected to test the upper boundary of the recommended operating flux range for the membrane. Increased fouling rates were observed initially with an overall downward trend in post-CEB TMP balance values over the approximately 2000 hours of Case 3 runtime. Two fouling events at runtime hours 5900 and 6700 increased post-CEB TMP balance levels temporarily, but Case 3 concluded with a post-CEB TMP balance of  $+0.016 \text{ bar}$  ( $+0.23 \text{ psi}$ ). Post-backwash TMP balance values were generally greater than the post-CEB TMP balance for the majority of Case 3. On the final day of testing, the post-backwash TMP balance was recorded to be  $+0.033 \text{ bar}$  ( $+0.48 \text{ psi}$ ). These TMP balance results indicate that the chemical maintenance protocol was effective at reducing flow resistance.

Operating TMP balance frequency distributions for the three flux cases are presented in Figure 3-8. The Case 2 (a) and Case 2 (b) columns incorporate TMP balance values with and without the two calcium carbonate fouling events, respectively. A comparison between the different operating fluxes reveals that the pilot experienced the lowest operating TMP balance levels at  $63.0 \text{ L/m}^2\text{-hr}$  ( $37.1 \text{ gal/ft}^2\text{-day}$ ). When the calcium carbonate fouling is excluded, the Case 2 flux of  $84.2 \text{ L/m}^2\text{-hr}$  ( $49.6 \text{ gal/ft}^2\text{-day}$ ) provided the second lowest operating TMP balance values, with the highest operating TMP balances occurring at  $106 \text{ L/m}^2\text{-hr}$  ( $62.3 \text{ gal/ft}^2\text{-day}$ ). These results are anticipated, because lower membrane fouling is generally observed at lower operating fluxes (Wu et al., 1999; Bacchin et al., 2006; Mosqueda-Jimenez et al., 2008). However, uncertainty remains as to the extent to which the three operating fluxes differ relative to fouling, because feed water quality and chemical maintenance protocols differed during the duration of testing. Parallel testing would be required to make a more accurate assessment, but Case 1 most likely yields the lowest operating cost relative to pressure development.



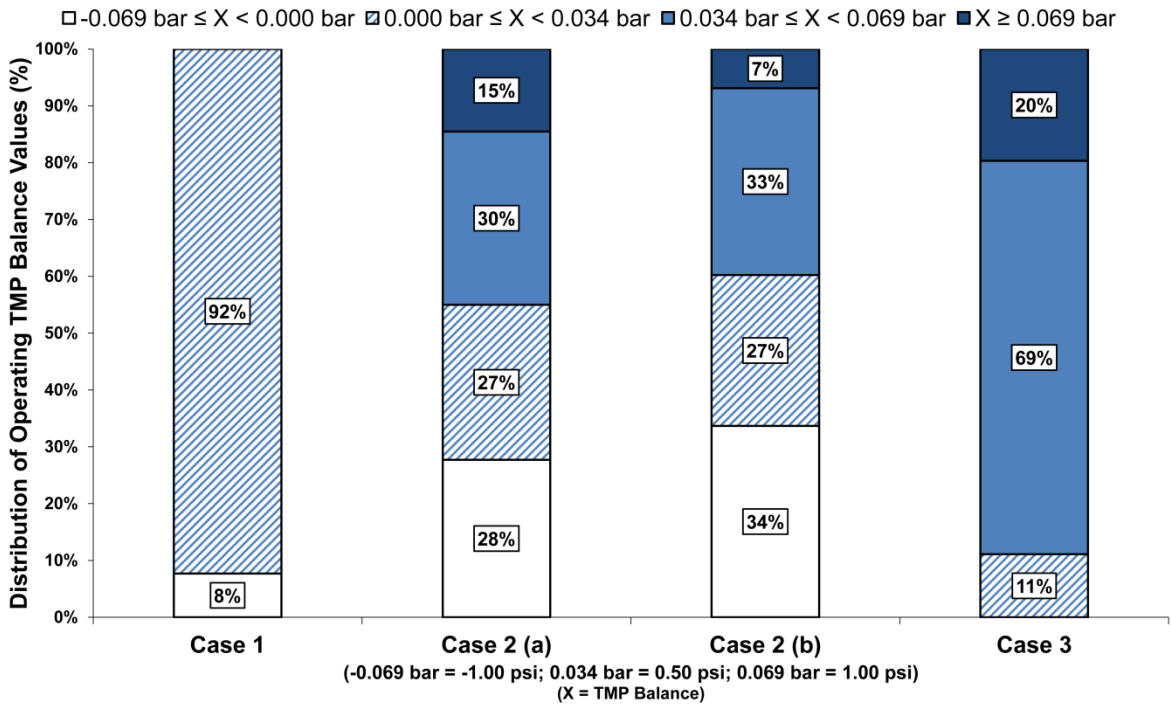


Figure 3-8 Manatee County UF Pilot – Frequency Distribution of Operating TMP Balance Values for Cases 1, 2, and 3

### 3.5.5.2.2. Statistical Comparison of Performance Monitoring Approaches

The efficient operation of membrane filtration processes is dependent on the appropriate selection of operating fluxes and the frequency of backwashes and chemical maintenance procedures. Therefore, it is important to closely monitor membrane performance to provide sufficient information for the decision making process. The Lake Manatee UF pilot was operated conservatively with respect to cleaning protocols to assess membrane performance at three flux values. From this data, a comparison has been made between the specific flux, TCTMP, and TMP balance evaluation methods.

Figure 3-9 presents a distribution of the per cycle specific flux, TCTMP, and TMP balance values for the three flux cases at  $\pm 1$  standard deviations from the mean. The purpose of Figure

3-9 is to highlight the differences between these three assessment approaches with respect to data interpretation, given that the three performance benchmarks are calculated from the same set of operating data. The three methods show the expected positive correlation between fouling and flux. However, the specific flux data shows a greater distribution of values around its mean than the TCTMP and TMP balance methods. This wider standard deviation for specific flux is the result of the non-linearity of the specific flux term at low TMP. Since the TMP balance is a summation of TCTMP values, as shown in Equations 3-8 and 3-9, the standard deviations for both assessment tools are equal, but the key distinction between the two pressure based methods is in the magnitude of the averages. The average for the TMP balance is less than that of the TCTMP, because the TMP balance identifies the pressure contribution associated with fouling and physical membrane deterioration.

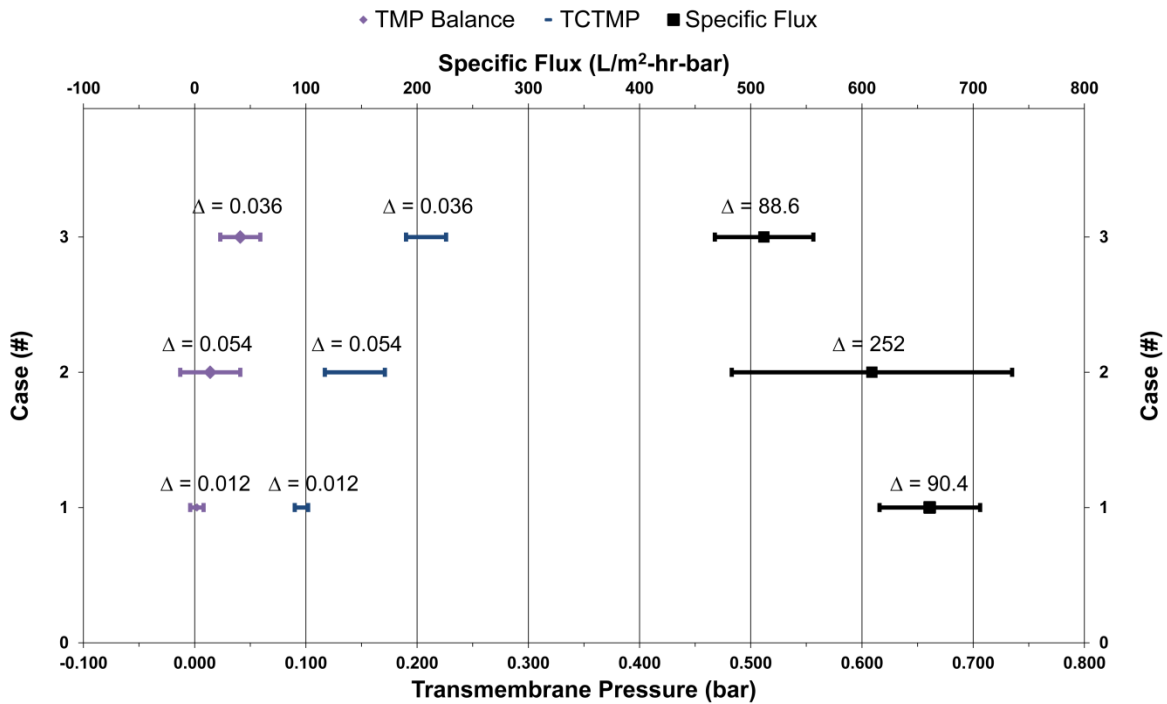


Figure 3-9 Manatee UF Pilot – Statistical Comparison for Per Cycle Fouling Assessment

### 3.6. Conclusions

The TMP balance provides a new approach for benchmarking membrane process performance and may be used as an alternative or supplement to traditional specific flux and TMP assessment techniques. While the specific flux is a valuable tool for normalizing process data with respect to temperature and pressure, the non-linearity of the specific flux at low TMP values results in exaggerated fouling trends. TCTMP provides information on the fouling of membrane processes but is limited as a tool for distinguishing between different types of fouling or comparing performance at different flux values. The TMP balance approach has been developed to address these issues, and the principle benefits the TMP balance are as follows:

- The performance of a membrane process is easily interpreted from the TMP balance, because the TMP balance is reported as a pressure change relative to a reference condition.
- The TMP balance identifies pressure variations associated with changes to the intrinsic membrane resistance and fouling layers.
- The TMP balance distinguishes between chemically unresolved, physically unresolved and operating pressure changes through calculation of post-CEB, post-CIP, post-backwash, and operating TMP balance values. This information may be used to determine the frequency of chemical and physical maintenance procedures.
- Calculation of the TMP balance allows for the comparison of process performance at different flux values.

### 3.7. Acknowledgments

The research reported herein was funded by UCF project agreements 16208085 and 16208088. Thanks are in order for the companies and municipalities involved in the acquisition, maintenance, and support activities associated with the two ultrafiltration pilots. The contributions of Harn R/O Systems, Inc. (Venice, FL), Horizon Industries, Inc. (Las Vegas, NV), Toyobo Co., Ltd. (Osaka, Japan), the Manatee County Utilities Department (Bradenton, FL), and the Alameda County Water District (Fremont, CA) are duly recognized and greatly appreciated. Additional thanks are offered to Dr. Jayapregasham Tharamapalan for his dedicated assistance with pilot testing activities.

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## **CHAPTER 4. FIVE COMPONENT OPTIMIZATION APPROACH FOR MEMBRANE FILTRATION PROCESSES USING TRANSMEMBRANE PRESSURE (TMP) VARIATIONS**

### 4.1. Abstract

The goal of ultrafiltration (UF) process optimization is to identify a set of operating parameters that allow membrane fouling to be managed and water production goals to be met. The study described in this paper demonstrates a five component systematic approach for the optimization of UF membrane processes on the basis of variations in transmembrane pressure. Terms are defined for assessing the performance of filtration, backwash, and chemical cleaning process events, and a new process performance benchmark, termed process utilization, is proposed to define the extent to which UF processes approach ideal performance. New measures for quantifying backwash and chemically enhanced backwash (CEB) performance are also presented. Backwash duration was identified as a major factor influencing process recovery and utilization, and increases in operating pressures and chemically unresolved fouling were correlated to increases in process recovery and utilization. Also, extending the interval between CEBs was demonstrated to form a protective fouling layer that improved backwash effectiveness for the filtration of conventionally pretreated surface water. The five component systematic optimization approach achieved a sustainable process recovery of 96.1% and process utilization of 93.5%.

Key words: Ultrafiltration, Optimization, Utilization, Recovery, Transmembrane Pressure, TMP, TMP Balance

## 4.2. Introduction

The need for advanced water treatment technologies is expected to increase globally as a result of projected water quality and availability issues; however, cost considerations are a potential barrier to the widespread implementation of energy intensive technologies such as ultrafiltration (UF) (Shannon et al., 2008). Accordingly, there is a need to increase the efficiency of UF processes by employing optimization strategies that reduce operating costs without sacrificing treated water quality and production reliability. A key component of UF process optimization is fouling management. Major cost considerations for UF processes, such as energy use and chemical consumption, are strongly influenced by membrane fouling. As a result, considerable research efforts have been expended to investigate the mechanisms by which fouling occurs and identify the constituents that contribute to fouling development such as natural organic matter (NOM), algae, and biopolymers (Lee et al., 2004; Kwon et al., 2005; Haberkamp et al., 2008).

Membrane fouling may be partially managed by feed water pretreatment. Common pretreatment approaches for natural waters include coagulation, preoxidation, and adsorption (Howe & Clark, 2006; Huang et al., 2009; Campinas & Rosa, 2010; Gao et al., 2011), because these technologies generally improve UF process performance by removing or altering foulants prior to filtration. In conjunction with pretreatment, UF operating parameters significantly affect the development and severity of membrane fouling. A variety of research has elucidated the interdependence between operating flux and fouling (Field et al., 1995; Howell, 1995; Wu et al., 1999), and the selection of a sustainable flux is necessary for efficient long-term operation (Bacchin et al., 2006). Additional factors of consequence to fouling management include the frequency and duration of backwash procedures (Kim & DiGiano, 2006; Smith et al., 2006) and the implementation of

chemical maintenance programs via chemically enhanced backwashes (CEBs) or clean-in-place (CIP) events (Yuan & Zydney, 2000; Katsoufidou et al., 2008; Strugholtz et al., 2005; Zondervan & Roffel, 2007; Porcelli & Judd, 2010; Liu et al., 2006).

The complex interactions between source water quality, pretreatment processes, membrane fouling, and process operating configurations present a significant challenge to UF performance improvement efforts. Laboratory studies have demonstrated the use of statistical analysis and empirical modeling techniques to identify an optimum set of operating conditions using water quality and operating data (Zularisam et al., 2009; Figueroa et al., 2011; Alventosa-deLara et al., 2012), and statistical methods have been employed at the pilot-scale to improve the performance of backwash and chemical cleaning procedures (Chen et al., 2003). However, full-scale implementation of statistical model based optimization techniques presents challenges in water treatment. The variability of source waters (Ouyang et al., 2006; Boyd & Duranceau, 2012a) and the dynamic operation of pretreatment processes yield a constantly changing set of input conditions for full-scale UF processes. Accordingly, pilot-scale studies are typically used to determine an acceptable set of UF operating parameters (Decarolis et al., 2001; Jang et al., 2005) with emphasis on stable operation rather than optimization.

