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Reducing Sulfuric Acid Pretreatment in a Nanofiltration Process Treating Surficial Groundwater

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REDUCING SULFURIC ACID PRETREATMENT IN A NANOFILTRATION PROCESS TREATING SURFICIAL GROUNDWATER

by

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B.S. Env.E. University of Central Florida, 2016

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ABSTRACT

Nanofiltration (NF) is a pressure driven membrane process employed in drinking water treatment that requires pretreatment for reliable operation. The objective of this research was to determine if NF membranes can proficiently operate with a decreased or eliminated dose of sulfuric acid pretreatment. When used as pretreatment, sulfuric acid prevents calcium carbonate scaling on NF membranes, yet is costly, hazardous, and imparts high sulfate concentrations to NF feed and concentrate streams. To conduct this research, a 0.324 million gallon per day (MGD) NF pilot plant was operated for 3,855 run-hours at a flux rate of 15 gallons per square foot-day. The NF pilot unit's process performance, productivity, and water quality were monitored while the sulfuric acid dose was gradually decreased, controlled by monitoring pH that ranged from pH 6.5 (80 mg/L sulfuric acid dose) to pH 7.0 (no sulfuric acid dose). NF pilot productivity, as measured by specific flux, was found to decline when sulfuric acid was eliminated by 2.33 percent, 9.61 percent, and 4.08 percent in the first stage, second stage, and total pilot system, respectively, with no distinguishable increase in pressure drop. Noticeable water quality trends include approximately 75 percent sulfate decrease in feed and concentrate streams, and 20 percent increase of calcium hardness and alkalinity in the permeate stream. After piloting, superimposed elemental imaging analysis revealed that the second stage, tail-end membrane surface was fouled with iron disulfide, calcium carbonate, clay, and natural organic matter. However, flux recovered to normal operating conditions after a membrane cleaning was performed. Results of the pilot study indicated that sulfuric acid could be eliminated from the full-scale NF pretreatment process; however, membrane cleaning frequencies could increase. If applied to the full-scale NF process, elimination of sulfuric acid pretreatment would reduce annual chemical costs by over $70,000.

To my parents, whose unrelenting love and support has allowed me to grow and strive to achieve more than I’ve ever thought possible.

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LIST OF ACRONYMS AND OTHER ABBREVIATIONS

AWC	American Water Chemicals
AWWA	American Water Works Association
AX	anion exchange
DBP	disinfection by-product
DOC	dissolved organic carbon
gfd	gallons per day per feet squared
gpd	gallons per day
gpm	gallons per minute
I-stat	Industrial Statistic
IX	ion exchange
J_W	water flux
J_{SP}	specific flux
LRD	Loxahatchee River District
LSI	Langelier Saturation Index
MF	microfiltration
MFI	modified fouling index

MGD	million gallons per day
NF	nanofiltration
nm	nanometer
NOM	natural organic matter
NPF	Normalized permeate flow
NSP	Normalized salt passage
NSR	Normalized salt rejection
P_D	pressure drop
psi	pounds per square inch
psig	pounds per square inch gauge
RO	reverse osmosis
RPD	Relative Percent Difference
RSI	Ryznar Stability Index
SDI	Silt Density Index
SCADA	Supervisory control and data acquisition
S&DSI	Stiff and Davis Stability Index
Town	Town of Jupiter Water Utilities

TDS	total dissolved solids
TSS	total suspended solids
TOC	total organic carbon
UCF	University of Central Florida
UF	ultrafiltration
USEPA	United States Environmental Protection Agency
UCL	Upper Control Limit
UWL	Upper Warning Limit
WTF	Water Treatment Facility
WTP	Water Treatment Plant
µS/cm	microSiemans per centimeter

CHAPTER 1. INTRODUCTION

Nanofiltration (NF) is a pressure driven membrane separation process that relies on a semi-permeable membrane and is used in water treatment and other separation processes. NF is often referred to as membrane softening, which is one of the major uses of the technology. In water treatment, NF processes are used for the removal of hardness (divalent cations), disinfection by-product precursors (natural organic carbon), pesticides (synthetic organic compounds), and color reduction. NF processes require pretreatment to improve the quality of the feed water to a condition that would result in reliable operation of the membranes. In the absence of adequate pretreatment, the membrane surface becomes rapidly covered by incompatible material present in the feed water, resulting in membrane fouling which is detected by a decrease in membrane productivity with time.

Recently, NF processes have been used to replace aging lime softening processes in water treatment due to the competitive cost and superior quality of the membrane treated water (Bergman, 1995). NF membranes are constructed in polyamide thin-film composite configurations that are comprised of semipermeable material with nanometer (nm) size pores. Pressure drives water through the semipermeable material, separating water from constituents larger than the pore size. NF membranes can achieve 95 percent and 40 percent removal of divalent ions and monovalent ions, respectively (Mukiibi and Feathers, 2009). The ions that are separated from the source water flow into the reject water, otherwise known as the concentrate stream, or become fixed on the membrane. When ions consisting of a salt are concentrated beyond their solubility limits, they can precipitate (scale) within the membrane concentrate channel. Calcium carbonate, calcium sulfate, and silica are the more common membrane scalants in drinking water treatment applications (Howe et al., 2012). However, pretreatment unit operations can reduce scale and ultimately protect membranes.

In general, pretreatment techniques rely on physical or chemical means. Physical pretreatment removes suspended solids, which prevent particulates from plugging the membrane. Physical pretreatment techniques include, but are not limited to: sand filtration, cartridge filtration, or ultrafiltration membrane filtration. Chemical pretreatment prevents sparingly soluble salts from precipitating on to the membrane surface, hence thwarting scale. Chemical pretreatment typically includes scale inhibitors or acid addition. Scale inhibitors (or antiscalants) prevent the precipitation of ions by disrupting crystallization and are employed to control sparingly soluble salts such as calcium sulfate, barium sulfate, strontium sulfate, calcium fluoride and silica. Acids are employed to control calcium carbonate scaling by lowering the feed pH, shifting bicarbonate alkalinity in the aqueous phase and preventing the formation of calcium carbonate onto the membrane surface. The addition of acid depresses water pH through the membrane process and into post-treatment, yielding superior hydrogen sulfide stripping via degasification. However, with advancements in membrane technology and scale inhibitor formulation, the addition of acid pretreatment may be decreased or eliminated without altering the efficiency of the system (Kinser et al., 2008). Acid addition increases anion content in the water (i.e. sulfate from sulfuric acid or chloride from hydrochloric acid) which can alter the precipitation of sparingly soluble salts. In addition, mineral acids such as sulfuric acid and hydrochloric acid are considered hazardous materials and require special handling requirements as mandated by the Occupational Safety and Health Administration (OSHA) that establishes minimum health and safety standard for workers handling hazardous materials. Detailed sulfuric acid unloading procedures and safety guidelines are found in government publications (Occupational Safety and Health Administration, 2017).

NF processes require pretreatment to improve the quality of the feed water to a condition that would result in reliable operation of the membranes. In the absence of adequate pretreatment, the membrane surface becomes covered by incompatible material present in the feed water resulting in a decrease in membrane productivity, which can increase operational costs. The fundamental objective of this research was to determine if NF membranes can proficiently operate with a decreased or eliminated dose of sulfuric acid pretreatment.

CHAPTER 2. LITERATURE REVIEW

In drinking water treatment, membrane technology is applied to remove contaminants from water by a driving force delivered across a semipermeable media (Howe et. al, 2012). Membranes can be categorized by driving force, which includes temperature gradient, concentration gradient, pressure gradient, or electrical potential. Pressure driven membranes are namely microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), and reverse osmosis (RO), and are often classified by solute exclusion size, or pore size, ranging from 0.1 µm to 0.0001 µm (Duranceau and Taylor, 2011). MF and UF remove particles via a sieving mechanism while NF and RO remove particles via a diffusion-controlled separation process (AWWA, 2007). NF is often grouped with RO, and is sometimes referred to as “loose RO”, as it requires less pressure and allows monovalent ions to pass through while removing divalent ions, color, and organic matter from water (Van Der Bruggen, 2013; Hilal et al., 2004).

An Overview of Nanofiltration

Nanofiltration (NF) membranes are commonly comprised of a thin, semipermeable polymer material fabricated in a spiral wound configuration that separates particles from water by means of pressure. Feed water travels tangentially through the membrane surface in a spiral path into a center collection tube, known as permeate, while rejected contaminants do not pass through the membrane and are instead collected on the outer diameter of the membrane, known as concentrate. Figure 2-1 depicts the structure of a spiral-wound membrane element. The semipermeable material has a pore size of 1 nanometer (nm), which can reject natural organic matter (NOM) and divalent ions from water, but rejection of monovalent ions ranges from 20-70 percent (Baker, 2004).

Rejection refers to the percentage of solute concentration that does not pass through the membrane. In drinking water application, NF membranes are used for brackish water desalination, softening, and disinfection by-product (DBP) control (Howe et al., 2012; Choi et al., 2001).

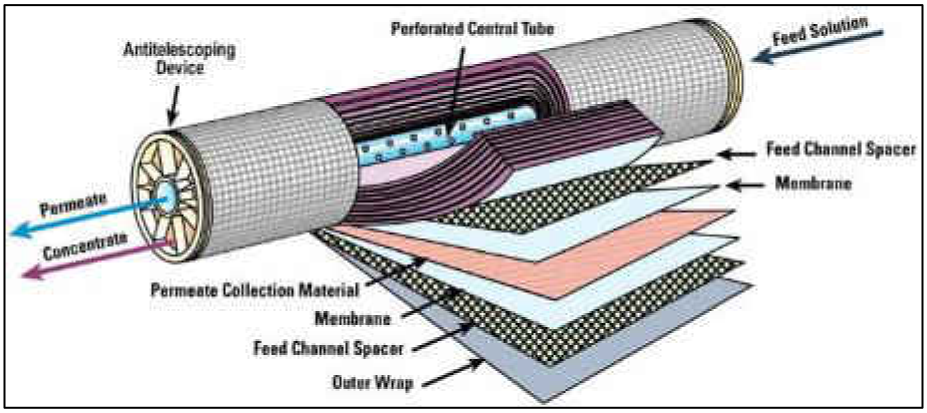


Figure 2-1: Configuration of Spiral-Wound Membrane Element (LIXUS, 2013).

Membrane performance is affected by feed temperature, feed water composition, feed pressure, and recovery rate (percentage of water treated). Membrane performance is often evaluated by normalized permeate flow (NPF), normalized salt rejection (NSR,) or pressure drop (P_D). NPF indicates permeate flow as a function of temperature, net driving pressure (NDP), and membrane condition (Crittenden et al., 2012). NSR indicates how well the membrane rejects salts, and is a function of temperature and permeate flow. NSR can be reported as normalized salt passage (NSP), which indicates how much salt is passing through the membrane. P_D is the change in pressure between feed and concentrate streams. P_D can indicate feed pressure requirements and is used in conjunction with NPF and NSR to evaluate fouling of a membrane.

Fouling

Fouling is the loss of performance of a membrane due to accumulation of dissolved or suspended particles on its surface or within its pores (Koros et al., 1996). Fouling is detected by a decrease of NPF or increase in P_D, resulting in higher energy considerations to drive water through the membrane. Fouling is often irreversible but may be eliminated by vigorous cleaning. Foulants can be classified as particulate, biological, organic, or inorganic. It is important to note that particulate fouling is often detected in the first stage of a membrane process. Fouling indices such as the silt density index (SDI) and modified fouling index (MFI) are used to estimate fouling and pretreatment requirements for NF processes.

Silt Density Index (SDI)

The Silt Density Index is a timed filtration test that measures static resistance of water flowing through a 0.45 µm laboratory grade nitrocellulose membrane filter at 30 psig (pounds per square inch gauge) (ASTM, 2001). The time needed to filter 500 mL of water is taken at t = 0, 5, 10, and 15 minutes. The SDI is calculated using Equation 2-1.

$$SDI = \frac{100\left[1 - \left(\frac{t_i}{t_f}\right)\right]}{t} \tag{2-1}$$

Where,

$t_i = time\ to\ filter\ initial\ 500\ mL\ of\ water\ (taken\ at\ t = 0\ min)$

$t_f = time\ to\ filter\ final\ 500\ mL\ of\ water\ (taken\ at\ t = 15\ min)$

$t = total\ time\ of\ test$

Modified Fouling Index (MFI)

The Modified Fouling Index (MFI) uses the same calculation as the SDI, but varies in that volume is logged every 30 seconds over a 15-minute time frame (Schippers and Verdouw, 1980). The inverse of the flow rate can be plotted against the volume filtered to determine the initial block of filtration, solids formation, and failure of a membrane. Table 2-1 presents the ranges of SDI and MFI required for membrane processes to operate.

Table 2-1: Fouling Indices for RO and NF (Duranceau, 2006)

Fouling Index	Range (s/L^2)	Application
MFI	0-2	Reverse Osmosis
	0-10	Nanofiltration
SDI	0-2	Reverse Osmosis
	0-3	Nanofiltration
	0-10	Electrodialysis reversal

NF membranes can process feed waters with a SDI of 3, but encounter issues with foulants not predicted by the SDI, such as biological and organic fouling (Duranceau & Taylor 2011).

Scaling

Membrane scaling is a form of fouling, where precipitation occurs on the membrane by the concentration of a species past their solubility limits, and is a function of pressure, temperature and pH (Singh, 2006). The mechanism behind scale formation is concentration polarization, first recorded by Sherwood et al. in 1965. Concentration polarization is a buildup of rejected solute in a boundary layer near the membrane surface. The concentration of solute at the membrane surface is higher than the feed water, thus creating a gradient. The high concentration solute is pulled into the boundary layer through convection, and is removed by diffusion (Schafer et. al 2005). Concentration polarization causes the NDP to increase, consequentially decreasing NPF. Figure 2-2 illustrates the concentration polarization mechanism.

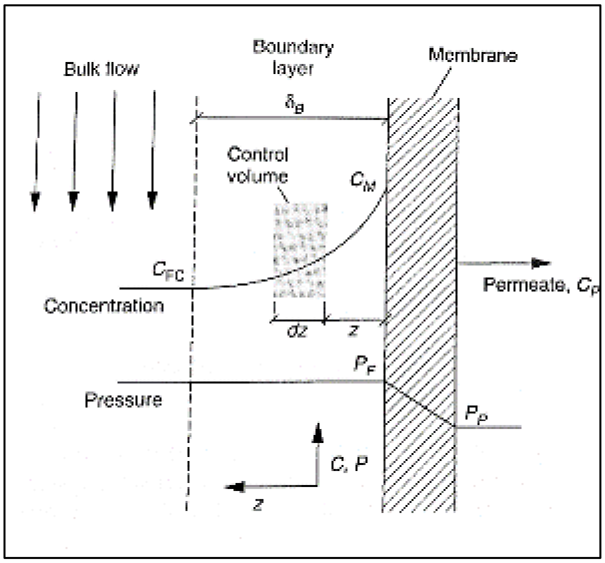


Figure 2-2: Schematic of Concentration Polarization (Howe et al., 2012)

The most common scalants are inverse-solubility salts such as calcium carbonate ($CaCO_3$), calcium sulfate ($CaSO_4$), silica, barium sulfate ($BaSO_4$), strontium sulfate ($SrSO_4$), and calcium orthophosphate ($Ca_3(PO_4)_2$) (Howe et al., 2012; AWWA 2007; Wilf et al., 2007; Chong & Sheikholeslami, 2001). Scale formation is affected by temperature, pressure, flow velocity, and operating pH (Luo & Wan, 2013; Antony et al., 2011). Scale is most likely to form at the tail end of a membrane process. When concentrated with solute, feed water may become supersaturated with ions and precipitate as it travels through the membrane process. Source waters with large concentrations of divalent ions such as calcium and barium encounter membrane scale over time. However, theoretical indices can predict the tendency of scale to form, namely calcium carbonate.

The Langelier Saturation Index (LSI), Stiff and Davis Stability Index (S&DSI), and Ryznar Saturation Index (RSI) are common methods that determine calcium carbonate ($CaCO_3$) solubility in water. It is important to note that the aforementioned scaling indices distinguish only thermodynamic driving forces of scale formation, and do not calculate the rate or quantity of scale formation (Antony et al., 2011).

Langelier Saturation Index (LSI)

The Langelier Saturation Index (LSI) is an equilibrium model which compares the pH of a water to a calculated saturation pH of water with $CaCO_3$, and is based on pH, alkalinity, temperature, total dissolved solids (TDS), and calcium hardness. The increase of the aforesaid parameters yields a higher tendency to form $CaCO_3$ scale. The LSI is used when TDS is less than 10,000 mg/L. The LSI equation is defined as Equation 2-2 and was derived by Wilfred F. Langelier (Langelier, 1936).

$$LSI = pH - pH_s \tag{2-2}$$

The pH_s term denotes a calculated pH in which water is saturated with $CaCO_3$, and is calculated using Equation 2-3.

$$pH_s = pK'_2 - pK'_s + pCa^{2+} + pAlk \tag{2-3}$$

Where,

$pK'_2 = acid\ dissociation\ constant\ of\ biocarbonate$

$pK'_s = solubility\ constant\ for\ CaCO_3$

$pCa^{2+} = negative\ logarithm\ of\ calcium\ concentration$

$pAlk = negative\ logarithm\ of\ alkalinity\ concentration$

The calculation of pH_s was modified by Nordell in 1961, shown as Equation 2-4.

$$pH_s = (9.3 + A + B) - (C + D) \tag{2-4}$$

Where,

$$A = \frac{Log_{10}[TDS] - 1}{10}$$

$$B = -13.12 * Log_{10}(°\mathrm{C} + 273) + 34.5$$

$$C = Log_{10}[Ca^{2+} as\ CaCO_3] - 0.4$$

$$D = Log_{10}[alkalinity\ as\ CaCO_3]$$

If the LSI is negative, the solution is undersaturated with $CaCO_3$. This condition dissolves $CaCO_3$, creating a corrosive environment. If the LSI is zero, the solution is in equilibrium with $CaCO_3$. If the LSI is positive, the solution is supersaturated with $CaCO_3$. This condition precipitates $CaCO_3$, initiating scale.

Stiff and Davis Saturation Index (S&DSI)

The Stiff and David Saturation Index (S&DSI) is a modified version of the LSI, and is based on pH, calcium, TDS, and alkalinity. It is used when TDS is greater than 10,000 mg/L. The S&DSI is defined as Equation 2-5 and was derived by Henry Stiff and Lawrence Davis (Stiff and Davis, 1952).

$$S\&DSI = pH - pCa - pAlk - k \tag{2-5}$$

Where,

$pCa = \ logarithm\ of\ calcium\ molarity$

$pAlk = logarithm\ of\ alkalinity$

$k = empirical\ constant\ accounting\ for\ ionic\ strength\ and\ temperature$

The S&SDI indicators are the same as the LSI indicators. A negative S&SDI has a tendency to corrode, a positive S&SDI has a tendency to scale, and a zero S&SDI is in equilibrium.

Ryznar Stability Index (RSI)

The Ryznar Stability Index is another modification of the LSI, which is based on scaling observed in municipal water systems. The RSI equation is defined as Equation 2-6 and was derived by John Ryznar (Ryznar, 1944).

$$RSI = 2pH_s - pH \tag{2-6}$$

If the RSI is less than 6, there is a tendency to precipitate $CaCO_3$. If the RSI is greater than 7, there will be no tendency to precipitate or dissolve $CaCO_3$. If the RSI is greater than 8, there is a tendency to dissolve $CaCO_3$.

Strategies to control membrane fouling and scaling include selection of membrane and operational design, cleaning regiment, and pretreatment.

Scale Control Measures

The chemistry of slightly soluble salts (such as $CaCO_3$) present in source water is the key driving force for pretreatment chemicals in NF and RO membrane processes (Kinslow and Hudkins, 2004). Pretreatment of raw water is often required prior to membrane treatment. For example, source water with hardness concentrations exceeding 180 mg/L as $CaCO_3$ is classified as very hard, and should be pretreated prior to NF (McGowan, 2000). Pretreatment can increase efficiency of treatment by reducing fouling and scaling, consequently increasing the lifespan of membranes. The subsequent techniques have been employed to mitigate scale on a membrane.

Scale Inhibitor Addition

Scale inhibitors (or antiscalants) are chemicals added prior to membrane treatment which impede materialization and precipitation of scale, and can operate by slowing the growth of crystalline precipitates, chelating dissolved ions to stay dissolved at higher concentrations, or dispersion (AWWA, 2007). However, scale inhibitors do not limit scale formation, but delay the onset of precipitation. Scale inhibitors can be classified into three groups by their molecular structure: phosphates, phosphonates, and polycarboxylates (Antony et al., 2011). Scale inhibitors are widely used in both RO and NF drinking water applications and can be administered at small doses (less than 5 mg/L) without altering feed water quality characteristics. With recent advancements in formulation, scale inhibitors may be used to replace acid feed to control calcium carbonate scale in RO membrane systems (Ning and Netwig 2002; Hydranautics, 2008).

Acidification

Acidification is the addition of acid to the feed water stream to decrease the pH prior to membrane treatment. In drinking water treatment, acid is added to drop the feed pH to 5-7 pH units, to increase the solubility of scale, primarily consisting of $CaCO_3$ (Prihasto et al., 2009). At a low pH, carbonic acid (H_2CO_3) and bicarbonate (HCO_3^-) are kept from dissociating to carbonate (CO_3^{2}), which can bond with calcium (Ca^{2+}) to form $CaCO_3$ scale. Figure 2-3 and Equations 2-8 and 2-9 illustrate the carbonate equilibria, where Equation 2-10 presents the chemical bond of $CaCO_3$.

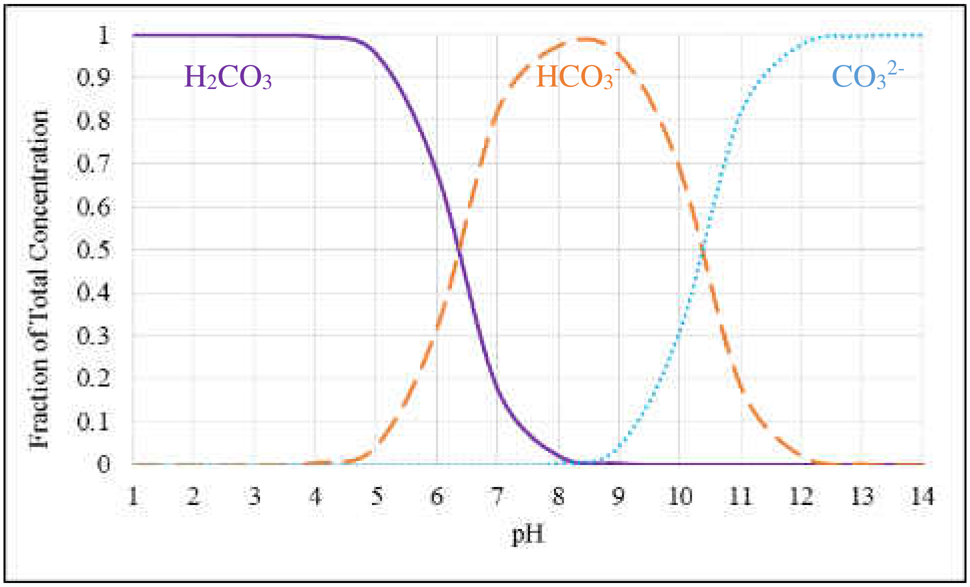


Figure 2-3: Carbonic Acid Equilibrium

$$CO_2(aq) + H_20 \leftrightarrow H_2CO_3(aq) \qquad (2\text{-}7)$$

$$H_2CO_3(aq) \leftrightarrow H^+(aq) + HCO_3{}^-(aq) \qquad pK_1 = 6.33 \qquad (2\text{-}8)$$

$$HCO_3{}^-(aq) \leftrightarrow H^+(aq) + CO_3{}^{2-}(aq) \qquad pK_2 = 10.35 \qquad (2\text{-}9)$$

$$Ca^{2+} + CO_3{}^{2-} \leftrightarrow CaCO_3 \qquad (2\text{-}10)$$

Typically, hydrochloric (HCl) or sulfuric (H_2SO_4) acid is used to decrease the feed water pH. Sulfuric acid is often favored over hydrochloric acid due to the superiority of sulfate ion rejection compared to chloride ion rejection (Hydranautics, 2008). However, sulfuric acid can increase scaling potential for sulfate salts, such as calcium sulfate ($CaSO_4$) and barium sulfate ($BaSO_4$).

