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Evaluation of the Impact of Membrane Change at a Membrane Softening Water Treatment Plant

by

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Evaluation of the Impact of Membrane Change at a Membrane Softening Water Treatment Plant

Michael Keen

ABSTRACT

At the water treatment plant in Dunedin, Florida, reverse osmosis membranes remove the hardness from groundwater sources. Reverse osmosis membranes remove salts, pathogens, and organics from the feed water but can create an aggressive permeate. The membranes strip most ions in the process and the resulting permeate, if not subjected to blending on post treatment, has a tendency to leach metals from lead and copper pipes in the distribution networks. To prevent such problems, the permeate needs to be blended with partially treated raw water or to be chemically treated to re-mineralize and add alkalinity back into the water. In the last decade nanofiltration treatment has gained an increasing foothold in the water treatment industry especially as a water softener. Although nanofiltration membranes also have a high removal rate for organics and pathogens, the separation process is more selective towards multivalent ions (e.g., Ca^{2+}, and Mg^{2+}) than monovalent (e.g., Na^{+}) ions.

Most membrane softening plants blend minimally treated raw water with the membrane permeate as a means to reduce the aggressiveness of the water. However, blending can cause issues with disinfection byproducts and pathogen re-introduction. With nanofiltration membranes, fewer mono-valent ions are rejected which creates a more stable permeate and can reduce the blended water ratio. Since it is unlikely that most plants that use membrane filtration for water softening will be able to stop blending entirely, any improvement or sustainability of water quality at a reduced blend ratio should be viewed favorably within the water treatment industry. The study evaluates three nanofiltration membranes: TFC-SR, NF-90, and ESNA1-LF in relation to the reverse osmosis TFC-S RO membrane currently in use at Dunedin. Water flux and salt rejection of the permeate water were compared using solutions of NaCl, $MgSO_4$ and $CaCl_2$. Since the Langelier Saturation Index (LSI) is one of the main tests of the blended finished water and is used to judge water quality prior to its release into the distribution system, this study created a 0%, 10%, 15%, 20%, 30%, and 100% blend ratio for each membrane to compare and contrast the change in the LSI. The TFC-SR membrane showed the most promise in lowering the blend ratio while improving the aggressiveness of the finished water by showing a lower rejection for divalent ions. The TFC-SR membrane also showed an improvement in the LSI relative to the other membranes over the total range of blend ratios.

1. INTRODUCTION

The Dunedin Water Treatment Plant (DWTP), operated by the city of Dunedin, Florida, is a reverse osmosis (RO) water softening plant that currently produces about 3.9 MGD (million gallons per day) of high quality water for the residents of the city. Groundwater taken from local wells which tap into the Upper Floridan Aquifer (UFA) constitutes the source water. The raw water can be classified as hard to very hard with a hardness value of 160-190 mg/L $CaCO_3$, and it has a low to moderate total dissolved solids (TDS) content of 580-600 mg/L (Crittenden and Montgomery Watson Harza, 2005). Hardness values are categorized in Table 1. The hard water must be softened to reduce scaling throughout the distribution system and in homes and offices. DWTP accomplishes this by removing the magnesium and calcium ions through RO membrane filtration. The raw water also has elevated levels of iron and manganese which needs to be removed via the greensand filter pretreatment process before the feed water reaches the RO membranes to prevent scaling since these ions can easily precipitate out of the water. Various water quality parameters over the past two years for the DWTP can be seen in Table 2. The DWTP currently has to blend its RO permeate in an 80/20 blend ratio with minimally treated raw water in order to minimize the aggressiveness of permeate when released into the distribution system. Aggressive finished water can corrode the metal in the distribution system pipes, and the corrosion can cause serious health concerns if the metal is either lead or copper.

However, the blending process has a potential to create problems of its own by increasing the likelihood of non-compliance with regards to disinfection byproducts (DBPs) such as haloacetic acids (HAAs) and trihalomethanes (THMs). The absence of RO membrane filtration on the bypass water means that some natural organic matter (NOM) in the raw water has the potential to serve as precursor to halogenated DBPs. DBP creation happens when NOM reacts with chlorine either in the chlorination prior to the raw water entry into the plant or after disinfection in the post treatment. Studies have shown that about 25% of halogenated compounds formed are THMs and 18-20% HAAs (Reckhow and Singer, 1984; Fleischaker and Ramdtke, 1983). The Environmental Protection Agency (EPA) has placed limits on the amount of DBPs released to consumers and the environment. The limits were enacted because DBPs have been proven to be carcinogens linked to bladder and rectal cancers (Morris et al., 1992). Through the implementation of the Stage 1 Disinfection Byproducts Rule (Stage 1 DBP), the EPA has set maximum contaminant levels (MCLs) for total THMs and five HAAs. The agency set the MCLs at 80 parts per billion (ppb) for THMs like chloroform, bromoform, bromodichloromethane and dibromochloromethane. MCLs for monochloroacetic, dichloroacetic, trichloroacetic, monobromoacetic and dibromoacetic acids were set at 60 ppb (EPA, 1998).

Another issue with blending minimally treated waters to meet finished water demands comes from the cost associated with chemically treating the blended water. Additional chlorine has to be added to properly disinfect the blended bypass water. Switching the DWTP from a RO to a nanofiltration (NF) membrane system has the potential to lessen blending needs by creating a less aggressive permeate while still meeting all the requirements under the EPA's Stage2 DBP rule. Membrane change can also have the added benefit of possibly meeting the Long Term 2 Surface Water Treatment Rule (LT2) generally applied to plants treating surface water. Currently, the DWTP is classified as a groundwater treatment plant. Under the current plant classification DWTP must test their groundwater wells for *Escherichia coli* which are quite costly. Being reclassified under the LT2 would cut down on the required well monitoring under Florida Department of Environmental Protection (FDEP) rules governing the treatment of groundwater. If DWTP can get reclassified as a surface water treatment plant by the FDEP, it would only have to show the appropriate removal in the plant's treatment train of certain pathogenic microorganisms like *Cryptosporidium parvum* to meet the rule requirements. This would save the DWTP the costs of monitoring the wells and let the plant maintain focus on the efficiency of the treatment processes.

Table 1: Water Hardness and TDS Categories

Hardness	Range (mg/L of $CaCO_3$)
Soft	0 to <60
Moderately Hard	60 to <120
Hard	120 to <180
Very Hard	>180

(Crittenden and Montgomery Watson Harza, 2005)

Table 2: Water Quality Data for 8/10/07 & 8/11/08

Parameters	Units	Raw '07	Raw '08	Feed '07	Feed '08	Perm '07	Perm '08	Conc '07	Conc '08
Field Parameters:									
Specific Conductance	umhos/cm		1005		1002		167		3840
Water Temp.	°C		25.1		25.1		25.3		25.4
pH			7.12		7.12		6.12		7.57
Inorganics									
Total Alkalinity as $CaCO_3$	mg/L	160	190	120	180	10	23	470	930
Chloride	mg/L	190	190	200	180	45	35	790	820
Fluoride	mg/L	0.19	0.22	0.17	0.24	0.14	0.032	0.56	0.47
Nitrate (as N)	mg/L	0.54	0.14	0.53	0.15	0.14	0.097	1.1	0.34
Sulfate	mg/L	37	33	100	32	1.5	0.39	500	160
TDS	mg/L	600	580	600	530	84	80	2600	2400
TOC	mg/L	2	2.1	1.9	1.9	0.5	0.5	10	11
Total Phosphorus	mg/L P	0.066	0.079	0.075	0.21	0.011	0.01	0.36	0.94
Turbidity	NTU	0.85	0.95	0.1	0.05	0.15	0.05	0.1	0.1
Metals									
Barium	mg/L	0.03	0.027	0.021	0.021	0.01	0.005	0.096	0.11
Calcium	mg/L	90	96	100	93	6	4.6	480	460
Iron	mg/L	0.61	0.43	0.02	0.02	0.02	0.02	0.02	0.02
Iron, Dissolved	mg/L	0.1	0.41	0.02	0.02	0.02	0.02	0.02	0.02
Potassium	mg/L	4.1	4.6	3.8	4.9	1.1	1.2	14	13
Magnesium	mg/L	14	13	14	13	0.76	0.95	68	65
Manganese	mg/L	0.02	0.018	0.01	0.019	0.01	0.01	0.041	0.095
Sodium	mg/L	94	80	100	76	29	22	340	300
Dissolved Silica as SiO_2	mg/L	26	27	25	27	6.3	6.1	110	115
Strontium	mg/L	0.28	0.29	0.29	0.3	0.019	0.016	1.5	1.6

Data provided by Southern Analytical Laboratories, Inc. 110 Bayview Blvd. Oldsmar, Fl 34677

Note: Raw = raw well water; Feed = water after pretreatment and anti-scalant injection going to the RO membrane; Perm = membrane permeate; and Conc = membrane concentrate.

1.1 Purpose

This project will look into the replacement of the current RO membranes with NF membranes at the Dunedin Water Treatment Plant in Dunedin, Florida. The study will focus on maintaining and improving water quality, creating non-aggressive finished water, and increasing savings in plant operations. Using different blend ratios from three different NF permeates, this project hopes to show that effluent quality as defined by a corrosivity and scalability index (Langelier Saturation Index - LSI) can be maintained or improved, and costs can be reduced.

1.2 Research Objectives

The objectives of this research are:

1. To quantify the effectiveness of three NF membranes compared to the membrane currently being used in terms of the cascading impact on plant operations, blend ratio, finished water quality, and possible plant reclassification.

2. To analyze finished water quality as a function of the blend to permeate ratio using different NF membranes with respect to plant operations and the potential for plant reclassification.

2. PLANT OVERVIEW

The DWTP receives its raw water from a group of wells in Pinellas County. See Appendix 1 for an overview of the plant's 21 wells and raw water collection system. The source water comes from Zone A of the Upper Floridan Aquifer (Carnahan et al., 1995). The shallowest and freshest permeable area, Zone A has an average depth of 180 ft with a range of 115 to 250 ft (Broska and Barnette, 1999). The plant is located at 1401 County Road 1, Dunedin, Florida, which is southwest of Tampa. The plant has been operational since 1992.

The finished water distribution system has over 7.5 miles of transmission piping, four 2-million gallon ground storage tanks, and approximately 138 miles of distribution piping (Dunedin, 1992). Currently the DWTP can produce 9.5 MGD, but has been permitted by Southwest Florida Water Management District (SWFWMD) for 6.6 MGD. From a peak demand of 4.7 MGD in 1998, the yearly demand has steadily decreased over the years as stricter water conservation (due to increase in water rates) and a higher demand for reused water from the Dunedin Wastewater Treatment Plant (DWWTP) began to affect the local water consumption. The recent average daily demand falls below 3.9 MGD. During the daily operation of the DWTP, the plant operators take measurements of various water parameters by which they assess the quality of different streams and judge the efficiency of the various treatment trains. An overview of all the measurements taken at the various plant locations is shown in Appendix 3.

The RO treatment train comprises four two-stage skids. The first stage includes twenty six pressure vessels and the second stage has thirteen. Each pressure vessel contains seven membrane elements. Each membrane element is a Koch TFC 9921-S polyamide spiral wound module (8 ½”diameter, 40” length). The 8 ½” elements have been phased out of commercial production and replaced by the now common 8” diameter element. Any new 8 ½” membrane modules will have to be specially made by the manufacturer. According to Rick Lesan, an R&D engineer with Koch Membrane Systems, brine seals can be placed on the smaller 8” elements and made to fit in the 8 ½” pressure vessels. During the two stage process, about 75% of the feed water is converted into permeate. The first stage recovers 50%, and another 50% of the first stage concentrate is recovered. Pictures of the RO skids and other plant components are shown in Figure 1 below.

Currently, at the DWTP, the raw water is pre-treated by four processes before reaching the RO membranes. The processes are (in order): pre-chlorination, greensand filtration, cartridge filtration (5 micron cartridge filters), and anti-scalant injection. After cartridge filtration, some of the water bypasses the anti-scalant and RO processes so it can be blended with the RO membrane permeate. Following the RO membrane process, the water is subjected to five post-treatment processes: blending, degasification for CO_2 removal, fluoridation, pH adjustment, and disinfection for chlorine residual in distribution system. The RO concentrate is sent directly to the Dunedin Wastewater Treatment Plant for disposal. An overview DWTP schematic can be found in Appendix 2.

Four Skids at DWTP

Blue Pressure Vessels on Skid 4

Spiral Wound Membrane Element

End View of a Skid

Figure 1: Pictures of RO Skid at the DWTP

2.1 Pretreatment

Chlorine is added to the raw water to help complete the oxidation of hydrogen sulfide (H_2S) which causes bad odors in water. Some treatment centers have established greensand filters as an effective method of sulfide removal (Boyle, 2005). By performing pre-chlorination on the raw groundwater, the DWTP improves the greensand filters by removing the initial oxidation demand with chlorine instead of potassium permanganate which is added specifically for the greensand process (Boyle, 2005). After potassium permanganate is added to the water and has time to react with the greensand can oxidize, filter, and adsorb the contaminants (Boyle, 2005). Currently, two of the five greensand filters use a manufactured greensand called Greensand Plus ^{TM}. The other three use conventionally mined glauconite greensand. Both types of greensand have similar performance traits (Boyle, 2005). These traits include the oxidation of iron, manganese and sulfide, avoidance of THMs or HAAs production, minimization of turbidity and sulfide oxidizing bacteria, and reduction of a portion of the color content of the raw water (Boyle, 2005). The next step is cartridge filtration (nominal 5 µm) which removes particulates to protect the RO membranes downstream against impaction or deposition. The anti-scalant (polyacrylic acid – General Electric's Betz Hypersperse MDC 700) injections reduce the scaling of the RO membranes caused by certain carbonate and sulfate compounds by allowing the foulant's potential to exceed their solubility constant without precipitating out of solution. In Figure 2 below, various sections of the pretreatment process are shown.

Greensand Filters

Cartridge Filters

Feed Water Pumps Just After Anti-scalant Injection

Figure 2: Pictures of Various Pretreatment Systems

2.2 Post Treatment

The first post-membrane treatment process is blending of RO permeate with water that bypasses the anti-scalant injection and the RO membranes. The blend is comprised of 80% permeate and 20% bypass water. The 80/20 blend ratio allows the bypass water to remineralize the permeate which has had most of the minerals and alkalinity removed during RO treatment. However, CO_2 in the feed water is not removed by RO due to its small size and neutral charge, and it has to be taken out at the degasification post treatment stage (Schaefer, 2005). A diagram of the bypass water and permeate flows is shown in Figure 3. The bypass water splits off from the feed water after the cartridge filter and before the anti-scalant injection. It combines with the 1st and 2nd stage permeate right after the RO process but before degasification. Blending stabilizes the aggressive water at a lower cost than injecting chemicals into the water.

The blended water undergoes daily tests for corrosiveness and scalability as measured by the Langelier Saturation Index (LSI). The LSI tool measures the potential of the water to form chemical scale and its ability to corrode the pipes in the distribution system. A positive LSI value means the water has the potential to form scale, and a negative value describes the corrosive nature of the water. The plant operators perform the test on the finished water in the storage tanks, on the clearwell tanks, and on water collected from the farthest point in the distribution system. The types and quantity of the plant measurements, the location of the samples taken, and whether the water quality tests are performed in-house or by outside laboratories are shown in Appendices 3 and 4. Five water variables are needed to calculate the LSI. The variables are temperature, calcium hardness, total alkalinity, total dissolved solids, and pH. Both calcium hardness and total alkalinity are in terms of calcium carbonate. The DWTP currently aims for a slightly positive finished water LSI. This positive number means the water will more likely scale than corrode.

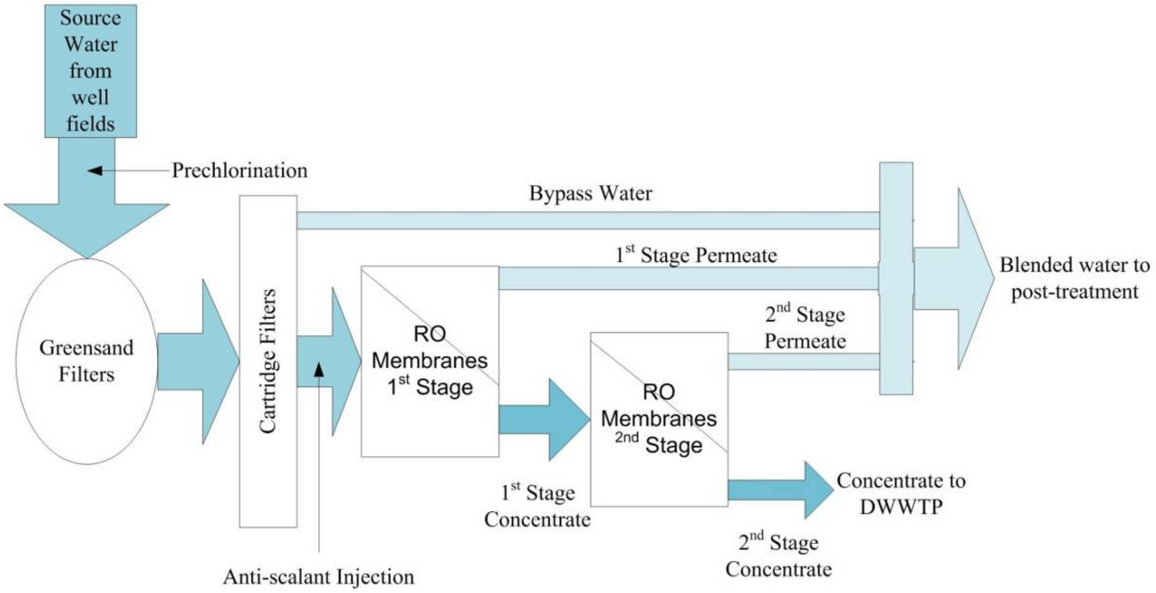


Figure 3: Water Flow Diagram

2.3 Other Post Treatment

The blended water goes through a series of post-treatment processes as seen in Appendix 2. The post-treatment train includes degasification, fluoridation, the injection of sodium hydroxide for pH adjustment, and chlorination. Some of the post treatment systems are shown in Figure 4 below. Degasification removes any residual hydrogen sulfide and CO_2. Carbon dioxide is found in groundwater and may also have been formed if the pH was lowered enough due to the injection of the anti-scalant prior to membrane treatment. If the pH was lowered significantly it could cause the carbonate within the water to change to carbon dioxide. Fluoride in the form of hydrofluosilicic acid is injected into the water to help promote healthy teeth and reduce cavities. The adjustment of pH before the effluent reaches the distribution system is to stabilize the water for public consumption. Chlorine injection disinfects any biological contaminants within the water. Pathogens are usually removed through the membrane process but may be reintroduced when the permeate is blended with unfiltered water. Enough chlorine is added to create a residual disinfection throughout the distribution system. However, high doses of chlorine can also lead to the formation of THMs or HAAs when it comes into contact with certain DBP precursors (NOM) found in the bypass water.

Degasification Towers

Chemical Storage Tanks

Figure 4: Pictures of Various Post Treatment Systems

2.4 Concentrate Disposal

In Dunedin, the concentrate of the DWTP flows by a direct pipeline to the Dunedin Wastewater Treatment Plant (DWWTP). Before the concentrate leaves the DWTP, it undergoes a pH adjustment with sodium hydroxide to around 8.4. Because of the thorough pretreatment of the feed water in the greensand filters, we can assume that when concentrate gets to the DWWTP, it has low concentrations of iron (Fe), and manganese (Mn) as verified in Table 2.

3. LITERATURE REVIEW

3.1 Membrane Filtration

There are several types of membrane filtration currently used in municipal water treatment plants. Each type of membrane can be loosely defined by the types of material rejected (Crittenden and Montgomery Watson Harza, 2005). Although rejection mechanisms for the different types of membranes can be quite different, each of the membranes uses pressure to produce the permeate (Crittenden and Montgomery Watson Harza, 2005). Each membrane type uses the differences in permeability (of water constituents) as a separation mechanism (Baker, 2004). During the membrane process, water is pumped touching the surface of the membrane resulting in permeate and concentrate streams. The membrane material is designed to be highly permeable to some components of the feed stream while being less permeable to others (Crittenden and Montgomery Watson Harza, 2005). During the filtration process, low permeability constituents of the solution stay on the feed side of the membrane while more permeable ones are passed through the membrane. The resulting product stream is relatively free of impermeable constituents (Crittenden and Montgomery Watson Harza, 2005).