In addition to statistical modeling efforts, optimization research has focused on enhancing the functionality and implementation of filtration, backwash, and cleaning events. For example, the incorporation of air injection into routine backwashes increased membrane foulant removal (Remize et al., 2010) for a direct filtration membrane process, and the initiation of backwashes based on transmembrane pressure (TMP) reduced backwash water consumption and energy requirements during the treatment of wastewater effluent (Smith et al., 2006). Performance

improvements have also been realized by quantifying energy costs for alternative operating configurations (Xu & Gao, 2010), identifying threshold filtration and backwash durations for fouling (Ye et al., 2010), evaluating process changes via trial-and-error procedures, and upgrading existing process equipment (White & Kosterman, 2010). The variety of optimization research ideas published in the literature point to the potential for meaningful improvement in the performance of existing and future UF processes. This paper presents the development of a systematic optimization approach to improve UF process performance for both pilot- and full-scale applications and demonstrates the use of new tools for the evaluation of membrane processes at the pilot-scale during surface water treatment.

#### 4.3. Methods and Materials

##### 4.3.1. UF Pilot Test Location

The Lake Manatee Water Treatment Plant (WTP) in Manatee County, Florida, which is operated by the Manatee County Utilities Department, was selected as the pilot testing site. The facility practices alum coagulation for the removal of organics from the Lake Manatee Reservoir. An organic polymer is added during flocculation to promote the formation of a settleable floc, and the settled water is pH adjusted with lime as needed. Additionally, a maintenance dose of chlorine is added in the post-mix to limit algae growth on the basin walls. During seasonal taste and odor events, powdered activated carbon is added to the raw water prior to coagulation.

##### 4.3.2. UF Membrane and Pilot Unit Description

The fully-automated pilot unit was fitted with a single hydrophilic Durasep UPF0860 inside-out hollow fiber UF membrane manufactured by Toyobo CO., Ltd. The Durasep membrane was

composed of polyvinylpyrrolidone–modified polyethersulfone (PES) with an active surface area of 40 m<sup>2</sup> (430 ft<sup>2</sup>) providing an approximate 150,000 dalton cutoff. Feed and filtrate turbidity, pressure, and flow data were recorded at two minute intervals, and two chemical injection systems were installed for chemical maintenance purposes.

#### 4.3.3. UF Pilot Operations

The UF pilot operated in a constant flux direct flow configuration and filtered settled surface water from the Lake Manatee WTP. Filtrate was used to perform backwashes and CEBs. During backwashes, filtrate was first pumped out the bottom and then out the top end of the module at a flux equal to three times the filtration flux. The CEB process involved an injection of chemical during a backwash, followed by a 10 minute soak, and concluding with an extended backwash.

#### 4.3.4. UF Pilot Operating History

Prior to the start of optimization testing, the UF pilot and membrane were used in a series of evaluations over an approximately two year period. CIPs were conducted before the optimization study commenced to restore membrane performance. The CIP procedure consisted of the recirculation of chemical for approximately one hour, a thirty minute soak, and a subsequent rinse. A low pH citric acid CIP was performed first followed by a high pH sodium hypochlorite CIP. Optimization testing commenced in December, 2011 and concluded in March, 2012.

#### 4.3.5. Water Quality Testing

The water quality sample plan developed for the research called for the collection of pH, temperature, turbidity, alkalinity, total hardness, total organic carbon (TOC), dissolved organic carbon (DOC), and UV 254 data. Temperature and turbidity data were automatically recorded at

two minute intervals using equipment onboard the UF pilot. Additional water quality data was provided courtesy of the Manatee County Utilities Department. Alkalinity, hardness, and pH data were measured daily; whereas, TOC, DOC, and UV 254 analyses were conducted weekly.

#### 4.3.6. Method of Data Compilation

The process data collected during operation was compiled and assigned runtime values. Since the UF pilot recorded data at two minute intervals, data collected prior to flux stabilization following backwashes or CEBs was excluded by removing values outside a range of  $\pm 3$  standard deviations from the mean of adjacent points.

#### 4.3.7. Method of Performance Monitoring

UF pilot performance was monitored using the TMP balance approach (refer to Chapter 3) that identifies changes to membrane fouling resistance and intrinsic membrane resistance based on variations in temperature corrected TMP (TCTMP) relative to a reference pressure. The reference pressure is selected according to the application and may be either that of a new process at steady state, a chemically cleaned process, or a process operating at a level of acceptable performance. A simplified version of the TMP balance calculation is presented as Equation 4-1. In the equation, TCTMP measurements are chronologically organized into sequences (J) and cycles (K). An operating sequence consists of consecutive filtration and backwash events; whereas, an operating cycle is comprised of a series of sequences culminating in a CEB. An additional summation may be added to the TMP balance equation to incorporate CIP events if desired. The  $\Delta$ Reference term, defined mathematically in Equation 4-2, adjusts



TMP balance data to the reference condition in instances where the first TCTMP value in a data set is not the reference pressure.

$$TMP\ Balance_{ijk} = \Delta Reference + \left( \sum_{k=1}^K \sum_{j=1}^{J_k} \sum_{i=1}^{n_{jk}} (TCTMP_{i+1,jk} - TCTMP_{ijk}) \right) \quad (4-1)$$

$$\Delta Reference = TCTMP_{ijk} - TCTMP_{Reference} \quad (4-2)$$

Where,

Subscript  $i$  refers to the TCTMP value

Subscript  $j$  refers to the sequence number

Subscript  $k$  refers to the cycle number

The magnitude of the TMP balance quantifies the resistance change in units of pressure, and the sign denotes position relative to a zero TMP balance. TMP balance values of zero indicate that the process is operating at the reference condition; whereas, TMP balance values greater than zero indicate an increase in the resistance to flow. Negative TMP balance values are indicative of a decreased resistance to flow and may occur if the reference condition is not representative of a clean, acclimated membrane. TMP balance values are used to distinguish between different types of fouling. For instance, operating TMP balance values are calculated during filtration events and quantify the pressures required to produce filtrate. Calculation of the post-backwash TMP balance indicates the pressure contribution of physically unresolved resistance changes, and post-CEB TMP balance values quantify the pressure contribution of chemically unresolved resistance changes.

## 4.4. Results and Discussion

### 4.4.1. Characterization of Process Events via Pressure Variation

The operation of UF membrane processes may be viewed as a sequence of individual filtration, backwash, CEB, and CIP events, termed process events. Process events determine the operating TMP by affecting membrane fouling and integrity and may be quantified numerically by calculating the pressure difference associated with each event. Equations 4-3 through 4-5 present the calculations for the  $\Delta\text{Filtration}$ ,  $\Delta\text{Backwash}$ , and  $\Delta\text{CEB}$  terms. The process event terms provide tools for identifying process operating issues and optimizing process performance. For example, pressure changes during filtration are primarily influenced by mass removal and compression of the fouling layer. A positive  $\Delta\text{Filtration}$  value denotes increased flow resistance during filtration, and the magnitude of the  $\Delta\text{Filtration}$  term may be used to make decisions concerning filtration duration and monitor changes in feed water quality. Negative  $\Delta\text{Backwash}$  and  $\Delta\text{CEB}$  values indicate a decreased flow resistance resultant from these foulant removal functions and allow for an assessment of physical and chemical cleaning protocol effectiveness.

$$\Delta\text{Filtration} = TCTMP_{i,j,k} - TCTMP_{i+n,j,k} \quad (4-3)$$

$$\Delta\text{Backwash} = TCTMP_{i,j+1,k} - TCTMP_{i+n,j,k}, \quad (4-4)$$

$$\Delta\text{CEB} = TCTMP_{i,j,k+1} - TCTMP_{i+n,j+o,k} \quad (4-5)$$

Where,

Subscript  $n$  refers to the last TCTMP value of sequence  $j$

Subscript  $o$  refers to the last sequence of cycle  $k$

#### 4.4.2. Assessment of Cleaning Performance

The assessment of cleaning performance is important for process optimization, because the identification of ineffective or unnecessary cleaning events enables changes to operating protocols. However, the number of backwashes and CEBs conducted during long-term operation may make it difficult to assess overall cleaning performance based on individual event data. Accordingly, this paper proposes the calculation of backwash and CEB residual pressure (RP) terms to facilitate data interpretation by generalizing cleaning performance over a time interval, such as hours, days, or weeks, rather than on a per event basis. The generalized cleaning performance is derived in Equations 4-6 and 4-7 by uniformly distributing the unresolved pressure development over a specified time interval. Thus, higher RP values indicate increased unresolved resistance development. The time interval selected is dependent on the analysis being conducted. If monitoring for changes in performance, shorter time intervals should be used such that significant variations in pressure are not masked by previous data; whereas, a general summary of cleaning performance may be determined using longer time intervals.

$$\text{Backwash Residual Pressure} = \frac{\sum \Delta \text{Filtration} + \sum \Delta \text{Backwash}}{\text{Runtime}} \quad (4-6)$$

$$\text{CEB Residual Pressure} = \frac{\sum \Delta \text{Filtration} + \sum \Delta \text{Backwash} + \sum \Delta \text{CEB}}{\text{Runtime}} \quad (4-7)$$

#### 4.4.3. Process Production Benchmarks

The selection of operating parameters, such as filtration duration and backwash flux, affects both the total and net filtrate production of UF processes. Improvements in the net filtrate volume may be achieved by varying relevant operating parameters in accordance with an optimization strategy. Process production benchmarks, which include the process recovery and a new process

utilization benchmark, provide a means for comparing different UF process operating configurations on the basis of net filtrate production.

#### 4.4.3.1. UF Process Recovery

In UF processes, backwashes and CEBs are often conducted using filtrate, and the volume of filtrate consumed during these maintenance activities determines the net filtrate volume. The process recovery, or simply recovery, for direct filtration UF processes is the ratio of the net filtrate volume to the feed volume over a specified interval of time (MWH, 2005). Accordingly, the process recovery, presented as Equation 4-8, represents the percentage of the feed volume that is available as product water.

$$\% \text{ Process Recovery} = \frac{V_{Fil} - V_{BW} - V_{CEB}}{V_{Feed}} \times 100 \quad (4-8)$$

Where,

$V_{Fil}$  is the total filtrate volume, L (gal)

$V_{BW}$  is the total backwash volume, L (gal)

$V_{CEB}$  is the total CEB volume, L (gal)

$V_{Feed}$  is the total feed volume, L (gal)

#### 4.4.3.2. UF Process Utilization

While the process recovery characterizes process performance on the basis of usable filtrate, the recovery calculation is not sensitive to downtime. A new benchmark, termed the process utilization, accounts for the loss of filtrate production associated with backwashes, forward

flushes, CEBs, valve actuations, and fiber integrity tests. Process utilization values quantify the extent to which the process approaches ideal performance. As presented in Equation 4-9, the process utilization is calculated as the ratio of the net filtrate volume to the theoretical maximum filtrate volume ( $V_{FIL,MAX}$ ) that could be produced assuming constant filtrate production over a specified time interval.

$$\% \text{ Process Utilization} = \frac{V_{FIL} - V_{BW} - V_{CEB}}{V_{FIL,MAX}} \times 100 \quad (4-9)$$

Where,

$V_{FIL,MAX}$  is theoretical maximum filtrate volume, L (gal)

#### 4.4.4. Optimization Approach

This study developed and tested a five component systematic UF optimization approach to improve process recovery and utilization values while maintaining sustainable process operation.

The five component optimization approach is as follows:

- 1) Develop a test plan to incrementally increase production benchmark values by systematically varying operating parameters. Optimization test plans should be realistic for the feed water quality being treated and consider the recommendations and requirements of the membrane and equipment manufacturers.
- 2) Monitor process performance using the TMP balance to check for developments of physically and chemically unresolved membrane fouling.

- 3) Assess process event performance by using the  $\Delta$ Filtration,  $\Delta$ Backwash, and  $\Delta$ CEB terms and by calculation of backwash and CEB residual pressure values.
- 4) Assess the distribution of operating TMP balance values recorded for each operating configuration.
- 5) Identify the operating configuration that maximizes process recovery and utilization while maintaining sustainable process operation.

#### 4.4.5. Lake Manatee UF Optimization Study

##### 4.4.5.1. Optimization Test Plan

The goal of optimization testing was to achieve sustainable UF process performance at a minimum process recovery of 95% and process utilization of 92%. Typical UF processes operate at recoveries between 95% and 98% (MWH, 2005). A six-phase test plan, presented in Table 4-1, was developed to incrementally increase the process recovery at a constant flux of 82.9 L/m<sup>2</sup>-hr (48.9 gal/ft<sup>2</sup>-day). Phase 1 represented the most conservative set of test parameters with a process recovery of 91.8%, and a significant increase in the recovery was achieved in Phase 2 by decreasing the duration of the backwash up and backwash down events by 10 seconds each. In Phase 3, the process recovery was further improved by decreasing the frequency of CEBs from 7 to approximately 3.5 cycles per week. The duration of filtration events was then increased in Phases 4, 5, and 6 to achieve a process recovery of >95.0% and process utilization of >92%.

##### 4.4.5.2. Feed Water Quality

Feed water quality data for the UF pilot is organized according to optimization test phase in Table 4-2. TOC, DOC and UV 254 values decreased from December, 2011 to March, 2012;

whereas, total alkalinity and total hardness values were observed to increase over the same timeframe. Turbidity and pH values remained consistent during testing, and feed water temperatures ranged between 20 and 24 °C.

