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Eric J. Lynne
South Dakota State University

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NANOFILTRATION MEMBRANE PILOT STUDIES FOR DISINFECTION BY-PRODUCT CONTROL

BY

ERIC J. LYNNE

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NANOFILTRATION MEMBRANE STUDIES FOR DISINFECTION BY-PRODUCT CONTROL

This thesis is approved as a creditable and independent investigation by a candidate for the Master of Science degree and is acceptable for meeting the thesis requirements for this degree. Acceptance of this thesis does not imply that the conclusions reached by the candidate are necessarily of the major department.

Delvin E. DeBoer, Ph.D., P.E. Date
Major Advisor
Civil & Environmental Engineering Department

Bruce W. Berdanier, Ph.D., P.E., L.S. Date
Department Head
Civil & Environmental Engineering Department

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ABSTRACT

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Watertown, South Dakota currently uses conventional softening to treat ground water to remove hardness, iron and manganese, and natural organic matter. The distribution system has experienced elevated concentrations of disinfection by-products, which will require additional treatment to comply with future limits set by the Stage 2 Disinfectant/Disinfection By-Products Rule. A nanofiltration membrane system has been proposed to remove additional natural organic matter from the softened water. Removing the natural organic material disinfection by-product precursors should reduce the concentration of disinfection by-products. The use of nanofiltration membranes has been previously documented to reject total organic carbon, while allowing desirable levels of hardness and alkalinity to remain in the water.

A study using a 4” diameter, single element pilot plant study compared six nanofiltration membranes from various manufacturers. Koch TFC-SR2, Koch TFC-SR3, Trisep XN45-TSF, Hydranautics ESNA1-LF, Hydranautics HydraCoRe-70pHT, and Dow/Filmtec NF270 were operated at 15, 50, and 80 percent recovery to analyze each membrane’s performance. Water analyses were performed and membranes were selected for further studies if they exhibited high total organic carbon rejection, low simulated distribution system disinfection by-product formation, and reject stream total dissolved solids concentrations below 1000 mg/L. The Koch TFC-SR3, Trisep XN45-TSF, and Hydranautics ESNA1-LF membranes were selected for further study. A larger pilot plant was utilized to further test the selected membranes using a 2:2:1:1 array of twenty-one 4" diameter elements. Three membrane models were operated at flux rates of 9, 12, and 15 gallons per day per square foot to determine an optimum flux setting for full scale design. Water quality parameters were also analyzed to provide additional basis for membrane selection. The efficacy of nanofiltration to reduce disinfection by-products was also compared to chloramination.

Koch TFC-SR3, Trisep XN45-TSF, and Hydranautics ESNA1-LF exhibited total organic carbon rejections in excess of 90 percent for every test setting during final testing. The excellent organic rejections corresponded to disinfection by-product removals in excess of 90 percent for many of the flux settings. No trends were established between flux rate and disinfection by-product removal. However, increasing flux rates were shown to cause decreasing specific flux rates. A membrane fouling study was performed for 30 days to analyze the specific flux decline from organic and inorganic foulants. No significant fouling was observed for Hydranautics ESNA1-LF or Trisep XN45-TSF. Dependent on several economical factors, an optimum operating setting was not established.

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LIST OF ABBREVIATIONS

°C	degrees celcius
µS/cm	microsiemens per centimeter
$CaCO_3$	calcium carbonate
DBP	disinfection by-product
DOC	dissolved organic carbon
EDTA	ethylenediaminetetraacetic acid
EPA	Environmental Protection Agency
ft	feet
gfd	gallons per minute per foot squared
gpm	gallons per minute
HAA5	haloacetic acids
lb	pound
LSI	Langlier saturation index
m	meter
MCL	maximum contaminant level
MF	microfiltration
mg/L	milligrams per liter
MGD	million gallons per day
mL	milliliters
MWCO	molecular weight cut-off
NDP	net driving pressure
NF	nanofiltration
NH_3	ammonia
NH_4	ammonium
NOM	natural organic matter
psi	pounds per square inch
RO	reverse osmosis
SBS	sodium bisulfite
SDDENR	South Dakota Department of Environment and Natural Resources
SDI	silt density index
SDS	simulated distribution system
SF	specific flux
SUVA	specific ultraviolet light absorbance
TCF	temperature correction factor
TDS	total dissolved solids
THM	trihalomethane
THMFP	trihalomethane formation potential
TOC	total organic carbon
TTHM	total trihalomethanes
UF	ultrafiltration

UV_{254}	ultraviolet light at 254 nm
WEERC	Water and Environmental Engineering Research Center
WMU	Watertown Municipal Utilities
D/DBP	disinfectant and disinfection by-product

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CHAPTER ONE – INTRODUCTION

1.1. Background

The Watertown Municipal Utilities (WMU) water treatment plant (WTP) is facing new water quality standards that include more stringent disinfection by-product (DBP) levels to be enforced by the Stage 2 Disinfectant/Disinfection By-Product (D/DBP) Rule. In addition to providing safe drinking water, WMU desires to expand the plant capacity and update the aging water treatment infrastructure. To avoid increased DBP levels WMU is seeking the best available technique for natural organic matter (NOM) removal. NOM has been proven to be a precursor to DBPs when free chlorine is used for disinfection. Nanofiltration (NF) membranes were examined in this study because of their ability to selectively remove NOM and hardness, while leaving moderate levels of desirable alkalinity and total dissolved solids (TDS) in the treated water (Crittenden et al., 2005; AWWA, 1999).

Watertown Municipal Utilities obtains their groundwater from shallow, alluvial wells in the Big Sioux Aquifer (named the Conifer well field), of which many wells contain TOC concentrations ranging from 4.5-6.0 mg/L. Through the existing conventional softening WTP the average total organic carbon (TOC) concentrations are lowered to 2.5-4.0 mg/L. The future well site, named Rauville, has raw water TOC similar to the existing WTP filter effluent, around 2.5 mg/L.

The overall schematic for a proposed alternative is shown in Figure 1.1. Four million gallons per day (MGD) will be NF product and approximately four MGD will be

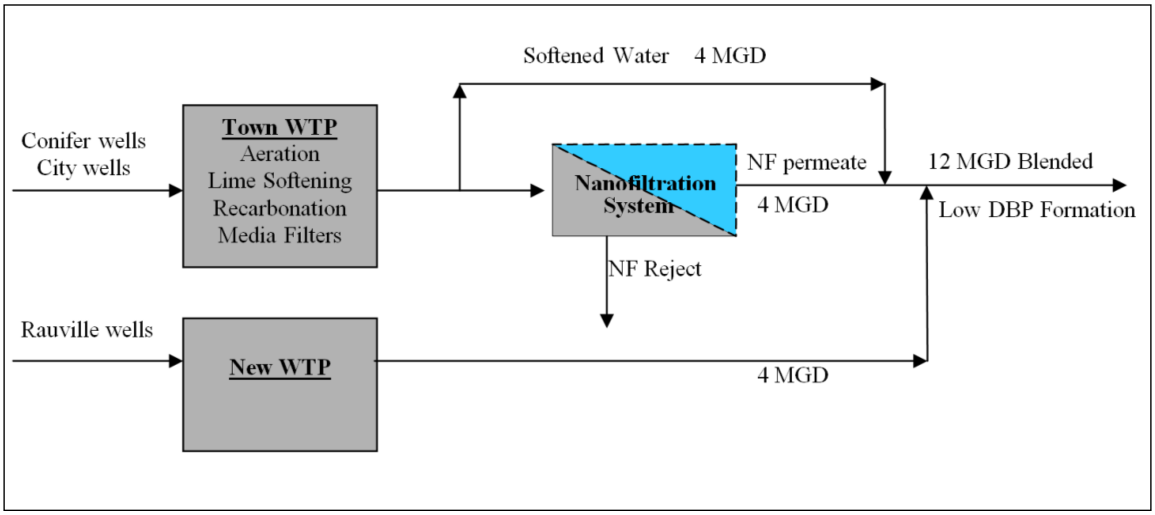


Figure 1.1 – Proposed WTP Flow Schematic (Chmielewski 2008)

bypassed, depending on the product quality. The proposed WTP addition will also add 4 MGD to bring the total to 12 MGD. Since chlorinated permeate DBP levels from NF systems are typically well below the Environmental Protection Agency (EPA) limit of 80 μg/L and 60 μg/L for total trihalomethanes (TTHM) and five haloacetic acids (HAA5), a portion of the NF system feed water will bypass the membranes to produce a blend that meets the D/DBP regulations.

1.2. Objective

The purpose of this project was to determine if treatment of the existing filter effluent using nanofiltration membranes can remove sufficient TOC to assure low DBP levels in the NF permeate. The low concentration of DBP in the permeate is necessary to create a blended water quality that will assure compliance with the D/DBP rule. A single element pilot test was implemented to select candidate membranes for further testing. Three candidate membranes would then be tested in a 21 element pilot skid to properly imitate a full scale system. Engineering design criteria necessary for full-scale implementation would be obtained from this test.

The full scale NF membrane concentrate would be disposed in the Big Sioux River. South Dakota's Department of Environment and Natural Resources (SDDENR) classifies the beneficial use of the Big Sioux River as a domestic water supply, thereby enforcing a TDS discharge limit of 1000 mg/L (SDDENR 2008). Depending on the membrane characteristics and NF system settings, the concentrate stream may exceed this TDS limit. Furthermore, the NF membrane still must reduce DBPs substantially to facilitate a high blend ratio. Therefore, understanding the influence of blend ratios on DBP production and characteristics of the NF concentrate were important for this study.

1.3. Scope of Study

The project involved the operation of two NF pilot plants at a ground water treatment facility. Prior to acquiring the membranes, a water quality analysis was performed to understand potential operational characteristics of candidate NF systems. Experiments were performed during the single element membrane screening test to compare TOC and TDS rejection capabilities for each of six different elements. From the single element results, the optimum NF membrane was determined by the highest TOC rejection and lowest TDS rejection. In addition, a laboratory blend of NF permeate with feed water was examined to determine if the blended water would meet the Stage 1 and Stage 2 Disinfection By-Product Rules. The 21-element pilot plant compared three of the six membranes from the screening test. The larger pilot plant verified the rejection characteristics of organic and inorganic material for the selected membranes. Simulated distribution system (SDS) tests of various samples also demonstrated the effectiveness of NF membranes for reducing DBPs. The operating pressures and temperatures for varying flux rates were recorded to verify optimum membrane performance settings. The fouling characteristics were monitored to determine long-term permeability decline. The results of this research provide insight on the application of NF membranes for softening and NOM removal in a ground water treatment facility. Local water suppliers with similar influent water quality can utilize this information to help them evaluate alternative treatment processes.

CHAPTER TWO – LITERATURE REVIEW

2.1. Introduction

A literature review was conducted to provide background information on DBPs, spiral wound membrane filtration, foulant control methods, effects of membrane system settings on flux and recovery, and organic and inorganic contaminant rejection. The effects of flux settings, NOM, TDS, and ammonia rejection, and membrane fouling on membrane operations are described in the literature review and tested during the experimental process. Examples of pilot scale tests are also discussed in the literature review.

2.2. Disinfection By-Products

Organic DBPs are created when chemical disinfectants, such as free chlorine, combine with NOM. The extent of DBP formation depends on treatment conditions and water quality variables such as the type and dosage of disinfectant, reaction time, pH, temperature, season, type and amount of organic matter, bromide, ammonia, and carbonate alkalinity (Gagliano 2006, Garvey and Tobiason 2003). Total trihalomethanes (TTHM – chloroform, bromoform, bromodichloromethane, and dibromochloromethane) and haloacetic acids (HAA5 – monochloro-, dichloro-, trichloro-, monobromo-, dibromo-acetic acid) are the common forms of DBPs created when chlorine or chloramine is used for disinfection (USEPA 2006).

Several epidemiological studies have linked extreme DBP levels and/or chronic DBP exposure to bladder cancer and potentially to reproductive or developmental health effects. To ensure public safety the EPA implemented Stage 1 and Stage 2 of the Disinfectants and Disinfection By-Products Rule, which places maximum contaminant levels (MCLs) on TTHM and HAA5 of 80 μg/L and 60 μg/L, respectively. Stage 1 of the Rule required the system to meet these MCLs based on a calculated running annual average of the samples collected throughout the entire distribution system (USEPA 1998). Stage 2 changed the compliance MCL calculation to a locational running annual average (LRAA) (USEPA 2006). The EPA suggests controlling DBPs by limiting the amount of DBP precursors available to react with disinfectants (USEPA 1998).

2.2.1. Factors Affecting DBP Formation

As stated previously, DBP formation depends on many factors. In this study only source water NOM, pH, disinfectant type, and disinfectant dose will be considered. Other factors such as reaction time, temperature, and bromide were held relatively constant throughout the study and will not be discussed.

The source water NOM concentration has a direct impact on the resulting DBP formation. Typically ground water sources have a relatively consistent NOM concentration, while surface water and ground water under the influence of surface water will have seasonal NOM concentration variations. The ground water quality is well specific, as quality will change with varying location and depth. For a low turbidity ground water source, dissolved organic carbon is the main source of NOM (Crittenden et al. 2005). Each water source has a specific composition of NOM constituents commonly classified by size and functionality (Liang and Singer 2003). Generally, NOM is a complex, heterogeneous mixture of hard-to-identify compounds. Non-polar or humic

NOM is hydrophobic and is readily removed by coagulation when compared with polar or non-humic NOM (Hwang et al. 2002). NOM consists of low molecular weight acids, amino acids, proteins and polysaccharides, fulvic acids and humic acids that have a wide range of molecular weights (Crittenden et al. 2005). Higher molecular weight organics exhibit higher TTHM formation potential than organics with lower molecular weights (Reckhow and Singer 1990).

The pH has been demonstrated to directly influence DBP formation. A higher pH, 8 or greater, will favor higher THM growth, while HAA growth increases at a lower pH of 6 (Liang and Singer 2003, Brereton and Mavinic 2002). In a ground water treatment plant using conventional softening the final pH typically ranges from 8.3 – 9.0 (Qasim et al. 2000, DeVille 2008). In this pH range, it has been documented that TTHM formation potential is greater than the associated HAA5 formation potential (Gagliano 2006).

The type of disinfectant applied for microbial disinfection can also drastically change DBP formation. The use of free chlorine residual forms many DBPs, however ultraviolet light and chlorine dioxide create no organic DBPs. Ozone and chloramine have low potential to form DBPs. Chloraminated water may exhibit THMs and HAAs that are believed to be caused from free chlorine residuals in the water prior to ammonia addition (Crittenden et al. 2005).

The disinfectant dose has been shown to impact DBP formation. Higher dosages of chlorine create more THMs than smaller dosages (Brereton and Mavinic 2002). Chlorine applied to water containing ammonia must achieve breakpoint chlorination to oxidize the ammonia before creating free chlorine residual (Crittenden et al. 2005). The limiting concentration of free chlorine that enables significant DBP formation has been established at 0.3 mg/L. Concentrations below this threshold minimum do not form significant DBP values, nor provide strong disinfection (USEPA 2006).

2.2.2. Treatment Processes and Operations to Reduce DBPs

Instead of removing DBPs after they have been formed, specific treatment processes may be installed to remove NOM prior to disinfection. Enhanced coagulation or softening, chemical oxidants, activated carbon, ion exchange, and reverse osmosis or nanofiltration membranes are effective operations and processes to remove NOM.

Enhanced coagulation or enhanced softening is a modification of an existing treatment process to optimize NOM removal. In enhanced coagulation the organics bind to a metal ion coagulant through adsorption (Liang and Singer 2003). Enhanced softening utilizes the precipitation of magnesium hydroxide floc to adsorb up to 40-80% of the NOM (Crittenden et al. 2005). Waters with higher specific ultraviolet absorbance values are more amenable to removal of organic material by coagulation than waters with low specific ultraviolet absorbance values. Coagulation has been shown to remove more HAA precursors than THM precursors (Liang and Singer 2003). The EPA has listed enhanced coagulation and enhanced softening as a best available technique for NOM removal in the Stage 1 Disinfectant/Disinfection By-Product Rule (USEPA 1998). Conventional water treatment is most effective at removing non-polar NOM (Hwang et al. 2002).

Chemical oxidants may also be used to oxidize the NOM disrupting their ability to create DBPs. Preoxidants like chlorine dioxide, potassium permanganate, and ozone are typically applied for their strong oxidation potential and low DBP formation (Crittenden et al. 2005). The chemical oxidant's effectiveness must be evaluated for both TOC and DBP reduction.

NOM may also adsorb onto activated carbon, although the capacity for activated carbon to remove TOC is small relative to the taste and odor removal capacity. Activated carbon is best at removing the polar NOM (Hwang et al. 2002). The use of granular activated carbon or powdered activated carbon is considered expensive and a last resort for organic removal, therefore, activated carbon is less commonly applied for TOC removal. Biologically active carbon filters effectively use a bacterial film to decompose the organics. (Crittenden et al. 2005).

Ion exchange resins have been developed specifically for NOM removal. These smaller and magnetized cationic resins attract the negatively charged NOM. Although NOM removals are highly dependent on the NOM characteristics, typical removals are around 50% (Crittenden et al. 2005). Ion exchange is most efficient at removing polar NOM (Hwang et al. 2002). Ion exchange resins can be regenerated using chloride or hydroxide. Disposal of the rejected brine typically limits its application, due to the high TDS concentration (Crittenden et al. 2005).

Reverse osmosis (RO) can physically remove NOM from the water source using diffusion. However, similar to ion exchange the RO process implementation may be limited by a high TDS reject stream. Reverse osmosis is most efficient at rejecting polar

NOM. (Hwang et al. 2002). Having near similar rejections of TOC, nanofiltration has also shown effectiveness at removing NOM from water in many studies (Hwang et al. 2002, Allgeier and Summers 1995, Tan and Sudak 1992). A major advantage for NF is its ability to retain TDS in the finished water, allowing NF to be implemented where RO was not feasible.

2.3. Membrane Filtration

There are four types of pressure-driven membrane filtration processes, microfiltration (MF), ultrafiltration (UF), NF, and RO. Typically the membrane processes are differentiated by the materials that are rejected. MF rejects particles, sediment, algae and bacteria. UF membranes have smaller pores and reject all same material as microfilters as well as small colloids and viruses. NF and RO membranes operate using higher pressures to separate dissolved material from a liquid. NF uses molecular size sieving and diffusion to reject particles and solutes larger than 1 nanometer in size. RO can reject monovalent ions in addition to all the previous particles using diffusion (Crittenden et al. 2005). The particle size exclusion capabilities of various membranes is shown in Figure 2.1. Spiral wound NF membranes represent the extreme left of the nanofiltration separation process box, rejecting only a portion of aqueous salts and a majority of humic acids. Aqueous salts like calcium and magnesium are divalent ions, with a larger ionic size than monovalent ions. These divalent ions can be selectively rejected by certain NF membranes.

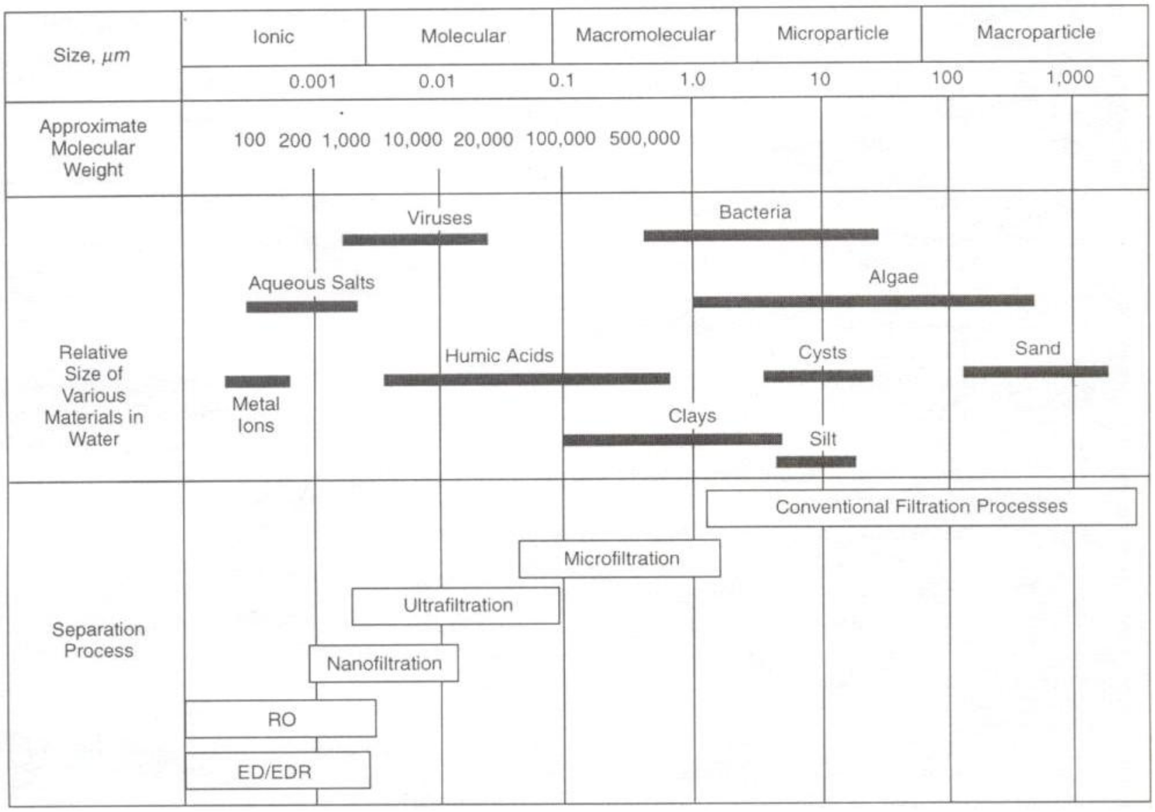


Figure 2.1 – Membrane Size Comparison (AWWA 1999)

The permeate from a pressure-driven membrane system is the processed water that passes through the membranes. The reject, or concentrate, flow is the remaining water and constituents that did not pass through the membranes. Typical NF membranes are able to remove salts, hardness, pathogens, turbidity, DBP precursors, synthetic organic compounds, and sulfate (AWWA 1999).

NF membrane characteristics vary widely by manufacturer but are commonly compared by their molecular weight cut-off (MWCO) and solute rejection. The MWCO (measured in Daltons) is the size of exclusion based on constant laboratory conditions (Taylor and Jacobs 1996). NF membranes that reject a majority of NOM have a MWCO value in the range of 300 to 1000 Daltons (AWWA 1999). Solute rejections are determined by challenging the membrane with a known concentration of a salt solution such as chloride or magnesium sulfate. These values give the design engineer a basic understanding of the reject and permeate water quality for a particular membrane (Qasim et al. 2000).

NF membrane filtration utilizes two techniques, straining and diffusion, to reject particles and dissolved material, respectively, from the water. For straining, constituents in the water are being rejected by the size of the pore openings. Diffusion uses pressure to overcome a concentration gradient and drive liquid through the membrane. Since water diffuses across the membrane faster than the larger dissolved ions, the contaminants are rejected (Crittenden et al. 2005, AWWA 1999).

Another major difference between the types of membrane classifications is in the method of waste production and removal. In a MF or UF membrane filtration apparatus, the membranes are periodically backwashed to remove any of the particles that have collected on the membrane surface. This particulate matter is then settled out and the water is recovered. Since spiral wound NF membranes typically are not backwashed, a high enough cross flow velocity must be maintained to flush away dissolved foulants in the concentrate stream, which tend to be scale-forming (Crittenden 2005). Membrane manufacturers typically specify a minimum cross flow velocity such that a 5:1 ratio of feed water flow to permeate flow is maintained across every section of membrane. The rejected dissolved solids and accompanying water become the concentrate stream which must be further processed or disposed (Dow 2008).

2.3.1. Permeate Flux through NF Membranes

The term flux describes the recovery of product water per unit area of membrane surface. A higher flux rate requires a smaller surface area in a treatment system, which lowers the capital investment and enables a smaller facility footprint (Qasim et al. 2000). Typical flux rates for RO and NF membranes range from 7-25 gallons per square foot per day (gal/ft^2-d) or abbreviated more commonly as “gfd.” The optimum flux rate depends on the quality of the feed water. Pure water will flow through at a high flux rate, around 25 gfd, while increased turbidity and ionic concentrations will lower the maximum allowable flux rate (Dow 2008).

Calculating the flux of permeate and solutes through a membrane enables designers to model membrane systems. While there are several theories on permeate flux, the homogenous solution diffusion model is based on the following fundamental equations (AWWA 1999, Taylor and Jacobs 1996).

$$J = k_w \cdot (\Delta P - \Delta \Pi) \tag{2.1}$$

$$J = \frac{Q_p}{A} \tag{2.2}$$

$$J_s = k_s \cdot \Delta C \cdot 0.012 \tag{2.3}$$

$$J_s = \frac{Q_p \cdot C_p \cdot 0.012}{A} \tag{2.4}$$

$$R = \frac{Q_p}{Q_f} \tag{2.5}$$

in which: J = permeate flux through membrane (gfd)
k_w = water mass transfer coefficient (gfd/psi)

ΔP = transmembrane pressure differential (psi)
$\Delta \Pi$ = osmotic pressure differential (psi)
Q_p = permeate flow rate (gpd)
A = active membrane area (ft^2)
Js = solute flux through membrane ($lb/d/ft^2$)
k_s = solute mass transfer coefficient (gpm/ft^2)
ΔC = solute concentration differential (mg/L)
C_p = permeate solute concentration (mg/L)
R = recovery (decimal fraction)
Q_f = feed water flow rate (gpd)

Equation 2.1 states that flux of the solvent through the membrane is based on the solvent mass transfer coefficient, the pressure differential across the membrane and the osmotic pressure. As the pressure gradient across the membrane increases, the solvent flux will increase. Conversely, as the osmotic pressure increases, the solvent flux will decrease. Osmotic pressure is the potential energy created by the solute concentration gradient across the membrane. Equation 2.2 is used to calculate the permeate flux when the area and permeate flow are known.

Equation 2.3 describes the solute flux as a function of the solute mass transfer coefficient and concentration differential. As the solute concentration differential increases, the solute flux increases. Equation 2.4 relates the known parameters of permeate flow, permeate concentration and area to determine the solute flux. Equation 2.5 determines the product water recovered from the feed water flow and the permeate flow. The recovery value is important for understanding the system performance.

As observed from these equations, there are several operating conditions that have a significant impact on a membrane system’s performance. The operating pressure is critical to the entire principle as it provides the driving force to promote permeation of water through the membrane. Correspondingly, with varying pressures the output water quantity and quality changes. Other factors that affect permeation include recovery, feed water solute concentration, and temperature (Dow 2008, AWWA 1999).

2.3.2. Net Driving Pressure

Higher pressure typically yields greater permeate flow; however the gross operating pressure is not a proper representative for all systems. The net driving pressure (NDP) accurately represents the impact of the applied pressure after accounting for permeate back pressure and the osmotic pressure. The NDP is described by the following equations (AWWA 1999, Taylor and Jacobs 1996).

$$NDP = \Delta P - \Delta \Pi \qquad \textbf{(2.6)}$$

$$\Delta P = \frac{P_f + P_c}{2} - P_p \qquad \textbf{(2.7)}$$

$$\Delta \Pi = \frac{\Pi_f + \Pi_c}{2} - \Pi_p \qquad \textbf{(2.8)}$$

in which:
P_f = feed water pressure (psi)
Pc = concentrate pressure (psi)
Pp = permeate pressure (psi)
Πf = osmotic pressure of the feed water (psi)
Πc = osmotic pressure of the concentrate (psi)
Πp = osmotic pressure of the permeate (psi)

Equation 2.6 shows that the NDP is a function of the pressure differential and the osmotic differential. As the pressure differential increases, the NDP increases. However, as the osmotic pressure increases, the NDP decreases. Equation 2.7 and 2.8 describe the calculations for finding the pressure and osmotic pressure differentials, respectively. The differentials each use the average of the feed water and concentrate pressures minus permeate back pressure. Taylor and Jacobs (1996) also suggest that the solvent mass transfer coefficient (k_w) will determine the maximum solvent flux, regardless of how much pressure is applied. The solvent mass transfer coefficient, also commonly termed specific flux (SF), ranges from 0.10 – 0.20 gfd/psi for RO systems. In NF systems the SF range is higher (0.15 – 0.45 gfd/psi) due to variations in membrane characteristics (Bellona et al. 2008).

Typical NDP values for NF membranes range from 45 – 75 psi at a flux rate of 14 gfd on a brackish groundwater. When the flux was increased to 20 gfd the feed pressures ranged from 76-100 psi (Kumar et al. 2006). Bellona and others (2008) also found similar pressures of 50 – 70 psi to obtain a flux rate of 18 gfd when applied to reclaimed wastewater.

According to the homogenous solution diffusion model, the solute diffusion is unaffected by changes in pressure and will only progress at a constant rate. Therefore, as pressure is increased more solvent (water) is permeated and the solute concentration in the permeate will be diluted (AWWA 1999).

2.3.3. Recovery

Since the recovery is the percentage of feed water that has permeated through the membrane, higher recovery values can maximize source water utilization. Recovery rates of 75 to 90% are common for NF systems, which corresponds to 10 to 25% rejected to waste. The higher recovery settings produce extremely concentrated reject water. At these high recovery rates the solute rejection may decrease due to an increased concentration gradient (Qasim et al. 2000). The highest operational recovery rate is determined by the limiting salt. The limiting salt is the cation and anion pair in the feed water that will be first to form a precipitate and scale on the surface of the membrane during treatment. The limiting salt can be determined from the solubility products of potential salts and the actual concentrations necessary to form precipitates. The maximum recovery setting can be extended beyond the limiting salt's recovery setting through the use of proper pretreatment techniques (Crittenden et al. 2005). The problems associated with salt precipitation and pretreatment techniques will be discussed in subsequent sections.

A single 40-inch long membrane element is typically only capable of 5 – 20% recovery (Dow 2008). To obtain a total system recovery of 75 to 90% the elements must be arranged appropriately to maximize their combined recovery. A membrane system typically is designed with arrays, or rows of membrane elements in series. The first series will only recover a portion of the total recovery, so the reject water is recycled into a second series of elements. Figure 2.2 illustrates the application of an array system, where the concentrate from the first series becomes the feed water for the second series. This setup is repeated until the desired recovery can be achieved. Multiple arrays are operated in parallel to obtain a design permeate flow (AWWA 1999). As the recovery is increased, the specific flux decreases due to the higher pressure required to overcome the higher osmotic pressure (Kumar et al. 2006).