Aqueous carbon dioxide (CO_2) reacts with water to form carbonic acid, as shown in Equation 2-7. Depressed pH allows CO_2 to remain aqueous and pass through the membrane and into the permeate stream. However, elevated concentrations of such gases require post-treatment utilizing degasifiers (Tharamapalan, 2012; AWWA, 2007). Depressed pH can also lead to the formation of hydrogen sulfide (H_2S), if the appropriate concentrations of hydrogen (H^+) ions and sulfide (S^{2-}, HS^-) ions are present (Gare, 2002). Figure 2-4 and Equations 2-11 and 2-12 display the H_2S equilibrium. H_2S is a noxious gas, and must be removed in post-treatment, such as aeration (Duranceau & Taylor, 2011). Degasifiers can obtain a highly efficient H_2S rejection if the permeate pH is suppressed. Lyn and Taylor (1992) reported that untreated sulfide will be oxidized with chlorine, which yields poor aesthetic water quality, namely elevated color and turbidity. However, municipal water systems are required to post-treat prior to consumer distribution. NF permeate post-treatment processes include degasification, pH adjustment, corrosion control, and disinfection (AWWA, 2007).

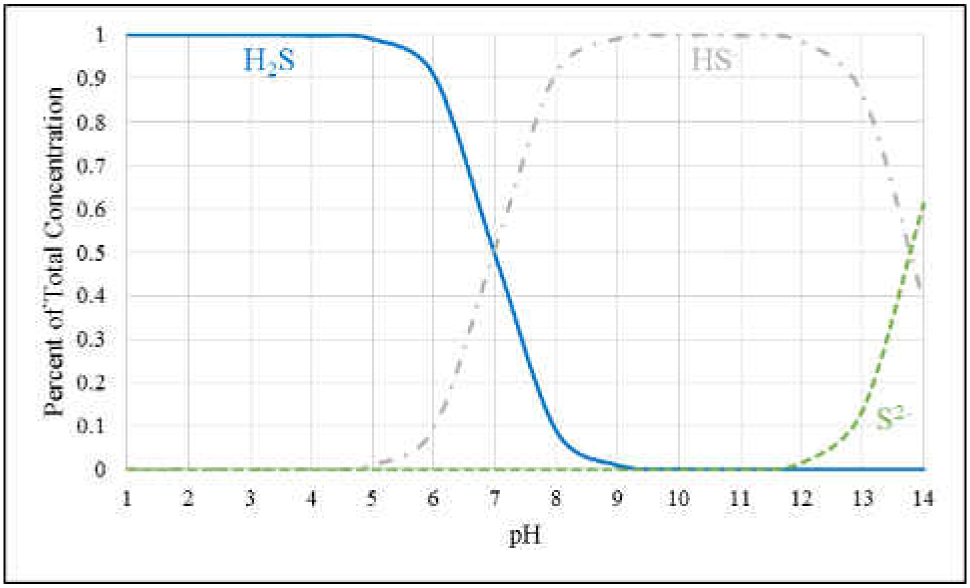


Figure 2-4: Hydrogen Sulfide equilibrium

$H_2S(g) + H_2O \leftrightarrow H_3O^+ + HS^-(aq)$ $pK_1 = 7.0$ (2-11)

$HS^-(aq) + H_2O \leftrightarrow H_3O^+ + S^{2-}(aq)$ $pK_2 = 13.8$ (2-12)

Due to the recent advancements in organic scale inhibitors, Ning and Netwig (2002) investigated performance of RO with various scale inhibitors and acid dosages and discovered that acid can be eliminated if scale inhibitor formulation and dosage is optimized, yielding major savings in operational and maintenance costs. Tharamapalan and Duranceau (2013) conducted a similar study to eliminate sulfuric acid pretreatment prior to a RO membrane process in Sarasota, FL. It is important to note that the gradual decrease of sulfuric acid occurred while scale inhibitor dose remained constant. Pilot testing revealed a minor specific flux decline (0.21 gfd/psi) with discontinuation of acid. However, it was recommended to eliminate acid pretreatment feeding the full-scale membranes. This was conducted by gradually decreasing the acid dose. Finally, after elimination of acid, continuous monitoring for scale was conducted utilizing a two-membrane observation device (known as a “canary”) installed at the end of the RO train.

Scale Remediation Measures

In source waters with high divalent ion concentrations, scale formation is inevitable and thus will eventually accumulate on the membrane surface. To remedy this, membranes must be cleaned. Cleanings are usually accomplished via a high pH or low pH soak. High pH cleaners remove fouling, specifically biofouling and colloidal fouling, while low pH cleaners remove scale and iron oxides (Johnson, 2006). It is recommended to follow manufacturer's guidelines for membrane cleaning by monitoring membrane productivity and cleaning when advised.

CHAPTER 3. EXISTING CONDITIONS

The Town of Jupiter's Water Utility serves approximately 88,000 residents of Northern Palm Beach and Southern Martin Counties on the east coast of Florida. Unlike the balance of South Florida, the Jupiter Area has no connection to the regional water supply system, which includes inland Lake Okeechobee. The primary source of fresh water supply to this region of Florida is a shallow aquifer located approximately 150 feet below the ground surface. When drawn down from over-pumping, the shallow aquifer can result in environmental damage to wetland areas, including saltwater intrusion from the nearby Atlantic Ocean and reduction of base flows to the nationally designated "wild and scenic" Loxahatchee River, which bisects the community.

The Town of Jupiter (Town) Water Treatment Facility (WTF) has been in operation since 1963, and has undergone several improvements in treatment process and capacity to meet the United States Environmental Protection Agency's (USEPA) Safe Drinking Water Act's water quality regulations. The existing treatment mechanisms that the Town utilizes are reverse osmosis (RO), nanofiltration (NF), and anion exchange (AX), totaling a treatment capacity of up to approximately 30 MGD. In August 2010, the Town of Jupiter, FL commissioned a 14.5 MGD NF Water Treatment Plant (WTP) at its Central Boulevard complex. The NF plant was constructed to replace the Town's aging lime softening facility, historically operated in conjunction with the Town's 13.7 MGD brackish groundwater RO WTP, which is coupled with a 1.8 MGD AX process for organics removal. This chapter highlights the existing NF treatment process in Jupiter, FL, which was utilized in this research.

Site Overview

The Town employs NF membranes to treat surficial groundwater. The Town has 53 surficial groundwater production wells that can pump up to 28.3 MGD of water to their NF treatment facility. The wells are located approximately 150 feet below ground level. The Town primarily relies on the surficial groundwater wells in the wet season due to the abundance of surficial ground water. The wells are distributed around the western areas of the Town, which are predominantly residential. The wells range in age from 3 to 43 years old. The water quality of the surficial wells is high in carbon dioxide, color, hydrogen sulfide, hardness, iron, total organic carbon (TOC), and turbidity (Wilder, 2012). Figure 3-1 presents the locations of the Town's surficial wells.

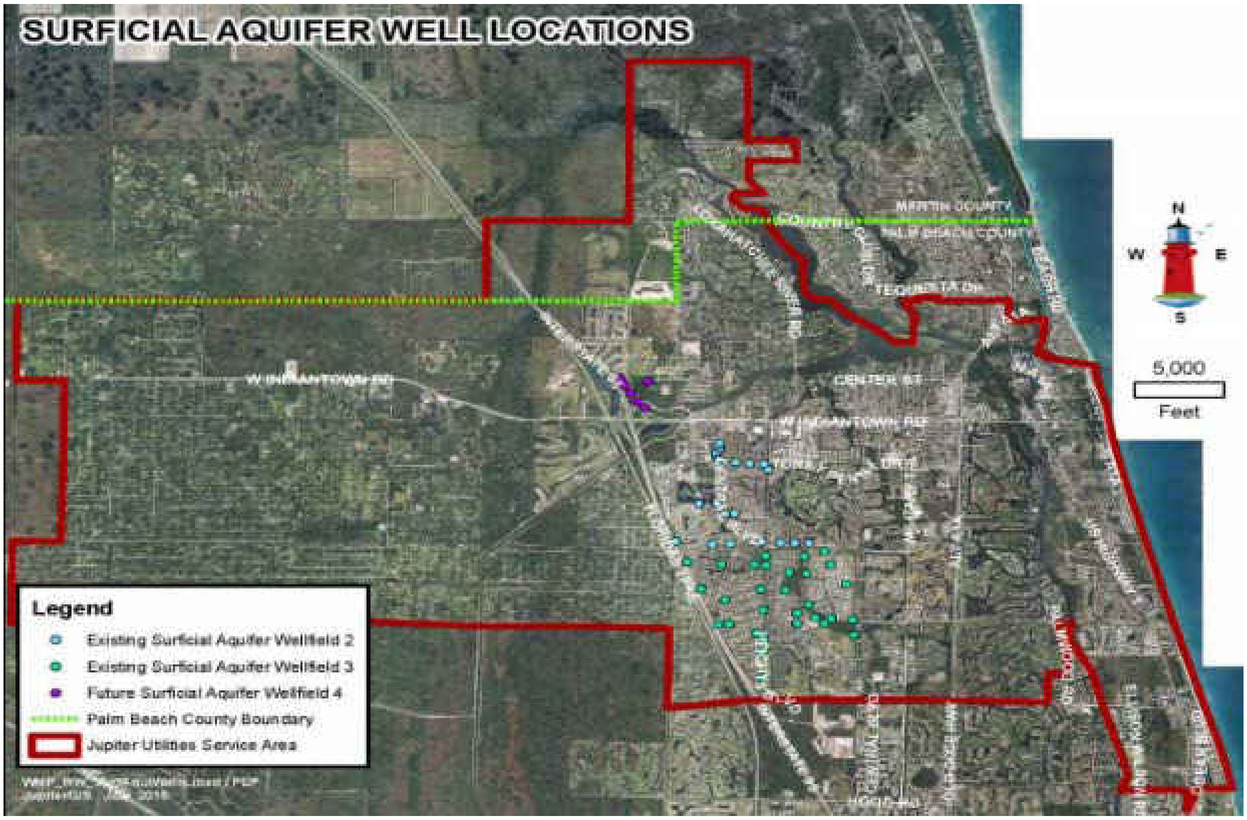


Figure 3-1: Town of Jupiter Surficial Well Locations

Surficial water pumped from the wells is blended at the head of the water treatment plant. This 'raw' water is treated in a series of three stages: pretreatment, treatment, and post-treatment, which will be described herein. Table 3-1 presents average water quality parameters for raw water and pretreated feed water.

Table 3-1: Town of Jupiter Average NF Raw and Feed Water Quality

Water Quality Parameter	Raw Water	Feed Water
pH	7.05	6.46
Alkalinity (mg/L as $CaCO_3$)	300	309
Conductivity (µs/cm at 25°C)	766	761
Total Dissolved Solids (mg/L)	503	477
Calcium (mg/L as $CaCO_3$)	307	303
Hardness (mg/L as $CaCO_3$)	323	325
Temperature (°C)	25.1	24.1
Chloride (mg/L)	55.0	52.5
Sulfate (mg/L)	26.3	105
Dissolved Organic Carbon (mg/L)	10.5	10.8

NF Membrane Process Pretreatment

Initially, raw water goes through pretreatment comprised of sand filtration, sulfuric acid addition, scale inhibitor addition, and cartridge filtration. Sand filtration removes small particles via large pressurized vessels filled with sand media. Water then flows through cartridge filters, which filter out particles greater than 5 micron in diameter. The water is dosed with an American Water

Chemical brand scale inhibitor (AWC 102 Plus) at a dose of 2 mg/L. A 93 percent sulfuric acid solution is added simultaneous to the scale inhibitor to decrease the pH from 7.0 to 6.5. The average dose of sulfuric acid is 80 mg/L, however is controlled by feed pH. The purpose of the scale inhibitor is to control the precipitation of solubility of salts, whereas the purpose of sulfuric acid is to control the precipitation of calcium carbonate. It is important to note that the limiting salt, or the salt that reaches its saturation first as a water becomes more concentrated when passing through a membrane, is calcium sulfate (Crittenden et al., 2012).

NF Membrane Process Treatment

Subsequent to pretreatment, water travels through NF membranes that reject natural organic matter and divalent ions, such as calcium and magnesium. The Town's NF process is operated in a two-stage array where feed is sent through a series of membrane elements contained in pressure vessels, yielding permeate and concentrate flow streams. The first stage concentrate (or interstage) becomes the second stage feed and is processed by a second set of membrane elements contained in pressure vessels, also yielding permeate and concentrate streams. The purpose of the two-stage system is to increase system recovery. Figure 3-2 highlights a two-stage membrane schematic with accompanying variables used in mass and flow balance calculations shown in Equations 3-1 to 3-5. In these equations, Q_F, Q_{S1P}, Q_I, Q_{S2P}, Q_{TP}, and Q_C are the feed, first stage permeate, interstage, second stage permeate, total permeate, and concentrate flow rates, respectively. Additionally, C_F, C_{S1P}, C_I, C_{S2P}, C_{TP}, and C_C feed, first stage permeate, interstage, second stage permeate, total permeate, and concentrate concentrations, respectively. R is the overall water recovery (flow based), and rejection is percentage constituent removal (concentration based).

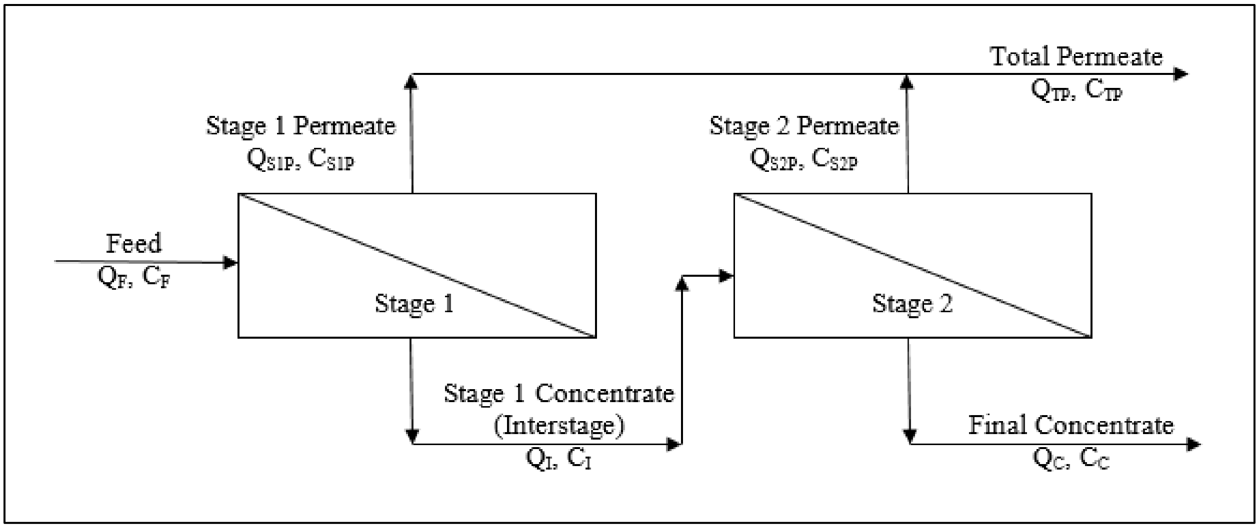


Figure 3-2: Two-stage Membrane Process Schematic

$$Q_F = Q_{TP} + Q_C \tag{3-1}$$

$$Q_{TP} = Q_{S1P} + Q_{S2P} \tag{3-2}$$

$$Q_F C_F = Q_{TP} C_{TP} + Q_C C_C \tag{3-3}$$

$$R = \left(\frac{Q_{TP}}{Q_F}\right) * 100 \tag{3-4}$$

$$Rejection = \frac{C_F - C_{TP}}{C_F} * 100 \tag{3-5}$$

The Town’s NF process configuration is unique in that it employs a split-feed, center-port configuration. Feed water is pressurized and is fed on both sides of the train and travels through three elements, where concentrate is collected in the middle and permeate is collected on the ends. The intermediate concentrate follows the same flow regime as the first stage, where flow is routed to the ends and travels through three elements, and concentrate is collected in the center. Utilizing center port pressure vessels, a NF train can be designed wherein a more optimal hydraulic system could be achieved. Through a reduction in hydraulic losses associated with higher numbers of membrane elements linked in series, membrane productivity or flux can be increased. This configuration requires a lower osmotic pressure difference across the membrane surface, which saves energy when compared to a traditional NF configuration. Figure 3-3 illustrates the Town's NF process, and highlights the split-feed center-port configuration.

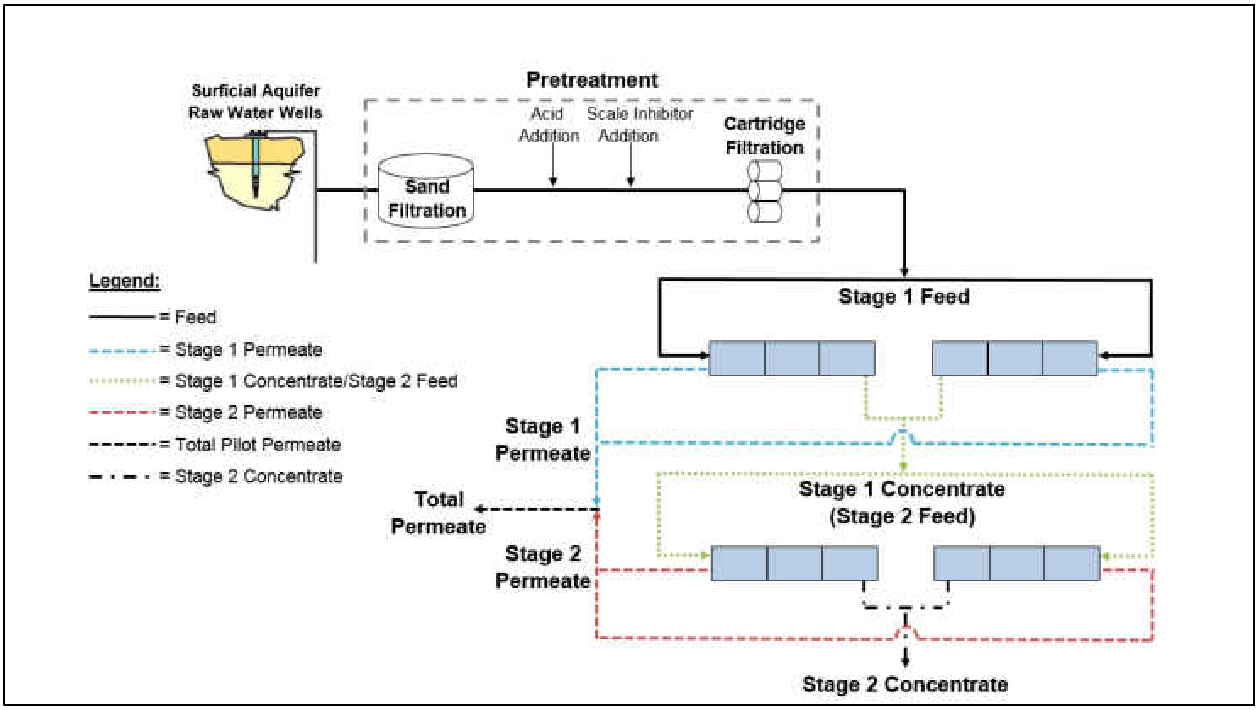


Figure 3-3: Town of Jupiter Center-port Split-feed NF Process

NF Membrane Process Post-Treatment

Succeeding NF treatment, permeate water goes through post-treatment, entailing degasification and odor control, disinfection, pH adjustment, and mineralization. Degasification removes dissolved gasses from water, specifically hydrogen sulfide and carbon dioxide from treated water. An odor control device takes the hydrogen sulfide laden air and introduces it to a high pH solution which takes the contaminants out of the air. The treated water is primarily disinfected with chlorine gas and secondarily disinfected with ammonia to form chloramines. Post-treated NF permeate is blended with RO product water at a ratio of 50.8 percent RO to 49.2 percent NF. Sodium hydroxide (or caustic) is added to pH adjust to 8.0. Subsequent to treatment, water is conveyed to the distribution system.

Figure 3-4 illustrates the Town's water treatment schematic, encompassing RO, NF, and AX treatment. Regarding the NF process, raw water is pretreated with sand filtration, sulfuric acid addition, scale inhibitor addition, and cartridge filtration. The Town retails the NF reject water, or concentrate, to a local wastewater facility for reclaimed use, per Rule 62-610.865 F.A.C. However, the reclaimed water must meet primary and secondary drinking water standards, per FDEP Chapter 62-550 (Stanley et al., 2009). There is concern regarding the sulfate concentration in concentrate water, which is due to the addition of sulfuric acid pretreatment. Therefore, the Town partnered with University of Central Florida (UCF) to examine the feasibility of reducing sulfuric acid pretreatment dose.

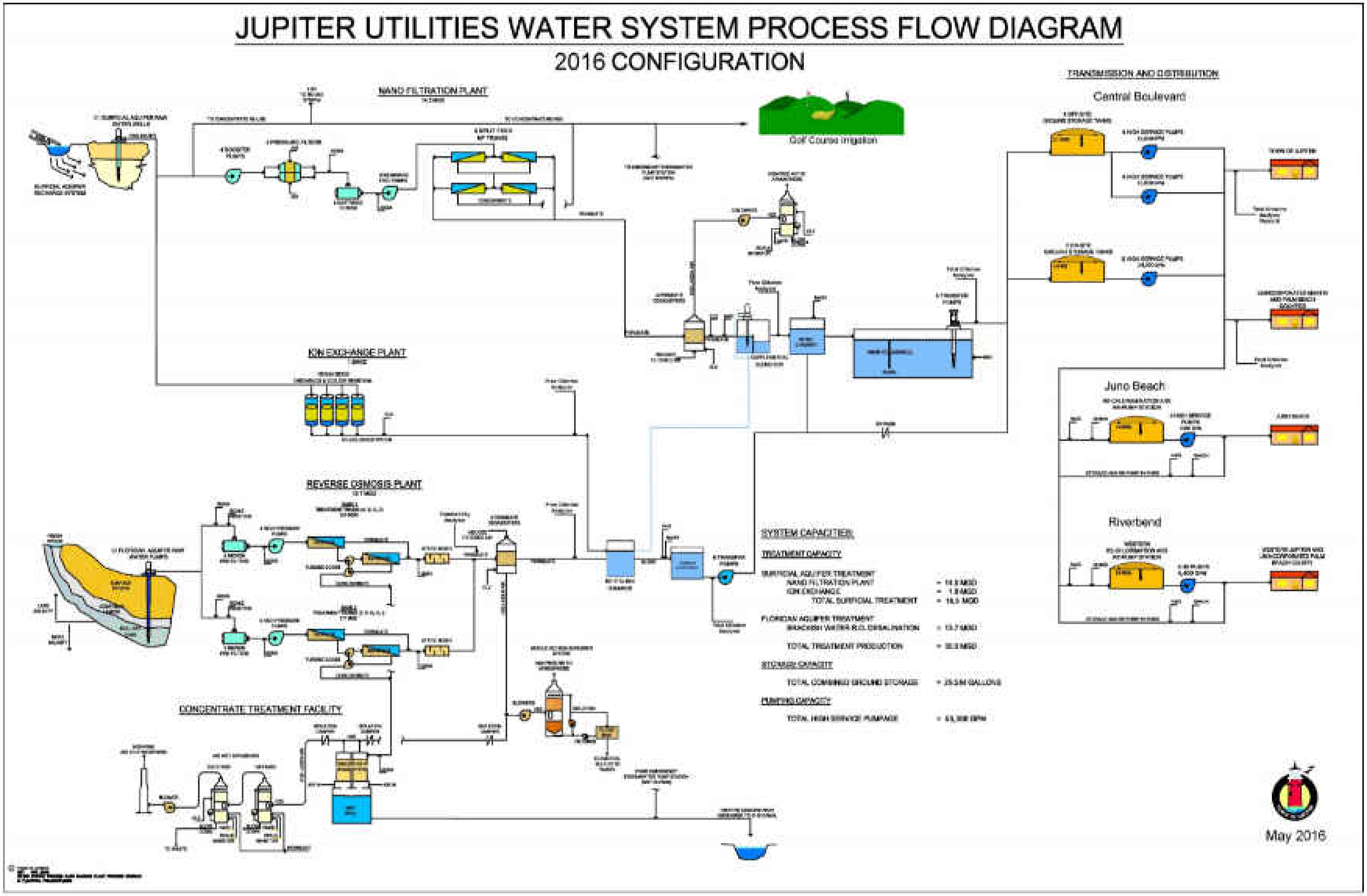


Figure 3-4: Town of Jupiter Water Treatment Plant Schematic (Courtesy of Town of Jupiter, 2016)

CHAPTER 4. MATERIALS AND METHODS

The procedure and materials applied in this study are presented in this chapter. Standard methods for drinking-water analysis described in this section were applied under local (pilot plant) conditions for accuracy and precision purposes. However, the use of standard methods does not in itself maintain that reliable and accurate results will be obtained. In the context of analytical work, quality control was applied specifically to generate data for the purpose of assessing and monitoring how acceptable the analytical methods were and how well the pilot process was operating.