Table 4-1 Optimization Test Plan for the Lake Manatee UF Pilot

<b>Optimization Phase #</b>	<b>1a,b</b>	<b>2</b>	<b>3</b>	<b>4</b>	<b>5</b>	<b>6</b>
Filtration Duration (min)	45	45	45	<b>50</b>	<b>60</b>	<b>75</b>
Backwash Duration (sec)	60	<b>40</b>	40	40	40	40
# Sequences / Cycle	31	31	<b>62</b>	62	62	62
# Cycles / Week	7.0	7.0	<b>3.5</b>	<b>3.2</b>	<b>2.6</b>	<b>2.1</b>
<b>UF Process Recovery (%)</b>	<b>91.8</b>	<b>94.0</b>	<b>94.8</b>	<b>95.3</b>	<b>96.1</b>	<b>96.9</b>
<b>UF Process Utilization (%)</b>	<b>87.0</b>	<b>89.8</b>	<b>91.4</b>	<b>92.3</b>	<b>93.5</b>	<b>94.8</b>

Table 4-2 Lake Manatee UF Pilot Feed Water Quality Summary

<b>Water Quality Parameter</b>	<b>Phase 1a</b>	<b>Phase 1b</b>	<b>Phase 2</b>	<b>Phase 3</b>	<b>Phase 4</b>	<b>Phase 5</b>	<b>Phase 6</b>
<b>pH</b>	6.20	6.24	6.22	6.15	6.20	6.15	6.21
<b>Temperature (°C)</b>	20.3 ± 0.3	18.9 ± 1.2	17.1 ± 0.5	18.5 ± 0.8	19.6 ± 0.8	21.9 ± 0.5	23.8 ± 0.6
<b>Turbidity (NTU)</b>	1.02 ± 0.14	1.13 ± 0.11	1.29 ± 0.24	1.21 ± 0.17	1.14 ± 0.12	1.27 ± 0.33	1.18 ± 0.11
<b>Total Alkalinity (mg/L as CaCO<sub>3</sub>)</b>	9.30 ± 1.17	10.5 ± 0.61	10.1 ± 2.05	11.2 ± 1.51	15.8 ± 2.51	15.1 ± 1.59	17.1 ± 2.36
<b>Total Hardness (mg/L as CaCO<sub>3</sub>)</b>	112 ± 2	113 ± 3	115 ± 3	121 ± 3	127 ± 4	141 ± 4	152 ± 5
<b>Calcium Hardness (mg/L as CaCO<sub>3</sub>)</b>	83 ± 4	83 ± 5	83 ± 3	89 ± 3	93 ± 4	94 ± 5	99 ± 5
<b>Magnesium Hardness (mg/L as CaCO<sub>3</sub>)</b>	29 ± 3	30 ± 5	31 ± 4	33 ± 3	35 ± 5	47 ± 5	53 ± 5
<b>TOC (mg/L as C)</b>	8.26 ± 0.67	7.01 ± 1.09	6.99 ± 0.17	6.52 ± 0.37	6.36 ± 0.37	6.79 ± 1.43	5.51 ± 0.54
<b>DOC (mg/L as C)</b>	6.73 ± 0.17	6.58 ± 0.38	6.07 ± 0.24	6.06	6.00 ± 0.10	5.83 ± 1.22	5.26 ± 0.31
<b>UV 254</b>	.114 ± .006	.109 ± .013	.106 ± .001	.119 ± .019	.095 ± .011	.095 ± .006	.084 ± .009

### 4.4.5.3. Optimization Performance Summary

The performance of UF membrane processes may be monitored using the TMP balance, and TMP balance values reported after backwash or CEB events quantify the extent of physically or chemically unresolved pressure development, respectively. Figure 4-1 presents the post-backwash and post-CEB TMP balance values recorded at the end of each cycle during optimization testing. The data shows an initial increase in physically and chemically unresolved pressure development during Phase 1a. The pressure increase was resolved in Phase 1b, and a gradual increase in the TMP balance was then observed in subsequent test phases as process benchmark values increased.

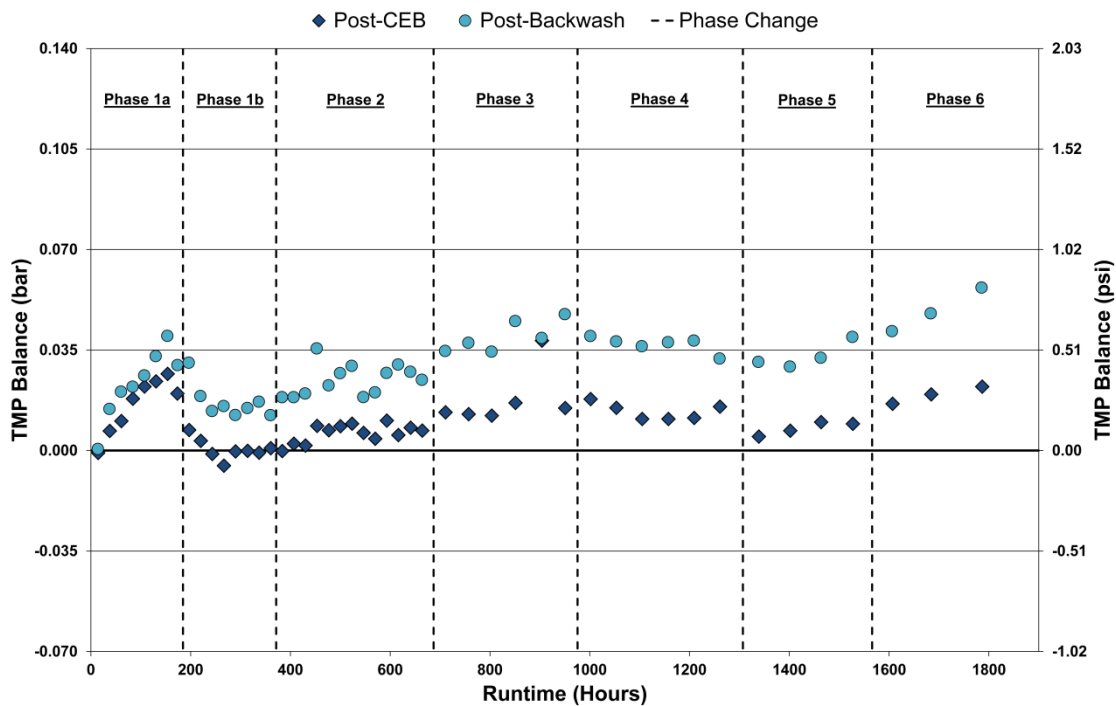


Figure 4-1 Post-backwash and Post-CEB TMP Balance Results for the Lake Manatee UF Pilot



#### 4.4.5.4. Process Event Evaluation

##### 4.4.5.4.1. Filtration

The magnitude of pressure changes during filtration relates to the quantity and behavior of accumulated foulant material at the membrane surface. Figure 4-2 presents the distribution of  $\Delta$ Filtration values for the UF pilot on a percentage basis. The results indicate that the magnitude of  $\Delta$ Filtration measurements increased concurrently with increasing process recovery and utilization. The lowest  $\Delta$ Filtration values were observed during Phase 1, and modifications to the backwash duration and CEB frequency parameters in Phases 2 and 3 increased the percentage of  $\Delta$ Filtration values recorded between the pressure range of +0.007 to +0.014 bar (+0.10 to +0.20 psi). In Phases 4 through 6, the percentage of  $\Delta$ Filtration measurements with values greater than or equal to +0.014 bar (+0.20 psi) increased as the filtration time was lengthened, and fifty-six percent of the Phase 6  $\Delta$ Filtration data exceeded +0.014 bar (+0.20 psi).

##### 4.4.5.4.2. Backwashes

Backwashes are used to reduce the resistance developed during filtration and typically account for the majority of UF maintenance water requirements. As such, the optimization of backwash procedures is critical for increasing UF process recovery. The backwash RP values reported in Table 4-3 compare UF pilot backwash performance at the different process benchmark values. The first increase in process recovery was achieved during Phase 2 by decreasing the backwash duration from 60 to 40 seconds. Shortening the backwash duration increased backwash RP for Phase 2; however, unanticipated backwash performance improvements were then observed in the subsequent test phases.

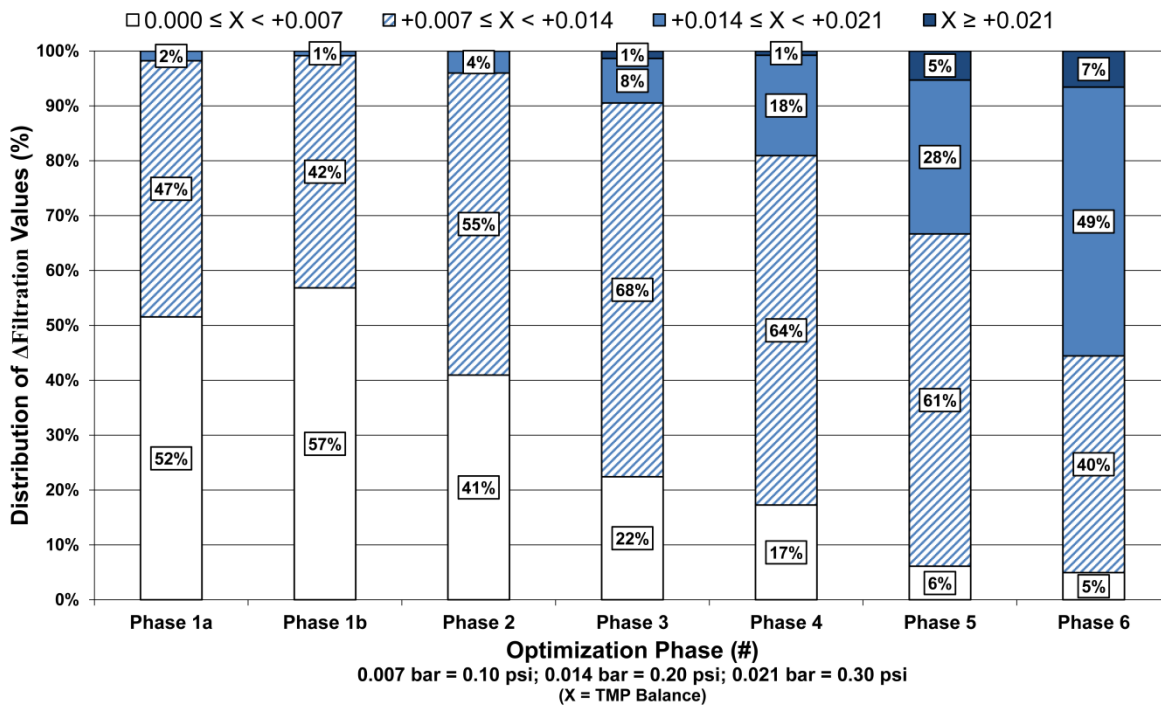


Figure 4-2 Pressure Distribution of ΔFiltration Values

Table 4-3 Backwash Performance Results for Optimization Phases 1 - 6

Phase #	ΣΔFiltration, bar (psi)	ΣΔBackwash, bar (psi)	Runtime, hours	Backwash RP, bar/day (psi/day)
Phase 1a	1.52 (22.0)	-1.42 (-20.6)	174	+0.013 (+0.19)
Phase 1b	1.50 (21.7)	-1.39 (-20.1)	187	+0.014 (+0.21)
Phase 2	2.95 (42.8)	-2.70 (-39.2)	304	+0.020 (+0.28)
Phase 3	3.40 (49.4)	-3.27 (-47.4)	286	+0.012 (+0.17)
Phase 4	3.95 (57.3)	-3.81 (-55.2)	325	+0.011 (+0.15)
Phase 5	3.03 (44.0)	-2.94 (-42.6)	251	+0.009 (+0.13)
Phase 6	3.43 (49.7)	-3.29 (-47.8)	321	+0.010 (+0.14)

An assessment of post-backwash TMP balance data, displayed graphically in Figure 4-3, provides an explanation for the improved backwash RP values following Phase 2. During the first two optimization phases, increases in the post-backwash TMP balance were approximately

linear for each cycle. As the process runtime between CEBs was increased in Phases 3 through 6, post-backwash TMP balance development trends transitioned from linear to predominantly logarithmic functions. Figure 4-4 presents post-backwash TMP balance data recorded during one of the Phase 5 cycles. The backwash RP was comparable to that of Phase 2 for the first 19 runtime hours but then improved significantly to a value of +0.005 bar/day (+0.07 psi/day) during the remaining 41 hours. Since the  $\Delta$ Filtration values remained consistent before and after the transition at  $+0.011 \pm 0.003$  bar ( $+0.16 \pm 0.04$  psi) and  $+0.012 \pm 0.003$  bar ( $+0.17 \pm 0.05$  psi), respectively, the backwash performance improvements suggest the development of a protective fouling layer (Munoz-Aguado et al., 1996; Lee et al., 2009) on the UF membrane fibers that enabled improved physical foulant separation subsequent to layer formation. Thus, extending the CEB interval reduced the rate of physically unresolvable fouling development for a significant portion of the runtime in Phases 3 through 6, which translated to a reduction in cumulative backwash RP values.

#### 4.4.5.4.3. Chemical Cleaning

Chemical maintenance is required to remove membrane fouling that is not resolved by physical backwashes. Table 4-4 presents the CEB history for the optimization study along with the average  $\Delta$ CEB, the post-CEB TMP balance, and the CEB RP values for each phase. The initial CEB protocol consisted of consecutive citric acid and sodium hypochlorite CEBs; however, an issue with the citric acid injection pump during Phase 1a limited the chemical maintenance procedures to sodium hypochlorite CEBs only. The injection issue was corrected prior to commencement of Phase 1b, and sodium hydroxide was added to the sodium hypochlorite CEB solution to increase the pH above 10 during sodium hypochlorite CEBs.