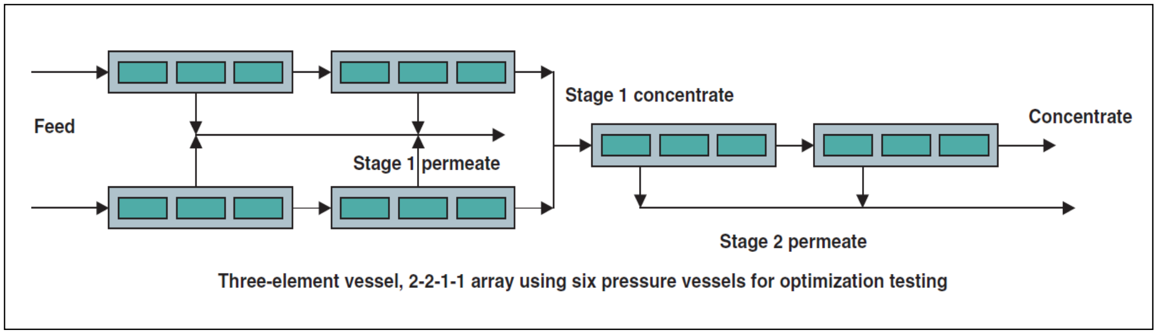


Figure 2.2 – Membrane Array Schematic (Kumar et al. 2006)

2.3.4. Temperature

Temperature has a direct impact on membrane permeate flux (AWWA 1999). Understanding temperature's effects will help diagnose system changes and requirements for design (Qasim et al. 2000). Converting the permeate values to 25°C provides a universal comparison for all temperatures (Taylor and Jacobs 1996). This provides a conversion to equally compare tests which were performed at different temperatures.

The flux of permeate increases as temperature increases because the viscosity decreases. The Hagen-Poiseuille equation describes slow viscous flow through a circular cross section, which is very applicable to membrane permeate flux. Using the Hagen-Poiseuille equation to correct a flux rate back to the reference temperature of 25°C the formula appears as Equation 2.9. The θ value varies between membrane manufacturers but typically is around 1.03. The equation can be modified for use as a temperature correction factor (TCF) as in Equation 2.10, with a different temperature correction constant, U, provided by each manufacturer (Taylor and Jacobs 1996).

$$\log \frac{J_{T^\circ C}}{J_{25^\circ C}} = \log \frac{\mu_{25^\circ C}}{\mu_{T^\circ C}} = (T-25)\cdot \log \theta \qquad \textbf{(2.9)}$$

in which: T = arbitrary temperature in degrees Celcius
J_T = permeate flux at an arbitrary temperature in degrees Celcius
J_{25} = permeate flux at the reference temperature
μ_{25} = permeate viscosity at the reference temperature
μ_T = permeate viscosity at an arbitrary temperature
θ = temperature correction constant

$$\frac{J_{T°C}}{J_{25°C}} = TCF = e^{U(\frac{1}{298}-\frac{1}{273+T})} \qquad \textbf{(2.10)}$$

in which: U = temperature correction constant
(Hydranautics = 2700, Trisep = 2900, Dow = 3020, Koch = 3100)

The logarithmic basis for the temperature correction equations yields a non-linear relationship between temperature and flux. For a temperature of 10°C, the associated TCF ranges from 0.62 – 0.58 depending on the U value selected. Therefore, the flux at 10°C is about 60% of what it would be at 25°C. As a rule of thumb, the temperature effects on flux are regarded to be about 3% for every degree Fahrenheit (AWWA 1999).

2.3.5. Ammonia Rejection Studies

While the rejection of inorganic salts has been studied extensively, the rejection of ammonia is not well documented. Free ammonia is commonly reported as NH_3-N while it's ionized form, ammonium, is reported as NH_4^+-N. The relationship between these two forms of reduced nitrogen is in equilibrium at all times, but the concentrations of each species depend upon pH. As the pH decreases, the hydrogen ion concentration increases providing more available protons for the free ammonia to combine with and form ammonium ions. The reaction also reverses as pH increases. The equilibrium constant (K_{eq}) between these two forms is $10^{-9.25}$ at 20°C. Therefore, at the equilibrium pH of 9.25, water contains 50% free ammonia and 50% ammonium.

Kurama et al. (2002) analyzed the removal of soluble ammonium ions from a surface water source containing 6.5 mg/L NH_4-N at pH of 7.6. Applying the ammonium feed water to a RO membrane system removed ammonium to 0.2 mg/L. The same ammonium feed water applied to Celgard N30F and NF-PES-10 membranes yielded permeate ammonium concentrations of 4.75 and 5.75 mg/L, respectively. The percent rejection for the respective NF membrane calculates to 27% and 12% using Equation 2.11 (AWWA 1999).

$$R = \frac{C_f - C_p}{C_f} \tag{2.11}$$

in which:
R = rejection (decimal fraction)
C_f = concentration in the feed (mg/L)
C_p = concentration in the permeate (mg/L)

A study performed on non-nitrified reclaimed wastewater monitored the rejection of ammonia for seven NF membranes (Bellona et al. 2008). The feed water applied to the membranes contained 32 – 37 mg/L free ammonia at a pH of 6.1 – 6.3. The test was performed at flux rates of 13 and 18 gfd with varying recovery rates. The ammonia rejections ranged from 35.9 – 96.5% as shown in Table 2.1. A higher specific flux corresponds to a lower ammonia rejection. No correlation was noted between varying flux or percent recovery.

Table 2.1. Ammonia Rejections for Various NF Membranes (Bellona et al. 2008)

Membrane Manufacturer	Membrane Model Name	Pretreatment	Initial Specific Flux (gfd/psi)	Ammonia Rejection (%)
Koch	TFC-S	Microfiltration pH adjustment, antiscalant, and chloramination	0.23	91.5
Hydranautics	ESNA1-LF		0.15	96.5
Filmtec	XLE		0.29	92.4
	NF90		0.30	88.2
	NF200		0.22	49.2
	NF4040		0.37	47.0
	NF270		0.45	35.9

The effect of pressure, temperature, and pH on ammonia ion rejection was studied using a Koch TFC-S NF membrane (Koyuncu 2002). A direct increase in pressure was correlated to increased rejection of ammonia ions. At 46 psi the rejection was 80%, and then as pressure was increased to 87 psi the rejection increased steadily to 88%. The TFC-S NF membrane exhibited a MWCO of approximately 200 Daltons, placing it towards the RO end of the NF range, which explains the higher rejections compared to those experienced by Kurama et al. (2002). Although membrane pores tighten at lower temperatures, no change was experienced on rejection. The pH, however, had a strong impact on ammonia ion rejections. As shown by Figure 2.3 the rejections increased gradually until a pH of 8.5. Repulsion between the positively charged membrane and the positively charged ammonia ion apparently occurred at lower pH values (pH 2 – 3). With increasing pH the membrane's charge changed from positive to neutral and then to negative. The negative membrane charge at pH values greater than 8.5 created an attractive force between the positive ammonia ion that reduced the membrane's ability to reject the positive ammonia ions (Braeken et al. 2006, Koyuncu 2002).

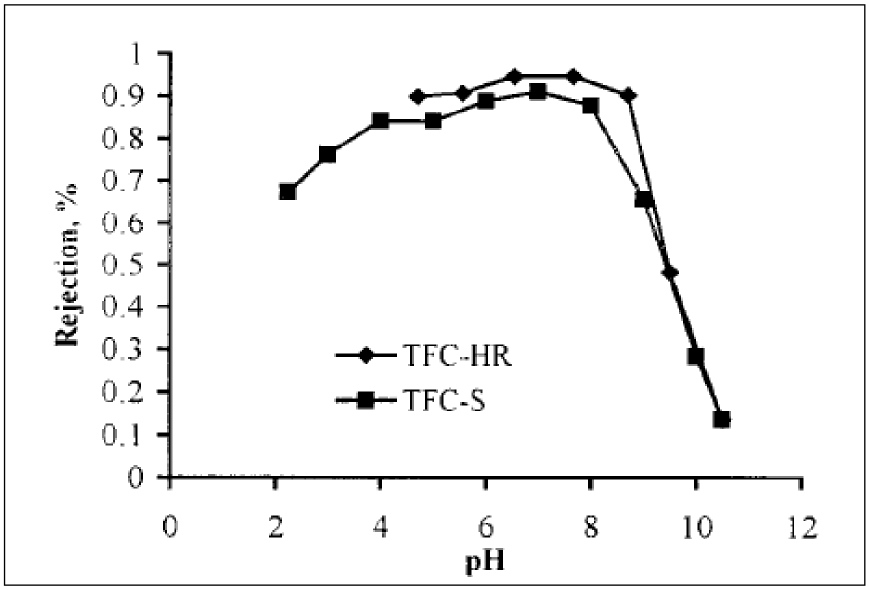


Figure 2.3 – Effect of pH on Ammonia Ion Rejection (Koyuncu 2002)

2.3.6. NOM Rejection Studies

NF membranes have been shown to provide significant NOM rejection indicated by high TOC and ultraviolet light (UV_{254}) rejections. The characteristics of the NOM can be quantified by measuring the specific ultraviolet light absorbance (SUVA) of the water. Equation 2.12 relates UV_{254} to dissolved organic carbon (DOC) to provide the SUVA value.

$$SUVA = \frac{100 \bullet UV_{254}}{DOC} \qquad \textbf{(2.12)}$$

in which: SUVA = Specific ultraviolet-light absorbance (L/mg-m)
UV_{254} = Ultraviolet-light absorbance at 254 nm (1/cm)
DOC = Dissolved organic carbon (mg/L)

For a low turbidity groundwater, the TOC can be assumed equal to the DOC (Allgeier et al. 2005). Higher SUVA values indicate a larger fraction of hydrophobic organic material. Typically found as unsaturated hydrocarbons, the hydrophobic material is considered difficult to remove through conventional treatment (Crittenden et al. 2005).

Recent studies on NF membranes are shown in Table 2.2. Bellona et al. (2008) studied the use of seven NF and four RO membranes on reclaimed wastewater and found all eleven membranes could provide greater than 92% rejection of TOC. The remaining studies shown on Table 2.2 correlated the removal of TOC with DBP reduction. The DBP reduction is denoted as percent removal of trihalomethane formation potential (THMFP) and these results can be directly correlated to the TOC removals. High TOC removals correspond with high DBP removals, reinforcing the fact that NOM is a DBP precursor (Falls 2002).

Although dissolved material rejection by NF membranes is typically governed by diffusion, the larger dissolved molecular compounds may also be rejected simply through sieving. One method to determine which principle governs is to increase the system pressure and recovery and monitor organic rejection. If the percent rejection does not change then sieving is the dominant mechanism (AWWA 1999). Other methods for predicting organic material rejection have been developed through NF studies that focused on specific rejection mechanisms (Verliefde et al. 2008, Braeken et al. 2006, Van der Bruggen et al. 1999, Visvanthan et al. 1998). The research found organic removal is controlled by the combination of size exclusion, electrostatic repulsion, and hydrophobic interactions with the membrane.

Table 2.2. NOM Rejection Using NF Membranes based on work reported by Bellona et al. (2008) and Mody (2004)

Membrane Manufacturer	Membrane Trade Name	Water Source	Pretreatment	TOC			THMFP		
				Feed mg/L	Permeate mg/L	Percent Removal	Feed µg/L	Permeate µg/L	Percent Removal
Koch	TFC-HR	West Basin Water Recycling Plant, CA	Microfiltration pH adjustment, antiscalant, and chloramination			98.6			
	TFC-ULP					97.7			
	TFC-S					94.3			
Hydranautics	ESPA2					98.6			
	ESNA1-LF					92.5			
Filmtec	XLE					98.9			
	NF90					97.1			
	NF200					92.4			
	NF4040					93.5			
	NF270					93.5			
Toray	TMG10					96.7			
Osmonics	DS-5-DK	Lake Manatee, FL	Conventionally treated surface water with enhanced coagulation	4.7	0.4 - 0.9	81 - 91	325	39	88
	DS-5-DL			4.7	0.2 - 0.3	95 - 96	325	17	95
Filmtec	NF90			4	0.1 - 0.3	95 - 98	154	17	89
	NF200			4	0.1 - 0.3	95 - 98	154	15	90
	NF270			3.8	0.1 - 0.3	94 - 96	154	17	88
Hydranautics	ESNA			3.8	0.4 - 0.9	77 - 90	154	56	64
Koch	TFC-S			3.7	0.2 - 0.5	86 - 94	154	33	79
Trisep	XN40			3.7	0.7 - 0.9	76 - 82	154	88	43
	TS80			3.4	0.1 - 0.2	95 - 96	154	7	95
Filmtec	NF200B	Ohio River, KY	Conventionally treated surface water			66.5			15
	NF200					27			30
Hydranautics	LFC1					93			72
Koch	TFC-S					58			7
Filmtec	NF45	Biscayne Aquifer, FL	Conventionally treated surface water and cartridge filter	12.1	1.1	93	342	38	89
	NF200B	Lake Meade, VA		3.3	0.3	91	75	10	87
Hydranautics	NTR7450	Caloosahatchee River, FL		7.1	2.1	71	252	80	68
Koch	TFC-S	Rio Grande River, TX		2.9	0.18	94	214	18	93
Hydranautics	LFC1	Hillisborough River, FL	Microfiltration	2.0 - 16	<0.5		46 - 1062	3.3 - 6	
Koch	CALP			3.0 - 15	0.5 - 0.8		124 - 1037	34 - 60	
Filmtec	NF50	Village of Golf, FL				93			98
	NF50	Acme District, FL				90			97

Steric size exclusion refers to the basic sieving mechanism, which rejects particles larger than the pores of the NF membrane (Bellona et al. 2008). Although the molecular weight is most commonly used to describe a compound's size, Van der Bruggen et al. (1999) correlated other size factors to rejection. The Stokes diameter, equivalent molar diameter, and diameter from energy minimization calculations were determined to provide a more accurate prediction than just the molecular weight alone. Although each diameter calculation is slightly different, they all provide a good rejection model based on the compound's geometry.

As mentioned during the ammonia rejection section, the membrane surface can possess a charge. The charge on a membrane depends on its polymeric construction and pH (Braeken et al. 2006). Many membranes on the market have a neutral to negative charge when used for neutral pH feed water. As seen in Figure 2.4 the Hydranautics HydraCoRe membrane has a strong negative charge. Contrary to the positively charged ammonia ions, the negatively charged NOM compounds are repelled by a negatively charged membrane (Bartels et al. 2002). Following Coulomb's law the negatively charged membranes will also attract positive cations, which reduces the TDS level in the reject stream. The process of permeating primarily positive ions creates a charge differential across the membrane. The extreme charge differential forces some negative ions to permeate in an effort to maintain electroneutrality; this process is also known as the Donnan effect. The Donnan effect reduces NOM rejection for negatively charged membranes (Visvanathan et al. 1998).

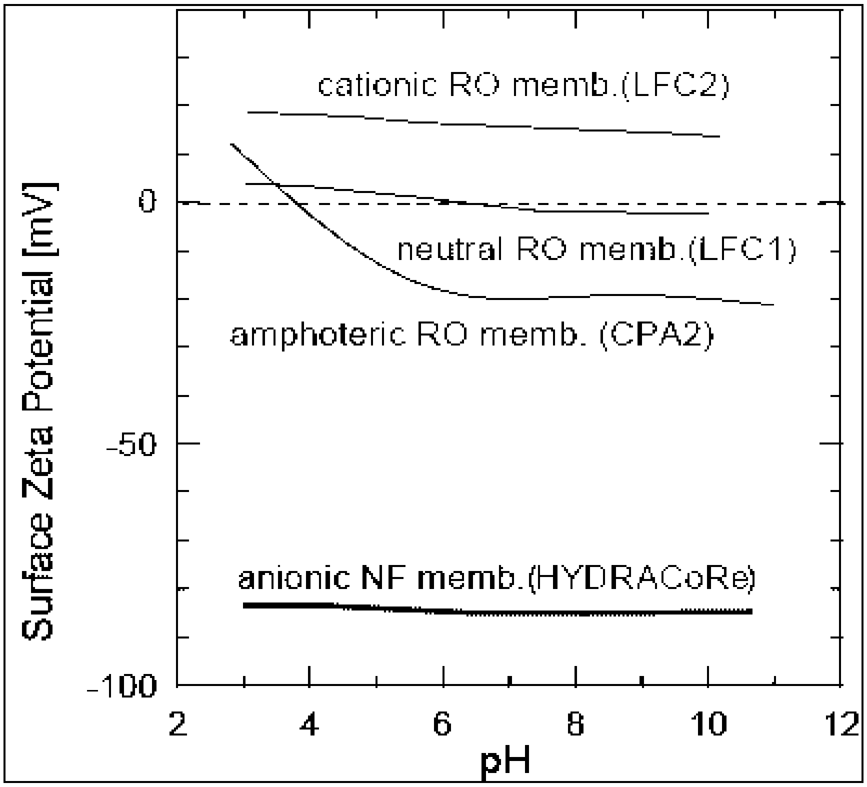


Figure 2.4 – Membrane Electrostatic Charge Comparison (Bartels et al. 2002)

Visvanathan and et al. (1998) tested the effects of metal salts on organic rejections. Using a negatively charged membrane, they found that increasing either magnesium or calcium ions caused a decrease in UV_{254} rejection. The researchers attributed this to the Donnan effect and to coiling of the NOM humic acid chains. Humic acid chains may complex with metal ions and coil causing a reduction in their overall negative charge. The coiling process tightens the organic molecule and squeezes out water; converting the NOM from hydrophilic (water attracting) to hydrophobic (water repelling). This process reduces NOM rejection as more humic acids are allowed to pass through the membrane.

As discussed in previous sections, the NOM in water can be either hydrophilic or hydrophobic. If treated with conventional softening prior to membranes, the hydrophobic portion is removed in the softening process, thus leaving the hydrophilic portion to be treated by NF (Hwang et al. 2002). A contact angle measurement using Milli-Q water determines the hydrophobicity. A contact angle between 0° and 90° is classified as hydrophilic (Braeken et al. 2006). A selection of six membranes studied by Hobbs et al. (2006) exhibited contact angles ranging from 51.7° – 55.3°. The compound's hydrophobicity can be determined by the n-octanol water partition coefficient (K_{ow}) (Uyak et al. 2008). The literature did not show a significant correlation between contact angle and NOM rejection, however it was noted by Braeken et al. (2006) that hydrophobic compounds adsorb strongly to the membrane surface.

2.4. Fouling Potential and Protection

Fouling is a term that defines loss of membrane performance due to the accumulation of suspended or dissolved material on the surface or within the matrix of the membrane (Crittenden et al. 2005). Fouling can be temporary or permanent and develop quickly or over several years. The accumulation of foulants reduces the active area of the membrane surface causing flux to decrease (Qasim et al. 2000). The most common foulants can be categorized as silt and colloidal deposition, microbial growth, inorganic salt scaling, and organic carbon accumulation (AWWA 1999).

Silt and colloidal fouling is caused by particles that become trapped in a membrane's feed spacer (AWWA 1999). To ensure proper membrane performance, the manufacturers stipulate a maximum silt density index (SDI) of 5.0. The SDI value corresponds to the amount of particulate matter in water. Typical ground water SDI values are below 3.0, while surface waters may exceed 5 without proper pretreatment (Dow 2008). A 5.0 micron fiber prefilter is typically installed to safeguard against unwanted particulate matter (AWWA 1999).

Microbial growth occurs in systems with high levels of organisms in their source water; however the majority of accumulation develops during improperly controlled system shutdowns. The microbial organisms secrete biofilms that cling to the polyamide membrane surface causing irreversible fouling. The addition of chlorine will kill any organisms that may pose a microbial fouling threat. However, many membranes are chlorine intolerant, so sodium bisulfate (SBS) must be used to reduce any remaining chlorine and also as a preservative (AWWA 1999).

Inorganic salt scaling occurs when the limiting salt becomes supersaturated. If system conditions are severe, many compounds may become supersaturated. The degree of saturation is measured by the Langlier Saturation Index (LSI). A LSI value below zero is under-saturated, while positive values indicate supersaturation. A solution that has reached supersaturation will precipitate crystals (AWWA 1999). The crystals clinging to the surface of the membrane block water flow. Common crystalline scales that need to be monitored are calcium carbonate, calcium sulfate, calcium fluoride, barium sulfate, and strontium sulfate. Calcium scales are a major foulant as it is found in most source water (Ghafour 2002). Certain scaling compounds like strontium sulfate, pictured in Figure 2.5, will form permanent deposits inside the membrane pores.

Figure 2.5 – Strontium Sulfate Inorganic Scale (Malki 2008)

Applying proper pretreatment techniques can prevent substantial scale from fouling the membrane. Acid has been used effectively to lower the pH of the water, thus converting carbonate alkalinity into bicarbonate or carbonic acid. This procedure ensures very few carbonate ions are available to form precipitates of carbonate hardness (AWWA 1999). Acid pretreatment is not able to control the precipitation of non-carbonate hardness compounds. In fact, if sulfuric acid is used, the levels of sulfate ions will actually increase leading to other precipitates. To inhibit many types of scaling an antiscalant chemical can be dosed alone or in conjunction with acid (Malki 2008). The proprietary polymeric antiscalants have been shown to provide scaling protection for solutions that far exceed saturation. This advantage allows a membrane system to operate at higher recoveries, while the antiscalant minimizes scale formation (AWWA 1999).

Organic carbon can contribute to membrane fouling, either by adsorption of the dissolved fraction onto the membrane material or obstruction by the particulate fraction (AWWA 1999). As large particles of NOM are sieved from the water, an organic mesh tends to accumulate on the membrane surface. Increasing flux rates correspondingly increases the buildup of NOM fouling. Figure 2.6 illustrates the need for a cross flow velocity to flush away the accumulating particles (Thorsen and Flogstad 2006). Thus, lower fluxes may be necessary for membrane filtration treating water with significant organic carbon content. The tendency for a membrane to be affected by NOM is partially influenced by the nature of the organic matter in the water. Studies suggest that the

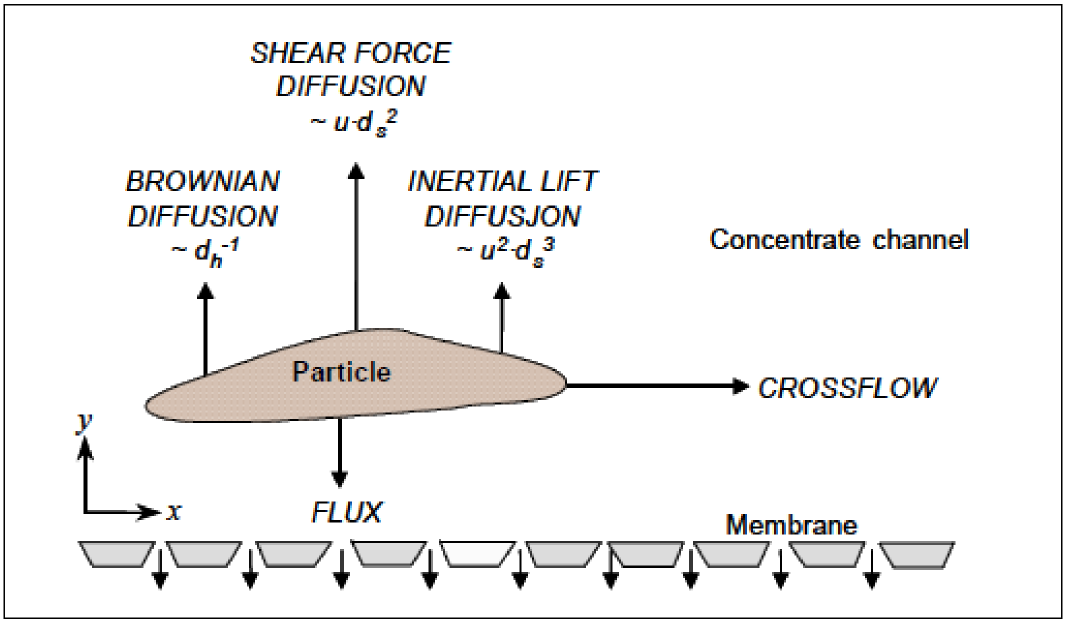


Figure 2.6 – Forces on Feed Water Particles (Thorsen and Flogstad 2006)

hydrophobic fraction of NOM contributes more significantly to membrane fouling (Allgeier et al. 2005). The literature shows that significant fouling of a NF membrane can diminish any presumed benefits of lower operating pressures as compared to a RO system (Bellona et al. 2008). Hobbs et al. (2006) studied surface roughness characteristics of various membranes and found increasing surface roughness correlates to higher initial membrane fouling. Based on the magnitude and frequency of surface irregularities the researchers determined that smooth membranes experience a lower flux decline.

The occurrence of significant flux decline varies with water quality and membrane characteristics. The majority of initial flux decline can be established by 100 hours of testing, however continual foulant buildup will cause further flux decline (Liikanen et al. 2003). Although extensive fouling can lead to lower flux rates, a 336 hour study never experienced significant fouling when the 3.93-4.70 mg/L TOC feed water was applied (Tan and Sudak 1992).

To restore the membrane's capacity, the elements are cleaned with a strong acid to dissolve scale buildup and a strong base to remove organic material. The temperature and cross flow velocity are increased to optimize the cleaning procedure (AWWA 1999). The system is typically cleaned when the flux has declined 15 – 20%. Prior to cleaning the membrane elements in the last vessel should be inspected to determine the dominant cause of fouling. Preventative measures can then be taken to help extend the time between cleaning. Fu et al. (1994) monitored flux decline, which resulted in membrane cleanings on 50 to 60 day intervals for feed water that contained approximately 10.6 mg/L TOC.

2.5. Pilot Testing

Pilot scale testing can be used to facilitate the selection of a NF membrane or a group of membranes that will be used for the design of a treatment facility. Membranes can be selected for pilot study based on the manufacturer's water quality models. A pilot skid is compact treatment unit that only treats a fraction of the full scale design. The information gathered from pilot testing can be used for more precise design calculations. Typical pilot studies are performed as bench, single element, or arrayed multiple element pilot tests (Allgeier et al. 2005).

If the feed water supply is limited a bench scale pilot test may be performed as it requires a lesser amount of water. The bench scale test uses a 26 square inch flat section of membrane to treat water. While the test is small, reasonable results can be obtained for operating pressure, flux, and fouling. Since the feed water flow rate is limited, the results may also be easily skewed if varying water quality is an issue. Additionally, it can be difficult to simulate the full scale system recovery using a bench scale test (DiGiano et al. 2000). Through the use of proper concentrate recycle flows the system can achieve very high recovery levels (80 – 90%). This flexibility allows the unit to simulate different portions of the full scale system without demanding large amounts of water or electricity (Allgeier and Summers 1995).

A simple yet more accurate representation of full scale systems can be accomplished using a single element pilot test (Bellona et al. 2008). The test uses one four-inch element, 40 inches long to treat water. The membrane industry terms the 4” diameter and 40” long elements as 4040 elements. The use of an actual membrane element provides an accurate representation for the cross-flow velocity and turbulence encountered inside a full scale system. Also, proper pretreatment chemicals can be applied to ensure few variables are left unknown (Dow 2008).

The larger, multi-element, arrayed pilot tests are used to verify system performance and gather system data that can facilitate design of the full scale system. The costs associated with a larger pilot are dependent upon the number of membrane elements used, the feed water required, and the operator demand (Blau et al. 1992). The use of a larger pilot can verify performance of a smaller pilot test, or simulate situations not achievable in other tests (Bellona et al. 2008).

The variations between membrane construction and performance can be quickly compared with the use of a pilot-scale test. The performance of NF membranes for control of DBP precursors cannot be predicted from manufacturer’s information alone. The use of pilot scale tests can provide a means for further membrane selection (Mody 2004). The degree of pilot testing is a function of available funding, however the results may help offset the costs for testing by reducing conservative design values. The previous literature of established membranes may be used for performance predictions, however new untested membranes will typically require a pilot test (Allgeier et al. 2005).

CHAPTER THREE – METHODS AND MATERIALS

3.1. Introduction

Phase I of this project employed a single element pilot system to select NF membranes that rejected DBP precursors and discharged a concentrate stream of under 1000 mg/L TDS. Phase II of the pilot study employed a 21 element pilot plant to examine the success of TOC removal and determine optimum system settings required for full scale design. During Phase I, the flux rate was constant enabling fair comparison of the different NF membranes. During Phase II, the flux rate was variable, while recovery was held constant. In addition to system parameters, the feed water quality fluctuated systematically and caused variable conditions for alkalinity, ammonia, conductivity, DBP, hardness, pH, TOC, and UV_{254}. Experiments were conducted at the Watertown Town Water Treatment Plant from June 2008 to March 2009. The Phase I and II pilot plant configurations and analytical procedures are described in the following sections.

3.2. Feed Water Source

Figure 3.1 illustrates the current 6 MGD WTP unit operations and processes. The feed water for all pilot testing was pumped directly from the existing WTP gravity media filter effluent prior to chlorination. Due to several system variables prior to the filter effluent, the feed water quality varied. Water quality variations were also caused by variations in quality between the ground water wells. The WTP uses wells within city limits constantly, and draws supplemental water from the Conifer wells during high

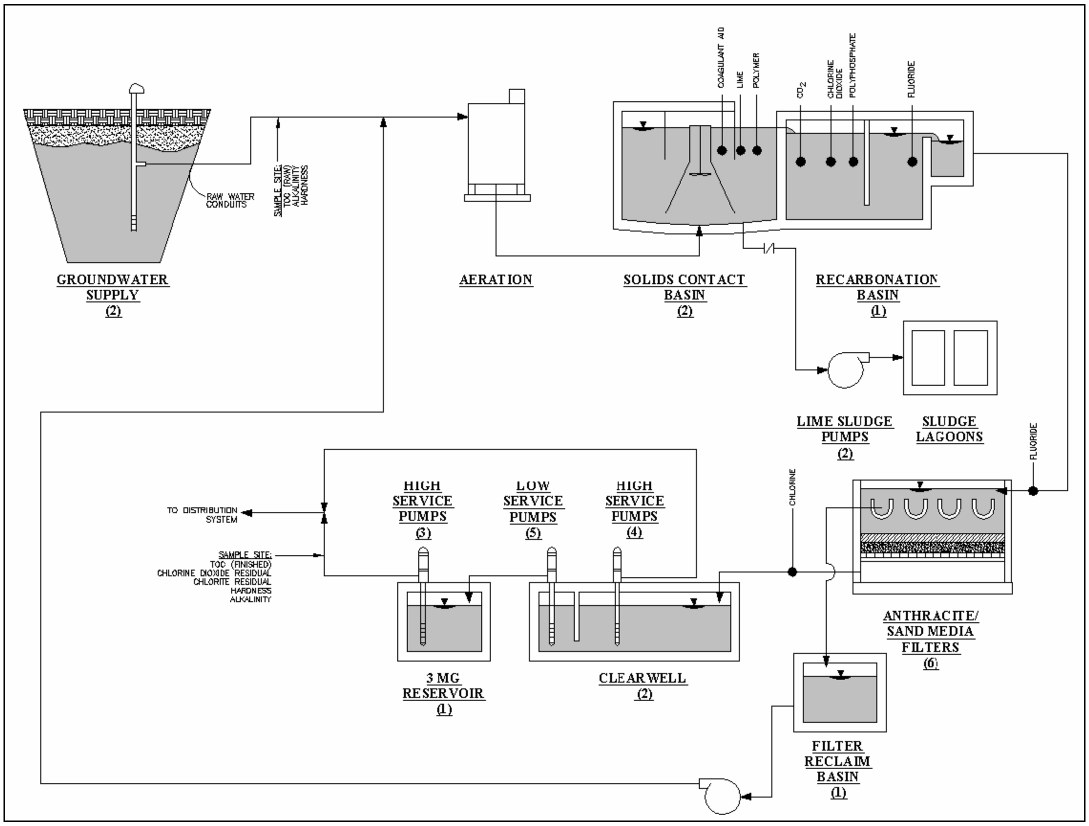


Figure 3.1 – Watertown Water Treatment Plant (Bergantine 2007)

demand. The Conifer well field is located in a wildlife refuge northwest of Watertown near the Big Sioux River. The Conifer wells have very high NOM content with naturally occurring free ammonia. A future WTP expansion will use water from the Rauville well field north of Watertown in addition to the Conifer well water source.

