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Relationship between biofilm removal and membrane performance using Dunedin reverse osmosis water treatment plant as a case study

Joshua E. Goldman
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Relationship between Biofilm Removal and Membrane Performance using Dunedin Reverse Osmosis Water Treatment Plant as a Case Study

by

Joshua E. Goldman

A thesis submitted in partial fulfillment of the requirements for the degree of Master of Science Department of Environmental Science and Policy College of Arts and Sciences University of South Florida

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Date of Approval: July 11, 2007

Keywords: spiral wound membrane, polyamide membrane, membrane autopsy, membrane cleaning, membrane fouling

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Relationship between Biofilm Removal and Membrane Performance using Dunedin Reverse Osmosis Water Treatment Plant, as a Case Study

Joshua E. Goldman

ABSTRACT

Membrane biofouling is a common occurrence in water treatment plants that utilize reverse osmosis (RO). As bacteria and biofilm material build up on the membrane surface, it becomes more difficult for clean water to permeate through the membrane, and more pressure is required to produce the same amount of water. When pressures become critically high, membranes must be cleaned. This process is expensive in terms of chemical cost, labor, and downtime. Even after membranes have been cleaned, they can re-foul quickly if the cleaning did not effectively remove the biofilm.

The water treatment plant in Dunedin, FL, which uses RO for treating groundwater, has experienced membrane biofouling since it began operation in 1992. Without the means to systematically evaluate a multitude of cleaning strategies on the bench scale, cleaning optimization must be conducted on the production skid level, which restricts the evaluation of alternative protocols. This problem is typical for many RO plants. The objectives of this project are: (1) using a multi-level and systematic approach, develop cleaning strategies for biofouled membranes that will lead to improved cleaning and decreased operational costs; (2) develop other cleaning strategies that will add to the scientific knowledge base; (3) quantify the effects of improved protocols; and (4) determine the policy implications of
developed protocols in terms of cost suitability to Dunedin and elsewhere in Florida.

This project consists of three phases, with phases progressively more similar to the water production environment. In the first phase, a series of bench tests were performed in the laboratory. Fouled membrane swatches were soaked and agitated in different cleaning solutions for different lengths of time, at different temperatures and pH. Protein and carbohydrate assays were then performed on both the cleaning solution and the membrane swatch to determine which conditions yield most complete removal of protein and carbohydrate from the membrane surface. Results indicate that carbohydrate removal does not appear to depend strongly on pH or temperature. Protein removal increases with increasing pH and is slightly greater at higher temperatures.

The second phase of testing employed a 4”x6” stainless steel flat-sheet module in which cleanings were performed under different conditions to document corresponding changes in water flux and salt rejection. Operational parameters were based on pertinent literature and optimization results from Phase 1. Results indicate that water flux increases in response to cleaning at increasing pHs and increasing temperatures with best performances occurring after 30 minutes of cleaning. Salt rejection appears to decrease with pH. The most effective cleaning protocols, determined through trials in Phases 1 and 2, were put to the test again in Phase 3 where cleanings were performed on a specially constructed single-element cleaning system (for 8.5” x 40” elements), designed to clean a membrane element in isolation. This phase also served as final verification of new cleaning protocols before implementation on the production scale. Results from this phase were inconclusive due to mechanical problems.
A multi-level, systematic cleaning evaluation leads to better understanding of the dependence of biofilm material removal and membrane performance on critical factors such as temperature, pH, time of cleaning, and chemical dose, which results in improved cleaning protocols and ultimately cost savings to RO water utilities such as Dunedin.
1. Introduction

Reverse osmosis technology for drinking water production has gained considerable attention in the past decade due to increased freshwater scarcity (AWWA et al., 1996). Reverse osmosis membranes remove salts, allowing utilities to use hard water, brackish water, or seawater to produce potable water. Reverse osmosis membranes can also remove dissolved organic compounds which are potential precursors to chlorine disinfection byproducts such as trihalomethanes or haloacetic acids.

Membrane technology for producing potable water is in use worldwide, mostly in places where water scarcity is an issue, such as the Middle East and the Southwestern United States. Since the energy required to generate high pressure is expensive, membrane technology is mostly limited to richer areas of the world. Membrane softening is used widely in Florida (AWWA et al., 1996).

The City of Dunedin, in West Central Florida, built a reverse osmosis water treatment plant in 1992 (see Figure 1). Since that time, biofouling has increased operational costs by necessitating frequent skid cleanings and membrane autopsies to determine the cause of reduced productivity. Biofouling is the buildup of a bacterial layer on the membrane surface. Skid cleanings can be expensive due to the high cost of cleaning, skid downtime, and hourly labor. Autopsies can vary in cost from $2500 to $5000, depending on the type of analyses required. If cleaning methods can be improved so
that less frequent cleaning is required, operational costs could be significantly reduced.

Federal and state policies regulate the substances that can be safely used for the treatment of drinking water. This is a constraint in developing improved cleaning strategies for Dunedin. According to regulations in the state of Florida, membrane cleaning chemicals must be certified by NSF International, The Public Health and Safety Company™, under Standard 60: Drinking Water Treatment Chemicals.
Most of the certified cleaning chemicals are proprietary products developed by chemical companies like Dow, or by membrane manufacturing companies like Koch. This limits the number of choices of substances that can currently be used to clean membranes in Dunedin. However, testing with substances that are not NSF 60 approved will add to the set of scientific knowledge that may eventually lead to new formulas being approved.

1.1 Objectives

The objectives of this project are as follows:

1) Using a multi-level and systematic approach, develop cleaning strategies for biofouled membranes that will lead to improved cleaning and decreased operational costs;

2) To develop other cleaning strategies that will add to the scientific knowledge base;

3) To quantify the effects of improved protocols; and

4) To determine the policy implications of developed protocols in terms of cost suitability to Dunedin and elsewhere in Florida.
1.2 Dunedin Reverse Osmosis Water Treatment Plant

The city of Dunedin’s water treatment plants treats fresh groundwater from their local well field. All of the City’s wells draw water from the Surficial Aquifer. The water treatment plant consists of four reverse osmosis skids. The reverse osmosis process is completed in two stages. In the first stage, feed water passes through 26 first stage pressure vessels in the skid and is separated into permeate and concentrate. The concentrate from the first stage then passes through 13 second stage pressure vessels. Each pressure vessel accommodates 7 membrane elements. During the two stage process, 75% of the feed water is converted into potable water; 50% in the first stage and another 50% in the second stage.

Currently, each skid is cleaned approximately once every 3-4 months. The current cleaning protocol consists of forward and reverse flushes, salt solution soaks, and exposure to high and low pH solutions. The total time required to clean both stages can exceed five days. Table 1 describes the current protocol in detail.
Table 1: Details of the Current Cleaning Protocol at Dunedin (from 10/17/06)

<table>
<thead>
<tr>
<th>Skid Cleaning</th>
<th>Type</th>
<th>Direction</th>
<th>pH</th>
<th>Temp</th>
<th>Flowrate (L/min)</th>
<th>Pressure (psi)</th>
<th>Time (hr)</th>
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<td></td>
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<td>Reverse</td>
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<td>10.91</td>
<td>25</td>
<td>3400</td>
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<tr>
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<td>Flush</td>
<td>Reverse</td>
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<td>20-32</td>
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<td>20-32</td>
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<tr>
<td>9 hr Forward Flush</td>
<td>Flush</td>
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<td>10.5-11</td>
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<td>10.5-11</td>
<td>20-32</td>
<td>1360-1820</td>
<td>42-56</td>
<td>9</td>
</tr>
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<td>Flush</td>
<td>Reverse</td>
<td>Perm</td>
<td>Perm</td>
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<td>Flush</td>
<td>Reverse</td>
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<td>Perm</td>
<td>Perm</td>
<td>3400</td>
<td>30</td>
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Total Time (hr) 86
2. Literature Review

2.1 Background

Reverse osmosis membranes are at the extreme end of the membrane filtration spectrum (see Figure 2). They can remove dissolved materials from water as small .001 microns and 100 AMUs. They are made of semi-permeable that allows water molecules to pass through but rejects most dissolved salts and organics. The process of reverse osmosis can be compared to osmosis, during which water diffuses through a membrane, moving from an area of low salt concentration to an area of high salt concentration until the concentrations on both sides of the membrane are at equilibrium. The pressure required to stop the diffusion of water during osmosis is called osmotic pressure. During reverse osmosis, pressure exceeding the osmotic pressure is applied to the high concentration side of the membrane, forcing the water through the membrane to the low concentration side. The result is that the high concentration side becomes even more concentrated and the low concentration side becomes even more diluted.

The water that permeates through the membrane from the concentrated side is called permeate. The water high concentration water that remains on the high pressure side is called concentrate. The amount of pressure required to move water through the membrane during reverse osmosis is dependent upon the salt concentration of the source water. The more salty the source water,
the more pressure is required to further concentrate it. Typical operating pressure required for removing hardness ranges from 55-125 psi. Brackish water requires operation ranging from 150 to 600 psi, and seawater can require up to 1000 psi (McClellan, 2006). The relationship between osmotic pressure, concentration, and temperature is described by Van’t Hoff’s equation:
\[ \pi = \Phi C \eta NC_s RT \]  

(2.1)

where \( n \) is the osmotic pressure, \( \Phi \) is the osmotic pressure coefficient, \( N \) is the number of ions in solution, \( C_s \) is the solution concentration, \( R \) is the universal gas constant, and \( T \) is the temperature. Table 2 illustrates some general rules relating salt concentration to osmotic pressure.

**Table 2: Osmotic Pressure of Water Containing Dissolved Solids**

<table>
<thead>
<tr>
<th>TDS (mg/L)</th>
<th>Osmotic Pressure (psi)</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>1</td>
</tr>
<tr>
<td>1,000</td>
<td>10</td>
</tr>
<tr>
<td>35,000</td>
<td>350</td>
</tr>
</tbody>
</table>

Adapted from McClellan (2006)

Reverse osmosis membrane used for water treatment are usually sold as spiral wound elements (see Figure 3). This structure allows for a lot of surface area to be housed in a small package. Several elements are placed in a row, inside a long tube called a pressure vessel. Separation occurs as feedwater flows from the feed end of the element, through the permeate spacer. Clean water permeates through the membrane and collects in the permeate spacer, which is glued on three sides. This causes the water to be pushed towards the center collection tube. Water flows through the tube from one element to the next until it reaches the end of the pressure vessel and is collected for use.
Reverse osmosis membranes are generally divided into two categories, based on the type of material from which they are made. Membranes made from cellulose acetate (CA) were first developed in the 1960’s. These membranes have a relatively smooth surface and are not adversely affected for oxidizing chemicals. CA membranes can be irreversibly damaged by biofouling. CA membranes are more expensive to use because they require acidification to minimize hydrolysis a higher net driving pressure than PA membranes. These requirements can results in high chemical and energy costs compared to PA membranes. These limitations have resulted in their replacement by polyamide (PA) membranes over the 1990’s (Tricep, n.d.).

Polyamide membranes are a newer technology in use currently by most water treatment plants, including Dunedin’s water treatment plant. PA membranes are made by forming a thin PA film on the finely
porous surface of a polysulfone supporting membrane by an interfacial reaction between the reactant pair trimesoyl chloride and m-phenylenediamine. Although there are significant advantages to PA membranes over cellulose acetate membranes in terms of operations cost and performance, there are several characteristics of PA membranes that make them more susceptible to biofouling including an intolerance to oxidants such as chlorine, a high degree of surface roughness, and a more a hydrophobic surface (SST and OCWD, 2000).