Research Objectives

The fundamental objective of this research was to determine if NF membranes can proficiently operate with a decreased or eliminated dose of sulfuric acid pretreatment. The goals of investigating the reduction of sulfuric acid from a NF pretreatment process are as follows:

1. Produce improved water quality in the concentrate stream – the Town sells the NF concentrate consisting of membrane rejected NF water to the Loxahatchee River District (LRD) Wastewater Facility to blend with wastewater effluent per F.A.C. Rule 62-610.865, which is used to irrigate local golf courses. Sulfuric acid pretreatment yields a high sulfate concentration in the concentrate stream which is of concern to the Town.
2. Produce improved water quality in the permeate stream – NF permeate provides stability (in alkalinity and calcium hardness) when blended with corrosive RO permeate.
3. Retain sustained membrane performance, corresponding slight membrane fouling or scale.

NF Pilot Plant Description

To accomplish the above-mentioned goals, a NF pilot-scale unit in Jupiter, FL commissioned in December of 2014 was utilized in this research. The pilot unit was designed to simulate the existing full-scale membrane process in the Town's facility. The pilot unit (shown in Figure 4-1) contains a pretreatment system comprised of cartridge filters, scale inhibitor addition, and sulfuric acid addition. Feed water enters the pilot membranes at 267 gallons per minute (gpm). The array of the membranes is 7:2, with 7 pressure vessels housing 6 membranes each in the first stage of treatment and 2 pressure vessels housing 6 membranes each in the second stage, reaching a total of 54 membranes. The membranes in the pilot are analogous to membranes used in the full-scale process (NF270; Dow Filmtec). The water recovery of the pilot unit is 85 percent. The NF pilot unit is located in the same room as the NF full-scale process, shown in Figure 4-2.

The pilot unit contains a water quality sampling panel, and supervisory control and data acquisition (SCADA) control system (shown in Figure 4-4). Figure 4-2 presents a comparison between pilot-scale and full-scale NF processes in Jupiter, FL. It is important to note that the water flux of the pilot and full-scale process are equivalent, with a flux of 14.9 gal/sfd and 15.1 gal/sfd for the pilot unit and full-scale process, respectively. It is also important to note that the NF pilot is dimensionally analogous to that of the full-scale process, as the pilot unit houses the same membranes, and operates at the same recovery as the full-scale NF process.

Figure 4-1: NF Pilot Plant

Figure 4-2: Full-scale NF trains (left) and Pilot-scale NF Unit (right) (Duranceau, 2015)

Table 4-1: Full Scale and Pilot Scale Comparison (Black, 2015)

Item	Full-Scale	Pilot-Scale
Total membrane area (ft^2 per train)	194,400	21,600
Average design production capacity (MGD)	2.899	N/A
Peak design production capacity	14.5 MGD (2,013 gpm/train)	225 gpm
Max. approved feed flow (gpm)	N/A	275 gpm
Salt Rejection (%)	40	40
% Recovery per element (DOW)	15%	15%
% Recovery per Stage	first stage = 67%; second stage = 47%	N/A
% Recovery for system	85%	N/A
Design flux (gal/d/ft^2)	14.9	15.1
Water Mass Transfer Coefficient	N/A	N/A
Maximum operating pressure (psig) (DOW)	600	600
Membrane modules per train	486	54
Membrane modules in first stage	378	42
Membrane modules in second stage	108	12
Membranes per pressure vessel	6	6
Array	3.5:1	3.5:1
Pressure vessels per train	81	9
Pressure vessels in first stage	63	7
Pressure vessels in second stage	18	2
Permeate flow in first stage (gpm)	1,610	179 (12.8 gpm per vessel)
Feed flow in to second stage (gpm)	775	N/A
Permeate flow in second stage (gpm)	405	44.8 (11.2 gpm per vessel)
% of first stage permeate in total permeate	80	80
% of second stage permeate in total permeate	20	20

NF Pilot Unit Research Use

The pilot was utilized to monitor incremental decrease in sulfuric acid dosage pretreatment. The study was completed in the feed pH range of 6.5 to 7.0 pH units, where a feed pH of 6.5 indicated baseline conditions including the full operational sulfuric acid dosage of 80 mg/L, and a feed pH of 7.0 indicated no sulfuric acid pretreatment dosage. The current pH of the pretreated feed water that the Town relies on to supply the full-scale NF membranes is 6.5 pH units, hence the initial point of the study. Sulfuric acid dose was monitored by pH, and each incremental decrease corresponded to a 0.1 pH unit increase of feed water. Therefore membrane performance and water quality were monitored based on feed pH. It is important to note that the NF pilot unit recovery was not changed throughout the study and thus remained at 85 percent water recovery. Figure 4-3 presents the sulfuric acid tank and pump set up configuration. The flow of sulfuric acid was adjusted by decreasing the frequency (speed) of the dose, while the duration of the dose (stroke) remained constant. Decreasing the sulfuric acid dose to a specific feed pH occurred by a trial and error process. After the pump speed was decreased, the system was operated for a minimum of 14 minutes and 15 seconds before sampling, as determined in a response tracer study on the same NF pilot unit by Black and Duranceau (2016). Subsequent to the pump alteration, feed pH was measured to determine if the acid dose was successfully decreased. If not, the pump speed was altered until the desired pH was reached.

Figure 4-3: Scale Inhibitor Tank (left) and Sulfuric Acid Tank (right)

Figure 4-4: NF Pilot SCADA System (left) and Sampling Panel (right)

Frequent collection and analysis of membrane performance and water quality parameters from raw, feed, permeate, and concentrate streams were conducted at pH operating points of 6.5, 6.7, 6.8, 6.9 and 7.0. The pilot unit SCADA system recorded pH, conductivity, pressure, feed turbidity, and flow rate in ten-minute increments. A weekly collection of water analyzing for pH, temperature, conductivity, total dissolved solids (TDS), alkalinity, calcium hardness, color, and turbidity was conducted at the Town's on-site laboratory (Jupiter, FL). A weekly collection of water for the analysis of assorted metals, anions, dissolved organic carbon (DOC), and UV_{254} was conducted at UCF's Drinking Water Laboratories (Orlando, FL). The total duration of the sulfuric acid reduction study was 536 days, with a total NF pilot run time of 3,855 hours, as shown in Table 4-2. It is important to note that the NF pilot ran for approximately 2,100 hours prior to the inauguration of this study.

Table 4-2: Timeline of Sulfuric Acid Reduction Study

pH	Duration at pH	Total run time hours at pH
6.5	January 2016 - March 2016	557
6.7	April 2016 - August 2016	1,434
6.8	September 2016 - February 2017	819
6.9	March 2017 - May 2017	444
7.0	June 2017 - July 2017	601
Total	**January 2016 – July 2017**	**3,855**

NF Pilot Membrane Performance Calculations

Downloaded SCADA data was used to determine NF pilot process performance of the NF pilot system. Normalized permeate flow (NPF), pressure drop (P_D), normalized salt passage (NSP), specific flux (J_{SP}), and water flux (J_W) were calculated in accordance with Equations 4-1 to 4-6.

$$NDP(psi) = \Delta P - \Delta\pi = \left(P_{CF,ave} - P_P\right) - (\pi_{CF,ave} - \pi_P) \tag{4-1}$$

$$NPF(gpm) = Flow_{TP} * (\frac{NDP_S}{NDP})(TCF) \tag{4-2}$$

$$P_D(psi) = P_F - P_C \tag{4-3}$$

$$NSP(\%) = \left(\frac{TDS_{TP}}{TDS_F}\right)(\frac{Q_{TP}}{Q_{TP,S}}) \tag{4-4}$$

$$J_{sp}(\frac{gal}{ft^2day - psi}) = (\frac{Q_{TP}}{S.A_{membrane} * NDP}) \tag{4-5}$$

$$J_w(\frac{gal}{ft^2day}) = k_w(\Delta P - \Delta\pi) \tag{4-6}$$

Normalized data was used to compare current NF performance to a standard performance unaffected by fluctuating operating conditions. Normalized data shows membrane performance decline by a decrease in membrane J_{SP}, NPF, or an increase NSP. Net driving pressure (NDP) is the difference between applied pressure and osmotic pressure across the membrane process. NPF is calculated by multiplying the total permeate flow (Q_{TP}) by standard net driving pressure (NDP_s) over measured net driving pressure (NDP) and a temperature correction factor (TCF). For this research, it was assumed that the TCF was 1. P_D is the difference in feed (P_F) and concentrate (P_C) pressures. NSP is a ratio between the TDS concentrations of the total permeate (TDS_{TP}) and feed (TDS_F) streams multiplied by permeate flow (Q_{TP}) divided by standard permeate flow ($Q_{TP,S}$). J_{SP} is the product of Q_{TP} and NDP divided by membrane area. J_W is the product of mass transfer coefficient for water flux (k_w) and NDP. For this research, membrane performance was calculated for first stage, second stage, and overall system.

NF Pilot Water Quality Collection and Analysis

Sample collection and water quality evaluations were conducted in accordance with Standard Methods for the Examination of Water and Wastewater (Standard Methods) (Rice et al., 2012) and Laboratory Quality Assurance Procedures for the Environmental Systems Engineering Institute within UCF (Real-Robert, 2011). The protocols and testing procedures presented in the aforementioned documents established the sampling, handling, transport, and analytical methodology requirements for the analysis conducted in this research work. Table 4-3 and Table 4-4 present the laboratory methods conducted in this research.

Table 4-3: List of Methods and Equipment for Water Quality Analysis

Test	Test Location	Method	Equipment Description	Method Detection Level
Alkalinity	Town WTF/ UCF Laboratory	SM: 2320 B. Titration Method	Sulfuric Acid Burette Titration	5 mg/L as CaCO3
Calcium	UCF Laboratory	SM: 3120 B. Inductively Coupled Plasma (ICP) Method	Inductively Coupled Plasma Spectrometer - Perkin Elmer Optima 2100 DV	0.01 mg/L
Chloride	Town WTF/ UCF Laboratory	SM: 4110 B. Ion Chromatography; SM: 4500 B. Argentometric Method	Ion Chromatography - Dionex ICS-1100 with AS40 Automated Sampler	0.004 mg/L
Color (True)	Town WTF/ UCF Laboratory	SM: 2120 C. Spectrophotometric-Single-Wavelength Method	HACH DR 2700 Spectrophotometer	1 cpu
Conductivity	Town WTF	SM: 2510 B. Laboratory Method	Myron L Ultrameter 4P II	0.01 µS/cm
Hardness	Town WTF/ UCF Laboratory	SM: 2340 B. Hardness by Calculation; SM: 2320 C. EDTA Titrimetric Method	EDTA Burette Titration	0.1 mg/L

Test	Test Location	Method	Equipment Description	Method Detection Level
Magnesium	UCF Laboratory	SM: 3120 B. Inductively Coupled Plasma (ICP) Method	Inductively Coupled Plasma Spectrometer - Perkin Elmer Optima 2100 DV	0.03 mg/L
pH	Town WTF	SM: 4500-H+ B. Electrometric Method	Oakton pH Testr 30; Accumet Research AR 60	0.01 pH units
Silica	UCF Laboratory	SM: 3120 B. Inductively Coupled Plasma (ICP) Method	Inductively Coupled Plasma Spectrometer - Perkin Elmer Optima 2100 DV	0.02 mg/L
Sodium	UCF Laboratory	SM: 3120 B. Inductively Coupled Plasma (ICP) Method	Inductively Coupled Plasma Spectrometer - Perkin Elmer Optima 2100 DV	0.03 mg/L
Sulfate	UCF Laboratory	SM: 4110 B. Ion Chromatography	Ion Chromatography - Dionex ICS-1100 with AS40 Automated Sampler	0.018 mg/L
Temperature	Town WTF	SM: 2550 B. Laboratory and Field Methods	Oakton pH Testr 30; Accumet Research AR 60	0.01 °C
TOC	UCF Laboratory	SM: 5130 C. Persulfate-Ultraviolet or Heated-Persulfate Oxidation Method	Teledyne Tekmar Total Organic Carbon Fusion UV/Persulfate Analyzer	0.01 mg/L
Total Dissolved Solids (TDS)	Town WTF/ UCF Laboratory	SM: 2540 C. Total Dissolved Solids Dried at 180 C	Myron L Ultrameter 4P II	4 mg/L
Turbidity	Town WTF/ UCF Laboratory	SM: 2130 B. Nephelometric Method	HACH 2100N Laboratory Turbidity Meter	0.01 NTU
UV_{254}	UCF Laboratory	SM: 5910 B. Ultraviolet Absorption Method	HACH DR 5000 Spectrophotometer	0.01 cm^{-1}

Table 4-4: Preservation and holding times for water quality analysis

Parameter	Collection Amount/ Vessel	Preservative	Holding Time
Alkalinity	200 mL plastic or glass	Refrigerate 4 °C	14 days
Anions (Cl^-, $SO_4^{2-)}$)	100 mL plastic or glass	Refrigerate 4 °C	28 days
Metals (Ca^{2+}, Mg^{2+}, Na^+, Si)	100 mL plastic or glass	HNO_3 to pH < 2	6 months
pH	50 mL plastic or glass	N/A	Analyze Immediately
TOC	100 mL glass	Refrigerate 4 °C H_3PO_4 to pH < 2	7 days
UV_{254}, Color, Turbidity	100 mL plastic or glass	N/A	Analyze Immediately

Before data was presented, a statistical analysis was conducted to decrease the data set size and eliminate invalid instrument readings. Data outside control limits, (+/- 3 standard deviations from the mean) were not included in the data sets.

Laboratory Quality Control

Laboratory quality control measures (Method 1020 B. Quality Control from Standard Methods) were utilized to produce reputable data. Reagents used for chemical analysis were at least analytical grade. Glassware used in the study was washed with laboratory grade detergent, rinsed with 1:1 HCl and cleansed with distilled water prior to collection. Distilled water was produced using a Barnstead-Thermolyne distillation unit. Deionized water was produced using a Thermo Scientific Barnstead Water Purification System, and used for chemical analysis.

Accuracy

The accuracy of a sample set is determined by spike recovery experiments. A known concentration of an analyte was added to a sample to detect accuracy. Percent recovery is calculated using

Equation 4-7. Generally, percent recovery is accepted within the range of 80 to 120 percent (Rice et al. 2012). In this study, every fifth sample was spiked to check accuracy.

$$\%Recovery = \frac{C_{sample+spike} - C_{sample}}{C_{spike}} * 100 \tag{4-7}$$

Where,

$C_{sample} = concentration\ of\ the\ sample\ (\frac{mg}{L})$

$C_{sample+spike} = concentration\ of\ spiked\ sample\ (\frac{mg}{L})$

$C_{spike} = concentration\ of\ known\ spike\ added\ (\frac{mg}{L})$

Percent recovery can be graphed and represented as an accuracy control chart to detect equipment accuracy. Upper control limits (UCL) and lower control limits (LCL) are plus or minus three standard deviations, and are calculated using Equation 4-8. Upper warning limits (UWL) and lower warning limits (LWL) are plus or minus two standard deviations, are calculated using Equation 4-9.

$$UCL/LCL = x_{ave} \pm 3s \tag{4-8}$$

$$UWL/LWL = x_{ave} \pm 2s \tag{4-9}$$

Where,

$x_{ave} = mean\ of\ percent\ recoveries$

$s = standard\ deviation\ of\ percent\ recoveries$

Precision

The precision of a sample set is determined by duplicates. A duplicate is the analysis of two independent samples prepared from one aliquot. Precision of a sample can be calculated by relative percent difference (RPD) or the industrial statistic (I-stat), shown in Equations 4-10 and 4-11, respectively. In this study, every fifth sample was duplicated to check sample collection, handling, and preparation techniques.

$$\%RPD = \frac{S - D}{\frac{S + D}{2}} * 100 \tag{4-10}$$

$$I - stat = \left|\frac{S - D}{S + D}\right| \tag{4-11}$$

Where,

$S = sample\ concentration\ (\frac{mg}{L})$

$D = duplicate\ sample\ concentration\ (\frac{mg}{L})$

RPD or I-stat can be graphed and represented as a precision control chart to detect deviations in sample preparation procedure. The UWL and UCL were calculated in accordance with Equations 4-8 and 4-9.

The developed precision and accuracy control charts for this research can be found in Chapter 5.

CHAPTER 5. RESULTS AND DISCUSSION

A NF pilot plant located at Jupiter Water Utilities water treatment campus in Jupiter, FL was monitored for changes in water quality and membrane performance whilst sulfuric acid pretreatment was decreased and scale inhibitor dose remained constant. This chapter presents the results obtained from this study.

NF Pilot Performance Results

NF performance was collected via a SCADA system. The data was further manipulated mathematically to obtain NPF, P_D, NSP, J_{SP}, and J_W. Results include first stage, second stage, and total system membrane performance. NF performance can be ascertained by the evaluation of membrane productivity decline, which often infers fouling or scale formation.

Table 5-1 presents averaged membrane performance parameters for the NF pilot unit. Figure 5-1 illustrates the NPF for the NF pilot unit throughout the sulfuric acid reduction study period. The NPF compares measured permeate flow to a standard condition, and is normalized by a TCF and NDP to distinguish between normal phenomena (i.e. fluctuations in feed pressure, feed conductivity, and feed pressure) and changes due to fouling conditions. The NPF is measured in gpm. The elimination of sulfuric acid yielded total system NPF loss of 4.48 percent, while first and second stage incurred a 3.22 percent and 9.61 percent loss, respectively. The decrease in NPF corresponds to fouling. However, the steep decrease in NPF experienced in the second stage suggests scale. Water passing the membrane gradually becomes more concentrated with dissolved solids that have been retained on the feed water side of the membrane as water permeate through the membrane. If the concentration of any sparingly soluble substance exceeds solubility limits, it precipitates on the membrane. Hence, scale usually occurs in the second stage concentrate stream of membrane processes. In this study, the most likely scale to form is calcium carbonate due to the nature of the water quality emanating from the Floridan aquifer, which is limestone based. Nonetheless, a decrease in the NPF did not exceed greater than 10 percent, which is the membrane manufacturer's recommended level that triggers the initiation of a membrane cleaning.

Figure 5-2 illustrates the P_D over the sulfuric acid reduction study. P_D is the loss of pressure between the feed and concentrate stream of a membrane system, measured in psi. P_D is due to friction and energy loss of water as it flows through the membrane and associated appearances. However, an increase of pressure required in a membrane system can correspond to an accumulation of foulants (i.e. particles, scale) on the membrane surface. Thus, P_D is frequently and consistently monitored and trended for observation and analysis by membrane operators. During the pilot study, the total system incurred a 0.672 percent increase in P_D. The first and second stage displayed similar trends. This data indicates no significant change over time, suggesting that membrane fouling did not increase energy requirement of the membranes. The membrane manufacturer recommends that an increase of 10 to 15 percent in pressure drop across a membrane process train may be fouled, and membrane elements should be cleaned to regain productivity.

Table 5-1: Total NF System Average Performance

pH	NPF (gpm)	Delta Pressure (psi)	Salt Passage (%)	Specific Flux (gfd/psi)	Water Flux (gal/sfd)
pH 6.5	250	5.33	49.0	0.639	15.0
pH 6.7	249	5.41	53.9	0.635	15.0
pH 6.8	243	5.43	57.2	0.627	15.0
pH 6.9	239	5.43	59.8	0.619	15.0
pH 7.0	239	5.30	61.1	0.613	15.1

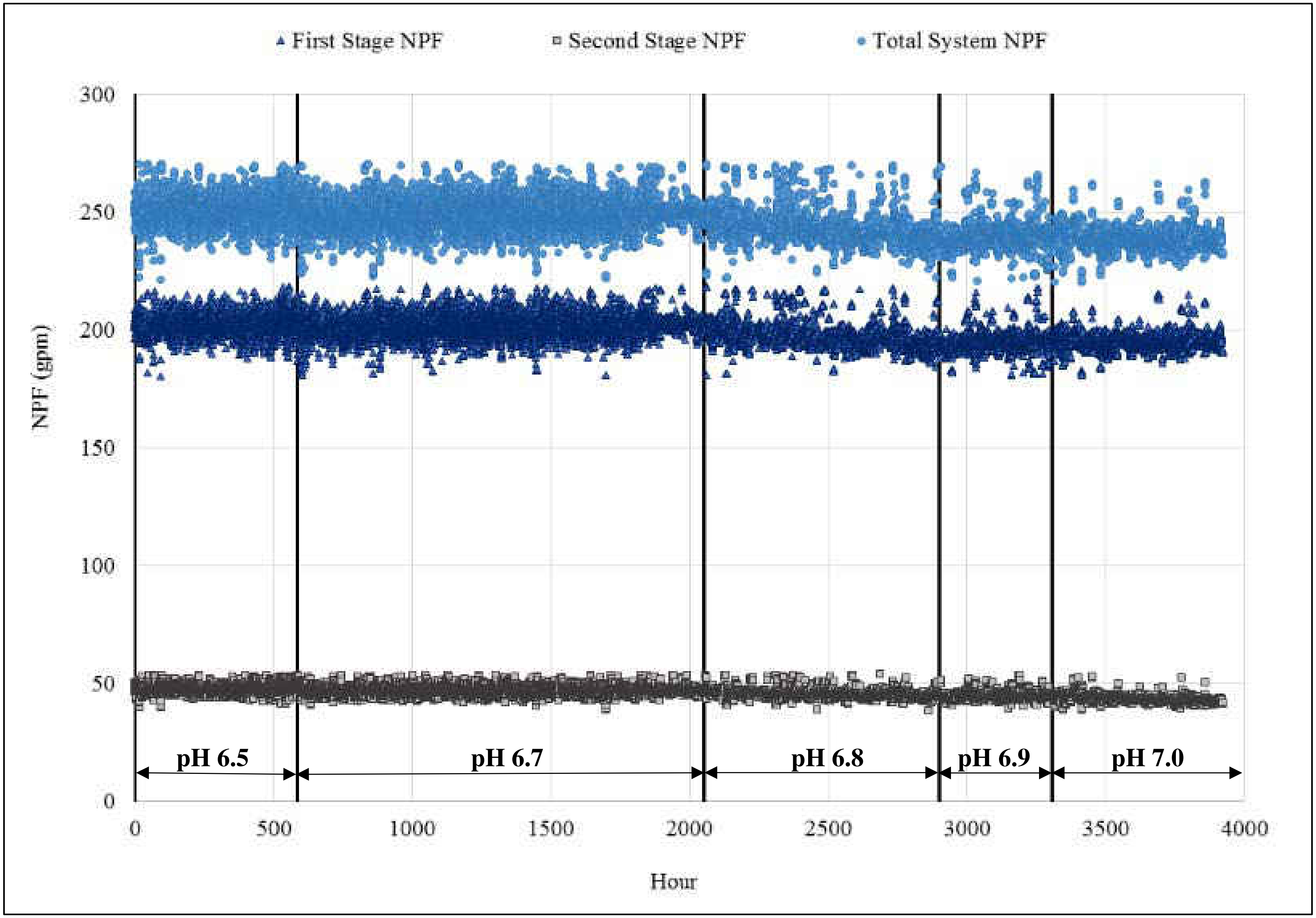


Figure 5-1: Normalized Permeate Flow (NPF)