The water treatment processes employed at the WTP are typical of a lime softening system (see Figure 3.1). After being pumped from shallow wells, the water is aerated, and then fed to a solids contact basin. The water is dosed with lime, coagulant aid, and polymer. The pH in the solids contact basin is maintained in the range of 10.5 to 11.0 to enhance the softening process and optimize TOC removal. The pH is lowered in the recarbonation basin with carbon dioxide. Chlorine dioxide is added to oxidize NOM and polyphosphate is dosed to prevent filter encrustation. Fluoride is added before the water passes through the dual media (anthracite and sand) filters. After filtration, the water is breakpoint chlorinated to create a free chlorine residual in the distribution system. Filter backwash water is supplied from the clear well. When chlorinated backwash water mixes with naturally occurring ammonia, chloramines are created and are detectable in the filter effluent.

The softened water quality is shown in Table 3.1. The 2006 average TOC was 2.8 mg/L, however, higher values are commonly experienced during the summer when the Conifer wells are used extensively.

3.3. Preliminary Water Quality Testing

Prior to acquiring the membranes for this study, a water quality analysis was performed to understand how the NF membranes might perform. Additionally, each well’s quality was tested to understand the variability between sources. An SDI test was performed on the filter effluent, as well as the raw WTP influent and at the well fields. The TOC, UV_{254}, and free ammonia were measured at each well, and also at the WTP influent and filter effluent. Methods for these analyses are presented in Section 3.7

Table 3.1. Softened Water Quality for Watertown Treatment Plant (Chmielewski 2008)

Parameter	Units	Concentration[1]	Concentration[2]
Calcium	mg/L	39.5	56.2
Magnesium	mg/L	27.9	15.7
Sodium	mg/L	20.2	16.6
Potassium	mg/L	4.7	4.0
Carbonate	mg/L	0	6
Bicarbonate	mg/L	41	27
Sulfate	mg/L	186	179
Chloride	mg/L	1.14	22
Nitrate	mg/L	0.1	0.3
Fluoride	mg/L	1.14	1.2
Iron	mg/L	<0.03	<0.03
Manganese	mg/L	<0.02	0.02
Total Dissolved Solids	mg/L	359	336
Total Hardness	mg/L as $CaCO_3$	213	205
Total Alkalinity	mg/L as $CaCO_3$	34	32
pH	-	7.92	9.05
Temperature	°C	14	N/A
Parameter	**Units**	**Concentration[3]**	
Silica	mg/L	17.5	
Aluminum	mg/L	Not Detected	
Boron	mg/L	Not Detected	
Bromide	mg/L	Not Detected	
TOC	mg/L	2.8	

Notes:

1) Based on a Public Health laboratory report dated 6/29/2004.
2) Based on a Public Health laboratory report dated 4/17/2007.
3) Based on 2006 average

3.4. Phase I of Pilot Testing

The Phase I NF membrane screening pilot test skid contained a 4” diameter single element pressure vessel with adjustable pressure and concentrate recycle. The unit was rented from the Layne-Christensen Company and operated inside the WTP building. The single element unit was equipped with a 5.0 micron 10” long prefilter, a high pressure feed pump, and a single 4” diameter and 40” long pressure vessel. Also provided were all the appropriate pressure and flow meters to monitor system settings. Sample taps were provided to obtain easy access to feed, concentrate, and permeate water samples. All water was sent to drain, both reject and permeate. The single element skid is pictured in Figure 3.2.

The high pressure feed pump, Grundfos model CRN 3-19, was capable of 15 gpm and 426 ft of head. A variable frequency drive motor was used to accurately adjust the feed water pressure. Two chemical feed systems were supplied with the single element

Figure 3.2 – Phase I Single Element Pilot Plant

pilot skid. Antiscalant and sodium bisulfite (SBS) were dosed at 2 mg/L and 6 mg/L, respectively. The antiscalant used for all experiments was A-102 Plus from American Water Chemicals, Inc. The neat antiscalant chemical was diluted 1 part antiscalant to 350 parts distilled water to facilitate uniform dosages using reasonable pumping rates. The SBS used for all experiments was 38% pure, supplied from Hawkins, Inc. For the single element pilot test the SBS was diluted 1 part SBS to 100 parts distilled water to facilitate uniform dosages using pumping rates in the operating range of the supplied chemical feed pumps. 15 gallon plastic chemical tanks were used to store the diluted chemicals. The supplied diaphragm chemical feed pumps were Liquid Metronics Incorporated model P121-352SI with a maximum output of 0.20 gph. The chemical pumps were calibrated several times throughout the testing to ensure accurate dosages of each chemical.

Each of the six NF membranes listed in Table 3.2 were tested at 12 gfd. After installing each trial membrane the feed water was applied slowly to remove air voids. Next, the applied feed water pressure was increased gradually to achieve the desired permeate flow for a 12 gfd flux rate. Initially, the concentrate valve was fully open, while the recycle valve was closed. The recycle valve remained closed during the first two hours of operation to cleanse the membrane of preservatives and establish equilibrium. To simulate the lead elements of a full scale system, the applied pressure was increased until 15% recovery was obtained. If needed, the concentrate valve was closed to induce resistance in order to achieve the desired flows on Table 3.3. To simulate the average element in a full scale system, the system was operated at 50% recovery with high recycle flow and low concentrate flows. The variable frequency drive

Table 3.2. Summary of Tested NF Membranes

General Specifications		Manufacturer Specifications					Project Specifications	
Membrane	Manufacturer	Salt Rejection %	pH Range	Pure Water Flow gpd	Element Area ft^2	Material	Element Used at:	Sample Label
TFC - SR 2	Koch Membrane Systems, Wilmington, MA	10-30 NaCl** 95 $MgSO_4$*	4 - 9	3100	85	Proprietary	Single Element Pilot	K2
TFC - SR 3	Koch Membrane Systems, Wilmington, MA	99.4 $MgSO_4$*	4 - 10	1500	85	Proprietary polyamide	Single Element Pilot, 2:2:1:1 Vessel Pilot	K3
XN45-TSF	Trisep, Goleta, CA	95 $MgSO_4$****	2 - 11	2000	85	Polyamide	Single Element Pilot, 2:2:1:1 Vessel Pilot	T
ESNA1 - LF	Hydranautics, Oceanside, CA	90 NaCl***	3 - 10	2100	85	Composite Polyamide	Single Element Pilot, 2:2:1:1 Vessel Pilot	HE
HydraCoRe 70pHT	Hydranautics, Oceanside, CA	70 NaCl***	1 - 13.5	N/A	70	Sulfonated Polyethersulfone	Single Element Pilot	HH
NF270	Dow/Filmtec, The Dow Chemical Co., Midland, MI	97 $MgSO_4$****	2 - 11	2500	82	Polyamide	Single Element Pilot	DF

MgSO4 - magnesium sulfate, NaCl - sodium chloride, NF – nanofiltration
Test Conditions: *5000 mg/l MgSO4, **2000 mg/l NaCl, ***500 mg/l NaCl, ****2000 mg/L MgSO4

Table 3.3. Desired Flows for Phase I Pilot Testing

Membrane	Membrane Area ft^2	Recovery Rate %	Feed Flow gpm	Permeate Flow gpm	Recycle Flow gpm	Reject Flow gpm	Recycle + Reject Flow gpm
Koch TFC-SR2	85	15	4.72	0.71	0.00	4.01	4.01
		50	1.42	0.71	2.29	0.71	3.00
		80	0.89	0.71	2.82	0.18	3.00
Koch TFC-SR3	85	15	4.72	0.71	0.00	4.01	4.01
		50	1.42	0.71	2.29	0.71	3.00
		80	0.89	0.71	2.82	0.18	3.00
Trisep XN45-TSF	85	15	4.72	0.71	0.00	4.01	4.01
		50	1.42	0.71	2.29	0.71	3.00
		80	0.89	0.71	2.82	0.18	3.00
Hydranautics ESNA1-LF	85	15	4.72	0.71	0.00	4.01	4.01
		50	1.42	0.71	2.29	0.71	3.00
		80	0.89	0.71	2.82	0.18	3.00
Hydranautics HydraCoRe 70pHT	70	15	3.89	0.58	0.00	3.31	3.31
		50	1.17	0.58	2.42	0.58	3.00
		80	0.73	0.58	2.85	0.15	3.00
DOW Filmtec NF270	82	15	4.56	0.68	0.00	3.87	3.87
		50	1.37	0.68	2.32	0.68	3.00
		80	0.85	0.68	2.83	0.17	3.00

was used to seamlessly adjust feed water pressure in order to obtain the calculated flows. To simulate the end elements of a full scale system, the applied pressure was increased until 80% recovery was obtained. To match the desired flows, the concentrate valve was typically adjusted to allow less concentrate flow, thus increasing the recovery.

The membranes in Table 3.2 selected for testing were suggested by the manufacturers to have excellent TOC rejection, yet allow moderate concentrations of divalent ions to permeate. Based on the manufacturer's specifications of salt rejection and pure water flow, the TFC-SR3 and XN45-TSF were predicted to have water quality closer to RO permeate than the other four membranes. Table 3.2 also contains each element's respective sample identification, which was used as the labels for figures in Chapter 4.

It is important to note the element surface area varies among the tested membranes, which requires different flow rates to maintain the same flux, as seen in Table 3.3. The tested flux for Phase I was held constant at 12 gfd. This flux setting resulted in permeate flows ranging from 0.58 – 0.71 gpm. When operated at greater than 15% recovery, the recycle flow was increased to obtain a 3.0 gpm cross flow velocity. A 3.0 gpm cross flow velocity ensured approximately a 5:1 ratio of concentrate water flow to permeate flow was maintained. During system operation, parameters of pressure, temperature, and flow were recorded.

After removing an element from the testing apparatus, the element was soaked in a 1% SBS solution to prevent microbial growth during storage. The elements were immersed in the preservative for 48 hours, removed and allowed to drip dry, then immediately placed into plastic bags and sealed tightly.

After Phase I results were analyzed the membranes that could provide adequate DBP reduction and concentrate TDS concentrations of under 1000 mg/L would be selected for further comparison during Phase II. If multiple membranes met the DBP reduction and concentrate TDS criteria, other performance criteria like specific flux and permeate alkalinity could be used to screen the membranes. Three membranes were selected to compare further during the Phase II testing.

3.5. Phase II of Pilot Testing

The Phase II pilot testing procedure was performed using a 2:2:1:1 array of 4-inch diameter 40-inch long spiral wound elements selected from the results of Phase I. As illustrated in Figure 3.3, the 2:2:1:1 vessels each contained 3, 4, 3, 4 elements, respectively. This pilot scale unit simulates the hydrodynamic conditions of a two-stage full-scale treatment process with seven 8-inch diameter elements per vessel. The unit, shown in Figure 3.4, was rented from the Koch Membrane Systems Company. The use of stages eliminated the need for a concentrate recycle flow. The pilot unit was capable of adjustable inlet pressure and concentrate flow. The multi element unit was equipped with dual 5.0 micron prefilters, a high pressure feed pump, four first-stage pressure vessels, a high pressure interstage booster pump, and two second-stage pressure vessels. Also

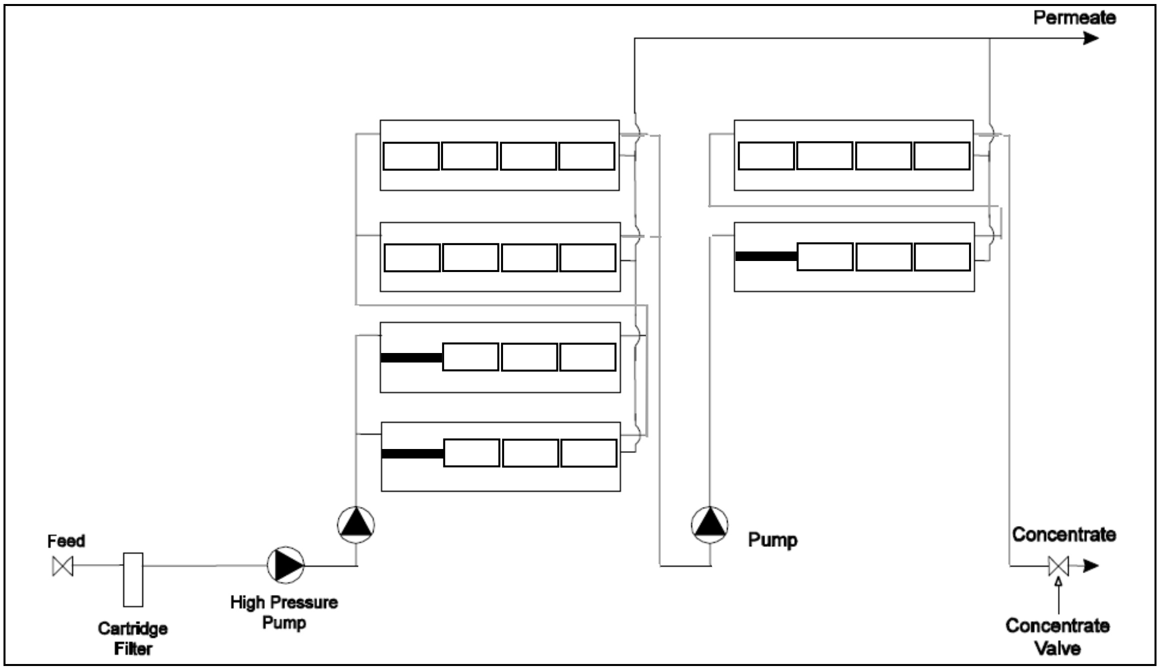


Figure 3.3 – Two Stage NF Pilot System with Interstage Pump

Figure 3.4 – Phase II Pilot Plant

provided were all the appropriate pressure and flow meters. Conductivity and pH electrodes continuously monitored system water quality. The unit was equipped with a data logging and control system to monitor and log flux, pressure, and water quality parameters; pH, temperature, and conductivity.

The high pressure feed pump, Grundfos model CRN5-22, was capable of 30.4 gpm and 533 ft of head. A constant speed, 7.5 horsepower Baldor motor was used to drive the feed water pump. The interstage booster pump, Grundfos model CRN3-11, was capable of 15.9 gpm and 246 ft of head. A constant speed 2.0 horsepower Baldor motor was used to drive the booster pump.

Chemical feed systems were supplied with the multi-element pilot skid. Antiscalant and SBS were dosed at 2 mg/L and 6 mg/L, respectively, similar to the single element pilot testing. The antiscalant used for all experiments was A-102 Plus from American Water Chemicals, Inc. The neat antiscalant chemical was diluted 1 part antiscalant to 75 parts distilled water to facilitate uniform dosages using reasonable pumping rates. The SBS used for all experiments was 38% pure, supplied from Hawkins, Inc. SBS was diluted 1 part SBS to 25 parts distilled water to facilitate uniform dosages using reasonable pumping rates. 100 liter plastic chemical tanks were used to store the diluted chemicals. Acid dosing for pH control was also available. Acid was fed from a 55 gallon drum of 15% hydrochloric acid at variable rates to achieve a target pH of 8.5 – 9.0. The supplied diaphragm chemical feed pumps were Liquid Metronics Incorporated model P131-398SI with a maximum output of 0.42 gph. The chemical pumps were calibrated several times throughout the testing to ensure accurate dosages of each chemical.

Three of the six membranes listed in Table 3.2 were selected for Phase II testing. The membranes were Koch Membrane Systems TFC-SR3, Trisep XN45-TSF, and Hydranautics ESNA1-LF. Twenty one elements for each of these membranes were installed in the pilot plant.

The objective of Phase II was to determine the best performing membrane and its corresponding optimum flux rate. To test this, the pilot system was set at 85% recovery and allowed to stabilize for one week at each flux rate of 9, 12, and 15 gfd. The optimum flux setting would be determined by a combination of specific flux, permeate quality, and reject quality. The selection of the design flux rate must not be overlooked. As detailed in the literature review, extremely high fluxes can accumulate organic fouling on the membrane surface. During each flux setting, the pilot plant's computer logged water quality data.

After installing each set of membranes the feed water was applied slowly to remove air voids. Next, the applied feed water pressure was increased gradually by opening the inlet needle valve. Table 3.4 shows the desired flows used to balance the system flows to achieve the desired permeate fluxes of 9, 12, or 15 gfd. To achieve equal flux rates for the first and second stage, a booster pump was utilized to replenish pressure lost during the first stage. A needle valve on the discharge side of the booster pump was adjusted to control the boost pressure. Initially, the concentrate valve was fully open to remove any preservative chemicals. After two hours of flushing, the concentrate valve was partially closed to increase the percent recovery to 85%. Each flow was dependent on every valve position, such that several fine adjustments were necessary to reach the desired flows.

The status of the pilot plant was checked every four hours at which the pH and flows would be verified and adjusted to maintain the desired set points. The system

Table 3.4. Desired Flows for Phase II Pilot Testing

Flux	**Membrane Area**	**Recovery**	**Feed Flow**	**Permeate Flow**	**Reject Flow**
gfd	ft^2	%	gpm	gpm	gpm
9	1785	85	13.2	11.2	2.0
12	1785	85	17.5	14.9	2.6
15	1785	85	21.9	18.6	3.3

pressures and flows were recorded daily to monitor any changes. Weekly samples were obtained and analyzed for water quality. Conductivity tests were performed twice per week on each pressure vessel permeate to ensure proper performance of seals. Unusually high levels of conductivity indicated a malfunctioning seal that needed to be fixed before any useful data could be obtained.

After acquiring the data from flux testing, the Hydranautics ESNA1-LF membrane was chosen to perform a fouling study. Using the same startup procedure as flux testing, the fouling study loaded the membrane at the highest flux, 15 gfd, for 30 days. During this process, the hydraulics and water quality parameters were monitored for flux decline. The flux decline was also monitored hydraulically for Trisep XN45-TFS to compare with the Hydranautics ESNA1-LF results. System conditions were checked and recorded similar to the flux testing. The amount of flux decline during one month would be an indicator for the cleaning needs required at full scale.

3.6. Sampling

Pilot plant samples were obtained directly from each unit's built-in sample ports. Filter effluent feed water, recycle water, concentrate water, and permeate water were each collected in 500 mL amber glass bottles. In order to ensure that fresh samples were obtained from each sample port, three volumes of sample water were used to rinse the sample container prior to collection. The samples were taken to the on-site lab for analysis or preparation for analysis at an off-site laboratory. Blended water was created using a graduated cylinder to measure the appropriate amounts of both filter effluent and NF permeate water.

Phase I pilot plant samples were analyzed for conductivity, pH, UV_{254}, total hardness, alkalinity, and ammonia on-site. TDS, TOC, SDS-THM, and SDS-HAA were prepared on-site and sent to an off-site laboratory for complex analysis. These parameters were analyzed for each membrane at each recovery setting on the feed water, permeate and blended permeate. Samples were only analyzed for THM and HAA at the 15 and 50 percent recovery settings to conserve financial resources.

Phase II pilot plant samples were analyzed for conductivity, pH, UV_{254}, total and calcium hardness, alkalinity, and ammonia on-site. TDS, TOC, SDS-THM, and SDS-HAA were prepared and preserved on-site and sent to an off-site laboratory for these analysis according to the schedule in Table 3.5. Weekly tests were performed on feed, permeate, and a blend of permeate and feed water. The testing of SDS-THM samples were performed three times per week to cover slight variations in feed water quality.

Table 3.5. Phase II Pilot Plant Sampling Regime

Analysis	**Feed Frequency**	**NF Permeate Frequency**	**44% Permeate: 56% Feed Blend Frequency**
SDS-THM	Three per week	Three per week	Three per week
SDS-HAA	Weekly	Weekly	Weekly
UV_{254}	Weekly	Weekly	n/a
TOC	Weekly	Weekly	n/a
TDS	Weekly	Weekly	n/a
Hardness	Weekly	Weekly	n/a
Alkalinity	Weekly	Weekly	Weekly
Calcium	Weekly	Weekly	Weekly
pH	Daily	Weekly	Weekly

SDS-HAA samples were only performed weekly due to information obtained during the literature review that indicated a greater threat for THMs than HAAs for this source water.

Samples were collected according to *Standard Methods for the Examination of Water and Wastewater* (1998) and analyzed before the recommended holding time had expired.

3.7. Water Quality Parameter Analytical Procedures

The majority of the analytical procedures for the pilot plant were conducted in accordance with *Standard Methods for the Examination of Water and Wastewater* (1998), with a few exceptions for other methods. The analyses performed by the author included silt density index, ammonia, free and total chlorine, monochloramine, pH, calcium hardness, total hardness, alkalinity, conductivity, total dissolved solids. The author also prepared samples for simulated distribution tests for THM and HAA analysis. Analyses performed by the South Dakota State University Water and Environmental Engineering Research Center (WEERC) personnel included total organic carbon and quality control checks on chlorine and ammonia concentrations. Analysis for THM and HAA concentrations were performed by Energy Labs in Rapid City, South Dakota. The standard methods used during the course of the experiment are summarized in Table 3.6.

Table 3.6. Methods Used for Sample Analysis

PARAMETER	NAME OF METHOD	METHOD
SDI	Standard Test Method for SDI of Water	ASTM D4189-07
Ammonia	Indophenol Method	HACH 10200
Free Chlorine	DPD Colorimetric Method	SM 4500 CI G
Total Chlorine	DPD Colorimetric Method	SM 4501 CI G
Monochloramine	Indophenol Method	HACH 10200
pH	Electrometric Method	SM 4500-H^+ B
Calcium Hardness	EDTA Titrimetric Method	SM 2340 B
Total Hardness	EDTA Titrimetric Method	SM 2340 C
Alkalinity	Titration Method	SM 2320 B
Conductivity	Laboratory Method	SM 2510 B
TDS	Total Dissolved Solids Dried at 180°C	SM 2540 C
TOC	High Temperature Combustion Method	SM 5310 B
UV_{254}	UV Absorbing Organic Constituents	SM 5910 B
SDS-TTHM	Formation of THMs and other DBPs	SM 5710 C
SDS-HAA5	Formation of THMs and other DBPs	SM 5710 C

3.7.1. Silt Density Index

The SDI test was conducted according to procedures described in ASTM D-4189. In this procedure, the water sample pressure is regulated to 30 psig and forced through a 47 mm diameter, 0.45 micron membrane filter. The time to filter 500 ml of water is measured at the start of the test and then re-measured after 15 minutes of continuous flow of water through the filter. The SDI is calculated using the following equation.

$$SDI = \frac{1 - t_i / t_f}{T} 100 \qquad \textbf{(3.1)}$$

in which: SDI = Silt Density Index
t_i = initial time in seconds required to filter 500 ml of sample
t_f = time in seconds required to filter 500 ml of sample after test time T
T = test time in minutes (15 minutes)

The SDI tests were conducted at the Watertown WTP on filter effluent, raw influent, and wells 3, 10, 11-20, and 21-26. Filtered water was supplied from the effluent pipe of the third filter from the west side of the plant (designated Filter 6). The filter had been operating over 3 hours prior to the SDI test on the filter effluent. Water plant personnel provided a pump to pressurize the water from the each source to greater than 30 psig. The pump was connected to each source and water was allowed to flow through the pump for several minutes before beginning the SDI test procedure.

Pressure was regulated to 30 psig throughout the duration of the SDI test using a pressure regulator and attached gage. The pressure was pre-adjusted using a trial membrane setup, so as to be very close to the required pressure when the SDI test began.

The SDI test was first completed on the filtered water and then on the raw water. After a trial setup with a spare membrane to adjust the pressure to 30 psi, a fresh membrane was placed in the filter apparatus and the air eliminated from the test system. The pump motor was engaged and the ball valve opened to allow water to flow through the membrane. As soon as the water flow was stabilized (within approximately 2-3 seconds) the time to filter 500 ml of water was determined with a stopwatch. The time for filtering 500 mL was re-measured at 5, 10 and 15 minutes elapsed time from the start of the test. Water temperature was recorded as well as the filter manufacturer and type.

The filter used for all SDI tests was a Millipore 0.45 µm HAWP (Mixed Cellulose Ester). A glass 500 mL graduated cylinder was used to measure the 500 mL sample.

3.7.2. Ammonia

A portable HACH DR-890 colorimeter and appropriate Monochlor F powder pillows and free ammonia reagent solution were used to quantify the concentration of free ammonia in the water samples. Free ammonia measurements were determined using HACH's patented Indophenol Colorimetric Method 10200.

The colorimetric method's accuracy is limited to a maximum detectable concentration of 0.55 mg/L NH_3-N. To measure higher concentrations, dilutions were prepared with distilled water. The dilution accuracy was checked against an ammonia ion sensitive electrode at the WEERC laboratory.

3.7.3. Disinfectant Residual

A portable HACH DR-890 colorimeter and appropriate DPD powder pillows were utilized to quantify the concentration of both free and total chlorine in the water samples. Chlorine measurements were determined in accordance with *Standard Methods* DPD Colorimetric Method (4500-CI G). Residual combined chlorine was determined by subtracting the free chlorine concentration from the total concentration. Additionally, using the HACH DR-890 monochloramine concentrations were determined using HACH's patented Indophenol Colorimetric Method 10200.

The colorimetric method has interferences with oxidizable material leading to possible inaccuracies. To verify the accuracy of the onsite method, samples were transported to the WEERC laboratory for chlorine analysis on a HACH AutoCAT 9000 using the more accurate amperometric method.

3.7.4. Calcium Hardness

Calcium hardness was analyzed according to Standard Methods 2340-C, Ethylenediaminetetraacetic Acid (EDTA) Method. A buret was used to dispense the titrant (0.020 N EDTA).

The procedure for calcium hardness required a sample volume of 50 mL. The 50 mL of sample was then dispensed into a 100 mL beaker with a stir bar and placed onto a magnetic stirrer. One scoop of HACH CalVer indicator powder was added to the stirring sample, followed by two mL of 8 N NaOH. The sample was then titrated with the buret until the color changed from pink to light blue. The number of milliliters titrated would be multiplied by a factor to achieve a result in mg/L as CaCO3. For example, for the 50 mL sample, the milliliters of titrant were multiplied by twenty.

3.7.5. Total Hardness

Total Hardness was analyzed according to Standard Methods 2340 C., using EDTA. A buret was used to dispense the titrant (0.020 N EDTA).

Similar to the analysis for calcium hardness, the amount of sample needed for total hardness was 50 mL. The sample was measured with a plastic 50 mL graduated cylinder. The sample was then poured into a 100 mL beaker with a stir bar and placed onto a magnetic stirrer. One mL of HACH Hardness 1 Buffer Solution was added to the diluted sample followed by one scoop of ManVer indicator. The sample was then titrated from pink to light blue. The number of digits required to titrate the sample were recorded and multiplied by a conversion factor (20) to obtain the total hardness measured in mg/L as CaCO3.

3.7.6. pH

The pH of the sample was analyzed according to Standard Methods 4500-H+ B., pH value by Electrometric Method. The pH instrument used was a Thermo Electron Corporation Orion portable pH meter, model 290 A+.

The portable pH meter was calibrated at the beginning of the day, using pH standards of 4.0, 7.0 and 10.0. Once the meter was calibrated with the standards, pH measurements could be taken for water samples.

3.7.7. Alkalinity

Total alkalinity was analyzed according to Standard Methods 2320 B., Titration Method. A buret was used to dispense the titrant (0.020 N Sulfuric Acid).

The alkalinity test required 50 mL of sample to complete the analysis. The volume of sample needed was measured with a graduated cylinder to 50 mL. The sample was poured into a 100 mL beaker with a stir bar and placed onto a magnetic stirrer. A pH electrode was placed into the sample to measure the pH during the course of titration. Four to six drops of brom cresol green methyl red indicator was added to the sample. The sample was then titrated with sulfuric acid to a pH of 4.5, which corresponded to a color change from blue to light pink. The volume of titrant was multiplied by 20 to mg/L as calcium carbonate (CaCO3).

3.7.8. Conductivity

Conductivity was analyzed according to Standard Methods 2510 B Laboratory Method. A HACH Sension5 conductivity meter was used to measure the conductivity of the sample.

The conductivity meter was calibrated using 1000 µS/cm standard with automatic temperature correction. The results of each test were corrected to 25 degrees C using the automated temperature compensation within the conductivity meter. With the calibration stored in the conductivity meter, analysis could be completed by placing the electrode in the water sample.

3.7.9. Total Dissolved Solids

Total dissolved solids were performed on samples collected at various locations through the pilot plant. Total dissolved solids were measured on the filter effluent (feed to the pilot plant), concentrate, and permeate water.

To conduct the test, a 180°C preheated evaporating dish was weighed, and the weight was recorded. The sample of water was filtered through a prepared glass-fiber filter disk and 100 mL of the filtered water was introduced to the dish with a pipette. The dish was placed into a 180°C oven for 24 hours. The weight of the dish and dried residue was measured to determine the amount of residue in the dish. The total dissolved solids were calculated by using the following equation:

$$\text{mg TDS / L} = \frac{(A - B) \times 1000}{\text{sample volume, ml}} \qquad \textbf{(3.2)}$$

in which: A = weight of dried residue + dish, mg
B = weight of dish, mg

3.7.10. UV_{254}

The UV_{254} test was performed according to Standard Methods 5910 B, Ultraviolet Absorption Method using a Shimadzu UV1600U Double Beam UV Visible Spectrophotometer. The Shimadzu has locations for both the sample, and the reference or blank. Two 5-ml cuvettes filled with nanopure water were used to zero the instrument. Next, one cuvette was rinsed three times with the sample and filled. Kimwipes were used to remove moisture from the side of the cuvettes prior to analysis. Air bubbles were allowed to float to the surface prior to analysis. UV_{254} samples were recorded to the nearest thousandth in cm^{-1}.