3.2 High Pressure Filtration

The main difference between low and high pressure filtration is the removal mechanisms. In low pressure filtration (microfiltration or ultrafiltration), the removal mechanism relies solely on particle size exclusion (Crittenden and Montgomery Watson

Harza, 2005). On the other hand, high pressure filtration (reverse osmosis or nanofiltration) relies mainly on diffusion and to some degree on size exclusion in the case of nanofiltration (Schaefer et al., 2005). In high pressure diffusion membranes, the water is separated from the solution by overcoming the osmotic pressure within the solution. In these membranes, greater pressures are needed to overcome the higher osmotic pressures in different solutions (Baker, 2004). In the water treatment industry, reverse osmosis membranes are usually used to produce potable water from saline or brackish waters (Crittenden and Montgomery Watson Harza, 2005). The nanofiltration membranes are generally used to soften hard water and freshen brackish water (Crittenden and Montgomery Watson Harza, 2005). Most of the high pressure membranes in drinking water treatment use a spiral wound design which enable cross-flow filtration (Schaefer et al., 2005).

3.3 Spiral Wound Membranes and Cross Flow Filtration

In Figure 5, a detailed schematic of a spiral wound module (SWM) shows an internal view of the different layers that make up the membrane element. Multiple leaves comprised of membrane sheets, feed channel spacers and permeate collection material wrap around a central permeate tube. The membranes are glued on three sides with the fourth side providing the opening toward the feed flow (Schwinge et al., 2004). Since the feed flows over the surface of the membrane, the filtration system is termed cross flow filtration (CFF). The feed channel spacers act to separate the membrane leaves and cause interference to the feed flow, which helps the water to become turbulent and keeps fouling of the membrane surface down (Schwinge et al., 2004; Baker, 2004). As the water transfers across the membrane it then travels spirally around the permeate material and exits out of the porous permeate tube in the center (Schwinge et al., 2004). The SWM maximizes the active surface area of the membranes while reducing the size of the system which allow water treatment plants to keep their footprints small.

3.4 Comparison of Nanofiltration and Reverse Osmosis Membranes

Reverse osmosis membranes accomplishes the separation of dissolved solutes from water without regard to valence charge (Crittenden and Montgomery Watson Harza, 2005). RO can effectively remove most constituents from water, but is not selective in the removal (Schaefer et al., 2005). Unlike typical RO membranes, NF membranes have the ability to selectively reject certain electrolytes and low molecular weight dissolved constituents (Bartels et al., 2008). Created during the 1960s, NF membranes are mainly used to soften water because they have the ability to selectively reject those ions like Ca^{2+} and Mg^{2+} that are the main causes of hardness (Schaefer et al., 2005). In Florida, there are many water treatment plants that use NF membranes to soften their groundwater, such as, Deerfield Beach, Hollywood, and Boca Raton. At these plants, the NF membranes have been packed in spiral wound modules (SWM). The NF membrane plants that treat hard water in Florida use arrays of SWM in parallel and in series to meet their permeate demands. Multiple membranes sit inside of pressure vessels which connect to each other. Groups of pressure vessels connected in parallel are usually called stages. Stages can either be connected in parallel or in series depending on the permeate needs.

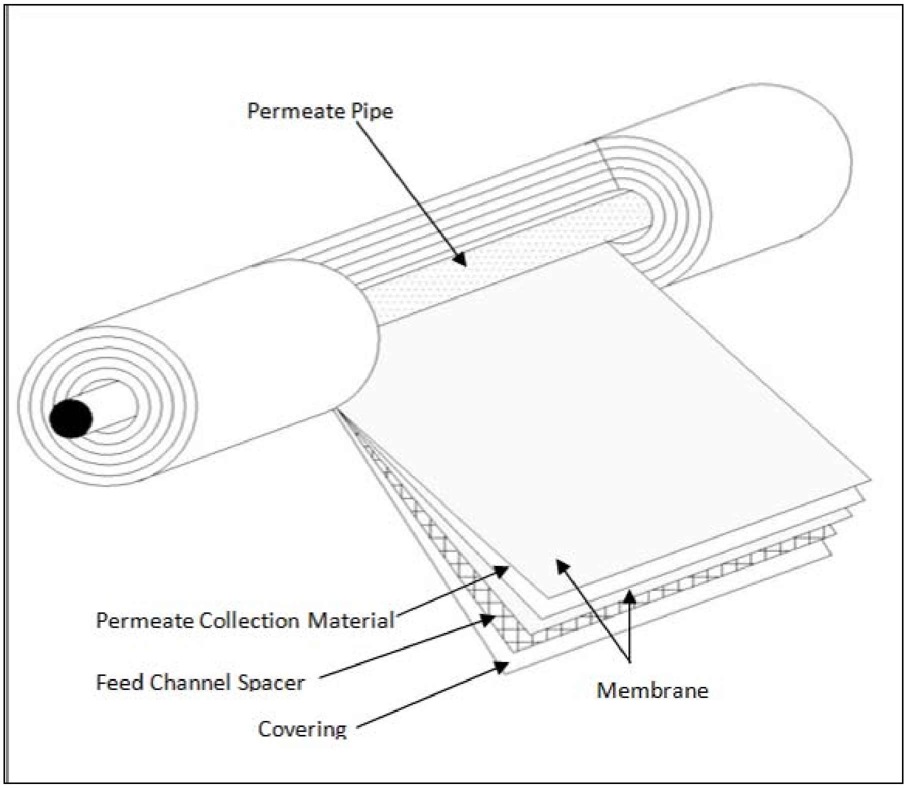


Figure 5: Diagram of a Spiral Wound Membrane

(Based on Koch Membrane System’s spiral wound membrane diagram)

3.5 Nanofiltration Rejection Mechanisms

Nanofiltration (NF) uses pressure to separate the solutes from the solution. The effective pressure (P_e) is the difference in the change of operating pressure (P) and the change in the osmotic pressure (π) from the concentrate to the permeate side of the membrane. Many phenomena can describe the transport of solutes across the membrane, but P_e is the driving force for water flux.

$$\Delta P_e = (\Delta P - \Delta \pi) \qquad (1)$$

NF membranes have been termed “loose” RO membranes or “tight” ultrafiltration (UF) membranes, but their solute removal mechanisms are uniquely different from either RO or UF (Sharma and Chellam, 2006; Schaefer, 2005; Bartels et al., 2008). According to Schaefer et al. (2005), NF membranes have three unique properties that set them apart. These distinctive properties are a high rejection of negatively charged multivalent ions, varied rejections of sodium chloride, and a rejection of non-charged, dissolved materials and positively charged molecules based on size and shape. To accomplish this range of rejection, NF membranes apply both the sieving (steric hindrance) effect and the Donnan (electrostatic) effect (Wang et al., 2002; Schaep et al., 1999). See Figure 6 for the different membrane filtration spectrums and Table 3 for a list of comparative rejection values for different membrane types.

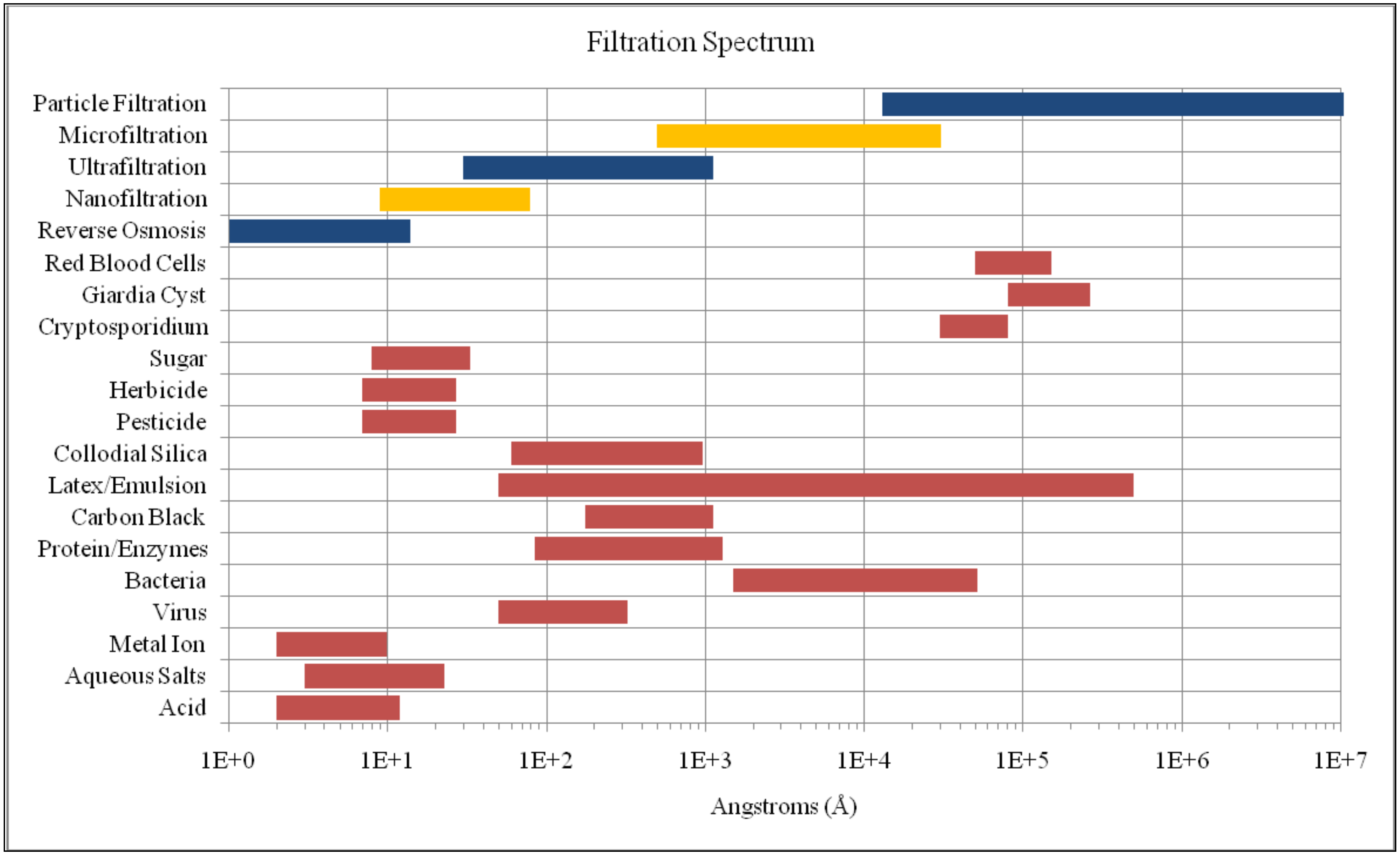


Figure 6: Membrane Filtration Spectrum

(Based on Osmonics Inc. spectrum chart)

Table 3: Comparative Rejection Values

Species	*RO*	*Loose RO*	*NF*	*UF*
Sodium Chloride	99%	70-95%	0-70%	0%
Sodium Sulfate	99%	80-95%	99%	0%
Calcium Chloride	99%	80-95%	0-90%	0%
Magnesium Sulfate	>99%	95-98%	>99%	0%
Humic Acid	>99%	>99%	>99%	30%
Virus	99.99%	99.99%	99.99%	99%
Bacteria	99.99%	99.99%	99.99%	99%

(Based on a similar table (Schaefer, 2005), from Bjarne Nicolaisen of Osmonics, Inc.)

The leading method used to describe the solute removal mechanism of NF membranes comes from the Donnan-steric partitioning pore model (DSPM) (Bowen et al., 1996; Schaep et al., 2001; Labbez et al., 2002; Labbez et al., 2003; Bandini and Vezzani, 2003). In the DSPM, the NF membrane is considered a charged porous layer and takes into account three parameters: effective pore size, effective ratio of membrane thickness to porosity, and effective charge density (Peeters et al., 1998; Bandini and Vezzani, 2003; Mohammad and Takriff, 2003).

However, the DSPM model has a problem in predicting the rejection of divalent ions (Vezzanni and Bandini, 2001; Schaep et al., 2001). To help in the predictive model, dielectric exclusion (DE) portioning has been used to explain the high rejections encountered in such divalent ions as Mg^{2+} (Schaep et al., 2001; Bandini and Vezzani, 2003).

The DE model is based on the difference between the dielectric constant of the membrane and the bulk solution (Bandini and Vezzani, 2003).

In DE, the separation mechanism does not take into account the charge of the ion. The dielectric constant is the expression used to identify the degree that a material will concentrate electric flux (Bandini and Vezzani, 2003). Electric flux is the movement of charge through a material. The differing electrostatic fields cause an interaction between the ions and the polymeric surface in which the dielectric constant of the aqueous solution is much higher than the surface. At the boundary between these two fields, the ions cause a charge of the same polarity as the reference ion thus repelling the charged ions independent of its sign.

3.6 Nanofiltration Fouling

Outside of costs associated with the pressure required for membrane filtration one of the biggest problems encountered during membrane treatment comes from the constant fouling of the membranes. This causes decline of permeate flux and loss of product quality (Baker, 2004). Koros et al. (1996) defined fouling as "…the process resulting in loss of performance of a membrane due to deposition of suspended or dissolved substances on its external surfaces, at its pore openings, or within its pores." Schaefer et al. (2005) lists some of the causes and control strategies of membrane fouling, as summarized in Table 4. Any type of fouling on the membrane can lead to reduced recovery, higher operational costs, higher energy demand, increase of cleaning frequency, and a reduction in the useful life of the membrane element (Vrouwenvelder et al., 2003; Manttari et al., 1997; Bonne et al., 2000).

As seen in Table 4, most of the operational controlling of fouling occurs before the water makes contact with the membrane. The preventive treatment of the raw water is the key to limiting fouling of the membranes.

Table 4: Potential Membrane Fouling Sources and Control Strategies (Schafer et al., 2005)

Origins of Fouling	*Fouling Control*
Scaling: substances exceeding their solubility product	Operate below solubility limit, pretreatment: reduce pH to 4-6, low recovery, and anti-scalants. Pre-oxidation of metals.
Deposition of colloidal matter or dispersed fines	Pretreatment using filtration, microfiltration (MF) or Ultrafiltration (UF)
Organic fouling	Pretreatment using filtration, MF, UF, ion exchange, ozone, enhanced coagulation or carbon adsorption
Biofouling: colonization by bacteria	Hydrodynamics, operation below critical flux, chemical cleaning, pretreatment: disinfection or UF, MF, Hydrodynamics, operation below critical flux, chemical cleaning

3.6.1 Scaling

Calcium carbonate, calcium sulfate, silica complexes, barium sulfate, strontium sulfate and calcium fluoride have been identified as leading causes of scale formation on membranes (Baker, 2004). Scaling occurs when the concentration of one of these species exceeds the solubility constant and starts to precipitate out of the solution onto the membrane. Scaling can be greatly affected by pH, temperature, fluid velocity, time and salt concentration in the concentrate (Schafer, 2005). Certain cations like Mg^{2+} and Ca^{2+} can increase the precipitation and colloidal formation of silica complexes

(Sheikholeslami and Bright, 2002). It has also been noted in the same study that iron and manganese even at low concentrations can also increase the fouling potential of silica compounds. However, the greensand filtration at the DWTP removes the majority of the iron and manganese during the pretreatment phase.

Since groundwater results from the flow of surface water through different types of sediment it becomes naturally mineralized and can sometimes have significant levels of scale forming species. The DWTP has a high scaling potential because of the concentration of certain minerals in the water such as Mg^{2+} and Ca^{2+} which the plant was designed to remove. Nederlof et al. (2000) studied different pretreatment methods for controlling membrane fouling and concluded that scaling must be addressed with the addition of anti-scalants or pH adjustment. At one time in DWTP, anti-scalant was added and the pH of the feed water was adjusted but over time the plant operators have discontinued the process. Without pretreatment of the water, plant operators could reduce the recovery of the membranes to control scaling (Schafer et al., 2005). At a reduced recovery, the likelihood of a critical buildup in scale forming species would be lowered because the concentrate would not be likely to reach a supersaturated state. However, many water treatment plants need to maintain a certain recovery to meet their area's water demand, and therefore use chemical pretreatment methods.

3.6.2 Colloidal Matter

Particles defined by their small size, state of hydration, and surface charge make up the foulant group known as fine colloids (Viessmann et al., 2009). The negative surface charge of the suspended particulate keeps them from aggregating and falling out of the solution (Viesmann et al., 2009, Schafer et al., 2005). These charges affect the particulates through electrostatic double layer (EDL) interactions. The negatively charged particulates attract a covering of positively charged ions by an electrostatic attraction, and the stable layer of positive ions is surrounded by a moving diffuse zone of counterions. The attraction between ions is reduced in the diffusive zone the further away the ions roam from the stable layer (Viessmann et al., 2009). The EDL of two similarly charged particles will repel each other, and with proximity the repelling force increases (Sawyer et al., 2003). Water with high ionic strength has the potential to compact the EDL thus increasing the ability of the particles to get together and at a certain point in the process the Van der Waals force can overcome the EDL repulsion and let the colloids form aggregates and settle on membrane surfaces (Sawyer et al., 2003). The Van der Waals force is the intermolecular attractive force which all particles possess in varying strengths according to their composition and density. A strong enough cross-flow velocity in the membrane treatment system can create turbulent flow and keep much colloidal matter from depositing on the membranes. In a membrane water treatment plant, the cross-flow velocity decreases as the water flows through the pressure vessels. The reduction in cross-flow velocity closer toward the end membrane element means the water flow can become more laminar, which will increase the susceptibility to chemical or colloidal fouling (Gwon et al., 2003). The prevalent methods of reducing any colloidal fouling at the DWTP are the application of cartridge filtration before the feed pumps and maintaining a strong cross flow velocity.

3.6.3 Organics

Studies have shown that humics, non-humics, polysaccharides and proteins dominate organic membrane fouling (Violleau et al., 2005). Organic material comes from human activities, natural organic matter (NOM), or compounds formed during disinfection processes. It may also be formed through the addition of compounds during the transmission or treatment of water (Crittenden and Montgomery Watson Harza, 2005). Since much of the water at the DWTP is treated minimally before it gets to the membranes and the source wells are well protected, the majority of the organic matter in the DWTP comes from NOM. According to Schafer et al. (2005), the NOM can form a gel on the surface of the membrane through adsorption. NOM can also build up a cake layer through deposition by organic colloids or restrict the pores once the organic molecules have penetrated the membrane. Total organic carbon (TOC) commonly measures the concentration of NOM in the water. Like most groundwater, the raw water at DWTP has a low concentration of TOC as shown in Table 2. Although organic fouling can occur in municipal water treatment facilities, it is more common in other membrane applications such as industrial processes where RO membranes are used to treat a process stream (Baker, 2004).

3.6.4 Biofouling

Biofouling (biological fouling) is the growth of biological organisms on either the permeate or concentrate side surface of the membrane (Baker, 2004). In water treatment facilities that use membranes, biofouling is hard to control because fouling can occur with only a few viable bacteria and can feed off of any organic material (usually a steady supply in the feed water) found in the water including dead bacteria (Flemming, 2002). At DWTP, studies by Carnahan et al. (1995) found that there was enough organic matter in the raw water to support *Pseudomonas* bacteria. Once attached to the surface of the membrane, biofilm is very hard to remove because the organisms excrete extra-cellular polymeric substances (EPS) that form a protective medium and adhesive for the microorganisms (Carnahan et al., 1995; Flemming, 2002). At DWTP biofouling of the membranes tends to occur more heavily on the feed side of the membrane element because the majority of the NOM and bacterium are removed by the membrane (Sagiv and Semiat, 2005). DWTP uses cleaning protocols to remove the buildup of biofoulants.

3.6.5 Concentration Polarization

Concentration polarization can significantly affect the operation of NF and RO membranes. Feed water at the DWTP has many constituents that make up the water's characteristics. Because these constituents permeate at differing rates, gradients of concentration can form on either the permeate or concentrate side of the membrane surface in a process called concentration polarization (Baker, 2004). In addition, the ions collecting at the boundary can change the osmotic pressure of the solution thus decreasing the water flux, but the placement of feed spacers and a significant cross flow velocity can mitigate the degree of concentration polarization (Schafer et al., 2005).

3.6.6 Membrane Compaction

Although membrane compaction does reduce the water flux of a membrane, it should not be confused with fouling (Bert, 1969; Schafer et al., 2005). As pressure increases within a membrane filtration process, water will travel through the membrane.

According to Bert's research, a newly created membrane lacks the ability to retain most of the water within its matrix as the water passes through and over time the increase in pressure used on a RO or NF membrane forces out the water reducing the membrane's hydration. As water is forced out of a particular area in the membrane matrix, it affects the permeability of the membrane because water flux is the movement of water through the membrane and a reduction in water content at any point leads to an overall reduction of permeability (Bert, 1969). To overcome this issue, this study setup a pre-compaction routine to temper the membranes before any experiments by running water through a membrane at a high enough pressure and timescale (Schafer et al., 2005).