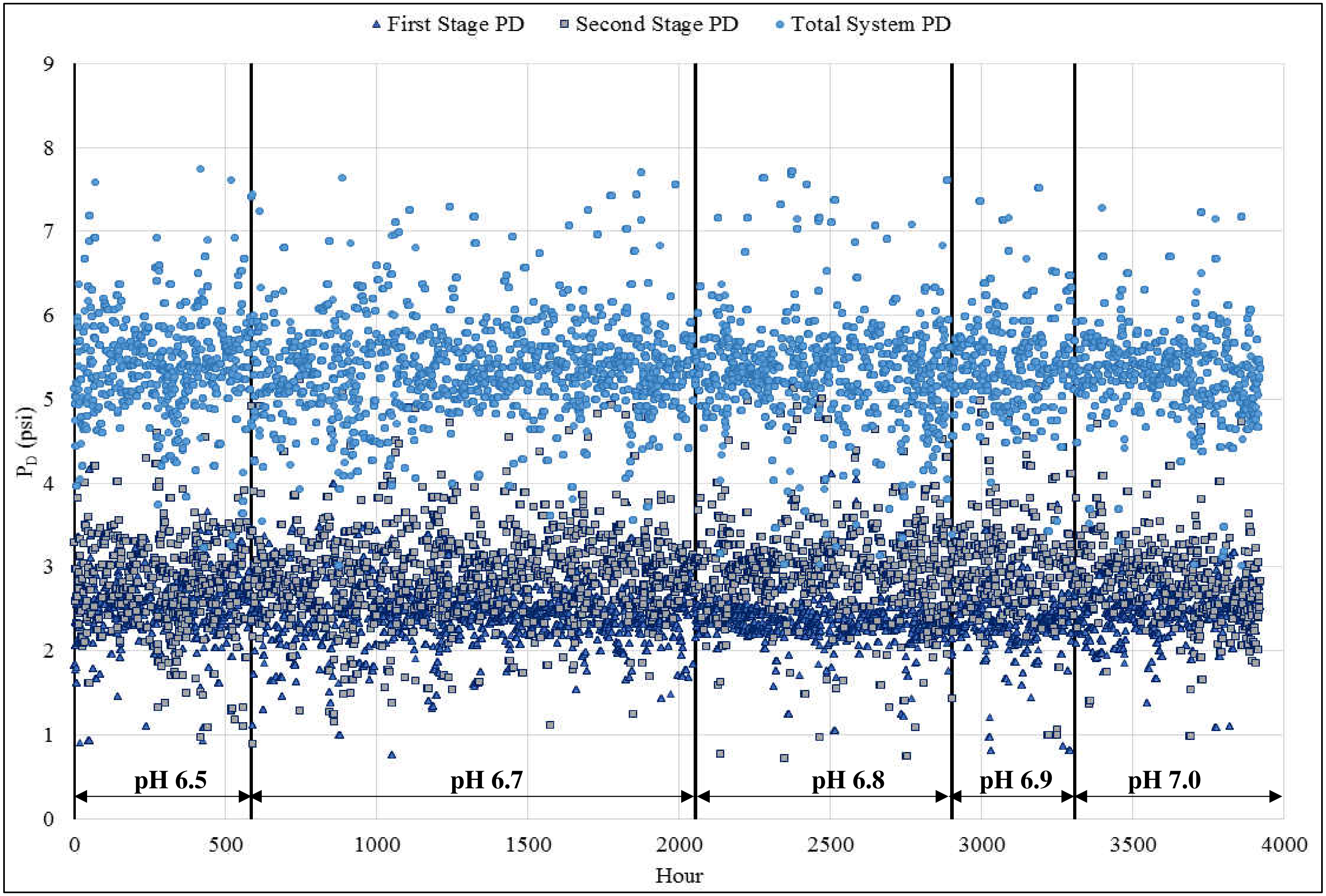


Figure 5-2: Pressure Drop (P_D)

Figure 5-3 presents NSP over the sulfuric acid reduction study. NSP measures the percentage of ionic compounds that pass through the membrane to the permeate stream. Like the NPF, the NSP compares measured salt passage to a standard condition, and is normalized to distinguish between normal phenomena and changes due to fouling conditions. It is important to note that NSP was calculated using TDS values, which were converted into conductivity values using conversion factors of 0.51 and 0.62 for permeate and feed TDS, respectively (Hubert and Wolkersdorfer, 2015). The elimination of sulfuric acid yielded an increase in NSP by 24.0 percent, 47.9 percent, and 24.5 percent in the first stage, second stage, and total system, respectively. Similar to the NPF, the steepest salt passage increase occurs in the second stage, suggesting scale buildup opposed to particulate fouling. However, the overall increase in the NSP is gradual, indicating that scale builds over time and is not triggered at a specific pH. The mechanisms behind the increase in NSP can be explained by concentration polarization and the Donnan effect. The accumulation of salt on a boundary layer near the membrane surface creates points of localized high concentration that increase salt passage through the membrane. The rate of salt diffusion into the boundary layer is greater than the rate of diffusion, causing salt diffusion through the membrane. The accumulation of scale can also cause abrasion on the membrane surface, creating spaces for additional salt passage (Holferty, 2014). The Donnan effect refers to the condition where charged particles fail to distribute evenly across a semi-permeable membrane (Donnan, 1995; Sarkar et al., 2010). As the amount of sulfuric acid decreases in the feed stream, divalent ions (Ca^{2+}, Mg^{2+}) that usually bond with sulfate (SO_4^{2-}) must bond with other existing ions in the water stream, in this case chloride (Cl^-). Divalent ions bonded with two monovalent ions have a lower molecular weight, increasing the percentage that they pass through the membrane.

Per the membrane manufacturer, experiencing a 10 to 15 percent increase of total system NSP should indicate that a cleaning is required. However, the manufacturer determines salt passage using magnesium sulfate ($MgSO_4$) as the ‘salt’ and thus is not a proper description of true salt passage. Nonetheless, an increasing trend in NSP suggests that fouling in the second stage may be occurring as scale formation, and should be cleaned to recover membrane productivity.

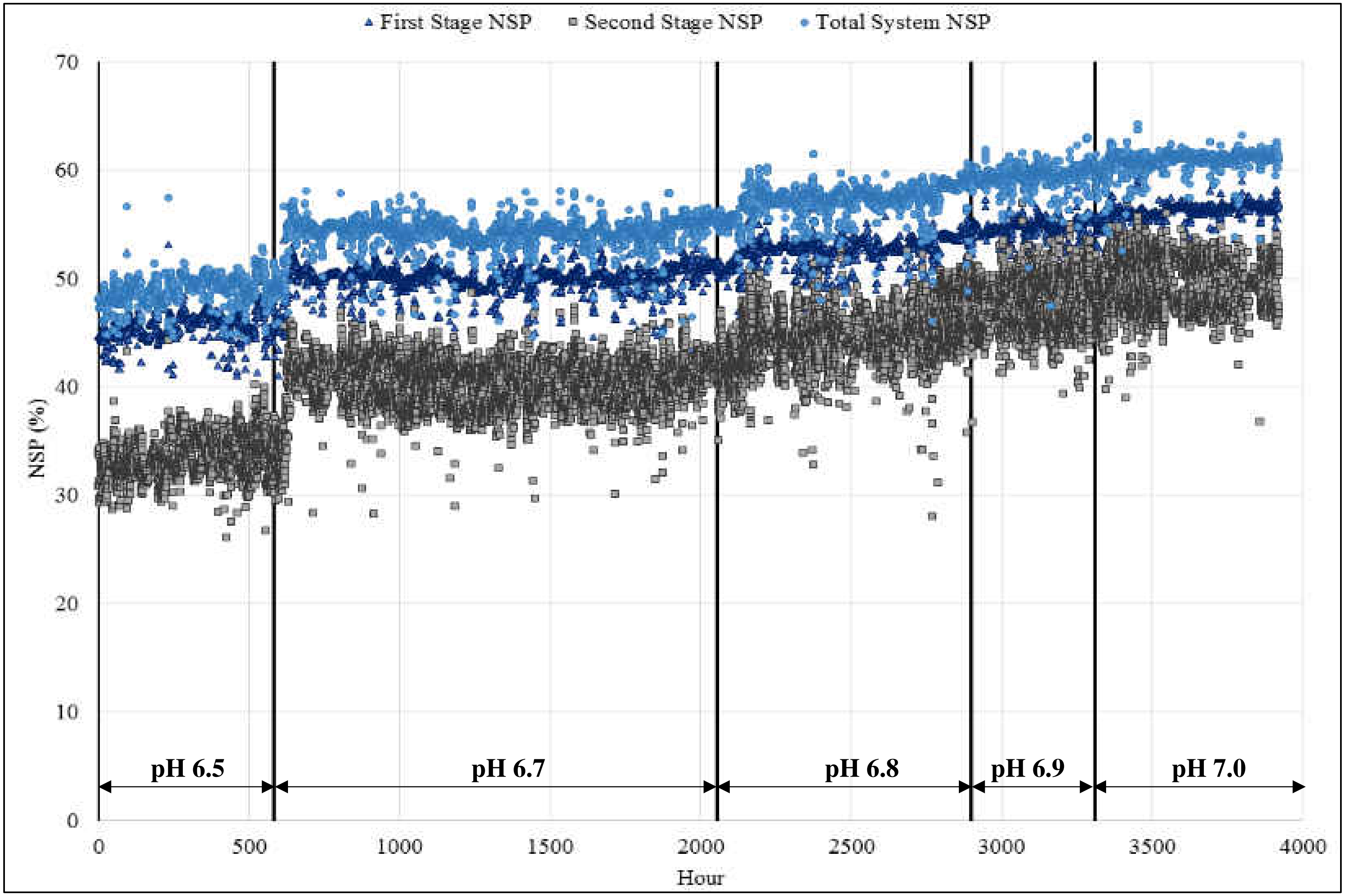


Figure 5-3: Normalized Salt Passage (NSP)

Figure 5-4 illustrates J_W recorded throughout the study. J_W is a measure of the flow of permeate water per unit area of membrane, and is measured in gallons per day per feet squared (gfd). First stage and total system J_W remain unchanged, while second stage flux experiences a 2.00 percent drop when the feed pH was changed to 7.0 from 6.9. It is likely that the decrease in J_W is due to scale formation. The accumulation of crystalline salt on the membrane surface plugs the pores on the membrane surface, thus decreasing permeate flux. However, the specific decrease at pH 7.0 means that salt formation began affecting the membrane pores when acid was completely removed.

Figure 5-5 presents J_{SP} taken over the study. J_{SP} is the flux of a membrane over the TMP, and is measured in gallons per day per feet squared psi (gfd/psi). J_{SP} is also known as the mass transfer coefficient for water, which is a diffusion rate constant responsible for relating the rate of mass transfer, surface area available for mass to transfer, and driving force for mass transfer, or concentration gradient (Crittenden et al., 2012). J_{SP} may be the most accurate membrane performance gauge as the parameter is normalized by pressure, which is desirable to identify changes in productivity produced by fouling and not other operational error. J_{SP} declines by 2.33 percent, 9.61 percent, and 4.08 percent, in the first stage, second stage, and total system, respectively. Similar to the NPF and the NSP, second stage incurs the largest J_{SP} decrease, suggesting that fouling is occurring the second stage and may predominantly be due to scale formation.

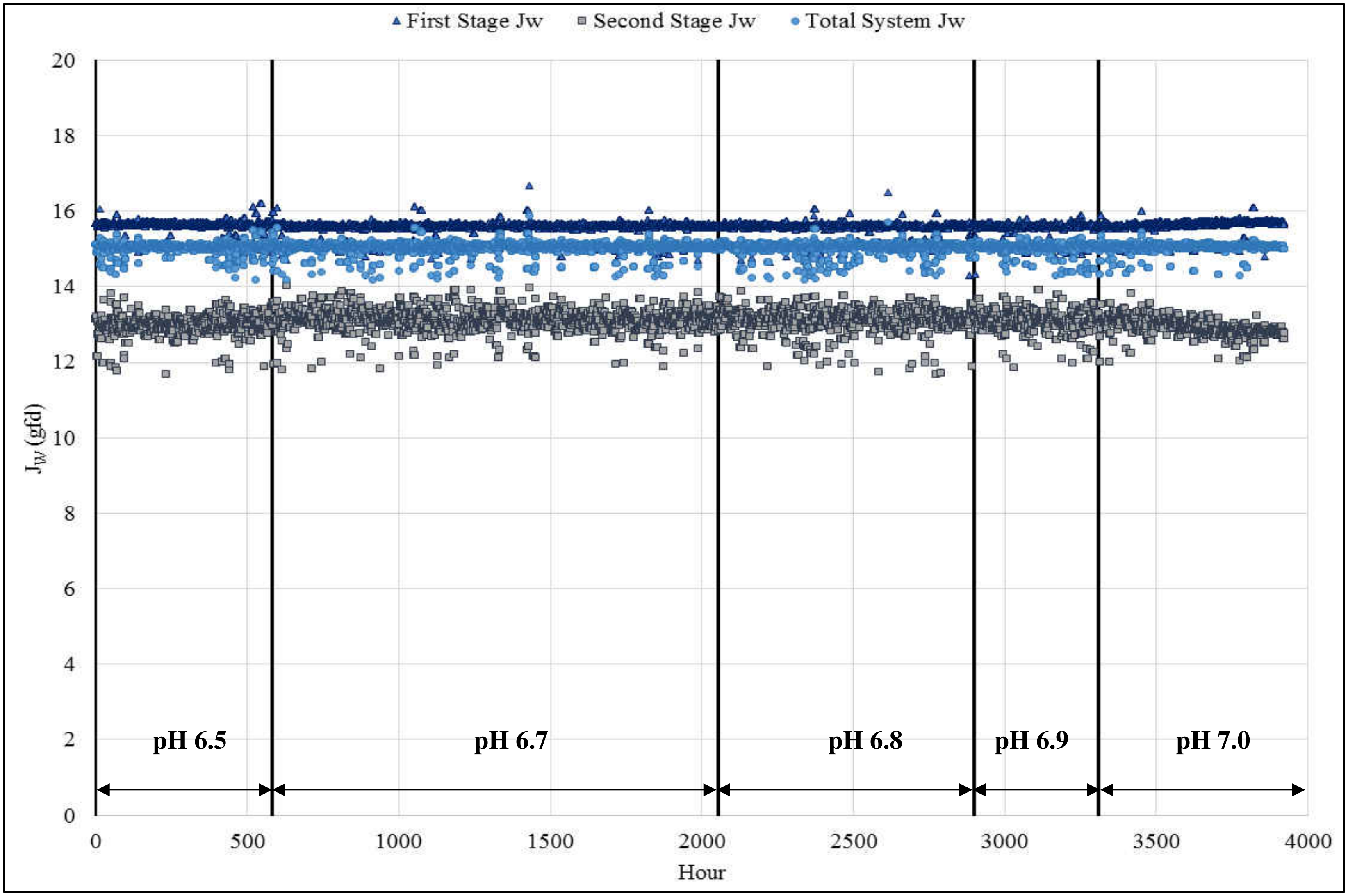


Figure 5-4: Water Flux (Jw)

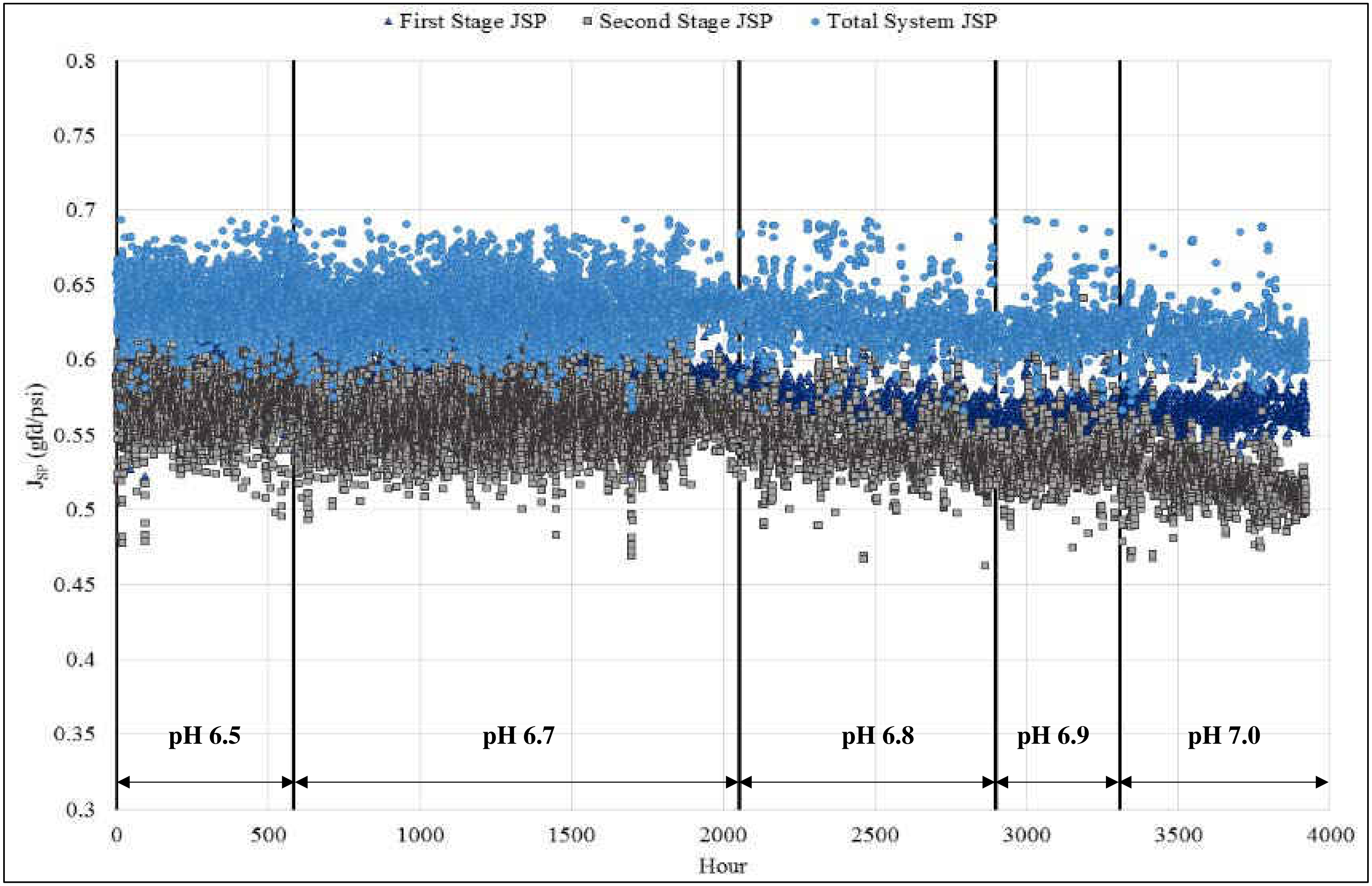


Figure 5-5: Specific Flux (J_{SP})

NF Pilot Water Quality Results

Water quality was monitored throughout the sulfuric acid elimination study. Pertinent water quality results include pH, conductivity, sulfate, calcium hardness, and alkalinity. Magnesium, silica, sodium, chloride, color, temperature, and TOC, remained unchanged throughout the study and therefore will not be discussed herein, but are presented in Appendix C. Table 5-2 displays water quality results for permeate and concentrate streams. Figure 5-6 displays pH over the duration of the study. It is important to note that water quality of the raw stream does not stay constant throughout the duration of the study, which is assumed to be due to seasonal rainfall patterns and drought. The decrease of sulfuric acid resulted in a corresponding increase in the pH of feed, permeate, and concentrate streams. Permeate pH is lower than feed pH due to the passage of protons through the membrane, thus reducing pH in the permeate stream, and conversely increasing pH in the concentrate stream. In downstream treatment (such as degasification), lower permeate pH is favored as the gaseous form of hydrogen sulfide (H_2S) is dominant, allowing effective stripping to proceed. As the permeate pH increases, the percent of available H_2S to remove decreases and shifts to aqueous bisulfide (HS^-), decreasing overall stripping efficiency, as demonstrated in Figure 2-4. Aqueous HS^- must be converted to gaseous and strippable H_2S, accomplished via Le Châtelier’s Principle. Table 5-3 presents percentages of H_2S and HS^- concentrations based on feed and permeate pH values obtained from the study. It should be noted that these values are theoretical, and were not experimentally tested due to lack of a post-treatment degasification pilot unit.

Biological Activity Reaction Tests (BART) were conducted for permeate water at corresponding feed pHs of 6.5, 6.7, and 7.0. The tendency for bacteria to form in permeate stream can negatively affect degasification efficiency. However, bacteria favors slightly acidic to neutral pH for growth so it is expected that permeate water will permit the tendency to grow bacteria. At a feed pH of 6.5, permeate water tested positive for heterotrophic aerobic bacteria (HAB), acid producing bacteria (APB), and sulfate reducing bacteria (SRB). At a feed pH of 6.7, permeate water tested positive for APB and SRB, but at an order of magnitude less than the lower pH permeate. At a feed pH of 7.0, permeate water tested positive for iron reducing bacteria (IRB), APB, slime-forming bacteria (SLYM) and SRB, also at low magnitudes. Permeate water does have the capacity to grow bacteria at the three pH values tested. Though, an increase in permeate pH decelerates the growth of bacteria. Data from this component of the research can be found in Appendix D.

Table 5-2: Total Permeate (TP) and Final Concentrate (FC) Water Quality

	pH		**Conductivity (µS/cm)**		**Sulfate (mg/L)**		**Calcium Hardness (mg/L as CaCO3)**		**Alkalinity (mg/L as CaCO3)**	
Feed pH	TP	FC	TP	FC	TP	FC	TP	FC	TP	FC
6.5	6.38	6.72	469	2080	2.76	736	162	1080	179	524
6.7	6.61	6.99	523	1910	1.91	465	185	959	200	625
6.8	6.62	7.10	534	1860	2.22	368	190	940	213	682
6.9	6.67	7.11	562	1830	1.67	259	195	878	212	745
7.0	6.76	7.17	583	1790	1.72	173	198	792	219	763

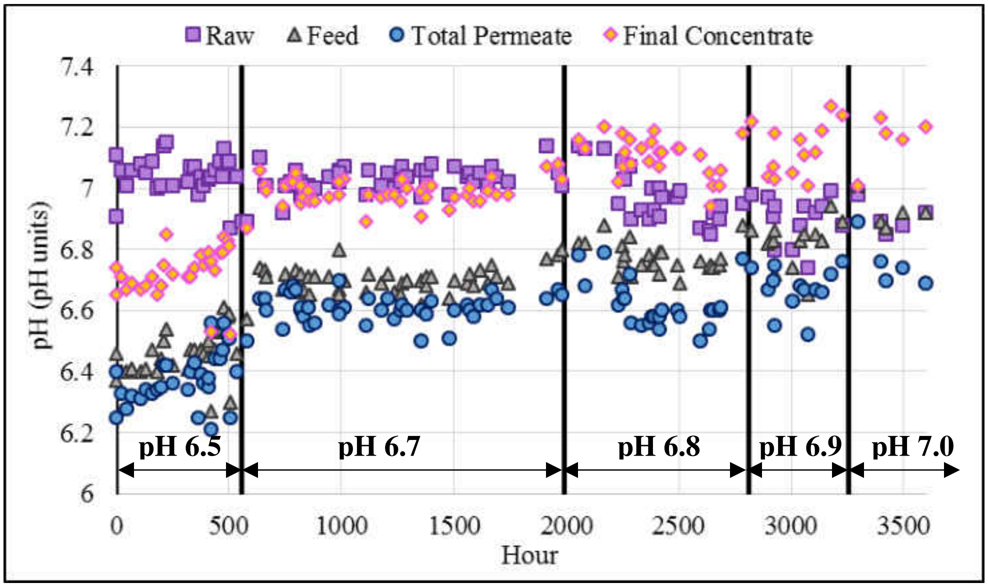


Figure 5-6: pH Values

Table 5-3: Theoretical Components of Hydrogen Sulfide (H2S) and Bisulfide (HS^-) based on Permeate pH

Feed pH	Permeate pH	% H_2S (g)	% HS^- (aq)
6.46	6.38	80.3	19.7
6.70	6.61	70.6	29.4
6.77	6.62	70	30
6.81	6.67	67.6	32.4
6.92	6.76	62.9	37.1

Figure 5-7 illustrates the conductivity recorded over the duration of the study. Conductivity is directly related to TDS, and is a measure of the ability of water to conduct an electric current, reported in microSiemans per centimeter (uS/cm). As the sulfuric acid dose decreases, conductivity increases in the total permeate stream by 24.3 percent, and decreases in the concentrate stream by 14.0 percent. The increase of pH causes carbonic acid (H_2CO_3) to partially dissociate to bicarbonate (HCO_3^-), which reacts with monovalent cations to form compounds that can pass through the membrane, hence increasing permeate concentration and decreasing concentrate concentration. Permeate conductivity increase is not desirable as it represents a higher concentration of charged ions in solution, as the goal is to remove total dissolved solids from the feed water supply. However, concentrate conductivity decrease is desirable as less charged ions are in solution.