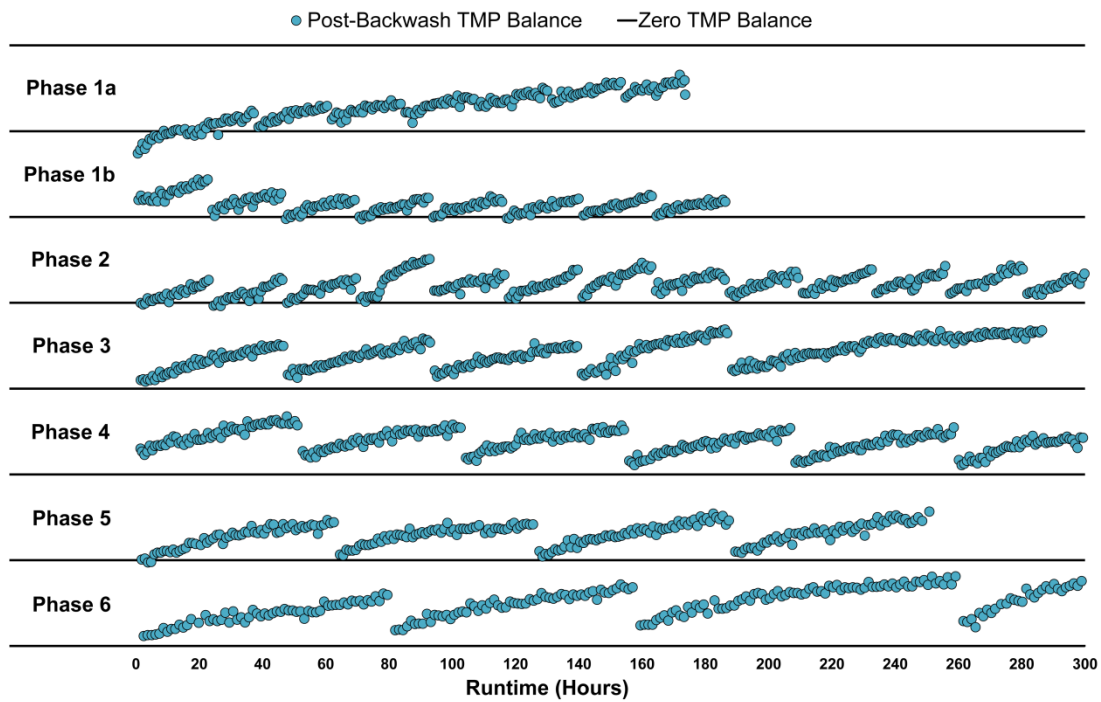


Figure 4-3 Post-backwash TMP Balance Results for Optimization Phases 1 – 6

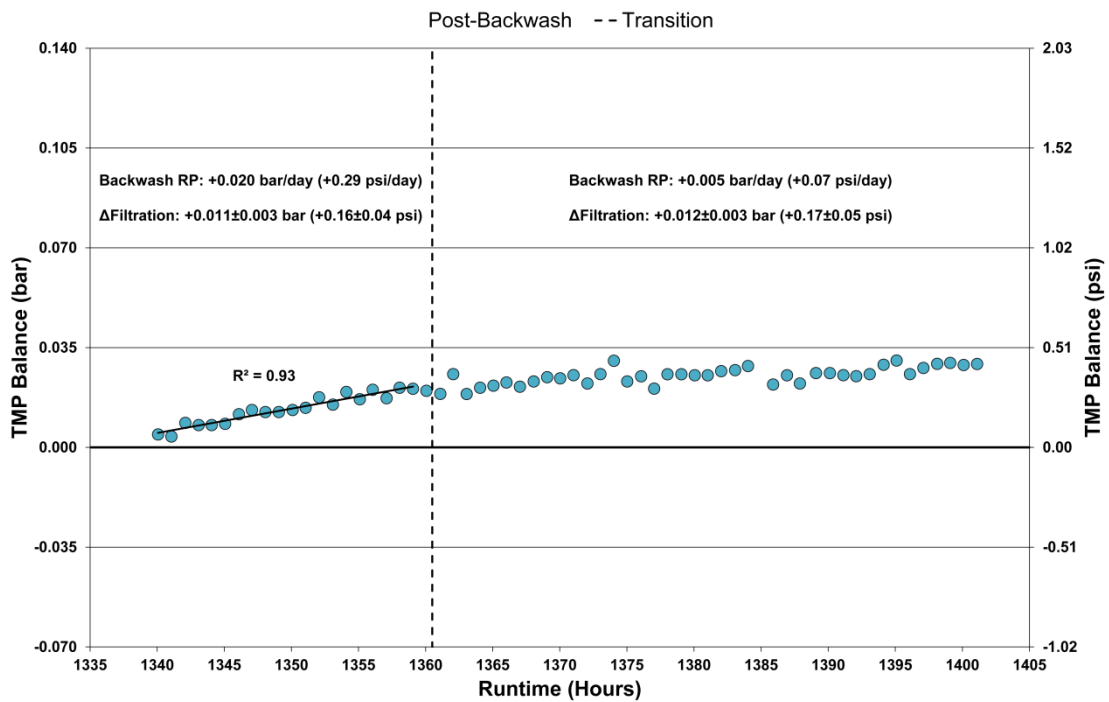


Figure 4-4 Non-linear Post-backwash TMP Balance Data for a Phase 5 Cycle

Table 4-4 CEB Performance Results for Optimization Phases 1 - 6

Phase #	Chemical	Average $\Delta$ CEB, bar (psi)	Average Post-CEB TMP Balance, bar (psi)	CEB RP, bar/week (psi/week)
Phase 1a	1	0.007 (0.11)	+0.016 (+0.23)	0.035 (0.50)
Phase 1b	2,3	0.016 (0.24)	0.000 (0.00)	-0.017 (-0.25)
Phase 2	2,3	0.019 (0.27)	+0.006 (+0.09)	0.003 (0.05)
Phase 3	2,3	0.026 (0.38)	+0.014 (+0.20)	0.005 (0.07)
	2	0.001 (0.01)	---	---
Phase 4	2,3	0.024 (0.34)	+0.014 (+0.20)	0.000 (0.00)
Phase 5	2,3	0.025 (0.37)	+0.008 (+0.12)	-0.003 (-0.05)
Phase 6	2,3	0.029 (0.43)	+0.019 (+0.28)	0.023 (0.34)

1 = Sodium Hypochlorite, 2 = Citric Acid, 3 = Sodium Hypochlorite + Sodium Hydroxide

The information in Table 4-4 allows for a direct comparison between the performance impacts of the different CEB protocols. During Phase 1a, sodium hypochlorite CEBs were ineffective at restoring membrane performance as evidenced by an increase in the post-CEB TMP balance and an elevated CEB RP. A significant improvement in performance was observed in Phase 1b when citric acid and high pH sodium hypochlorite CEBs were incorporated into the chemical maintenance protocol. Average post-CEB TMP balance values were 0.000 bar (0.00 psi) during this phase with a negative CEB RP value indicating the removal of previously developed fouling resistance. An evaluation of citric acid CEB effectiveness in Phase 3 revealed that citric acid had a negligible influence on TMP reduction with a  $\Delta$ CEB of only -0.001 bar (-0.01 psi); however, citric acid CEBs were not removed from the optimization test plan to avoid varying an additional operating parameter. A gradual increase in chemically unresolved resistance was generally observed with increasing process recovery and utilization. Phase 5 was an exception, because a two week pilot shutdown following Phase 4 reduced membrane fouling resistance as evidenced by the reduction in average post-CEB TMP balance values.

#### 4.4.5.5. Operating Pressure Assessment

Pressure requirements contribute significantly to UF process operating costs and may be quantified with the operating TMP balance. The distribution of operating TMP balance values, presented graphically in Figure 4-5, provides a method of ranking the optimization phases as a function of the pressures observed during filtration. Operating TMP balance values differed notably between Phases 1a and 1b, which demonstrates the impact of poor CEB performance on operating pressure. The backwash duration and CEB frequency decreases in Phases 2 and 3 also contributed to operating pressure increases. A five minute increase in the filtration time between Phases 3 and 4 did not appreciably influence the operating TMP balance; however, the seventy-five minute filtration time in Phase 6 yielded the highest operating pressures of the optimization study.

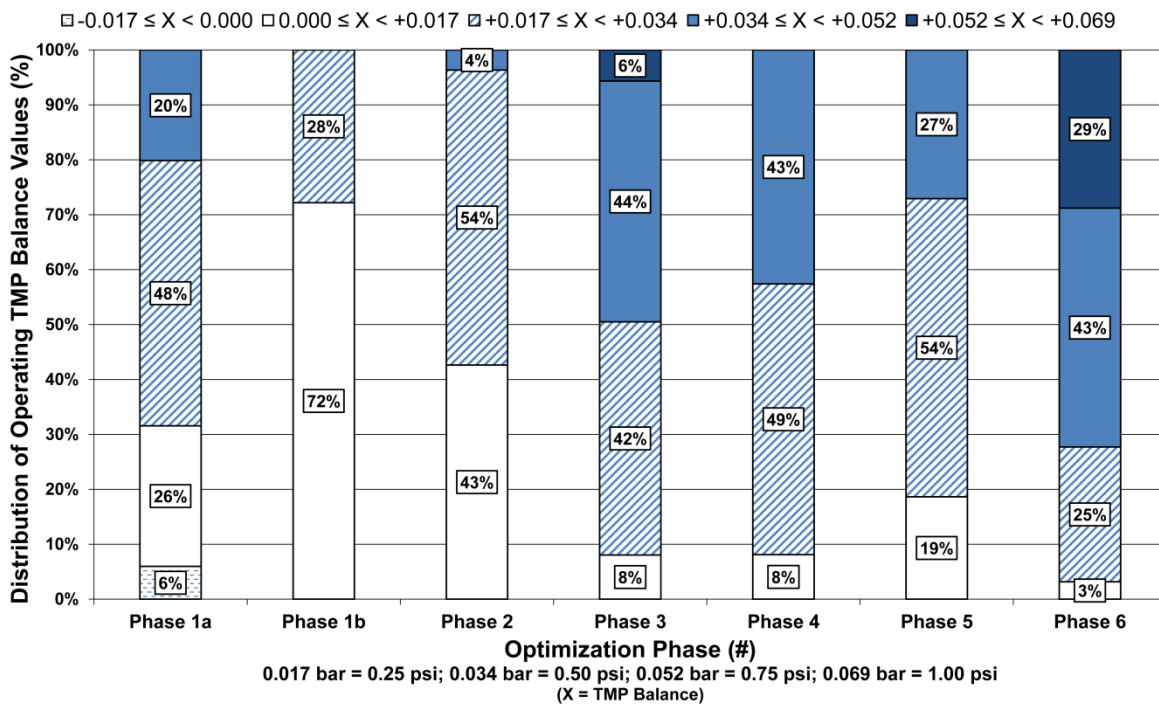


Figure 4-5 Distribution of Operating TMP Balance Values for Optimization Phases 1 - 6

#### 4.4.5.6. Findings

The goal of the optimization study was to systematically identify an operating configuration that yielded process recovery and utilization values greater than 95% and 92%, respectively. Optimization Phases 4, 5, and 6 met the target process performance benchmark criteria; however, UF process performance declined during test Phase 6 as evidenced by an upward trend in the post-CEB TMP balance and elevated operating TMP balance values. While the Phase 6 backwash RP of +0.010 bar/day (+0.14 psi/day) was on par with previous phases, the CEB RP value of +0.023 bar/day (+0.34 psi/day) indicates that the chemical maintenance protocol was unable to adequately manage physically unresolved resistance development. The CEB performance decline may have resulted from factors such as a compression of the foulant layer at the higher Phase 6 operating pressures, a change in the feed water quality, or an inadequate CEB frequency.

Stable process performance was observed during optimization test Phases 4 and 5. The backwash and CEB RP values were comparable between the two phases, and the post-CEB TMP balance data did not indicate an upward trend in chemically unresolvable resistance. Phase 5 yielded a greater volume of net filtrate production, because the increase in process utilization from 92.3% to 93.5% resulted in both greater total filtrate volume and decreased backwash and CEB filtrate consumption. Therefore, the Phase 5 configuration provided the best results on the basis of process performance and sustainability. To further differentiate between the two phases, a cost-benefit analysis should be performed, because the maximum sustainable performance may not be the most economical.

#### 4.5. Conclusions

In surface water treatment, the feed water source for UF membranes is variable and subject to both seasonal changes in source water quality and the performance of pretreatment processes. Accordingly, operating protocols for UF processes should be dynamic to maintain production targets while minimizing the occurrence of unnecessary maintenance activities. The five component optimization approach provides tools for identifying UF process operating configurations that achieve sustainable performance and improve process output. Optimization of an UF pilot with conventional alum coagulation pretreatment yielded sustainable process operation at process recovery and utilization values of 96.1% and 93.5%, respectively. This study also demonstrated the following:

- Backwash and CEB residual pressure calculations successfully identified changes in physical and chemical maintenance performance.
- A protective fouling layer effect was observed following extension of the CEB interval. The corresponding improvements in backwash effectiveness were accompanied by higher operating pressures.
- Post-CEB TMP balance values (i.e. chemically unresolved membrane fouling) generally increased with increasing process recovery and utilization.

#### 4.6. Recommendations

A cost-benefit analysis using local energy costs, chemical costs, and water rates is recommended to further differentiate between operating parameter configurations, because the increased operating pressures at higher process recovery and utilization values may offset the revenue



generated by increased water production. However, other factors, such as the benefits of minimizing chemical waste management requirements and reducing source water consumption should also be considered. Cleaning chemical optimization studies are recommended to minimize both the number and concentration of chemicals used during CEB events, as citric acid CEBs may have been unnecessary in this study. The impact of CEB chemical selection on other treatment processes should also be considered, as citric acid chemical waste streams are known to interfere with conventional surface water coagulation during backwash water recycle (Boyd et al., 2012b).

#### 4.7. Acknowledgments

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## **CHAPTER 5. SILICON DIOXIDE AS A SUPPORT LAYER FOR POWDERED ACTIVATED CARBON IN THE PRE-COATING ENHANCEMENT OF ULTRAFILTRATION MEMBRANES**

### 5.1. Abstract

In this study, silicon dioxide ( $\text{SiO}_2$ ) and powdered activated carbon (PAC), with particle diameters of  $\leq 45 \mu\text{m}$ , are evaluated as pre-coating materials for the filtration of an undiluted, organic surface water. The applicability of the transmembrane pressure (TMP) balance approach for the analysis of pre-coated membrane performance is also demonstrated. Utilization of the TMP balance enables the direct comparison of uncoated and pre-coated membranes on the basis of membrane fouling. Pressure changes for  $\text{SiO}_2$  pre-coated membranes exceeded an uncoated control membrane by greater than a factor of three after  $100 \text{ L/m}^2$  of specific filtrate production; however, the  $\text{SiO}_2$  pre-coat was effectively separated from the membrane during backwashing. PAC provided effective organic carbon removal and reduced membrane fouling initially, but ineffective separation of pre-coated PAC during backwashing resulted in the consistent development of physically unresolved membrane fouling. To address performance issues associated with individual  $\text{SiO}_2$  and PAC pre-coatings, this study demonstrates the first use of  $\text{SiO}_2$  as a support layer for PAC in a membrane pre-coating application. The combined  $\text{SiO}_2$ -PAC pre-coating successfully reduced physically unresolved membrane fouling and enhanced UF membrane organics removal capabilities.

Key Words: Silicon Dioxide, Powdered Activated Carbon, Ultrafiltration, Enhancement, Pre-coat, Pre-deposit, Layer

## 5.2. Introduction

The concept of pre-coating ultrafiltration (UF) membranes with removable media provides intriguing prospects for reducing fouling and enhancing membrane contaminant removal capabilities. To date, several researchers have investigated the pre-coating of UF membranes for drinking water treatment. Galjaard et al. (2001a) discuss a process for depositing solids on membrane filters called Enhanced Pre-Coat Engineering (EPCE<sup>®</sup>), and Cai and Benjamin (2011) refer to a similar pre-coating process as microgranular adsorptive filtration ( $\mu$ GAF). In these membrane pre-coating process schemes, a thin layer of solids is intentionally deposited onto UF membrane surfaces prior to filtration. Depending on the media, pre-coating UF membranes may significantly increase runtimes (Kim et al., 2010), improve backwash effectiveness (Galjaard et al., 2001b), and decrease permeability loss (Galjaard et al., 2003).