2.2 Membrane Biofouling

Membrane fouling generally falls into four categories: inorganic fouling, organic fouling, colloid fouling, and biological fouling. Biological fouling is commonly referred to as biofouling. The first three types are more easily controlled because they can be mitigated by limiting the amount of foulant in the feed water (Flemming, 2002). Biofouling is more difficult to control because even if almost all of the bacteria in the feedwater are inactivated or removed during pre-treatment, a few surviving bacteria can re-colonize a membrane surface very quickly by living off any biodegradable material, including dead bacteria (Flemming, 2002). Bacterial aggregates that have attached to a surface are generally referred to as “biofilms”, a term that describes both the bacteria and the organic macromolecules (polysaccharides, proteins, nucleic acids, and other polymeric compounds) that provide habitat, protection, and cohesive forces to the bacterial community (Flemming & Wingender, 2001). Because bacteria grow and reproduce, biofilm accumulates geometrically over time while other types of foulants grow arithmetically over time (AWWA et al., 1996).
Bacterial adhesion onto surfaces in water systems is a common occurrence in a multitude of natural and engineered environments (Flemming & Wingender, 2001a). In fact, 99% of the microorganisms on Earth reside in biofilms. They are an extremely successful adaptation, allowing bacteria to survive high amounts of biocide, perhaps two to three times the amount that would be lethal to suspended cells (Flemming, 2002).

Biofouling does not affect all areas of the membrane equally. Fouling is much more prevalent on the feed side of the membrane envelope (including spacer) than the product side. This is because most membranes effectively filter out the bulk of bacteria and the organic matter that they use as food. Biofouling also tends to affect the first membrane element in a pressure vessel more intensely than the others (Sagiv & Semiat, 2005).

Membrane biofouling causes several systemic problems including loss of permeate flux, decrease in salt rejection, increase in differential pressure, changes in pore size distribution (PSD), and irreversible membrane damage. Differential pressure is the difference between feed pressure and concentrate pressure. Permeate flux through a fouled membrane is described by the equation:

\[ J = \frac{\Delta p - \sigma_k \Delta \pi}{\mu \left( R_m(t) + R_c(\delta_c(t)) + \ldots + R_{cp}(D,J) \right)} \]  

(1.2)

where \( J \) is permeate flux, \( \delta_c \) is the thickness of the cake (or gel) layer, and \( D \) is the diffusivity of the material in the concentration polarization layer. The terms, \( R \), represents resistance of different material. \( R_m \) is membrane resistance, \( R_c \) is resistance due to the cake layer, and \( R_{cp} \) is resistance due to concentration polarization. Other resistance terms
can be added as needed. \( \mu \) is the absolute viscosity of the water, \( \Delta p \) is the pressure differential across the membrane surface, and \( \sigma_k \) is an empirical constant. As the thickness of the foulant layer increases, resistance increases, and overall flux decreases (AWWA et al., 1996).

Biofilm is responsible for the loss of permeate flux for a few reasons. First, particulates can physically clog membrane pores, leaving less space for water to pass through. Second, a layer of biofilm can cause significant resistance compared to other types of foulant layers because of the gel-like structure of the macromolecules. In many water treatment facilities, systems are configured to produce a steady amount of permeate over time. As a consequence, feed pressure must be increased over time to maintain flux. The effects of biofouling tend to be more apparent in water treatment facilities that treat more than 1 million gallons per day (MGD) because electrical costs associated with pumping are so high (AWWA et al, 1996). The good news is that most of the loss of flux caused by biofouling is most likely due to transport impedance rather than any changes to the membrane itself. Therefore, effective cleaning may be able to restore membrane performance. However, EPS (extra-cellular polymeric substances) excreted by bacteria in the biofilm can cause some damaging chemical changes to membrane itself (AWWA et al., 1996). Another consequence of biofouling is loss in salt rejection. This occurs because the biofilm reduces turbulent mixing at the boundary layer, increasing the accumulation of solutes near the boundary layer, a phenomenon called concentration polarization. Increasing concentration polarization causes an increase in mass transport, due to increased diffusion gradient (AWWA et al., 1996). It has also been shown by Kosutic & Kunst (2002), that biofouling can cause irreversible changes to the PSD of a membrane if cleaning is not done in a timely manner.
Studies show that irreversible damage can occur after only 200 hours after uninterrupted service. Normal pore size in reverse osmosis membrane ranges from 1.2 nm to 1 nm. Over time, in response to biofouling, the fraction of tight pores decreases while the fraction of wide pores increases. This is undesirable because tight pores more effectively filter water. In addition, EPS can cause new, aggregate pores to form (Kosutic & Kunst, 2002). Lastly, biofouling can cause irreversible damage to the membrane. Ridgway (1988) and Sinclair (1982) demonstrated biodegradation of cellulose acetate membranes, but this type of membrane is in declining use as most facilities have moved to TFC (thin film composite) membrane over the last 15 years. There has not been any direct evidence of biodegradation of TFC membranes, but the potential exists because these types of membranes contain aromatic ring and amide bond structures that contain nitrogen and carbon, substances that can potentially be degraded by bacteria (AWWA et al., 1996).

The only way to observe the surface of a spiral wound reverse osmosis membrane is to cut it out of its fiberglass shell. This process is called a membrane autopsy. According to a review of 150 membrane autopsies by scientists at Permacare, a division of Nalco, biofouling was the most frequently observed problem (Darton & Fazel, 2002). According to a survey of 78 reverse osmosis membranes done by Liu et al. (1991), 83% of the facilities surveyed had “above average” problems with biofouling (AWWA et al., 1996). Biofouling is clearly one of the most significant problems experienced by reverse osmosis water treatment facilities. When such a high percentage of membrane are shown to have “above average” levels of biofouling, one must question the validity of the average. Nevertheless, membrane biofouling is a widespread problem.
Biofilm formation is preceded by the adsorption of organic materials to the membrane surface (Al-Ahmad et al., 2000). This process changes the surface chemistry of the membrane, increasing the potential for bacterial adhesion. Bacterial adhesion occurs in two stages, primary and secondary. Primary adhesion is controlled by the physicochemical nature of the surface of the bacterial cell. Bacterial cells are initially attracted to the membrane surface by Brownian motion (diffusion), gravitational settling, convective transport, or independent motility (e.g. flagella) (AWWA et al., 1996) The Derjaguin-Landau-Verwey-Overbeek (DVLO) theory describes the attraction or repulsion of a particle to a surface as the sum of the double layer forces and the van der Waals forces (Splendiani et al., 2006). This theory is often used to simply describe foulant-foulant and membrane-foulant interactions.

The electrical double layer forces are related to the charge on the surface of the membrane and to the charge on the surface of the particle. Due to their chemical structure, bacteria typically have a negatively charged surface (Liikanen, et al., 2002). In an aqueous system, the surface of negatively charged particles will be surrounded by a layer of positively charged ions. A layer of negatively charged ions will surround the positively charged ions in another concentric layer, and so on until the particle is effectively neutralized. The electrical potential at the outermost layer of ions is termed the zeta potential. When the zeta potential is high (positive or negative), van der Waals forces are overcome, and particles are repelled from each other and from similarly charged surfaces. As the zeta potential approaches zero, the system becomes unstable. Van der Waals forces dominate and particles aggregate and attach to surfaces (Malvern Instruments, 2001).
Two important factors in reverse osmosis systems that influence zeta potential are ionic strength and pH. As salt concentration increases in the aqueous medium, the electrical double layer is compressed. This decreases zeta potential, and particles come in closer proximity to each other, where van der Waals forces dominate. Zeta potential is also affected by pH. At high or low pH levels, particles will tend to acquire a negative or positive charge, respectively. At some middle pH level, the particles will tend to acquire a neutral charge, and the system will become unstable. Membrane surface charge will also change based upon the pH of the electrolyte solution flowing through it or across it. When the solution is at a pH between 5.8 and 6.3, a normal range for drinking water production, a polyamide, thin-film membrane will carry a slightly negative charge (Childress & Elimelech, 1996). As the pH of the solution increases, the membrane will acquire a more intensely negative charge. At lower pH levels, membranes acquire a positive charge (Childress & Elimelech, 1996). Both the pH and conductivity of the feedwater have a significant effect on the stability of a system.

Another important chemical factor to consider is the hydrophobicity of the membrane surface. Thermodynamic theory explains why there is increased sorption of bacteria onto hydrophobic surfaces. Essentially, it takes less energy for bacteria to adhere to hydrophobic surfaces than to hydrophilic surfaces and more energy for them to detach. This is due to chemical and physical forces governing the free energy of adhesion to these surfaces (Pedri et al., 2004). Bacteria preferentially adhere to hydrophobic surfaces, including polyamide reverse osmosis membranes. Hydrophobic components of bacteria, such as flagella or pili, can easily displace water from the membrane surface, increasing adhesion potential (Splendiani et al.,
Finally, the last important chemical factor that controls primary adhesion is “salt bridging” by divalent cations. Commonly present divalent cations, such as calcium and magnesium can promote adhesion by connecting to the membrane surface and then attracting negatively charged bacteria that would otherwise be repelled (Liu et al., 1997).

While the chemical attributes of the system are very important in understanding primary adhesion, certain physical components are also significant. One such factor is the independent motility potential of the bacteria. If the chemical attributes of a system are such that bacteria are allowed to come close to a membrane surface, then bacteria use structures such as flagella or cilia to overcome any electrostatic repulsion between the bacterial surface and the membrane surface (Splendiani et al., 2006).

Another physical factor is membrane surface roughness. If all other factors are equal, the degree of biofouling on membrane surface is positively correlated with the degree of roughness of a membrane surface. Surface roughness contributes to membrane biofouling in two ways. Firstly, it increases the surface area of the membrane, so there is more space for bacteria to attach and grow. Secondly, surface roughness produces tangential colloidal forces that immobilize colloids or particles acting as colloids, attracting them to the membrane surface (Elimelech et al., 1997). Investigations through atomic force microscopy (AFM) have shown that the surface of polyamide membranes is rougher than that of cellulose acetate membranes (Elimelech et al. 1997).

Once bacteria have successfully attached to a membrane surface, they will begin to grow and multiply at a rate which is the function of the amount of biodegradable material in the feedwater
(AWWA, et al., 1996). At this stage, the bacterial attachment is still reversible though mild fluid shear or change in chemical conditions (AWWA et al., 1996). However, soon after primary adhesion and initial growth, bacteria begin to emit extra-cellular polymeric substances (EPS) (Flemming, 1997). EPS can significantly change the surface properties of a membrane, promoting further bacterial growth and attachment. *Secondary adhesion* occurs when bacteria adhere to a surface that has already been coated with EPS.

The structure of EPS changes according to the nature of the bacterial colony with which it is associated. However, in all cases EPS consist mainly of polysaccharides, proteins, nucleic acids, and lipids (Flemming & Wingender, 2001a). Table 3 illustrates the relative concentrations of each substance in biofilms. The polysaccharide category of EPS generally consists of glucose, fucose, mannose, glucose, fructose, pyruvate, and mannuronic or glucoronic acid-base complexes (Johansen et al., 1997).

<table>
<thead>
<tr>
<th>Component</th>
<th>Content in EPS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polysaccharides</td>
<td>40-95%</td>
</tr>
<tr>
<td>Protein</td>
<td>&lt;1-60%</td>
</tr>
<tr>
<td>Nucleic Acids</td>
<td>&lt;1-10%</td>
</tr>
<tr>
<td>Lipids</td>
<td>&lt;1-40%</td>
</tr>
</tbody>
</table>

Table 3: Composition of EPS and range of component concentration

EPS have several functions. Firstly, as the main component of most biofilms, they act to greatly enhance structural integrity (Flemming & Wingender, 2001a). The biofilm matrix is extremely stable. Part of the reason for this is that there are three different types of forces that contribute to its adhesiveness: electrostatic interactions, hydrogen bonds, and London dispersion forces (Flemming...
Under different conditions, each of these becomes important. Biofilm behaves as a gel as long as the shear forces remain below a certain level. Above that level, it behaves as a highly viscous liquid (Flemming & Wingender, 2001a). Because biofilms are highly adhesive and elastic, they can be very difficult to remove from surfaces using shear force. The presence of divalent cations, especially calcium, has been shown to significantly increase the strength of biofilms by forming “salt bridges” (Flemming & Wingender, 2001a).