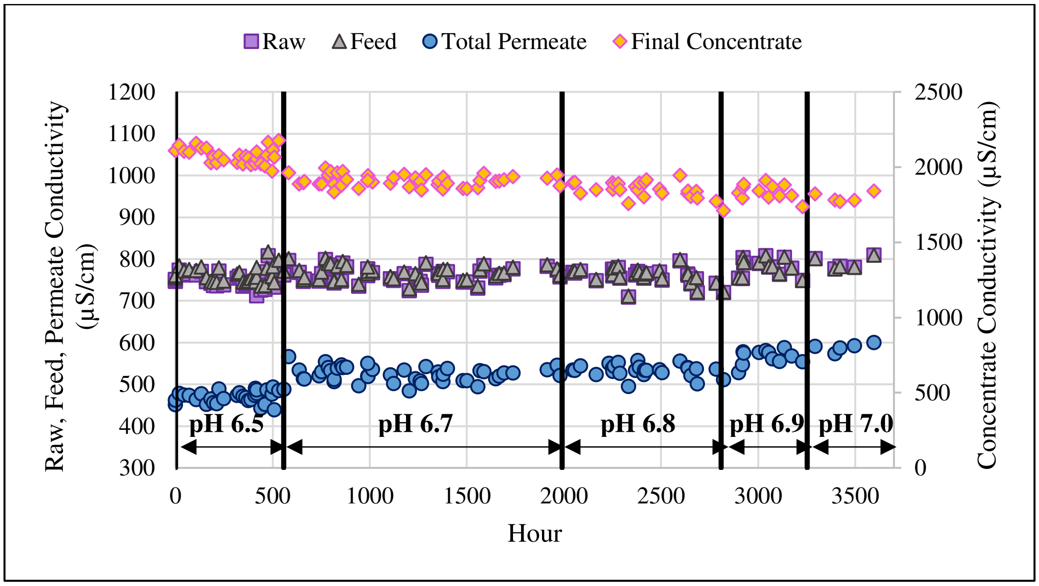


Figure 5-7: Conductivity Values

Figure 5-8 presents sulfate concentration over the duration of the study. Sulfate in the concentrate and feed streams decreased by 76.4 percent, and 74.0 percent, respectively. A decrease in the concentrate stream's sulfate concentration is desirable to the Town as they retail NF concentrate to LRD for water reclamation and irrigation purposes. Sulfate removal decreases from 97.3 percent at pH 6.5 to 93.7 percent at pH 7.0. However, permeate sulfate concentration remained below 3 mg/L throughout the duration of the study, which is lower than the secondary maximum contaminant level of sulfate for 250 mg/L advised by the USEPA.

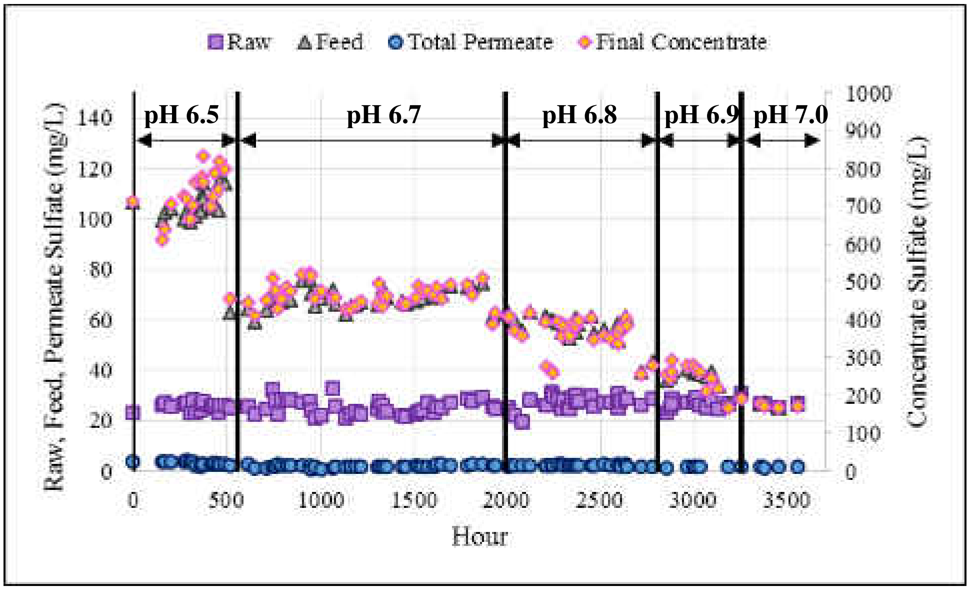


Figure 5-8: Sulfate Values

Figure 5-9 presents alkalinity concentration over the duration of the study. Alkalinity is a measure of the capacity of water to neutralize acid, and is measured in mg/L as $CaCO_3$. Permeate stream alkalinity increased from 179 mg/L at pH 6.5 to 219 mg/L at pH 7.0. However, the concentration is lower than the USEPA guideline of 500 mg/L. An increase of alkalinity in the NF permeate increases buffer capacity of water. Full-scale NF permeate is subsequently blended with RO permeate, therefore a higher alkaline and higher pH NF permeate would provide stability to combat corrosive brackish RO permeate. Alkalinity in the concentrate increased from 524 mg/L at pH 6.5 to 763 mg/L at pH 7.0.

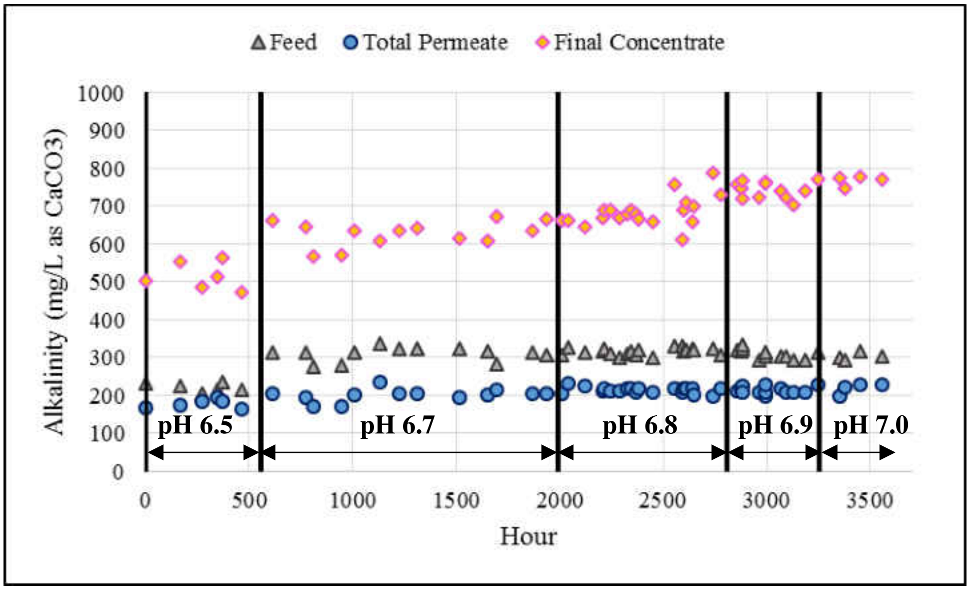


Figure 5-9: Alkalinity Values

Figure 5-10 presents calcium hardness data (mg/L as $CaCO_3$) collected over the duration of the study. It should be noted that concentrate calcium hardness concentration was calculated from a mass balance, as high concentrations cannot be read on the associated laboratory instrument. Calcium hardness removal decreased from 46.6 percent at pH 6.5 to 31.5 percent at pH 7.0. This phenomena can be described by the Donnan effect, whereupon calcium (Ca^{2+}) ions bond with sulfate (SO_4^{2-}) ions from sulfuric acid, forming calcium sulfate ($CaSO_4$, MW 136.14 g/mol) which is partially removed in a NF process. When the sulfuric acid dose is decreased, Ca^{2+} ions must bond with monovalent anions, (i.e. chloride), forming calcium chloride ($CaCl_2$, MW 110.98 g/mol). $CaCl_2$ has a higher likelihood of passing through the membrane when compared to $CaSO_4$, hence the decreased calcium removal.

Total permeate experienced a 22.2 percent increase in calcium hardness concentration, while final concentrate experienced a 26.7 percent decrease in calcium hardness concentration At a feed pH of 6.5, permeate water has a hardness of 162 mg/L as $CaCO_3$ and thus is classified as hard water. As the feed pH increases to 7.0, permeate water hardness increases to 198 mg/L as $CaCO_3$, classified as very hard water (McGowan, 2000). Hard water causes scale deposition in water distribution systems and heated water applications, reducing the efficiency of heat exchangers and residential water heaters by forming insoluble metal carbonates.

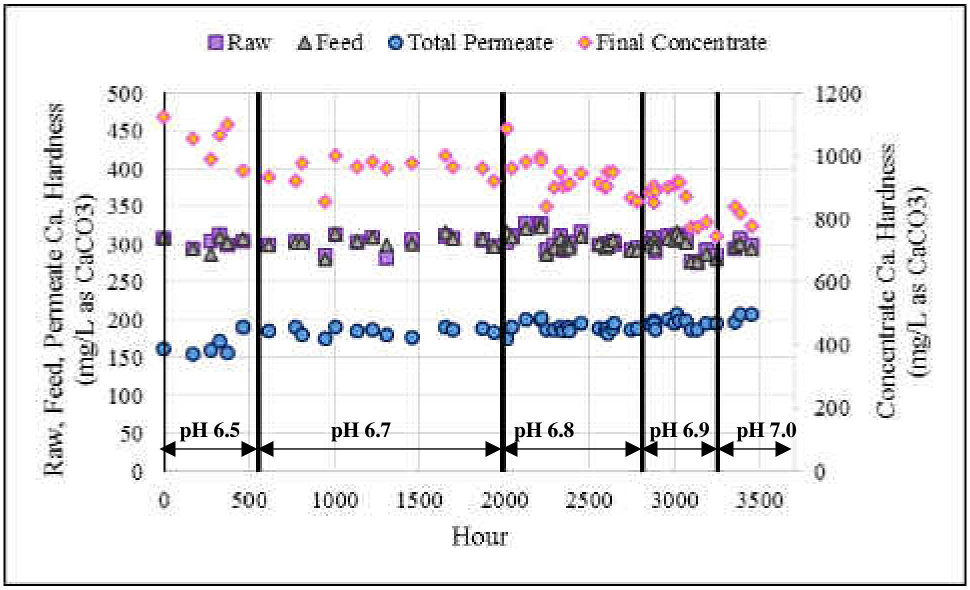


Figure 5-10: Calcium Hardness Values

Table 5-4 presents LSI, RSI, and SDI values over the duration of the study. Averages of pH, TDS, temperature, calcium, and alkalinity over each pH were used to calculate the indices in accordance with equations in Chapter 2. As the sulfuric acid dose decreases, the LSI increases, indicating feed water becoming more prone to form calcium carbonate scale. Conversely, the RSI decreases as the feed pH increases, also indicating a similar shift in water characteristic. The SDI does not fluctuate with an increase in pH, indicating no particulate fouling on the membrane surface. It should be noted that the S&DI index was not calculated due to TDS concentration of the target water streams reading below 10,000 mg/L.

Table 5-4: LSI and RSI Values

Target Feed pH	Actual Feed pH	LSI	RSI	SDI
6.5	6.46	-0.638	7.82	1.18
6.7	6.69	-0.273	7.26	1.18
6.8	6.77	-0.159	7.15	1.18
6.9	6.81	-0.084	7.16	1.19
7.0	6.92	0.010	7.06	1.18

Membrane Autopsy Results

Subsequent to the sulfuric acid elimination study, American Water Chemicals (AWC) conducted a membrane autopsy on the last membrane element of the second stage of the NF process. It should be noted that prior to the autopsy, the NF pilot was run for approximately 6,000 hours and had not been previously cleaned. Approximately 2,100 of the run time hours occurred prior to the sulfuric acid elimination study, whereas the last 3,855 hours included the sulfuric acid elimination study. According to AWC, initial testing revealed membrane flux was approximately 20 percent below the manufacturer's specification of 31.25 gfd, but salt rejection and differential pressure were within the expected range. After soaking in deionized water for 24 hours and retested, flux increased to 21 percent above the manufacturer's specification. The membrane was then cleaned with a basic chemical (AWC C-226) at pH 12.3 for six hours at 25 °C and retested. Flux increased by 40 percent from the deionized water clean flux (37.83 gfd to 53.08 gfd). The membrane was further cleaned with an acidic chemical (AWC C-234) at pH 1.7 for 4 hours at 25 °C and retested. Flux decreased by 21.3 percent when compared to the high pH clean flux (41.75 gfd vs 58.03 gfd).

Overall, membrane flux increased by approximately 34 percent after the complete cleaning regimen.

Figure 5-11 illustrates superimposed elemental imaging technology used to determine the topography, morphology, and elemental composition of the membrane surface. The foulant on the membrane surface comprised of iron disulfide (FeS_2), limestone ($CaCO_3$), silts, clays, and organics corresponding to large amounts of sulfur (S), iron (Fe), calcium (Ca), and silica (Si) ions seen in Figure 5-11 left. However, a membrane cleaning test comprised of high and low pH cleaners removed the foulant on the membrane surface, and flux was recovered to normal operating levels. Comparison of the two images depicted in Figure 5-11 indicated that the foulant shown initially had been completely removed as only carbon (C) ions on the cleaned membrane surface (right) remained (solid red image). It should be noted that the majority of membrane surfaces comprise of polyethersulfone or polysulfone, a carbon based material. The removal of the foulant with a membrane cleaning means the foulant damage is reversible and can be cleaned and returned to previous operating conditions.

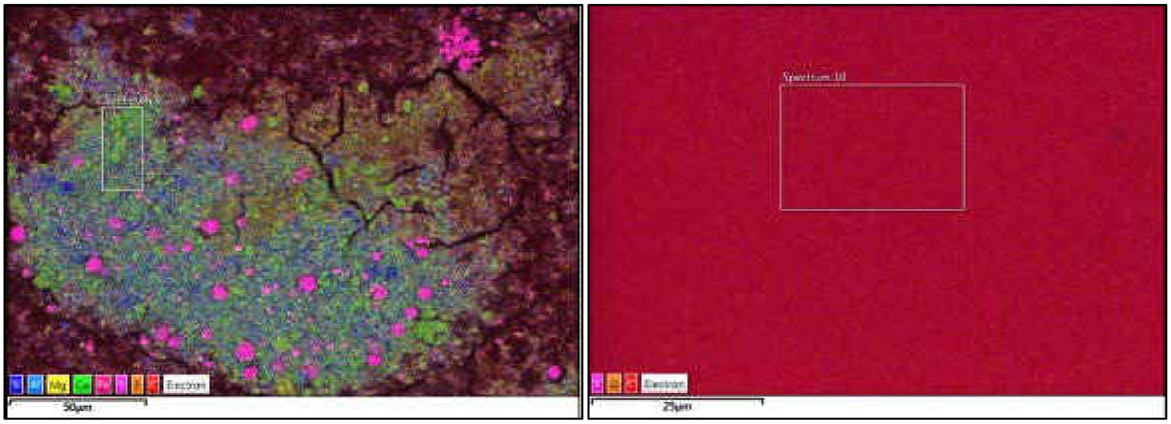


Figure 5-11: Superimposed Elemental Imaging of Membrane Surface Pre (left) and Post (right) Clean

BART tests revealed the dominant presence of heterotrophic aerobic bacteria and slime forming bacteria, with sulfate reducing bacteria and iron related bacteria also present. Other pertinent data regarding the membrane autopsy can be found in Appendix E. According to AWC's membrane autopsy, the fouling on the membrane can be removed via a cleaning regimen using deionized water, and acidic and basic cleaning chemicals.

Results Summary

The following presents a summary of the membrane performance and water quality data for permeate and concentrate streams taken throughout the duration of the study. Figure 5-12 presents percent changes in the NF system for each pH monitored compared to pH 6.5 (full scale sulfuric acid dose, baseline conditions). As sulfuric acid is decreased, total system membrane performance steadily declines, as seen by NPF and J_{SP} loss, and NSP increase.

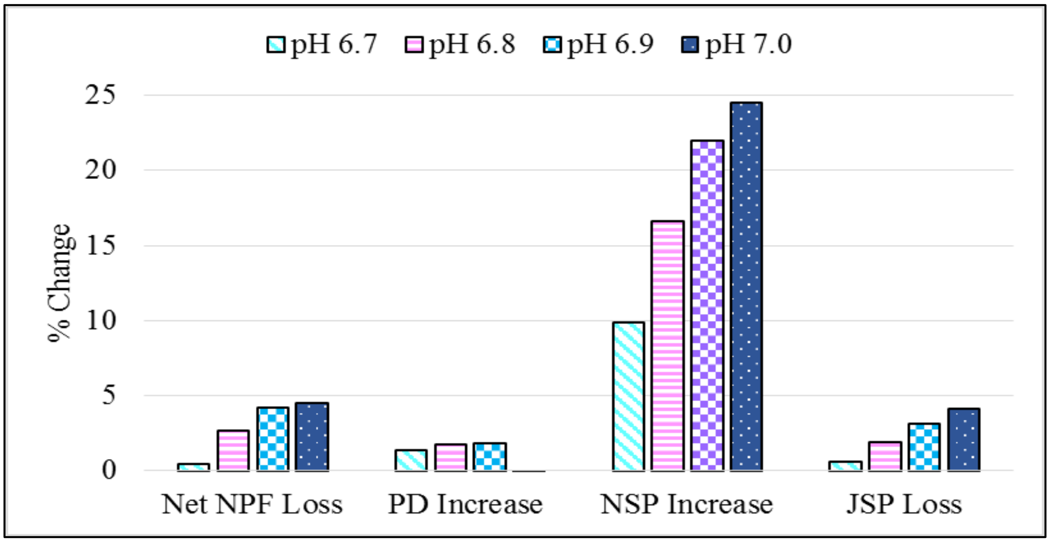
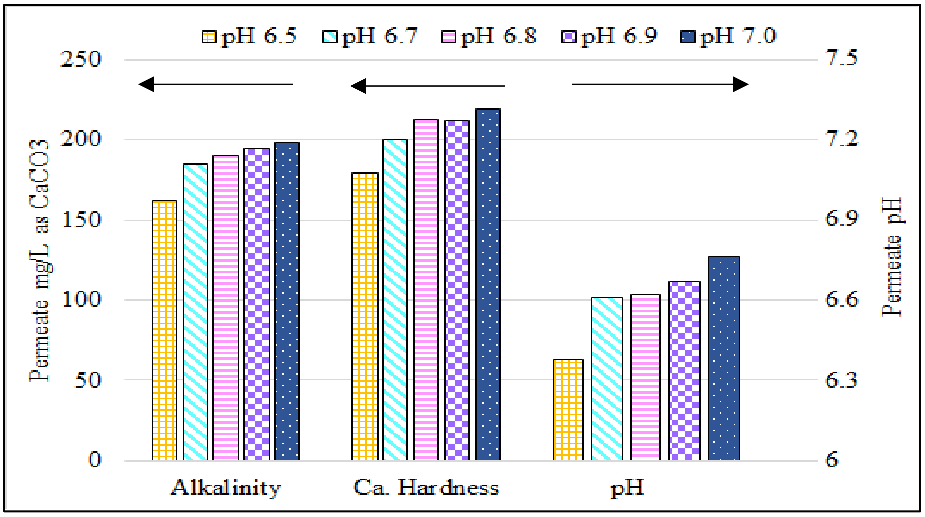


Figure 5-12: Total NF System Percent Change Compared to pH 6.5 (initial conditions)

Figure 5-13 presents permeate stream alkalinity and calcium hardness concentrations at each pH monitored compared to pH 6.5 (full scale sulfuric acid dose, baseline conditions). As sulfuric acid is decreased, permeate stream alkalinity concentration, calcium hardness concentration, and pH steadily increase. An elimination of sulfuric acid yielded an overall increase of alkalinity and calcium hardness by 40 and 36 mg/L, respectively.



Note: Arrows represent the axis corresponding to each parameter

Figure 5-13: Average Alkalinity, Calcium Hardness, and pH values for Permeate Stream

Figure 5-14 presents concentrate stream water quality percent changes in the NF system for each pH monitored compared to pH 6.5 (full scale sulfuric acid dose, baseline conditions). As sulfuric acid is decreased, concentrate pH, and alkalinity concentration steadily increase. Conversely, conductivity, sulfate concentration, and calcium hardness concentration steadily decrease.

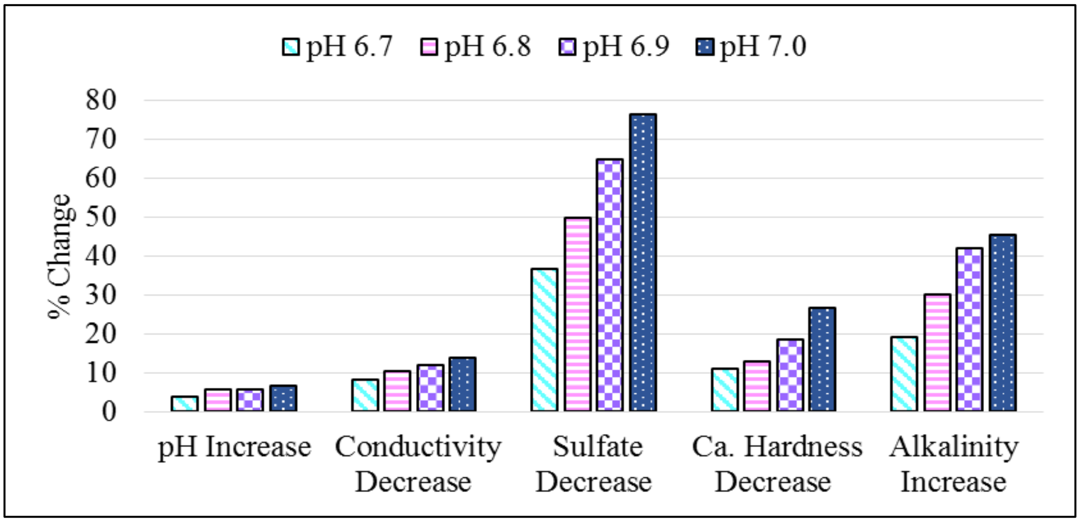


Figure 5-14: Concentrate Stream Water Quality Percent Change Compared to pH 6.5 (initial conditions)

Quality Control Results

Quality control measures were conducted in accordance with Standard Methods, described in Chapter 4, and presented herein. Data sets were analyzed for accuracy and precision. Samples were spiked and analyzed for percent recovery, and plotted on an accuracy control chart. Accuracy control charts for sulfate and calcium analyses are presented in Figure 5-15 and Figure 5-16, respectively. Samples were also duplicated and analyzed for relative percent difference, and plotted on a precision control chart. Precision control charts for sulfate, alkalinity, and calcium hardness are presented in Figure 5-17, Figure 5-18, and Figure 5-19, respectively.