A variety of pre-coating materials have been tested to varying degrees as individual coatings, including silicon dioxide ( $\text{SiO}_2$ ) and powdered activated carbon (PAC). The implementation of  $\text{SiO}_2$  membrane pre-coating has faced significant challenges. Published research has reported accelerated fouling rates for  $\text{SiO}_2$  pre-coated membranes (Galjaard et al., 2001; Kim et al., 2008), and the hydrophilicity and negative surface charge of  $\text{SiO}_2$  particles (Yang et al., 2009) limits the applicability of  $\text{SiO}_2$  as an adsorbent for natural organic matter (NOM). Adsorption experiments with  $\text{SiO}_2$  have confirmed poor NOM removal capacity (Chen et al., 2006; Bui & Choi, 2010). Increased fouling rates and negligible NOM removal have rendered  $\text{SiO}_2$  as a less attractive pre-coating material in comparison to an adsorbent such as PAC; however, additional research is warranted for  $\text{SiO}_2$ , because its intrinsic properties suggest alternative pre-coating applications.



The integration of PAC with UF membranes combines the adsorption capabilities of PAC with the solids separation provided by UF membranes. While PAC-UF systems have been extensively studied in the past, previous applications have involved the use of PAC pretreatment via reactors or direct feed water injection rather than membrane pre-coating. A number of studies have reported improved UF membrane performance as the result of PAC addition (Jack & Clark, 1998; Mozia et al., 2005; Kim et al., 2007a; Lee et al., 2007; Smith & Vigneswaran 2009; Campinas & Rosa, 2010; and Hu et al., 2010); however, the integration of PAC can also reduce the performance of UF processes and enhance membrane fouling (Lin et al., 1999; Lin et al., 2000; Lin et al., 2001; Zhang et al., 2003; Li and Chen, 2004; Zhao et al., 2005). From the perspective of membrane pre-coating, PAC was demonstrated to decrease fouling rates relative to an uncoated membrane and result in significant natural organic matter (NOM) removal (Kim et al., 2008). However, the development of physically irreversible fouling is also a documented issue (Galjaard et al., 2001b).

The goal of the present research study is to identify a new method for enhancing UF contaminant removal capabilities while protecting the membrane from irreversible fouling. Accordingly, a new application of SiO<sub>2</sub> is proposed in which SiO<sub>2</sub> serves as a support layer for PAC. This paper presents an evaluation of membrane performance with individual SiO<sub>2</sub>, PAC, and combined SiO<sub>2</sub>-PAC pre-coating layers. Process data is assessed using the transmembrane pressure (TMP) balance approach (refer to Chapter 3), and the applicability of the TMP balance approach for analyzing pre-coated membrane processes is discussed.

### 5.3. Materials

#### 5.3.1. UF Membrane Test Equipment

Two bench-scale UF membrane test units (Figure 5-1) were designed, constructed, and equipped with Masterflex<sup>®</sup> L/S<sup>®</sup> positive displacement pumps and Masterflex<sup>®</sup> Tygon<sup>®</sup> tubing (Cole-Parmer, Vernon Hills, IL, USA) to provide a constant volumetric flow during experimentation. The tubing connected into a schedule 80 PVC pipe network with appropriate valves and fittings. Process pressure was monitored using a PX302-100GV pressure transducer and recorded automatically using an OM-DAQ-USB-2401 data acquisition unit (Omega Engineering, Inc., Stamford, CT, USA).

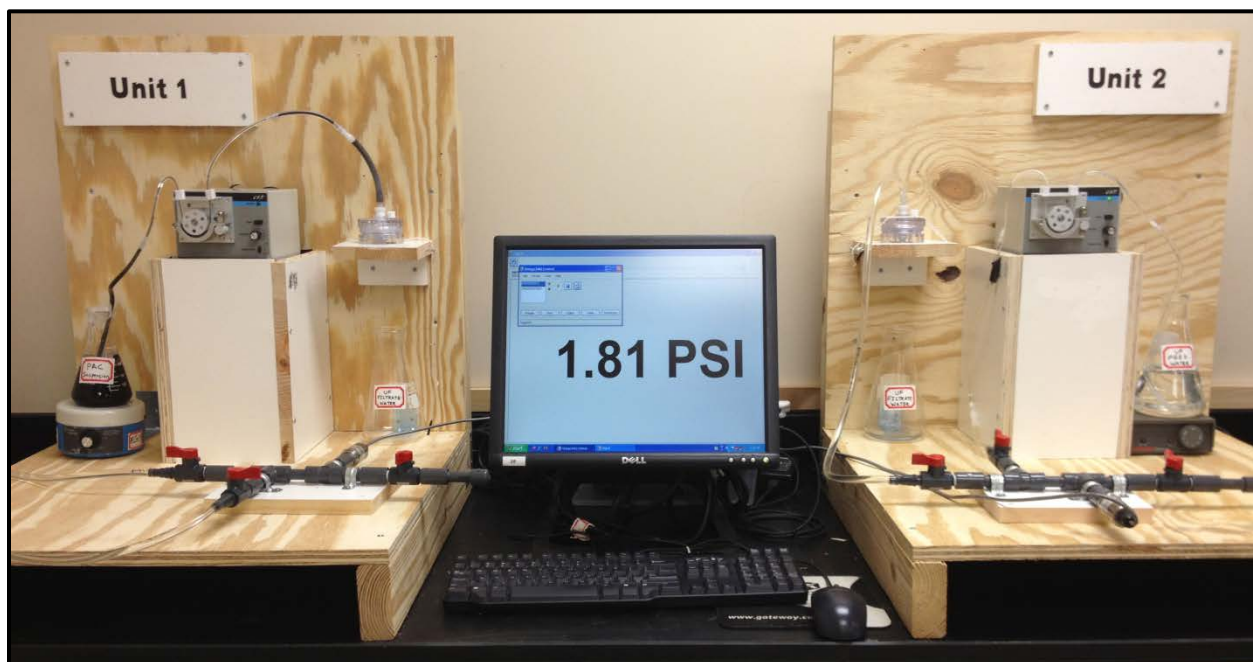


Figure 5-1 UF Membrane Test Units

### 5.3.2. UF Membrane

Hydrophilic polyethersulfone (PES) Nadir<sup>®</sup> UP 150 ultrafiltration membranes (Microdyn-Nadir GmbH, Wiesbaden, Germany) with a molecular weight cutoff of 150,000 daltons (pore size of  $\approx 0.04 \mu\text{m}$ ) were selected for testing.

### 5.3.3. UF Membrane Pre-Coating Materials

#### 5.3.3.1. SiO<sub>2</sub>

SiO<sub>2</sub> experiments were conducted with 100% by weight crystalline SiO<sub>2</sub> (Spectrum Chemical Manufacturing Corp., New Brunswick, NJ, USA) with a nominal particle diameter of  $0.45 \mu\text{m}$  (325 mesh).

#### 5.3.3.2. PAC

PAC experiments were conducted with Aqua Nuchar (MeadWestvaco Specialty Chemicals, North Charleston, SC, USA). Londono (2011) demonstrated that Aqua Nuchar remains intact under turbulent conditions, and a PAC that maintains integrity during pre-coating was desired to minimize particle size distribution variability during testing. The PAC was sieved to provide a particle size distribution of  $\leq 0.45 \mu\text{m}$  (325 mesh).

### 5.3.4. Surface Water

Surface water was collected from Lake Claire located on the University of Central Florida (Orlando, FL, USA) campus and pre-filtered using glass-fiber filters for the removal of large diameter particles and debris. The pre-filtered Lake Claire samples were stored within amber

glass bottles in a dark cooler at 4 °C and allowed to reach ambient temperature prior to use.

Table 5-1 presents a water quality summary for the pre-filtered Lake Claire surface water.

Table 5-1 Water Quality Data: Pre-filtered Lake Claire Surface Water

<b>pH</b>	<b>Temperature</b>	<b>Turbidity</b>	<b>Alkalinity</b>	<b>Total Hardness</b>	<b>Organic Carbon</b>	<b>UV 254</b>
---	°C	NTU	mg/L as CaCO <sub>3</sub>	mg/L as CaCO <sub>3</sub>	mg/L as C	cm <sup>-1</sup>
7.74	21.0	0.25	39.2	49.1	13.2	0.432

#### 5.4. Methods

##### 5.4.1. UF Membrane Preparation

UF membranes were cut into 47 mm diameter disks from flat sheets, rinsed with distilled water, and soaked in distilled water for a minimum of 12 hours prior to use.

##### 5.4.2. UF Membrane Pre-coating Procedure

Separate suspensions of SiO<sub>2</sub> and PAC were prepared within a fume hood by adding a measured weight of material to distilled water to achieve a target concentration. The SiO<sub>2</sub> and PAC suspensions were continuously mixed during application to the membrane surface. Pre-coating occurred at a constant flow rate for a set time interval to achieve target mass loadings of approximately 80 and 160 g/m<sup>2</sup> of membrane surface area. Following pre-coating, distilled water was pumped through the membrane at a flux of 100 L/m<sup>2</sup>-hr (58.9 gal/ft<sup>2</sup>-day) for a minimum of 15 minutes to compact the pre-coated material prior to lake water filtration.

#### 5.4.3. UF Test Procedure

Baseline pressure data was established with distilled water prior to lake water filtration. An Erlenmeyer flask containing undiluted Lake Claire water served as a feed reservoir. Feed water temperatures were recorded periodically. Experiments were conducted at a target flux of 100 L/m<sup>2</sup>-hr (58.9 gal/ft<sup>2</sup>-day), and flows were monitored using a calibration column and stopwatch. Backwashes were initiated at pre-determined specific filtrate volume intervals, where the specific filtrate volume is the volume of water produced per unit of membrane surface area. The backwash procedure consisted of an initial distilled water rinse followed by a five minute backwash using distilled water at a flux rate of 200 L/m<sup>2</sup>-hr (117.8 gal/ft<sup>2</sup>-day). After backwashing, unresolved membrane fouling was assessed by filtering distilled water for a minimum of 15 minutes and recording the pressure when stable.

#### 5.4.4. Organic Carbon Analysis

Composite filtrate samples were collected in specific filtrate volume increments of 15 L/m<sup>2</sup> and diluted with distilled water. Organic carbon concentrations were determined by the persulfate-ultraviolet oxidation method using a Fusion Total Organic Carbon Analyzer™ (Teledyne Tekmar, Mason, OH, USA). Laboratory quality control measures were conducted in accordance with the *Standard Methods for the Examination of Water and Wastewater* (American Public Health Association et al., 2005).

#### 5.4.5. UF Performance Assessment Method: TMP Balance Approach

UF pilot performance was monitored using the TMP balance approach that identifies changes to membrane fouling resistance and intrinsic membrane resistance based on variations in

temperature corrected TMP (TCTMP) relative to a reference pressure. The reference pressure is selected according to the application and may be either that of a new process at steady state, a chemically cleaned process, or a process operating at a level of acceptable performance. A generic temperature correction factor (TCF) for normalizing TMP values to 20 °C is presented in Equation 5-1, and Equation 5-2 presents a simplified version of the TMP balance calculation. In Equation 5-2, TCTMP measurements are chronologically organized into sequences (J); where an operating sequence consists of consecutive filtration and backwash events. The  $\Delta Reference$  term, defined mathematically in Equation 5-3, adjusts the first TCTMP value in a data set to the TMP balance by subtracting the reference pressure.

$$Temperature\ Correction\ Factor = \frac{1.002\ centipoise}{1.777 - 0.052T + 6.25 \times 10^{-4}T^2} \quad (5-1)$$

Where,

T = actual water temperature, °C

$$TMP\ Balance_{ij} = \Delta Reference + \left( \sum_{j=1}^J \sum_{i=1}^{n_j} (TCTMP_{i+1,j} - TCTMP_{ij}) \right) \quad (5-2)$$

$$\Delta Reference = TCTMP_{ij} - TCTMP_{Reference} \quad (5-3)$$

The magnitude of the TMP balance quantifies the resistance change in units of pressure, and the sign denotes position relative to a zero TMP balance. TMP balance values greater than zero indicate an increase in the resistance to flow, and negative TMP balance values indicate a decreased resistance. TMP balance values may be used to distinguish between different types of fouling. For instance, operating TMP balance values, calculated during filtration events, quantify the pressures required to produce filtrate, and post-backwash TMP balance values indicate the pressure contribution of physically unresolved resistance.

## 5.5. Results and Discussion

### 5.5.1. Implementation of the TMP Balance for Pre-Coating Evaluations

The TMP balance isolates the pressure contribution of membrane foulants and physical changes to the membrane material by accounting for the intrinsic resistance of the membrane ( $R_M$ ). Particle deposition during membrane pre-coating adds an additional layer of resistance to flow, referred to in this study as the intrinsic pre-coat resistance ( $R_{PC}$ ). Figure 5-2 presents a graphical depiction of a pre-coated membrane with the intrinsic resistance factors shown. At a given flux, the membrane and the pre-coating media offer a resistance to flow that translates into a TMP value. A modified form of the resistance-in-series model, as presented in Equation 5-4, shows that the total intrinsic pressure resistance ( $TMP_{M-PC}$ ) is determined by the summation of the intrinsic pressure resistances of the membrane ( $TMP_M$ ) and the pre-coat ( $TMP_{PC}$ ). For pre-coated membranes, the value of  $TMP_{M-PC}$  is used as the reference pressure in Equation 5-3 for adjusting pressure data to the zero TMP balance baseline. When the intrinsic pressure resistances for different pre-coating media and masses are quantified, the TMP balance enables different pre-coating combinations to be directly compared on the basis of fouling relative to the same zero TMP balance reference.

$$TMP_{M-PC} = J\mu(R_M) + J\mu(R_{PC}) = TMP_M + TMP_{PC} \quad (5-4)$$

Where,

$J$  is the volumetric flux,  $L/m^2$ -hr (gal/ft<sup>2</sup>-day)

$\mu$  is the absolute viscosity, cp (lb/ft-s)

$R_M$  is the intrinsic membrane resistance,  $m^{-1}$  ( $ft^{-1}$ )

$R_{PC}$  is the intrinsic pre-coat resistance,  $m^{-1}$  ( $ft^{-1}$ )

$TMP_M$  is the intrinsic membrane pressure resistance, bar (psi)

$TMP_{PC}$  is the intrinsic pre-coat pressure resistance, bar (psi)

$TMP_{M-PC}$  total intrinsic pressure resistance, bar (psi)

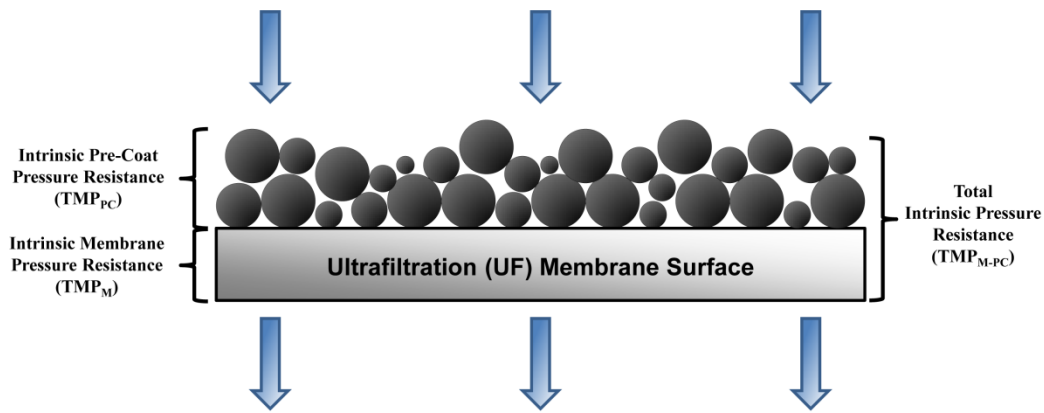


Figure 5-2 Intrinsic Resistances of a Pre-Coated UF Membrane

The intrinsic pressure resistance for pre-coated membranes at different flux values may be obtained from a plot of TCTMP versus volumetric flux. A linear relationship is known to exist between TCTMP and volumetric flux for an unfouled UF membrane filtering clean water (Yeh & Wu, 1997; Chellam et al., 1998; Cheryan et al., 1998), and this study demonstrated linear TCTMP-volumetric flux relationships for  $SiO_2$  (Figure 5-3) and PAC (Figure 5-4) pre-coated membranes as well. Once these equations are established, the total intrinsic pressure resistance may be determined for any applicable operating flux, and the TMP balance may be adjusted to account for the pressure variations associated with flux changes (refer to Appendix A).