The second function of EPS is to act as an ecological habitat for bacteria. One essential part of this function is the way EPS condition the membrane surface. In coating the membrane surface, EPS reduce repulsive forces between the membrane surface and the bacteria (Flemming, 2002). Bacteria will attach at a much faster rate to a surface that has been coated with biofilm. Once bacteria are attached, the biofilm allows the bacteria to stay in one place over a relatively long period of time, and synergistic relationships can develop among inhabitants (Flemming & Wingender, 2001a). Particles in the water can adhere to the biofilm, or dissolved organics can be sorbed to its surface, providing nutrients to the inhabitants of the biofilms. It has also been shown that bacteria in biofilms are much less susceptible to biocides than suspended bacteria. EPS react with and consume oxidizing agents before they reach the bacteria (Flemming & Wingender, 2001b). Biofilms are particularly protective against free chlorine opposed to chloramines. This is most likely due to transport limiting factors (LeChevallier, et al., 1988). EPS also retain water, protecting against dessication if water becomes scarce (Flemming, 2002). In these ways, biofilms nurture and protect bacteria, encouraging survival and growth.
2.3 Cleaning Strategies: Physical and Chemical

In most cases, membrane performance can be improved by effective cleaning (Darton & Fazel, 2002). However, cleaning can be expensive and may cause damage to the membrane over time. On average, facilities employing membranes spend 5-20% of their operating budget on membrane cleaning (Madaeni et al., 2001). Repeated cleanings with NaOH, in particular, can cause membrane damage over time (Darton & Fazel, 2002).

Membrane cleaning is a complicated process because the fundamental mechanisms of fouling are very complex (Kosutic & Kunst, 2002). Knowledge about the particular membrane foulants present, most effectively gained through a destructive autopsy, is the most helpful in selecting a chemical cleaning protocol. Results from our membrane autopsy are presented in the next section.

Effective membrane cleanings that target biofilm should consist of three processes: retarding growth, minimizing binding energies, and chelating metals (Carnahan et al, 1995). There are several different categories of chemicals that are generally considered in membrane cleaning. The most common categories include high pH chemicals, low pH chemicals, surfactants, enzymes, and chelating agents. Commercial cleaners often contain mixtures of several of these chemical categories, but exact concentrations are not released due their proprietary nature (Ang et al., 2006). Therefore, when cleaning studies are performed using proprietary chemicals, it can be difficult to relate the results to cleaning mechanisms because exact proportions of ingredients are not known. Biocides are less common in membrane cleaning as opposed to use in cleaning other parts of a drinking water
system because biocides usually contain oxidizing agents to which most membranes are extremely sensitive.

High pH chemicals are effective because they increase the surface charge and zeta potential at bacterial surfaces. This, in turn, increases electrostatic repulsion between the membrane surface and the suspended bacteria and can increase “solubility” of bacteria by up to three orders of magnitude (Ang et al., 2006). In addition, high pH solutions create electrostatic repulsion between active sites on the membrane surface, effectively opening it up (Liikanen et al, 2002). NaOH is a very common choice in this category, especially in Florida, because is included in the list of chemicals approved for use in drinking water systems.

Low pH chemicals are commonly used to clean membranes that have been fouled with inorganic matter. Most inorganic foulants have increased solubility at low pH conditions. As is the case with NaOH, citric acid is a common choice in Florida because it is on the list of chemicals approved for use in drinking water systems.

Both high and low pH cleanings may act as a biocide to pH sensitive bacteria. Soaking in a concentrated NaCl (1 M) solution can also cause bacterial death to bacteria specifically adapted to freshwater conditions (Ang et al., 2006). However, bacterial death does not necessarily cause biofilm removal.

Surfactants are in wide use as an experimental method for removal of biofilms, due to their detergent action. They are also ingredients in several proprietary chemical products, made for use in industrial or municipal applications. Surfactants are surface-active agents that work at the liquid-solid interface. These molecules contain both a hydrophilic and a hydrophobic portion (Liu et al, 2007). The addition of surfactants to a chemical protocol produces several effects.
Above a certain concentration, surfactant molecules surround bacteria and organic particles, forming micelles that help to move normally insoluble material into a semi-liquid phase (Ang et al., 2006). Surfactants also align their hydrophobic portion with the membrane surface and orient their hydrophilic portion into the aqueous phase, effectively decreasing hydrophobic interactions between the membrane surface and suspended bacteria (Ang et al., 2006). Lastly, they can help increase the negative charge associated with the bacterial surface, increasing the effect of electrostatic repulsion (Splendiani et al., 2006). Sodium dodecyl sulfate (SDS) is believed to be the most common surfactant used in proprietary cleaning chemicals (Ang et al., 2006).

Another class of chemicals commonly used for cleaning is enzymes. Enzymes are biological molecules designed to break down carbohydrates for digestion. Enzymes can break down the polysaccharide component of EPS, significantly weakening the biofilm matrix. Because the proportions of different polysaccharides in a particular biofilm are not generally known, a combination of enzymes is usually more effective (Johansen et al., 1997). Although combined enzyme solutions are available from major chemical companies, they tend to be expensive and more difficult to handle than other cleaning chemicals, so their use has been limited (Johansen et al., 1997).

Chelating agents have been used in membrane cleaning to remove scaling because they dissolve precipitates and complex with metals (Ang et al., 2006). They may also be useful in removing biofilm if it has been strengthened with divalent cations such as calcium. Chelating agents, such as EDTA, complex with divalent cations and remove them from the biofilm, destroying “salt bridges” and weakening the biofilm structure (Hong & Elimelech, 1997).
There are many chemical and physical variables to consider in the cleaning process, so it has been difficult to relate results to a single variable or even multiple variables in past attempts at cleaning optimization. A study by Chen et al. (2003), employing fractional factorial analysis, concluded that the most significant physical factors were: the pressure during forward flush, the duration of backwash, the production interval between physical cleaning, and the interaction between the latter two factors. The study showed that the most important chemical factors were: the concentration of high pH cleaning solution, the temperature of high pH cleaning solution, and whether a forward flush or a backwash was done after chemical cleaning. The most significant interaction was between the temperature and the pressure of the high pH cleaning solution. The results of that study can serve as a guide toward optimization. However, that study used only one type of cleaning chemical, so it did not investigate the effect of changing the chemical cleaning solution.

Several other studies have also been conducted to compare the effectiveness of cleaning chemicals and to optimize their effectiveness by varying chemical and physical parameters. However, these studies have mostly concentrated on membranes in which the primary fouling agent was natural organic matter (NOM). These studies are still important to consider because membranes fouled by NOM are most likely biofouled, as well (Ang, et al. 2006). Chemical and physical parameters studied by Ang et al. (2006) included chemical type, dose/concentration, pH, time, crossflow velocity, temperature, and pressure. Overall results indicate that chemical parameters have a greater effect than physical parameters and that they should be optimized first. Specifically, efficiency almost always increased with chemical concentration and dose. However, dose mattered with some
chemicals more than others. Surfactants were only effective at concentrations near or equal to the critical micelle concentration (CMC). For SDS, this happens between 5 and 8 mM. The effectiveness of EDTA varied with concentration but was most effective at 2 mM. The effect of time was only important when dose was optimized. In these cases, time increased effectiveness for up to an hour, after which it was no longer important. The effect of crossflow velocity was very similar, but it had even less impact on effectiveness than time. The effect of temperature was rather dramatic. This is because increased temperature increased the rate of reaction and the transport rate between the chemical and the organic material. In addition, increased temperature can cause the biofilm to swell, decreasing its structural integrity (Ang et al., 2006). A study conducted by Li and Elimelech (2004), which employed atomic force microscopy to measure membrane adhesion, concluded that the chemical cleaning of membranes fouled by NOM is only effective when salt bridging is first eliminated by chelating agents.

The study described in this thesis aimed to optimize the cleaning process for the City of Dunedin using the guiding principles gleaned from the literature. In addition, the removal of protein and carbohydrates, the main components of biofilm, were quantified by the application of high and low pH cleanings. The next section contains a description the methodology developed to address these issues.
3. Materials and Methods

3.1 Overview

Prior to experimentation, a professional membrane autopsy was performed by researchers at the Orange County Water District. Another membrane autopsy was subsequently performed at USF. These autopsies provided baseline data regarding the extent and type of membrane biofouling. Specific details are discussed in this section. Results are discussed in the next section.

The experimental methodology consisted of three phases. In Phase 1, laboratory bench tests were performed to measure the effects of cleaning temperature, time of cleaning, and cleaning pH on protein and carbohydrate removal. In Phase 2, the performance of cleaned membrane was measured in a flatsheet module (FSM). Data gathered in these two phases were combined to optimize several cleaning parameters including pH, temperature, and time. Because these methods required only small swatches of membrane rather than entire membrane elements, several tests were able to be performed in a short time. Optimized cleanings were performed on a single element cleaning system (SECS) in Phase 3. Data from all phases were considered in the determination of the most effective cleaning protocols. During Phases 1 and 2, laboratory analyses of the cleaned membranes were performed in order to gather further information regarding effectiveness and mechanisms of the cleanings. These analyses include visual analysis of Scanning Electron Microscope (SEM) images and protein and carbohydrate assays.
3.2 Membrane Material

Thin Film Composite (TFC) reverse osmosis membrane produced by Koch Membrane Systems was used in the following experiments. Detailed specifications for model number 9921-S can found in Appendix 4. Fouled membranes came directly from Dunedin’s reverse osmosis skid and virgin membrane material was donated by Koch Membrane Systems.

3.2 Membrane Autopsy

A membrane autopsy was performed in August of 2006, to provide baseline fouling data. The purpose of the autopsy was to describe the type of fouling experienced by Dunedin’s membranes and to quantify the amount of foulant present. MicroMemAnalytical, Inc., a division of the Orange County Water District of Orange County, CA, was selected to perform the autopsy and to train us on autopsy techniques.

A membrane element was removed from the feed end of pressure vessel number 9 from Dunedin’s Skid 4. It was packed in ice and shipped to Micromem Analytical, located in Fountain Valley, CA. Upon arrival at Micromem Analytical, the membrane was unpacked and placed on a table. A circular saw (see Figure 4) was used to cut the endcaps off the membrane and to cut a line in the fiberglass casing, so it could be removed.
After the fiberglass casing was removed from the membrane, it was brought into the lab for further analysis. First, photographs were taken of the membrane surface (see Figure 5). Then, a razor blade was used to scrape biofilm material from the surface of the membrane. Scrapes were taken from the feed, middle, and end of the sheet.

The biofilm from each scrape was weighed and normalized to the area from which it was taken. Protein and carbohydrate assays (the procedures are described in Appendix 1) were performed on membrane swatches cut from each section of the membrane. Membrane swatches were also examined with a light microscope. Additional samples were dried for use in the ATR-FTIR. Spectra were taken for each membrane area. Other analyses performed include: total bacteria count, microbial community profile, and atomic force microscopy. Procedures are described in Appendix 2, and results are discussed in the next section.
3.3 *Phase 1: Laboratory Bench Tests*

The goal for the first experimental phase was to quantify the effects of pH, temperature, and time on protein and carbohydrate removal. Laboratory bench tests were performed in the laboratory at USF by me, Russell Ferlita, a fellow graduate student, and Michael Keen, an undergraduate research assistant for Dr. Daniel Yeh. These tests were designed to measure the relative removal of protein and carbohydrate from a membrane swatch by different cleaning solutions, under different conditions. Six bench tests were performed, in total. Experimental design for each test is illustrated in Table 4.