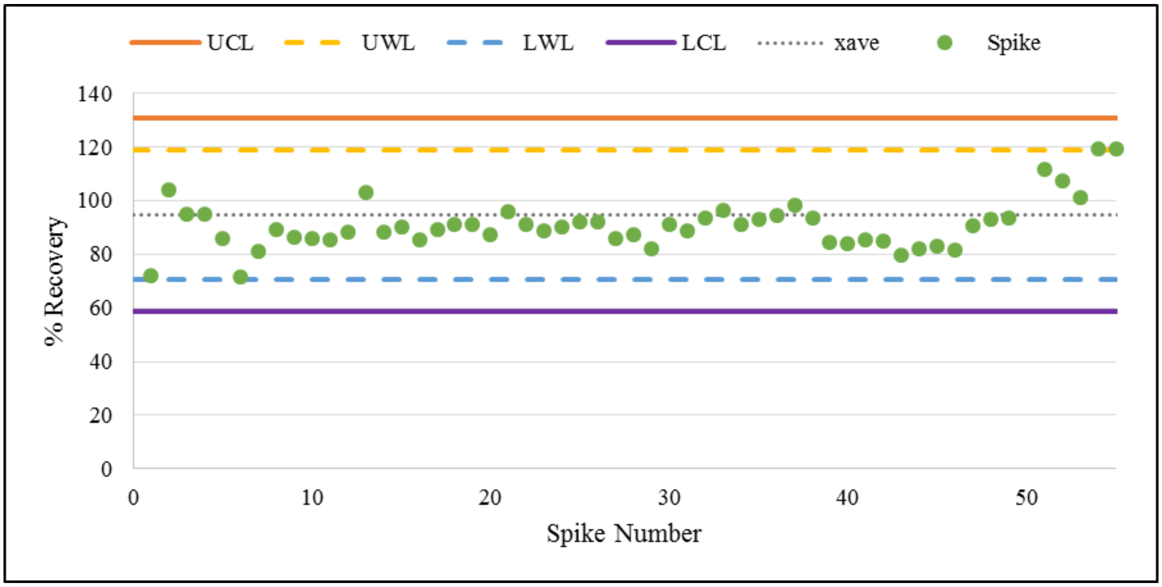


Figure 5-15: Sulfate Accuracy Control Chart

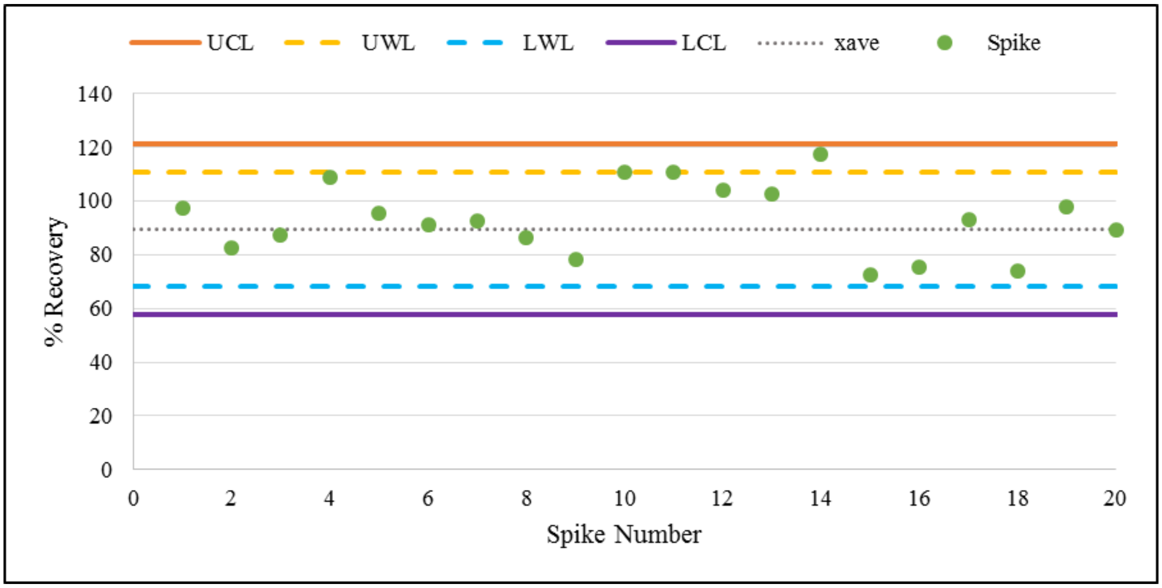


Figure 5-16: Calcium Hardness Accuracy Control Chart

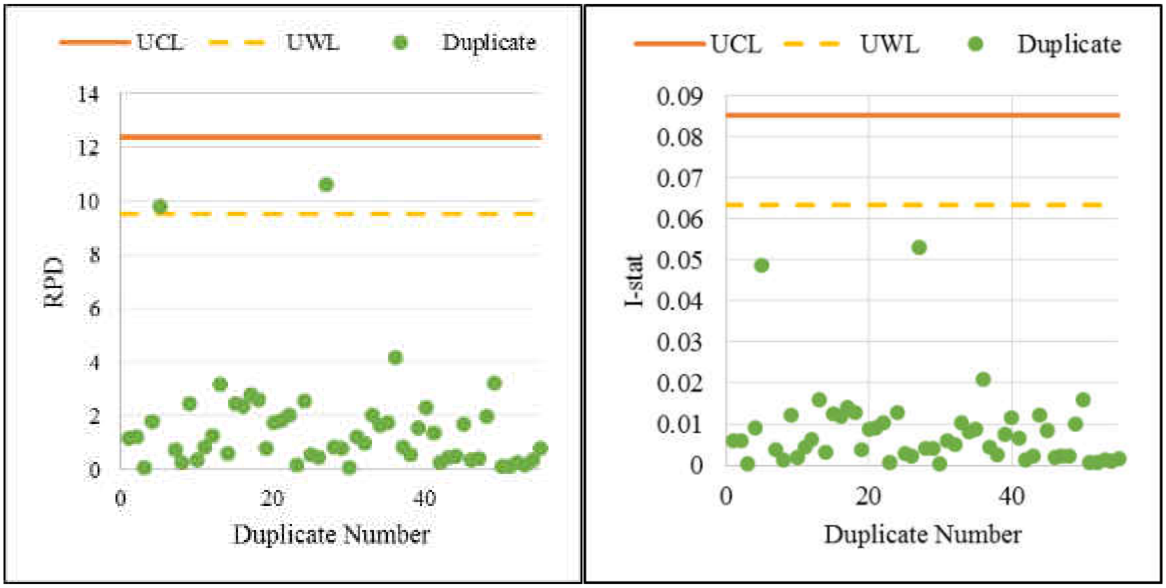


Figure 5-17: Sulfate Precision Control Chart

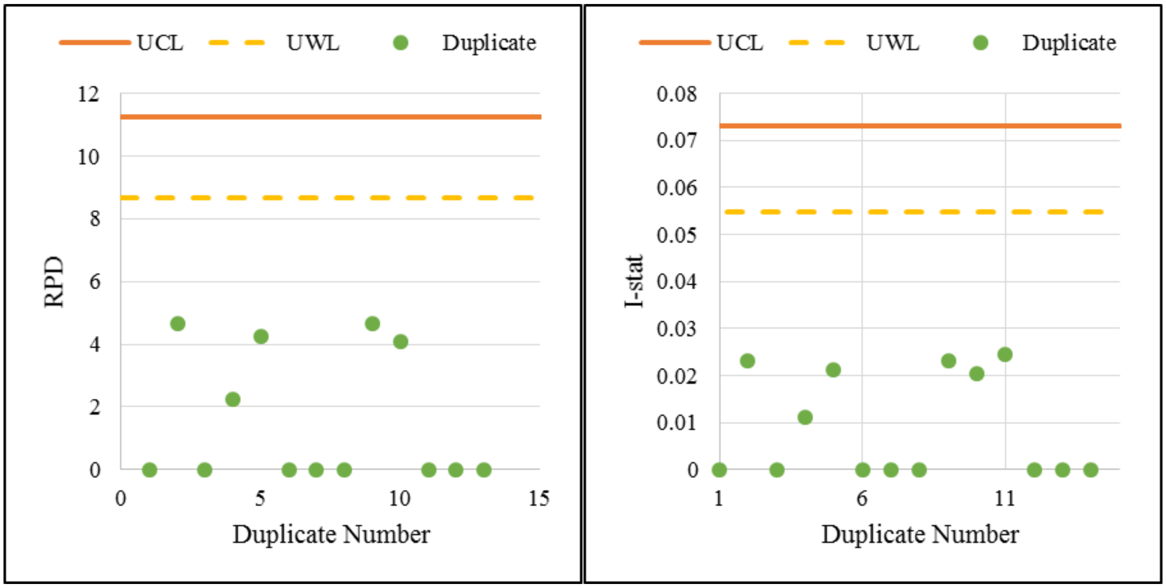


Figure 5-18: Alkalinity Precision Control Chart

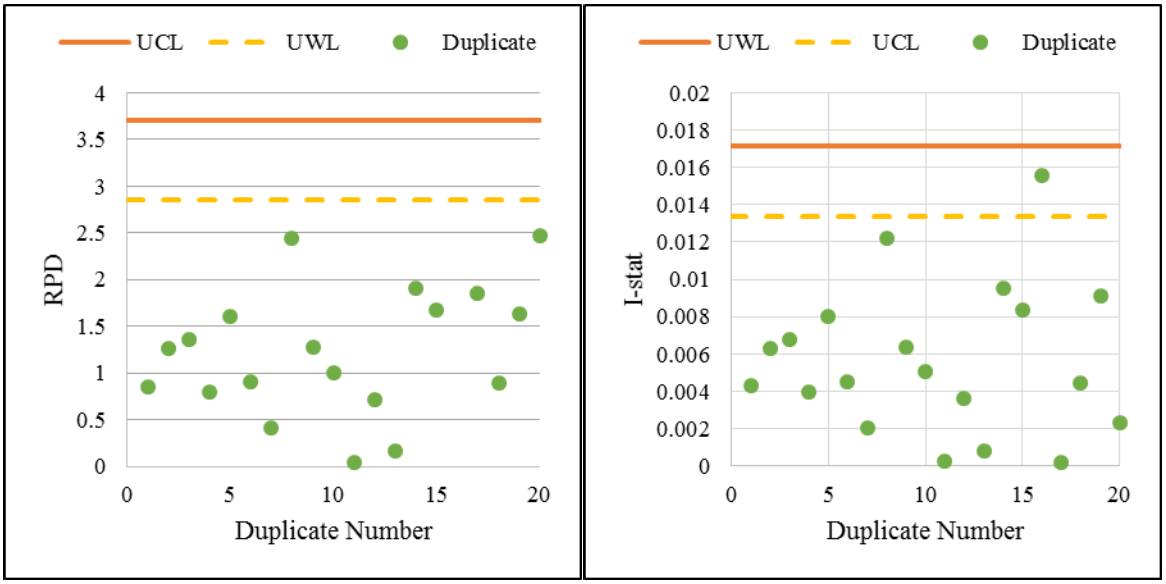


Figure 5-19: Calcium Hardness Precision Control Chart

CHAPTER 6. CONCLUSIONS

In this research, a 0.324 million gallon per day (MGD) pilot plant was operated for 3,855 run-hours to simulate the elimination of sulfuric acid from a 14.5 MGD full-scale NF pretreatment process while keeping other aspects of pretreatment constant (sand filtration, cartridge filtration, and scale inhibitor dose). The primary goal of this research was to decrease or eliminate sulfuric acid in the pretreated feed to a NF pilot unit without compromising membrane productivity, and permeate or concentrate water quality streams.

General conclusions made based on the results obtained from this research are as follows:

- NF pilot productivity, as measured by specific flux (J_{SP}), was found to decline when the sulfuric acid was eliminated by 2.33 percent, 9.61 percent, and 4.08 percent in the first stage, second stage, and total pilot system, respectively, with no noticeable corresponding increase in pressure drop (P_D).
- The total system normalized permeate flow (NPF) experienced a 4.48 percent loss, while the first and second stage incurred 3.22 percent and 9.61 percent loss, respectively, with the elimination of sulfuric acid.
- The elimination of sulfuric acid resulted in a net normalized salt passage (NSP) increase of 24.0 percent, 47.9 percent, and 24.5 percent in the first stage, second stage, and total system, respectively.
- The decrease and elimination of sulfuric acid caused a slight gradual decrease in NPF, J_{SP}, and water flux (J_W) primarily detected in the second stage. This suggests that scale has

formed, and was verified via membrane autopsy. However, the slight decline in membrane productivity did not warrant an immediate membrane cleaning.

- The elimination of sulfuric acid yielded a decrease in concentrate conductivity, calcium hardness concentration, and sulfate concentration by 13.9 percent, 26.7 percent, and 76.5 percent, respectively. The significant decrease in sulfate would allow the Town to continue to retail concentrate water to the neighboring wastewater plant without exceeding the discharge permit.
- The elimination of sulfuric acid yielded a decrease in permeate sulfate concentration by 37.6 percent, and an increase in alkalinity and calcium hardness concentrations by 22.3 and 22.2 percent, respectively. The increase of alkalinity imparts stability to the water when blended with corrosive reverse osmosis permeate. Conversely, increase of calcium hardness presents the potential problem of calcium carbonate scale in the distribution system. Conductivity also increases in the permeate stream by 24.3 percent, which can be explained by the Donnan effect.
- As sulfuric acid dose is decreased, the LSI increased, theoretically increasing the capacity of feed water to precipitate scale on the membrane surface. It should be noted that the significant decline in membrane performance occurs when the LSI goes from negative to positive, which occurs at a target feed pH of 6.9.
- A decrease in sulfuric acid pretreatment yielded a lower percentage of readily strippable H_2S in the permeate stream.

- With sulfuric acid pretreatment, the NF processes' limiting salt is calcium sulfate. However, with the removal of sulfuric acid, the limiting salt becomes calcium carbonate, which was verified via membrane autopsy.
- After piloting had concluded, superimposed elemental imaging analysis revealed that that the tail membrane surface was fouled with iron disulfide, calcium carbonate, clay, and NOM. However, the foulant was reversible as flux was recovered to normal operating conditions after a membrane cleaning with deionized water, low pH acid, and high pH base.

Table 6-1 presents the potential cost reduction if the Town wishes to reduce or eliminate the sulfuric acid dose, assuming acid is $0.63/gallon (Black et al., 2016). If the Town were to eliminate acid pretreatment, they would reduce their annual chemical costs by $70,080. Eliminating acid pretreatment compromises some membrane performance, yet implementing a consistent cleaning regimen may recover membrane performance to initial operating conditions. However, it is probable that the Town will decrease, but not eliminate sulfuric acid pretreatment in lieu of saving some membrane productivity and membrane cleaning costs.

Table 6-1: Sulfuric Acid Reduction Cost Reduction Opportunities

pH	Feed Sulfate (mg/L)	Sulfuric Acid dosage (mg/L)	Cost of Chemical ($/year)	Chemical Cost Reduction ($/year)
6.5	105	80	70,080	0
6.7	68.3	48	56,064	28,032
6.8	58.5	32	42,048	42,048
6.9	38.7	16	28,032	56,064
7.0	27.3	0	0	70,080

CHAPTER 7. RECOMMENDATIONS

If attainable, pilot plants are strongly recommended to evaluate possible modifications to a treatment process. Pilot plants are a useful tool that can determine optimal treatment operation without manipulating full-scale treatment processes.

As demonstrated in this study, sulfuric acid can be eliminated without compromising productivity or permeate water quality. If the Town elects to decrease or eliminate sulfuric acid pretreatment in the full-scale system, normalized permeate flow (NPF), pressure drop (P_D), normalized salt passage (NSP), specific flux (J_{SP}), and general water quality should be closely monitored to determine trends that signify scale formation and thus a cleaning. Per the manufacturer's specification, a cleaning should occur when NPF decreases greater than 10 percent, NSP increases 5 to 10 percent, or pressure drop increases 10 to 15 percent per the manufacturer's specification. At a minimum, it is recommended to decrease sulfuric acid pretreatment as it not only yields superior permeate and concentrate water quality, but it also saves annual chemical cost and diminishes hazard for membrane operators.

This study focused on one set of operating conditions in which scale inhibitor dose, scale inhibitor chemical, and recovery rate remained constant throughout the research. It is recommended that water purveyors and researchers conduct experiments that provide a range of variation in these parameters to optimize pretreatment in terms of operation and cost. It is also recommended to evaluate the effects of post-treatment when such parameters are varied.

APPENDIX A. LOG SHEETS AND MATERIALS USED IN RESEARCH

Table A-1: Study Log Sheet for Manual Collection

Sulfuric Acid Reduction Study Log Sheet

Date/Day: ________________ Operator: ________________

Time: ________________ Wells Running: ________________

Hour Meter: ________________

Parameter	Total Permeate	Raw	Feed	Final Concentrate
pH				
Temperature				
Conductivity				
TDS				
Analyzed at Town Laboratory				
Turbidity				
Alkalinity			x	
Chloride			x	
Calcium Hardness			x	
Color				

APPENDIX B. MEMBRANE PERFORMANCE DATA RECORDED DURING STUDY

Table B-1: Averaged Normalized Permeate Flow (NPF) (gpm) Data

Parameter	pH 6.5	pH 6.7	pH 6.8	pH 6.9	pH 7.0
First Stage NPF	202 ± 4	202 ± 4	198 ± 5	195 ± 4	196 ± 4
Second Stage NPF	47.6 ± 1.8	46.9 ± 1.7	45.6 ± 1.9	44.5 ± 1.7	43.0 ± 1.3
Total System NPF	250 ± 6	249 ± 6	243 ± 7	239 ± 5	239 ± 4

Table B-2: Averaged Pressure Drop (P_D) (psi) Data

Parameter	pH 6.5	pH 6.7	pH 6.8	pH 6.9	pH 7.0
First Stage P_D	2.54 ± 0.37	2.44 ± 0.35	2.37 ± 0.25	2.39 ± 0.31	2.49 ± 0.30
Second Stage P_D	2.82 ± 0.55	2.93 ± 0.53	3.01 ± 0.56	3.01 ± 0.53	2.79 ± 0.48
Total System P_D	5.33 ± 0.83	5.41 ± 0.80	5.43 ± 0.81	5.43 ± 0.72	5.30 ± 0.80

Table B-3: Averaged Normalized Salt Passage (NSP) (%) data

Parameter	pH 6.5	pH 6.7	pH 6.8	pH 6.9	pH 7.0
First Stage NSP	45.5 ± 1.2	50.0 ± 1.2	52.6 ± 1.2	55.0 ± 1.0	56.5 ± 0.6
Second Stage NSP	33.5 ± 1.8	40.4 ± 2.2	44.5 ± 2.4	48.3 ± 2.5	49.5 ± 2.0
Total System NSP	49.0 ± 1.2	53.9 ± 1.3	57.2 ± 1.3	59.8 ± 1.1	61.1 ± 0.6

Table B-4: Averaged Specific Flux (J_{SP}) (gfd/psi) Data

Parameter	pH 6.5	pH 6.7	pH 6.8	pH 6.9	pH 7.0
First Stage J_{SP}	0.585 ± 0.013	0.584 ± 0.013	0.572 ± 0.015	0.564 ± 0.012	0.566 ± 0.010
Second Stage J_{SP}	0.572 ± 0.021	0.563 ± 0.021	0.548 ± 0.023	0.535 ± 0.021	0.517 ± 0.015
Total System J_{SP}	0.639 ± 0.016	0.635 ± 0.016	0.627 ± 0.017	0.619 ± 0.015	0.613 ± 0.014

Table B-5: Averaged Water Flux (J_W) (gal/sfd) Data

Parameter	pH 6.5	pH 6.7	pH 6.8	pH 6.9	pH 7.0
First Stage J_W	15.6 ± 0.1	15.6 ± 0.1	15.6 ± 0.2	15.6 ± 0.2	15.7 ± 0.1
Second Delta J_W	13.0 ± 0.3	13.1 ± 0.3	13.1 ± 0.3	13.1 ± 0.3	12.8 ± 0.2
Total System J_W	15.0 ± 0.1	15.0 ± 0.1	15.0 ± 0.1	15.0 ± 0.1	15.1 ± 0.1

APPENDIX C. WATER QUALITY DATA RECORDED DURING STUDY

Table C-1: Averaged Temperature (°C) Data

Parameter	pH 6.5	pH 6.7	pH 6.8	pH 6.9	pH 7.0
Raw	24.1 ± 0.1	25.3 ± 0.5	25.4 ± 0.9	25.1± 0.6	25.9 ± 0.2
Feed	24.1 ± 1.0	25.3 ± 0.5	25.4 ± 0.8	25.1 ± 0.6	25.8 ± 0.2
Permeate	23.9 ± 1.0	25.4 ± 0.6	25.4 ± 1.2	25.2 ± 0.7	25.9 ± 0.1
Concentrate	24.2 ± 0.8	25.4 ± 0.5	25.5 ± 0.8	25.1 ± 0.6	26.1 ± 0.4

Table C-2: Averaged pH Data

Parameter	pH 6.5	pH 6.7	pH 6.8	pH 6.9	pH 7.0
Raw	7.05 ± 0.07	7.02 ± 0.05	6.98 ± 0.08	6.90 ± 0.08	6.90 ± 0.05
Feed	6.46 ± 0.08	6.70 ± 0.07	6.77 ± 0.08	6.81 ± 0.05	6.92 ± 0.08
Permeate	6.38 ± 0.09	6.61 ± 0.07	6.62 ± 0.08	6.67 ± 0.07	6.76 ± 0.07
Concentrate	6.72 ± 0.09	6.99 ± 0.07	7.10 ± 0.06	7.11 ± 0.08	7.17 ± 0.08

Table C-3: Averaged Conductivity (µS/cm) Data

Parameter	pH 6.5	pH 6.7	pH 6.8	pH 6.9	pH 7.0
Raw	751 ± 20	762 ± 18	759 ± 18	777 ± 26	782 ± 21
Feed	761 ± 19	767 ± 18	762 ± 18	778 ± 26	782 ± 21
Permeate	469 ± 18	523 ± 18	534 ± 14	562 ± 23	583 ± 17
Concentrate	2080 ± 51	1910 ± 43	1860 ± 43	1830 ± 55	1790 ± 39

Table C-4: Averaged TDS (mg/L) Data

Parameter	pH 6.5	pH 6.7	pH 6.8	pH 6.9	pH 7.0
Raw	435 ± 12	440 ± 15	456 ± 26	461 ± 29	497 ± 40
Feed	477 ± 11	466 ± 18	468 ± 26	471 ± 25	450 ± 40
Permeate	239 ± 7	294± 21	290 ± 28	304 ± 16	292 ± 56
Concentrate	1780 ± 5	1520 ± 50	1500 ± 65	1390 ± 60	1350± 26

Table C-5: Averaged Alkalinity (mg/L as $CaCO_3$) Data

Parameter	pH 6.5	pH 6.7	pH 6.8	pH 6.9	pH 7.0
Feed	309 ± 11	309 ± 20	316 ± 9	311 ± 12	304 ± 10
Permeate	179 ± 11	200 ± 17	213 ± 8	212 ± 9	219 ± 12
Concentrate	524 ± 33	625 ± 32	682 ± 39	745 ± 24	763 ± 27

Table C-6: Averaged Sulfate (mg/L) Data

Parameter	pH 6.5	pH 6.7	pH 6.8	pH 6.9	pH 7.0
Raw	25.7 ± 1.7	25.4 ± 2.8	26.9 ± 2.7	26.8 ± 2.0	27.1 ± 1.9
Feed	105 ± 5	68.3 ± 3.8	58.5 ± 7.3	38.7 ± 2.4	27.3 ± 1.9
Permeate	2.76 ± 0.64	1.91 ± 0.51	2.22 ± 0.27	1.67 ± 0.31	1.72 ± 0.18
Concentrate	736 ± 58	465 ± 30	368 ± 46	259 ± 25	173 ± 9.0