3.7 Blending

As stated in Chapter 2 Plant Overview, once the feed water passes through the membrane system, many water treatment plants (such as DWTP) will blend the water with minimally treated raw water known as bypass water. The blending ratios depend on the constituent characterization of the bypass and permeate waters. Other factors that could influence the blending ratio are water recovery needs, production costs, and regulatory constraints. Because a RO or "tight" NF filtration process can strip most everything out of the feed water leaving it very aggressive, a good blend will alleviate the amount of chemicals needed for treatment to correct for corrosivity or scaling if the pretreatment is sufficient. A proper blend will reduce the costs associated with chemically treating the water by remineralizing it. Along with a slightly positive LSI, remineralization includes an increased bicarbonate alkalinity and pH for the treated water (Withers, 2005). However, the blend has certain drawbacks such as introducing NOM back into the finished water which can lead to DBPs once chlorine is added for disinfection. DBP formation can cause problems when trying to meet regulatory limits set by the EPA.

3.7.1 Organics

The origin of NOM is complex and varied. NOM is derived from multiple sources in the natural environment including secretions from the metabolic activity of organisms (Crittenden and Montgomery Watson Harza, 2005). NOM can also develop from the decay of organic matter or from excretions of life forms (Crittenden and Montgomery Watson Harza, 2005). Basically, NOM comprises four different types of organic matter: carbohydrates, lipids, amino acids or nucleic acids, and the products of abiotic and biotic reactions between other NOM or inorganic molecules (Crittenden and Montgomery Watson Harza, 2005). Humic substances are a major component of NOM (50-80% of dissolved organic matter), and are known DBP precursors (Thurman, 1985; Chadik and Amy, 1983). Being very complex, NOM has usually been measured with a bulk indicator like total organic carbon (TOC) (Crittenden and Montgomery Watson Harza, 2005; Dalvi et al., 2000). The effectiveness of NF in the removal of the type of NOM that acts as a DBP precursor has been documented (Smith et al., 2002; Chellam et al., 2000). Taylor et al. (1987) found that RO did not remove NOM precursors significantly more effectively than NF membranes, but required greater pressure and had a reduced flux.

3.7.2 Disinfection Byproducts

Factors including TOC, bromide ion concentration, pH, temperature, ammonia concentration, and carbonate alkalinity affect the types and concentrations of DBPs (Garvey et al., 2003). Some of the most common disinfectants (chlorine, ozone, chloramines) used in drinking water create their own DBPs (Richardson, 1998). The EPA first regulated DBPs in 1979 with the THM rule and in 1998 it introduced the Stage 1 Disinfectants/Disinfection Byproducts rule (Stage 1 D/DBP Rule) (U.S. EPA 1979, 1998). This rule created and adjusted maximum contaminant levels (MCLs) for certain known DBPs. In 2003, the EPA added the Stage 2 Disinfectants/Disinfection Byproducts Rule (Stage 2 D/DBP Rule) which specifies that utilities will have to meet MCLs calculating a yearly average at the compliance monitoring station instead of a yearly average over the whole network (U.S. EPA 2003, 1998). DBPs have been linked to certain cancers in animals and humans, and studies suggest that the exposure routes in humans can be through ingestion, inhalation and dermal absorption (Lavoie, 2000; Aggazzotti et al., 1998; Xu et al., 2002). At the DWTP, chlorine is the only disinfection chemical added to the water after blending.

3.7.3 Chlorination

DBP formation is also usually dependent on chlorine dose rates and contact time (Dalvi et al., 2000). There are several reasons why chlorine disinfection remains popular even though it can cause DBPs. The chlorination fact sheet affirms chlorination as a useful disinfection process and states that it is a well established technology. The fact sheet states that chlorination is presently more cost effective than other disinfectants in most cases, it can prolong protection throughout the distribution system, and it offers flexible dosing control (U.S. EPA, 1999). However, the EPA also lists several drawbacks to chlorination like increased chloride content. In high chlorine demand systems higher chlorine concentrations are needed. *Cryptosporidium parvum* and *Giardia lamblia* have shown resistance to chlorine and long term chlorination effects on the environment are unknown.

3.8. Scaling and Corrosion Prediction with LSI

3.8.1 Langelier Saturation Index (LSI)

The LSI measures a solution's ability to dissolve or deposit calcium carbonate and has been used in the water industry to predict water's tendency to either corrode or scale (Gebbie, 2000). Both corrosion and scaling are factors that affect the public health, and corrosion products that leach off of distribution pipes can shield microorganisms from disinfectants (Melidis et al., 2007). The speciation in water of the carbonate system is directly dependent on pH (Crittenden and Montgomery Watson Harza, 2005; Langelier, 1936). At the DWTP, the plant operators try to maintain a slightly positive LSI number. A small amount of scale on the surface of the pipes can shield the pipe material from water thus giving it a certain amount of protection against corrosion. The reactions between calcium and carbonates are the primary focus of the LSI (Langelier, 1936; Withers, 2005). According to Langelier, the index is the difference between the pH of the solution and the pH_s (pH of saturation). The pH of saturation is the equilibrium pH once all forms of alkalinity have been adjusted so that water is only saturated in calcium carbonate (Langelier, 1936; Withers, 2005). A negative number represents a corrosive nature. A positive number means that the water has the ability to scale in the form of calcium carbonate, while zero indicates that the water is balanced.

The larger the positive or negative number the greater its ability to create scale or corrode (Langelier, 1936).

The following equations calculate the LSI.

$$LSI = pH - pH_s \quad (2)$$

$$pH_s = (9.3+A+B)-(C+D) \quad (3)$$

$$A = (\log_{10}(TDS)-1)/10 \quad (4)$$

$$B = -13.12*\log_{10}(°C+273)+34.55 \quad (5)$$

$$C = \log_{10}(Ca^{2+} \text{ as } CaCO_3 \text{ mg/L})-0.4 \quad (6)$$

$$D = \log_{10}(\text{Alkalinity as } CaCO_3 \text{ mg/L}) \quad (7)$$

According to Equations 3-8, TDS, total alkalinity, calcium hardness, pH and temperature affect the outcome of the LSI values. The variables within the LSI equations will have differing degrees of influence on the calculated outcomes. Below in Figure 7, a specific range of LSI values was compared to the individual variables while keeping the other parameters constant. The LSI values in the figure were calculated with four of the five following constants: temperature at 25°C, pH at 7, TDS at 550 mg/L, total Alkalinity at 150 mg/L as $CaCO_3$, and calcium hardness at 140 mg/L as $CaCO_3$. The resulting graphs give an idea of how much influence the individual variables have in the outcome of the calculated LSI values. According to the graphs, the least influential parameter is TDS as it can fluctuate over many magnitudes of values while only minimally changing the LSI value. Unlike the other parameters, TDS has an inverse relationship with LSI in that at lower values the TDS will produce a more positive LSI. Temperature and pH each have linear relationships with the LSI. As the values raise so does the LSI. However, pH has a greater influence since it can change the LSI to a greater degree by only fluctuating within a small pH range. The temperature produces a measured change in LSI as it increases. Within normal operating temperature range of 20°C -25°C, the temperature will only minimally change the LSI. Finally, the calcium hardness and total alkalinity have a logarithmic relationship with LSI. Both variables have a greater degree of influence at the lower concentrations, but their ability to significantly change the LSI lessens at higher concentrations.

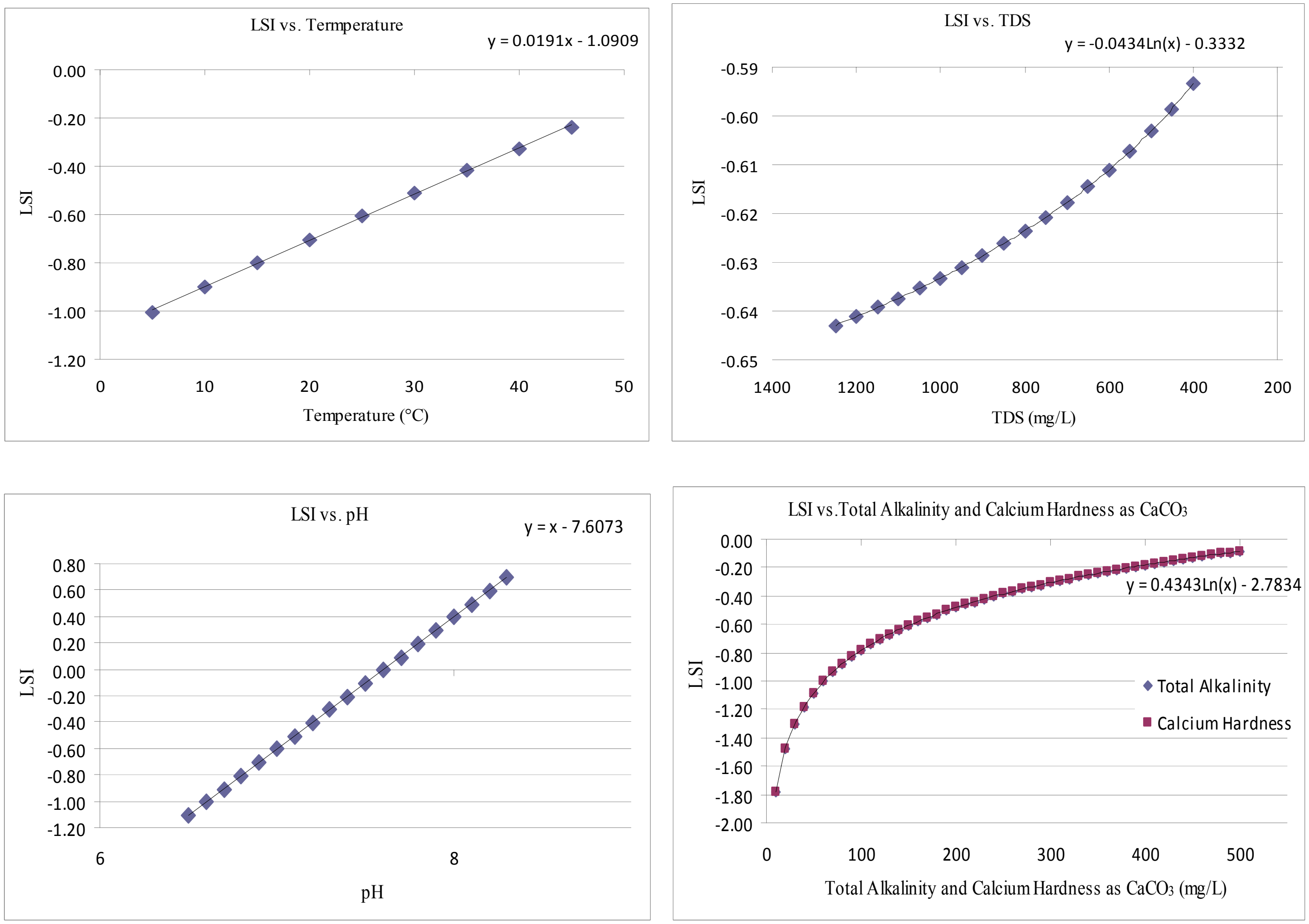


Figure 7: LSI Values vs. LSI Parameters

3.8.2 Lead and Copper Rule

In 1991, the U.S. EPA enacted the Lead and Copper Rule (LCR) for drinking water suppliers because of the adverse health effects of copper and lead corrosion (U.S. EPA, 1991). Neither metal is prevalent in drinking water, but copper pipes and lead solder can undergo an oxidation/reduction reaction with water, dissolved oxygen, and other oxidants (Xiao et al., 2007). The reaction can precipitate these metals in the water and will then come into contact with potable water consumers. To combat the aggressiveness of certain waters to leach the metals, the DWTP and other treatment centers use LSI or another such index to determine the aggressiveness of the finished water.

3.8.3 Stage 2 Disinfectants and Disinfection Byproducts Rule

The Stage 2 Disinfectants and Disinfection Byproducts Rule (Stage 2 DBPR) enacted by the U.S. EPA in January 2006, focuses on the reduction and elimination of DBPs in drinking water from both surface and groundwater sources. The main change from the Stage 1 Disinfectants and Disinfection Byproducts Rule was the method of compliance in reporting contaminant concentrations. Before the Stage 2 DBPR, many treatment plants averaged the DBP measurements over their entire distribution system. This meant that many plants could actually exceed their maximum contaminant levels (MCLs) if the average reported value was lower (Richardson, 2003). According to the EPA, the Stage 2 DBPR covers the DBPs formed when water treatment plants use disinfectants like chloramines and chlorine to reduce the pathogens in the finished water. The two most prevalent groups of DBPs are THMs and HAA5 which can form when chlorine interacts with NOM (Crittenden and Montgomery Watson Harza, 2005). The

DWTP uses chlorine as their disinfectant and therefore they have issues regarding DBP formation. According to the EPA's Stage 2 DBP Rule guidance manual, pH adjustment, filtration, NF and RO processes and chlorination adjustment are methods used to reduce DBP formation within water treatment plants.

3.8.4 Long Term 2 Enhanced Surface Water Treatment Rule

In 2006 along with the Stage 2 DBP Rule, the EPA created the Long Term 2 Enhanced Surface Water Treatment Rule (LT2 Rule) to minimize illnesses associated with certain pathogens in the drinking water that are resistant to some disinfectants like chlorine. Among others, these pathogens include *Giardia* and *Cryptosporidium*. Surface water and groundwater that is influenced by surface water are subject to this rule. The rule classifies systems into one of four categories called bins (U.S. EPA, 2006). The bin categories are determined by monitoring results for *E. coli* which is cheaper than monitoring tests for pathogens like *Cryptosporidium*. The higher the bin the more removal the treatment plant must provide with the highest bins having to show a further (1.0 – 2.5 log) reduction in *Cryptosporidium* levels above the 3.0 log required by the LT2 for meeting turbidity requirements. Although the well water for the DWTP is not considered to be influenced by surface water, the plant would like to explore the possibility of being placed under this rule as it might help in reducing costs associated with well testing. Currently, the plant must test wells for *E. coli* in their wells and so many tests can be cost prohibitive. Being classified under the LT2 Rule would allow the plant to show compliance by providing certain treatment processes approved by the EPA for reducing these pathogens.

4. METHODS AND MATERIALS

4.1 Overview

Historical data collected from DWTP which consisted of reports from Southern Analytical Laboratories (SAL) and data gathered by plant operators during the routine operation of the DWTP were used to chart the historical changes in water quality and operational variables. This data can be found in graphical format in the Appendix 10. Data gathered from these sources and used for this thesis project include parameters such as cross-flow velocity, feed flow, and operational pressure ranges. Table 5 lists the parameters used in this study.

Table 5: Operational Values at the DWTP

Parameter	Ranged Value	Units
Cross-Flow Velocity	13.7-12.8	m/min
Feed Flow	1371-1280	GPM
Feed Pressure	112-120	psi
Feed pH	6.80 (+/- 0.1)	

The study comprised three phases. In phase I, plant operational parameters and historical data were gathered. Samples for TDS analysis of the raw water, feed water, bypass water, permeate, and concentrate streams were also collected. In phase II, a flow cell system was designed and built to test four flat sheet membranes with distilled water and solutions of $MgSO_4$, NaCl, and $CaCl_2$. The test resulted in the identification of the flux in distilled water and the flux in three different salt solutions using the four membranes. Flux is the flow of water through the membrane expressed as flow per area. In phase III, membrane performance was tested using actual feed water from the DWTP. The permeate of the feed water from the four different membranes used in this study was blended at different volumetric proportions with the bypass water (post-cartridge filter). Total alkalinity, calcium hardness, pH, conductivity, and temperature were measured for each of the blended waters. Using this information, calculations were made of the LSI for each blend.

4.2 Membrane Materials

The project tested four membranes including the KOCH membrane currently used at the DWTP; the project also tested three other membranes. The choice of membranes and a short list of their published rejections and other specifications are listed in Table 6. These are based on the data sheets provided by the manufacturers, which have been summarized in Appendices 6-9.

Table 6: List of Membranes and Their Published Characteristics

Manufacturer	Filmtec	Hydranautics	Koch	Koch
Model Number	*NF90*	*ESNA1-LF*	*TFC-S**	*TFC-SR2*
Membrane Type	Polyamide TFC	Polyamide TFC	Polyamide TFC	Polyamide TFC
Nominal Surface Area (m^2)	37	37	38	35.8
NaCl Rejection %	85-95	--	--	--
$MgSO_4$ Rejection %	>97	--	99.25	95
$CaCl_2$ Rejection %	--	84-96	--	--
Max Operating Press. (psi)	595	603	350	500
Typical Operating Press. (psi)	--	--	75-125	50-100
pH Range Continuous Operation	3-10	3-10	4-11	4-9
Free Chlorine Tolerance (ppm)	<0.1	<0.1	<0.1	<0.1
Diameter (203 mm)	7.9 in	7.89 in	8 in	8 in

*Current membrane used at the DWTP.

4.3 Flat Sheet Membrane System

The flow cell system used for this study was designed and fabricated by Mr. Bob Riley of Separation Systems (San Diego, CA). It was constructed from 316 stainless steel and can sustain a pressure up to 800 psi. Stainless steel Swagelok fittings were used to connect the flow cell, meters, and valves. The cell has two rubber O-ring seals as shown in Figure 8. The first seal surrounds the feed channel and the other wraps around the membrane area both of which help maintain the integrity of the pressurized process during operation. Above the flow channel lies a sintered steel section slightly larger than the feed channel which allows the permeate to move outside of the flow cell. The sintered steel helps maintain the integrity of the membrane as the feed pressure is distributed evenly over the entire membrane. Inside the feed channel are an entry for feed flow and an exit for concentrate flow depending on how the flat sheet module is connected to the system. A flexible tube is attached to the permeate exit at the top of the flow cell to capture the permeate for collection and testing. The top and bottom portions of the flow cell are attached by six steel bolts.

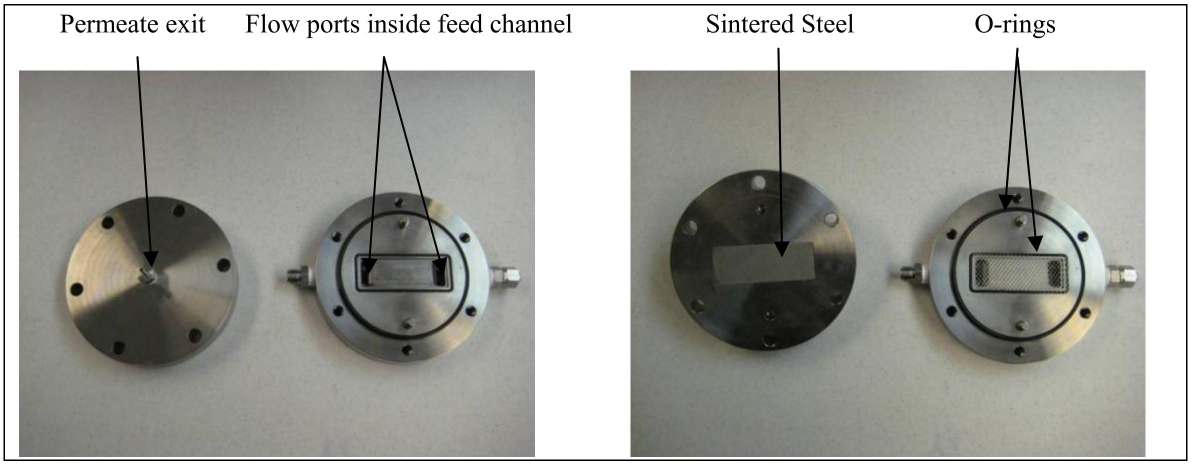


Figure 8: Separation Systems Flow Cell Front and Back

Along with the fittings, all stainless steel tubing and the digital pressure transducer (S Model with digital readout) came from Swagelok. The Swagelok pressure transducer and a Swagelok analog pressure gage was installed before the back pressure needle valve. The back pressure valve maintains the pressure within the flat sheet module by reducing the aperture the water can flow through thus building up pressure. A schematic for the flat sheet system can be found in Figure 9. The system also uses Swagelok needle valves to control and adjust the water flow throughout the system. The system used a McMillan S-111 flow meter with a metering range between 0.5-5 L/min. For those sections of the system that did not use Swagelok tubing, standard flexible tubing was used. A Hydra-Cell M-03 positive displacement pump with 3 gal/min flow capacity along with an Emerson 2-hp motor were used to pump the water through the system. The system uses a Polyscience P-series refrigerated recirculating chiller to control the temperature of the water during system operation. The ¼ hp chiller can maintain refrigerated temperatures between -10°C to 40°C. The chiller used copper coils connected to the chiller reservoir to transfer heat out of the system reservoir in a closed loop system. Figure 10 shows pictures of the system setup.