**Table 4: Bench Test Parameters**

<table>
<thead>
<tr>
<th>Test Date</th>
<th>Cleaning Time (min)</th>
<th>pH range</th>
<th>Temp (°C)</th>
<th>Chemicals Used</th>
<th>Time Sonicated (min)</th>
<th>Cleaning Solution Volume (mL)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3-11-07</td>
<td>30</td>
<td>2.5-11</td>
<td>25</td>
<td>NaOH/Citric Acid</td>
<td>20</td>
<td>20</td>
</tr>
<tr>
<td>3-24-07</td>
<td>30</td>
<td>2.5-11</td>
<td>25</td>
<td>NaOH/Citric Acid</td>
<td>30</td>
<td>15</td>
</tr>
<tr>
<td>4-16-07</td>
<td>60</td>
<td>2.5-7</td>
<td>25</td>
<td>HCl</td>
<td>45</td>
<td>15</td>
</tr>
<tr>
<td>5-18-07</td>
<td>120</td>
<td>2.5-12</td>
<td>25</td>
<td>NaOH/Citric Acid</td>
<td>50</td>
<td>15</td>
</tr>
<tr>
<td>5-22-07</td>
<td>120</td>
<td>2.5-7</td>
<td>25</td>
<td>HCl</td>
<td>60</td>
<td>15</td>
</tr>
<tr>
<td>5-31-07</td>
<td>120</td>
<td>2.5-12</td>
<td>35</td>
<td>NaOH/Citric Acid</td>
<td>60</td>
<td>15</td>
</tr>
</tbody>
</table>

Fouled membrane swatches were obtained from the feed sections of two sacrificed membrane elements from Skid 4 in Dunedin’s Water Treatment Facility. Both membrane elements had been previously autopsied, so they were already cut and unrolled. Swatches measuring approximately 2.5cm x 4cm (10 cm²) were cut from the most fouled section of the sheet using tweezers and a razor blade. All swatches were taken from the area just above the glue line, on the feed end of the element. The swatches were then measured and placed in labeled Petri dishes, in sets of three. Each dish was
labeled according the cleaning conditions to which the three swatches would be subjected. Dishes were separated into three color coded sections so membranes could be easily located and identified. These colors corresponded with three sets of color coded scintillation vials, into which the swatches would eventually be placed for cleaning.

High and low pH cleaning solutions were then prepared using anhydrous sodium hydroxide, anhydrous citric acid, or anhydrous hydrochloric acid, depending on the design for the particular experiment. All chemicals were procured from Fisher Chemical. Amounts of each chemical needed to adjust the pH to the required level were calculated according to mass action, charge balance, and mass balance equations. Solution pH was then measured and manually adjusted, if necessary.

Once the pH solutions were adjusted appropriately, they were transferred into scintillation vials. Scintillation vials were organized into sets of triplicates for each pH. Each vial received 15 mL of cleaning solution and a membrane swatch. The vials were quickly placed into a LAB-LINE Incubator/Shaker and gently shaken for various lengths of time, according the specific design. Temperature inside the agitator was also adjusted according to experimental design. It was measured periodically with a mercury thermometer to ensure accuracy.

When the cleaning was finished, carbohydrate and protein assays were performed on the cleaning solution. Complete descriptions of the assays are contained in Appendix 1. Treated membranes were then placed into a second set of labeled scintillation vials, containing 15 mL of de-ionized (DI) water. The vials were placed into a sonicator for various lengths of time to extract the remaining foulant from the membrane surface. As we gained
experience using the sonicator, it became clear that complete removal of residual foulant required an hour of sonication. After sonication, membranes swatches were removed from the scintillation vials and discarded. Another protein and carbohydrate assay was then performed on the remaining liquid in the vials.

The absorbance of both assays was measured by the HACH DR/4000U ultraviolet spectrophotometer. The Each condition was run in triplicate, so three absorbance values were recorded for each condition. Absorbance values were then converted to concentration (mg/L) according to a calibration curve prescribed by each method. This value was then multiplied by the known volume of liquid in which the protein and/or carbohydrate was suspended to yield a mass (mg). Finally, the mass was divided by the measured area of the membrane from which the protein and/or carbohydrate was removed to yield a mass/area (mg/cm²). Final data points were an average of the three mass/area values for each condition. For each condition, mass/area data from the cleaning solution vial (representing removal through cleaning) was compared to mass/area data from the sonicated vial (representing remaining foulant) to calculate fractional removal during cleaning. Percent removal was calculated by dividing the mass/area removed during cleaning, by the sum of the mass/area remaining and the mass/area removed. This calculation was performed for both carbohydrate and protein data. Results are discussed in the subsequent section.

3.4 Phase 2: The Flat Sheet Module

The goal for the second experimental phase was to identify several effective cleaning protocols based on a combination of
performance data from a flat sheet module (FSM) and laboratory data. Several chemical and physical variables, including pH, temperature, and time, were selected for testing, based on the literature review and other research described in the previous sections. Like the laboratory bench test, the FSM was economically efficient because it only required a relatively small piece of expensive membrane material to be used per cleaning run. More tests could be conducted at a lower cost and in less time than if testing was done at the skid level.

The FSM consisted of several components that were configured to measure membrane performance and record data. The main components of the system (see Figure 6 and Figure 7) included a pump, valves, tubing, an Osmonics flow cell, and clamps to hold the membrane sheet, flow and pressure gauges, data loggers, probes (temperature, pH, and conductivity), and a central computer.

![Figure 6: Process Diagram for the Flat Sheet Module (FSM)](image)
The flow cell accommodated flat sheets of membrane measuring 90cm by 150cm and had a feed channel depth of 7.874mm. Feed spacer and permeate spacer material from an autopsied membrane element was placed in the cell with the membrane flatsheet. The entire system was located on the production floor at Dunedin’s water treatment plant.

Cleanings in the FSM were performed at a flowrate of .3 L/min, yielding a crossflow velocity of 1.38 m/min. Although this differs from conditions in the skid, in which the crossflow velocity is about 10 m/min, results are still comparable to each other, and it is reasonable to assume that cleanings would only improve at a higher flowrate. Cleaning tests were run in duplicate to reduce errors due to chance. Thirty-two membrane cleanings, shown in Table 5, were performed in total.

Membrane cleanings were done in three parts. The first part was a pre-test where baseline performance conditions were identified for the fouled membrane sheet. Fifteen liters of second stage RO permeate were procured and mixed with 15 grams of NaCl in a five gallon bucket, to create a 1000ppm salt water solution. The bucket was then moved to the work area and covered with a lid which had been cut to provide access to the water through a small, circular hole at the top. The work area also contained a PC, running Windows.
2000, with two applications for datalogging installed. LoggerPro, by Vernier Software and Technology, is the application designed to work with the Vernier datalogger and BoxCarPro, by ONSET Computer Corporation, is the application that collects data from the ONSET HOBO Weather Station. A pH meter, connected to the Vernier data logger, was placed in the water through the hole in the lid, and the pH of the solution was recorded on a spreadsheet within LoggerPro. Next, the pH meter was removed because of interference with other probes, and a conductivity probe, connected to the Vernier datalogger, was placed in the water. A temperature probe connected to the HOBO Weather Station was also placed in the water. Permeate from the FSM was collected through a small tube that was taped to the side of a tipping bucket rain gauge, so it would drip into the gauge. A pulse detector was connected to the bottom of the gauge so a signal would be sent to the HOBO Weather Station and logged each time the bucket tipped inside the gauge. Permeate flowrate was calculated by multiplying the number of tips per minute by the volume of the receptacle. The volume of the receptacle at the point of tipping varied over time depending on how fast the water flowed. This relationship was characterized and used in the permeate flow calculation. The rain gauge emptied at the bottom into a small tray with a hole drilled into the bottom. Tubing connected the tray to the bottom of a small graduated cylinder containing a conductivity meter. As the water rose in the cylinder it exited through a hole drilled near the top where tubing connected it back to the five gallon bucket. The concentrate effluent tube was also placed into the bucket. Both permeate and concentrate were returned to the beginning of the loop to be recirculated.
A fouled membrane sheet was placed into the FSM, and the pump was turned on, circulating water through the system. Back pressure was applied using the valve located directly after the FSM. The feed valve and back pressure valve were adjusted until the pressure reached approximately 120 psi and feed flowrate was approximately 0.3 liters per minute. Feed flowrate and pressure were logged using voltage meters connected to the Vernier datalogger. Each meter was calibrated prior to the experiments by characterizing the relationship of each variable to voltage. Water was allowed to run through the system until conductivity values became relatively constant. This generally took between five and ten minutes, and then logging commenced. Both the Vernier datalogger and the HOBO Weather Station logged data once per minute into their respective applications. Data was taken for a total of fifteen minutes.

LoggerPro data was saved in a .txt file, and BoxCarPro data was saved in an .xls file. It was then pasted into another excel spreadsheet where secondary variables were calculated and temperature correction was performed. This spreadsheet was partially developed by Ana Garcia of Dr. Yeh’s research group. Temperature correction was based on standard calculations from three standard applications (NORMPro by Fluid Systems, RODATA by Hydronautics, and FTNORM by Dow) that are used in many reverse osmosis water treatment facilities.
Table 5: Cleaning Test Parameters in the FSM

<table>
<thead>
<tr>
<th>Cleaning #</th>
<th>Chemical</th>
<th>Temp</th>
<th>Time (min)</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>NaOH</td>
<td>22-27°C</td>
<td>15</td>
<td>10.5-11.5</td>
</tr>
<tr>
<td>2</td>
<td>NaOH</td>
<td>22-27°C</td>
<td>15</td>
<td>10.5-11.5</td>
</tr>
<tr>
<td>3</td>
<td>NaOH</td>
<td>22-27°C</td>
<td>30</td>
<td>10.5-11.5</td>
</tr>
<tr>
<td>4</td>
<td>NaOH</td>
<td>22-27°C</td>
<td>30</td>
<td>10.5-11.5</td>
</tr>
<tr>
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<td>NaOH</td>
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<td>45</td>
<td>10.5-11.5</td>
</tr>
<tr>
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<td>45</td>
<td>10.5-11.5</td>
</tr>
<tr>
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<td>60</td>
<td>10.5-11.5</td>
</tr>
<tr>
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<td>NaOH</td>
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<td>10.5-11.5</td>
</tr>
<tr>
<td>9</td>
<td>NaOH</td>
<td>35-40°C</td>
<td>15</td>
<td>10.5-11.5</td>
</tr>
<tr>
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<td>NaOH</td>
<td>35-40°C</td>
<td>15</td>
<td>10.5-11.5</td>
</tr>
<tr>
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</tr>
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<td>10.5-11.5</td>
</tr>
<tr>
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<td>60</td>
<td>10.5-11.5</td>
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<tr>
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<td>10.5-11.5</td>
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<td>Citric Acid</td>
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<td>2.2-3.0</td>
</tr>
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<td>2.2-3.0</td>
</tr>
<tr>
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<td>30</td>
<td>2.2-3.0</td>
</tr>
<tr>
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<td>30</td>
<td>2.2-3.0</td>
</tr>
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<td>10.5-11.5</td>
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<td>22-27°C</td>
<td>45</td>
<td>10.5-11.5</td>
</tr>
<tr>
<td>23</td>
<td>KochKleen</td>
<td>35-40°C</td>
<td>45</td>
<td>10.5-11.5</td>
</tr>
<tr>
<td>24</td>
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<td>45</td>
<td>10.5-11.5</td>
</tr>
<tr>
<td>25</td>
<td>RO Permeate</td>
<td>22-27°C</td>
<td>15</td>
<td>~7</td>
</tr>
<tr>
<td>26</td>
<td>RO Permeate</td>
<td>22-27°C</td>
<td>15</td>
<td>~7</td>
</tr>
<tr>
<td>27</td>
<td>RO Permeate</td>
<td>22-27°C</td>
<td>30</td>
<td>~7</td>
</tr>
<tr>
<td>28</td>
<td>RO Permeate</td>
<td>22-27°C</td>
<td>30</td>
<td>~7</td>
</tr>
<tr>
<td>29</td>
<td>RO Permeate</td>
<td>35-40°C</td>
<td>45</td>
<td>~7</td>
</tr>
<tr>
<td>30</td>
<td>RO Permeate</td>
<td>35-40°C</td>
<td>45</td>
<td>~7</td>
</tr>
<tr>
<td>31</td>
<td>Fisher Blend</td>
<td>35-40°C</td>
<td>45</td>
<td>10.5-11.5</td>
</tr>
<tr>
<td>32</td>
<td>Fisher Blend</td>
<td>35-40°C</td>
<td>45</td>
<td>10.5-11.5</td>
</tr>
</tbody>
</table>
These applications normalize permeate flow based on the equation:

\[ QN = Qt \times \left( \frac{NDPr}{NDPt} \right) \times \left( \frac{TCFt}{TCFr} \right) \]  