Table C-7: Averaged Chloride (mg/L) Data

Parameter	pH 6.5	pH 6.7	pH 6.8	pH 6.9	pH 7.0
Raw	51.2 ± 6.8	52.7 ± 6.5	52.3 ± 4.1	55.9 ± 4.9	56.6 ± 5.8
Feed	52.5 ± 5.4	52.6 ± 6.7	52.7 ± 4.2	55.9 ± 5.0	56.6 ± 5.7
Permeate	50.1 ± 7.1	51.6 ± 6.5	49.1 ± 4.4	51.4 ± 4.8	50.8 ± 4.7
Concentrate	74.8 ± 8.1	79.9 ± 9.4	79.2 ± 6.4	84.8 ± 6.9	88.4 ± 6.9

Table C-8: Averaged Calcium Hardness (mg/L) Data

Parameter	pH 6.5	pH 6.7	pH 6.8	pH 6.9	pH 7.0
Raw	305 ± 7	303 ± 9	305 ± 11	301 ± 10	292 ± 11.
Feed	303 ± 11	304 ± 9	305 ± 7	300 ± 10	289 ± 10
Permeate	162 ± 6	185 ± 5	190 ± 7	195 ± 6	198 ± 8
Concentrate	1080 ± 57	959 ± 38	940 ± 53	878 ± 40	792 ± 34

Table C-9: Averaged Magnesium (mg/L) Data

Parameter	pH 6.5	pH 6.7	pH 6.8	pH 6.9	pH 7.0
Raw	4.97 ± 0.33	5.09 ± 0.31	5.05 ± 0.29	5.12 ± 0.27	5.29 ± 0.49
Feed	5.05 ± 0.37	5.11 ± 0.30	5.06 ± 0.31	5.14 ± 0.27	5.8 ± 0.48
Permeate	1.55 ± 0.18	1.73 ± 0.10	1.79 ± 0.09	1.89 ± 0.09	1.99 ± 0.10

Table C-10: Averaged Sodium (mg/L) Data

Parameter	pH 6.5	pH 6.7	pH 6.8	pH 6.9	pH 7.0
Raw	21.6 ± 2.1	22.8 ± 2.0	22.1 ± 1.4	22.9 ± 1.7	23.6 ± 2.0
Feed	21.6 ± 2.2	22.9 ± 1.9	22.1 ± 1.4	23.0 ± 1.7	23.3 ± 2.2
Permeate	17.9 ± 1.6	19.6 ± 1.8	19.4 ± 1.1	20.5 ± 1.5	20.4 ± 1.1

Table C-11: Averaged Silica (mg/L) Data

Parameter	pH 6.5	pH 6.7	pH 6.8	pH 6.9	pH 7.0
Raw	11.5 ± 0.5	11.8 ± 0.6	11.9 ± 0.5	12.7 ± 0.5	15.1 ± 1.3
Feed	11.7 ± 0.4	12.0 ± 0.5	12.3 ± 0.6	12.7 ± 0.5	15.0 ± 1.4
Permeate	10.8 ± 0.4	11.3 ± 0.4	11.4 ± 0.5	11.9 ± 0.5	14.1 ± 1.2

Table C-12: Averaged Color (CU) Data

Parameter	pH 6.5	pH 6.7	pH 6.8	pH 6.9	pH 7.0
Raw	43 ± 7	41 ± 5	41 ± 3	41 ± 3	40 ± 2
Feed	34 ± 8	39 ± 5	38 ± 2	39 ± 3	38 ± 2
Permeate	< 5	< 5	< 5	< 5	< 5
Concentrate	247 ± 43	262 ± 27	259 ± 17	270 ± 8	269 ± 11

Table C-13: Averaged DOC (mg/L) Data

Parameter	pH 6.5	pH 6.7	pH 6.8	pH 6.9	pH 7.0
Raw	106 ± 1	10.7 ± 0.38	10.7 ± 0.53	10.3 ± 0.6	9.79 ± 0.41
Feed	10.8 ± 0.2	10.8 ± 0.34	10.6 ± 0.59	10.3 ± 0.6	9.86 ± 0.38
Permeate	< 0.25	< 0.25	< 0.25	< 0.25	< 0.25
Concentrate	74.9 ± 1.6	79.7 ± 3.2	83.4 ± 6.4	78.2 ± 1.9	76.6 ± 2.2

Table C-14: **UV$_{254}$ (cm^{-1}) Raw Data**

Parameter	pH 6.5	pH 6.7	pH 6.8	pH 6.9	pH 7.0
Raw	0.413 ± 0.013	0.415 ± 0.015	0.414 ± 0.017	0.405 ± 0.010	0.407 ± 0.009
Feed	0.410 ± 0.008	.0416 ± 0.016	0.418 ± 0.018	0.409 ± 0.011	0.411 ± 0.009
Permeate	0.04 ± 0.001	.006 ± 0.002	0.006 ± 0.003	0.006 ± 0.002	0.06 0.001

APPENDIX D. BART TEST DATA

Table D-1: Permeate BART Test Results at Feed pH 6.5

Day	**HAB** **Bleached from bottom to top** **Bleached from top to bottom**	**IRB** **Foam or brown slime ring forms around ball and/or at the bottom of the tube** **Green or red cloudy** **Black solution**	**APB** **Change from purple to yellow-orange** **Cloudy solution**	**SLYM** **Cloudy Solution** **Slime Growth at Bottom** **Blackened liquid** **Glowing Ring with UV**	**SRB** **Black slime ring forms around ball and/or at the bottom of the tube** **Cloudy, gray solution**
0	No reaction	No reaction	No reaction	No reaction	No reaction
1	No reaction	No reaction	No reaction	No reaction	No reaction
2	Bleaching at top - Anaerobic Aggressive ~575,000 CFU/mL	No Reaction	No Reaction	No Reaction	No Reaction
3	Not Measured	Not Measured	Not Measured	Not Measured	Not Measured
4	Positive See Day 2	No Reaction	Bleaching at Base Moderate ~4500 CFU/mL	No Reaction	Cloudy solution - Anaerobic Some black particulates in base and around ball – Combo aerobic/anaerobic Aggressive ~27,000 CFU/mL
5	Positive See Day 2	No Reaction	Positive See Day 4	No Reaction	Positive See Day 4
6	Positive See Day 2	No Reaction	Positive See Day 4	Solution appears cloudy, but positive reaction is not definitive Not glowing	Positive See Day 4
7		No Reaction	Positive See Day 4	Cloudy Solution – Slime forming bacteria Not glowing Not aggressive ~100 CFU/mL	Positive See Day 4
8		No Reaction	Positive See Day 4	Positive See Day 6	Positive See Day 4

Table D-2: Permeate BART Test Results at Feed pH 6.7

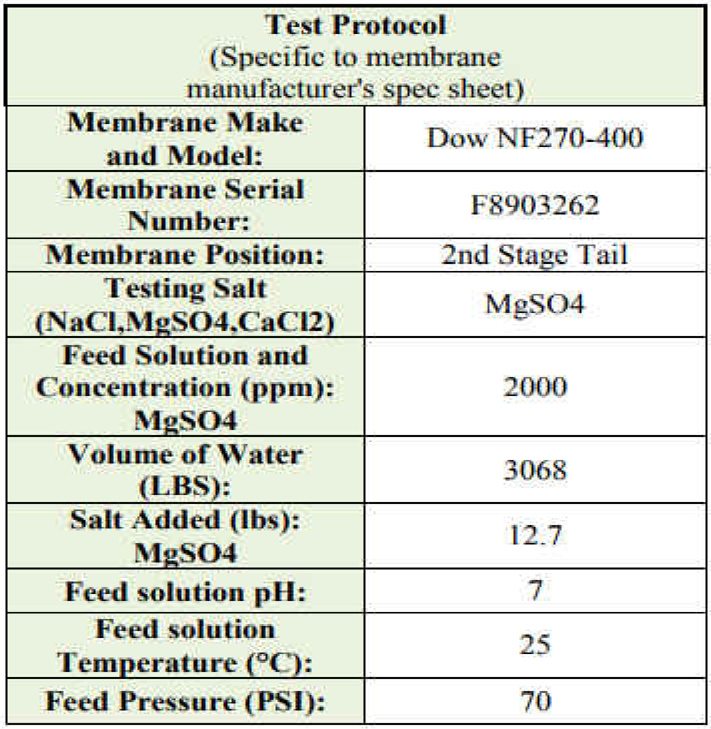
Day	HAB Bleached from bottom to top Bleached from top to bottom	IRB Foam or brown slime ring forms around ball and/or at the bottom of the tube Green or red cloudy Black solution	APB Change from purple to yellow-orange Cloudy solution	SLYM Cloudy Solution Slime Growth at Bottom Blackened liquid Glowing Ring with UV	SRB Black slime ring forms around ball and/or at the bottom of the tube Cloudy, gray solution
0	No reaction	No reaction	No reaction	No reaction	No reaction
1	No reaction	No reaction	No reaction	No reaction	No reaction
2	No reaction	No reaction	No reaction	No reaction	No reaction
3	Not Measured	Not Measured	Not Measured	Not Measured	Not Measured
4	No reaction	No reaction	Very slight bleaching at base, but positive reaction is not definitive	No reaction	Very minor growth at base, but positive reaction is not definitive
5	No reaction	No reaction	Bleaching at Base Moderate ~450 CFU/mL	No reaction	Growth observed at base – Dense anaerobic SRB consortium Aggressive ~6,000 CFU/mL
6	No reaction	No reaction	Positive See Day 5	No reaction	Positive See Day 5
7		Slight darkening of solution, but positive reaction not definitive	Positive See Day 5	Solution appears cloudy, but positive reaction is not definitive Not glowing	Positive See Day 5
8		Cloudy green/red solution- Pseudomonads and enteric bacteria Moderate ~25 CFU/mL	Positive See Day 5	Cloudy Solution – Slime forming bacteria Not glowing Not aggressive <20 CFU/mL	Positive See Day 5 Some additional growth around ball – Aerobic SRB

Table D-3: Permeate BART Test Results at Feed pH 7.0

Day	HAB Bleached from bottom to top Bleached from top to bottom	IRB Foam or brown slime ring forms around ball and/or at the bottom of the tube Green or red cloudy Black solution	APB Change from purple to yellow-orange Cloudy solution	SLYM Cloudy Solution Slime Growth at Bottom Blackened liquid Glowing Ring with UV	SRB Black slime ring forms around ball and/or at the bottom of the tube Cloudy, gray solution
0	No reaction	No reaction	No reaction	No reaction	No reaction
1	No reaction	No reaction	No reaction	No reaction	No reaction
2	No reaction	No reaction	No reaction	No reaction	No reaction
3	Not Measured	Not Measured	Not Measured	Not Measured	Not Measured
4	No reaction	Red, brown solution – IRB and enteric Cloudy – Heterotrophic bacteria Moderate ~9,000 CFU/mL	No reaction	No reaction	Very slight, minimal growth around ball and base, but positive reaction is not definitive
5	No reaction	Positive See Day 4	Very slight bleaching at base, but positive reaction is not definitive	No reaction	Growth under ball and at the base Aggressive ~6,000 CFU/mL
6	No reaction	Positive See Day 4	Bleaching at Base Moderate ~75 CFU/mL	Solution appears cloudy, but positive reaction is not definitive Not glowing	Positive See Day 5
7		Positive See Day 4	Positive See Day 6	Cloudy Solution – Slime forming bacteria Not glowing Not aggressive <20 CFU/mL	Positive See Day 5
8		Positive See Day 4	Positive See Day 6	Positive See Day 7	Positive See Day 5

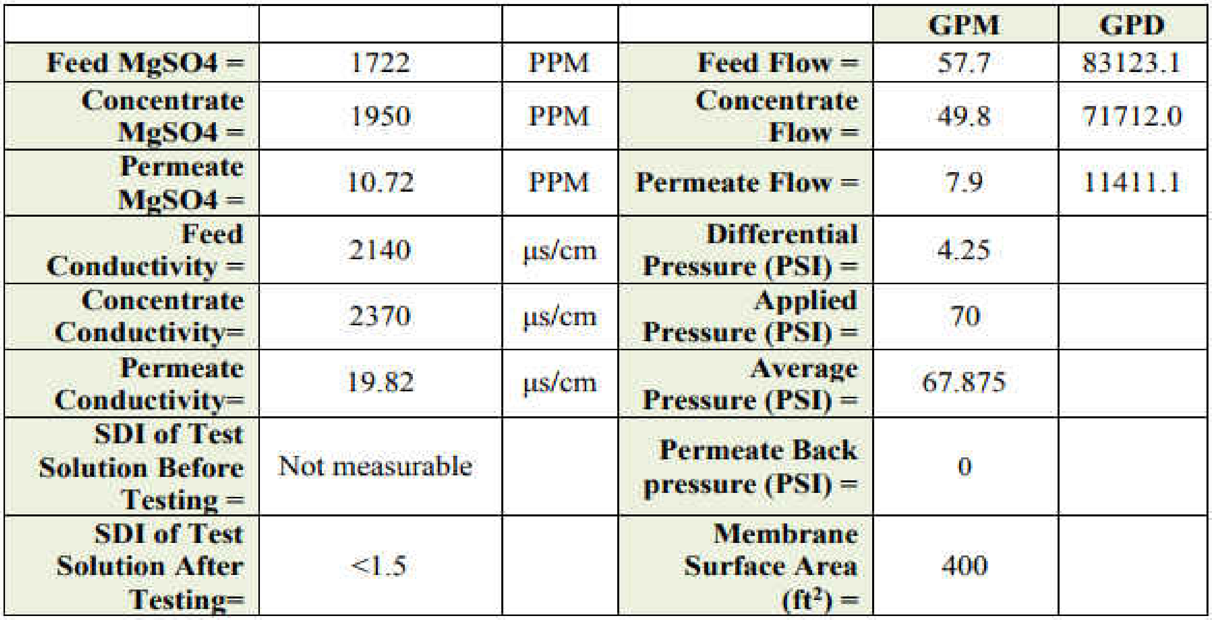
APPENDIX E. MEMBRANE AUTOPSY RESULTS

Table E-1: Initial Test Conditions



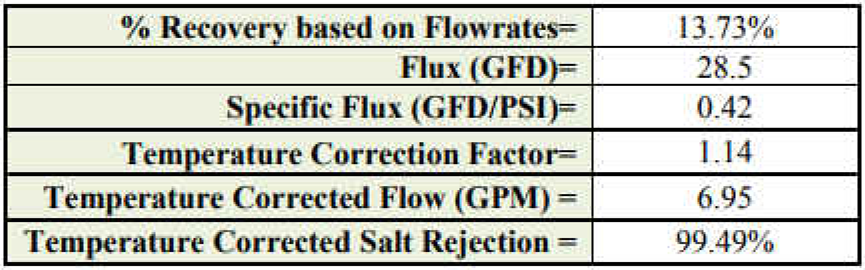
Test Protocol (Specific to membrane manufacturer's spec sheet)	
Membrane Make and Model:	Dow NF270-400
Membrane Serial Number:	F8903262
Membrane Position:	2nd Stage Tail
Testing Salt (NaCl,MgSO4,CaCl2)	MgSO4
Feed Solution and Concentration (ppm): MgSO4	2000
Volume of Water (LBS):	3068
Salt Added (lbs): MgSO4	12.7
Feed solution pH:	7
Feed solution Temperature (°C):	25
Feed Pressure (PSI):	70

Table E-2: Water Quality Characteristics and Membrane Conditions after Initial Test



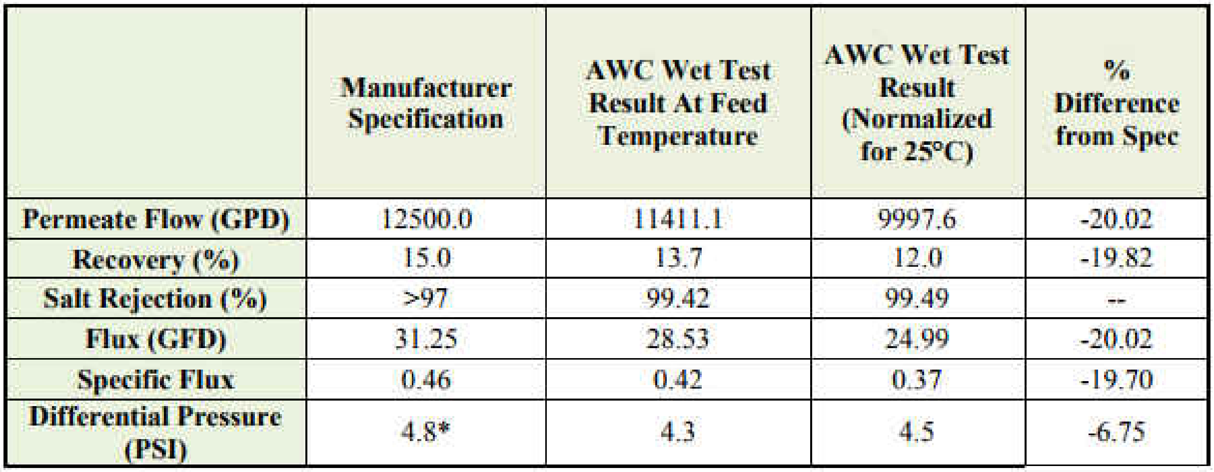
				GPM	GPD
Feed MgSO4 =	1722	PPM	**Feed Flow =**	57.7	83123.1
Concentrate MgSO4 =	1950	PPM	**Concentrate Flow =**	49.8	71712.0
Permeate MgSO4 =	10.72	PPM	**Permeate Flow =**	7.9	11411.1
Feed Conductivity =	2140	µs/cm	**Differential Pressure (PSI) =**	4.25	
Concentrate Conductivity=	2370	µs/cm	**Applied Pressure (PSI) =**	70	
Permeate Conductivity=	19.82	µs/cm	**Average Pressure (PSI) =**	67.875	
SDI of Test Solution Before Testing =	Not measurable		**Permeate Back pressure (PSI) =**	0	
SDI of Test Solution After Testing=	<1.5		**Membrane Surface Area (ft^2) =**	400	

Table E-3: Membrane Performance after Initial Test



% Recovery based on Flowrates=	13.73%
Flux (GFD)=	28.5
Specific Flux (GFD/PSI)=	0.42
Temperature Correction Factor=	1.14
Temperature Corrected Flow (GPM) =	6.95
Temperature Corrected Salt Rejection =	99.49%

Table E-4: Membrane Performance after Initial Test Compared to Manufacturer Specification



	Manufacturer Specification	AWC Wet Test Result At Feed Temperature	AWC Wet Test Result (Normalized for 25°C)	% Difference from Spec
Permeate Flow (GPD)	12500.0	11411.1	9997.6	-20.02
Recovery (%)	15.0	13.7	12.0	-19.82
Salt Rejection (%)	>97	99.42	99.49	--
Flux (GFD)	31.25	28.53	24.99	-20.02
Specific Flux	0.46	0.42	0.37	-19.70
Differential Pressure (PSI)	4.8*	4.3	4.5	-6.75

* Estimated based on Reynolds number (function of feed spacer height, temperature, flow velocity) and friction coefficient.

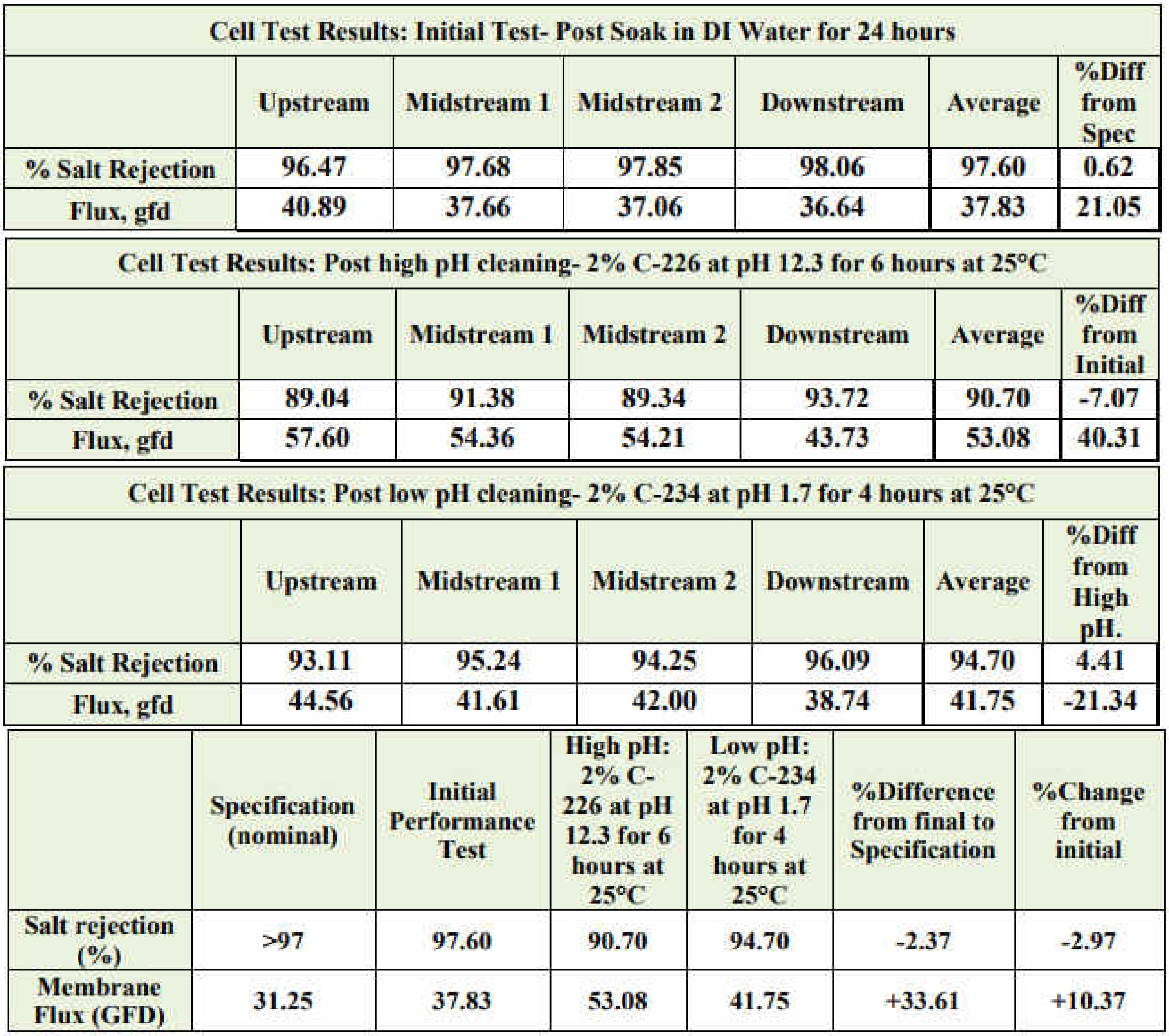
Table E-5: Bubble Test Results

		Results	Pass/Fail
Feed End	**Inner Diameter**	**No bubbles observed**	**Pass**
	Outer Diameter	**No bubbles observed**	
Concentrate End	**Inner Diameter**	**No bubbles observed**	**Pass**
	Outer Diameter	**No bubbles observed**	
Fiber glass shell	**Feed end**	**No bubbles observed**	**Pass**
	Middle	**No bubbles observed**	
	Concentrate End	**No bubbles observed**	

Table E-6: Contact Angle Test Results

	Foulant from membrane	Calculated Without Moisture
Moisture and Volatiles	**91.77%**	**--**
Organic Content	**1.75%**	**21.26%**
Inorganic Content	**6.48%**	**78.74%**

Table E-7: Cell Test Results Post Cleaning



Cell Test Results: Initial Test- Post Soak in DI Water for 24 hours						
	Upstream	Midstream 1	Midstream 2	Downstream	Average	%Diff from Spec
% Salt Rejection	96.47	97.68	97.85	98.06	97.60	0.62
Flux, gfd	40.89	37.66	37.06	36.64	37.83	21.05

Cell Test Results: Post high pH cleaning- 2% C-226 at pH 12.3 for 6 hours at 25°C						
	Upstream	Midstream 1	Midstream 2	Downstream	Average	%Diff from Initial
% Salt Rejection	89.04	91.38	89.34	93.72	90.70	-7.07
Flux, gfd	57.60	54.36	54.21	43.73	53.08	40.31

Cell Test Results: Post low pH cleaning- 2% C-234 at pH 1.7 for 4 hours at 25°C						
	Upstream	Midstream 1	Midstream 2	Downstream	Average	%Diff from High pH.
% Salt Rejection	93.11	95.24	94.25	96.09	94.70	4.41
Flux, gfd	44.56	41.61	42.00	38.74	41.75	-21.34

	Specification (nominal)	Initial Performance Test	High pH: 2% C-226 at pH 12.3 for 6 hours at 25°C	Low pH: 2% C-234 at pH 1.7 for 4 hours at 25°C	%Difference from final to Specification	%Change from initial
Salt rejection (%)	>97	97.60	90.70	94.70	-2.37	-2.97
Membrane Flux (GFD)	31.25	37.83	53.08	41.75	+33.61	+10.37

Table E-8: BART Test Results

Test	Test duration (days)	Day of failure	Population Cfu/mL
Iron related bacteria	8	6	500
Slime forming bacteria	8	1	1,800,000
Sulfate reducing bacteria	8	6	1200
Heterotrophic aerobic bacteria	4	1	7,000,000
Nitrifying bacteria	Positive/ Negative	Negative	--

APPENDIX F. DOW CHEMICAL COMPANY MEMBRANE SPECIFICATIONS AND CLEANING PROCEDURES FOR NF270 ELEMENTS

FILMTEC™ Membranes

FILMTEC NF270 Nanofiltration Elements for Commercial Systems

Features

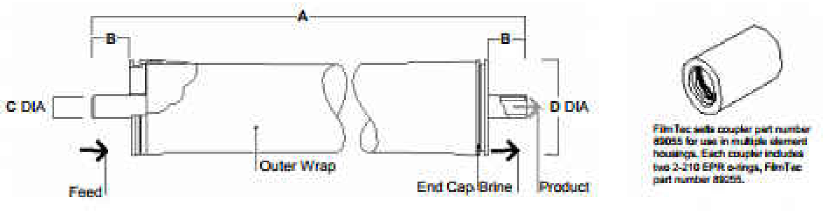
The FILMTEC™ NF270 membrane elements are ideal for removing a high percentage of TOC and THM precursors with medium to high salt passage and medium hardness passage. The FILMTEC NF270 membrane is an ideal choice for surface water and ground water where good organic removal is desired with partial softening.