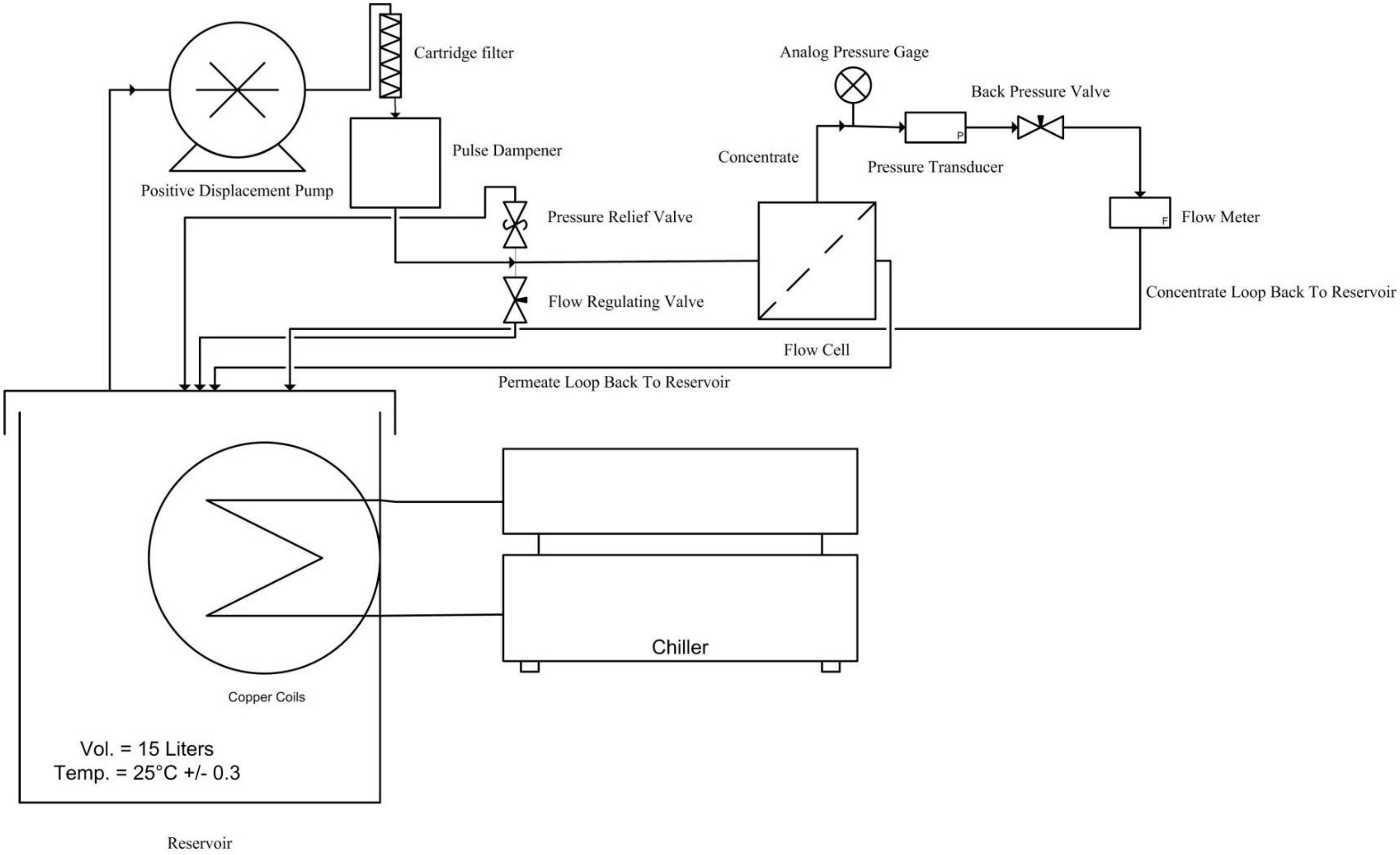
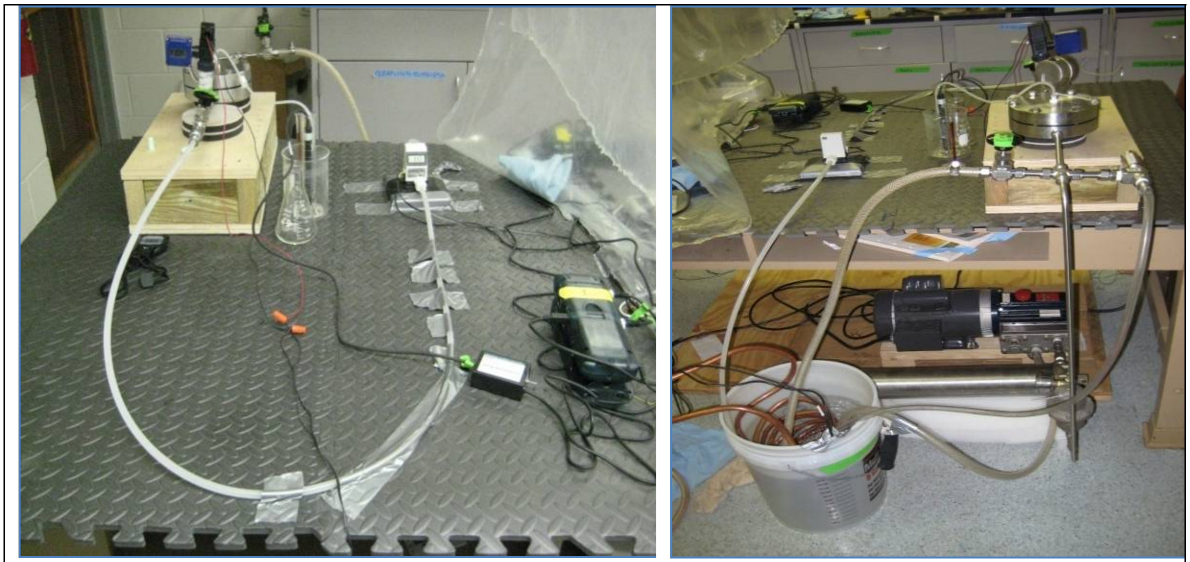


Figure 9: Overview Schematic of Flat Sheet System



Flat sheet module, Flow Meter,LabPro Datalogger

Reservoir, copper coil and HydraCell pump

Labtop computer with LoggerPro 3.1

Polyscience Chiller and tubing

Figure 10: Overview of Flat Sheet Membrane System

The system rerouted the water from the concentrate back into the reservoir to conserve ions. The data collection system was operated from a laptop and utilized Logger Pro 3.1 and LabPro software packages from Vernier. The data collection system gathered the feed/concentrate flow, reservoir temperature, pH of reservoir, and conductivity of the feed and permeates. Conductivity, temperature, and pH were collected using Vernier's ph-bta pH probe, con-bta conductivity probe, and tmp-bta stainless steel temperature probe. The manual data collection consisted of permeate flow and pressure readings from the pressure transducer. A 10 mL graduated cylinder and a stop watch calculated the permeate flow by measuring the time it took the permeate to reach 3 mL. Two permeate flow measurements were made and then averaged.

4.4 Phase I

Several goals were established for this phase. The first goal consisted of collecting plant data from the historical databases used by the plant operators. From this data experimental parameters such as feed flow were calculated for the flat sheet membrane system. This allowed the flat sheet system to mimic as closely as possible the current operating pressures, feed flow, feed pH and cross-flow velocity as displayed in Table 5. To calculate the cross-flow velocity of the flat sheet system the depth of the feed channel as well as the active area membrane width had to be measured. A Cen-Tech digital caliper measured both parameters. The depth of the feed channel was taken from the bottom of the channel to the top of the feed channel rubber seal (O-ring). The O-ring had a high density and it was assumed to compress very little if any during the pressurization process. The active membrane area was measured from midpoint to midpoint of the feed channel o-ring. The feed channel depth measured 2.72 mm and the active membrane width was 31.98 mm. Using the following equation, the feed flow (Q_f) was calculated using the plant's current cross flow velocity (V_{CF}). The feed flow was calculated to be 1.2 L/min based on the averaged cross flow velocity from DWTP's 2008 historical data. Both feed channel depth (F_{CD}) and active membrane area width (W_{cell}) as stated previously were measured.

$$V_{CF} = \frac{Q_f}{F_{CD} * W_{cell}} \tag{8}$$

The second goal of Phase I was to quantify the TOC from the different water flows as well as compare the measured conductivity with the TDS values to estimate a conversion factor. The samples taken from DWTP were stored in Boston Amber Round bottles from Fisher Scientific. Each water bottle was used multiple times, and each bottle always stored the same water source sample The sampling protocol consisted of running the water sample lines at the plant for five minutes. Then each bottle was rinsed with water from the sample port at least three times before the sample was taken. Once the samples made were transported to the University of South Florida campus, they were stored in a refrigerator until the proper experiments could be run. From the DWTP, samples of the raw water, feed water, post-cartridge filtrate (bypass), permeate, and concentrate were collected. These samples are plant-level samples and not taken from individual skids.

TDS experiments were conducted based on the Standard Methods 2540C, and conductivity was measured using the Cole-Parmer conductivity probe model 1481-61. This is the same probe that plant operators use at their on-site laboratory in the DWTP.

4.5 Phase II

Phase II consisted of gathering flux data and rejection data using distilled water and three separate salt solutions. The four solutions were run through the flat sheet system. The three salt solutions of 500 mg/L were NaCl, $MgSO_4$, and $CaCl_2$. Each experiment maintained feed pH at 6.8 (+/- 0.3), feed flow at 1.2 L/min (+/- 0.04 L/min), and water temperature at 25°C (+/- 0.4 °C). Before the membranes could be used each required a tempering preparation procedure. Each membrane used in the flat sheet module was soaked in distilled water for one hour prior to compaction. Once hydrated, the membranes were placed in the flat sheet module. Membrane compaction entailed running distilled water through the membrane in a recirculation mode for a 24 hour period at 120 psi. A second flow cell was attached to the first in series to double the quantity of membranes that could be compacted at one time. After compaction each membrane was stored in a Ziploc^{TM} bag with paper soaked in distilled water to keep it hydrated before and after each use. After compaction flux data were gathered using a solution of distilled water. After installation in the flow cell each membrane ran at pressures of 40, 60, 80, 100, 120 and 140 psi. The water flux (J_w) was calculated using the permeate flow (Q_p) and active membrane area (A_{cell}) in following equation:

$$J_W = \frac{Q_p}{A_{cell}} \tag{9}$$

Finally, the % rejection data were gathered using three solutions of $MgSO_4$, $CaCl_2$, and NaCl. Each solution consisted of a 500 mg/L concentration of these salts. The solutions ran at the same pressures as the flux experiments (40, 60, 80, 100, 120, and 140 psi). Unlike the water flux experiment, conductivity probes were placed in the receptacles holding the feed and permeate solutions. The conductance of the solutions was the bulk parameter used in determining % Rejection from the following equation.

$$\%R = \left(1 - \left(\frac{C_p}{C_f}\right)\right) * 100 \qquad (10)$$

C_p and C_f are the conductivity in µS/cm.

4.6 Phase III

The final phase of the project entailed using feed and bypass water gathered from the DWTP to create different ratios of blended water. Feed water and bypass water samples were collected in 15 L buckets with the same wash and storage procedure used with the amber Boston rounds. Each bucket had a lid and was stored in a refrigerator in the USF lab. The feed water was introduced through each of the four membranes in the flat sheet module system at a constant pressure of 120 psi. Once enough of the permeate was produced it was blended with the bypass water at volumetric ratios of 0%, 10%, 15%, 20%, 30%, and 100%. The Vernier probes measured conductivity, pH, and temperature of the blended water. After the blended water had been measured for these parameters, it was subjected to total alkalinity and calcium hardness tests using EPA approved Hach methods 8221 and 8222 respectively. Using the total alkalinity, calcium hardness, temperature, pH, and conductivity measurements of the blended water, the LSI was calculated for each blend ratio. Since the TFC-SR membrane reported much different LSI values than any other membranes tested, an additional test blending test was performed. To simulate the two stage RO process, the membrane was used to treat 50% of the water feed water. 500 mL of the permeate water from this portion of the experiment was stored in the refrigerator until needed. The 50% left in the container had been concentrated similar to the feed solution fed into DWTP's second stage RO process. Another 500 mL of the permeate was collected from the concentrated solution. The first and second stage permeates were mixed at a 2/3 to 1/3 volumetric ratio respectively. The amounts depended on what bypass blend was being created. Similar to the first blend experiment, the blend ratios were 0%, 10%, 15%, 20%, 30%, and 100%.

5. RESULTS AND DISCUSSION

5.1 Phase I

The historical data show that, for the past several years, the feed pressure at the DWTP has steadily decreased (Figure 11). From 2001-2005 the feed pressure increased from about 100 psi to a maximum around 130 psi. However, the pressure fell and then leveled at around 120 psi where it has been for the last couple of years. The reason for the increase in pressure was probably due to fouling of the membranes. New membranes were installed during late 2001 to early 2002. It took a while for them to reach an optimum performance between DWTP's cleaning protocols and daily fouling.

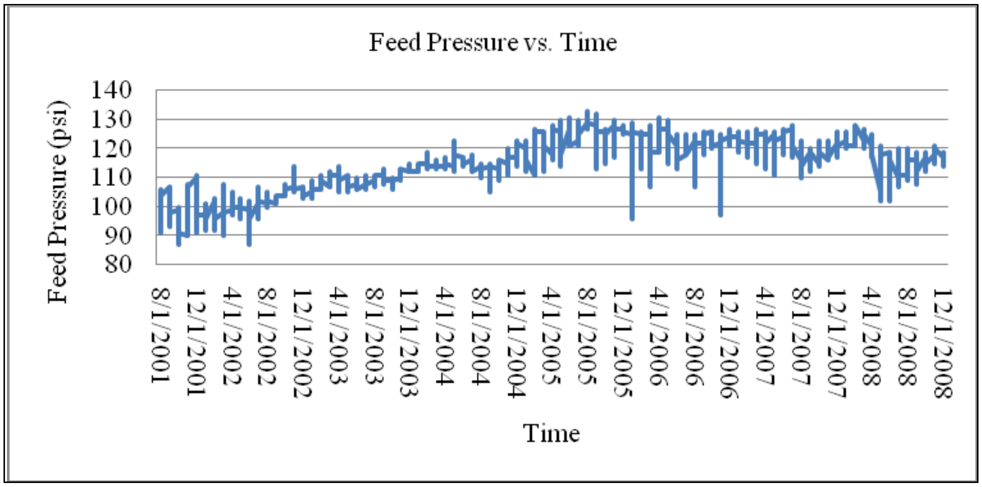


Figure 11: DWTP Feed Pressure Over a Seven Year Period

To calculate the LSI at the DWTP, the plant operators need to estimate the TDS. They do not measure TDS directly, but instead gather conductivity data from water samples using a conductivity meter at their onsite laboratory. The operators use the following equation to calculate the TDS value in mg/L based on their meter reading of conductivity.

$$TDS\left({}^{mg}\!/_{L}\right) = Conductivity\left({}^{\mu S}\!/_{cm}\right) * 0.61 \qquad (11)$$

The value of 0.61 represents a standard that the DWTP has been using since the beginning of operations. This equation was provided by their local engineers and probably represents a standard based on literature review instead of the analytical relationship between TDS and actual conductivity from the plant's water. According to published resources, the slope of the TDS vs. conductivity plot can fall in the range of 0.5-0.9 (Crittenden and Montgomery Watson Harza, 2005). The TDS versus actual conductivity data from experiments run during this project are placed in a composite graph seen in Figure 12. All conductivities were measured using the plant's conductivity meter. For the daily graphs of TDS vs. conductivity see Appendix 11. With a composite slope of 0.71, the results showed that the current slope factor used by DWTP was underestimating the TDS. The calculated slope factor probably represents the water better than the value currently in usage because it is determined from actual measurements.

Error in the estimates of conductivity and TDS in Figure 12 could arise from improper calibration of the conductivity meter at the DWTP or improper drying of the sample during TDS measurements. However, the variability in well sources used to create the raw water and future chemical changes of the well water due to salt water intrusion or other reasons could have an effect on these results and periodic testing will have to be done to maintain accuracy. Both the higher slope (0.71) and the current slope value (0.61) were used in calculating and reporting the results of the LSI in the next section.

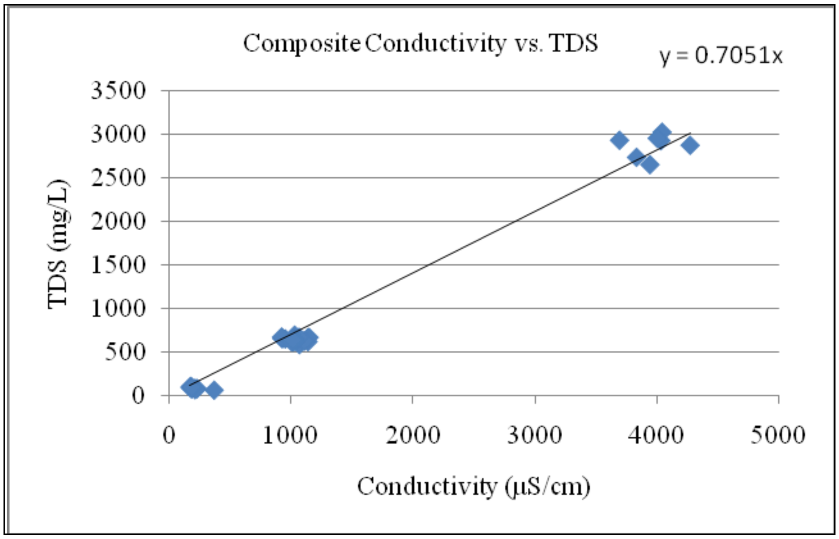


Figure 12: TDS vs. Conductivity Composite Graph

5.2 Phase II

In Phase II the object of the experiment was to determine the flux and % rejection of a 500 mg/L solution of NaCl, $CaCl_2$ and $MgSO_4$ for the various membranes. By determining the flux and rejections, the membrane's bench mark performance was assessed. During the testing of the membranes, experiments conducted at lower pressure values exhibited the most variability and error due to the constant fluctuation of pressure. The fluctuation was due to the amount of vibration in the system at those pressures. Between 40-60 psi, the system had a tendency to randomly increase or drop pressure and flow rate. Constant vigilance and adjustments had to be maintained to ensure relative stability within the system. Both the back pressure and flow adjustment had to be constantly attuned using the appropriate needle valves. However, over time the ability to maintain pressure and stability was improved. To maintain the concentration of the salts over time, the permeate was recycled into the feed reservoir. Figures 13-16, show plots of flux versus transmembrane pressure for each membrane using distilled water. The slopes of each chart represents the permeate flux coefficient, which are listed in Table 7.