(3.1)

where \( QN \) = Normalized flow rate (vol/t) at time t, \( Qt \) = Actual flow rate (vol/t) at time t, \( NDPr \) = Net Driving Pressure at reference point (units of pressure), \( NDPt \) = Net Driving Pressure at time t (units of pressure), \( TCFr \) = TCF for temperature at referenced conditions (no units), and \( TCFt \) = TCF for temperature at time t (no units). Because pressure is kept constant in the FSM, the pressure correction drops out of the equation. \( TFCt \) and \( TFCr \) were calculated using the equation:

\[ TCF = \exp \left\{ K \times \left[ \frac{1}{(273 \, ^{\circ}K + t)} - \frac{1}{298 \, ^{\circ}K} \right] \right\} \]  

(3.2)

where \( t \) is degrees Celsius, and \( K = 2640 \, ^{\circ}K \) for Koch membrane. Salt passage was also normalized with this equation, but the reciprocal of the TCF was used because by increasing flux, temperature actually decreases % rejection.

The next step in the process was to perform the actual cleaning of the membrane sheet. The sheet was left in the FSM while the bucket with the salt solution was replaced by a bucket containing 15L of cleaning solution which had varied composition based on the experimental design. The pH of the cleaning solution was measured and recorded. Then a temperature probe was placed in the bucket and remained there for the duration of the cleaning. Again, the cleaning solution was set to re-circulate by placing the permeate and concentrate effluent tubes into the bucket. If the cleaning was to be conducted at an elevated temperature, the entire bucket was placed into an electric heater. After the pump was turned on, the back
pressure valve and the feed valve were adjusted so that the flow rate was approximately 0.4 L/min and the pressure was approximately 40 psi. Cleaning times varied according to experimental design. Feed flowrate, feed pressure, and feed temperature were logged using LoggerPro for the length of the cleaning and later exported as a .txt file.

When the cleaning was finished, the FSM was flushed with permeate until the concentrate and permeate pH matched the feed pH. Then, a performance test, identical to the one done before the cleaning, was run. The two performance tests were compared in another spreadsheet, and the percent changes in temperature corrected specific flux, temperature corrected % rejection, and raw flow, were calculated. A comparison spreadsheet was generated for each cleaning run. The data from these comparison spreadsheets was compiled into another spreadsheet, so cleanings could be compared to each other and statistics could be generated. Results from this phase of the experiment will be discussed in the next section.

Prior to performing cleanings, the FSM was used to characterize virgin (unused) membrane in terms of flux and % rejection. This was done so that the performance of cleaned membranes could eventually be compared not only to that of fouled membranes but to virgin membrane, as well. The virgin membrane was compacted in the FSM, prior to characterization, by re-circulating RO permeate through it for 24 hours at a pressure of 120 psi and a flowrate of 0.3 L/min. Data for feed flowrate, permeate flowrate, feed conductivity, permeate conductivity, and feed temperature were collected once per hour. The last four hours of data, in which the numbers stabilized, were used to represent virgin membrane performance.
3.5 Phase 3: The Single Element Cleaning System

The objective of Phase 3 was to confirm the effectiveness of the protocols selected in experimental Phase 1 and narrow the selection down to a few, effective protocols. The SECS (see Figure 8 and Figure 9) was designed to feature conditions that more closely mimic the conditions in Skid 4 in Dunedin’s Water Treatment Facility and to help determine whether the cleaning protocols developed with the FSM are applicable to a whole membrane element. The main components of the system include a single element pressure vessel (on loan from the Bureau of Reclamation), a pump, two large water storage tanks, a tank warmer, a tank stirrer, PVC tubing, several valves, flow meters, and pressure gauges.

![Diagram of the Single Element Cleaning System](diagram.png)

Figure 8: Process Diagram for the Single Element Cleaning System

Courtesy of Bob Kyle, City of Dunedin
Four cleanings were performed on the SECS. Table 6 lists the parameters for each cleaning. As with cleanings in the FSM, the first stage in the process was to run a performance test on a fouled membrane element. Fouled membrane elements were taken from Skid 4. Only elements from the feed end of the pressure vessel were taken, because the presumption from the literature is that elements in that position will experience the most severe fouling. The performance pre-test was done using approximately 120 gallons of 1000ppm salt water solution. The solution was made using permeate from Dunedin’s RO skids mixed with salt until the conductivity reached approximate 2400 $\mu$S. This is comparable to the conductivity measured in the 1000ppm salt solution used for performance testing in the FSM. The SECS was designed to allow for recirculation of the permeate and the concentrate, for this part of the experiment. However, the SECS was
not designed for datalogging, so all measurements were taken by hand and recorded.

Table 6: Cleaning Test Parameters in the SECS

<table>
<thead>
<tr>
<th>Cleaning #</th>
<th>Chemical</th>
<th>Temp</th>
<th>Time (hr)</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>NaOH</td>
<td>Ambient</td>
<td>9</td>
<td>11</td>
</tr>
<tr>
<td></td>
<td>Citric Acid</td>
<td>Ambient</td>
<td>9</td>
<td>2.5</td>
</tr>
<tr>
<td>2</td>
<td>NaOH</td>
<td>Elevated</td>
<td>2</td>
<td>11</td>
</tr>
<tr>
<td></td>
<td>Citric Acid</td>
<td>Elevated</td>
<td>2</td>
<td>2.5</td>
</tr>
<tr>
<td>3</td>
<td>NaOH</td>
<td>Ambient</td>
<td>9</td>
<td>11</td>
</tr>
<tr>
<td></td>
<td>Citric Acid</td>
<td>Ambient</td>
<td>9</td>
<td>2.5</td>
</tr>
<tr>
<td>4</td>
<td>NaOH</td>
<td>Elevated</td>
<td>2</td>
<td>11</td>
</tr>
<tr>
<td></td>
<td>Citric Acid</td>
<td>Elevated</td>
<td>2</td>
<td>2.5</td>
</tr>
</tbody>
</table>

Once the pump was turned on, and water was re-circulating through the system, the concentrate recirculation valve was partially closed in order to increase system pressure. Unfortunately, the system could not sustain a pressure higher than 40 psi. Due to this limitation, performance tests were conducted at 40 psi rather than 120 psi, the pressure maintained in Dunedin’s RO Skids. System flow was maintained at approximately 15 gpm, slightly lower than the Skid condition of approximately 50 gpm. Performance tests lasted 30 minutes. Feedwater and permeate samples were gathered about every 10 minutes. Temperature, pH, and conductivity were measured in the feedwater sample, and conductivity was measured in the permeate sample. In addition, system flowrate and pressure were recorded based on the gauges installed on the SECS. Permeate flowrate was measured using a 1000mL graduated cylinder and a stopwatch. The cylinder was placed under the permeate tap for 15 seconds. The total volume gathered was then measured and divided by 15 to yield the flowrate in mL/sec. Because of the way the system
was piped, this method did yield a direct measurement of permeate production per time. Percent rejection was calculated by dividing the permeate conductivity by the feed conductivity, subtracting from one, and multiplying by 100.

After the performance test was completed, the cleaning was performed. The 120 gallon tank was filled and the pH was adjusted with NaOH or Citric Acid until the experimental design goal was reached. The temperature and pH of the cleaning tank were recorded prior to cleaning. During the cleaning, a feed sample was taken each hour for which the temperature and pH were recorded. Feed pressure, feed flowrate, and miscellaneous comments were also recorded once per hour. When the cleaning was finished, three permeate flushes were conducted. Each flush used approximately 80 gallons of permeate. The first and third flushes moved water from the feed to the permeate end of the element, while the second flush was in reverse, moving water from the permeate end to the feed end of the element. The SECS was designed with this capability in mind, and the change in direction was achieved by opening and closing valves. This is comparable to what is done on the skid level in Dunedin, during regular cleanings. Following the flushes, another performance test, identical to the one performed before cleaning, was conducted. The pre and post performance test were compared to determine the effects of cleaning. Results for this phase are discussed in the next section.

3.6 Policy Implications

The policy component of this project consisted of two parts. First, a cost analysis was performed, based on adoption of the suggested protocol, to estimate the cost savings potential to the City
of Dunedin. The analysis accounted for time, labor costs, chemical costs, and membrane costs. The second part of the policy component extrapolated the cost savings potential to all membrane based utilities in Florida. Cost savings was estimated based partially on the results of a survey of Florida membrane utilities (see Appendix 3). The survey gathered information regarding current cleaning protocols, fouling issues, plant size, and plant configuration. This information was used to determine whether a newly developed protocol would be applicable to other plants. The Florida DEP (Department of Environmental Protection) provided information regarding the number and type of reverse osmosis water treatment plants in Florida. These data were used to determine how many other plants in Florida were comparable to Dunedin.
4. Results and Discussion

4.1 Membrane Autopsy Results

A membrane autopsy was performed on an element from the first position of a pressure vessel from Dunedin’s Skid 4 in order to characterize the membrane and the foulant material more precisely. The autopsy consisted of several different analyses. A list and detailed description of the analyses are listed in Appendix 2. Results relevant to this study are presented here.

Photographic analysis was used to inspect the membrane for visual fouling patterns. Attenuated Total Reflection Fourier Transform Infrared (ATF-FTIR) was used to indentify molecular components of the biofilm. Protein and carbohydrate assays were used to quantify the amounts of protein and carbohydrates in the biofilm.

The photographic analysis (see Figure 5 from the previous chapter) revealed that the feed end of the membrane was much more fouled that the effluent end. This is consistent with the protein and carbohydrate assay results (see Figure 10) which show decreasing amounts of carbohydrate and protein with distance from the feed end of the element. This same pattern can also be observed in the ATR-FTIR data (see Figure 11). The wider peaks and valleys, evident on the feed end diagram, indicate more severe fouling. The sharper peaks on the middle and effluent end diagrams indicate less severe fouling.
Figure 10: Protein and Carbohydrate Assay Results from OCWD Membrane Autopsy

From Micromem Analytical (2006)
Figure 11: ATR-FTIR Spectra from Feed, Middle, and Effluent Membrane Sections

From Micromem Analytical (2006)
Overall autopsy results indicated that membrane biofouling was most severe at the feed end of the element and that biofouling in general was relatively mild in comparison to fouling observed in elements from other sources. Membrane autopsies at OCWD and elsewhere are often performed to determine the cause of membrane failure, in which case fouling is frequently very severe. In our case, the autopsy was performed to gather information regarding the extent and nature of fouling. Autopsy results represent a snapshot in time of the life of the membrane, not the overall condition of the skid. A second autopsy was performed at USF, and fouled membranes were individually cut and bagged for use in Phase 1 and Phase 2.