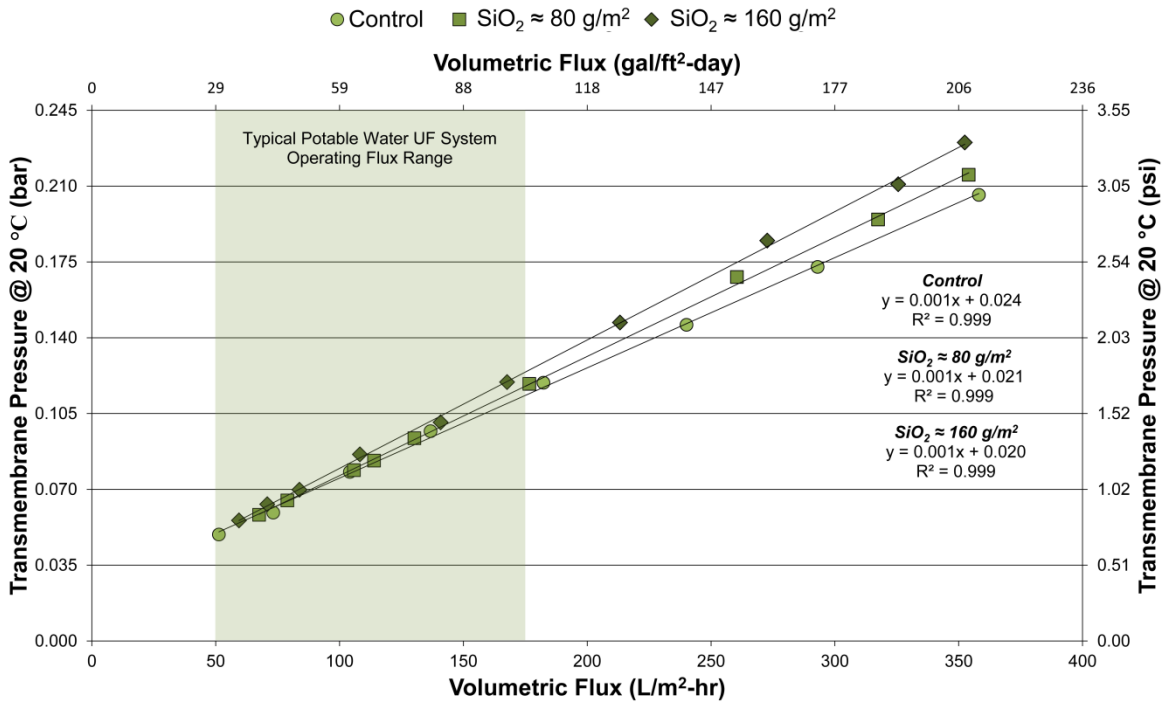


Figure 5-3 TCTMP versus Volumetric Flux for SiO<sub>2</sub> Pre-Coated UF Membranes

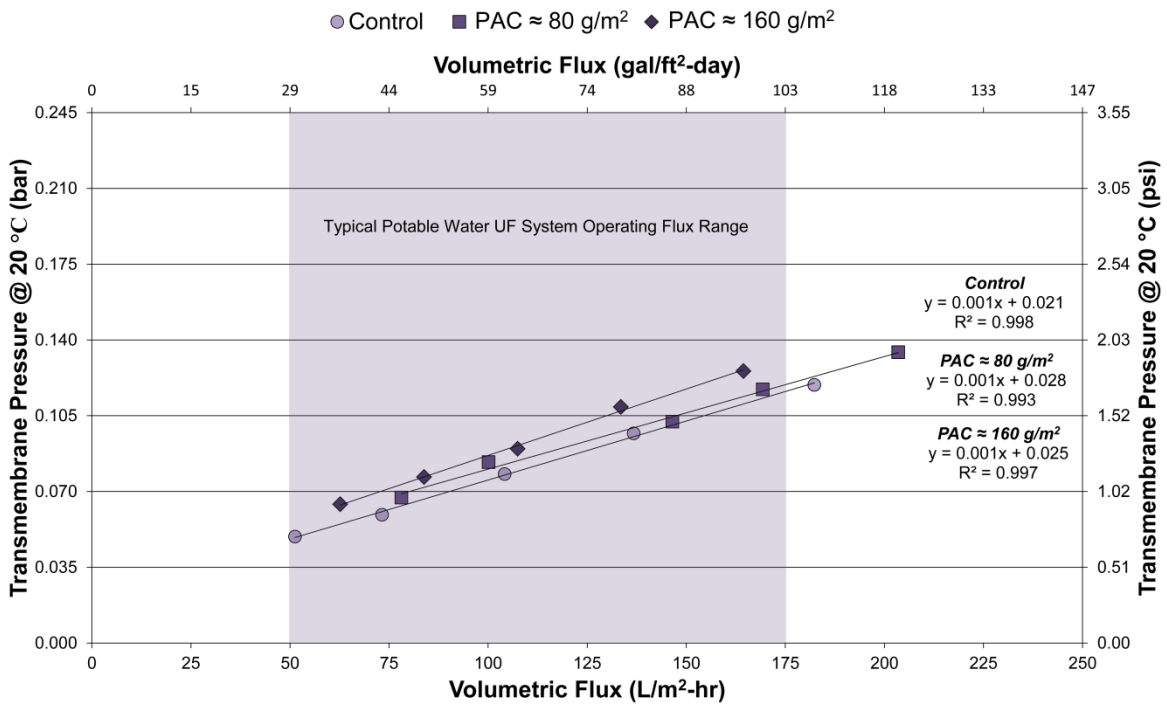


Figure 5-4 TCTMP versus Volumetric Flux for PAC Pre-Coated UF Membranes

### 5.5.2. TMP Balance Evaluation of SiO<sub>2</sub> Pre-Coat Performance

The SiO<sub>2</sub> pre-coating experiments operated at a constant flux of 100 L/m<sup>2</sup>-hr (58.9 gal/ft<sup>2</sup>-day) with pre-filtered Lake Claire feed water. SiO<sub>2</sub> mass loadings of approximately 80 g/m<sup>2</sup> and 160 g/m<sup>2</sup> were selected to approximate a desired layer depth of one and two particles, respectively. The 80 and 160 g/m<sup>2</sup> values were derived by assuming an ideal system with uniform particle diameters, a homogeneous particle suspension, and uniform particle settling during pre-coating. Backwashes were performed at 100 L/m<sup>2</sup> intervals for two sequences and then at 200 L/m<sup>2</sup> for a third sequence. Following each backwash event, a new layer of SiO<sub>2</sub> was deposited onto the membrane prior to filtration. An uncoated membrane served as an experimental control.

Figure 5-5 presents the TMP balance results for the SiO<sub>2</sub> pre-coating evaluation. The 80 g/m<sup>2</sup> and 160 g/m<sup>2</sup> SiO<sub>2</sub> mass loadings significantly increased fouling rates relative to the experimental control, and end-of-sequence TMP balance values exceeded control values by more than a factor of three. The resistance increases observed for the SiO<sub>2</sub> pre-coated membranes suggest the rapid formation of an organic gel layer on the SiO<sub>2</sub> particles, similar to the compressible gel layer demonstrated to develop on uncoated UF membranes during surface water treatment (Kim et al., 2007b).

Doubling the mass of SiO<sub>2</sub> from 80 to 160 g/m<sup>2</sup> did not appreciably affect the pressure rise, as evidenced by the proximity of the TMP balance trend lines. However, empirical evidence suggests that particle diameter plays a significant role in membrane fouling rates with SiO<sub>2</sub>. A related study conducted with 60.3 g/m<sup>2</sup> of 15 μm nominal diameter SiO<sub>2</sub> particles exceeded the TMP rise of an uncoated control membrane by approximately 0.790 bar (11.5 psi) after 25 L/m<sup>2</sup> of specific filtrate volume (Kim et al., 2008). In contrast, the 45 μm nominal diameter SiO<sub>2</sub>

coating in this study differed from the uncoated control membrane by only 0.045 bar (0.66 psi) at the same specific filtrate volume. Both studies filtered surface water at the same 100 L/m<sup>2</sup>-hr (58.9 gal/ft<sup>2</sup>-day) flux rate. Further research is needed to assess the impact of pre-coat particle size distributions on membrane fouling.

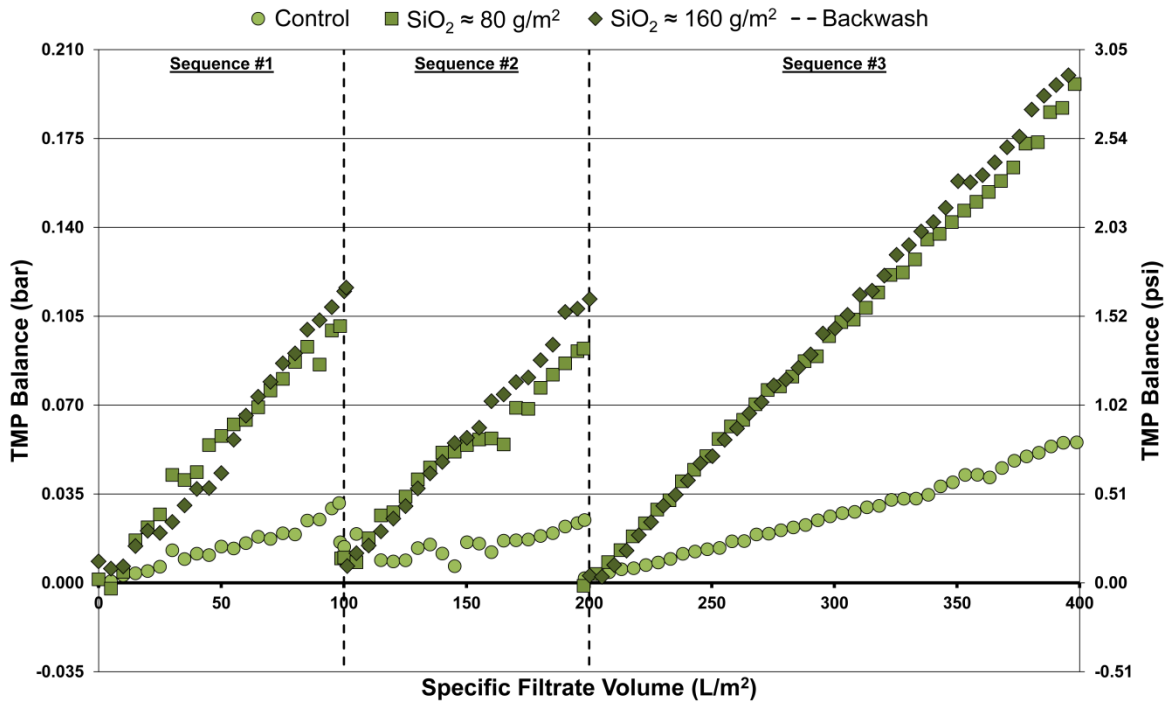


Figure 5-5 TMP Balance for SiO<sub>2</sub> Pre-Coating Experiments

Although the SiO<sub>2</sub> surface coating accelerated fouling rates during filtration, the SiO<sub>2</sub> layer was effectively removed from the membrane via backwash. Qualitative observations indicated a significant removal of the SiO<sub>2</sub> pre-coat during the rinse phase of the backwash procedure (Figure 5-6c) and a slight discoloration following backwash (Figure 5-6d). Post-backwash TMP balance results, which quantify the pressure contribution of physically unresolved membrane fouling, are presented in Figure 5-7. The post-backwash TMP balance values were generally lower for the SiO<sub>2</sub> pre-coated membranes than the control. Accordingly, the SiO<sub>2</sub> pre-coating

may have acted as a sacrificial layer to which physically irreversible membrane foulants preferentially adhered. Galjaard et al. (2003) achieved a similar protective effect using a diatomite pre-coat.

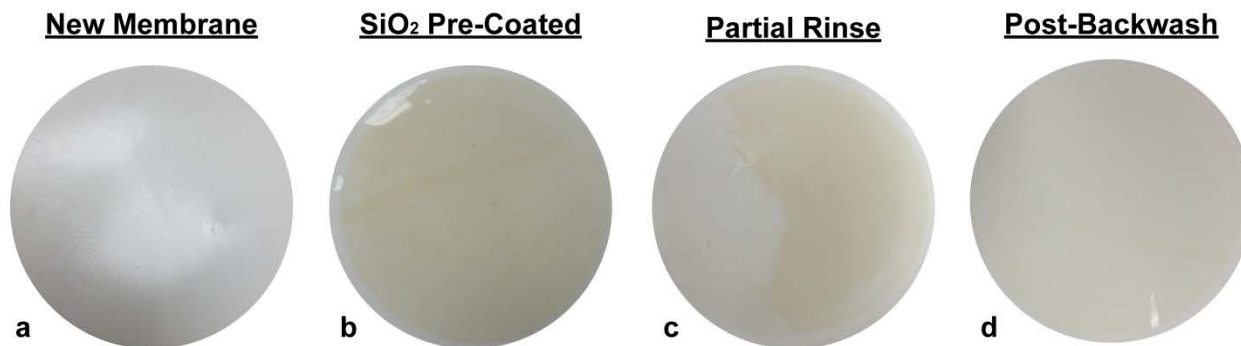


Figure 5-6 Images of SiO<sub>2</sub> Pre-Coated Membranes

### 5.5.3. TMP Balance Evaluation of PAC Pre-Coat Performance

#### 5.5.3.1. Assessment of Pre-Coated PAC Operating Performance

The experimental procedure employed during the SiO<sub>2</sub> experiments was replicated using PAC at the 100 L/m<sup>2</sup>-hr (58.9 gal/ft<sup>2</sup>-day) volumetric flux. PAC mass loadings of approximately 80 g/m<sup>2</sup> and 160 g/m<sup>2</sup> were selected to provide a gram for gram comparison with SiO<sub>2</sub> rather than on the basis of surface area coating. As shown in Figure 5-8, the 80 g/m<sup>2</sup> PAC pre-coated membrane yielded lower fouling rates relative to the control during the first sequence. However, gradual increases in fouling occurred with increasing specific filtrate volume. TMP balance values for both the 80 g/m<sup>2</sup> and 160 g/m<sup>2</sup> mass loadings exceeded the control in the third sequence with the 80 g/m<sup>2</sup> mass loading exhibiting the most severe fouling.