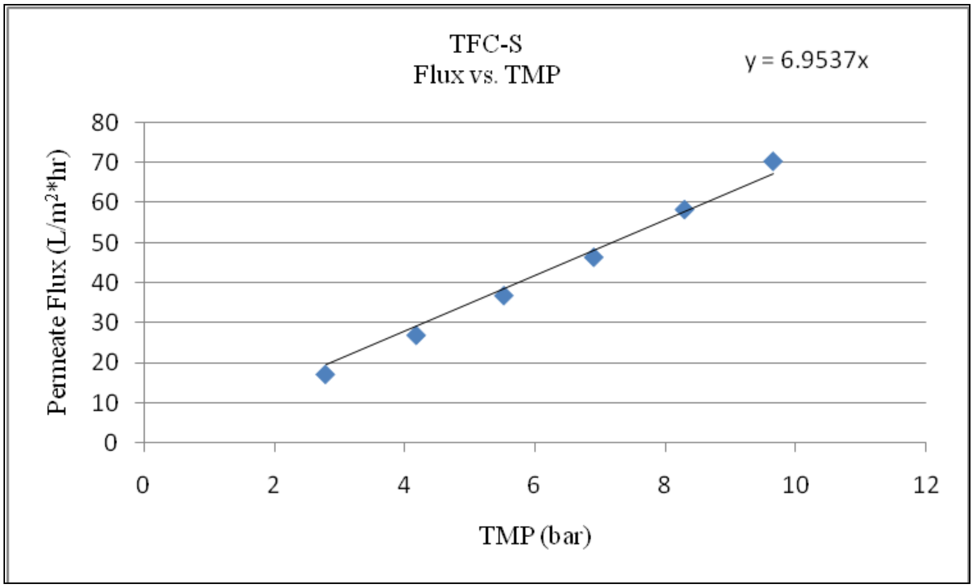


Figure 13: TFC-S Intrinsic Water Flux Plot

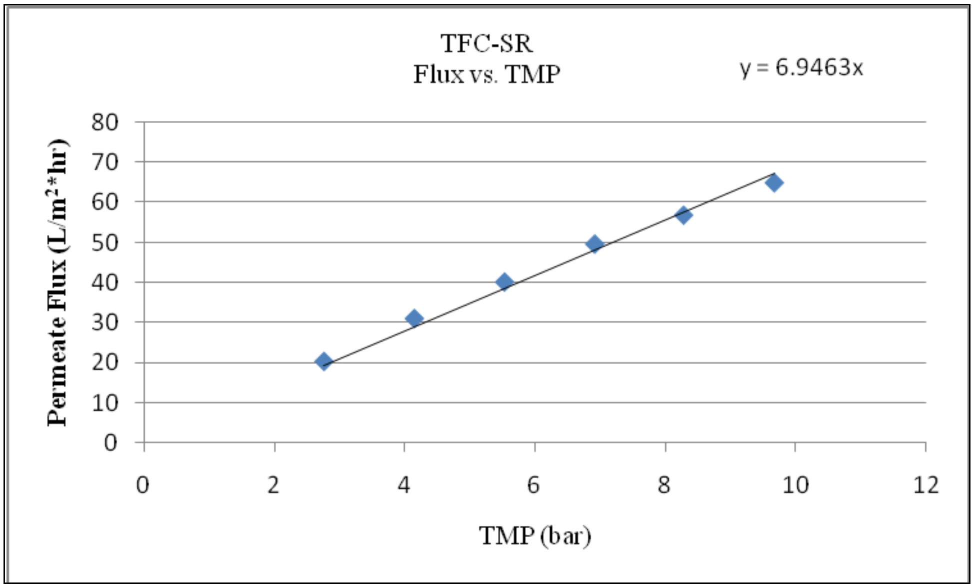


Figure 14: TFC-SR Intrinsic Water Flux Plot

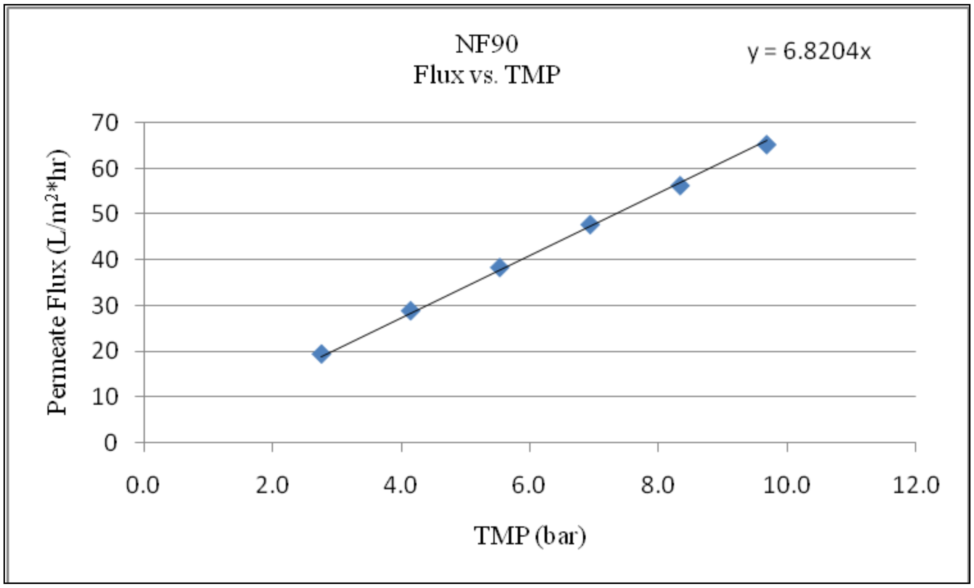


Figure 15: NF-90 Intrinsic Water Flux Plot

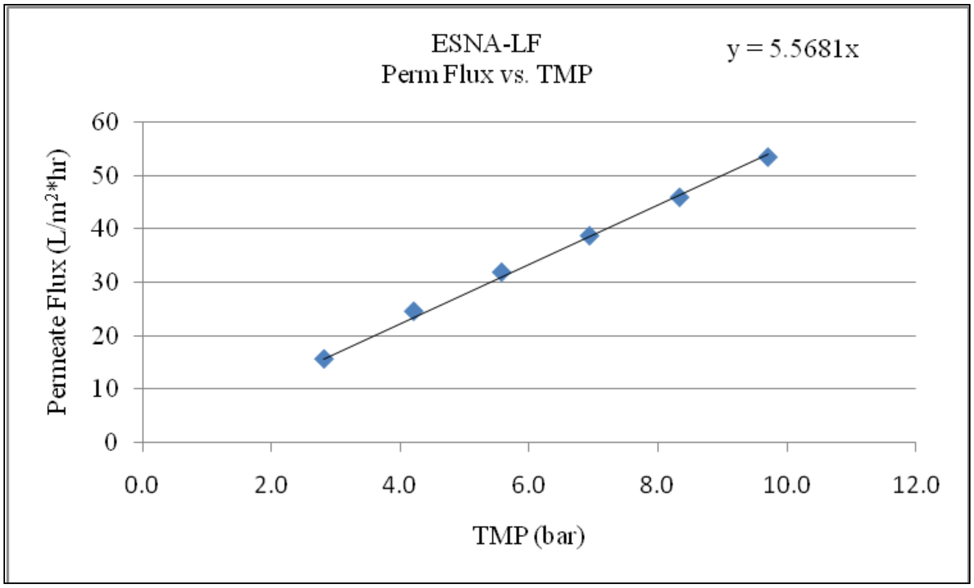


Figure 16: ESNA1-LF Intrinsic Water Flux Plot

The two KOCH membranes TFC-S and TFC-SR have similar permeability coefficients. The Film-Tec NF-90 had a slightly lower value while Dow's ESNA1-LF had the lowest permeability coefficient. The permeability coefficient is important because it gives one of the first indications of membrane fouling. As the membranes become fouled the coefficient will fall. The value will also fall when the TDS increases in water since the water will have a higher osmotic pressure to overcome. Since the coefficient is dependent on pressure, a higher coefficient relates to more production of water per active membrane area. This means that membranes with lower coefficients will need higher pressures to achieve production rates similar to other membranes with a higher coefficient. In Table 7, membrane resistance was also calculated. As expected, TFC-SR had the lowest resistance which indicates that less pressure will have to be applied to raise the water recovery than any of the other membranes.

Table 7: Membrane Permeability Coefficients and Resistance

Membrane	Water Permeability Coefficient (L/m^2*hr*bar)	Membrane Resistance (m^{-1})	Permeability* Coefficient for a 500 mg/L NaCl Soln. (L/m^2*hr*bar)	Membrane Resistance (m^{-1})	Permeability* Coefficient for a 500 mg/L $MgSO_4$ Soln. (L/m^2*hr*bar)	Membrane Resistance (m^{-1})	Permeability* Coefficient for a 500 mg/L $CaCl_2$ Soln. (L/m^2*hr*bar)	Membrane Resistance (m^{-1})
TFC –S	6.95	1.62E-4	6.24	1.80E-4	6.21	1.81E-4	6.33	1.78E-4
TFC-SR	6.95	1.62E-4	9.98	1.13E-4	9.10	1.23E-4	8.94	1.26E-4
NF-90	6.82	1.65E-4	6.11	1.84E-4	6.27	1.79E-4	6.23	1.80E-4
ESNA1-LF	5.56	2.02E-4	5.10	2.20E-4	5.06	2.22E-4	4.86	2.31E-4

*Data gathered from flux charts in Figures 11-14 and 17.

The % rejection for each membrane can be calculated using the following equation where ρ is the density of water (g/cm^3), A is the water permeability coefficient, B is the salt flux coefficient, and ΔP and Δπ are the pressure and osmotic pressure across the membrane respectively (Baker, 2004). The equation is the result of the combination of the equations for water flux and the salt concentration of the permeate side of the membrane.

$$R = \left(1 - \frac{\rho * B}{A(\Delta P - \Delta \pi)}\right) * 100\% \qquad (12)$$

However, this study used a simplified version of Equation 12 with the use of the permeate (C_p) and feed (C_f) bulk parameter of conductance. The new equation follows below.

$$R = \left(1 - \frac{C_P}{C_F}\right) * 100\% \qquad (13)$$

Table 8: Percent Rejection Tables for TFC-S and TFC-SR

Membrane	Salts	Operating Pressure (psi)	%Rejection	Membrane	Salts	Operating Pressure (psi)	%Rejection
TFC-S				*TFC-SR*			
	NaCl	40	85.7		NaCl	40	66.1
		60	87.9			60	66.3
		80	90.0			80	67.0
		100	91.7			100	66.8
		120	92.4			120	67.0
		140	92.7			140	67.2
	$MgSO_4$	40	95.8		$MgSO_4$	40	88.5
		60	96.9			60	88.7
		80	97.6			80	89.3
		100	97.9			100	89.5
		120	98.0			120	89.0
		140	98.7			140	89.1
	$CaCl_2$	40	90.6		$CaCl_2$	40	82.9
		60	93.0			60	83.3
		80	95.9			80	84.0
		100	97.3			100	85.8
		120	98.0			120	86.9
		140	98.1			140	87.7

Table 9: Percent Rejection Table for NF-90 and ESNA1-LF

Membrane	Salts	Operating Pressure (psi)	%Rejection	Membrane	Salts	Operating Pressure (psi)	%Rejection
NF-90				*ESNA1-LF*			
	NaCl	40	85.1		NaCl	40	83.5
		60	86.8			60	89.1
		80	89.9			80	91.4
		100	91.9			100	92.6
		120	92.4			120	92.8
		140	93.0			140	93.1
	$MgSO_4$	40	95.5		$MgSO_4$	40	94.6
		60	95.6			60	96.7
		80	96.4			80	97.1
		100	96.8			100	97.4
		120	97.1			120	97.7
		140	97.3			140	97.5
	$CaCl_2$	40	35.7		$CaCl_2$	40	95.1
		60	56.7			60	96.4
		80	73.6			80	97.4
		100	81.0			100	98.5
		120	85.4			120	98.9
		140	88.5			140	98.9

In Tables 8 and 9 above the percent rejection of the different salt solutions per membrane at different operating pressures are shown. See Figures 17 and 18 for graphical representations of the data in these tables. According to information in the tables and graphs, at the current plant operating pressure of 120 psi or 8.27 bar NF-90 and TFC-SR have lower rejections of magnesium and calcium ions. However NF-90 is closer to the other two membranes than to TFC-SR. TFC-S and ESNA-LF have similar rejection of the same ions at the same operating pressure. The rejection of monovalent sodium is much lower in TFC-SR membrane, but TFC-S, NF-90, and ESNA1-LF have similar rejections for the sodium ion. The data above suggest that both NF-90 and TFC-SR would give more mineralized water because of their lower rejections of divalent ions. At a lower operating pressure of 100 psi, the data suggests that NF-90 and TFC-SR would continue producing lower rejection values than either TFC-S or ESNA1-LF membranes.

Overall rejection performance of each membrane can be seen in Figure 17. The data show us that both TFC-S and NF-90 reject the salts at about the same percentage over the last range of pressures. Looking at the data for NF-90, the $CaCl_2$ numbers look different than would be expected based in comparison with the $MgSO_4$ numbers for the same membrane. NF-90 rejection for calcium drops significantly in the lower pressure ranges and is probably due to the issues associated with maintaining the proper water flow and pressure within the system. More tests will have to be conducted to see if the discrepancy is due to some error in the experiment. The trends show that both NF-90 and TFC-S would perform at roughly similar rejections even if operating pressures were lowered. Like the TFC-S, the NF-90 gives us slightly increasing rejection over a range of pressures. Since rejection is dependent on concentration of solutes and not pressure, the aberration in the data probably has something to do with fluctuations in temperature or flow. The data may be adjusted by normalizing it with the appropriate variable. Singularly, the ESNA1-LF membrane increases its rejection of all the salts to one degree or another at increasing pressures but the rejections become more or less stable around 100 psi or 6.9 bar. The rejection for most of these salts follows the same increasing pattern as the rejection of calcium by NF-90 and the error probably follows a similar explanation. At higher pressure ranges, ESNA1-LF gives slightly higher rejection values than the TFC-S and NF-90 membranes. Overall, the TFC-S, NF-90 and ESNA1-LF provided similar rejection of all salts between the 100-140 psi and 6.9-9.7 bar of operating pressure. This means that the only significant change is seen through the use of TFC-SR.

The performance of each membrane based on individual salt rejections is shown in Figure 18. For NaCl rejection, all membranes except for TFC-SR give similar rejections over the same operating pressures. TFC-SR gives a significantly lower rejection at below 70% over the same range of pressures. This increased NaCl concentration in the finished water with the use of TFC-SR would not affect the hardness, but would increase the conductivity. However, of all the LSI parameters the TDS value has the least effect according to Figure 7. Increased levels of sodium may also have implications for finished water taste since no post treatment will remove excess salinity.

For $MgSO_4$, TFC-S, NF-90 and ESNA1-LF had comparable rejections. The NF-90 and ESNA1-LF had slightly lower rejections, but the differences are between 1-2%. Switching out the current membranes with either ESNA1-LF or NF-90 would not necessarily change the Mg^{2+} concentration and therefore the total hardness to any significant degree. However, the usage of TFC-SR would increase the hardness due to Mg^{2+} because rejection would decrease by 7-9% across the relevant pressure ranges. At DWTP, according to Table 2 most of the hardness comes from calcium so the effect of less Mg^{2+} rejection might have a reduced amount of an impact than the rejection numbers would show. ESNA1-LF had the highest rejection of $CaCl_2$ than any other membrane so the hardness of the permeate would be even less than from TFC-S. Both the TFC-S and TFC-SR had similar rejections at lower pressures but between 100-140 psi and 6.9-9.7 bar, TFC-SR had around 4-6% lower rejections. The differences in rejection by the TFC-SR membrane would most likely increase the total hardness of the permeate. Again the lower rejection values of $CaCl_2$ for the NF-90 membrane are subject to scrutiny and further evaluations are needed to verify the anomalies. At the higher ranges, NF-90 falls between the performance of TFC-S and TFC-SR. With the use of NF-90 and TFC-SR the rejection of $CaCl_2$ is slightly lower than TFC-S at certain operating pressures.

The flux versus pressure curves for each membrane per each salt in Figure 19 show that the highest flux for any salt solution is retrieved from the TFC-SR membrane. A composite graph in Figure 20 shows the flux versus pressure curves for all the membranes of Figure 19. The trend lines in the graph have been approximated. Both the TFC-S and the NF-90 have similar fluxes across the different pressures, so no real benefit is seen in terms of permeate flux with a switch to NF-90. On the other hand, the ESNA1-LF has the lowest flux across the same range which means that higher pressure would have to be used to achieve the same amount of flux as the TFC-S or NF-90 membranes. Trying to maintain the current level of permeate quality by using ESNA1-LF may have the effect of increasing costs for DWTP since similar water recovery would mean higher feed pressures. Again TFC-SR shows the most positive difference than any other membrane. The TFC-SR membrane gives the greatest amount of flux over the range of operating pressures.

So at lower operating pressures, the TFC-SR would provide greater flux but reduced percent rejection enabling it to mineralize the water at a cheaper cost than any other alternative membrane.

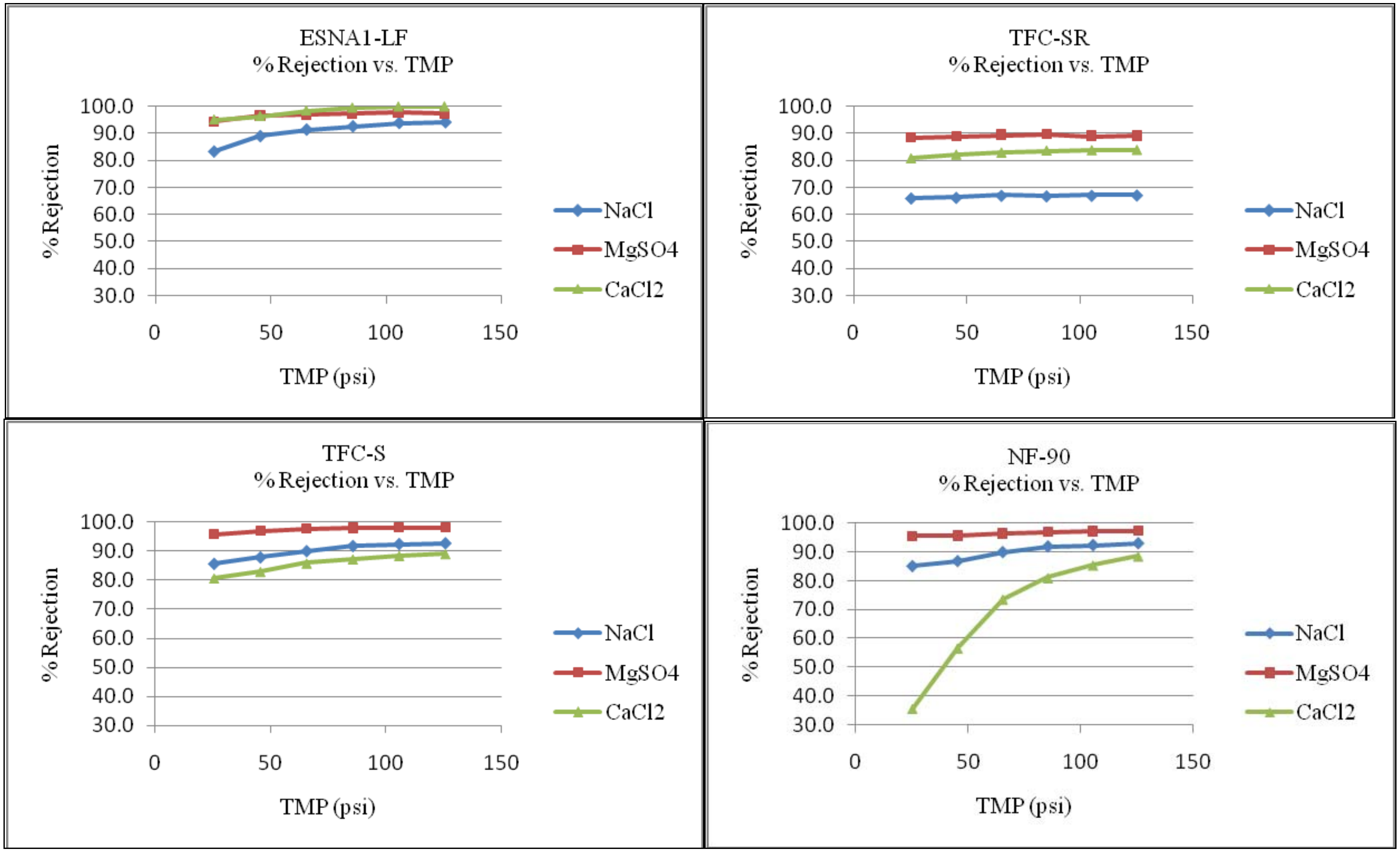


Figure 17: Percent Rejection vs. Transmembrane Pressure (TMP) (Per Membrane)

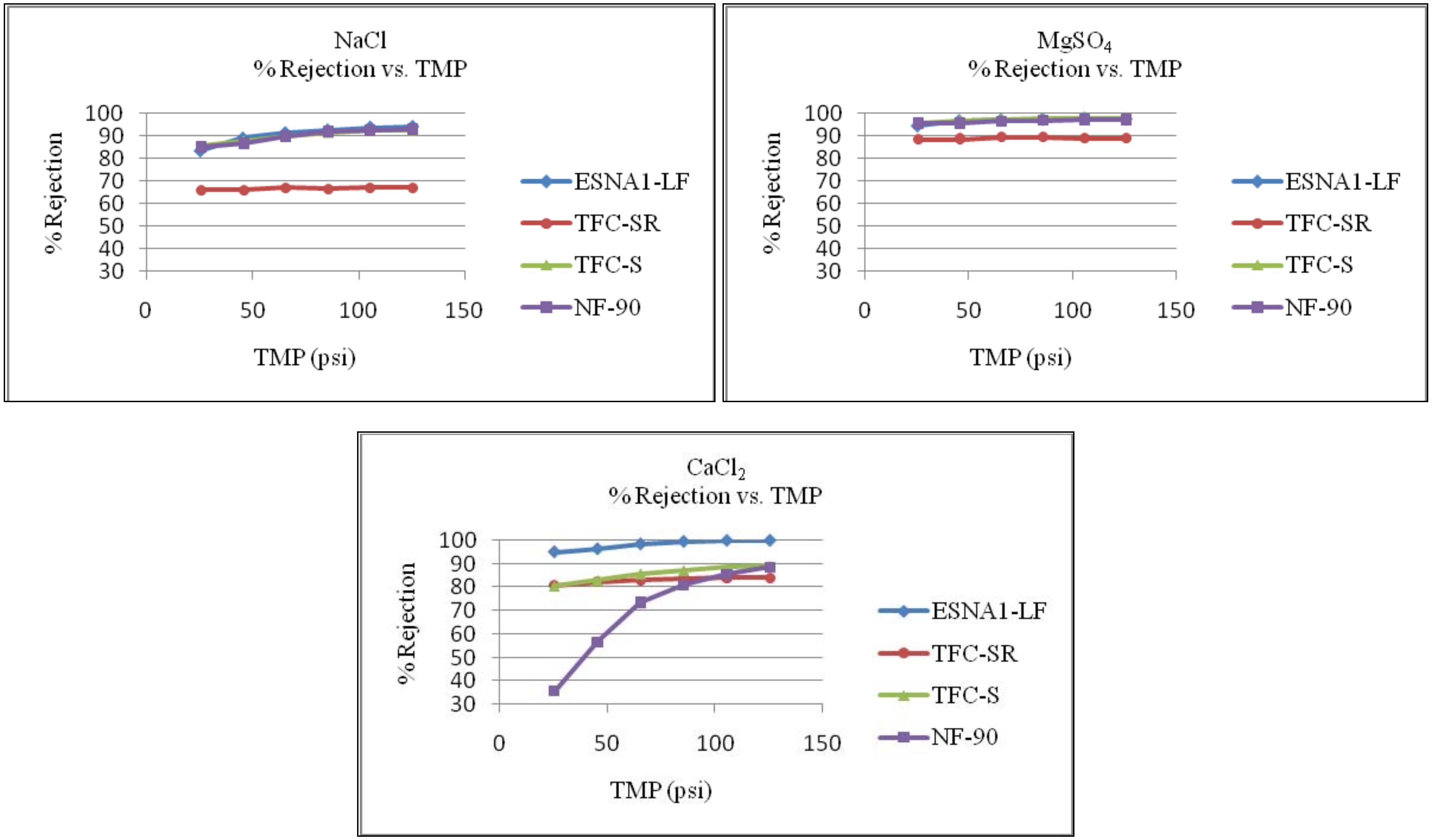


Figure 18: Percent rejection vs. Transmembrane Pressure (TMP) (Per Salt)