4.2 Phase 1: Laboratory Bench Tests

Six laboratory bench tests were performed, in total. Results from the first four tests are not presented in this section because these tests were not run with optimized parameters. Protein and carbohydrate assay procedures were adapted through trial and error from the procedures developed by the OCWD. As the bench test process was improved by prolonging the cleaning and sonication times, results became more consistent. The final two bench tests were run at optimized settings.

The protein and carbohydrate results are both highly sensitive to the way in which the calibration curve is generated. Calibration curves were generated during each experiment, but, due to error in dilution or measurement, they were not always similar. The protein calibration curves were more similar over time that the carbohydrate calibration curves (see Figure 12 and Figure 13). General protein and calibration curves were generated by averaging several individual curves. The
outlying curves were not included in the average (see Figure 14 and Figure 15). This approach was taken because errors in the calibration curve were most likely due to mis-calibrated pipettes. Dilutions were not done serially, so various pipettes were required to procure the necessary volumes. The actual samples to be measured were all taken with one of two pipettes and at single volumes, so error is less likely to be associated with the reaction and sample measurement process.

![Protein Calibration Curves](image_url)

*Figure 12: Protein Calibration Curves*
Figure 13: Carbohydrate Calibration Curves

Figure 14: Protein General Calibration Curve
Results indicate that there was not an equal amount of protein and carbohydrate present on the membrane surface, prior to cleaning (see Figure 16). In the later experiments, protein exceeds carbohydrate by an approximate 3 to 1 ratio (see Table 7). However, this ratio may not correlate directly with the ratio of the volume of bacterial cells to the volume of EPS in the biofilm. EPS can contain water channels, parts of dead bacteria, nutrients, enzymes, metabolites and oxygen (Coghlan, 1996), some of which will not show up at all in the carbohydrate assay and some which (like parts of dead bacteria) may be included in the results of the protein assay. It is likely that only some of the amount of protein measured by protein assay is from whole, bacterial cell material, while the amount of EPS present is likely underrepresented by the carbohydrate assay. The full extent of this effect is not known. In a mature biofilm, 75-95% of the volume is
occupied by the EPS matrix (Geesey et al., 1994), but much of that volume may be water. These assays may not be measuring the full amount of protein and carbohydrate present. However, there is no reason to believe that a greater proportion of total protein is being measured than that of carbohydrate or vice versa.

Protein and carbohydrate were not the only components of the biofilm. During the USF autopsy, total dry mass was measured by scraping biofilm from a known membrane area, drying it in an oven for one hour at 104°C, and measuring its mass. This mass also includes inorganic material. Protein and carbohydrate combined mass was approximately two thirds of the measured dry mass. Ash weight after incineration was also measured to determine the organic portion but the resulting mass was too small to measure.

Table 7: Comparison of Total Mass Measurements from Membrane Surface

<table>
<thead>
<tr>
<th>Data Source</th>
<th>Total Protein (µg/cm²)</th>
<th>Total Carbohydrate (µg/cm²)</th>
<th>Dry Mass (µg/cm²)</th>
<th>Ratio Protein : Carbohydrate</th>
</tr>
</thead>
<tbody>
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<td>USF Autopsy</td>
<td>62</td>
<td>47</td>
<td>151</td>
<td>1.3</td>
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<tr>
<td>OCWD Autopsy</td>
<td>32</td>
<td>42</td>
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<td>61</td>
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<td>3.1</td>
</tr>
</tbody>
</table>
Protein removal appears to correlate strongly with pH and weakly with temperature (see Figure 17). Between pH 9 and pH 12, correlation between pH and percent protein removal reaches above 97% with a slope of 2.722 (see Figure 18).

Carbohydrate removal does not appear to vary with pH or temperature (see Figure 19). Error ranges for the carbohydrate assay were much larger than those for data from the protein assay, so it is difficult to draw hard conclusions about carbohydrate removal. UV spectrometer reading errors could be caused by a density gradient in the treated liquid. The sulfuric acid required for the reaction caused the liquid to become more viscous and trap air bubbles.
Figure 17: Average % Protein Removal as a function of Time and pH

Figure 18: Strong Correlation between pH and % Protein Removal
At either temperature, the percent removal of protein is no higher than 14.3%, and the percentage removal of carbohydrate is no higher than 35.7%. However, a significant mass of material is still removed. Since there is significantly more protein than carbohydrate present prior to cleaning, a greater mass of protein is removed (see Figure 20).
The correlation between protein removal and pH can likely be explained by the change in surface chemistry caused by the cleaning solution. As the pH of the cleaning solution increases, the surface charge on the membrane and on the organic material (including protein and carbohydrates) increases, causing increased electrostatic repulsion between them.

One possible source of error in these experiments could be the dehydration of the membrane material. Although precautions against drying were taken (wrapping in plastic and refrigeration), the membrane material did get significantly more dry than the freshly autopsied material. Ease of removal could change over time and with drying. It is not known whether time and drying can also cause differential/preferential removal/detection percentages for carbohydrates or protein.
Percent removal of protein and carbohydrate was also measured over wider pH ranges. Results indicate that protein removal is greatest at higher pH levels and least at lower pH levels (see Figure 21). Due to a high degree of error in the carbohydrate removal measurements, it cannot be determined whether pH influences carbohydrate removal.

**Figure 21: Percent Removal of Protein and Carbohydrate as a function of pH on 5-18-07**

**Error bars represent max and min values**
4.3 Phase 2: Flatsheet Module Results

The Flatsheet Module (FSM) was used to measure the effects of time, temperature, pH and chemical composition on salt water flux and permeate flux. High pH cleanings were performed with NaOH, KochKleen, or Fisher Detergent at pH levels between 10.5 and 11.5. Normal pH cleanings were performed with RO permeate at pH levels between 5.5 and 7. Low pH cleanings were performed with Citric Acid at pH levels between 2 and 3. “Ambient temperature” refers to cleanings performed at room temperature. Room temperature was approximately 23-28°C. “Elevated temperature” refers to cleanings that were heated. Solutions were heated to temperatures between 35°C and 40°C. The full list of test conditions and results are reported in Table 8. The last column, percent recovery of flux, refers the comparison between cleaned membrane flux and virgin membrane flux, measured from unused, compacted membrane. A complete description of the pre and post tests for each of the 32 cleaning is listed Appendix 5.

The dependence of specific flux on temperature is often estimated by the equation:

\[ J_c = J_o \Theta^{T-25} \]  

(4.1)

where \( J_c \) is the specific flux at temperature \( T \), \( J_o \) is the specific flux at reference conditions (25°C), \( \Theta \) is an empirical constant factor, and \( T \) is temperature. The temperature correction constant (\( \Theta \)) could not be determined the from the pre cleaning and post cleaning data set,
because the observed flux did not depend on temperature in a consistent fashion. This may be due to errors in measurement. The methods used to measure both percent rejection and specific flux (flow) were necessarily time delayed. For instance, the percent rejection was measured in a graduated cylinder below the tray used to capture permeate from the rain gauge. The water may have been in the tray for a few minutes before reaching the conductivity meter. The temperature associated with measurement was taken in the reservoir and may be different than what was experienced by the membrane at that time. It is reasonable to assume that the percent rejection and flux measurements are actually associated with a time before the one recorded with them and a temperature after the one recorded with them. Since $\Theta$ could not be calculated, temperature correction was performed according to the industry standard method, described in the previous section. However, after examining the results of the correction, it is reasonable to conclude that some over-correction occurred. If this was the case, specific flux was underestimated at higher temperatures and over-estimated at lower temperatures, and the opposite would be true for percent rejection.

When cleanings at high pH are compared with cleanings at low pH, there results a positive correlation between pH and percent change in permeate flux (see Figure 22). However, this data is associated with a high degree of error. Biofilm and/or other foulant layers create resistance against flux, so flux increases when they are removed or reduced. Percent rejection has been shown to decrease with increasing pH. This could indicate that foulant layers are also acting as additional barriers for salts, so rejection decreases as they are removed or reduced. More likely, the membrane may have been
slightly damaged by high pH conditions. Further research will be required to determine the cause of this trend.

Table 8: Full List of FSM Cleanings and Results

<table>
<thead>
<tr>
<th>Cleaning Description (Time (min)-Chemical-Temp)</th>
<th>Pre-Q</th>
<th>Post-Q</th>
<th>% Δ Q</th>
<th>Pre-%Rc</th>
<th>Post-%Rc</th>
<th>% Δ Rc</th>
<th>Pre-Jc</th>
<th>Post-Jc</th>
<th>% ΔJc</th>
<th>% Recovery of Flux</th>
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<tr>
<td>15-NaOH-Ambient</td>
<td>14.3</td>
<td>14.6</td>
<td>2.2</td>
<td>78.1</td>
<td>85.2</td>
<td>8.3</td>
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<td>7.3</td>
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<td>14.6</td>
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<td>79.7</td>
<td>81.1</td>
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<td>2.1</td>
<td>7.6</td>
<td>7.5</td>
<td>-1.3</td>
<td>95.50</td>
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</table>
**Figure 22: Specific Flux and Rejection as function of pH**

**Figure 23: Four Cleanings Performed for 15 minutes**
Four cleanings were performed for 15 minutes (see Figure 23). The only cleaning protocol shown to improve specific flux after that time period was NaOH at an elevated temperature. Citric Acid at an elevated temperature increased rejection but decreased specific flux. Chelating action by the Citric Acid may have modified the structure of the biofilm but failed to remove it.

Six cleanings were performed for 45 minutes (see Figure 24). Most cleanings appeared to improve specific flux and decrease percent rejection, but many cleanings exhibited a high degree of variability, making conclusions more difficult. Fisher Detergent, a combination of NaOH, and surfactants, produced the greatest improvement in specific flux and greatest decrease in percent rejection, but similar results were achieved using pure NaOH. It is worth noting that ten out of the twelve cleanings performed resulted in increased specific flux, and percent rejection improved in eight of the twelve cases. In general, 45 minute cleanings resulted in improved membrane performance.

When percent improvement of specific flux due to NaOH cleanings are compared over time and temperatures, a clear trend can be seen (see Figure 25). Cleanings performed at elevated temperatures increase flux by approximately 5-7%, on average, compared to those performed at ambient temperature. As these cleanings are essentially chemical reactions between the cleaning solution, the membrane surface, and the foulant, it follows that adding heat will increase the speed and intensity of cleaning. After 30 minutes, it appears that cleaning efficiency (relative to specific flux) levels off. It is interesting to note that the cleanings performed at ambient temperature never achieve the amount of flux improvement as those performed at elevated temperature, even after 60 minutes.
This suggests that higher temperatures are necessary to release the full potential of high pH cleanings.

**Figure 24: Six Cleanings Performed for 45 minutes**
Figure 25: NaOH Cleanings at Ambient and Elevated Temperatures over Time. All cleanings were performed at a pH in the range 10.5-11.5.

Figure 26: Comparison of High and Low pH Cleanings at 30 Minutes
Cleanings performed with Citric Acid at an elevated temperature for 30 minutes resulted in performance changes that were very consistent among individual cleaning runs (see Figure 26). Percent rejection increased while specific flux decreased. This is the opposite of what occurred as the result of cleaning for 45 minutes with NaOH. The Citric Acid cleaning solution (in the reservoir) often took on a greenish yellow tint over time. This suggests that the cleaning resulted in the dissolution of some foulant. Citric acid is a chelator, so the greenish yellow tint may be the result of iron and/or calcium dissolution, as those are the most prevalent metals in the feedwater. Citric Acid cleaning has a significantly positive effect on percent rejection suggesting that metal scale and/or complexed biofilm is responsible for the decreased percent rejection.