3.7.11. Total Organic Carbon

The TOC test was performed according to Standard Methods 5310 High Temperature Combustion Methods using a Shimadzu TOC-V CSH/CSN total organic carbon analyzer. Samples were collected in a 40 mL glass vial that was acidified with 80 μL of concentrated hydrochloric acid. Once the samples were collected and returned to the WEERC laboratory they were stored in a 4°C refrigerator until analysis.

3.7.12. Simulated Distribution System Trihalomethanes (SDS-THM)

The SDS-THM test measures the potential to form THMs by placing finished water in conditions similar to those encountered in the distribution system. It can also be used to analyze the effectiveness of an alternative disinfectant, such as chloramines. In this case, the SDS-THM tests were used to compare the permeate quality from various membranes as well as to compare chlorination with chloramination. Before collecting SDS-THM samples, the pH, temperature, and free chlorine levels of the sample were measured, according to methods described previously. These parameters provide an estimate of the condition of water entering the distribution system. For the membrane comparison, samples were collected before and after membrane treatment to determine their rejection ability. For the disinfectant comparison, one sample was chloraminated in the lab while the other sample was taken directly from the clearwell.

Water samples for the SDS-THM test were collected and placed into 500 mL amber glass bottles that had been washed with soap and hot water, rinsed three times with RO water, rinsed with 50/50 nitric acid, and rinsed three times with nanopure water. Containers were filled completely and capped such that no air bubbles remained.

The solids contact clarifier was selected as the onsite incubator as it maintained a temperature similar to the distribution system. Samples immersed just under the clarifier water surface remained at 14°C during the 3-day test. After the 3-day incubation period, three 40 ml THM sample vials were immediately collected from each SDS container and stored at 4°C until analysis was performed. The samples were also analyzed for free chlorine, temperature, and pH. Duplicate samples were analyzed for quality assurance and multiple tests were prepared to evaluate the varying feed water quality.

The sample vials were obtained from and tested by a commercial laboratory, which used EPA method 524.2 to analyze the THM concentrations. This method uses purge and trap gas chromatography/mass spectrometry. Prior to collecting samples, the vials were pretreated with ascorbic acid then filled at the onsite laboratory. When collecting samples, the vials were filled half-full and acidified to a pH<2 by adding a provided ampule of hydrochloric acid. Each THM vial was filled without overflowing, capped with no air bubbles, and transported to the lab for analysis prior to the 14-day storage limit.

3.7.13. Simulated Distribution System Haloacetic Acids (SDS-HAA)

Similar to the SDS-THM test, the SDS-HAA test measures the potential to form HAAs by placing finished water in conditions similar to those encountered in the distribution system. It can also be used to analyze the effectiveness of an alternative disinfectant, such as chloramines. In this case, the SDS-HAA tests were only used to compare the permeate quality from various membranes. Before collecting SDS-HAA samples, the pH, temperature, and free chlorine levels of the sample were measured, according to methods described previously. These parameters provide an estimate of the condition of water entering the distribution system. For the membrane comparison, samples were collected before and after membrane treatment to determine the membrane's rejection ability.

Water samples for the SDS-HAA test were collected and placed into 500 mL amber glass bottles that had been washed with soap and hot water, rinsed three times with RO water, rinsed with 50/50 nitric acid, and rinsed three times with nanopure water. Containers were filled completely and capped such that no air bubbles remained.

The same incubator as SDS-THM samples was used for the SDS-HAA samples. After the 3-day incubation period, three 40 ml HAA sample vials were immediately collected from each SDS container and stored at 4°C until analysis was performed. The SDS samples were also analyzed for free chlorine, temperature, and pH. Duplicate samples were analyzed for quality assurance and multiple tests were prepared to evaluate the varying feed water quality.

The sample vials were obtained from and tested by a commercial laboratory, which used EPA method 552.2 to analyze the HAA concentrations. This method uses liquid/liquid extraction with acidic methanol, gas chromatography with an electron capture detector. Prior to collecting samples, the vials were pretreated with ammonium chloride to provide 100 mg/L residual when filled at the onsite laboratory. When collecting samples, the vials were filled half-full and acidified to a pH<2 by adding a provided ampule of hydrochloric acid. Each THM vial was filled without overflowing, capped with no air bubbles, and transported to the lab for analysis prior to the 14-day storage limit.

CHAPTER FOUR – RESULTS AND DISCUSSION

4.1. Introduction

The objectives of this research project were to optimize the selection and performance of NF membranes chosen for future WTP expansion. The source water quality was evaluated prior to performing the pilot tests. A single element pilot plant was used during Phase I to uniformly examine the performance of six NF membranes at three recovery settings. A twenty-one element pilot plant was used during Phase II to uniformly evaluate the performance of three NF membranes at three flux settings. The results obtained throughout the course of the study are discussed in these sections.

4.2. Preliminary Water Quality Testing

Prior to pilot testing, the water was tested for SDI, TOC, UV_{254}, and ammonia. The results from these tests were interpreted to understand the potential behavior of the NF pilot tests as well as the behavior of the existing WTP.

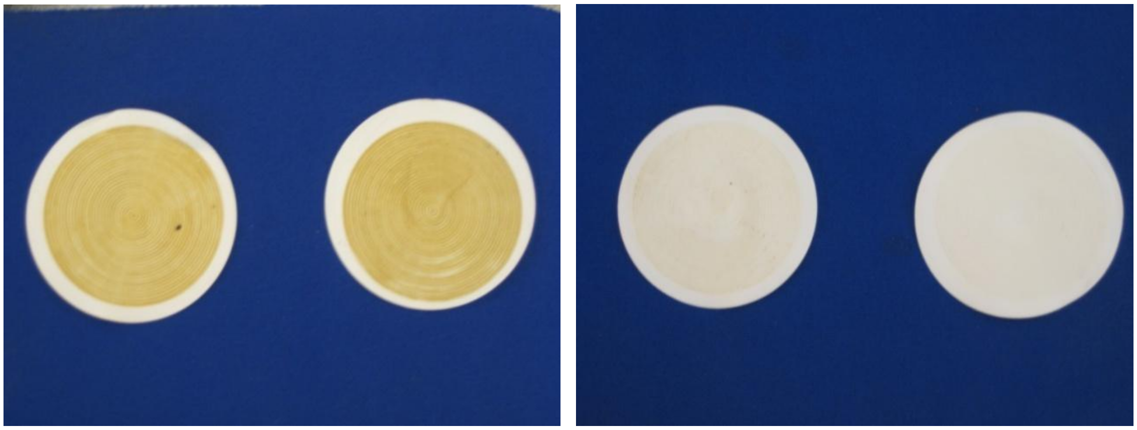
SDI testing was performed on several locations to determine if the water had low enough suspended matter to be treated by NF. A series of tests were conducted on June 23-25, 2008 to obtain information on the water quality of the filter number six effluent, plant inlet header, and of all available wells. The plant influent header produces a composite of all wells that were running on the day of the test - Wells 3 and 10 samples were obtained directly from the well head, and Wells 11-20 and Wells 21-26 samples were obtained from a header at the well field that contains a composite of water being produced by these wells. In conjunction with the SDI test procedure, the temperature was reported. The analysis of the raw water was performed to provide information that would be needed should direct nanofiltration of the raw water be considered.

The 15 minute SDI test results are shown in Table 4.1. A clean water SDI is represented by a value near zero, while turbid water is represented by a value above five. The raw well water SDI ranges from 1.2 – 3.3 with Well 10 being the lowest. After transmission to the WTP, the raw water SDI increases to 3.5 – 4.4. The increase is likely from iron oxidization as the water is pumped several miles. After conventional softening and dual media gravity filters, the treated water SDI is reduced to 1.0 – 1.2. The water temperature during the SDI testing was 12°C at the wells and 14°C at the filter effluent.

Images of SDI testing filters, shown in Figure 4.1, illustrate the difference between the raw and treated water. The dirtier filter corresponds to the higher SDI value. The maximum allowable SDI for direct nanofiltration is 5.0, therefore all of these water sources could be amenable to NF. A water source with SDI between 3.0 and 5.0 can be applied to a NF system, however, significant fouling will be a problem and the NF system will require frequent cleaning. Applying the NF pilot tests to the filter effluent

Table 4.1. SDI_{15} Test Results

	SDI_{15}		
Source	**Maximum**	**Minimum**	**Mean**
Filter Effluent	1.2	1.0	1.1
WTP Influent	4.8	3.5	4.2
Well 3	3.3	2.4	2.9
Well 10	1.5	1.2	1.4
Wells 11-20	3.2	3.1	3.2
Wells 21-26	2.6	2.6	2.6



a) WTP Influent b) Filter Effluent

Figure 4.1 – SDI Filter Images

provided the best available source to demonstrate NF membrane performance without a concern of fouling due to suspended solids.

The TOC test accurately provides the total organic carbon level, but is costly and usually must be run off-site, requiring shipping and analytical turn-around time. The use of a TOC surrogate like UV_{254} can provide a quick and easy check on the TOC concentration. After collecting several TOC and UV_{254} samples from the wells, a strong correlation can be inferred between UV_{254} and TOC as indicated by an R^2 value close to 1.0. Figure 4.2 shows a plot of UV_{254} and TOC for wells 3, 3A, and 10 – 15, which are regularly used by the WTP. The R^2 value for the raw water samples was 0.90.

As noted in the literature, the use of UV_{254} is limited as it can only detect the amount of NOM containing unsaturated carbon bonds. At high concentrations, especially prior to treatment, there appears to be a moderate correlation of UV_{254} and TOC. However, as shown in Figure 4.3, at low concentrations found in the treated water, which has had a majority of the unsaturated carbon removed, the correlation is more predictable

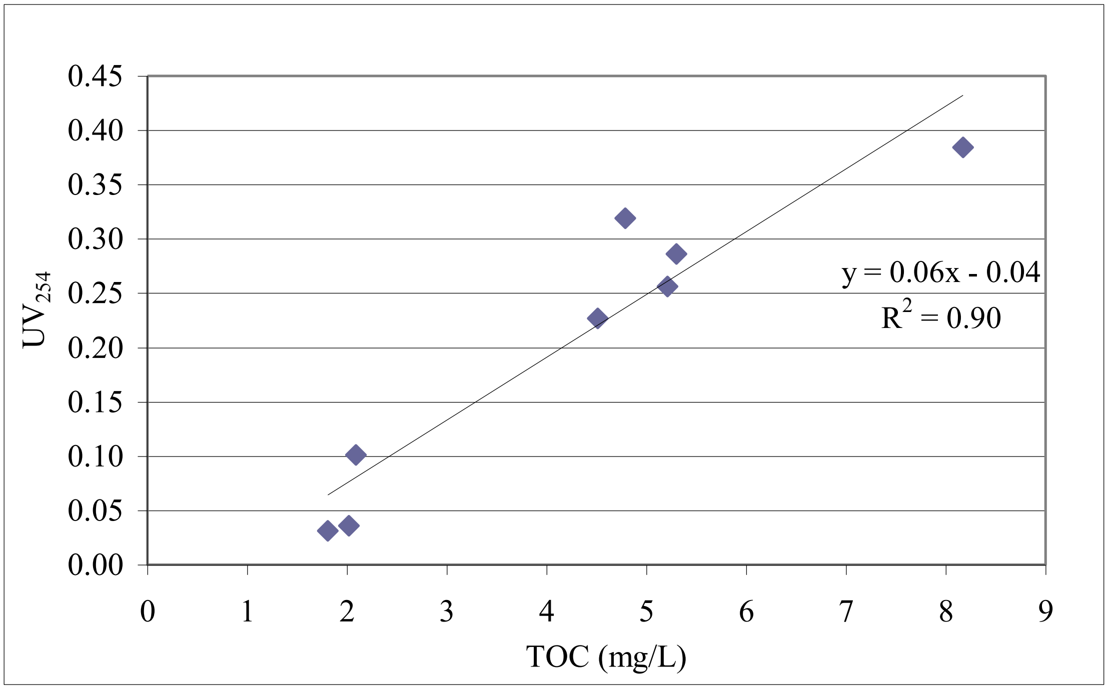


Figure 4.2 – UV_{254} Comparison to TOC for Raw Water

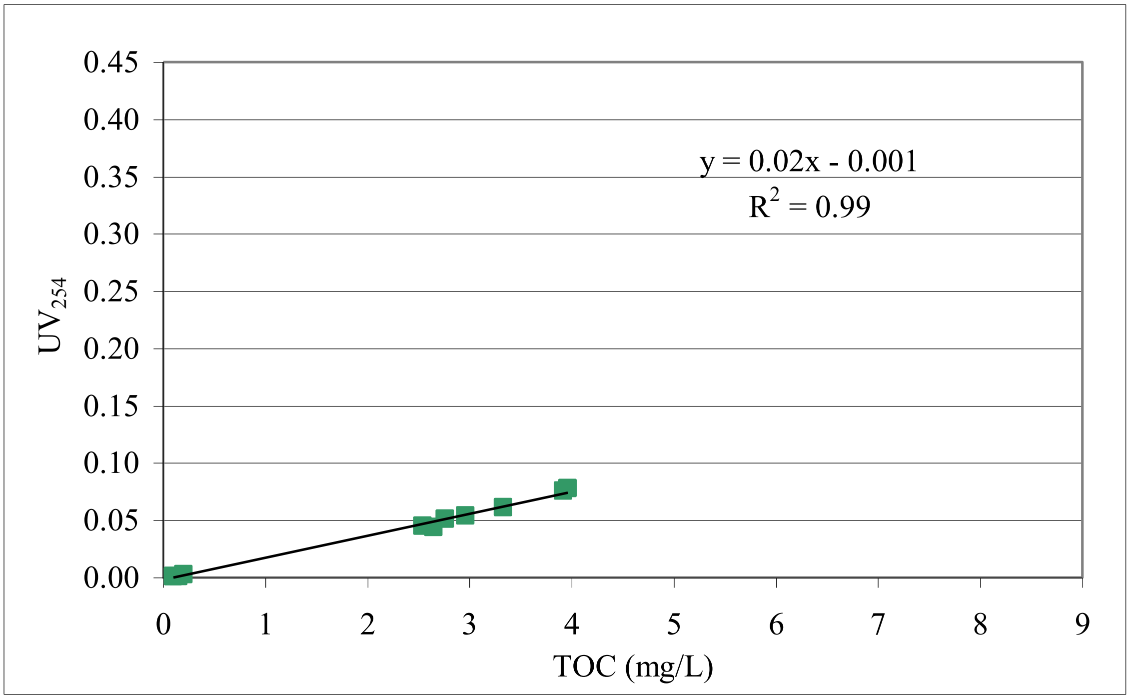


Figure 4.3 – UV_{254} Comparison to TOC for Treated Water

based on the R^2 statistic of 0.99. Additionally, the results from the treated water plotted along a lower slope than that the slope of the raw water.

The TOC and naturally occurring ammonia were also examined for each well to better understand which wells had the greatest influence on the concentrations of these parameters. A detailed table of each well's respective quality is shown in Appendix A. Wells 3, 3A, and 10 have relatively low average TOC and ammonia concentrations of 1.97 and 0.16 mg/L respectively, while Wells 11 – 28 have higher average TOC and ammonia concentrations of 5.77 and 1.39 mg/L, respectively. Since not all the TOC or ammonia is removed during the conventional softening process, the TOC and ammonia concentrations in the effluent from the gravity filters depends on which wells are pumping into the system. Typically, the WTP staff used the lowest numbered wells to meet the base demand, and added additional wells from the higher numbered wells as demand increased. The winter months had lower demand and typically Wells 3, 3A, and 10 – 15 were used. During the summer months when demand was highest, all the remaining wells were operated.

The feed water (water treatment plant filter effluent) quality applied to the NF pilot plants is shown in Table 4.2. The concentrations shown in Table 4.2 are compiled from all the samples during both pilot plant Phases. The filter effluent pH ranged from 8.63 to 9.72. Conductivity can be used as a surrogate for TDS when the correct multiplication factor is known. After performing several tests the TDS of the filter effluent was determined to be approximately 64% of the conductivity value, which is consistent with the literature. This value would fluctuate depending on which wells were

Table 4.2. Filter Effluent Water Quality – Phase I and II

Parameter	Maximum	Minimum	Average
pH	9.72	8.63	9.19
TDS (mg/L)	306	227	275
Conductivity (mS/cm)	475	372	412
Total Hardness (mg/L $CaCO_3$)	196	136	155
Calcium Hardness (mg/L CaCO3)	100	58	77
Alkalinity (mg/L CaCO3)	70	23	44
TOC (mg/L)	3.64	2.54	3.12
UV_{254} (cm^{-1})	0.166	0.044	0.064
Ammonia (mg/L NH_3-N)	1.20	0.50	0.67
SDS-THM (µg/L)	82	24	40
SDS-HAA (µg/L)	72	21	46

in operation. The filter effluent hardness is normally around 155 mg/L as $CaCO_3$, and calcium comprises approximately half of the total hardness. The TOC ranged from 2.54 to 3.64 mg/L. The concentrations of naturally occurring ammonia ranged from 0.50 to 1.20 mg/L NH_3-N. Both TOC and ammonia were sensitive to well selection. The SDS testing of THM and HAA formation determined average concentrations 40 and 46 µg/L respectively, after three day incubation.

Breakpoint chlorination of the treated water requires the complete destruction of free ammonia before a strong free chlorine residual can be created. In theory, as the ratio of chlorine to ammonia increases, the type and concentration of chlorine residual formed in the water changes. These changes are illustrated in Figure 4.4.

Up to a chlorine to ammonia ratio of approximately 5:1, chloramine is created. At chlorine to ammonia ratios between 5:1 and 7.6:1 the chloramine is destroyed. At chlorine to ammonia ratios greater than 7.6:1, free chlorine is formed. After the

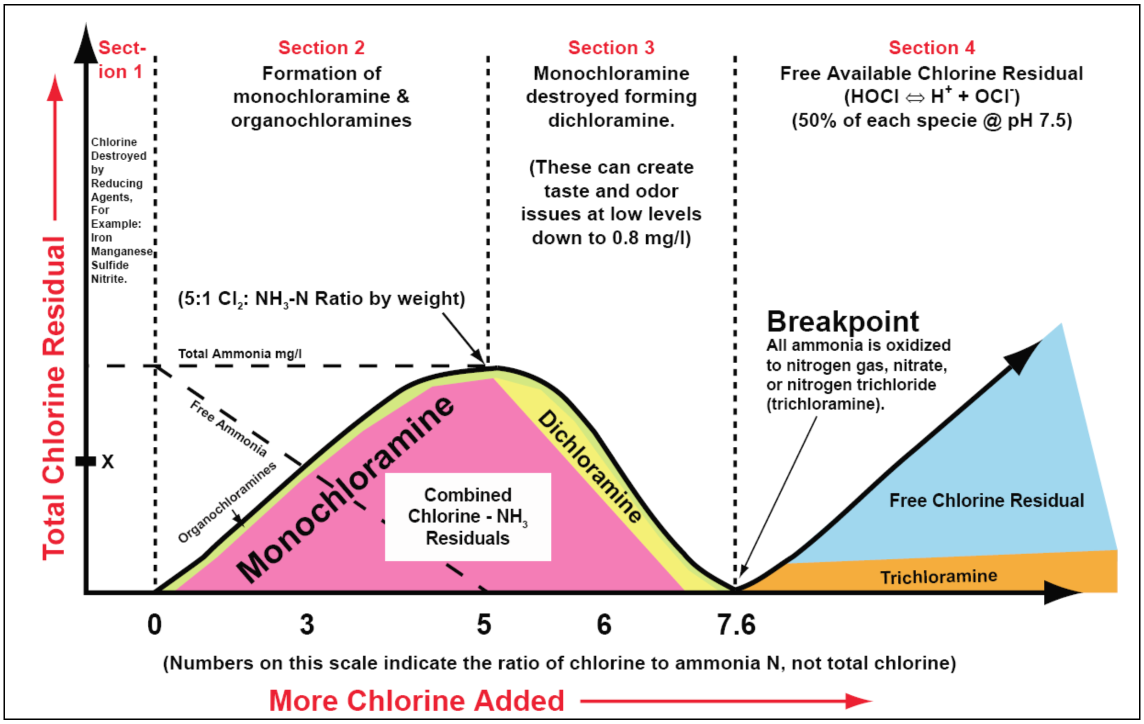


Figure 4.4 – Theoretical Breakpoint Chlorination Curve (Solar Bee 2008)

breakpoint, residual combined chlorine compounds of trichloramine are also created (Crittenden et al. 2005)

WMU doses chlorine to their water to achieve breakpoint chlorination and establish a free chlorine residual in their distribution system. The naturally occurring free ammonia in the well water requires the WTP to dose chlorine at rates higher than systems without ammonia. WMU desires to continue using a free chlorine residual after implementing TOC removal processes (such as nanofiltration). Relative to this study, the chlorine demand by ammonia must be accommodated in the SDS testing procedure to enable the test to depict the THM/HAA concentrations that would occur after the treatment improvements have been implemented.

An additional option would be for the system to operate with a chloramine residual in the distribution system. Chloramine residual operations would require the system to lower the chlorine dosage to achieve a 4:1 chlorine to ammonia ratio. The benefits of chloramine would be to provide a more persistent residual in the distribution system and to lower the concentrations of DBPs. The disbenefits would include potential for nitrification in the distribution system and the fact that chloramine is a weaker disinfectant than free chlorine.

Breakpoint chlorination experiments were performed to verify the chlorine to ammonia ratios necessary for simulated distribution system testing. The chloramination testing was used to achieve a chloramine residual and to understand when to expect free chlorine residual beyond the breakpoint. Samples of chloraminated water and free chlorinated water collected during the breakpoint chlorination experiments were analyzed for THMs.

Figure 4.5 illustrates the breakpoint curve created with varying ratios of chlorine to ammonia. Chloramination of the raw water 1.05 mg/L of ammonia yielded monochloramine residual of at least 3.5 mg/L. Chlorine to ammonia ratios to achieve the peak chloramine residual (approximately 5:1) and the breakpoint (approximately 8:1) were exhibited as expected based on the literature. Free ammonia was present up to the 5:1 chlorine to ammonia ratio, and absent at ratios greater than 5:1. Mono-, free, and total chlorine residuals tracked with each other as expected by chlorine chemistries.

A second chloramination study was performed on raw water with 0.50 mg/L of naturally occurring ammonia, which yielded 1.5 mg/L monochloramine. Since this

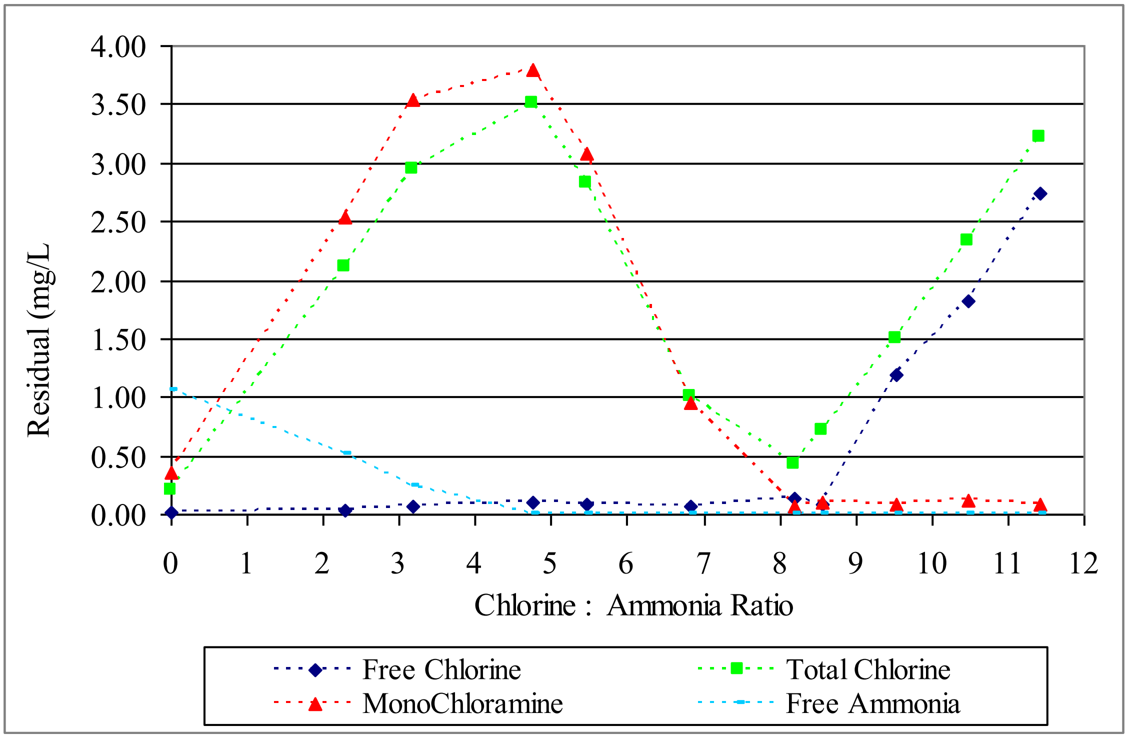


Figure 4.5 – Breakpoint Chlorination Curve of Membrane Feed Water

residual is in a range expected for distribution system chloramine residuals, samples from this second study were used to compare the THM formation potential of breakpoint chlorinated and chloraminated water. Two samples of breakpoint chlorinated water and chloraminated water were analyzed for THMs. The THM results are shown in Figure 4.6. As compared to breakpoint chlorinated water (approximately 57 µg/L TTHM) the TTHM concentration of the chloraminated water was approximately 10 µg/L. The chlorination to chloramination conversion provides a 82% decrease in TTHM formation.

Although the conversion to chloramination would alleviate WMU's THM problem, the conversion doesn't add any extra capacity, which is also needed. The second option evaluated for THM reduction is nanofiltration membranes. The

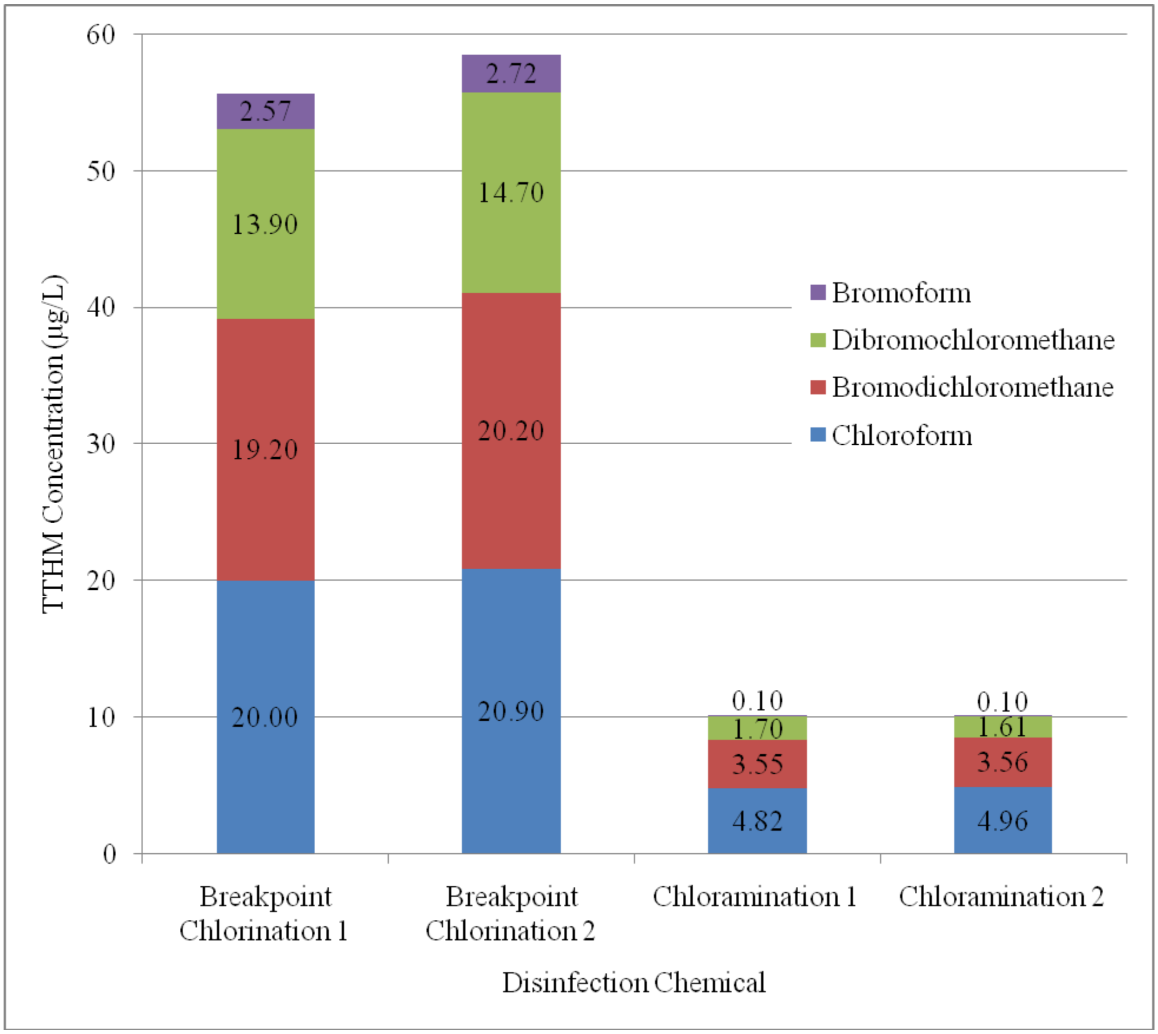


Figure 4.6 – Chloramination THM Results

implementation of a NF membrane system will also provide the utility the opportunity to increase water production capacity and selectively reject DBP precursors.

4.3. Phase I Pilot Studies

The planned WTP expansion will utilize NF membranes to reduce the THM and HAA concentrations entering the distribution system. To minimize the costs associated with the Stage 2 Disinfectant/Disinfection By-Products Rule compliance, a blend of permeate and conventionally softened water will be established. The blend has been determined based on 4.0 MGD of flow from the existing softening system, and an additional 4.0 MGD of feed water applied to an NF membrane system operating at 85% recovery. This equates to 3.4 MGD of flow from the NF permeate. The blended stream must have less than 80 µg/L TTHMs, and to ensure this a 10% safety factor will be added. Therefore, the blend water should have no more than 72 µg/L TTHMs. Considering the historical worst case scenario, where the existing softened water contains 120 µg/L TTHM, the NF permeate must exhibit 87% reduction of TTHMs.