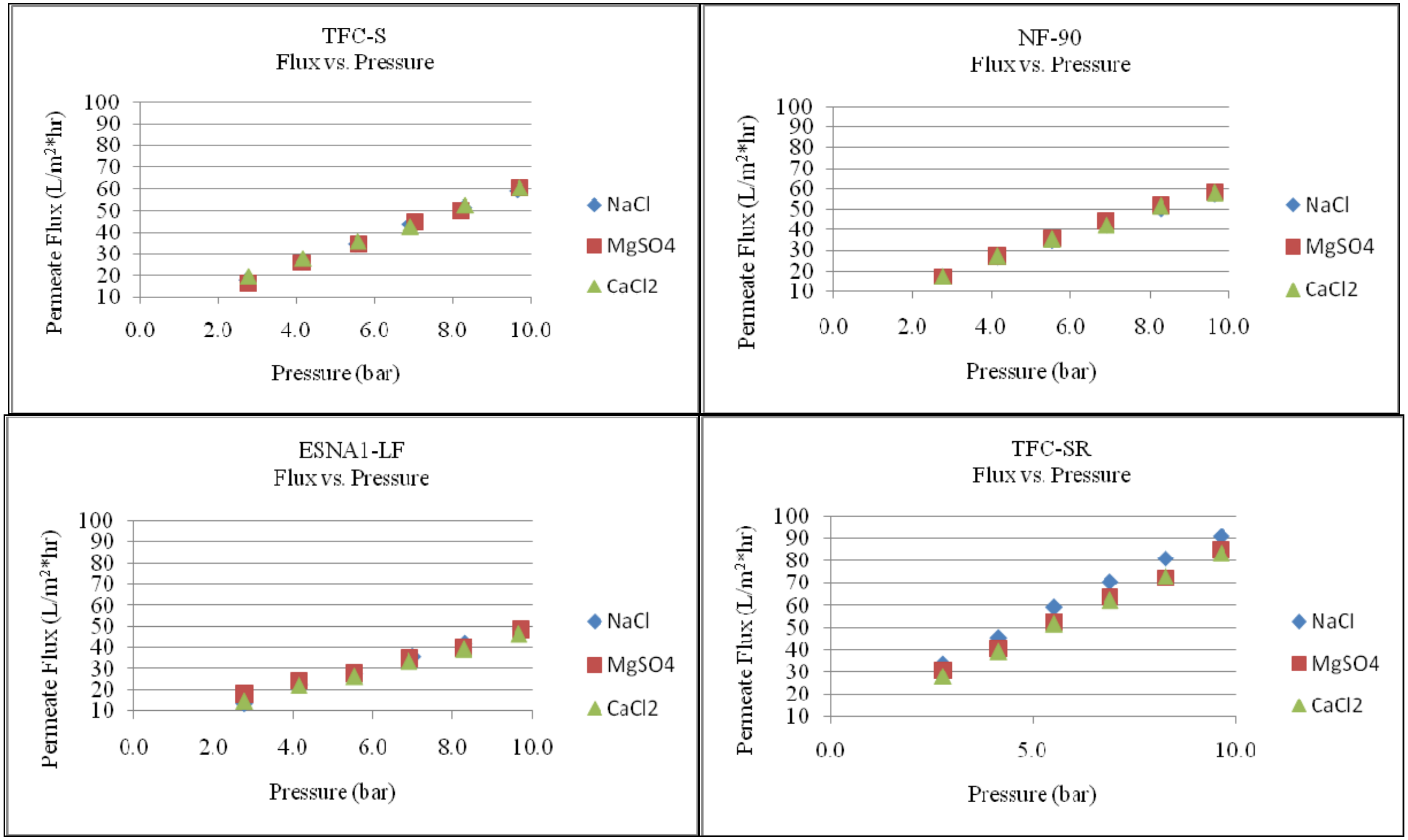


Figure 19: Flux vs. Pressure Graphs (Per Salt-Membrane)

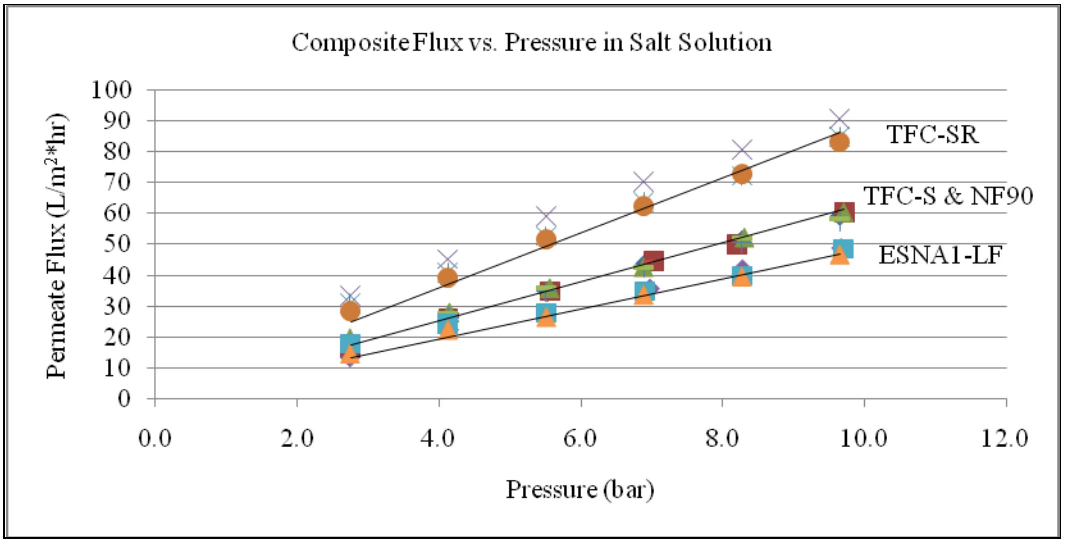


Figure 20: Composite Flux in Salt Solutions Per Membrane

5.3 Phase III

The final phase of the project entailed computing the LSI values for various blend ratios for each membrane using DWTP feed water and bypass water. Analysis of the data would suggest which membrane would make the appropriate finished water with the smallest amount of blend. According to Figures 21 and 22, using the corrected slope factor of 0.71 had negligible effect on the LSI numbers. In line with the performance of each membrane, the NF-90, TFC-S and ESNA1-LF had slightly different LSIs at the various blend ratios, while TFC-SR was the most divergent. Individual LSI parameters can be seen in Table 10.

Table 10: Water Quality Data from LSI Versus Blend Ratio Experiments

	pH	Temp (°C)	Cond (µS/cm)	TDS (mg/L)	TDS* (mg/L)	Total Alk (mg/L as CaCO3)	Cal Hard (mg/L as CaCO$_3$)	LSI	LSI*
NF90									
10%	6.92	25.1	127.6	77.8	90.6	28	32	-2.00	-2.01
15%	6.94	25.5	181.2	110.5	128.7	30	46	-1.80	-1.81
20%	6.99	25.4	221.3	135.0	157.1	48	56	-1.47	-1.48
30%	7.19	25.3	243.8	148.7	173.1	62	88	-0.97	-0.98
TFC-S									
10%	6.70	24.7	192.4	117.4	136.6	28	32	-2.25	-2.25
15%	6.90	24.9	222.7	135.8	158.1	40	50	-1.70	-1.71
20%	7.07	25.1	235.4	143.6	167.1	50	64	-1.32	-1.33
30%	7.18	25.1	247.8	151.2	175.9	66	94	-0.93	-0.94
TFC-SR2									
10%	7.32	25	261.1	159.3	185.4	90	112	-0.58	-0.59
15%	7.41	25.6	257.7	157.2	183.0	80	124	-0.49	-0.49
20%	7.41	25.2	260.4	158.8	184.9	88	132	-0.43	-0.43
30%	7.51	25.2	262.6	160.2	186.4	100	148	-0.22	-0.23
ESNA1-LF									
10%	6.67	25	170.4	103.9	121.0	36	36	-2.10	-2.11
15%	6.80	24.8	210.8	128.6	149.7	38	50	-1.82	-1.83
20%	6.92	24.8	230.7	140.7	163.8	46	74	-1.45	-1.46
30%	7.26	25.1	245.2	149.6	174.1	64	96	-0.85	-0.86

(*Calculated with adjusted slope factor)

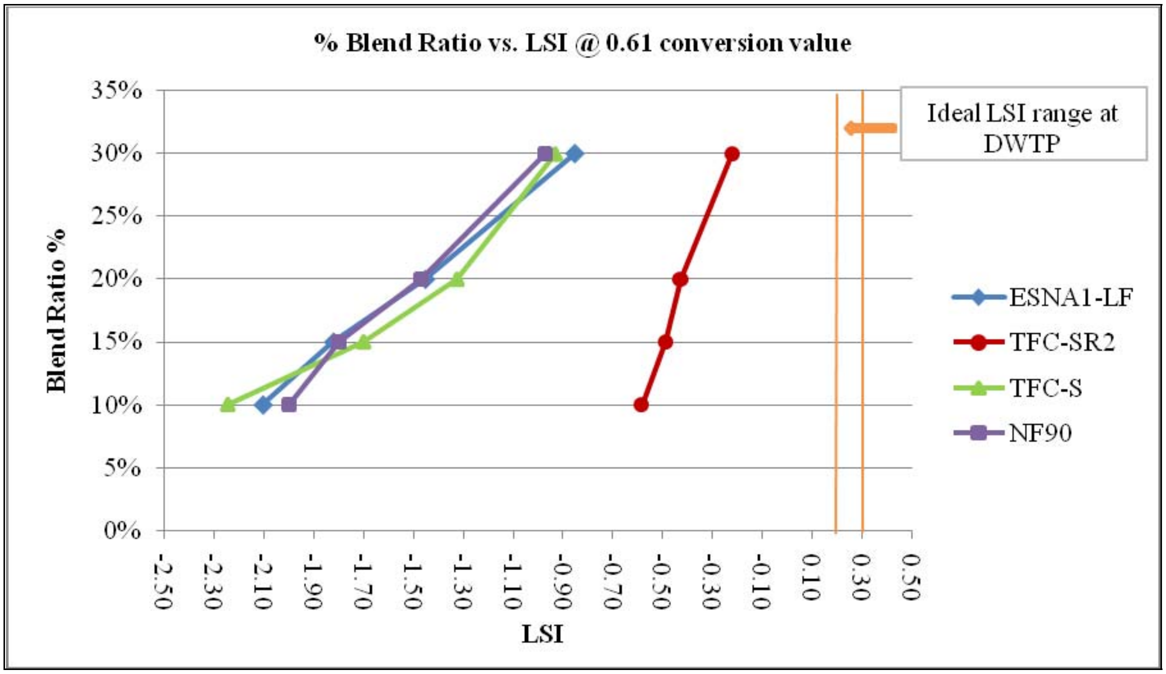


Figure 21: Percent Blend Ratio vs. LSI

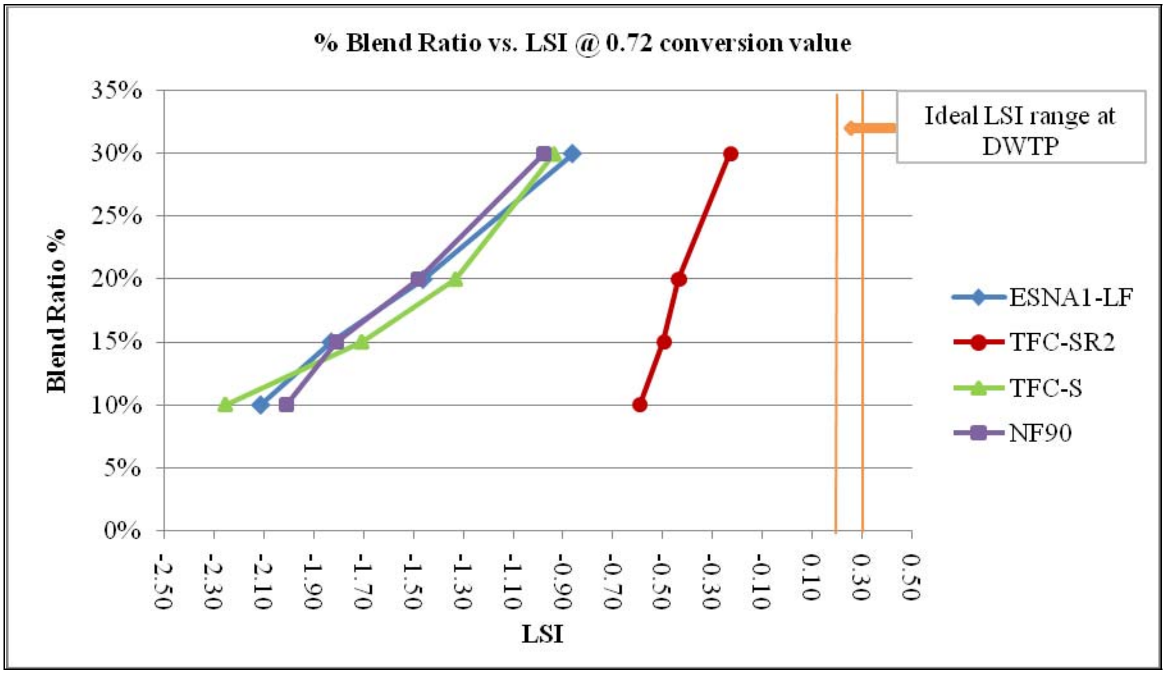


Figure 22: Blend Ratio vs. LSI (@ 0.72)

The LSI for TFC-SR is noticeably lower at all blends than any other membrane. Figures 21 and 22 follow the percent rejection values in that the most noticeable difference between the membranes was the TFC-SR element. Since the finished water at DWTP had been pH adjusted, degasified and chlorinated, the LSI values based on permeate and bypass water without benefit of any post treatment shown above will be more negative. After the additional post membrane treatment changes of pH adjustment, CO_2 removal, and chlorination the LSIs from the laboratory blends should increase in proportion to the finished water tested at DWTP if all chemical additions remain constant. The ability of the finished waters to become corrosive will remain or degrade for most of the membranes since their LSI values are not affected to the same degree as the TFC-SR.

In all the blend ratios, the TFC-SR has the strongest potential to reach the desired objective with the minimal effort. TFC-SR ranges between -0.17 and -0.53 LSI. Of the three membranes TFC-S, NF-90 and ESNA1-LF, at the highest ratio of 30%, the NF-90 had the lowest LSI of -0.92 while ESNA1-LF was -0.81. However, these numbers indicate a higher blend ratio than is currently in use at DWTP. At blends of 20% to 15%, TFC-S gives the highest LSI values. Since this is the membrane currently in use, neither the NF-90 nor the ESNA1-LF would be a better alternative. However, they have higher LSI values at the 10% blend, but relative to the current TFC-S blending value at 20% their LSI both fall below 0.7-0.79 of the TFC-S LSI value. This means that the best candidate for membrane change at the DWTP is the TFC-SR.

Not only does its LSI value increase over all blend ratios, but it provides more mineralized finished water. The TFC-SR will be the main focus for the rest of the discussion due to the operational similarities in the other three membranes.

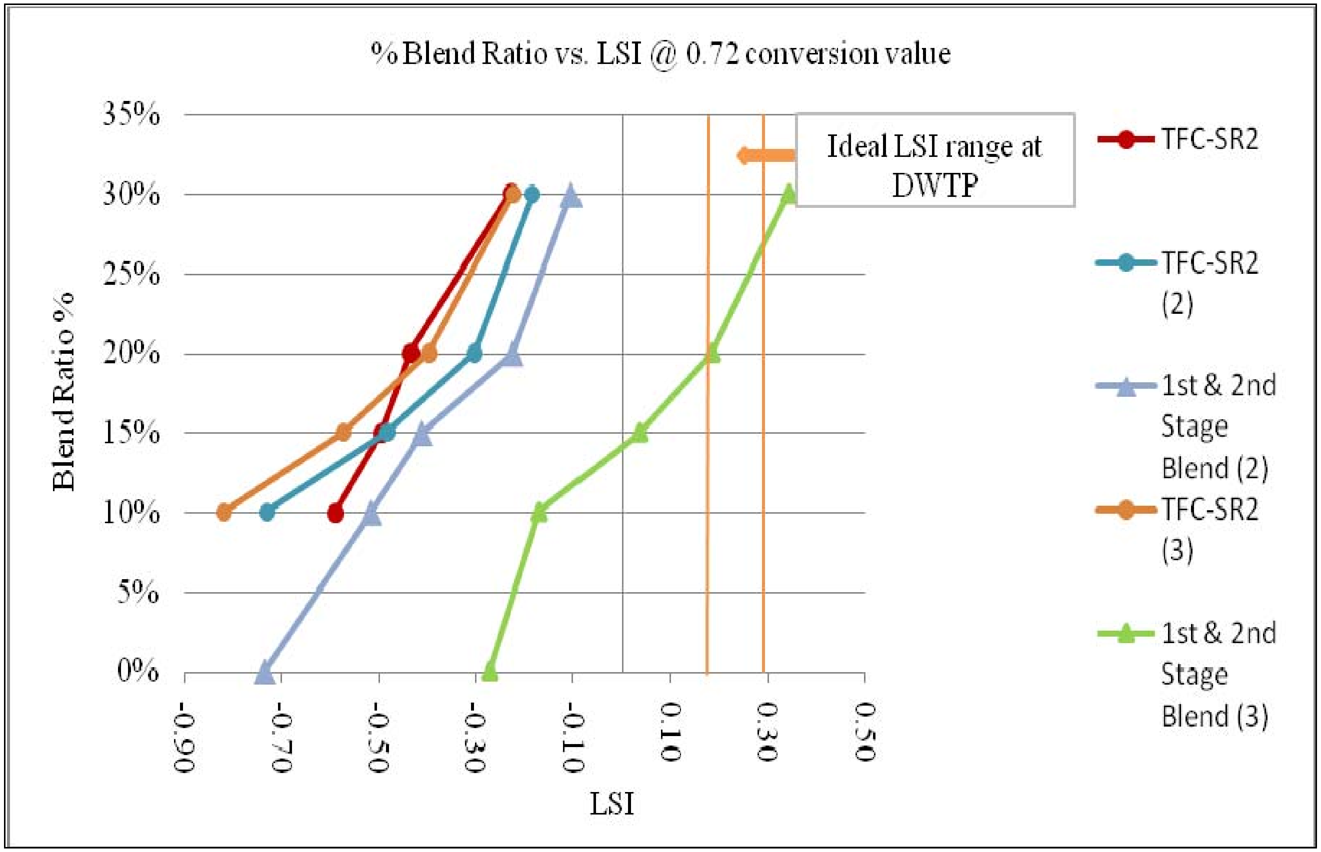


Figure 23: 1st and 2nd Stage Blend Ratios vs. LSI

Figure 23 shows the 0% and 100% blend ratio versus LSI for TFC-SR membrane. Also, the graph shows the combined first and second stage permeates blended at the same ratios. Since the objective of the DWTP is to produce a finished water with an LSI in the slightly positive range, the blends associated with the highest LSI values should be the most likely to achieve these results with the minimal amount of post membrane treatment. All three experiments with single stage permeate blends for the TFC-SR maintained roughly the same trend. There was some fluctuation in LSI but much of the difference could be attributed to the fact that different feed waters were used in all three trials. Overall, the membrane showed that it can produce a more positive LSI even with different feed water characteristics. Figure 23 shows that the 1st and 2nd stage blends tend to shift the trend in a more positive direction. However, the discrepancy between the two experiments could probably be attributed to the time it took to concentrate the feed water solution by 50%. During that time the feed and bypass water characteristics can change. Human error or equipment issues cannot be ruled out.