Cleanings performed with NaOH at an elevated temperature for 30 minutes resulted in performance changes that were more varied between individual cleaning runs (see Figure 26). It is likely that the effect on specific flux was positive, but, due to a high degree of variation, it is difficult to make a determination about the effect on percent rejection. NaOH works primarily to solubilize organic compounds by increasing electrostatic repulsion. NaOH cleaning generally results in increase of specific flux, suggesting that organic compounds in the biofilm are primarily responsible for decrease in specific flux. Since both types of cleaning result in performance improvements, it is likely that a protocol employing a combination of chemicals would result would be most beneficial.
4.4 Single Element Cleaning System (SECS) Results

Three cleanings were performed on the SECS, but system limitations made it difficult to draw conclusions from the results. The system has the potential to be extremely useful in the future, but a few modifications are necessary before it can be used for full scale cleanings. One recommended improvement is the installation of a larger pump, so the SECS will be capable of maintaining pressure conditions similar to the production skids. The centrifugal pump currently in place will only allow for system pressure up to 40 psi. This pressure is fine for cleanings but makes performance tests difficult. Additionally a permeate line flow meter will be required to accurately measure permeate flowrate. The tap and graduate cylinder method is inaccurate because of the way the permeate line is piped. Speedy tank filling could be achieved by installing a pump on the skid permeate line. The current setup employed hoses from the permeate line on the production skid, and 30 minutes or more are required to fill the tank, a process that must be done multiple times per cleaning. A permanent ladder should be installed near the tank to reduce chances of accident from the portable ladder as the SECS operator requires access to the top of the tank frequently during cleaning. Lastly, the tank heater thermostat should be altered to allow the tank temperature to reach 40°C. Presently, it is difficult to increase the temperature beyond 35°C, and it would be useful to match conditions set on FSM.

Some conclusions can be drawn from the three cleanings that were performed. In two of the cleanings (see Table 9), percent rejection could be measured accurately in the SECS after a broken connection piece was replaced. However, it is possible that percent
rejection would be different at 120 psi, as it was measured on the FSM and as it exists on Dunedin’s skids. Even if that is the case, these results do show the expected variability between results from the same type of cleaning. Based on this limited study, it does not appear that percent rejection was significantly improved by cleaning for two hours with each chemical at an elevated temperature (35°C).

Table 9: SECS Cleaning Results

<table>
<thead>
<tr>
<th></th>
<th>5/16/2007 - 2 hours NaOH/2 hours Citric Acid/Elevated Temp</th>
<th>6/1/2007 - 2 hours NaOH/2 hours Citric Acid/Elevated Temp</th>
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<td>Pre % Rejection</td>
<td>91.41</td>
<td>84.44</td>
</tr>
<tr>
<td>Post % Rejection</td>
<td>90.27</td>
<td>87.60</td>
</tr>
<tr>
<td>% Change</td>
<td>-1.26</td>
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It was also interesting to note the characteristics of the citric acid cleaning solution in terms of color and smell during the cleanings. The greenish yellow tint that was evident during citric acid cleanings in the FSM was even more apparent on the SECS. The water looked almost fluorescent green during one run. The NaOH cleaning solution became murky yellow and took on a musty smell. It also grew a deep (4 or 5 inch) layer of foamy bubbles over time. These characteristics of the cleaning solutions strongly suggest that these chemicals and heat are causing some type of reaction resulting in removal of some foulant material from the membrane surface, even if the improvements in performance are not obvious. As the system is improved, the potential for data collection will increase.
5. Conclusions and Recommendations

5.1 Connections between Removal and Performance

This study began as an investigation of biofouling and potential for cleaning protocol improvement for the city of Dunedin, but over a year and half it matured into a more general inquiry into the nature of biofilms, relative removal due to cleaning, and the connections between removal and performance. The Membrane Autopsies shed light on the intensity and nature of the biofouling, and the Bench Tests yielded information about relative removal of protein and carbohydrate (the major constituents of biofilm) under different conditions. The FSM measured membrane performance under similar conditions, allowing us to speculate about the relative effects of protein and carbohydrate on membrane performance.

The first important realization was that the extent of biofouling of the autopsied element from Dunedin was less than anticipated. Changes in pre-treatment and cleaning leading up to the time of the autopsy can affect the extent of biofouling observed. Also, it is important to note that the autopsy was performed on an element still in operation, and the element had not yet failed to perform, as is usually the case when they are sent for autopsy. It is likely that other types of fouling also affect membrane performance. This study was limited to elements in the first position in pressure vessels because they have been shown to be more affected by biofouling than elements in the later positions. It is possible that the elements towards the end
of the pressure vessel have been subject to scaling. The feedwater is treated with anti-scalant for scaling control, but it does contain calcium, magnesium, and iron.

The character of the biofilm is also important to consider in cleaning. According to Autopsy and Bench Test results, the ratio of protein to carbohydrate on the membrane surface is more than three to one on a mass basis. Therefore, a cleaning that is effective against protein will result in more removal. High pH cleanings, such as performed with NaOH, have been shown to more effectively remove protein from the membrane surface. Carbohydrate removal does not appear to vary with pH, but it does occur at no less than 17% (at 35°C) between pH 7 and 12.

Membrane performance is the surest indicator of cleaning effectiveness. Unfortunately, it does not yield direct information about mechanism of action. Therefore, performance data must be considered with removal and character data to get a total picture of what is occurring during cleaning. In order to do, a few assumptions must be made. First, we must assume that the removals measured during the Bench Tests will occur at the comparable percentages in the FSM. The major difference between the Bench Test process and the FSM is flow and pressure. Fast moving water and high pressure will generate shear stress on the biofilm and possibly aid in removal. Therefore, it is reasonable to think that removal will be easier in the FSM. There is no reason to assume that sheer stresses will affect protein and carbohydrate differently because they are both embedded in the biofilm. Second, we must assume that protein and carbohydrate removal is the most important effect of high pH on the membrane. However, lipids can represent up to 40% of biofilm material. If there were another substance affecting membrane
performance that was also removed at high pH, it would be a
confounding factor.

The other factor to consider is that FSM and Bench Test
swatches were all taken from the most biofouled portion of the
membrane element, the feed end. So, FSM performance is not
necessarily indicative of entire element or skid performance. However,
it is probable that swatches are more heavily fouled with biofilm than
with other foulants. Feedwater to the skids averages only 630 mg/L
total dissolved solids, so significant scaling is not expected (as would
be in the case of brackish groundwater or seawater. Therefore, it is
reasonable to assume that performance is mostly dependent on extent
of biofouling, so successful cleanings most likely resulted in some
biofilm removal.

FSM results showed that high pH cleanings resulted in the most
improvement of specific flux. The Bench Tests results showed that
high pH cleanings remove protein and carbohydrate from the
membrane surface. In keeping with the aforementioned assumptions,
it is reasonable to connect the presence of protein and carbohydrate to
reduced flux.

FSM results also showed that low pH cleanings resulted in the
most improvement in percent rejection. Low pH cleanings are known
to chelate metals. Therefore, the presence of metals may be
connected with reduced rejection. It is possible that a metal
complexed biofilm may cause decreased rejection compared to a
biofilm with no incorporated metal.
5.2 Recommendations to Dunedin

This was a preliminary study designed to improve Dunedin’s cleaning protocol, under the assumption that biofilm was the major problem at the plant. Further examination has shown that biofouling was not as severe as was originally thought for the lead element autopsied. More testing should be done to more thoroughly determine the extent of biofouling at Dunedin. First, elements from the middle and end of the Stage 1 pressure vessels should be autopsied. Then, similar elements from a pressure vessel in Stage 2 should be autopsied. Once the full extent of biofouling is known, it will be easier to determine the effectiveness of a protocol aimed directly at biofilm.

Dunedin’s current protocol calls for several, nine hour, high pH cleaning runs followed by a nine hour low pH cleaning. This study indicates that cleaning for that length of time is not necessary for biofilm removal and that after approximately 60 minutes, no improvement can been detected. Cleaning effectiveness has also been shown to improve with temperature. I have been told anecdotally that the current protocol is so long because it takes that long for the pump and friction to cause the cleaning solution to heat up. If electrical costs for 18 hours of pumping are greater than for 2-3 hours of heating, the plant may want to consider installing a tank heater or water heater.

High pH cleaning has been shown to increase flux, and low pH cleaning has been shown increase rejection. These are both important aspects of performance. More testing is required to determine what sequence of cleaning is most effective, but it makes the most sense to clean with low pH solution first to weaken the structure of biofilm and/or remove metals and then to clean with high pH to remove
biofilm. This sequence is likely to improve cleaning efficiency and should be tested on the FSM and the SECS.

5.3 Policy Analysis

Florida has more reverse osmosis water plants than any other state in nation. Reverse osmosis plants in Florida outnumber the closest competitor almost 3 to 1 (see Figure 27), and half of the nation’s reverse osmosis plants are located in Florida. An improved cleaning protocol in Florida has the potential to be very cost effective due to the high density of reverse osmosis plants in the state (FDEP, 2007).

The policy analysis was conducted to determine how the suggested protocol will affect the City of Dunedin and how that effect could be extrapolated to the state level. Of the 128 reverse osmosis plants listed by the FDEP, 30 plants are similar to Dunedin in that the use reverse osmosis for softening rather than desalination or other uses (see Figure 28). Plants that use reverse osmosis for brackish water treatment or desalination will have likely have different fouling patterns due to differences in water quality.
The suggested changes to Dunedin’s current protocol include purchasing a water heater for the cleaning tank and shortening the length of cleaning times. In this scenario, chemical costs would be reduced because the operators typically refill the tank and remix the solution at least once per cleaning. This would happen less often.
during a shorter cleaning cycle. A fifty percent chemical savings represents a conservative estimate. Labor costs would be reduced because cleaning times are shortened. Results indicate that cleaning past thirty minutes does not yield additional performance improvement.

Individual cleanings should be reduced to two or three hours, to start. Therefore, labor cost would be reduced by thirty-six hours per skid cleaning. A one-time cost for the purchase of a tank heater would be necessary, plus the yearly maintenance required to keep it in good condition and energy required to run it. It is possible that the new protocol could prolong membrane life. Cleanings tend to shorten membrane lifetimes. If the cleanings are more efficient, less cleaning will be necessary, effectively preserving membrane life. Also, shortened cleanings will reduce the exposure of the membrane to damaging chemicals. The length of the lifetime of the membranes at Dunedin is not yet known because the membranes are still operation after more than five years. The manufacturer’s warrantees expired after three years. Due to the large cost associated with replacing the membrane, increased lifetimes can potentially yield great cost savings. The longer the membranes are in use, the more cost effective they are. So, increasing the lifetimes from six to eight years is more beneficial in terms of cost savings than increasing lifetimes from ten to twelve years. The models below are meant to be conservative, so normal membrane lifetimes are assumed to be ten years.

Based on these assumptions, I have created a model to illustrate how the changes would affect Dunedin over ten years. One model uses the assumption that membrane lifetimes will not increase (see Table 10). The other model is based on a twenty percent increase in
membrane lifetimes (see Table 11). The output of these two models was then entered into a model of cost benefit to the state of Florida.

The model predicts that if Dunedin’s membrane lifetimes are not prolonged, the city will see $180,700 in savings over ten years (see Table 12). If lifetimes are prolonged by twenty percent, savings increases to $317,200 (see Table 13). Since Dunedin already uses the most inexpensive chemicals to clean membranes, their savings is relatively minor. However, the membrane cleaning survey indicates that other plants are using proprietary membrane cleaning products that can be significantly more expensive. Results from the FSM indicate that Kochkleen, a product in that category, does not produce significant increases in membrane performance over NaOH. Other plants may be able to save significantly by switching to NaOH and Citric Acid from more expensive products without any seeing any decline in cleaning efficiency. Of course, individual plants would run tests similar to those described here before making any cleaning protocol adjustments.