Product Specifications

Product	Part Number	Active Area ft² (m²)	Applied Pressure psig (bar)	Permeate Flow Rate gpd (m³/d)	Stabilized Salt Rejection (%)
NF270-2540	149986	28 (2.6)	70 (4.8)	850 (3.2)	>97.0
NF270-4040	149987	82 (7.6)	70 (4.8)	2,500 (9.5)	>97.0

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

Figure 1



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

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

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

1 inch = 25.4 mm

Operating Limits

• Membrane Type	Polyamide Thin-Film Composite
• Maximum Operating Temperature	113°F (45°C)
• Maximum Operating Pressure	600 psi (41 bar)
• Maximum Feed Flow Rate - 4040 elements	16 gpm (3.6 m³/hr)
- 2540 elements	6 gpm (1.4 m³/hr)
• Maximum Pressure Drop - tape wrapped	13 psig (0.9 bar)
- fiberglassed	15 psig (1.0 bar)
• pH Range, Continuous Operation[a]	2 - 11
• pH Range, Short-Term Cleaning (30 min.)[b]	1 - 12
• Maximum Feed Silt Density Index	SDI 5
• Free Chlorine Tolerance[c]	< 0.1 ppm

[a] Maximum temperature for continuous operation above pH 10 is 95°F (35°C).

[b] Refer to Cleaning Guidelines in specification sheet 609-23010 for NF90.

[c] Under certain conditions, the presence of free chlorine and other oxidizing agents will cause premature membrane failure. Since oxidation damage is not covered under warranty, FilmTec recommends removing residual free chlorine by pretreatment prior to membrane exposure. Please refer to technical bulletin 609-22010 for more information.

Important Information

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

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

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

Operation Guidelines

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

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

General Information

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

FILMTEC™ Membranes

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

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

http://www.filmtec.com

FILMTEC™ Membranes

Cleaning and Disinfection Procedures for FILMTEC™ NF200 and NF270 Elements

Introduction

The following are general recommendations for cleaning FILMTEC™ NF 200 and NF270 elements. More detailed procedures for cleaning a nanofiltration (NF) system are typically included in the operating manual provided by the system supplier. It should be emphasized that frequent cleaning is not required for a properly designed and properly operated NF system, however because of the NF 200 and NF270 membrane's unique combination of pH range and temperature resistance, cleaning may be accomplished very effectively.

The cleaning procedure for the piperazine-based nanofiltration membranes FILMTEC NF200 and FILMTEC NF270 differs from the procedure proposed for the polyamide-based FILMTEC FT30 membranes (FILMTEC BW30/TW30, FILMTEC BW30LE, FILMTEC XLE, FILMTEC SW30 and FILMTEC SW30HR).

There are two main reasons for the change:

- Alkaline cleaning at pH above 9 causes the membrane to swell. The net effect is an increase in flux (up to 40%) and a decrease in rejection. The effect disappears in normal operations, but can take up to 72 hours to disappear completely.
- Acid cleaning at pH below 4 causes the membrane to shrink. This becomes visible as an increase in rejection and a decrease in flux. The order of magnitude is less than with alkaline cleaners. Again this effect disappears during normal operation.

From an operations point of view, it is impractical to have to wait before the system stabilizes again. We have seen however, that the effect of the acid cleaner neutralizes the action of the alkaline cleaner (but not the other way around, as the alkaline effect is much stronger).

Cleaning Procedure

In normal operation, the membrane in nanofiltration elements can become fouled by mineral scale, biological matter, colloidal particles and insoluble organic constituents. Deposits build up on the membrane surfaces during operation until they cause loss in normalized permeate flow, loss of normalized salt rejection, or both.

Elements should be cleaned when one or more of the below mentioned parameters are applicable:

- The normalized permeate flow drops 10%
- The normalized salt passage increases 5 - 10%
- The normalized pressure drop (feed pressure minus concentrate pressure) increases 10 - 15%

If you wait too long, cleaning may not restore the membrane element performance successfully. In addition, the time between cleanings becomes shorter as the membrane elements will foul or scale more rapidly.

Cleaning Procedure (cont.)

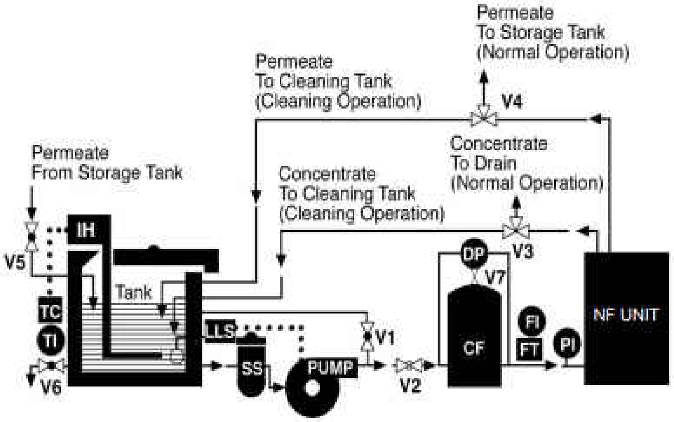
Differential Pressure (ΔP) should be measured and recorded across each stage of the array of pressure vessels. If the feed channels within the element become plugged, the ΔP will increase. It should be noted that the permeate flux will drop if feedwater temperature decreases. This is normal and does not indicate membrane fouling.

A malfunction in the pretreatment, pressure control, or increase in recovery can result in reduced product water output or an increase in salt passage. If a problem is observed, these causes should be considered first. The element(s) may not require cleaning. A computer program called FTNORM is available from FilmTec for normalizing performance data of FILMTEC™ RO and NF membranes. This program can be used to assist in determining when to clean and can be downloaded from our web site's Download Software section (http://www.dow.com/liquidseps/design/software.htm).

Safety Precautions

1. When using any chemical indicated here in subsequent sections, follow accepted safety practices. Consult the chemical manufacturer for detailed information about safety, handling and disposal.
2. When preparing cleaning solutions, ensure that all chemicals are dissolved and well mixed before circulating the solutions through the elements.
3. It is recommended the elements be flushed with good-quality chlorine-free water (20°C minimum temperature) after cleaning. Permeate water or deionized water are recommended. Care should be taken to operate initially at reduced flow and pressure to flush the bulk of the cleaning solution from the elements before resuming normal operating pressures and flows. Despite this precaution, cleaning chemicals will be present on the permeate side following cleaning. Therefore, the permeate must be diverted to drain for at least 30 minutes or until the water is clear when starting up after cleaning.
4. During recirculation of cleaning solutions, the maximum temperature must not be exceeded. The maximum allowed temperature is dependent on pH and membrane type. Table 1 contains information on the maximum allowed temperatures.
5. For elements greater than six inches in diameter, the flow direction during cleaning must be the same as during normal operation to prevent element telescoping, because the vessel thrust ring is installed only on the reject end of the vessel. This is also recommended for smaller elements. Equipment for cleaning is illustrated below.

Cleaning System Flow Diagram



TANK	Chemical Mixing Tank, polypropylene or FRP
IH	Immersion Heater (may be replaced by cooling coil for some site locations)
TI	Temperature Indicator
TC	Temperature Control
LLS	Lower Level Switch to shut off pump
SS	Security Screen–100 mesh
PUMP	Low-Pressure Pump, 316 SS or non-metallic composite
CF	Cartridge Filter, 5-10 micron polypropylene with PVC, FRP, or SS housing

DP	Differential Pressure Gauge
FI	Flow Indicator
FT	Flow Transmitter (optional)
PI	Pressure Indicator
V1	Pump Recirculation Valve, CPVC
V2	Flow Control Valve, CPVC
V3	Concentrate Valve, CPVC 3-way valve
V4	Permeate Valve, CPVC 3-way valve
V5	Permeate Inlet Valve, CPVC
V6	Tank Drain Valve, PVC, or CPVC
V7	Purge Valve, SS, PVC, or CPVC

Suggested Equipment

The equipment for cleaning is shown in the Cleaning System Flow Diagram. The pH of cleaning solutions used with FILMTEC™ NF 200 and NF 270 elements can be in the range of 1 to 11 (see Table 1), and therefore non-corroding materials should be used in the cleaning system.

1. The mixing tank should be constructed of polypropylene or fiberglass-reinforced plastic (FRP). The tank should be provided with a removable cover and a temperature gauge. The cleaning procedure is more effective when performed at a warm temperature, and it is recommended that the solution be maintained according to the pH and temperature guidelines listed in Table 1. It is not recommended to use a cleaning temperature below 20°C because of the very slow chemical kinetics at low temperatures. In addition, chemicals such as sodium lauryl sulfate might precipitate at low temperatures. Cooling may also be required in certain geographic regions, so both heating/cooling requirements must be considered during the design. A rough rule of thumb in sizing a cleaning tank is to use approximately the empty pressure vessels volume and then add the volume of the feed and return hoses or pipes. For example, to clean ten 8-inch diameter pressure vessels with six elements per vessel, the following calculations would apply:

   A. Volume in Vessels
   $V1 = \pi r^2 L$
   $= 3.14\ (4\ \text{in})^2\ (20\ \text{ft})\ (7.48\ \text{gal/ft}^3)\ /\ (144\ \text{in}^2/\text{ft}^2)$
   $V1 = 52$ gal/vessel ($0.2\ \text{m}^3$)
   $V10 = 52 \times 10 = 520$ gal ($1.97\ \text{m}^3$)

   B. Volume in Pipes, assume 50 ft. length total 4" Sch 80 pipe
   $Vp = \pi r^2 L$
   $= 3.14\ (1.91\ \text{in})^2\ (50\ \text{ft})\ (7.48\ \text{gal/ft}^3)\ /\ (144\ \text{in}^2/\text{ft}^2)$
   $= 30$ gals ($0.11\ \text{m}^3$)
   $Vct = V_{10} + Vp = 520 + 30 = 550$ gal.

Therefore, the cleaning tank should be about 550 gals ($2.1\ \text{m}^3$).

2. The cleaning pump should be sized for the flows and pressures given in Table 2, making allowances for pressure loss in the piping and across the cartridge filter. The pump should be constructed of 316 SS or nonmetallic composite polyesters.

3. Appropriate valves, flow meters, and pressure gauges should be installed to adequately control the flow. Service lines may be either hard piped or hoses. In either case, the flow rate should be a moderate 10 ft/sec (3 m/sec) or less.

Cleaning Elements In Situ

There are six steps in the cleaning of elements:

1. **Prepare and mix** the appropriate cleaning solution, and check pH of the solution. Ensure that all chemicals are dissolved and well mixed before circulating the solution to the elements. Any cleaning solution must be clear.

2. **Low-flow pumping.** Pump mixed, preheated cleaning solution to the vessel at conditions of low flow rate (about half of that shown in Table 1) and low pressure to displace the process water. Use only enough pressure to compensate for the pressure drop from feed to concentrate. The pressure should be low enough that essentially no or little permeate is produced. A low pressure minimizes redeposition of dirt on the membrane. Dump the concentrate, as necessary, to prevent dilution of the cleaning solution.

3. **Recycle.** After the process water is displaced, cleaning solution will be present in the concentrate stream. Then recycle the concentrate and permeate to the cleaning solution tank and allow the temperature to stabilize. Measure the pH of the solution and adjust the pH if needed.

4. **Soak.** Turn the pump off and allow the elements to soak. Sometimes a soak period of about 1 hour is sufficient. For difficult fouling an extended soak period is beneficial; soak the elements overnight for 10-15 hours. To maintain a high temperature during an extended soak period, use a slow re-circulation rate (about 10% of that shown in Table 1).

Table 1. Recommended feed flow rate per pressure vessel during high flow rate recirculation

Feed Pressure[1]		Element Diameter	Feed Flow Rate per Pressure Vessel	
(psig)	(bar)	(inches)	(gpm)	(m^3/hr)
20 - 60	1.5 - 4.0	2.5	3 - 5	0.7 - 1.2
20 - 60	1.5 - 4.0	4	8 - 10	1.8 - 2.3
20 - 60	1.5 - 4.0	8	30 - 40	6. - 9.1

[1] Dependent on number of elements in pressure vessel.

Table 2. pH range and temperature limits during cleaning

	Max. temp 25°C (77°F) pH range	Max. temp 35°C (95°F) pH range	Max. temp 45°C (113°F) pH range
FILMTEC™ NF200/NF270	1 - 12	1 - 11	3 - 10

5. **High flow pumping**. Feed the cleaning solution at the rates shown in Table 1 for 30-60 minutes. The high flow rate flushes out the foulants removed from the membrane surface by the cleaning. If the elements are heavily fouled, which should never happen, a flow rate ~50% higher than shown in Table 1 may aid cleaning. At higher flow rates excessive pressure drop may be a problem. The maximum recommended pressure drops are 1.0 bar (15 psi) per element or 3.4 bar (50 psi) per multi-element vessel, whichever value is more limiting. For 8" elements, the direction of flow during cleaning must be the same as during normal operation to avoid telescoping of the elements.

6. **Flush out.** NF permeate or deionized water are recommended for flushing out the cleaning solution. Prefiltered raw water or feed water should be avoided as its components may react with the cleaning solution: precipitation of foulants may occur in the membrane elements. The minimum flush out temperature is 20°C (68°F).

Cleaning Tips

1. It is strongly recommended to clean the stages of the NF system separately. This is to avoid having the removed foulant from stage 1 pushed into the 2nd stage resulting in minimal performance improvement from the cleaning. If the system consists of 3 stages, stage 2 and stage 3 should also be cleaned separately.

   For multi-stage systems, while each stage should be cleaned separately, the flushing and soaking operations may be done simultaneously in all stages. Fresh cleaning solution needs to be prepared when the cleaning solution becomes turbid and/or discolored. High-flow recirculation, however, should be carried out separately for each stage, so the flow rate is not too low in the first stage or too high in the last. This can be accomplished either by using one cleaning pump and operating one stage at a time, or by using a separate cleaning pump for each stage.

2. The fouling or scaling of elements typically consists of a combination of foulants and scalants, for instance a mixture of organic fouling, colloidal fouling and biofouling. Therefore, it is very critical that the first cleaning step is wisely chosen. FilmTec strongly recommends alkaline cleaning as the first cleaning step.

   Acid cleaners typically react with silica, organics (for instance humic acids) and biofilm present on the membrane surface which may cause a further decline of the membrane performance. Sometimes, an alkaline cleaning may restore this decline that was caused by the acid cleaner, but often an extreme cleaning will be necessary. An extreme cleaning is carried out at pH and temperature conditions that are outside the membrane manufacturer's guidelines or by using cleaning chemicals that are not compatible with the membrane elements. An extreme cleaning should only be carried out as a last resort as it can result in membrane damage.

   If the NF system suffers from colloidal, organic fouling or biofouling in combination with calcium carbonate, then a two- step cleaning program will be needed: alkaline cleaning followed by an acid cleaning. The acid cleaning may be performed when the alkaline cleaning has effectively removed the organic fouling, colloidal fouling and biofouling.

3. Always measure the pH during cleaning. If the pH increases more than 0.5 pH units during acid cleaning, more acid needs to be added. If the pH decreases more than 0.5 pH units during alkaline cleaning, more caustic needs to be added.

4. Long soak times. It is possible for the solution to be fully saturated and the foulants can precipitate back onto the membrane surface. In addition, the temperature will drop during this period, therefore the soaking becomes less effective. It is recommended to circulate the solution regularly in order to maintain the temperature (temperature should not drop more than 5°C) and add chemicals if the pH needs to be adjusted.

5. Turbid or strong colored cleaning solutions should be replaced. The cleaning is repeated with a fresh cleaning solution.

6. If the system has to be shutdown for more than 24 hours, the elements should be stored in 1% w/w sodium metabisulfite solution.

Cleaning Tips (cont.)

In addition to applying the correct cleaning sequence (alkaline cleaning step first), selecting the correct pH is very critical for optimum foulant removal. If foulant is not successfully removed, the membrane system performance will decline faster as it is easier for the foulant to deposit on the membrane surface area. The time between cleanings will become shorter, resulting in shorter membrane element life and higher operating and maintenance costs.

Most effective cleaning allows longer system operating time between cleanings and results in the lowest operating costs.

Cleaning Chemicals

Table 3 lists suitable cleaning chemicals. Acid cleaners and alkaline cleaners are the standard cleaning chemicals. The acid cleaners are used to remove inorganic precipitates including iron, while the alkaline cleaners are used to remove organic fouling including biological matter. Sulfuric acid should never be used for cleaning because of the risk of calcium sulfate precipitation. Permeate or deionized water should be used for the preparation of the cleaning solutions.

Table 3. Simple cleaning solutions for FILMTEC™ NF200/270 membrane

Cleaner Foulant	0.1% (W) NaOH and pH 11, 30°C max. or 1% (W) Na_4EDTA and pH 11, 30°C max.	0.1% (W) NaOH and pH 11, 30°C max. or 0.025 Na-DDS, pH 11, 30°C max.	0.1% STP and 1% Na_4EDTA or 0.1% TSP and 1% Na_4EDTA	0.1% (W) HCl	0.5% (W) H_3PO_4	2% (W) citric acid	0.2% (W) NH_2SO_3H	1% (W) $Na_2S_2O_4$
Inorganic salts (e.g. $CaCO_3$)				Preferred	Alternative	Alternative		Alternative
Sulfate scales ($CaSO_4$, $BaSO_4$)	Preferred	Alternative						
Metal oxides (e.g. iron)					Alternative	Alternative	Alternative	Preferred
Inorganic colloids (silt)		Preferred						
Silica	Alternative	Preferred						
Biofilms	Alternative	Preferred						
Organics	Alternative step 1	Preferred step 1	Preferred step 2					

Notes

1. (W) denotes weight percent of active ingredient.
2. Foulant chemical symbols in order used: $CaCO_3$ is calcium carbonate; $CaSO_4$ is calcium sulfate; $BaSO_4$ is barium sulfate.
3. Cleaning chemical symbols in order used: NaOH is sodium hydroxide; Na_4EDTA is the tetra-sodium salt of ethylene diamine tetraacetic acid and is available from The Dow Chemical Company under the trademark VERSENE™ 100 and VERSENE 220 crystals; Na-DDS is sodium salt of dodecylsulfate; STP is sodium triphosphate; TSP is trisodium phosphate; HCl is hydrochloric acid (Muriatic Acid); H_3PO_4 is phosphoric acid; NH_2SO_3H is sulfamic acid; $Na_2S_2O_4$ is sodium hydrosulfite.
4. For effective sulfate scale cleaning, the condition must be caught and treated early. Adding NaCl to the cleaning solution of NaOH and Na_4EDTA may help as sulfate solubility increases with increasing salinity. Successful cleaning of sulfate scales older than 1 week is doubtful.

Disinfecting NF Systems

If the plant has been infected by bacteria or mold, a disinfection must be carried out after the cleaning. The procedure is the same as for cleaning, except that the high flow pumping step can be skipped.

Hydrogen peroxide or **hydrogen peroxide/peracetic acid** solutions can be used at concentrations up to 0.2%. The biocidal efficacy of peracetic acid is much higher than that of hydrogen peroxide, but as most peracetic acid solutions also contain hydrogen peroxide, care must be exercised not to exceed the 0.2% concentration as a sum of both compounds. Continuous exposure at this concentration may eventually damage the membrane. Instead, periodic use is recommended.

Disinfecting NF Systems (cont.)

When hydrogen peroxide is applied, **the pH of the solution must be lower than 4.** A pH of 3 is recommended. This will ensure optimal biocidal results and longer membrane lifetime. If no acid is added to the hydrogen peroxide solution, the chemical attack on the membrane will be much faster. When a mixture with peracetic acid is used, pH adjustment is usually not required.

If an alkaline cleaning has preceded disinfection, the alkalinity has to be carefully rinsed out also from the permeate side (check pH!) before peroxide/peracetic acid is applied. Otherwise, the membrane might become oxidized.

Two other factors greatly influence the rate of hydrogen peroxide attack on the membrane: temperature and iron.

The disinfecting solution must not exceed 25°C (77°F). FILMTEC™ NF200/NF270 membrane samples tested with 0.5% hydrogen peroxide at 34°C (93°F) showed a very high salt passage after several hours. At 24°C (75°F) however, membrane samples demonstrated compatibility with 0.5% hydrogen peroxide after 96 hours.

Iron or other transition metals must not be present, because they catalyze membrane degradation in the presence of hydrogen peroxide solutions. NF200/NF270 samples were tested using a 0.15% solution of hydrogen peroxide and tap water containing iron. After 150 hours, the salt passage of the membrane began to increase dramatically.

For NF200/NF270 membrane systems, Dow recommends the following procedure for disinfection with hydrogen peroxide solutions:

1. Any type of deposit on the membrane or other parts of the system should be removed with an alkaline cleaner before disinfecting. Removal of these deposits, which harbor microorganisms, will maximize the degree of disinfection. After alkaline cleaning, flush the system with NF permeate.
2. Clean the NF system with acid, e.g. 0.1% by volume hydrochloric acid or 0.4% by volume phosphoric acid, to remove any iron from the membrane surface. Flush the unit with NF permeate.
3. Circulate a solution of 0.2% hydrogen peroxide (preferably containing peracetic acid) diluted with NF permeate and pH adjusted to 3-4 with HCl at a temperature below 25°C (77°F) for 20 minutes.
4. Flush out the disinfecting solution. Rinse the system.
5. Allow the elements to soak in the disinfecting solution for 2 hours.
6. Flush out the disinfecting solution. Rinse the system.

Other disinfectants iodine, quaternary germicides and phenolic compounds cause flux losses and are not recommended for use as disinfectants.

70% ethanol can be used for disinfection. **Brand name biocides** have also been tested for effects on the membrane performance. There are fully compatible and limited compatible biocides.

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

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