5.4 Implementation

5.4.1 Membrane Properties

The blend ratio impacts many different parts of the DWTP. Below in Figure 23, some of the more important relationships concerning the blend ratio are shown. Based on the experimental results, the most remarkable change in plant performance would be with the TFC-SR membrane. The NF-90 membrane exhibited lower LSI values than the current DWTP membrane at blend ratios less than 20%. Even though NF-90 had a more positive LSI value than the current DWTP membrane at the 10% blend, the NF-90 LSI was almost 50% more negative than the TFC-S LSI value at the current 20% blend ratio. Although NF-90 has a small improvement to flux and slightly lower rejection of divalent ions at the higher operating pressure ranges than TFC-S, switching to the NF-90 would not make any significant improvement to the current setup. Like the NF-90, ESNA1-LF also has a more negative LSI than TFC-S at the 10% blend ratio, but the flux is lower and the $MgSO_4$ rejection would not significantly change. Again the ESNA1-LF or NF-90 membranes would have a relatively insignificant impact on rejection, recovery, or in minimizing the allowable blend ratio. Overall, the TFC-SR membrane would be the best candidate for change because the rejection of divalent ions would decrease along with NaCl. The change in rejection and recovery would affect the plant's finished water by decreasing the aggressiveness of the water while improving the rate of recovery at a lower pressure due to a higher flux in ionic solution. If the blend ratio is lowered or removed then the membranes will have to increase recovery to maintain the same amount of finished water. With a potentially higher flux, the TFC-SR could probably accomplish it at a lower operating pressure.

At higher recoveries, the potential for fouling increases according to a review of the literature. If blending were removed from the treatment process, the recovery would have to increase by 20%. This increase could have a negative effect on the system by requiring the plant operators to increase their membrane fouling treatments. Also, higher rates of recovery might carry over into a reduction in the lifetime of the membrane because of increased usage.

Testing will have to be carried out to determine if increased fouling and a lowered life cycle of the membrane would happen if blending were reduced or eliminated.

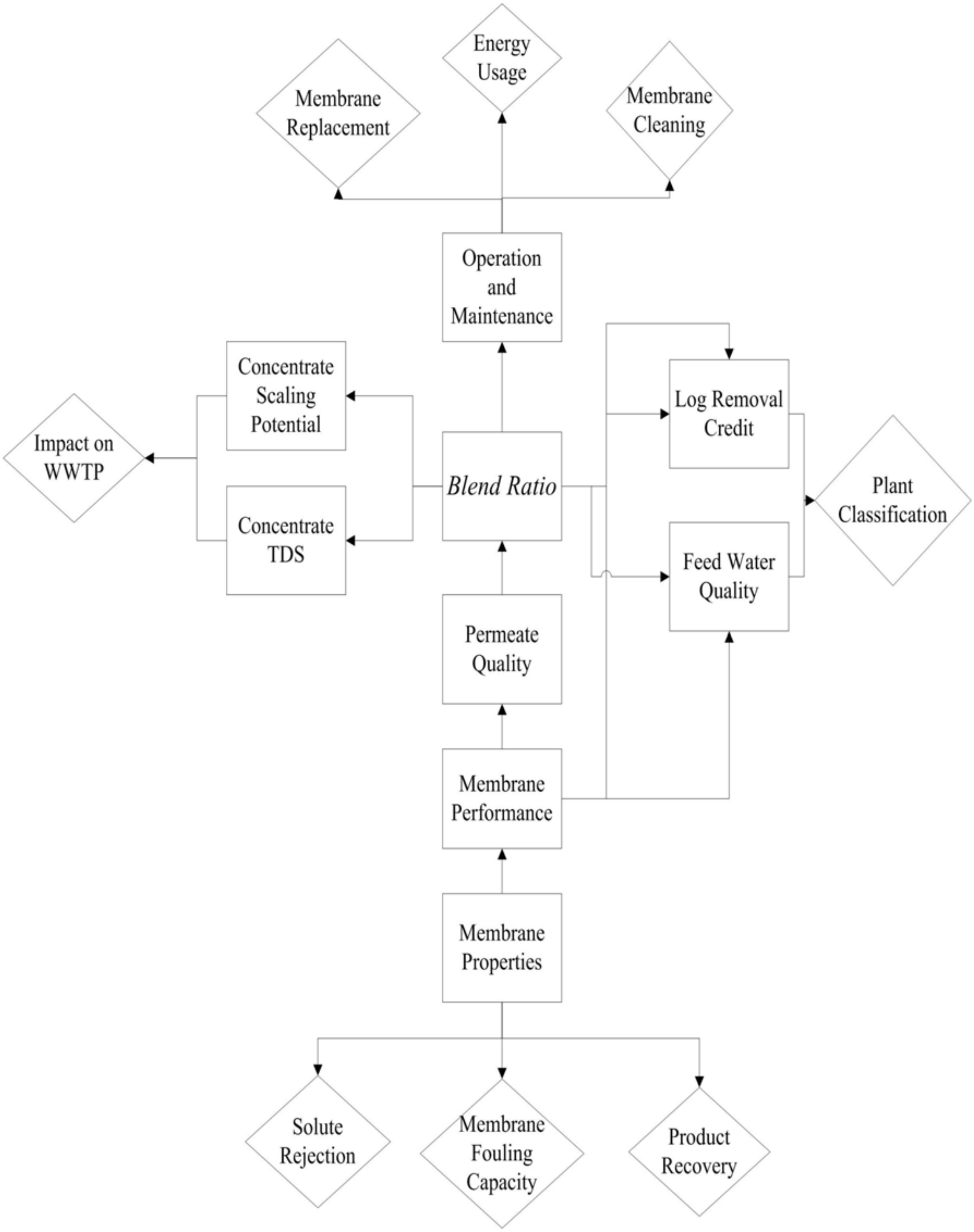


Figure 24: Blend Ratio Relationship Overview

5.4.2 Concentrate Disposal

The impact on concentrate disposal with the TFC-SR membrane would be a reduction in the TDS of the concentrate and thus a lowering of the ionic strength of the solution. This change would slightly lower hardness, alkalinity, and salinity as the concentrate would have reduced levels of Mg^{2+}, Na, and Ca^{2+}. Any scaling issues would be improved. The concentration of the ions would be reduced making it more difficult for the scale causing solutes to exceed their solubility constant. This would also affect silica scaling as the lack of Mg^{2+} and Ca^{2+} would reduce the ability for silica to cause scaling.

5.4.3 Operation and Maintenance

The most important aspect of any change in membrane or plant operation is the costs associated with it. This project did not look at actual costs in dollars because too many unknown factors would have made any estimate similar to a guess. Case in point is the actual replacement costs for the membranes. There are two choices available. DWTP can either replace the membranes with 8 ½” or 8” modules. Replacing the 8 ½” membranes would mean finding a manufacturer with the capabilities but similar price structure to make it affordable. Since the TFC-SR is made by their current membrane manufacturer it would not be that difficult to repackage the replacements, but other membrane manufacturers may include considerable cost increases. To replace the membranes with an 8” element would mean the use of brine seals or some other technology to make them fit in the current pressure vessels. This fix will have certain effects on plant processes that may include significant loss of pressure and possibly a reduction in flow through the pressure vessels. Maintenance due to fouling or mechanical issues might increase. Any comparison between the two membrane sizes will have to include more research into manufacturers and brine seal type technology than was in the scope of this paper.

However, some broad estimates towards higher or lower costs can be made by looking at the probable effects a change in membrane might entail. According to the experimental results, TFC-SR could operate at lower pressures while maintaining an increase in the LSI values. Operating at lower pressures would probably translate into increased energy savings, yet some of the savings might be negated through increased product recovery if the blend ratios were lowered or removed altogether. The reduced bypass water would include cost savings in the reduction of chlorine disinfection as more if not all of the water would pass through the membranes at lower blend ratios. The blended water would have reduced amounts of pathogens and thus reduced need for disinfection, although residual disinfection throughout the distribution system would have to be maintained. Since the LSI value for the TFC-SR treated water is more positive, reductions in pH control would probably come into effect. Other costs associated with the possible need to increase the amount of anti-scalant injected into the water might rise. Increased amount of feed water going into the system coupled with higher recoveries might increase the concentrations of the contaminants making it easier for them to overcome their solubility concentration.

5.4.4 Plant Reclassification

Any change to the membranes and blend ratio would also have an impact on the Stage 2 DBP Rule and the LT2 Rule. Changing to the TFC-SR membrane would affect the Stage 2 DBP Rule, since the membrane has the potential to decrease the amount of bypass water blend. A reduction in the amount of bypass water blended with permeate includes a reduction in NOM. Most NOM that reaches the RO/NF filters would be taken out at similar efficiencies due to the removal effects of these membranes. Less NOM means less DBP precursors making it easier for the plant to stay within the DBP MCLs.

A change to TFC-SR would only have a positive effect on the LT2 Rule if the no bypass water was blended. The LT2 gives treatment credits in log removal for various processes in the water treatment plant that affect the removal or inactivation of *Cryptosporidium*. Any blend with minimally treated raw water negates the possible credit received by the membrane filtration process. According to the LT2 Rule, the DWTP would most likely be placed in bin one category which is the least restrictive in terms of showing log removal. Without mandated monthly tests for *Cryptosporidium* over a 24 month period, this assumption cannot be verified. However, the plant's source water suggests that contamination by either *Cryptosporidium* or *Giardia* would be unlikely. If the DWTP was listed as a filtration treatment plant with the FDEP and categorized within bin one, then it would only have to provide the standard 3 log removal required for turbidity. The plant would most likely be considered a Filtered Treatment Center because filtration by Greensand and cartridge were used on both the feed and bypass streams.

If the plant was able to be reclassified and placed under the LT2 regulations *Cryptosporidium* testing would have to be implemented along with integrity tests on certain processes to verify the assessment of this paper.

6. CONCLUSION

Membranes ESNA1-LF, NF-90 and TFC-SR were compared to the existing membrane TFC-S as an evaluation of possible changes in the blend ratio and its subsequent effect on the DWTP's processes. In conclusion, the greatest change from any membrane replacement would be in the switch to the TFC-SR modules. At all pressure ranges regardless of the solution TFC-SR maintained higher flux than any other membrane. At operating pressures of 100 psi and 120 psi the TFC-SR flux for the various salt solutions increased by approximately 45% above the current membrane. The TFC-SR showed lower rejection for the three salts tested than the TFC-S. Using TFC-SR at the 120 psi and the 100 psi operating pressures the NaCl rejection fell around 27%, $MgSO_4$ fell around 8.5%, and $CaCl_2$ fell between 7.5% - 5.2%. No other membrane tested had more positive change in membrane flux and rejection values than the TFC-SR. The decreased rejections values equate into a less aggressive permeate than is currently produced at the DWTP.

The aggressiveness of the finished water was measured by the LSI. According to the experimental values, TFC-SR produced a more positive LSI over the 0% to 30% blend range in relation to TFC-S. At 0% blend, TFC-SR produced a slightly more positive and slightly more negative LSI than any other membrane at a 30% blend. The TFC-SR has the potential to eliminate blending at DWTP.

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APPENDICES

Appendix 1: Overview of the Dunedin Well Water Collection System

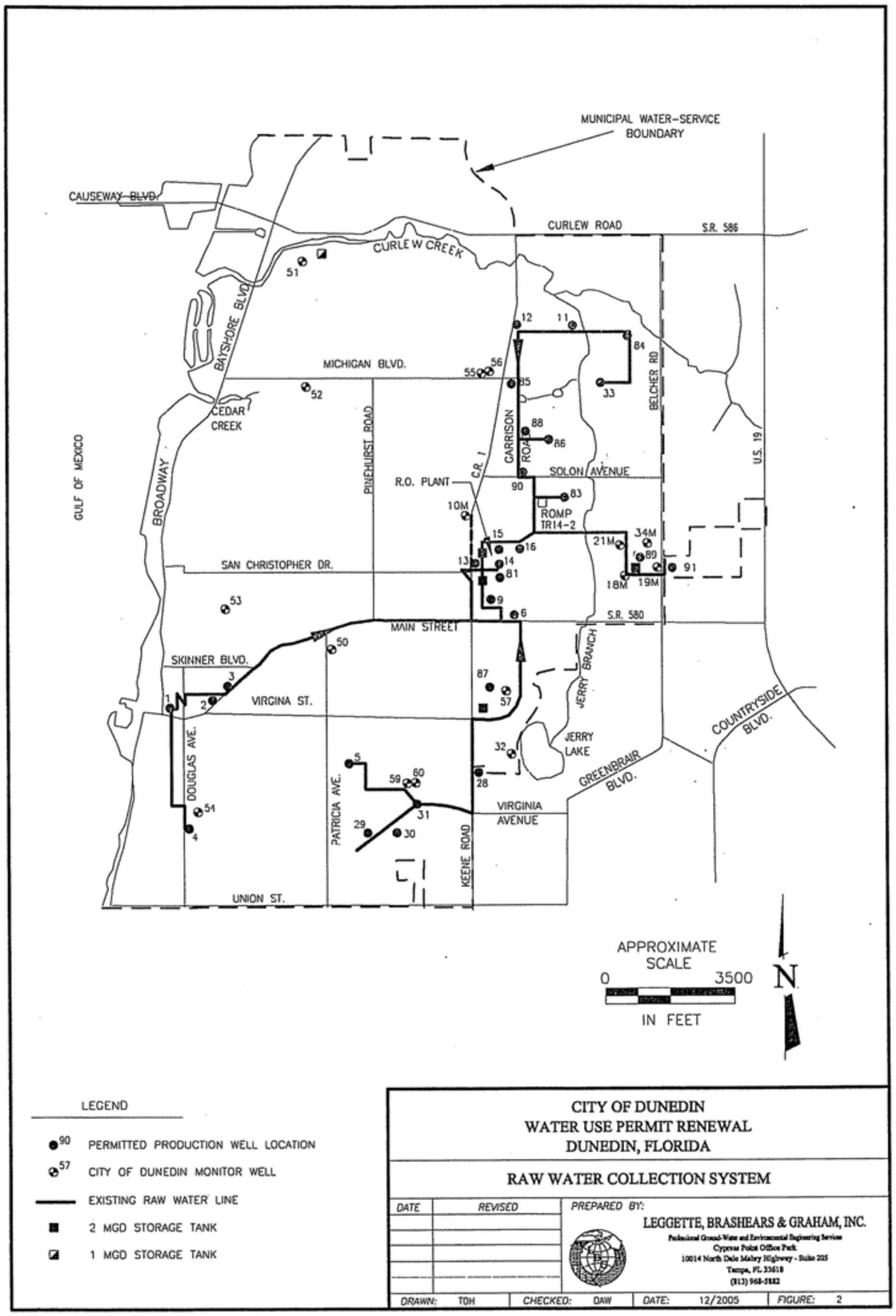

Figure 25: Dunedin Well System Collection Map

Appendix 2: Diagram of the Dunedin Water Treatment Plant

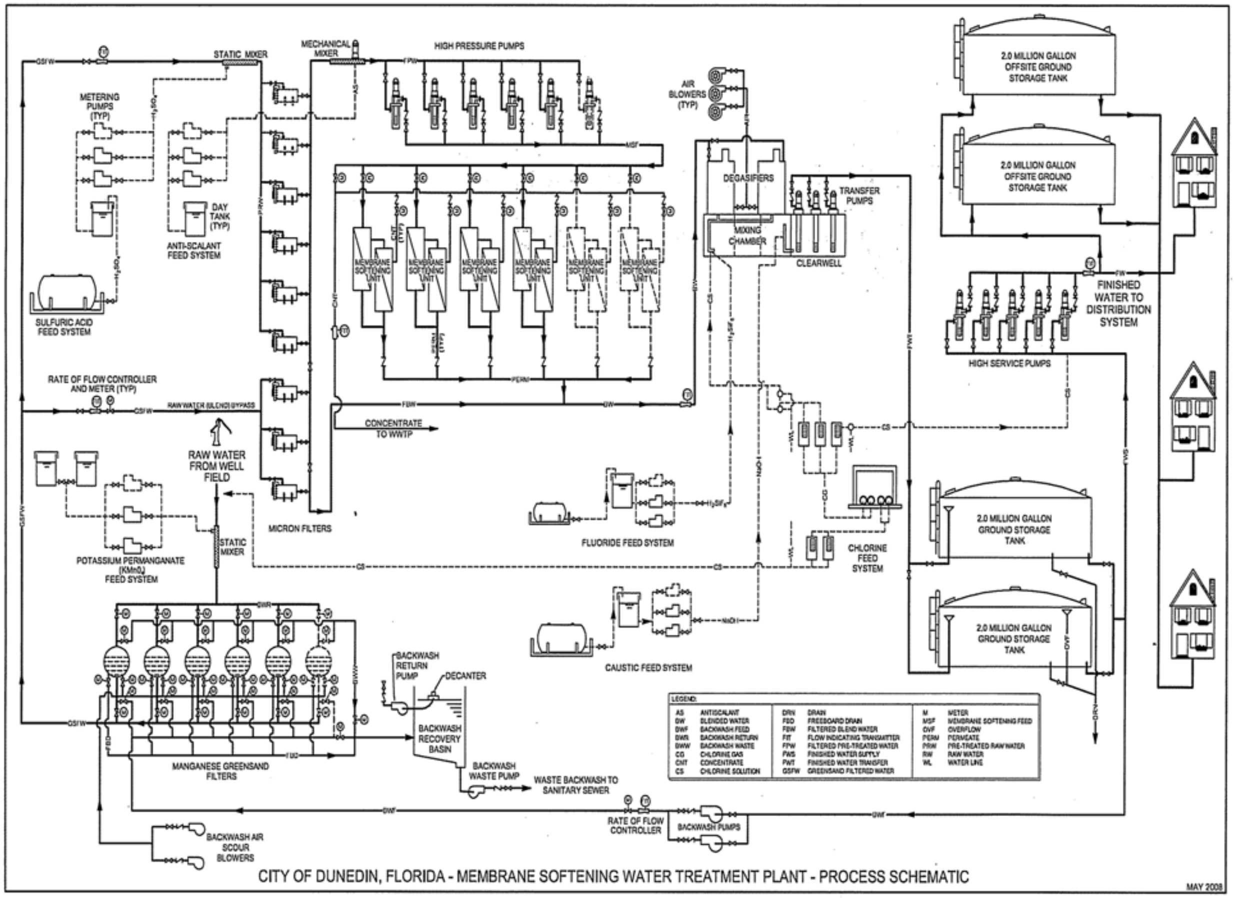

Figure 26: DWTP Plant Schematic

Appendix 3: Overview of All the Measurements and Locations at the DWTP

Table 11: Overview of the Measurements Performed at DWTP

Measurement	Plant	Lab*	Instrumentation**	Wells	Raw	Effluent	Clearwell	Concentrate	Feed	2 Cswy Blvd.	Interstage	Stage 1 Perm.	Stage 2 Perm.	Total Perm.	Concentrate	Green Sand Filters
Flow			x						1/m			1/m	1/m	1/m	1/m	6/d
Pressure			x						2/d, 1/m			1/m	1/m	1/m	1/m	
pH		x	x	1/6m	1/d	3/d	4/d	3/d	2/d, 1/m	1/d		1/m	1/m	1/m	1/m	
Temperature			x						2/d							
Conductivity		x		1/6m	1/d	3/d	4/d	1/d	2/d, 1/m		1d	1/d	1/d	1/d	1/d, 1/m	
Turbidity		x			1/d	3/d	4/d	1/d	2/d							
Alkalinity		x		1/6m	1/d	3/d	4/d	1/d								
Calcium Hardness		x			1/d	3/d	4/d	1/d	1/m			1/m	1/m	1/m	1/m	
Total Hardness		x			1/d	3/d	4/d	1/d								
Free Cl		x				6/d	12/d			1/d						
Total Cl		x							12/d							
Chlorides		x		1/m, 1/3m		3/d	4/d									
Flouride		x			1/d	3/d	4/d									
Sulfates		x		1/3 m												
Fe		x		1/6m	1/d	3/d	4/d									6/d

Appendix 3: (Continued)

Table 11: (Continued)