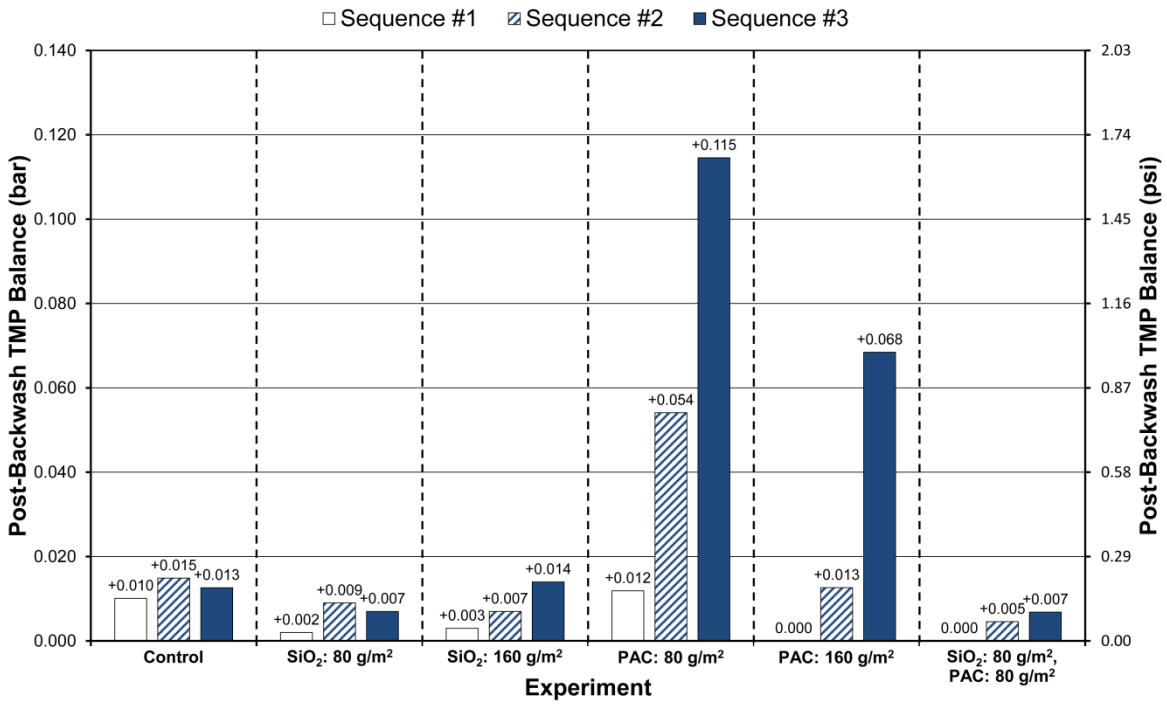


Figure 5-7 Post-Backwash TMP Balance Results

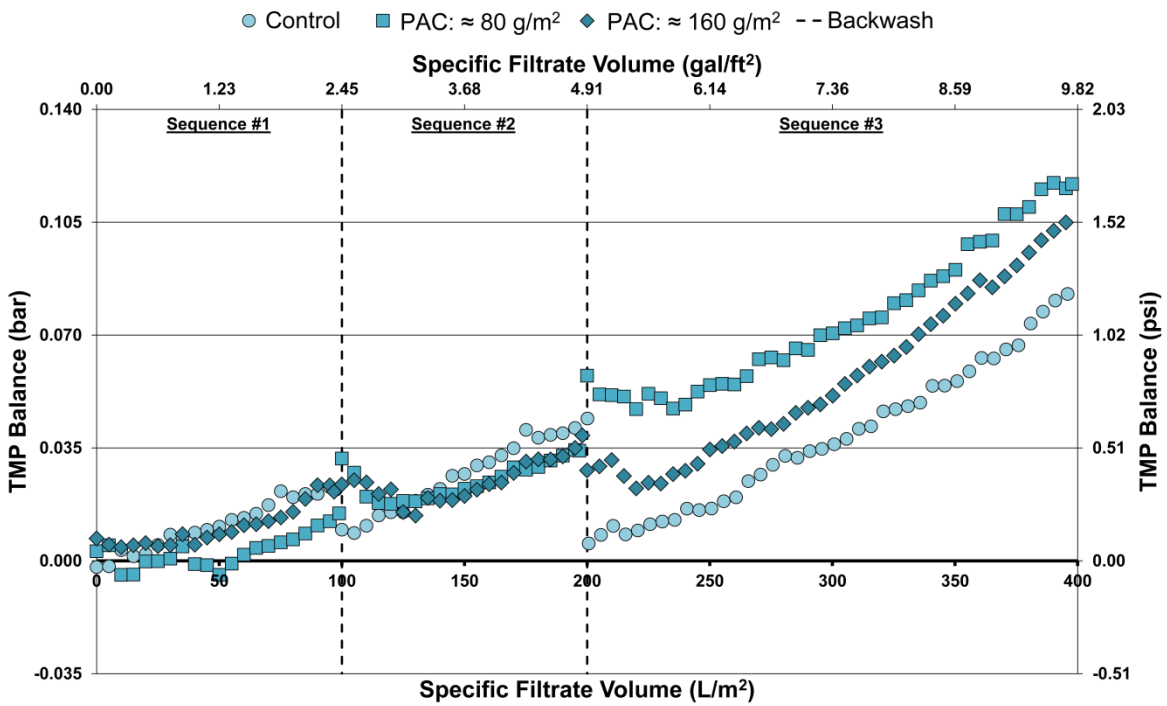


Figure 5-8 TMP Balance for PAC Pre-Coating Experiments

The gradual deterioration in PAC pre-coated membrane performance resulted from the development of physically unresolved membrane fouling. A visual assessment of the pre-coated membranes before and after backwashing (Figures 5-9b and 5-9c) indicated significant PAC retention at the membrane surface, and post-backwash TMP balance values (Figure 5-7) revealed consecutive increases in physically unresolved fouling from sequences 1 through 3. Maximum post-backwash TMP balance values occurred for the 80 g/m<sup>2</sup> mass loading, which implies a correlation between PAC mass and membrane fouling reduction. Kim et al. (2010) suggested that a pre-deposited adsorbent layer may be viewed as a thin packed bed and hypothesized that improvements in UF membrane performance were due to NOM removal and gel formation at the surface of the adsorbent layer. Correspondingly, increases in UF fouling rates have been correlated to theoretical breakthroughs for a thin packed adsorbent layer (Cai et al., 2008), and Galjaard et al. (2001b) reported membrane performance improvements at estimated adsorbent layer thicknesses of 3 and 5 particles. The results of this study are in agreement with these assertions, because the increase in adsorption sites and layer depth at 160 g/m<sup>2</sup> PAC loading yielded fouling reduction improvements consistent with the presence of a thin packed adsorbent bed.

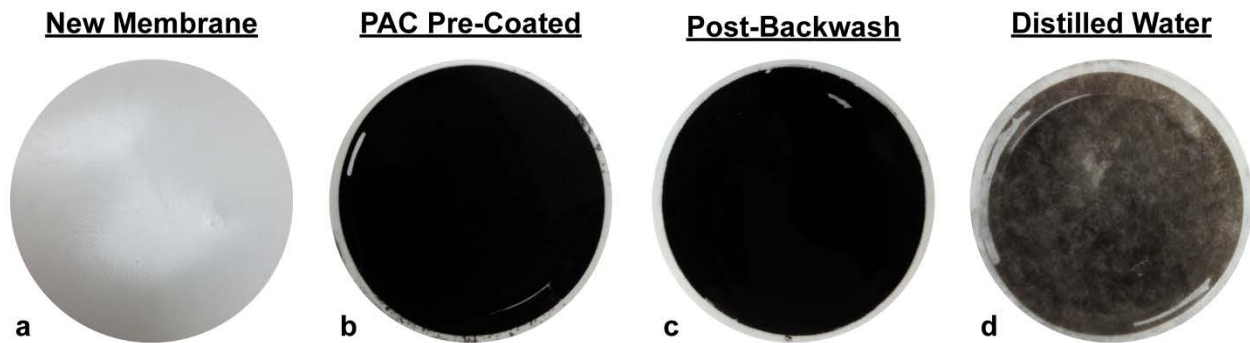


Figure 5-9 Images of PAC Pre-Coated Membranes

PAC fouling mechanisms were further assessed by filtering distilled water through a new, PAC pre-coated UF membrane and evaluating the backwash effectiveness. A notable improvement in PAC removal was observed visually (Figure 5-9d), but a PAC residue remained affixed to the membrane. While similar experiments have indicated that PAC alone does not cause irreversible fouling (Lin et al., 1999; Zhang et al., 2003; Li and Chen, 2004; Mozia et al., 2005; Campinas and Rosa, 2010), the post-backwash TMP balance data indicated a slight flow resistance increase of +0.001 bar (+0.02 psi).

The PAC particle size distribution of  $\leq 45 \mu\text{m}$  may have played a significant role in physically unresolved PAC fouling, because smaller diameter particles have been demonstrated to be more difficult to remove (Galjaard, 2001b). However, the PAC-UF interactions alone do not explain the severity of the observed physically unresolved fouling following lake water filtration. NOM is reported to act as a binding agent that links PAC particles to the membrane forming a backwash resistant layer (Lin et al., 1999; Zhang et al., 2003), and the filtration of the organic surface water in this study clearly exacerbated the fouling tendency of the PAC pre-coat and increased PAC retention at the membrane surface.

#### 5.5.3.2. Organic Carbon Removal with PAC Pre-Coat

Figure 5-10 presents organic carbon percent removal values as a function of specific filtrate volume. The uncoated control membrane provided percent removals of less than 4.3% during testing with the exception of an initial 29.8% carbon removal. The elevated initial organic removal, coupled with a first sequence physically unresolved fouling increase of +0.010 bar (0.15 psi), implies the adsorption of organic carbon onto the clean control membrane. The subsequent declines in control membrane carbon removal values suggest the occupation of

available adsorption sites. PAC pre-coated membranes yielded organic carbon removal values between 77.2% and 49.9%. In keeping with standard adsorption theory, maximum PAC organic carbon removals occurred at the beginning of each sequence and gradually declined with increasing specific filtrate volume.

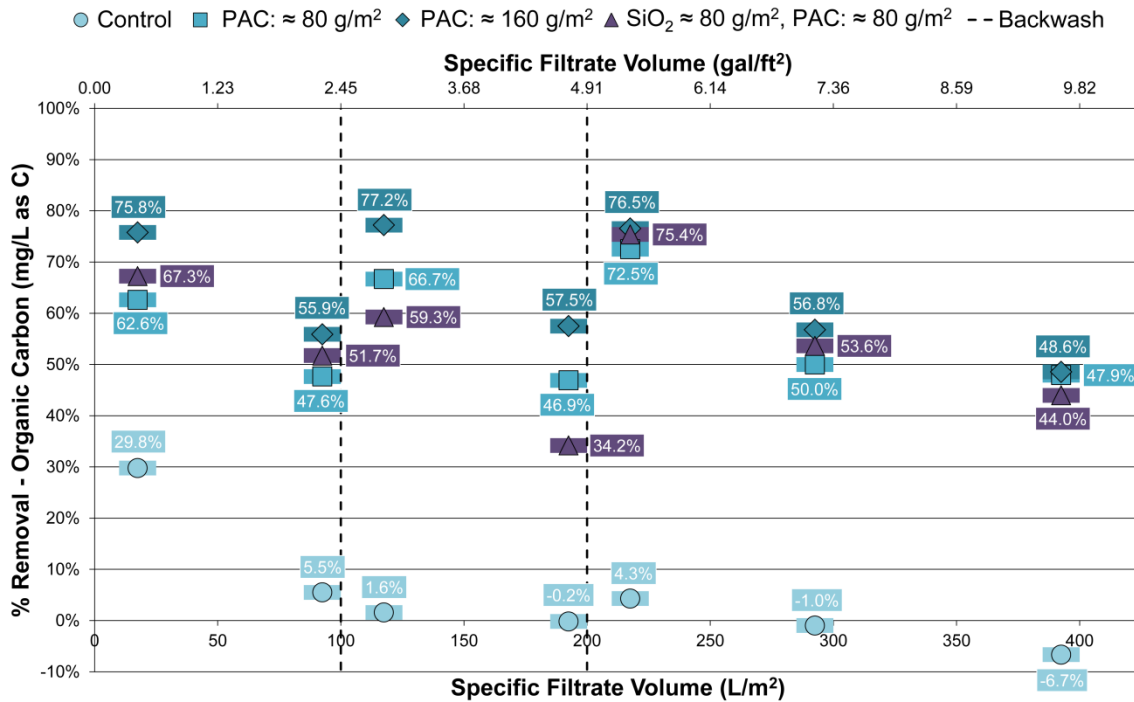


Figure 5-10 Organic Carbon Removal Values

#### 5.5.4. Combined SiO<sub>2</sub> – PAC Pre-Coating Demonstration

Strengths and weaknesses were identified for both the SiO<sub>2</sub> and PAC pre-coating materials. SiO<sub>2</sub> was effectively removed during backwashing but resulted in significant operating pressure increases. PAC demonstrated an ability to reduce operating pressure development and organic carbon concentrations but intensified physically unresolved fouling. Based on these strengths and weaknesses, a third experiment was designed to test whether layering PAC above pre-deposited



SiO<sub>2</sub> would enable effective backwashing, maintain acceptable operating pressures, and enhance organic carbon removal. For the test sequences, 80 g/m<sup>2</sup> of SiO<sub>2</sub> was applied to the membrane surface followed by an 80 g/m<sup>2</sup> layer of PAC.