During the Phase I single element pilot plant experiments, the actual flows did not match the desired flows for every membrane. The actual flows achieved for each of the six NF elements are listed in Table 4.3. Due to variations in the membrane permeability and pilot plant operation limits, the desired flows were only matched for membrane K3. The other five membranes each had slightly different flow values that affected recovery and flux rates. Although not ideal, the actual recovery rates were still very close to the desired recovery rates. The DF membrane had the highest recovery setting error 81.2% vs the desired 80%. This slight difference equates to a 1.5% error, which should not substantially affect the results of the test. Additionally, the actual flux rates were not always 12.0 gfd. The resulting flux rate for membrane K2 varied from 10.2 – 19.3 gfd. The flux rate for membrane T varied from 12.0 gfd only during the 80% recovery setting when a flux of 12.7 gfd was recorded. The flux rate for membrane HE varied from 10.6 – 15.6 gfd. The initial flows for membrane HH were based on 12 gfd and an assumed

Table 4.3. Actual Flows, Recovery Rates, and Flux Rates During Phase I Testing

Sample Label	Membrane	Membrane Area ft^2	Actual Permeate Flow gpm	Desired Recovery %	Actual Recovery %	Actual Feed Flow gpm	Actual Recycle Flow gpm	Actual Reject Flow gpm	Recycle + Reject Flow gpm	Actual Flux gpd/ft^2
K2	Koch TFC-SR2	85	0.60	15	15.8	3.80	0.00	3.20	3.20	10.2
			0.90	50	50.0	1.80	2.10	0.90	3.00	15.2
			1.14	80	80.3	1.42	2.82	0.28	3.10	19.3
K3	Koch TFC-SR3	85	0.71	15	15.0	4.72	0.00	4.01	4.01	12.0
			0.71	50	50.0	1.42	2.29	0.71	3.00	12.0
			0.71	80	80.0	0.89	2.82	0.18	3.00	12.0
T	Trisep XN45-TSF	85	0.71	15	15.0	4.72	0.00	4.01	4.01	12.0
			0.71	50	50.0	1.42	2.29	0.71	3.00	12.0
			0.75	80	80.0	0.94	2.81	0.19	3.00	12.7
HE	Hydranautics ESNA1-LF	85	0.63	15	15.0	4.72	0.00	4.01	4.01	10.6
			0.76	50	50.0	1.52	2.24	0.76	3.00	12.9
			0.92	80	80.0	1.15	2.77	0.23	3.00	15.6
HH	Hydranautics HydraCoRe-70pHT	70	0.63	15	15.0	3.89	0.00	3.31	3.31	12.9
			0.63	50	50.0	1.17	2.42	0.58	3.00	12.9
			0.63	80	80.0	0.73	2.85	0.15	3.00	12.9
DF	Dow/Filmtec NF270	82	0.68	15	15.0	4.56	0.00	3.87	3.87	12.0
			0.82	50	50.0	1.64	2.20	0.82	3.02	14.4
			0.95	80	81.2	1.19	2.80	0.22	3.02	16.7

area of 75 ft^2. The calculated flux was corrected to 12.9 gfd after it was learned the surface area was 70 ft^2. The flux rate for membrane DF varied from 12.0 – 16.7 gfd. The flux rates are dependent on the permeate flow and membrane area. The actual flux was typically higher than the desired rate for the 80% setting because the recycle flow was increased to maintain the cross flow velocity.

4.3.1. Membrane Comparison from Single Element Pilot Plant

The six NF membranes tested during Phase I were evaluated based on specific flux (SF) and contaminant rejection. The results are displayed in Table 4.4 and Appendix B.

Specific flux was calculated and adjusted for temperature. The temperature fluctuated from 14.5 – 20.5 °C and was highest during each 80% recovery setting. The recycled water was warmed by the high pressure pump and friction through pipes and fittings. Each temperature correction constant obtained from each manufacturer was applied to calculate the specific flux values at 25 °C, the results of which are shown in Figure 4.7. The adjusted specific flux ranged from 0.11 – 0.52 gfd/psi. The two membranes with the lowest adjusted SF were K3 and HH. The membrane with the highest adjusted SF was K2. High specific flux is a benefit because the membrane produces more water with less energy requirement.

The contaminant removal analysis focused on the TOC rejection to reduce DBP formation. Due to variable feed water concentrations, permeate quality was evaluated on a percent removal basis. Additionally, the concentrate TDS was monitored at the highest

Table 4.4. NF Membrane Performance Characteristics During Phase I Testing

Sample Label	Desired Recovery %	NDP psi	SF gfd/psi	Temp. °C	TCF	Adjusted SF @ 25°C gfd/psi	Concentrate TDS mg/L	% TOC Removal	% UV_{254} Removal	% THM Removal	% HAA Removal	% NH_3-N Removal
K2	15	28.5	0.36	14.6	0.686	0.52	-	93%	92%	79%	95%	27%
	50	49.5	0.31	16.4	0.734	0.42	-	86%	93%	82%	75%	24%
	80	60.0	0.32	17.0	0.751	0.43	1128	87%	86%	-	-	20%
K3	15	99.5	0.12	14.5	0.684	0.18	-	95%	97%	93%	95%	66%
	50	96.0	0.13	16.0	0.723	0.17	-	98%	99%	96%	84%	41%
	80	104.0	0.12	18.5	0.793	0.15	1155	98%	99%	-	-	54%
T	15	63.0	0.19	15.1	0.716	0.27	-	93%	96%	94%	95%	41%
	50	56.5	0.25	17.1	0.767	0.33	-	78%	95%	81%	89%	13%
	80	60.5	0.28	19.1	0.822	0.34	844	93%	98%	-	-	27%
HE	15	50.5	0.21	15.6	0.744	0.28	-	93%	94%	97%	85%	35%
	50	53.0	0.24	17.7	0.797	0.30	-	62%	74%	91%	90%	35%
	80	60.5	0.26	18.0	0.804	0.32	1122	93%	97%	-	-	49%
HH	15	159.5	0.08	15.8	0.749	0.11	-	85%	91%	76%	79%	3%
	50	147.0	0.09	18.5	0.817	0.11	-	89%	93%	74%	77%	0%
	80	140.0	0.09	20.5	0.870	0.11	574	91%	92%	-	-	14%
DF	15	47.5	0.25	15.6	0.719	0.35	-	99%	97%	93%	96%	46%
	50	52.5	0.23	16.8	0.751	0.30	-	98%	94%	95%	97%	41%
	80	59.0	0.22	17.4	0.767	0.28	1151	98%	98%	-	-	43%

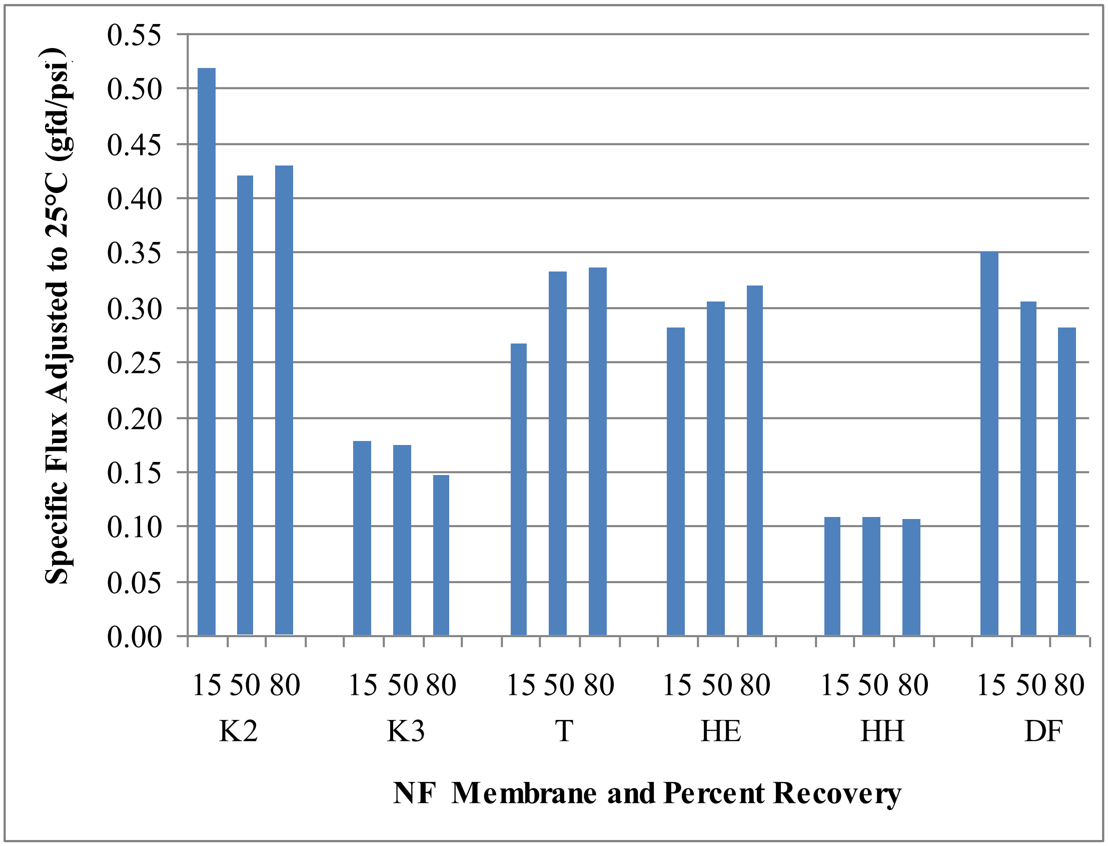


Figure 4.7 – Specific Flux with Varying Recovery During Single Element Tests

recovery setting to evaluate disposal options. A target ammonia rejection was not set, however the results were also compared.

The TOC rejection is plotted in Figure 4.8 for three recovery settings, 15, 50, and 80 percent, for each membrane. It is important to note that the TOC of the feed water increases as the percent recovery increases due to the recycled concentrate flow. The surrogate TOC parameter UV_{254} is also plotted alongside the respective samples. The rejection of TOC was extremely good, ranging between 62% and 99%, with 98% rejection exhibited by both K3 and DF membranes at 50 percent recovery. The

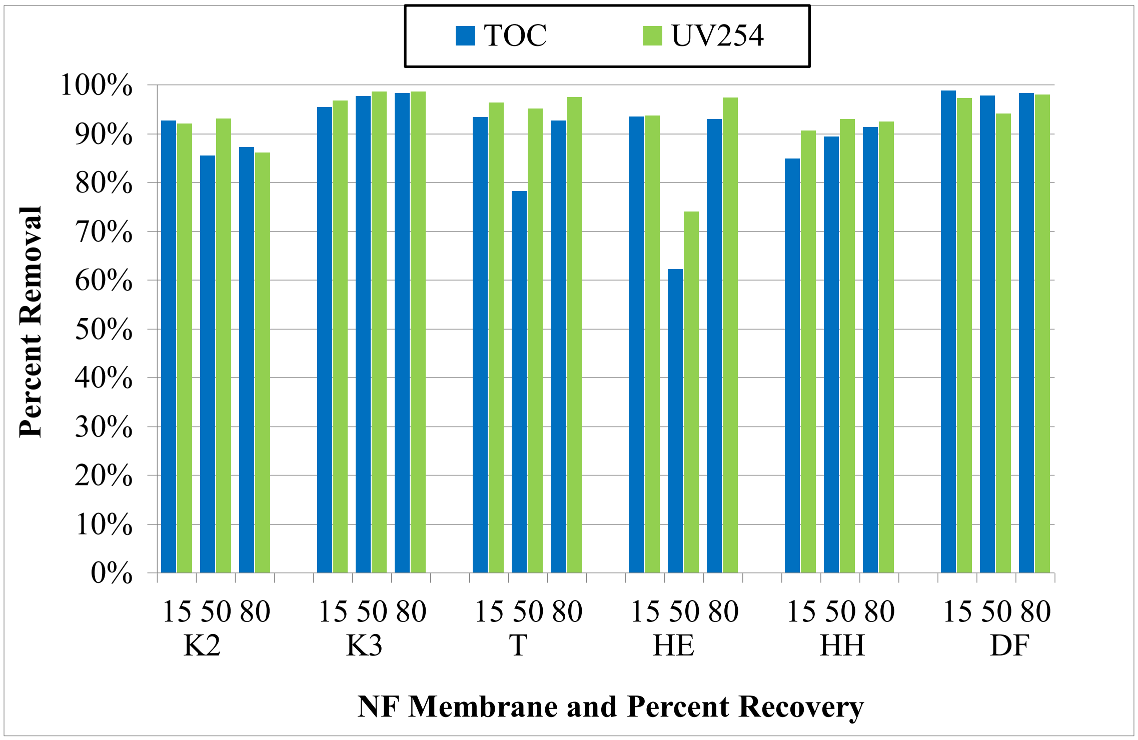


Figure 4.8 – TOC and UV_{254} Removal with Varying Recovery During the Single Element Tests

corresponding UV_{254} rejection compared closely to many of the TOC rejections. The UV_{254} removal is higher than the TOC removal for three-fourths of the sample group. The average percent difference between the TOC removal and the UV_{254} removal is 3.4%. Given the similarities between the TOC and UV_{254} percent removal results, the UV_{254} test provides fair and fast representation of organic removals through the membranes. However, for both T and HE membranes at 50 percent recovery, the TOC and UV_{254} removals were more than 15% different from each other. Therefore, the UV_{254} method should not be relied on solely, but used to supplement the TOC data, providing instantaneous results.

4.3.2. Disinfection By-Product Results

As a result of substantial DBP precursor (TOC) removal, the membrane permeate was shown to contain very low concentrations of DBPs and substantial DBP removals were obtained. The SDS-TTHM and SDS-HAA5 feed water to permeate percent reduction results are shown in Figures 4.9 and 4.10, respectively. As explained previously, the feed water blend required 87% removal of TTHMs in the NF permeate, as indicated by the bold, red horizontal line. The membranes that satisfy this requirement at both 15 and 50 percent recovery are K3, HE, and DF. Membrane T only satisfied the requirement at the 15 percent recovery setting. Membrane K3 had the highest average TTHM reduction at 94.5%.

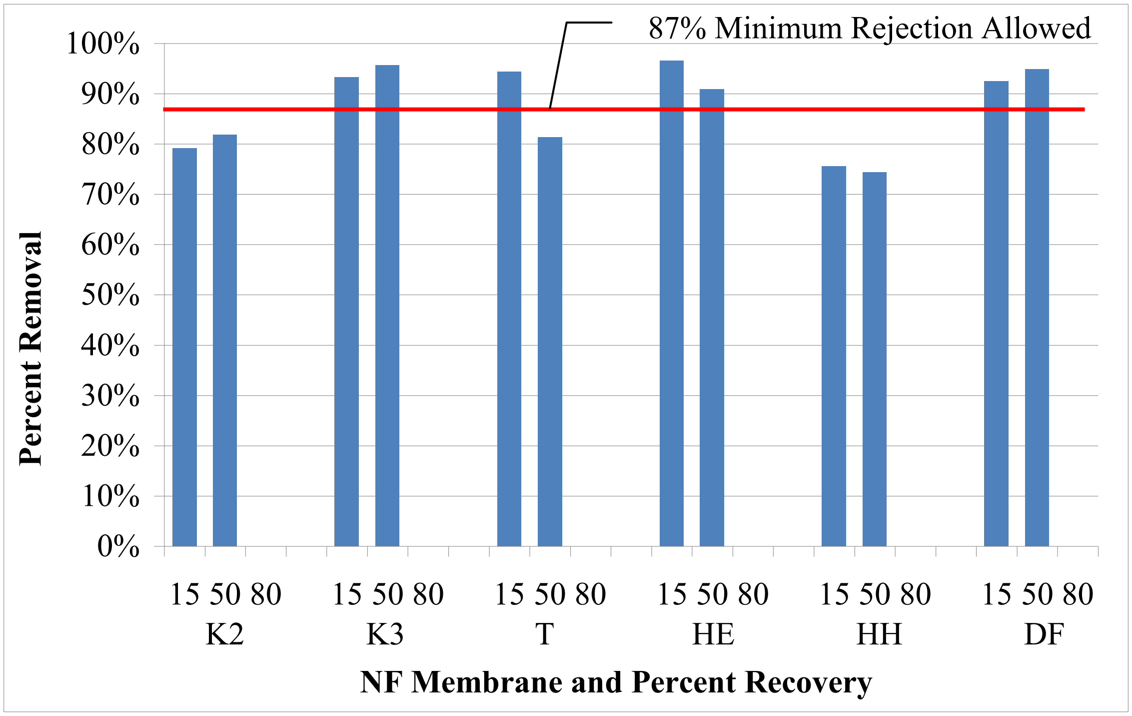


Figure 4.9 – Single Element SDS-TTHM Reduction

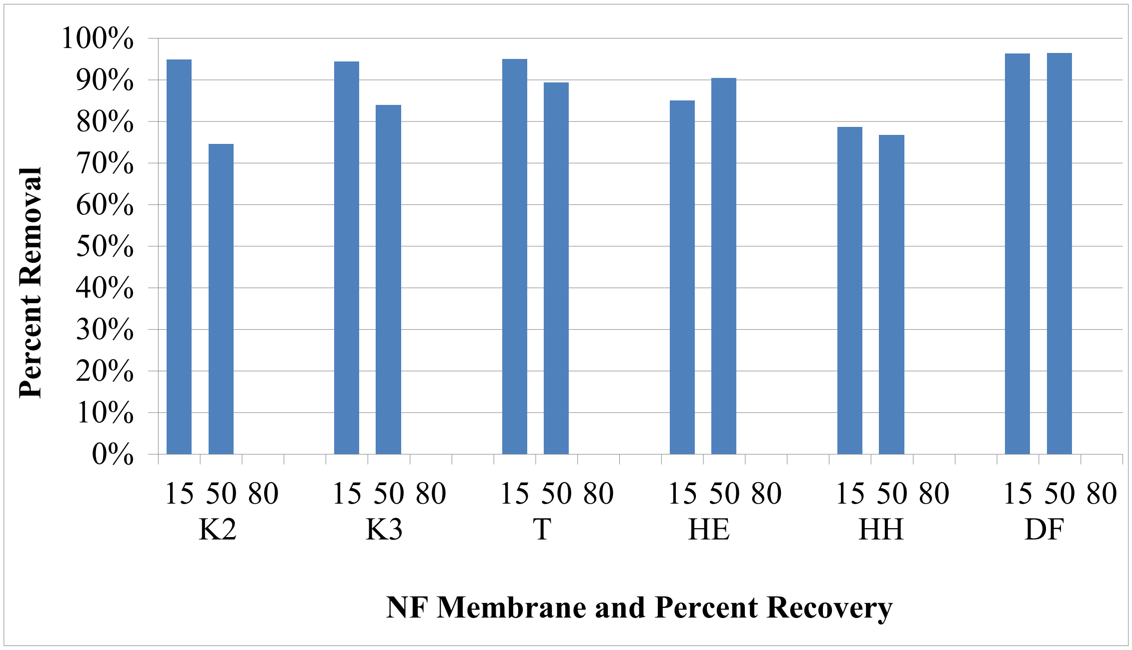


Figure 4.10 – Single Element SDS-HAA5 Removal

The corresponding high HAA5 reductions provided assurance that there would not be a concern with excessive HAA5 in the blend water. The highest individual concentration of HAA5 reported by WMU in the past two years was 47 µg/L, which is below the Stage 2 D/DBP MCL of 60 µg/L. Therefore, no reduction is required of the NF permeate for HAA5 values. HAA5 reduction values were all greater than 70%, wherein membrane DF exhibited the highest at 96% removal. Membrane selection would only consider the HAA5 removal if the TTHM removal and concentrate TDS parameters were satisfied by multiple membranes.

4.3.3. Membrane Concentrate

The membrane concentrate TDS was only evaluated at the 80% recovery setting. According to the literature, at the highest recovery setting the reject stream will have the highest concentration of dissolved matter. Although the 50% recovery setting is used to compare permeate, due to the pilot setup, the concentrate parameters were only representative at the design recovery setting. The results from the Phase I testing are illustrated in Figure 4.11. The bold, red horizontal line indicates the maximum allowable TDS in the concentrate for disposal. Membranes T and HH were the only elements to satisfy this requirement at 80% recovery. The other membranes all exhibited TDS concentrations above 1100 mg/L. These excessive TDS concentrations could be reduced below 1000 mg/L if a lower recovery rate was selected. The TDS limit was a key component for membrane selection in Phase I, however to facilitate better comparisons a study on concentrate disposal or treatment alternatives should be completed.

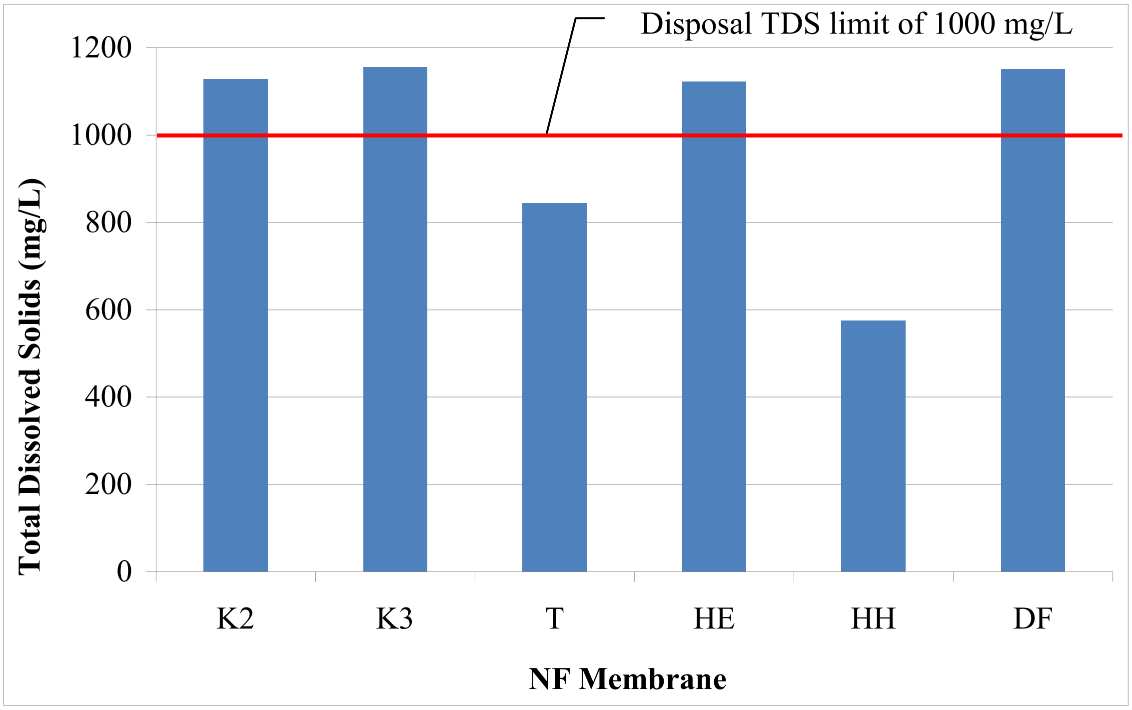


Figure 4.11 – Single Element Concentrate TDS at 80% Recovery

4.3.4. Effects of Varying Percent Recovery

The single element pilot plant was operated at 15, 50 and 80 percent recovery settings to simulate the respective lead, middle, and tail elements of a full scale treatment system. In the literature, it was noted that the specific flux decreases with increasing recovery rates. However, according to Figure 4.7 the adjusted specific flux only decreased for membranes K2, K3, and DF. The other membranes T, HE, and HH exhibited increasing or un-changing specific flux when recovery was increased.

During higher recoveries the reject flow becomes increasingly concentrated and can decrease permeate quality. Listed in Appendix B, the permeate pH values demonstrated a decreasing trend with increasing recovery rates. As shown in Figure 4.12, the permeate total hardness, alkalinity, and conductivity increase with increasing recovery rates. The total hardness and alkalinity are plotted in mg/L as $CaCO_3$ on the left side of the chart, while conductivity is plotted in µS/cm to the right.

Other permeate water quality parameters, like TOC and ammonia, can also be affected by varying recovery rates. As illustrated in Figure 4.8, the TOC rejection may either increase or decrease with increasing recovery rates. The inconsistent trends indicate the membrane characteristics affect TOC removal. A decreasing percent removal trend, as exhibited by membrane K2 is an example of the Donnan effect as noted in the literature review. An increasing percent removal trend, as exhibited by membrane HH is indicative of an extremely negatively charged membrane, which may not be hindered by the Donnan effect.

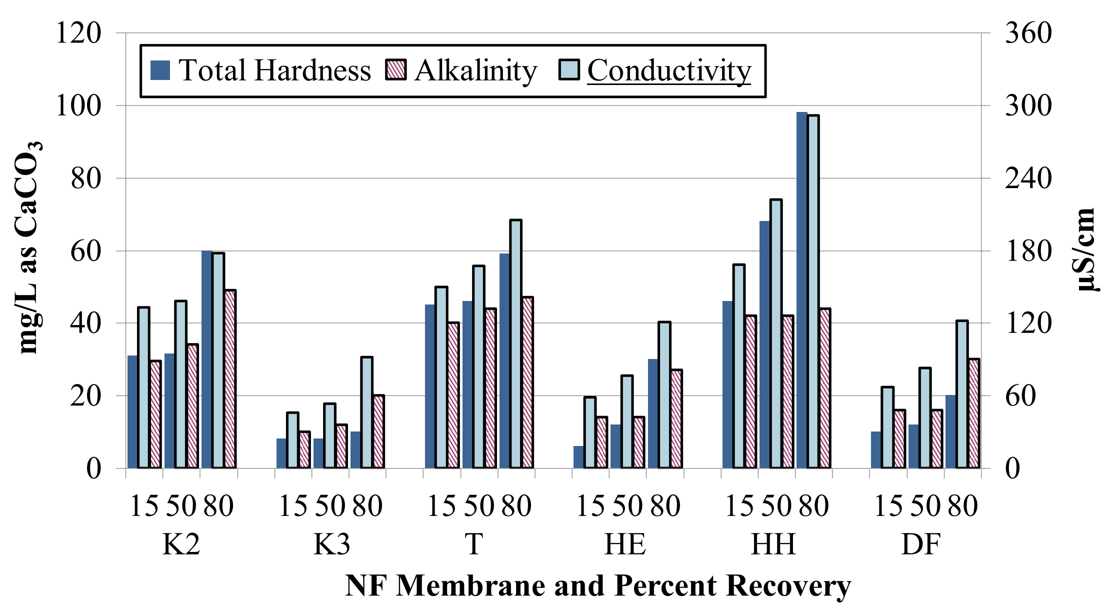


Figure 4.12 – Single Element Permeate Water Total Hardness, Alkalinity, and Conductivity

Ammonia removal results in Figure 4.13 indicate the removals are highly membrane specific. The highest feed water to permeate removals were exhibited by membrane K3 with an average of 54%. The lowest removals were exhibited by membrane HH with an average of 6%. The significant difference between these two membranes can be attributed to their MWCO values. Membrane K3's MWCO is approximately 300 Daltons, whereas membrane HH's MWCO is approximately 720 Daltons. Additionally, membrane HH's strong negative charge attracts the positively charged ammonia ions further reducing the removal. During this study, varying the recovery rate did not appear to have a consistent influence on the ammonia removal.

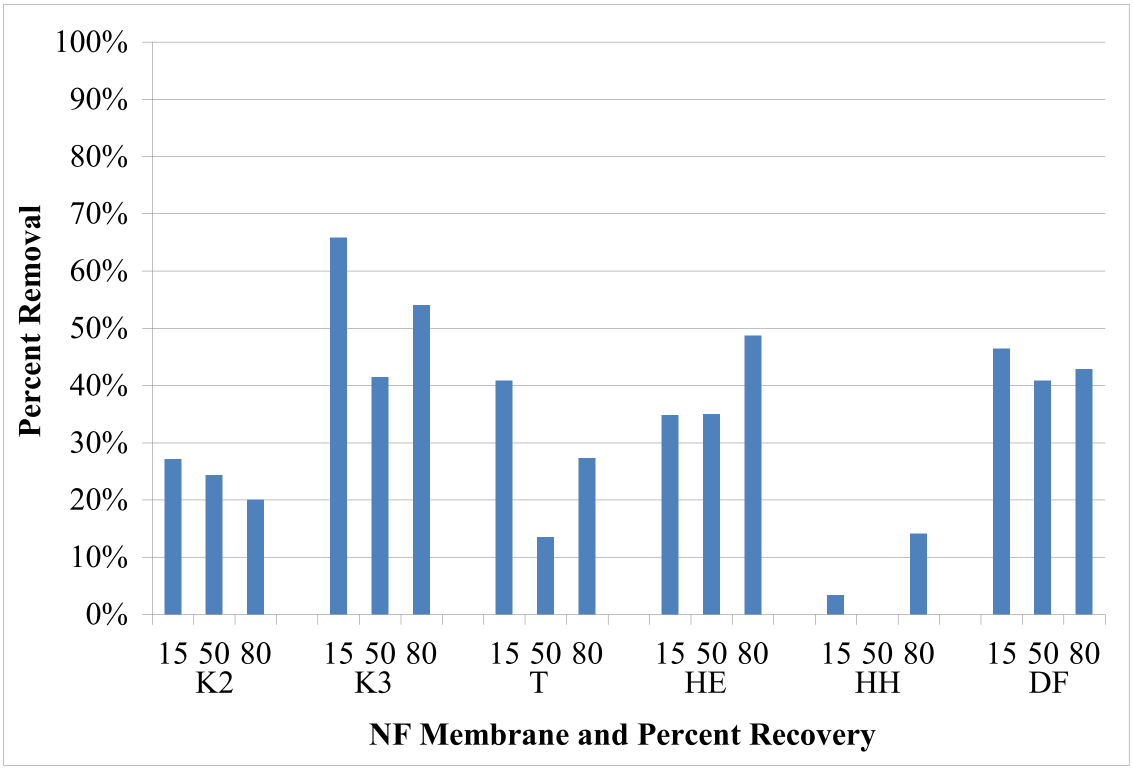


Figure 4.13 – Single Element NH_3-N Removal with Varying Recovery

Based on each membrane's ability to satisfy the required 87% TTHM removal and maintain a concentrate TDS below 1000 mg/L three membranes were selected. Koch TFC-SR3 (K3), Trisep XN45-TSF (T), and Hydranautics ESNA1-LF (HE) were chosen for further examination during Phase II testing. Trisep XN45-TSF was chosen because the average TTHM percent removal was 87.9% and the concentrate TDS at 80% recovery was 844 mg/L. Koch TFC-SR3 and Hydranautics ESNA1-LF were chosen because their average TTHM percent removal was 94.5% and 93.8%, respectively. Although Koch TFC-SR3 and Hydranautics ESNA1-LF did not satisfy the concentrate TDS limit exhibiting 1155 mg/L and 1122 mg/L, they were selected based on their high TOC rejections. The TDS limit was compromised as no other membrane satisfied both TTHM and TDS conditions. Membrane HH satisfied the concentrate TDS limit, however exhibited only 75% TTHM removal. The 87% TTHM removal requirement was not flexible, however the concentrate TDS discharge limit was being re-evaluated by the SDDENR.