Measurement	Plant	Lab*	Instrumentation**	Wells	Raw	Effluent	Clearwell	Concentrate	Feed	2 Cswy Blvd.	Interstage	Stage 1 Perm.	Stage 2 Perm.	Total Perm.	Concentrate	Green Sand Filters
Mn		x		1/6m	1/d	3/d	4/d									6/d
Br		x		1/6m												
NO_3		x		1/6m												
Dis. Silica		x		1/6m												
SO_4		x		1/6m												
TDS		x		1/3m, 1/6m												
As		x		1/6m												
Ca		x		1/6m												
Mg		x		1/6m												
K		x		1/6m												
Na		x		1/6m												
HS		x		1/6m												
TOC		x		1/6m												
Pressure Differential			x													1/d
LSI		x				3/d		4/d		1/d						

Appendix 4: List of Each Water Quality Lab Test at DWTP

Site	Time	Location	Type of Sample Testing	Testing Location
Wells:	Monthly		Chlorides, water levels	Lab**
	Quarterly		Sulfates, TDS, Chlorides	Lab**
	Bi-Annual testing of production wells		Conductivity (field), pH (field)	Field
			Alkalinity: Total, Bicarb, Carb	Lab**
			Br, Cl, NO3, Dis. Silica, SO_4, TDS, AS, Ca, Fe, Mg, K, Na	Lab**
			HS, TOC	Lab**
Skids 1-4				
	Daily	Feed	turbidity, pH, Conductivity, Temperature, Pressure	In-house
		Interstage	Conductivity	In-house
		Stage1 Permeate	Conductivity	In-house
		Stage2 Permeate	Conductivity	In-house
		Total Permeate	Conductivity	In-house
		Concentrate	Conductivity	In-house
	Monthly	Feed	Pressure, Conductivity, Flow, Calcium Hardness, pH	In-house
		1st Stage	Pressure, Flow, Calcium Hardness, pH	In-house
		2nd Stage	Pressure, Flow, Calcium Hardness, pH	In-house
		Permeate	Pressure, Flow, Calcium Hardness, pH	In-house
		Concentrate	Pressure, Conductivity, Flow, Calcium Hardness, pH	In-house
Green Sand Filters 1-5	Daily	Filters (1-5)	Flow	In-house
			Run Time	In-house
			Pressure Differential	In-house
			KMnO4 residual, levels	In-house
	Daily	Cartridge Filters 1-5	Fe, Mn	In-house

Appendix 4: (Continued)

Misc.			
	Raw	Fe, Mn	In-house
	Clearwell	Fe, Mn	In-house
	Effluent	Fe, Mn	In-house
	Raw	Flouride	In-house
	Clearwell	Flouride	In-house
	Effluent	Flouride	In-house
	Raw	pH, Alkalinity, Calcium Hardness, Total Hardness, Cl, Turbidity, Conductivity	In-house
	Clearwell	pH, Alkalinity, Calcium Hardness, Total Hardness, Cl, Turbidity, Conductivity	In-house
	Effluent	pH, Alkalinity, Calcium Hardness, Total Hardness, Cl, Turbidity, Conductivity, LSI*	In-house
	Concentrate	pH (3x), Alkalinity, Calcium Hardness, Total Hardness, Cl, Turbidity, Conductivity, LSI*	In-house
	2 Causeway Blvd, (Farthest pt. in distr. Sys.)	Cl, LSI*, pH	

	Plant	Rain levels	In-house
	North Head	Free & Total Cl	
	South Head	Free & Total Cl	
	West Head***	N/A	

*LSI = Langlier Saturation Index (scale and corrosive test)

**Testing done by Southern Analytical

***West headwork is not pre chlorinated

Appendix 5: List of Drinking Water Monitoring Done at the DWTP

Site	Time	Location	Type of Sample Testing
Distribution System	1/9 yrs	N/A	Asbestors
Distr. Sys.	1/yr	N/A	Nitrate & Nitrite
Distr. Sys.	1/yr	N/A	Inorganics
Distr. Sys.	1/yr	N/A	THCs & HAA5
Distr. Sys.	1/3yrs	N/A	Secondary Contaminants
Distr. Sys.	1/9yrs	N/A	Gross Alpha, Radium & Uranium
Distr. Sys.	1/3yrs	N/A	Volatile Organinc
Distr. Sys.	8/3yrs	N/A	Synthetic Organics
Distr. Sys.	# per mo./yr	N/A	Microbial Contaminants
Distr. Sys.	1/3yrs	N/A	Beta particle & photon radioactivity

**Testing done by Southern Analytical

Appendix 6: Specification Sheet for KOCH TFC-S Membrane

Name:	*KOCH TFC-S*
Type:	Reverse Osmosis

Product Specifications:

Product	Nominal Active Surface Area (m^2)	Product Water Flow Rate (m^3/d)	Stabilized Salt Rejection (%)
TFC-S	38		
$MgSO_4$		35.2	99.25

Comments:

1000 mg/l $MgSO_4$, 80 psi, 77°F (25°C) and 15% recovery.

Dimensions	Membrane Element Diameter	Permeate Tube Diameter	Membrane Element Length
	8 (in)	1.5 (in)	40 (in)

Operating Limits

Membrane Type	Polyamide TFC
Max. Operating Temperature	45 °C
Max. Operating Pressure	350 psig
Maximum Pressure Drop	10 psi
pH Range, Continuous Operation	4-11
pH Allowoble Short Term Cleaning	2.5-11
Maximum Feed Flow	75 gpm
Maximum Feed Silt Density Index	SDI 5
Free Chlorine Tolerance	<0.1 ppm

(Based on the KOCH TFC-S specification sheet)

Appendix 7: Specification Sheet for KOCH TFC-SR Membrane

Name:	*KOCH TFC-SR*
Type:	Nanofiltration

Product Specifications:

Product	Nominal Active Surface Area (m^2)	Product Water Flow Rate (m^3/d)	Stabilized Salt Rejection (%)
TFC-SR	35.8		
$MgSO_4$		58.7	95
NaCl		58.7	10-30

Comments:

5000 mg/l $MgSO_4$, 96 psi , 77°F (25°C) and 15% recovery.
2000 mg/l NaCl, 95 psi , 77°F (25°C) and 15% recovery.

Dimensions	Membrane Element Diameter	Permeate Tube Diameter	Membrane Element Length
	8 (in)	1.5 (in)	40 (in)

Operating Limits	
Membrane Type	Polyamide TFC
Max. Operating Temperature	113 °C
Max. Operating Pressure	500 psig
Maximum Pressure Drop	10/15 psi
pH Range, Continuous Operation	4-9
pH Allowoble Short Term Cleaning	2-11
Maximum Feed Turbidity	1 NTU
Maximum Feed Silt Density Index	SDI 5
Free Chlorine Tolerance	<0.1 ppm

(Based on the KOCH TFC-S specification sheet)

Appendix 8: Specification Sheet for FILMTEC NF-90 Membrane

Name: *FILMTEC NF-90*
Type: Nanofiltration

Product Specifications:

Product	Nominal Active Surface Area (m^2)	Product Water Flow Rate (m^3/d)	Stabilized Salt Rejection (%)
NF90	37		
NaCl		28.4	85-95
MgSO4		36	>97

Comments:

2,000 mg/l NaCl, 70 psi , 77°F (25°C) and 15% recovery.
2,000 mg/l MgSO4, 70 psi, 77°F (25°C) and 15% recovery.

Dimensions	Membrane Element Diameter	Permeate Tube Diameter	Membrane Element Length
	40 (in)	1.5 (in)	40 (in)

Operating Limits

Membrane Type	Polyamide TFC
Max. Operating Temperature	45 °C
Max. Operating Pressure	600 psig
Maximum Pressure Drop	15 psig
pH Range, Continuous Operation	3-10
pH Range, Short-Term Cleaning (30 min)	1-13
Maximum Feed Flow	70 gpm
Maximum Feed Silt Density Index	SDI 5
Free Chlorine Tolerance	<0.1 ppm

(Based on the FilmTec NF90 specification sheet)

Appendix 9: Specification Sheet for HYDRANAUTICS ESNA1-LF Membrane

Name:	*Hydranautics ESNA1-LF*
Type:	Nanofiltration

Product Specifications:

Product	Nominal Active Surface Area (m^2)	Product Water Flow Rate (m^3/d)	Stabilized Salt Rejection (%)
NF90	37		
$CaCl_2$		31	91

Comments:

500 mg/l $CaCl_2$, 70 psi , 77°F (25°C) and 15% recovery.

Dimensions	Membrane Element Diameter	Permeate Tube Diameter	Membrane Element Length
	7.99 (in)	1.125 (in)	36 (in)

Operating Limits

Membrane Type	Polyamide TFC
Max. Operating Temperature	45 °C
Max. Operating Pressure	600 psig
Maximum Pressure Drop	10 psi
pH Range, Continuous Operation	3-10
Minimum Ratio of Concentrate to Permeate Flow for any Element	5:1
Maximum Feed Flow	75 gpm
Maximum Feed Silt Density Index	SDI 5
Free Chlorine Tolerance	<0.1 ppm

(Based on the Hydranautics ESNA1-LF specification sheet)

Appendix 10: Historical Data of the Dunedin Water Treatment Plant

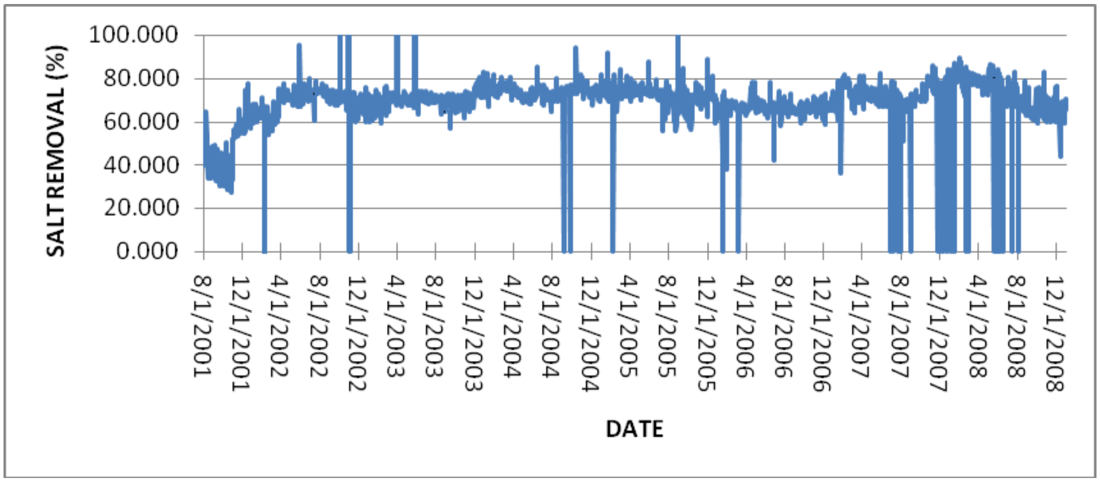

Figure 27: Historical %Salt Removal Over Time

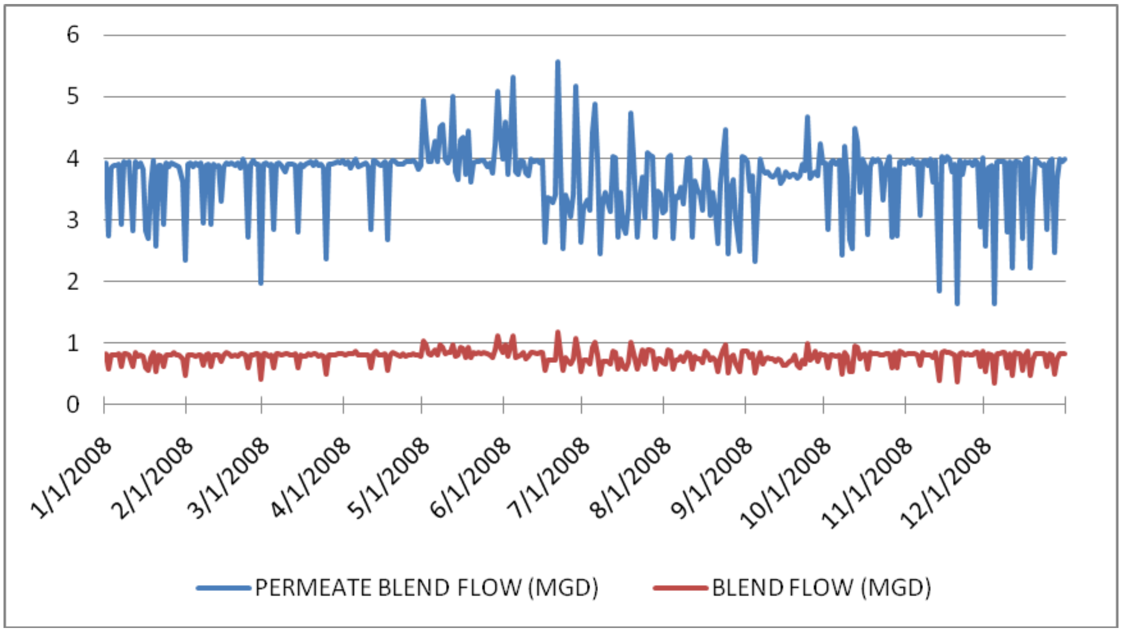

Figure 28: Historical Blend Flows

Appendix 11: TDS vs. Conductivity Graphs

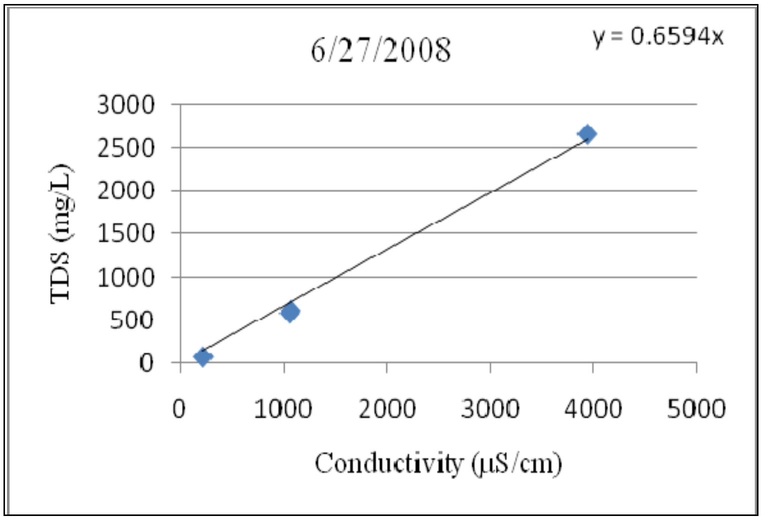

Figure 29: TDS vs. Conductivity for 6/27/2008

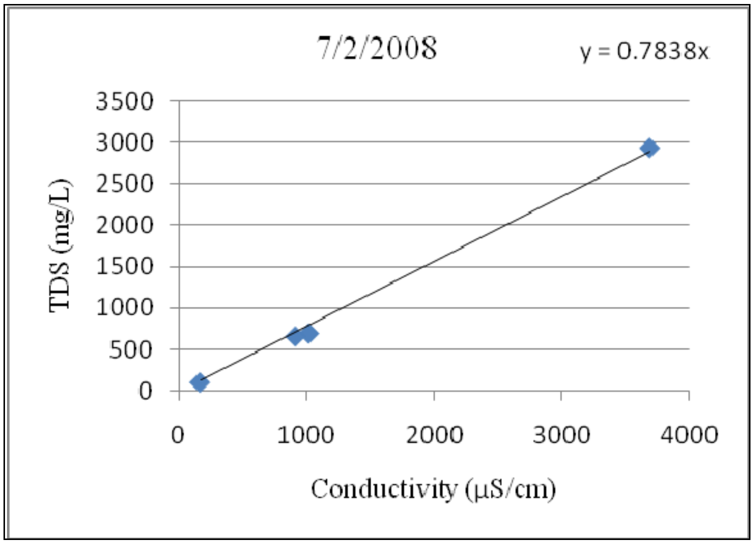

Figure 30: TDS vs. Conductivity for 7/2/2008

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Appendix 11: (Continued)

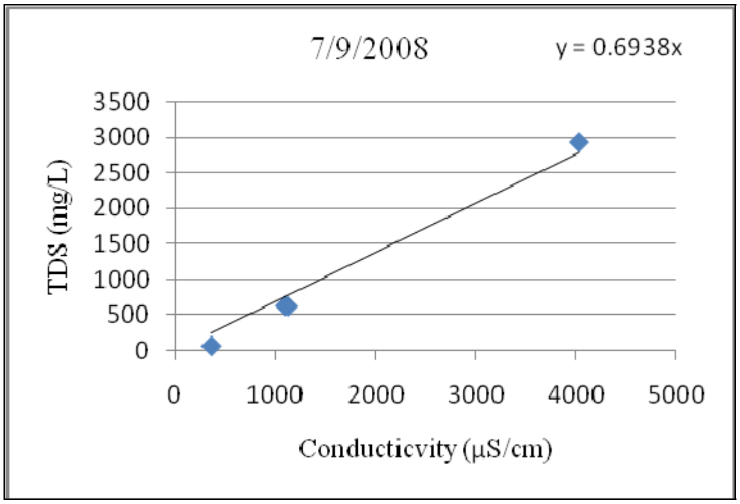

Figure 31: TDS vs. Conductivity for 7/9/2008

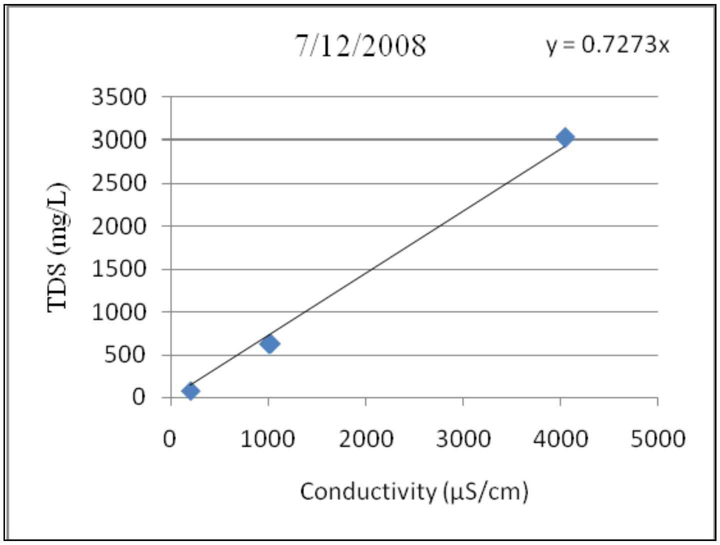

Figure 32: TDS vs. Conductivity for 7/12/2008

Appendix 11: (Continued)

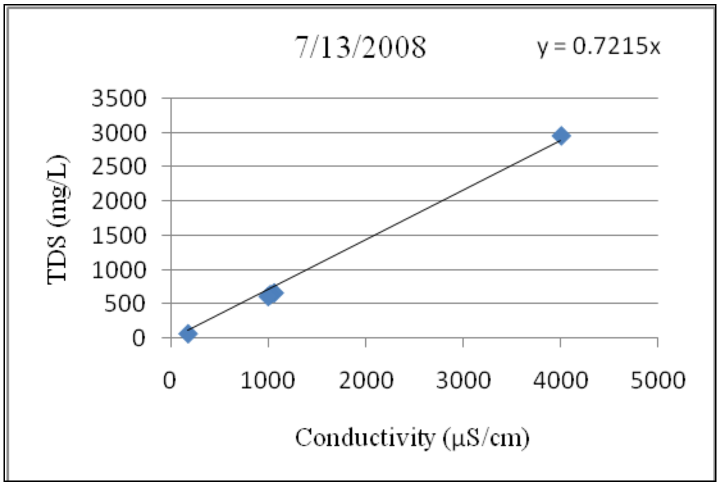

Figure 33: TDS vs. Conductivity for 7/13/2008

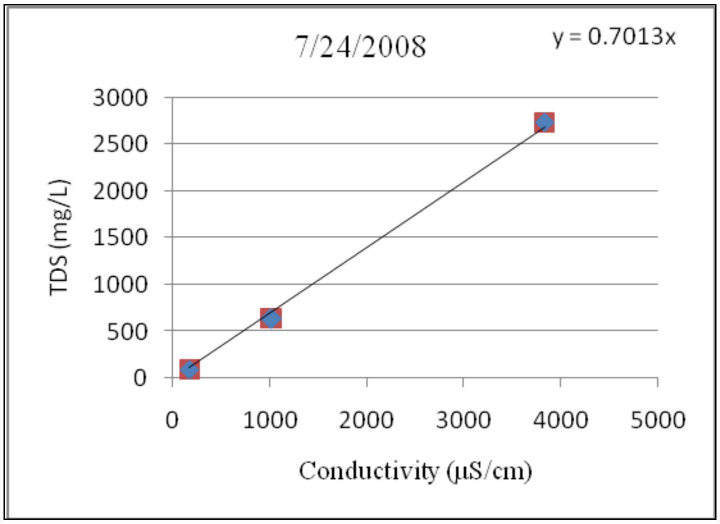

Figure 34: TDS vs. Conductivity for 7/24/2008