Figure 5-11 presents the TMP balance results for the SiO<sub>2</sub>-PAC pre-coating experiments. As observed with the PAC pre-coated membranes, TMP balance values were elevated at the start of each SiO<sub>2</sub>-PAC test sequence and declined over 10 to 20 L/m<sup>2</sup> of specific filtrate volume. These pressure trends suggest that newly deposited PAC particles tend to reconfigure in a manner that reduces flow resistance. Following the initial pressure decline at the start of each sequence, TMP balance values increased with increasing specific filtrate volume. Figure 5-12 compares the operating TMP balance values for the control, SiO<sub>2</sub>, PAC, and SiO<sub>2</sub>-PAC experiments. Operating pressures for the SiO<sub>2</sub>-PAC pre-coated membrane were elevated relative to the control, notably lower than the SiO<sub>2</sub>, and comparable to the PAC tests over the first 300 L/m<sup>2</sup> of filtrate production.

The SiO<sub>2</sub>-PAC combination effectively protected the membrane from physically unresolved pressure development. Qualitative observations identified substantial removal of the SiO<sub>2</sub>-PAC pre-coat during the initial rinse phase of the backwash procedure (Figure 5-13b) and a significantly reduced PAC residual after three sequences of operation (Figure 5-13c). Post-backwash TMP balance values (Figure 5-7) were lowest for the SiO<sub>2</sub>-PAC pre-coating experiments indicating an ability to reduce physically unresolved fouling development. Additionally, the organic carbon removal capabilities of the SiO<sub>2</sub>-PAC pre-coat were in keeping with the 80 and 160 g/m<sup>2</sup> PAC experiments (Figure 5-10).

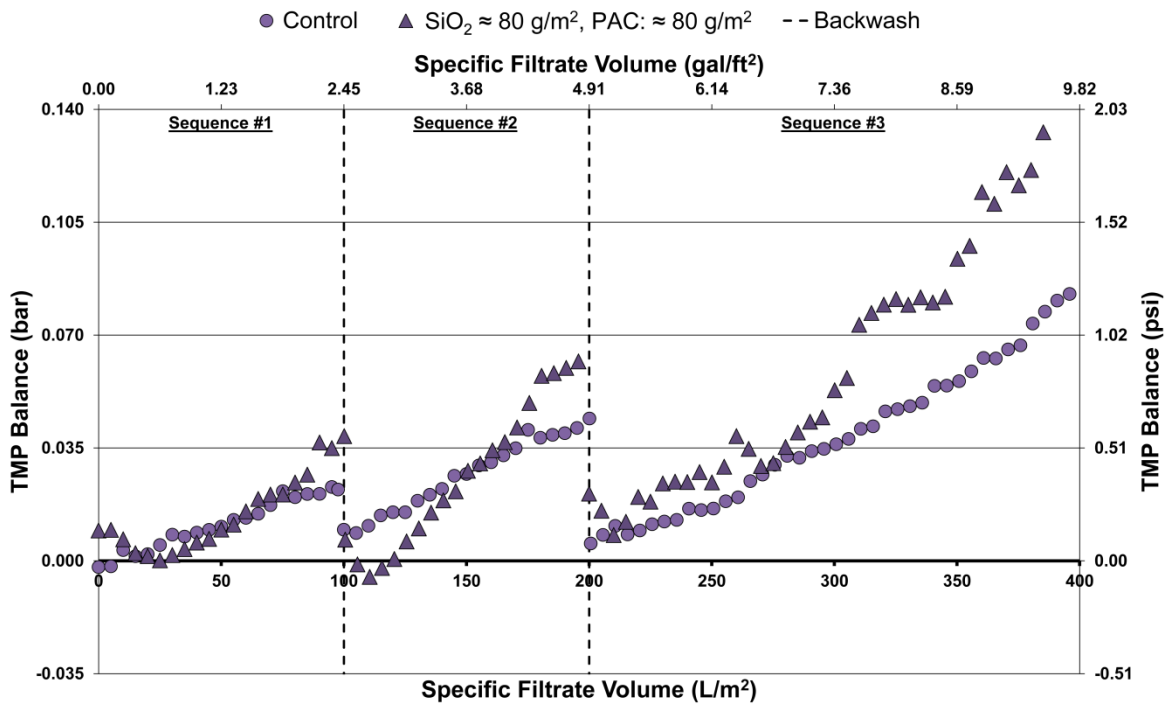


Figure 5-11 TMP Balance for SiO<sub>2</sub>-PAC Pre-Coating Experiments

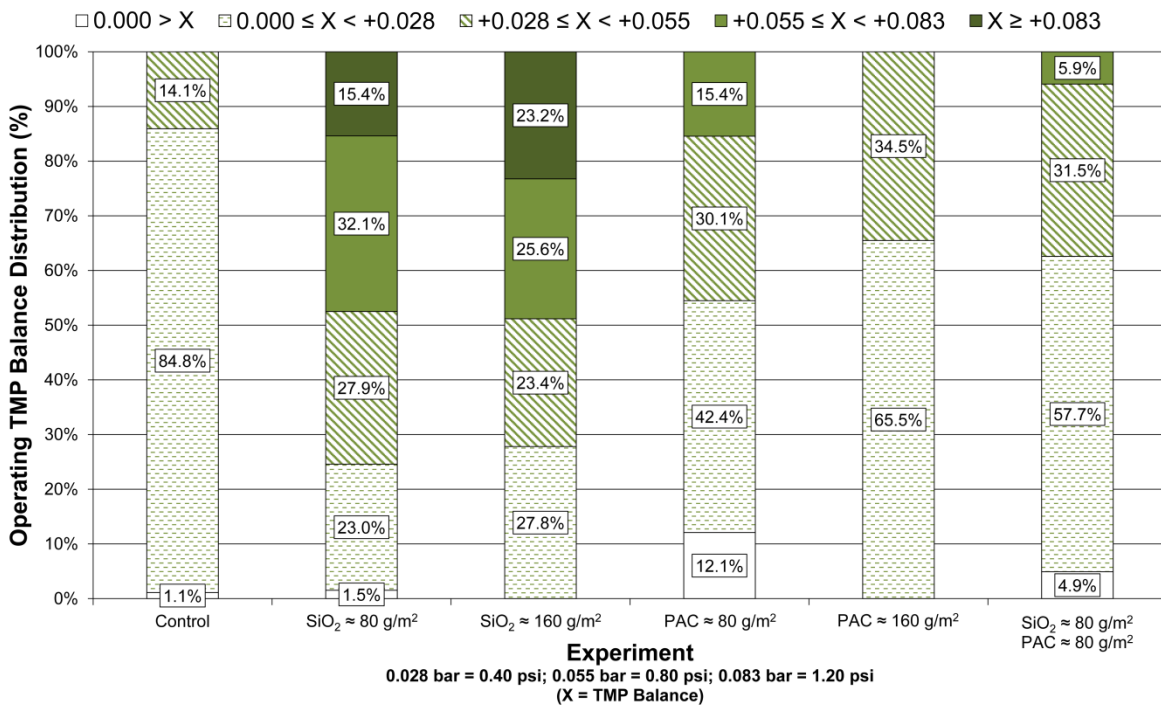


Figure 5-12 Operating TMP Balance Distribution Comparison Chart

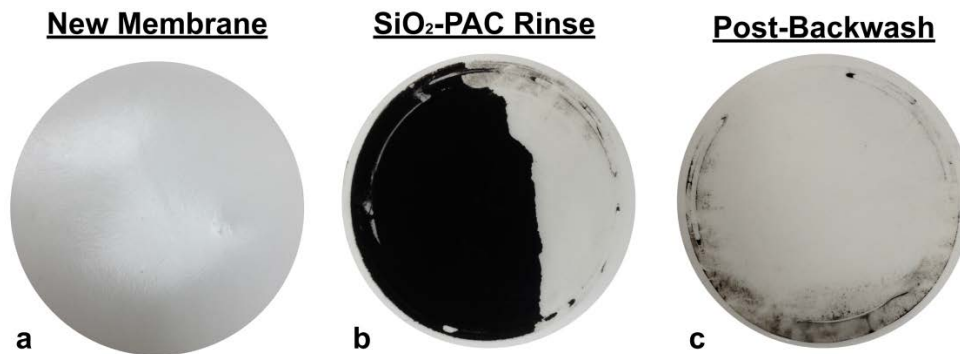


Figure 5-13 Images of PAC-SiO<sub>2</sub> Pre-Coated Membranes

## 5.6. Conclusions

SiO<sub>2</sub> and PAC were evaluated as pre-coatings for a PES UF membrane using the TMP balance approach. SiO<sub>2</sub> alone increased fouling rates and operating pressures for the UF process, but the SiO<sub>2</sub> layer was effectively removed from the membrane surface during backwashing. The SiO<sub>2</sub> layer also protected the membrane from physically unresolved fouling. PAC alone effectively removed organic carbon from the feed water but accelerated physically unresolved fouling development.

For the first time, this study evaluated the concept of layering PAC over a pre-coating of SiO<sub>2</sub>. SiO<sub>2</sub> was demonstrated to be an effective support layer that provided a barrier between the membrane fouling PAC and the membrane surface. The SiO<sub>2</sub>-PAC pre-coating resulted in lower physically unresolved fouling development than an uncoated membrane at the expense of increased operating pressure. Adding PAC onto the SiO<sub>2</sub> support also significantly enhanced organic carbon removal with maximum removals of 75.4%. The concept of pre-coating membranes with a SiO<sub>2</sub> support layer provides a new approach for enhancing the removal

capabilities of UF membranes and reducing physically unresolved fouling. Future research may look at the potential for extending UF runtimes with a SiO<sub>2</sub>-PAC pre-coating via incorporation of feed water pretreatment processes and by depositing other materials onto the SiO<sub>2</sub> support layer for organic and inorganic contaminant removal.

### 5.7. Acknowledgments

The research reported herein was funded by UCF project agreement 16208085. Thanks are in order to David Dickerson (Microdyn Technologies, Inc., Raleigh, NC) for the donation of the membranes used in this study and to the Manatee County Utilities Department (Bradenton, Florida) for the donation of the powdered activated carbon used during testing. The contributions of Andrea Cumming (University of Central Florida, Orlando, FL), Dr. Jayapregasham Tharamapalan, and Jonathan Harn (Harn R/O Systems, Inc., Venice, FL) are duly recognized and greatly appreciated.

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## CHAPTER 6. GENERAL CONCLUSION

- Pilot test protocols should provide sufficient time to identify the impacts of seasonal water quality changes on UF pilot performance.
- Dynamic cleaning protocols should be employed to adapt to changing water quality conditions to limit the unnecessary use of cleaning chemicals and improve UF process performance.
- The performance of a membrane process is easily interpreted from the TMP balance, because the TMP balance is reported as a pressure change relative to a reference condition.
- The TMP balance identifies pressure variations associated with changes to the intrinsic membrane resistance and fouling layers.
- The TMP balance distinguishes between chemically unresolved, physically unresolved and operating pressure changes through calculation of post-CEB, post-CIP, post-backwash, and operating TMP balance values.
- Calculation of the TMP balance allows for the comparison of process performance at different flux values.
- Operating protocols for UF processes should be dynamic to maintain production targets while minimizing the occurrence of unnecessary maintenance activities.
- The five component systematic optimization approach provides tools for identifying UF process operating configurations that achieve sustainable performance and improve process output.

- Optimization of an UF pilot with conventional alum coagulation pretreatment yielded sustainable process operation at process recovery and utilization values of 96.1% and 93.5%, respectively.
- Backwash and CEB residual pressure calculations successfully identified changes in physical and chemical maintenance performance.
- A protective fouling layer effect was observed following extension of the CEB interval. The corresponding improvements in backwash effectiveness were accompanied by higher operating pressures.
- Post-CEB TMP balance values (i.e. chemically unresolved membrane fouling) increased with increased process recovery and utilization.
- $\text{SiO}_2$  was effectively removed from the membrane surface during backwashing, but increased fouling rates and operating pressures for the UF system.
- Membrane fouling with  $\text{SiO}_2$  was found to be independent of  $\text{SiO}_2$  mass.
- PAC effectively removed organic carbon from the feed water but resulted in the development of physically unresolved fouling.
- For the first time,  $\text{SiO}_2$  was demonstrated to be an effective support layer that provided a barrier between the membrane fouling PAC and the membrane surface.
- The  $\text{SiO}_2$ -PAC pre-coating resulted in lower physically unresolved fouling development than an uncoated membrane at the expense of increased operating pressure.
- Adding PAC onto the  $\text{SiO}_2$  support significantly enhanced organic carbon removal relative to an uncoated membrane with maximum removals of 75.4%.

**APPENDIX A: SUPPLEMENTAL INFORMATION – ADDITIONAL TMP  
BALANCE FUNCTIONALITY FOR MEMBRANE PRE-COATING**

The linear relationship between TCTMP and volumetric flux enables the TMP balance to maintain the established zero TMP balance reference when the flux is changed. This is accomplished by accounting for the associated intrinsic pressure resistance change using the  $\Delta Flux$  term. In the  $\Delta Flux$  equation, the subscript  $m$  refers to the flux case, which corresponds to an operating flux value, and the *slope* is that of the line describing TCTMP versus volumetric flux for the process. Once the  $\Delta Flux$  term is calculated, it may be incorporated into the TMP balance equation as shown below.

$$\Delta Flux = slope (Flux_m - Flux_{m+1})$$

$$TMP\ Balance_{ijm} = \Delta Reference + \left( \sum_{m=1}^M \sum_{j=1}^{Jm} \sum_{i=1}^{n_{jm}} (TCTMP_{i+1,jm} - TCTMP_{ijm}) \right) + \sum_{m=1}^M \Delta Flux_m$$

Where,

Subscript  $m$  refers to the flux case

## **APPENDIX B: LABORATORY QUALITY CONTROL RECORDS**

Laboratory quality control was maintained using sample replicates and spikes. Tables Appendix-B1 and Appendix-B2 present the relative standard deviation (RSD) and recovery values for the organic carbon analysis discussed in Chapter 5. Replicate samples were in compliance at RSD values of  $\leq 20\%$ , and spiked samples were in compliance at values between 80% and 120%.

Table Appendix-B1 Organic Carbon Analysis – % RSD for Replicate Samples

<b>Replicate Set #</b>	<b>%RSD</b>
1	1.84
2	2.34
3	5.80
4	2.56
5	2.50
6	5.60
7	1.53

Table Appendix-B2 Organic Carbon Analysis – Percent Recovery for Spiked Samples

<b>Spike Set #</b>	<b>% Recovery</b>
1	99.9
2	99.6
3	98.4
4	98.8
5	100.1
6	96.8
7	99.1

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