4.4. Phase II Pilot Studies

The Phase II pilot plant was used to compare the three membranes chosen from Phase I testing. The membranes tested were Koch TFC-SR3 (K3), Trisep XN45-TSF (T), and Hydranautics ESNA1-LF (HE). The membranes were each tested at 9, 12, and 15 gfd flux rates. The Phase II experiments were able to maintain the desired flows as listed in Table 3.3 for the duration of each test, except for membrane K3 during 9 gfd flux rate. Membrane K3 was operated at 80% recovery and exhibited correspondingly lower permeate flows under the same feed flow rate. The 80% recovery setting was performed to simulate similar settings as exhibited during Phase I testing. However, the Phase II flows were adjusted to 85% recovery when WMU's surface water discharge permit was amended to permit concentrate flows with up to 2500 mg/L TDS. This increase from 1000 mg/L allowed WMU to consider operation of a full scale plant at higher recovery rates; such as 85%. Each flux rate was operated for one week's duration, however some tests ran longer than seven days due to technical difficulties.

During each flux setting, NDP and SF for the three membranes were recorded. The test results are displayed in Table 4.5. As mentioned in the literature, higher flux requires higher pressures, which held true for these experiments. The values shown in Table 4.5 are averages of several readings taken throughout each test. The NDP values

Table 4.5. NF Membrane Performance Characteristics for Phase II Pilot Plant

Sample Label	Flux gfd	NDP psi	SF gfd/psi	Temperature °C	TCF	Adj. SF @ 25°C gfd/psi	Concentrate TDS mg/L
K3	9*	88	0.10	16.6	0.740	0.14	1137
	12	126	0.10	14.3	0.679	0.14	1702
	15	165	0.09	14.4	0.681	0.13	1671
T	9	63.7	0.14	14.0	0.689	0.21	1287
	12	94.4	0.13	12.4	0.651	0.20	1376
	15	128.5	0.12	11.9	0.639	0.18	1288
HE	9	76.2	0.12	12.1	0.664	0.18	1783
	12	102.2	0.12	11.6	0.653	0.18	1875
	15	136.5	0.11	11.5	0.651	0.17	1983

* pilot test operated at 80% recovery, while other tests were operated at 85% recovery

were determined using the applied pressure differential only, the osmotic pressure differential was assumed to be negligible. Therefore, the NDP was the difference between the applied pressure and the permeate pressure. As flows increased with higher flux rates, the permeate pressure increased. The increased permeate backpressure was caused by headlosses on route to the drain. Permeate pressures were typically around 12, 24, and 34 psi for the respective flux rates of 9, 12, and 15 gfd. The NDP values ranged from 60.5 to 104 psi during Phase I at 80% recovery, while during Phase II NDP values during the 12 gfd flux rate ranged from 94.4 to 126 psi for the three selected membranes. The increased pressures from Phase I to Phase II were caused by lower water temperatures and the increased recovery rate from 80 percent to 85 percent. The pressures observed for membrane HE were substantially higher during Phase II testing, 102.2 psi as compared to 60.5 psi during Phase I.

To equally compare the flux rate testing, each SF was temperature corrected to 25°C with a temperature correction constant obtained from each manufacturer. The feed water temperature decreased gradually as Phase II continued into the winter months. The feed water temperature ranged from 16.6 to 11.5°C. The adjusted specific flux ranged from 0.13 to 0.21 gfd/psi. Membrane K3 exhibited the lowest adjusted SF, while membrane T exhibited the highest. The adjusted specific flux rates results are shown in Figure 4.14 to enhance the comparison of each membrane. The adjusted SF rates show a declining trend for membrane T with increasing flux rates. The other two membranes, K3 and HE, both exhibited lower adjusted specific flux rates (0.13 and 0.17 gfd/psi, respectively) at higher flux settings, but the decreases (0.01 gfd/psi for both membranes)

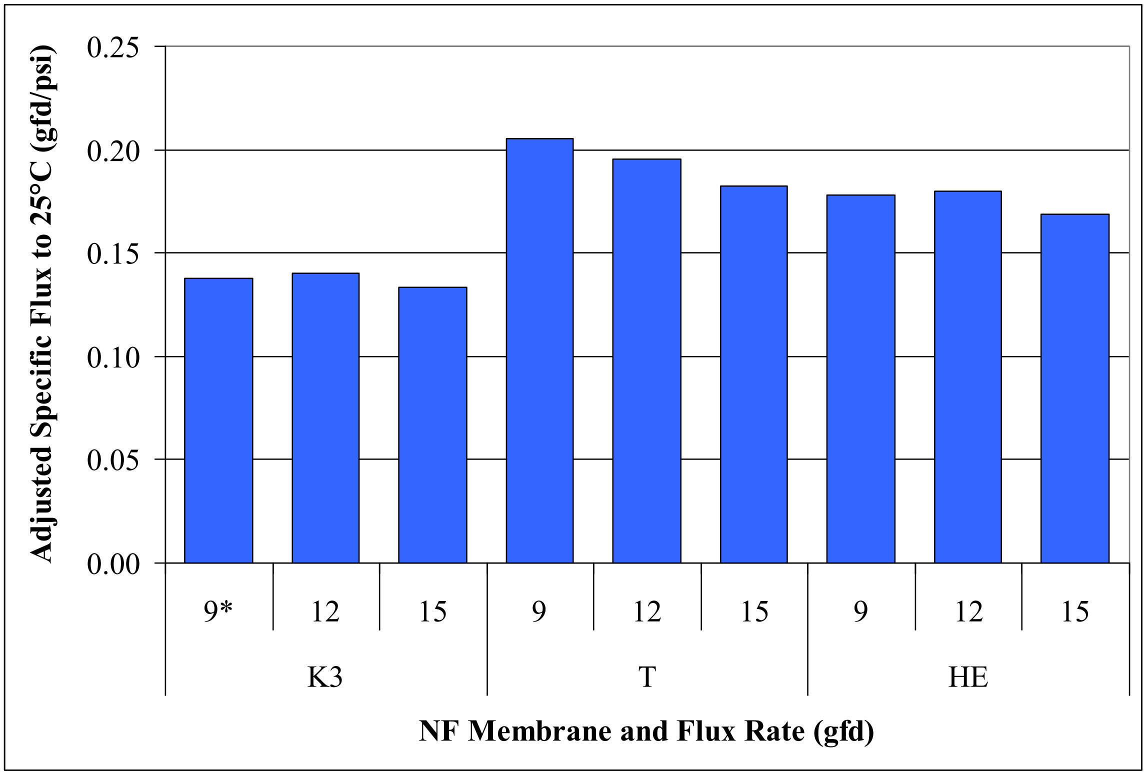


Figure 4.14 – Adjusted Specific Flux with Varying Flux Rates

were minimal compared to membrane T's decrease of 0.03 gfd/psi. The seemingly small value of 0.03 gfd/psi equates to a 14% drop in productivity, which is substantial. The results from Phase I are comparable for membrane K3, but membrane T and HE exhibited higher specific flux rates during Phase I than Phase II. Comparing both Phases at 12 gfd, the Phase I SF for membrane K3 was 0.15 gfd/psi compared to 0.14 gfd/psi during Phase II. However, membrane T exhibited a SF of 0.34 gfd/psi during Phase I, but only 0.20 gfd/psi during Phase II. Similar to membrane T, membrane HE exhibited a SF of 0.32 gfd/psi during Phase I, but only 0.18 gfd/psi during Phase II. The Phase II pilot plant was more accurate than Phase I, providing a continuous temperature reading and a stable NDP through the course of several days as compared to several hours. Therefore, the SF results from Phase II should be used to evaluate each membrane based on energy requirements. Membrane T exhibited the highest SF, 0.21 gfd/psi at the 9 gfd flux rate, and therefore would be selected based on energy performance.

All of the concentrate TDS concentrations exceeded the 1000 mg/L limit due to the increased recovery. Increasing the recovery to 85%, membrane T exhibited concentrate TDS around 1300 mg/L, which is approximately 54 percent larger than the 844 mg/L exhibited during Phase I at 80% recovery. The 9 gfd, 80% test for membrane K3 exhibited concentrate TDS of 1137 mg/L, similar to results from Phase I at 1128 mg/L.

4.4.1. Membrane Comparison from 21-Element Pilot Plant

Similar to Phase I, the contaminant removal analysis focused on the TOC rejection to reduce DBP formation. Due to variable feed water concentrations, permeate quality was evaluated on a percent removal basis. The percent removal values were calculated using the feed water and the respective membrane's permeate. A target ammonia rejection was not set, however the results were compared. Table 4.6 shows the respective feed water to permeate percent removals for TOC, UV_{254}, TTHM, HAA5, and ammonia for each flux setting during Phase II.

The TOC rejection is plotted in Figure 4.15 for three flux rates, 9, 12, and 15 gfd, for each membrane. The surrogate TOC parameter UV_{254} is also plotted alongside the respective samples. The rejection of TOC was extremely good, with all values above 92%. The highest removal (99%) was exhibited by membrane HE at both 9 and 12 gfd flux rates. The lowest removal (92%) was exhibited by membrane T at a flux rate of 15 gfd. The corresponding UV_{254} rejection plotted closely to many of the TOC rejections,

Table 4.6. NF Membrane Contaminant Rejections for Phase II

Sample Label	Flux gfd	% TOC Removal	% UV254 Removal	% TTHM Removal	% HAA5 Removal	% NH_3-N Removal
K3	9*	94%	98%	96%	81%	38%
	12	96%	98%	92%	90%	51%
	15	96%	98%	90%	90%	53%
T	9	95%	98%	85%	90%	29%
	12	97%	98%	91%	90%	30%
	15	92%	93%	92%	79%	42%
HE	9	99%	98%	95%	N/A	68%
	12	99%	98%	93%	88%	69%
	15	97%	98%	97%	97%	75%

* pilot test operated at 80% recovery, while other tests were operated at 85% recovery

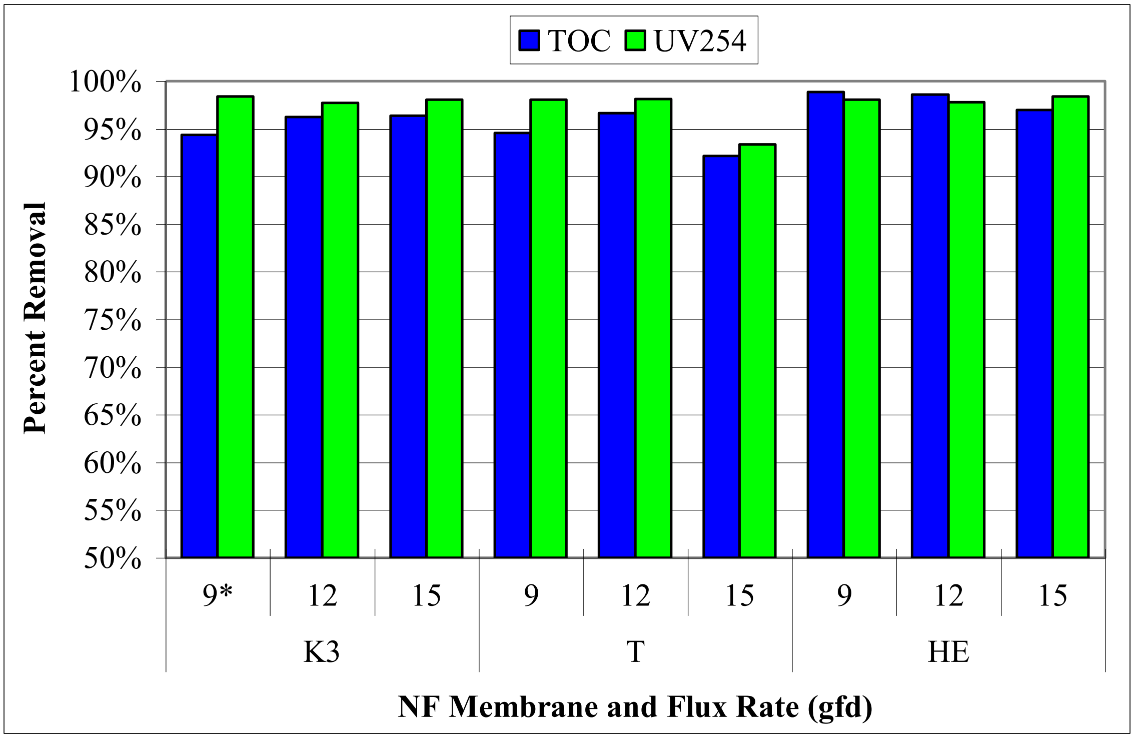


Figure 4.15 – Phase II TOC and UV_{254} Removal with Varying Flux Rates

with an average percent difference of 1.5%. The UV_{254} removal was 98% for all Phase II experiments except for membrane T at 15 gfd. The UV_{254} removal was higher than the TOC removal for a majority of the Phase II samples, which was equivalent to Phase I.

4.4.2. Disinfection By-Product Results

As a consequence of providing substantial DBP precursor removal, the Phase II membrane permeates were shown to contain very few DBPs. Although written in Table 4.6, the feed water to permeate SDS-TTHM and SDS-HAA5 percent removals are also shown in Figures 4.16 and 4.17, respectively. As explained previously, the feed water blend required 87% reduction of TTHMs in the permeate, as indicated by the bold, red

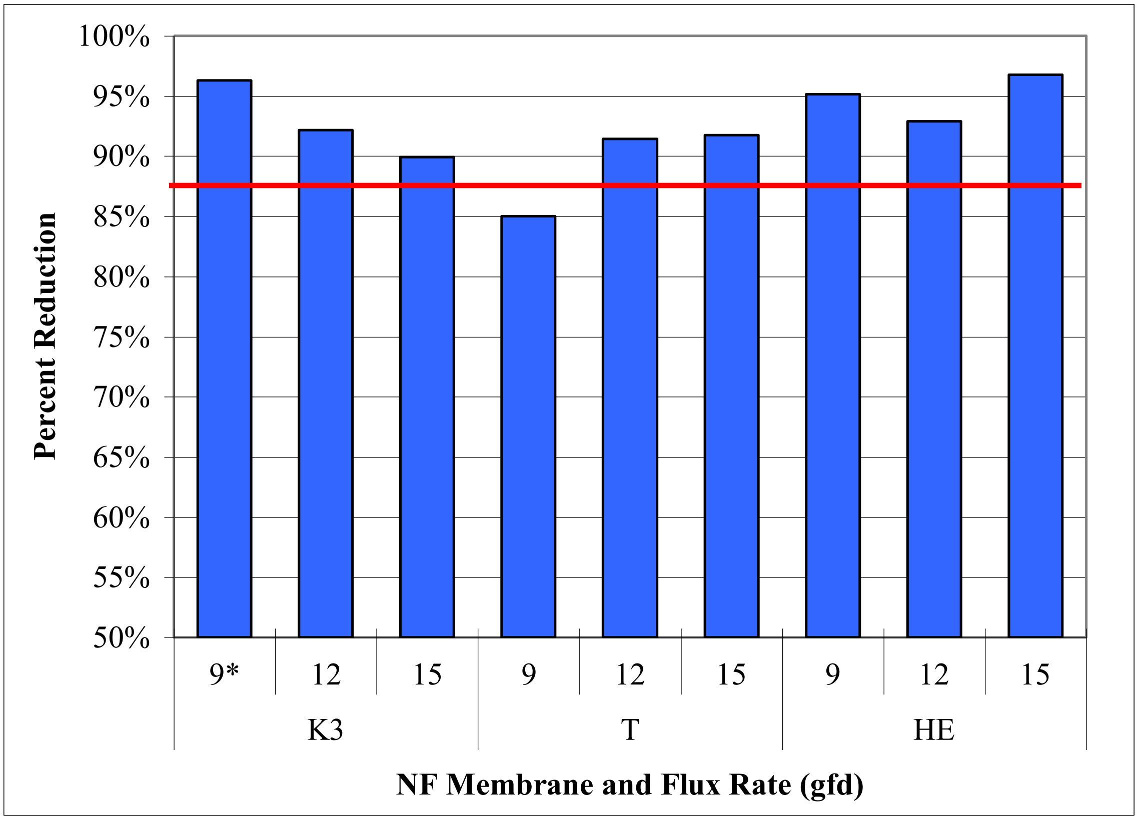


Figure 4.16 – SDS-TTHM Reduction with Varying Flux Rates

horizontal line. All membranes satisfy this requirement, except the 9 gfd flux rate for membrane T. This is not consistent with the lowest TOC rejection observed at 15 gfd for membrane T. Membrane HE had the highest average TTHM reduction at 97% when operated at the 15 gfd flux rate.

Based on the TTHM results, the use of Koch TFC-SR3 (K3), Trisep XN45-TSF (T), and Hydranautics ESNA1-LF (HE) membranes can sufficiently reduce DBP precursors to assure compliance with the D/DBP rule, when operated properly. The selection of either Koch TFC-SR3 or Hydranautics ESNA1-LF could be operated at 9, 12, or 15 gfd flux rate as each of these settings provide more TTHM removal than the

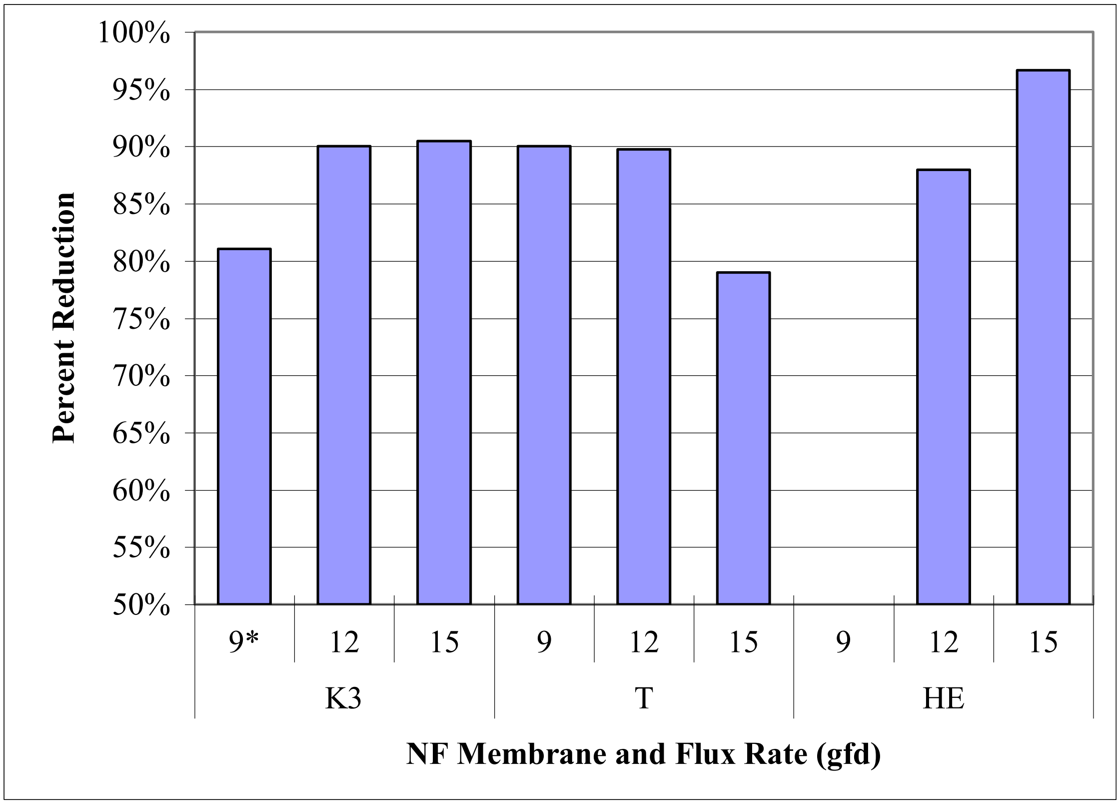


Figure 4.17 – SDS-HAA5 Reduction with Varying Flux Rates

87% reduction requirement to create a blended water that will comply with the D/DBP rule. The selection of Trisep XN45-TSF could be operated at 12 or 15 gfd flux rate to provide more TTHM removal than the 87% reduction requirement.

Similar to the high SDS-TTHM reductions, the SDS-HAA5 reductions were all above 79%. The highest HAA5 reduction (97%) was exhibited during the 15 gfd flux setting for membrane HE. The permeate HAA5 sample obtained during the 9 gfd flux rate for membrane HE was not valid, due to preservation error, for use in this comparison and was omitted.

The Phase II, 12 gfd flux rate, results for TTHM and HAA5 correlated well with the Phase I results. All three selected membranes exhibited over 90% reduction of TTHM during both Phases. During both tests membrane T exhibited slightly lower reductions than membrane K3 or HE. The HAA5 results were analogous having approximately 90% reduction for all membranes, while membrane HE exhibited slightly lower reductions. Although no HAA5 removal is required for the blended water, membrane permeate with substantial HAA5 removal is desirable.

4.4.3. Chlorine Residual Decay

The removal of TOC also affected the amount of chlorine decay during the SDS-TTHM and SDS-HAA5 tests performed on feed water and permeate. The feed water averaged 0.63 mg/L of free chlorine depletion during the 3-day incubation period, while permeate samples from the NF membranes were all much lower. As shown in the chlorine decay data in Appendix C, the average chlorine decay from membrane K3 was 0.09 mg/L during the three day test. Membrane T and membrane HE permeate exhibited chlorine demands of 0.10 and 0.16 mg/L respectively.

The application of a NF membrane system for WMU would offer substantial chlorine savings compared to an equivalent capacity conventional softening process. The lower ammonia concentration in NF permeate will require less initial chlorine for breakpoint chlorination. Additionally, the lower dose is complimented with a longer lasting residual free chlorine.

4.4.4. Performance of Membranes with Varying Flux Rate

The 21-element pilot plant was operated at 9, 12, and 15 gfd flux rates to determine the optimum system flux. The analysis of specific flux, constituent rejections, and concentrate TDS concentrations was done to determine the optimum settings for the three selected membranes.

In the literature, it was noted that a higher SF provides a more energy efficient treatment process that will save money with yearly operation costs when compared to membranes of lower SF. According to Figure 4.14, the adjusted specific flux decreases with increasing flux rates. There is a trade-off between specific flux and capital cost, as spending more capital may pay for itself during the design life. Operating the system at a higher flux, like 15 gfd, would require a lower capital cost than operating at lower flux rates of 9 or 12 gfd. Based on optimum SF, the membranes rank (in descending order) membrane T, HE, K3. For membrane HE and K3 the SF did not decrease when the flux was increased to 12 gfd, therefore the 12 gfd flux setting was most efficient.

The variation of flux rates also impacted the performance of permeate water quality. The TOC rejection shown in Figure 4.15 illustrates that membrane K3 exhibits an increasing rejection with increasing flux, membrane T does not exhibit a trend, and membrane HE exhibits a decreasing rejection with increasing flux. These trends appear membrane specific with possible correlations to the individual membrane characteristics. Without detailed information about each membrane's surface roughness or electrostatic charge, no further conclusions may be made.

The variation of flux with DBPs was shown previously in Figures 4.16 and 4.17 for TTHM and HAA5 respectively. The increasing flux rate for membrane K3 exhibited decreasing TTHM reduction, but increasing HAA5 reduction. Membrane T exhibited opposite trends from membrane K3, as the TTHM reduction was increasing, and the HAA5 was decreasing, with increasing flux rates. Membrane HE had no trend for TTHM reduction, but did exhibit an increasing trend for HAA5. Theoretically, as the organic matter was rejected through steric size exclusion and electrostatic repulsion, the Donnan effect reduces NOM rejection for negatively charged membranes. Therefore, at higher flux rates, when the membrane is rejecting more organic material, the Donnan effect permits some organic material to permeate. This trend was observed for membrane HE's TOC rejection, but not for DBP reduction. The DBP reduction trends may not be fully representative of the actual performance as feed water quality fluctuated and the laborious simulated distribution system testing may introduce error which may negate any trends exhibited.

The free ammonia rejection is displayed in Figure 4.18 for each tested flux rate. The membranes each exhibit increasing rejection with increasing flux rate. The highest rejection observed was for membrane HE operating at a flux rate of 15 gfd. The lowest rejection was observed during the 9 gfd flux setting for membrane T. These results correspond to the literature, which states how the increasing flow of permeate water dilutes the constant flux of permeating ammonia ions.

The permeate water quality characteristics of pH, hardness, and alkalinity values are listed in Appendix C. The pH values from Phase II are not comparable because acid

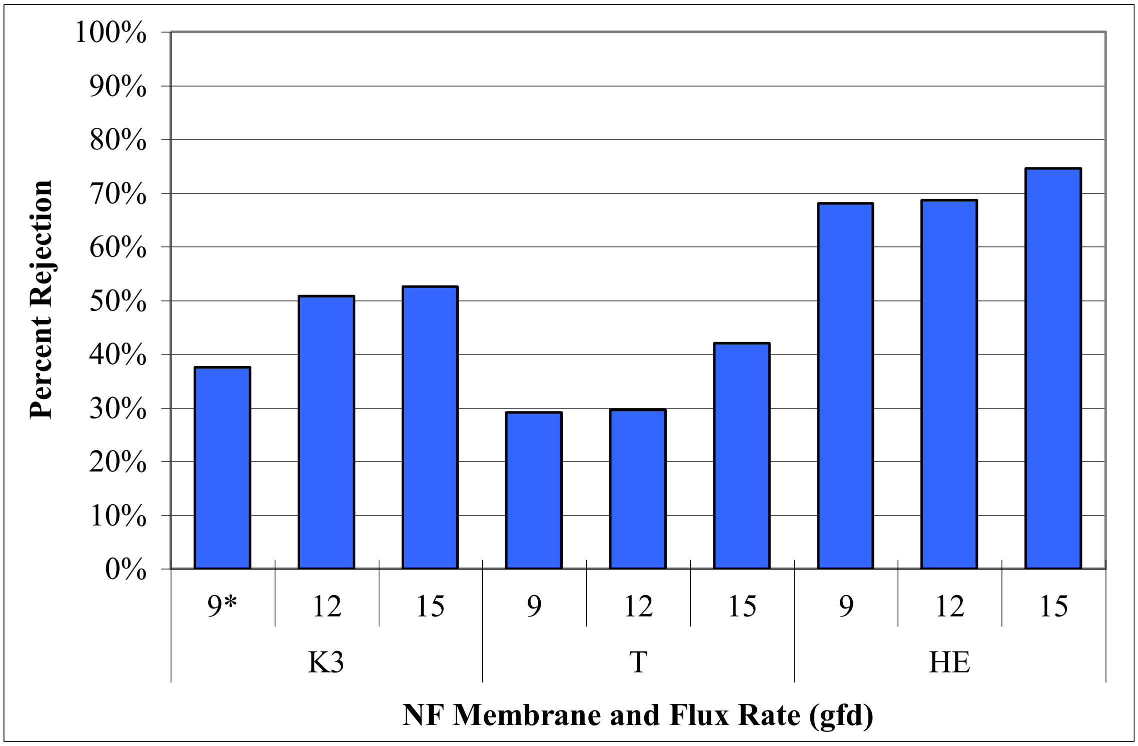


Figure 4.18 – NH_3-N Removal with Varying Flux Rates

was dosed for pH adjustment at variable rates. The total hardness values for membrane K3 and T correspond well to the Phase I results, however membrane HE exhibited significantly lower permeate concentrations. The average feed water total hardness concentration of 154 mg/L as $CaCO_3$ was reduced to less than 68 for all membranes, but membrane HE permeate exhibited almost undetectable hardness. The calcium hardness paralleled the total hardness concentration as calcium comprised a majority of the remaining hardness. The alkalinity rejections for Phase I and II correspond well together and are analogous to the hardness removals, as membrane HE and K3 removed a significant portion (~80%) while membrane T removed about 30%. The removal of hardness and alkalinity is not desirable, as it may promote corrosive water or require post treatment processes. In general, the removal of hardness and alkalinity were unaffected by changes in flux.

Permeate conductivity readings are also listed in Appendix C, these readings correspond between Phase I and Phase II as illustrated by Figure 4.19. The shaded box between 400 and 475 µS/cm represents the variable feed water concentration. The permeate conductivity values were from Phase I during 80% recovery, and from Phase II at 85% recovery; both were at 12 gfd flux rate. No trend was established with varying flux rates. The permeate conductivity appeared to trend up or down more with varying feed water conductivity rather than flux variations. The conductivity readings represent the dissolved ions in the water, often measured by the TDS concentration. The use of conductivity values provided a quick and simple check to the system's performance. To

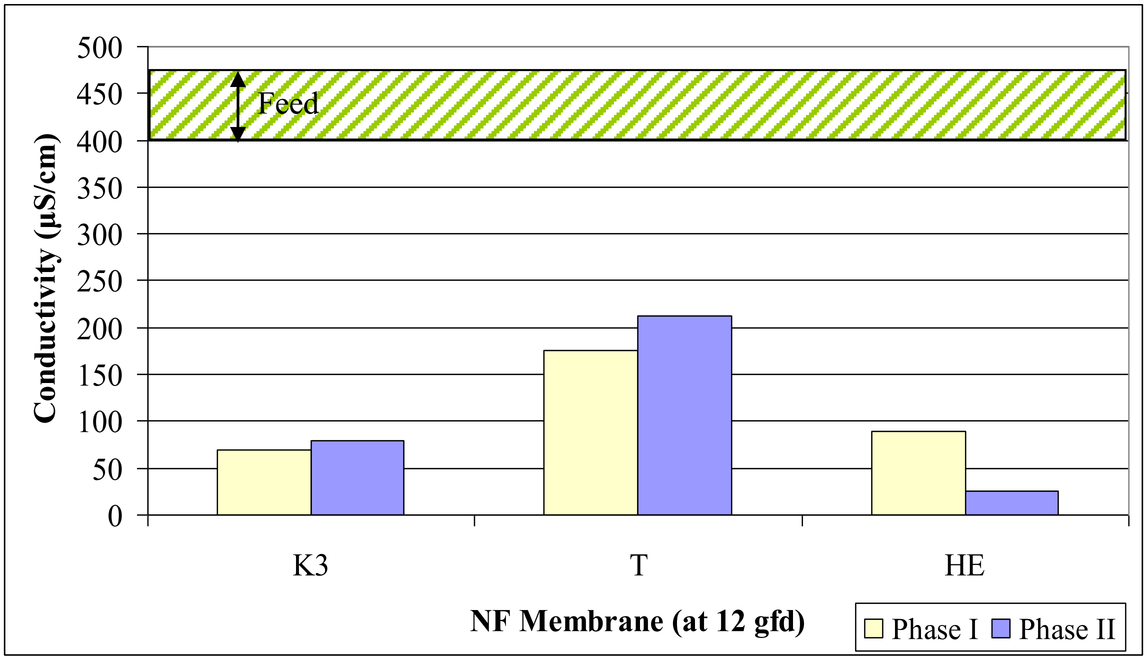


Figure 4.19 – Phase I and II Permeate Conductivity Values

properly evaluate the surrogate values, a conductivity to TDS correction factor was established. The literature suggests that the permeate, feed water, and concentrate each possess their own respective correction factor due to the varying ionic strengths of each sample. The experimental data support the literature, exhibiting a higher correction factor for concentrate than permeate.

The concentrate TDS concentration variation with increasing flux is not apparent for membranes K3 and T. However, membrane HE exhibits an increasing concentrate TDS concentration with increasing flux. Figure 4.20 illustrates the concentrate TDS for each membrane at varying flux rates.

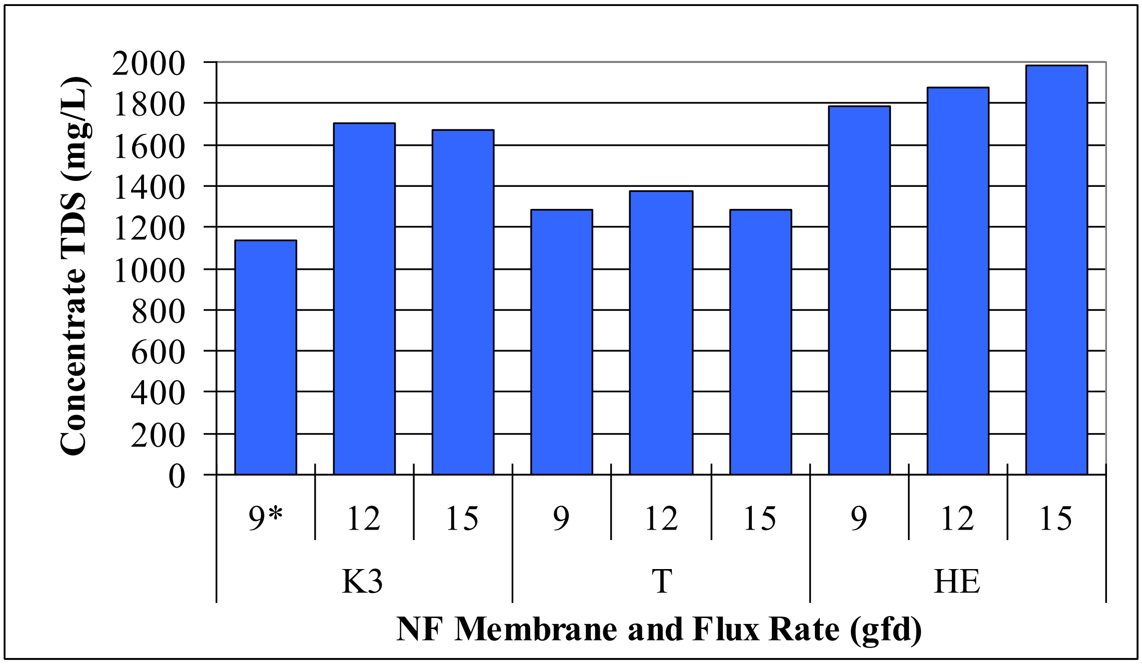


Figure 4.20 – Concentrate TDS with Varying Flux Rates

The water quality of the blended water for Phase II is shown in Table 4.7. When compared to the NF feed water and the NF permeate water quality, found in Appendix C, the blend was usually close to the weighted average of the combined blend. pH values deviated from the weighted average because they were dependent on alkalinity. The blend consisted of 44 parts NF permeate and 56 parts NF feed water (filter effluent). At 12 gfd flux rate, the feed water for membrane T contained an average of 35 µg/L TTHM and the permeate contained an average of 3 µg/L TTHM. After blending the two samples, the TTHM concentration was 29 µg/L. The blended water quality TTHM never exceeded the Stage 2 D/DBP Rule limit of 80 µg/L because the feed water was not above the TTHM MCL.

Table 4.7. 44/56 Blend of NF Permeate with Filter Effluent

Membrane	Flux (gfd)	Calcium (mg/L $CaCO_3$)	Alkalinity (mg/L $CaCO_3$)	pH	Ammonia (mg/L)	TTHM (µg/L)	HAA5 (µg/L)
K3	9*	47	23	8.67	0.58	24.6	28
	12	53	20	8.48	0.43	22.2	20
	15	48	28	8.93	0.43	19.7	13
T	9	40	28	8.83	0.45	22.0	17
	12	52	41	8.72	0.46	29.0	21
	15	56	33	8.65	0.42	22.8	17
HE	9	36	29	8.98	0.34	19.0	N/A
	12	32	20	8.98	0.34	18.0	29
	15	38	33	8.79	0.36	19.7	21

4.4.5. Phase II Fouling Study

Membranes HE and T were each tested in the Phase II pilot plant for 30 days to determine if fouling would significantly decrease membrane productivity. The literature suggested if a membrane were to exhibit fouling, there would be indicators within the first month. These indicators would be increased pressure, decreased flow, and increased head losses through the pressure vessel. The literature also indicated permeate quality may have higher rejections due to the pore blocking from foulant material.

Figure 4.21 shows the adjusted specific flux over the 30 days for both membrane

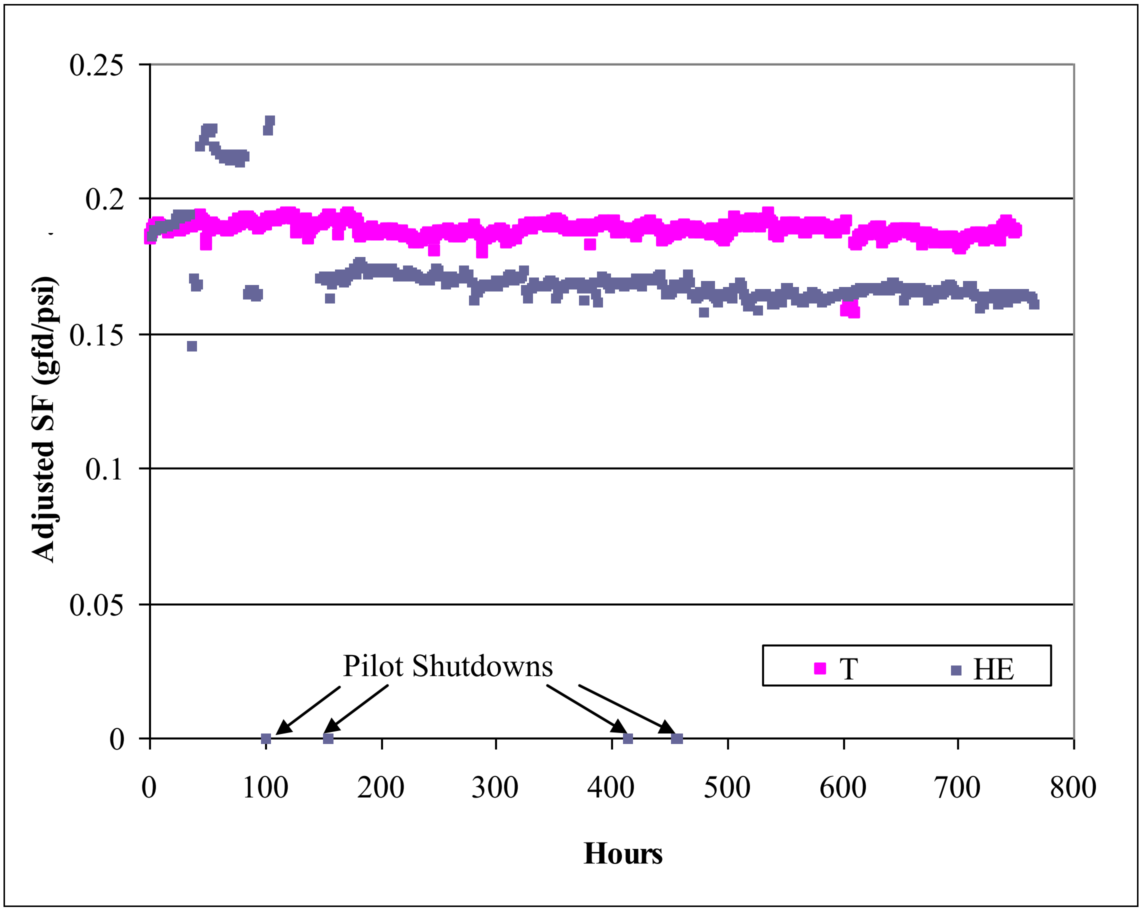


Figure 4.21 – Adjusted Specific Flux During 30-day Fouling Test

T and membrane HE. The data for membrane HE is not consistent until about 150 hours into the test. These inconsistencies were caused by pilot plant malfunctions independent of the test. Additionally, there are points plotted showing zero SF at approximately 100, 150, 410, and 450 hours. These zeros indicate data collected when the pilot plant was shut down during filter backwashing. Although the pilot plant may have been temporarily shut down more often than shown, not all shutdowns were recorded because the data was only logged every two hours.

Analysis of the fouling data indicates that neither membrane exhibited fouling to reach the 15% flux decline recommended by the manufacturer to initiate a cleaning cycle. Membrane T exhibited an average adjusted SF of 0.19 gfd/psi at the start of the test, which correlates well with previous data observed in Phase II. The average adjusted SF at the end of the 30 days was 0.3% lower than the beginning. This is significantly under the standard 15% to qualify as fouling. Membrane HE exhibited an average starting adjusted SF of 0.17 gfd/psi once the data were stable. The data at the end of the test shows an adjusted SF of 0.16, equating to a 5.2% decrease. The specific flux decline for membrane HE is also under the 15% guideline, and is not classified as significant fouling. Over a longer fouling test, both membranes would likely exhibit fouling and require a chemical clean, however the information provided in this research is not sufficient to extrapolate information about future data.

An analysis of membrane HE permeate after the 30 day fouling test indicated slightly lower permeate TOC concentrations, but the water quality parameters of UV_{254}, TDS, hardness, and alkalinity were mostly unchanged, indicating low levels of fouling.

The permeate conductivity for membranes T and HE have been plotted in Figure 4.22. The permeate conductivity for membrane T appears to increase slightly from around 150 µS/cm to around 180 µS/cm. Fouling would be noted with a decrease of permeate conductivity, therefore no fouling has occurred. Membrane HE permeate conductivity remained stable at around 30 µS/cm throughout the fouling test.

Water temperatures during the fouling test were the coldest of the entire study. Membrane T was exposed to water temperatures ranging from 10 to 11.5 °C, while membrane HE was exposed to water temperatures ranging from 8.5 to 10 °C. Although the membrane may have experienced fouling, some of the flux decline may be caused by

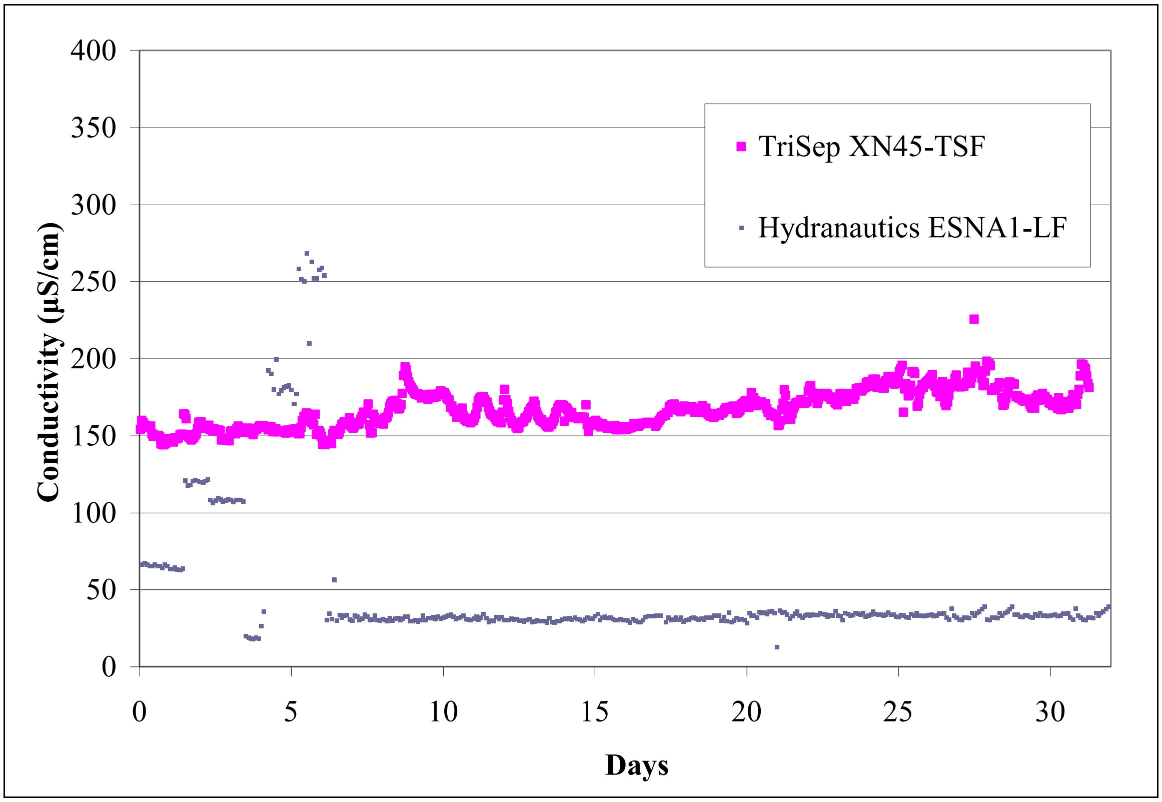


Figure 4.22 – NF Permeate Conductivity During 30-Day Fouling Test

an inaccurate temperature correction constant provided by the manufacturer, which may under estimate the performance at low temperatures.

CHAPTER FIVE – CONCLUSIONS AND RECOMMENDATIONS

5.1. Conclusions

Based on preliminary water quality data the existing water treatment plant effluent has the potential to form total trihalomethanes (TTHM) of 120 μg/L. Watertown Municipal Utilities desired alternative solutions to maintain compliance with the Stage 2 Disinfectant/Disinfection By-Product Rule. Chloramination, utilizing the naturally occurring free ammonia in Watertown Municipal Utilities' ground water source, was compared against the existing breakpoint chlorination process. Additionally, nanofiltration was extensively evaluated to select and establish optimum settings for design.

A blend of 44% nanofiltration permeate and 56% by-passed filter effluent was established to assure compliance with the Stage 2 Disinfectant/Disinfection By-Products Rule. The blend ratio was determined using the maximum potential TTHM of the feed water (120 μg/L) and the desired blend TTHM concentration of less than 80 μg/L TTHM. The calculated nanofiltration permeate TTHM concentration was established at 87% removal because varying feed water conditions caused fluctuating permeate TTHM concentrations.

The performance of six nanofiltration membranes (Koch TFC-SR2, Koch TFC-SR3, Trisep XN45-TSF, Hydranautics ESNA1-LF, Hydranautics HydraCoRe-70pHT, and Dow/Filmtec NF270) were evaluated using two phases of testing, a single element screening phase and a multi element pilot test with three of the selected membranes.

Filter effluent of conventionally softened ground water was applied to the membranes to determine which membrane would provide the lowest total trihalomethane permeate, while discharging a concentrate containing total dissolved solids below 1000 mg/L. The lowest permeate total trihalomethane concentration was desirable to maximize the blend of 44% permeate water, and 56% by-passed filter effluent. To assure the desired blend ratio complied with the Stage 2 Disinfectant/Disinfection By-Products Rule, 87% TTHM removal was required.

Phase I utilized a single element pilot plant set at 15, 50, and 80 percent recovery to facilitate the selection of three membranes for the second stage of testing. Phase II utilized a 21 element two-stage pilot plant set at 85% recovery with varying flux rates of 9, 12, and 15 gfd. The optimum flux setting was determined for each membrane based on adjusted specific flux and disinfection by-product removal. Following the flux testing, a 30-day fouling study was performed on both Trisep XN45-TSF and Hydranautics ESNA1-LF.

The following conclusions were made from the data collected during the experiments.

5.1.1. Preliminary Water Quality Testing

A. The average WTP influent SDI value of 4.2 identifies direct nanofiltration as an alternative treatment. The average filter effluent SDI value of 1.13 identifies the filter effluent as the best source for nanofiltration feed water.

B. Ground water with high TOC and ammonia can be successfully treated with chloramines to reduce DBP formation by 82%. During the chloramination testing the SDS-TTHM concentration was decreased to 10 µg/L. The use of chloramination was a viable alternative to maintain compliance with the D/DBP Rule.

5.1.2. Single Element Pilot

C. Four of the six nanofiltration membranes tested: Koch TFC-SR3, Hydranautics ESNA1-LF, Dow/Filmtec NF270, and Trisep XN45-TSF satisfied 87% TTHM reduction. Higher rejections of TTHM and HAA5 concentrations in the permeate correlated with higher rejections of TOC and UV_{254} rejection at the recoveries tested.

D. Two of the six nanofiltration membranes tested: Trisep XN45-TSF and Hydranautics HydraCoRe-70pHT exhibited concentrate total dissolved solids concentration below 1000 mg/L to satisfy the surface water discharge permit.

E. One of the six nanofiltration membranes tested: Trisep XN45-TSF satisfied both conditions of 87% total trihalomethane reduction and concentrate total dissolved solids below 1000 mg/L. Trisep XN45-TSF was selected as one of three membranes for Phase II analysis.

F. Koch TFC-SR3 and Hydranautics ESNA1-LF were selected for Phase II analysis based on their excellent permeate quality (>96% reduction of total trihalomethanes). However, since no other membranes satisfied the concentrate discharge of 1000 mg/L total dissolved solids limit, this criteria was compromised.

5.1.3. 21-Element Pilot Flux

G. The specific flux exhibited by Trisep XN45-TSF decreased from 0.21 to 0.18 gfd/psi as the flux rate was increased from 9 gfd to 15 gfd. However, the membrane's maximum total trihalomethane removal (92%) was exhibited at the 15 gfd flux rate. The permeate at 15 gfd contained 2.5 μg/L total trihalomethanes.

H. The specific flux exhibited by Hydranautics ESNA1-LF decreased from 0.18 to 0.17 gfd/psi as the flux rate was increased from 9 gfd to 15 gfd. However, the membrane's maximum total trihalomethane removal (97%) was exhibited at the 15 gfd flux rate. The permeate at 15 gfd contained 1.1 μg/L total trihalomethanes.

I. The specific flux exhibited by Koch TFC-SR3 decreased from 0.14 to 0.13 gfd/psi as the flux rate was increased from 9 gfd to 15 gfd. The membrane's maximum total trihalomethane removal (96%) was also exhibited at the 9 gfd flux rate. The permeate at 9 gfd contained 1.5 μg/L total trihalomethanes.

J. The specific flux was observed to decrease with increasing flux rate for all three membranes.

K. The optimum setting is a complex matrix of highest specific flux, highest flux, highest rejections, and lowest capital cost. Without the cost information, a precise optimum setting cannot be established.

L. Membrane selection to assure compliance with the D/DBP Rule would be satisfied by each of the three membranes as indicated by the low permeate TTHM concentrations and greater than 87% reduction of feed water TTHM. The South Dakota Department of Natural and Environmental Resources increased the 1000 mg/L total dissolved solids limitation to 2500 mg/L during this study, allowing the pilot testing to operate at a higher recovery rates. The concentrate TDS of all membranes examined in this pilot phase were less than 2500 mg/L, so the 2500 mg/L limit enables all three membranes to be employed in a full scale system.

M. The design criteria obtained includes: net driving pressure values ranging from 64 – 165 psi, specific flux values ranging from 0.13 – 0.21 gfd/psi, system recovery rate of 85 percent, and permeate water quality TTHM ranging from 1.1 – 2.5 μg/L to assure the blended water meets the TTHM MCL of the D/DBP Rule.

5.1.4. Fouling

N. Based on specific flux and permeate conductivity, no substantial fouling was observed during the 30-day test for either Trisep XN45-TSF or Hydranautics ESNA1-LF. The specific flux did not decrease for Trisep XN45-TSF and only decreased 5.2% for Hydranautics ESNA1-LF. The permeate conductivity was stable, or increasing, throughout the duration of the fouling test.

5.2. Recommendations

It is recommended that the cost information be obtained for each membrane including element prices, piping requirements, and energy demands. Without cost data, Trisep XN45-TSF is recommended for the blend’s ability to satisfy the D/DBP Rule MCL of 80 μg/L total trihalomethanes and maintain a concentrate TDS below 1000 mg/L. Compliance with these criteria require the Trisep XN45-TSF element to operate at 80 percent recovery and 12 gfd. Future experiments and evaluations may be conducted to prove the membrane's ability to increase the flux rate to 15 gfd, 80 percent recovery, provided the concentrate TDS does not exceed 1000 mg/L.

Based on the revised discharge permit, it is recommended that Watertown Municipal Utilities utilize the increased concentrate TDS limit and select Hydranautics ESNA1-LF. This membrane has exhibited better contaminant rejection thus providing more capability to blend at a more cost effective ratio. These recommendations are based on each membrane's performance alone; however the associated costs for each membrane alternative will dictate the final selection.

As a result of this research project, several options are proposed to further expand the success of future pilot plant operations. The following ideas are recommended to further develop the research:

A. During Phase I studies, maintain a consistent source water supply by using the same wells for the duration each test to eliminate water quality variability as a source of error.

B. During Phase I, adjust the pilot plant recovery until each membrane exhibits a concentrate TDS concentrations steady below 1000 mg/L.

C. During Phase II, only select one membrane for the fouling test and continue the test until fouling develops, and then conduct a chemical cleaning to restore the reversible fouling.

D. During Phase II, operate at higher flux rates to maximize the productivity from each membrane, and subsequently develop noticeable fouling.

E. If possible, locate all pilot plant skids indoors with a constant ambient temperature, or provide redundant heat sources if freezing temperatures may occur.

F. When installing the feed water piping, avoid placing a corporation stop on the top side of piping used for filter effluent, especially if the pipe may not be full during filter backwashing.

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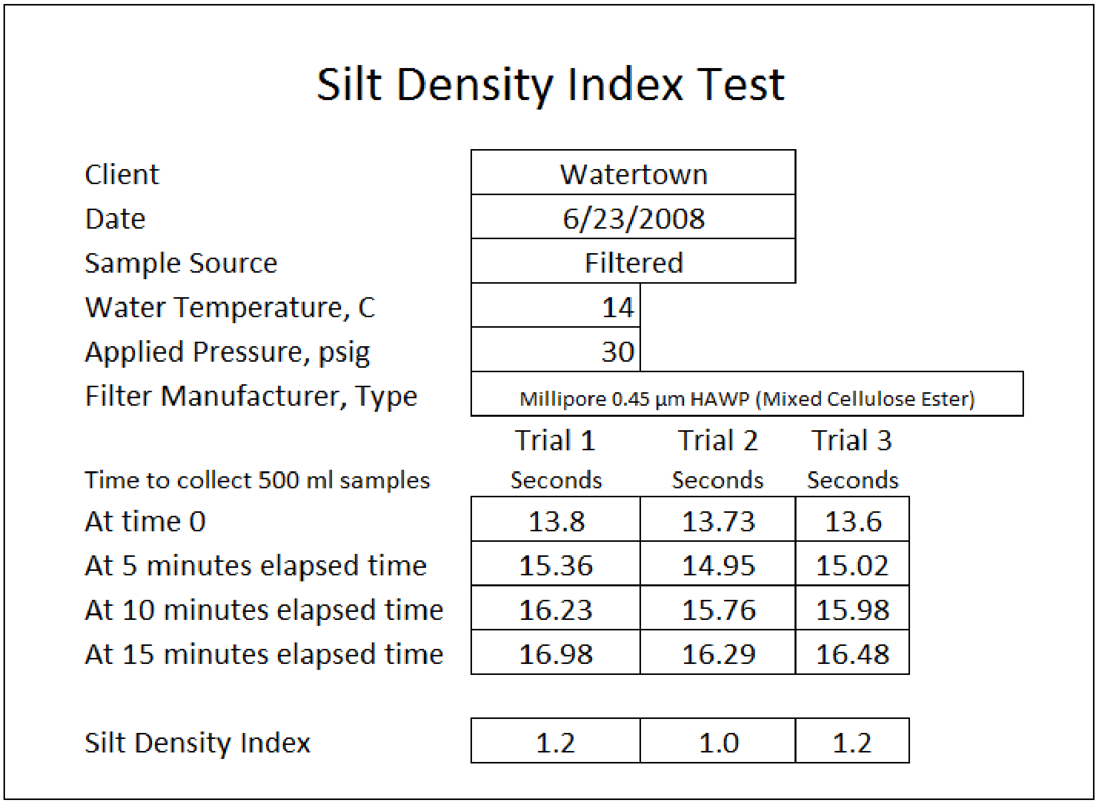
APPENDIX A: Preliminary Water Quality Testing Data



Silt Density Index Test

Client	Watertown
Date	6/23/2008
Sample Source	Filtered
Water Temperature, C	14
Applied Pressure, psig	30
Filter Manufacturer, Type	Millipore 0.45 µm HAWP (Mixed Cellulose Ester)

	Trial 1	Trial 2	Trial 3
Time to collect 500 ml samples	Seconds	Seconds	Seconds
At time 0	13.8	13.73	13.6
At 5 minutes elapsed time	15.36	14.95	15.02
At 10 minutes elapsed time	16.23	15.76	15.98
At 15 minutes elapsed time	16.98	16.29	16.48
Silt Density Index	1.2	1.0	1.2

Figure A.1 – Example of SDI Test Data Sheet

Table A.1. Water Source Analysis

Source	Date		UV_{254} (cm^{-1})		TOC (mg/L)		Free Ammonia (mg/L NH_3-N)
Well 3	6/27/2008		0.036		2.02		0.12
Well 3-A	6/27/2008		0.031		1.81		0.21
Well 10	6/27/2008		0.101		2.09		0.17
Average of Wells 3, 3A, and 10					1.97		0.17
Well 11	7/14/2008		0.256		5.21		1.05
Well 12	7/14/2008		0.286		5.3		0.72
Well 13	7/14/2008		0.319		4.79		0.68
Well 14	7/14/2008		0.227		4.51		0.84
Well 15	7/14/2008		0.384		8.17		0.84
Well 16	7/14/2008		0.236		6.48		1.20
Well 17	7/14/2008		0.338		5.83		0.96
Well 18	7/14/2008		0.235		6.61		0.80
Well 19	7/14/2008		0.343		4.26		0.92
Well 20	7/14/2008		0.081		3.68		0.56
Well 21	7/14/2008		0.359		6.78		1.88
Well 22	7/14/2008		0.213		6.74		2.20
Well 23	7/14/2008		0.397		5.28		2.25
Well 24	7/14/2008		0.428		5.51		1.62
Well 25	7/14/2008		0.355		4.99		2.04
Well 26	7/14/2008		0.409		6.38		2.25
Well 27	7/14/2008		0.298		6.96		2.35
Well 28	7/14/2008		0.360		6.38		1.88
Average of Wells 11-28					5.77		1.39
Raw Plant - Influent	6/24/2008		0.198		6.07		1.12
	7/14/2008		0.313		5.66		0.93
Filter 6 - Effluent	6/24/2008		0.078		3.96		0.82
	7/15/2008		0.076		3.92		1.05

Table A.2. Filter Effluent Water Quality – Phase I

Parameter	Maximum	Minimum	Average
pH	9.72	9.20	9.51
TDS (mg/L)	260	237	248
Conductivity (µS/cm)	414	372	391
Total Hardness (mg/L $CaCO_3$)	170	136	146
Alkalinity (mg/L CaCO3)	70	23	48
TOC (mg/L)	3.64	2.89	3.35
UV_{254} (cm^{-1})	0.166	0.048	0.074
Ammonia (mg/L NH_3-N)	1.2	0.56	0.74
SDS-THM (µg/L)	82	53	61
SDS-HAA (µg/L)	72	28	53

Table A.3. Filter Effluent Water Quality – Phase II

Parameter	Maximum	Minimum	Average
pH	8.99	8.68	8.80
TDS (mg/L)	306	227	272
Conductivity (µS/cm)	436	402	419
Total Hardness (mg/L $CaCO_3$)	166	142	154
Calcium Hardness (mg/L CaCO3)	100	83	90
Alkalinity (mg/L CaCO3)	44	38	41
TOC (mg/L)	3.04	2.6	2.83
UV_{254} (cm^{-1})	0.061	0.044	0.052
Ammonia (mg/L NH_3-N)	0.78	0.59	0.70
SDS-THM (µg/L)	46	24	33
SDS-HAA (µg/L)	58	21	37

APPENDIX B: Phase I Pilot Plant Data

Table B.1. Average Water Quality Concentrations in Feed Water and Permeate

Sample Label	**% Recovery**	**Feed TOC mg/L**	**Permeate TOC mg/L**	**Feed UV_{254} cm^{-1}**	**Permeate UV_{254} cm^{-1}**	**Feed NH_3-N mg/L**	**Permeate NH_3-N mg/L**
K2	15	3.32	0.25	0.063	0.005	1.02	0.75
	50	4.42	0.65	0.085	0.006	1.02	0.78
	80	8.16	0.86	0.154	0.018	1.20	0.96
K3	15	3.27	0.15	0.061	0.002	0.73	0.30
	50	3.80	0.09	0.069	0.001	0.82	0.48
	80	11.00	0.19	0.190	0.003	0.66	0.27
T	15	3.49	0.24	0.069	0.003	0.69	0.41
	50	6.11	1.33	0.103	0.005	0.76	0.54
	80	12.67	0.95	0.227	0.006	0.48	0.40
HE	15	2.89	0.19	0.048	0.003	0.66	0.43
	50	4.26	1.61	0.077	0.020	0.80	0.52
	80	11.56	0.78	0.208	0.005	0.62	0.32
HH	15	3.55	0.54	0.064	0.006	0.60	0.58
	50	6.25	0.66	0.114	0.008	0.60	0.60
	80	10.25	0.88	0.186	0.014	0.78	0.67
DF	15	3.55	0.04	0.072	0.002	0.71	0.38
	50	5.33	0.12	0.103	0.006	0.54	0.42
	80	12.83	0.22	0.237	0.005	0.45	0.30

Note: two samples were collected at each setting

Table B.2. Average Water Quality Concentrations in Feed Water and Permeate

Membrane	**% Recovery**	**Feed TTHM µg/L**	**Permeate TTHM µg/L**	**Feed HAA5 µg/L**	**Permeate HAA5 µg/L**	**Number of Samples Collected**
K2	15	53.0	11.0	63.0	3.2	1
	50	-	9.6	-	16.0	1
	80	-	-	-	-	1
K3	15	54.0	3.6	55.0	3.0	1
	50	-	2.3	-	8.8	1
	80	-	-	-	-	1
T	15	59.0	3.3	40.0	2.0	1
	50	-	11.0	-	4.3	1
	80	-	-	-	-	1
HE	15	58.0	2	28	4.2	1
	50	-	5.2	-	2.7	1
	80	-	-	-	-	1
HH	15	82.0	20.0	56.0	12.0	1
	50	-	21.0	-	13.0	1
	80	-	-	-	-	1
DF	15	72.0	5.4	52.0	1.9	1
	50	-	3.7	-	1.8	1
	80	-	-	-	-	1

Table B.3. Average Water Quality Concentrations in Membrane Permeate

Sample Label	**% Recovery**	**pH**	**Total Hardness mg/L $CaCO_3$**	**Alkalinity mg/L $CaCO_3$**	**Conductivity µS/cm^{-1}**
K2	15	9.81	31	30	133
	50	9.70	32	34	138
	80	9.55	60	49	177
K3	15	9.83	8	10	46
	50	9.75	8	12	53
	80	9.69	10	20	92
T	15	9.56	45	40	150
	50	9.58	46	44	167
	80	9.60	59	47	205
HE	15	9.72	6	14	58
	50	9.59	12	14	76
	80	9.48	30	27	121
HH	15	9.80	46	42	168
	50	9.63	68	42	222
	80	9.50	98	44	292
DF	15	9.74	10	16	67
	50	9.58	12	16	83
	80	9.44	20	30	122

Membrane Data Sheets

KOCH
MEMBRANE SYSTEMS

FLUID SYSTEMS® TFC® - SR®2 4" ELEMENT

Low Pressure, Selective Rejection Element

PRODUCT DESCRIPTION

Membrane Chemistry: Proprietary TFC® membrane
Membrane Type: TFC®-SR®2 membrane
Construction: Spiral wound with fiberglass outerwrap
Applications: Separation of higher molecular weight components (>300-400 dalton) and multivalent ions from solution
Feed spacer thickness: N1 element 27 mil (0.7 mm), N2 element 46 mil (1.1 mm)

SPECIFICATIONS

Part Number	Model	Permeate Flow		Rejection %		Membrane Area	
		gpd*	(m^3/d)	Chloride**	$MgSO_4$*	ft^2	(m^2)
8472000	4720 SR®2-N1	3,100	(11.7)	10-30	95	85	(7.9)
8472001	4720 SR®2-N2	2,350	(8.9)	10-30	95	63	(5.8)

* Test Conditions: 5,000 mg/l $MgSO_4$ in deionized water at 95 psi (655kPa) applied pressure, 15% recovery, 77°F (25°C) and pH 7.5.

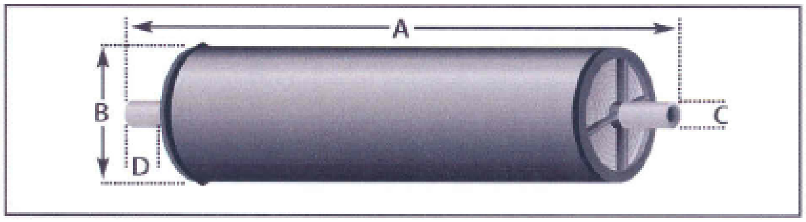
** Test Conditions: 2,000 mg/l NaCl solution at 55 psi (380kPa) applied pressure (50 psi (345 kPa) net pressure), 15% recovery, 77°F (25°C) and pH 7.5.

OPERATING & DESIGN INFORMATION*

Typical Operating Pressure: 50 - 100 psi (345 - 690 kPa)
Maximum Operating Pressure: 500 psi (3447 kPa)
Maximum Operating Temperature: 113°F (45°C)
Maximum Cleaning Temperature: 113°F (45°C)
Maximum Continuous Free Chlorine: <0.1 mg/l
pH Range - Allowable pH - Continuous Operation: 4.0 - 9.0
pH Range - Allowable pH - Clean-in-Place (CIP): 2.0 - 11.0
Maximum Differential Pressure Per Element: 10 psi (69 kPa)
Maximum Differential Pressure Per Vessel: 60 psi (414 kPa)
Maximum Feed Turbidity: 1 NTU
Maximum Feed SDI (15 Minute): 5

* Consult Process Technology Group for specific applications

NOMINAL DIMENSIONS



Model	A	B	C	D	Weight	Part Numbers		
	inches (mm)	inches (mm)	inches (mm)	inches (mm)	lbs (kg)	Interconnector	O-ring	Brine Seal
4720 SR®2-N1	40 (1,016)	4 (101.6)	0.75 (19.0)	1.0 (25.4)	10 (4.5)	0035267	0035458	0035702
4720 SR®2-N2	40 (1,016)	4 (101.6)	0.75 (19.0)	1.0 (25.4)	10 (4.5)	0035267	0035458	0035702

TFC® - SR®2 4" ELEMENT

Performance:

Performance specifications shown on the front side of this document are nominal values. Individual element permeate flows may vary ±20% from the values shown. Minimum rejection to $MgSO_4$ is 93% at the conditions shown.

Selective Rejection (SR®2) nanofiltration membrane performance is highly dependent on water chemistry, temperature, pH and solution concentration. Performance can only be accurately known through pilot study. KMS strongly recommends that the appropriate pilot studies are conducted to determine suitability for a given application.

System operating data should be normalized and key performance parameters tracked using KMS NORMPRO® software.

Operating Limits:

- **Operating Pressure**: Maximum operating pressure is 500 psi (3450 kPa). Typical operating pressure for TFC®-SR2 systems is in the range of 50-100 psi (345-690 kPa). Actual operating pressure is dependent upon system flux rate (appropriate for feed source) as well as feed salinity, recovery and temperature conditions.
- **Permeate Pressure**: Permeate pressure should not exceed feed-concentrate pressure by more than 5 psi (34 kPa) at any time (on-line, off-line and during transition).
- **Differential Pressure**: Maximum differential pressure limits are 10 psi (69 kPa) for a 40" (1,016 mm) long element. Maximum differential pressure for any length pressure vessel is 60 psi (414 kPa).
- **Temperature**: Maximum operating temperature is 113°F (45°C). Maximum cleaning temperature is 113°F (45°C).
- **pH**: Recommended range for continuous operation is pH 4.0-9.0. Allowable range for short term cleaning is pH 2.0-11.0.
- **Turbidity and SDI**: Maximum feed turbidity is 1 NTU. Maximum feed Silt Density Index (SDI 15 minute test) is 5.0. Experience has shown that feedwater with turbidity greater than 0.2 NTU generally results in frequent cleanings.
- **Recovery**: Maximum recovery is site and application specific. In general, single element recovery is approximately 15% for 40" (1,016 mm) long elements. Recovery limits should be determined using KMS ROPRO® program.

Chemical Tolerance:

- **Chlorine**: Exposure of TFC-SR2 membrane to free chlorine or other oxidizing agents such as permanganate, ozone, bromine and iodine is not recommended. TFC-SR2 membrane has a free chlorine tolerance of approximately 1,000 ppm-hours based on testing at 77°F (25°C), pH 8. This tolerance may be significantly reduced if catalyzing metals such as iron are present or if the pH and/or temperature are different. Sodium metabisulfite (without catalysts such as cobalt) is the preferred reducing agent. TFC-SR2 membrane has a chloramine tolerance of approximately 60,000 ppm-hours in the absence of free chlorine based on testing at 77°F (25°C), pH 8.
- **Cationic (Positively Charged) Polymers and Surfactants**: TFC-SR2 membrane may be irreversibly fouled if exposed to cationic (positively charged) polymers or surfactants. Exposure to these chemicals during operation or cleaning is not recommended.

Lubricants:

For element loading, use only approved silicone lubricant, water, or glycerin to lubricate O-rings and brine seals. The use of petroleum-based lubricants or vegetable-based oils may damage the element and void the warranty.

Service and Ongoing Technical Support:

KMS has an experienced staff of professionals available to assist endusers, and OEM's for optimization of existing systems and support with the development of new applications. Along with the availability of supplemental technical bulletins, KMS also offers a complete line of KOCHTREAT® and KOCHKLEEN® RO pretreatment and maintenance chemicals.

Koch Membrane Systems, Inc., www.kochmembrane.com
Corporate Headquarters: 850 Main Street, Wilmington, Massachusetts 01887-3388, USA, Tel. Toll Free: 1-888-677-5624, Telephone: 1-978-694-7000, Fax: 1-978-657-5208
European Headquarters: Koch Chemical Technology Group Ltd., The Granary, Telegraph Street, Stafford ST17 4AT, United Kingdom, Telephone: +44-178-527-2500, Fax: +44-178-522-3149

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KOCH
MEMBRANE SYSTEMS

FLUID SYSTEMS® TFC® - SR®3 4" ELEMENTS

Low Pressure, Selective Rejection Nanofiltration Elements

PRODUCT DESCRIPTION

Membrane Chemistry:	Proprietary TFC® polyamide
Membrane Type:	SR®3 – selective rejection nanofiltration membrane
Construction:	Spiral wound with fiberglass outerwrap
Applications:	Separation of higher molecular weight components (>300-400 dalton) and multivalent ions from various feed solutions
Options:	Feed spacer: 27 mil (standard) or 46 mil (N2)

SPECIFICATIONS*

Part Numbers	Model	Permeate Flow gpd	(m³/d)	Rejection %	Membrane Area ft²	(m²)	Feed Spacer mil (mm)
8472002	TFC® 4720 SR®3	1,500	(5.7)	99.4	85	(7.9)	27 (0.7)
8472005	TFC® 4720 SR®3-N2	950	(3.6)	99.4	63	(5.9)	46 (1.2)

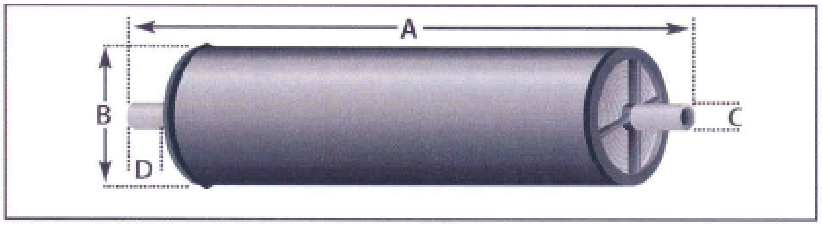
* Test Conditions: 5,000 mg/l $MgSO_4$ in deionized water at 95 psi (655 kPa) applied pressure, 15% recovery, 77°F (25°C), pH 7.5

OPERATING AND DESIGN INFORMATION*

Typical Operating Pressure:	200 - 600 psi (1,400 - 4,150 kPa)
Maximum Operating Pressure:	600 psi (4,150 kPa)
Maximum Operating Temperature:	122°F (50°C)
Maximum Cleaning Temperature:	113°F(45°C)
Maximum Continuous Free Chlorine:	<0.1 mg/L
pH Range – Continuous Operation:	4 - 10
pH Range – Short Term Cleaning:	1.7 - 11.5
Maximum Differential Pressure Per Element:	10 psi (69 kPa)
Maximum Differential Pressure Per Vessel:	60 Psi (414 kPa)
Maximum Feed Turbidity:	1 NTU
Maximum Feed SDI (15 Minute):	5

* Consult KMS Process Technology for specific applications.

NOMINAL DIMENSIONS



Model	A inches (mm)	B inches (mm)	C inches (mm)	D inches (mm)	Weight lbs (kg)	Part Numbers Interconnector	O-ring	Brine Seal
4720 SR3®	40.0 (1,016)	3.9 (99.1)	0.75 (19.0)	1.0 (25.4)	9.0 (4.1)	0035267	0035458	0035702
4720 SR3®-N2	40.0 (1,016)	3.9 (99.1)	0.75 (19.0)	1.0 (25.4)	9.0 (4.1)	0035267	0035458	0035702

TFC® - SR®3 4" ELEMENTS

Performance:

Performance specifications shown on the front side of this document are nominal values. Individual element permeate flows may vary +20/-15% from the values shown. Minimum hardness rejection is 99% at the conditions shown.

Selective Rejection (SR®3) nanofiltration membrane performance is highly dependent on water chemistry, temperature, pH, and solution concentration. Performance can only be accurately known through pilot study. KMS strongly recommends that the appropriate pilot studies be conducted to determine suitability for a given application.

System operating data should be normalized and key performance parameters tracked using KMS NORMPRO® software.

Operating Limits:

- **Operating Pressure**: Maximum operating pressure is 600 psi (4,150 kPa). Typical operating pressure for TFC®-SR3 systems is in the range of 200 psi (1,400 kPa) to 600 psi (4,150 kPa). Actual operating pressure is dependent upon system flux rate (appropriate for feed source) as well as feed salinity, recovery, and temperature conditions.
- **Permeate Pressure**: Permeate pressure should not exceed feed-concentrate pressure by more than 5 psi (34 kPa) at any time (on-line, off-line, and during transition).
- **Differential Pressure**: Maximum differential pressure limit is 10 psi (69 kPa). Maximum differential pressure for any length pressure vessel is 60 psi (414 kPa).
- **Temperature**: Maximum operating temperature is 122°F (50°C). Maximum cleaning temperature is 113°F (45°C).
- **pH**: Recommended range for continuous operation is pH 4-10. Allowable range for short-term cleaning is pH 1.7-11.5.
- **Turbidity and SDI**: Maximum feed turbidity is 1 NTU. Maximum feed Silt Density Index (SDI) is 5.0 (15-minute test). Experience has shown that feedwater with turbidity greater than 0.2 NTU generally results in frequent cleanings.
- **Recovery**: Maximum recovery is site and application specific. In general, single-element recovery is approximately 15% for 40" (1,016 mm) long elements. Recovery limits should be determined using the KMS ROPRO® program.

Chemical Tolerance:

- **Chlorine**: Exposure of SR3 membrane to free chlorine or other oxidizing agents such as permanganate, ozone, bromine and iodine is not recommended. SR3 membrane has a free chlorine tolerance of approximately 2,000 ppm-hours based on testing at 77°F (25°C), pH 8. This tolerance may be significantly reduced if catalyzing metals such as iron are present or if the pH and/or temperature are different. Sodium metabisulfite (without catalysts such as cobalt) is the preferred reducing agent. SR3 membrane has a chloramine tolerance of approximately 60,000 ppm-hours in the absence of free chlorine based on testing at 77°F (25°C), pH 8.
- **Cationic (Positively Charged) Polymers and Surfactants**: SR3 membrane may be irreversibly fouled if exposed to cationic (positively charged) polymers or surfactants. Exposure to these chemicals during operation or cleaning is not recommended.

Lubricants:

For element loading, use only approved silicone lubricant, water, or glycerin to lubricate O-rings and brine seals. The use of petroleum-based lubricants or vegetable-based oils may damage the element and void the warranty.

Service and Ongoing Technical Support:

KMS has an experienced staff of professionals available to assist endusers and OEM's for optimization of existing systems and support for development of new applications. KMS also offers a complete line of KOCHTREAT® and KOCHKLEEN® RO pretreatment and maintenance chemicals.

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PRODUCT SPECIFICATION

4" XN45 Nanofiltration Element Series

Model	Permeate flow GPD (m3/day)*	Average Salt Rejection (%)	Minimum Salt Rejection (%)
4040-XN45-TSF	2,000 (7.0)	95.00	92.00

Performance is based on the following test conditions: 2,000.0 ppm $MgSO_4$, 110.0 psi, 25°C, 15% recovery, pH 8.0, 30 minutes operation.

OPERATIONAL AND DESIGN DATA

Membrane Type	XN45 Polyamide Advanced Nanofiltration Membrane
Configuration	Spiral Wound,Fiberglass Outer Wrap
Active Membrane Area	85 ft² (7.9 m²)
Recommended Applied Pressure	40 - 200 psi (3 - 14 bar)
Maximum Applied Pressure	600 psi (41 bar)
Recommended Operating Temperature	35 - 113°F (2 - 45°C)
Feedwater pH Range	2 - 11 continuous
Chlorine Tolerance	0.5 ppm nominal, 1.0 ppm max
Maximum Feed Flow	20 GPM (4.5 m3/hr)
Minimum Brine Flow/Permeate Flow Ratio	5:1
Maximum SDI (15 minutes)	5.0
Maximum Turbidity	1 NTU

Element Weight : 15 (7)
Length (A) : 40.0 (1,016) Diameter (B) : 4.0 (101) Permeate Tube (C) : 0.75 (19.1)
Units in pounds and inches, units in paranthesis in kilograms and millimetes.
Mechanical Configuration: Filmtec Style Core Tube
Feed Spacer: 0.031" thick diamond spacer

* Permeate flow is clean water flux at standard conditions above. Not applicable for all feedwater conditions. Individual element's permeate flow may vary +/- 15%.

Engineered Membrane

SOLUTIONS

HYDRANAUTICS
High Performance Membrane Products
A NITTO DENKO CORPORATION

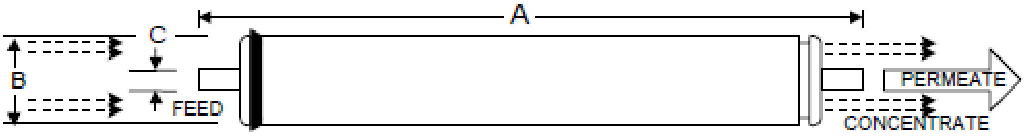
Membrane Element ESNA1-4040

Performance:	Permeate Flow:	2,100 gpd (8.0 m^3/d)
	Salt Rejection (average):	90 %
Type	Configuration:	Spiral Wound
	Membrane Polymer:	Composite Polyamide
	Nominal Membrane Area:	85 ft^2
Application Data	Maximum Applied Pressure:	600 psig (4.16 MPa)
	Maximum Chlorine Concentration:	< 0.1 PPM
	Maximum Operating Temperature:	113 °F (45 °C)
	Feedwater pH Range:	3.0 - 10.0
	Maximum Feedwater Turbidity:	1.0 NTU
	Maximum Feedwater SDI (15 mins):	5.0
	Maximum Feed Flow:	16 GPM (3.6 m^3/h)
	Minimum Ratio of Concentrate to Permeate Flow for any Element:	5:1
	Maximum Pressure Drop for Each Element:	10 psi

Test Conditions

The stated performance is initial (data taken after 30 minutes of operation), based on the following conditions:

500 PPM NaCl solution
75 psi (0.53 MPa) Applied Pressure
77 °F (25 °C) Operating Temperature
15% Permeate Recovery
6.5 - 7.0 pH Range



A, inches (mm)	B, inches (mm)	C, inches (mm)	Weight, lbs. (kg)
40.00 (1016)	3.95 (100.3)	0.75 (19.1)	8 (3.6)

Core tube extension = 1.05" (26.7 mm)

Notice: Permeate flow for individual elements may vary + or - 15 percent. All membrane elements are supplied with a brine seal, interconnector, and o-rings. Elements are enclosed in a sealed polyethylene bag containing less than 1.0% sodium meta-bisulfite solution and 10% propylene glycol, and then packaged in a cardboard box. All elements are guaranteed 80.0% minimum rejection.

HYDRANAUTICS
High Performance Membrane Products
A NITTO DENKO CORPORATION

QUALSEP HYDRACoRe 70 pHT

High flux, 720 Dalton MWCO thin-film, chlorine resistant Nanofiltration membranes designed specifically for color removal; and acid, caustic, and other chemical reclamation by rejecting color, proteins, fats, oils, and other macromolecular species.

Products & Guidelines:

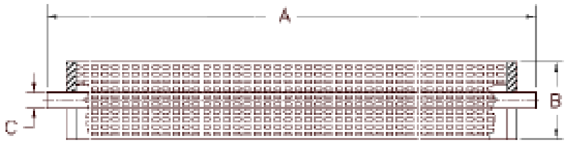
Model	Feed Spacer, inches (cm)	Area, ft2 (m2)	Dimensions, inches. (cm)			Feed Flow, GPM (m3/hr)	Max. Pressure Drop per Element, psi (bar)
			A	B	C		
HYDRACoRe 70pHT-4	0.046 (0.12)	70 (6.4)	40.0 (102)	3.98 (10.1)	0.75 (1.9)OD	30 (6.8)	15 (1.0)
HYDRACoRe 70pHT	0.046 (0.12)	275 (25)	40.0 (102)	7.90 (20.1)	1.125 (2.9)ID	80 (18.2)	15 (1.0)

Type

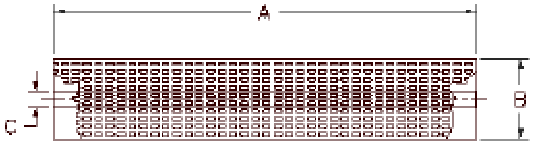
Configuration:	Sanitary Spiral Wound
Membrane Polymer:	Sulfonated Polyethersulfone

Application Data

Maximum Applied Pressure:	600 psig (bar)
Maximum Chlorine Concentration:	200 PPM
Maximum Operating Temperature:	158°F (70 °C)
Operating pH Range:	1 - 13.5
Cleaning pH Range:	1 - 13.5
Maximum Pressure Drop for a vessel	60 psi (4 bar)



4040



8040 (w/atds)

Notice: Elements are vacuum sealed in a polyethylene bag containing less than 1.0% sodium meta-bisulfite solution, and then packaged in a cardboard box. Hydranautics believes the information and data contained herein to be accurate and useful. The information and data are offered in good faith, but without guarantee, as conditions and methods of use of our products are beyond our control. Hydranautics assumes no liability for results obtained or damages incurred through the application of the presented information and data. It is the user's responsibility to determine the appropriateness of Hydranautics' products for the user's specific end uses.

08/29/05

Product Information

FILMTEC™ Membranes

FILMTEC NF270 Nanofiltration Elements for Commercial Systems

Features

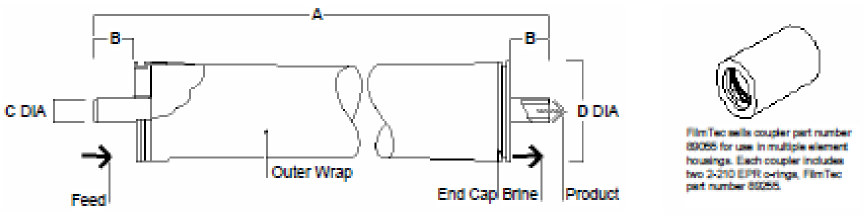
The FILMTEC™ NF270 membrane elements are ideal for removing a high percentage of TOC and THM precursors with medium to high salt passage and medium hardness passage. The FILMTEC NF270 membrane is an ideal choice for surface water and ground water where good organic removal is desired with partial softening.

Product Specifications

Product	Part Number	Active Area ft^2 (m^2)	Applied Pressure psig (bar)	Permeate Flow Rate gpd (m^3/d)	Stabilized Salt Rejection (%)
NF270-2540	149986	28 (2.6)	70 (4.8)	850 (3.2)	>97.0
NF270-4040	149987	82 (7.6)	70 (4.8)	2,500 (9.5)	>97.0

1. Permeate flow and salt rejection based on the following test conditions: 2,000 ppm $MgSO_4$, 77°F (25°C) and 15% recovery at the pressure specified above.
2. Permeate flows for individual NF270-2540 elements may vary by -20% / +30%. NF270-4040 individual elements may vary -15% / +50%.
3. Developmental products available for sale.

Figure 1



FilmTec sells coupler part number 89055 for use in multiple element housings. Each coupler includes two 2-210 EPR o-rings, FilmTec part number 89255.

Product	Dimensions – Inches (mm) A	B	C	D
NF270-2540	40.0 (1,016)	1.19 (30)	0.75 (19)	2.4 (61)
NF270-4040	40.0 (1,016)	1.05 (27)	0.75 (19)	3.9 (99)

1. Refer to FilmTec Design Guidelines for multiple-element systems.
2. NF270-2540 has a tape outer wrap. NF270-4040 has a fiberglass outer wrap.

1 inch = 25.4 mm

Operating Limits

• Membrane Type	Polyamide Thin-Film Composite
• Maximum Operating Temperature	113°F (45°C)
• Maximum Operating Pressure	600 psi (41 bar)
• Maximum Feed Flow Rate - 4040 elements	16 gpm (3.6 m^3/hr)
- 2540 elements	6 gpm (1.4 m^3/hr)
• Maximum Pressure Drop - tape wrapped	13 psig (0.9 bar)
- fiberglassed	15 psig (1.0 bar)
• pH Range, Continuous Operation[a]	2 - 11
• pH Range, Short-Term Cleaning (30 min.)[b]	1 - 12
• Maximum Feed Silt Density Index	SDI 5
• Free Chlorine Tolerance[c]	< 0.1 ppm

[a] Maximum temperature for continuous operation above pH 10 is 95°F (35°C).
[b] Refer to Cleaning Guidelines in specification sheet 609-23010 for NF90.
[c] Under certain conditions, the presence of free chlorine and other oxidizing agents will cause premature membrane failure. Since oxidation damage is not covered under warranty, FilmTec recommends removing residual free chlorine by pretreatment prior to membrane exposure. Please refer to technical bulletin 609-22010 for more information.

Important Information

Proper start-up of reverse osmosis water treatment systems is essential to prepare the membranes for operating service and to prevent membrane damage due to overfeeding or hydraulic shock. Following the proper start-up sequence also helps ensure that system operating parameters conform to design specifications so that system water quality and productivity goals can be achieved.

Before initiating system start-up procedures, membrane pretreatment, loading of the membrane elements, instrument calibration and other system checks should be completed.

Please refer to the application information literature entitled "Start-Up Sequence" (Form No. 609-02077) for more information.

Operation Guidelines

Avoid any abrupt pressure or cross-flow variations on the spiral elements during start-up, shutdown, cleaning or other sequences to prevent possible membrane damage. During start-up, a gradual change from a standstill to operating state is recommended as follows:

- Feed pressure should be increased gradually over a 30-60 second time frame.
- Cross-flow velocity at set operating point should be achieved gradually over 15-20 seconds.
- Permeate obtained from first hour of operation should be discarded.

General Information

- Keep elements moist at all times after initial wetting.
- If operating limits and guidelines given in this bulletin are not strictly followed, the limited warranty will be null and void.
- To prevent biological growth during prolonged system shutdowns, it is recommended that membrane elements be immersed in a preservative solution.
- The customer is fully responsible for the effects of incompatible chemicals and lubricants on elements.
- Maximum pressure drop across an entire pressure vessel (housing) is 30 psi (2.1 bar).
- Avoid static permeate-side backpressure at all times.

FILMTEC™ Membranes

For more information about FILMTEC membranes, call the Dow Liquid Separations business:

North America:	1-800-447-4369
Latin America:	(+55) 11-5188-9222
Europe:	(+32) 3-450-2240
Pacific:	+60 3 7958 3392
Japan:	+813 5460 2100
China:	+86 21 2301 9000

http://www.filmtec.com

Notice: The use of this product in and of itself does not necessarily guarantee the removal of cysts and pathogens from water. Effective cyst and pathogen reduction is dependent on the complete system design and on the operation and maintenance of the system.

APPENDIX C: Phase II Pilot Plant Data

Table C.1. Average Water Quality Concentrations in Feed Water and Permeate

Sample Label	**Flux gfd**	**Feed TOC mg/L**	**Permeate TOC mg/L**	**Feed UV_{254} cm^{-1}**	**Permeate UV_{254} cm^{-1}**	**Feed NH_3-N mg/L**	**Permeate NH_3-N mg/L**
K3	9*	3.01	0.17	0.061	0.001	0.72	0.45
	12	2.65	0.10	0.044	0.001	0.69	0.34
	15	3.04	0.11	0.052	0.001	0.59	0.28
T	9	2.76	0.15	0.051	0.001	0.55	0.39
	12	2.96	0.10	0.054	0.001	0.54	0.38
	15	2.54	0.20	0.045	0.003	0.5	0.29
HE	9	2.69	0.03	0.052	0.001	0.5	0.16
	12	2.85	0.04	0.045	0.001	0.51	0.16
	15	3.33	0.10	0.061	0.001	0.55	0.14

Table C.2. Average Water Quality Concentrations in Feed Water and Permeate

Sample Label	**Flux gfd**	**Feed TTHM µg/L**	**Permeate TTHM µg/L**	**Feed HAA5 µg/L**	**Permeate HAA5 µg/L**
K3	9*	40.3	1.5	58	11
	12	37.0	2.9	33	3.3
	15	30.7	3.1	21	2.0
T	9	32.0	4.8	41	4.1
	12	35.0	3.0	41	4.2
	15	30.3	2.5	30	6.3
HE	9	31.0	1.5	N/A	N/A
	12	29.5	2.1	49	5.9
	15	33.7	1.1	30	1.0

Table C.3. Chlorine Decay Results

Sample	**Chlorine Decay (mg/L)**
Raw	0.63
K3	0.09
T	0.10
HE	0.16

Table C.4. Average Water Quality Parameters of Membrane Permeate

Sample Label	**Flux gfd**	**pH**	**Total Hardness mg/L $CaCO_3$**	**Calcium Hardness mg/L $CaCO_3$**	**Alkalinity mg/L $CaCO_3$**	**Conductivity µS/cm**
K3	9*	8.66	8	6	13	72
	12	8.07	10	7	6	79
	15	8.91	7	6	9	65
T	9	8.95	47	22	23	183
	12	8.69	68	22	56	213
	15	8.68	43	21	19	168
HE	9	9.44	2	1	9	24
	12	9.24	1	1	7	26
	15	8.55	1	1	8	23

Table C.5. NF Membrane Fouling Data

Sample Label	**Adjusted SF**	**Time**	**SF Decline**
T	0.1884	Start	
	0.1878	End	0.32%
HE	0.1724	Start	
	0.1633	End	5.2%

Table C.6. Membrane HE Water Quality Comparison Before and After Fouling

Analysis	**Feed Start**	**Permeate Start**		**Feed End**	**Permeate End**
UV$_{254}$ cm^{-1}	0.061	0.001		0.047	0.001
TOC mg/L	3.33	0.1		2.76	0.05
Conductivity µS/cm	465	23		470	33
TDS mg/L	297	16		281	17
Total Hardness mg/L $CaCO_3$	196	1		189	3
Calcium mg/L $CaCO_3$	58	1		66	2
Alkalinity mg/L $CaCO_3$	39	8		49	9
pH	8.83	8.55		9.12	9.32