The extrapolation model is based on the assumption that twenty percent of the membrane softening plants in Florida can be compared to Dunedin in terms of fouling and cleaning. Only one plants in five plants surveyed was similar enough to possibly utilize the cleaning protocol. The model predicts that savings to Florida would be $1,084,200 over ten years, with no increase in membrane lifetimes and $1,903,200, over ten years, if membrane lifetimes were to increase by twenty percent. Estimated savings would increase if plants were switching to lower cost chemicals.

The modeled cost savings are crude estimates because there are many other variables that could be considered. Autopsy results indicate that Dunedin’s membrane had relatively low levels of
biofouling. Had the biofouling been worse, experimental results may have varied. Furthermore, the level of biofouling at each plant is different and is difficult to measure. Different biofilms can vary in terms structure and components. Also, there are many different brands and types of reverse osmosis membranes being used at different plants in Florida. Different membranes may react differently to the same protocol. Also, plants have different cleaning system configurations and may not be able to clean exactly the same way.
### Table 10: Model to Estimate 10 Year Cost Saving to Dunedin (Assume No Gain in Membrane Lifetimes)

<table>
<thead>
<tr>
<th>Variables</th>
<th>Approx Value</th>
<th>Year 1</th>
<th>Year 2</th>
<th>Year 3</th>
<th>Year 4</th>
<th>Year 5</th>
<th>Year 6</th>
<th>Year 7</th>
<th>Year 8</th>
<th>Year 9</th>
<th>Year 10</th>
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<td>320</td>
<td>480</td>
<td>640</td>
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<td>Labor Cost</td>
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<td>17920</td>
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<td>53760</td>
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<td>89600</td>
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<tr>
<td>Equipment Cost</td>
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<td>-100</td>
<td>-100</td>
<td>-100</td>
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<tr>
<td>Sum</td>
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<td>144540</td>
<td>162620</td>
<td>180700</td>
<td></td>
</tr>
</tbody>
</table>

**Assumptions:**

1. Labor hours saved are used elsewhere (this may not be true during overnight hours)
2. Tank heater cost approx $2000 to buy and $100/year to maintain
3. Each cleaning cost approximately $20 in chemicals
4. Approximately 16 cleanings are performed per year (4 on each skid)
5. Each cleaning takes approximately 22 hours to complete (Stage 1)
6. Labor hours cost approximately $20
Table 11: Model to Estimate 10 Year Cost Saving to Dunedin (Assume 20% Gain in Membrane Lifetimes)

<table>
<thead>
<tr>
<th>Variables</th>
<th>Approx Value</th>
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<th>Year 2</th>
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<th>Year 8</th>
<th>Year 9</th>
<th>Year 10</th>
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<tbody>
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<td>144540</td>
<td>162620</td>
<td>317200</td>
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</tr>
</tbody>
</table>

Assumptions:

1. Labor hours saved are used elsewhere (this may not be true during overnight hours)
2. Tank heater cost approx $2000 to buy and $100/year to maintain
3. Each cleaning cost approximately $20 in chemicals
4. Approximately 16 cleanings are performed per year (4 on each skid)
5. Each cleaning takes approximately 22 hours to complete (Stage 1)
6. Labor hours cost approximately $20
7. Membranes Are Purchased Once in 10 Year Period
Table 12: Model to Estimate 10 Year Cost Saving to Florida (Assume No Gain in Membrane Lifetimes)

<table>
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<tr>
<th>Variables</th>
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</thead>
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<td>Dunedin's Cost Savings/10 year</td>
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</tr>
<tr>
<td>Comparable RO Plants in FL</td>
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<tr>
<td>FL Savings/10 years</td>
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</table>

Assumptions

1. Most plants clean at ambient temperature
2. One fifth of the RO softening plants are comparable to Dunedin in terms of cost and protocol

Table 13: Model to Estimate 10 Year Cost Saving to Florida (Assume 20% Gain in Membrane Lifetimes)

<table>
<thead>
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<th>Variables</th>
<th>Approx Value</th>
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</thead>
<tbody>
<tr>
<td>Dunedin's Cost Savings/10 year</td>
<td>317200</td>
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<tr>
<td>Comparable RO Plants in FL</td>
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</tr>
<tr>
<td>FL Savings/10 years</td>
<td>1903200</td>
</tr>
</tbody>
</table>

Assumptions

1. Most plants clean at ambient temperature
2. One fifth of the RO softening plants are comparable to Dunedin in terms of cost and protocol
5.4 Future Research

This study was an important first step in tying biofilm removal to membrane performance. Further studies will be necessary to more completely understand the relationship between performance and removal and to optimize removal at the skid level.

A more complete characterization of the biofilm would be useful. If the biofilm contains divalent cations, they could be strengthening the biofilm. It is likely that this is the case because the feedwater has high concentrations of calcium and magnesium. It would be interesting to find out what species of bacteria inhabit the biofilm and how they affect the quantity and types of protein and carbohydrate present. Targeted enzyme treatments could be used if more were known about the specific carbohydrates in the biofilm. This information would be useful to Dunedin and be applicable to biofilm remediation elsewhere.

Further research is planned on the FSM, and a temperature control unit was procured to limit the effect of temperature on the results. This will prevent us from having to do tricky temperature correction calculations.

After other mechanical problems are fixed, I recommend a pH dependent experiments on the FSM and SECS that would better match the Bench Tests. It would be interesting to see if performance improvement were matched exactly to increased removal. It would also be useful to measure the removal of scale in a similar fashion to protein and carbohydrate on the Bench Tests.

In order to determine the optimal cleaning time, experiments will need to be extended to at least two hours. All cleaning runs should be
performed at ambient and elevated temperature to confirm our original findings.

These stages will require considerable work, but they will provide invaluable information about optimization that will be necessary before moving on the SECS. Dunedin has a limited amount of membranes that can be sacrificed for testing, so it is important to get the most out of the SECS runs. Once the SECS has been perfected, it will almost certainly yield results that are directly applicable to cleaning and the skid level.

Russell Ferlita and Michael Keen will be running a related experiment at Dunedin to try to optimize the process, as a whole. Part of this study will aim to reduce fouling rather than to remove it from the membranes.

Another area of research that should be pursued is re-fouling potential. It is likely that fouling will occur more quickly when the membrane surface is conditioned by a biofilm layer. Even if all the bacteria in a biofilm have been inactivated by biocides, it is reasonable to assume that secondary adhesion of new bacteria will occur if the biofilm has not been completely removed from the membrane surface. Moreover, the presence of EPS will likely facilitate growth of more biofilm. More complete EPS removal will likely lead to longer times between cleaning because fouling will occur more slowly.

I sincerely hope that my research will have a positive impact on the cleaning protocol for City of Dunedin’s water treatment plant. I am sure that, at the very least, my work will benefit others that explore the issue of membrane cleaning and biofouling at Dunedin and elsewhere.
Literature Cited


Separations Systems Technology (SST) and Orange County Water District (OCWD) (2000). *Polyamide Reverse Osmosis Membrane Fouling and Its Prevention: Oxidation-Resistant Membrane Development, Membrane Surface Smoothing, and Enhanced Membrane Hydrophilicity*. (SST REPORT NO. 1098-1)


Appendices
Appendix 1: Assay Descriptions

From OCWD

Title:

Carbohydrate Assay

Objective:
The purpose of this analysis is to measure the total carbohydrate concentration of a sample in question.

Reagents:

Phenol Reagent
A 25g aliquot of ultra-pure phenol is dissolved in 500mL DI water. Store in an all-glass container that will prevent exposure to light

Sulfuric Acid Reagent
2.5g of Hydrazine Sulfate in dissolved in 500mL Concentrated Sulfuric Acid

Sample Preparation:
1. A measured sample, mass or area depending on desired units, is placed into a vial
2. 3mL 0.1% Sodium Pyruvate is added to the sample
3. The sample is then sonicated for 10 minutes
4. The sample is vortex mixed prior to removal of any sample
Appendix 1 (Continued)

**Method:**

1. A 0.5mL aliquot of sample is added to a 100x15mm test tube
2. A 0.5mL aliquot of the Phenol Reagent is added to sample
3. A 2.5mL aliquot of the sulfuric acid reagent is rapidly added to the sample from a pipette while rapidly vortex mixing.
   
   **Note:** use a pipette pump that will allow complete rapid delivery of sulfuric acid reagent, taking care not to break tube with pipette tip.

   **Caution:** The sulfuric acid reagent generates excessive amounts of heat. Use proper safety attire and carry out the reaction in a fume hood.

4. The tubes are then covered with aluminum foil and allowed to cool at room temperature in a dark place for one hour (color is stable for 24 hours)
5. The optical density of the sample is measured at 490nm using a UV-VIS spectrophotometer
Appendix 1 (Continued)

**Calibration Curve:**
A stock solution of glucose (dextrose) is prepared by dissolving 0.01g in 100mL DI water. The following table is used for the calibration curve of the concentration of carbohydrates. Micro-pipetters and cuvets are used to make the dilutions/measure absorption spectra. Calibration samples are run in triplicate to ensure reproducibility of the data.

<table>
<thead>
<tr>
<th>Concentration</th>
<th>mL Dextrose Stock Solution</th>
<th>mL DI Water</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sugars (Dextrose)</td>
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<td>500</td>
</tr>
<tr>
<td>70</td>
<td>350</td>
<td>150</td>
</tr>
<tr>
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<td>5</td>
<td>450</td>
</tr>
<tr>
<td>0</td>
<td>0</td>
<td>500</td>
</tr>
</tbody>
</table>

Reference:
Appendix 1 (Continued)
From OCWD

Title:

Lowry Protein Assay

Objective:
The purpose of this analysis is to measure the total protein concentration of a sample in question.

Reagents:

4% Sodium Carbonate in 0.2N Sodium Hydroxide
- 0.8g NaOH dissolved in 100mL DI water
- 4.0g Na$_2$CO$_3$ dissolved in 96mL NaOH solution

2% Copper Sulfate
- 1.0g CuSO$_4$ dissolved in 49mL DI water

4% Sodium Tartrate
- 2.0g Sodium Tartrate dissolved in 48mL DI water (potassium tartrate may also be used)

Reagent D
- 10mL Reagent A, 0.1mL Reagent B, and 0.1mL Reagent C

Reagent E
- 1:1 mixture of Folin’s Reagent to DI water
Appendix 1 (Continued)

**Sample Preparation:**

1. A measured sample, mass or area depending on desired units, is placed into a vial
2. 3mL 0.1% Sodium Pyruvate is added to the sample
3. The sample is then sonicated for 10 minutes
4. The sample is vortex mixed prior to removal of any sample

**Method:**

1. 2.0mL of Reagent D is added to 2.0mL sample
2. Mixture is vortex mixed
3. Sample is allowed to sit for 10 minutes
4. 0.4mL Reagent E is added to the mixture
5. Sample is vortex mixed and allowed to sit for 30 minutes
6. The optical density of the sample is measured at 550nm using a UV-VIS spectrophotometer
Appendix 1 (Continued)

**Calibration Curve:**

A stock solution of Bovine Serum Albumin (BSA) is prepared by dissolving 0.05g in 100mL DI water, making sure to gently agitate as to prevent foaming of sample. The following table is used for the calibration curve of the concentration of protein. Micro-pipetters and cuvets are used to make the dilutions/measure absorption spectra. Calibration samples are run in triplicate to ensure reproducibility of the data.

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<thead>
<tr>
<th>mg/L Concentration Protein (BSA)</th>
<th>mL BSA Stock Solution</th>
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<tbody>
<tr>
<td>100</td>
<td>1.00</td>
<td>4.00</td>
</tr>
<tr>
<td>75</td>
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<td>0</td>
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</tbody>
</table>

**References:**

Appendix 2: OCWD Autopsy Procedures

(Prepared by Orange County Water District)

Light Microscopy:
Light microscopy was performed with an Olympus SZ-40 dissecting microscope and an Olympus AX-70 upright microscope equipped for surface illumination. Images were acquired using an Optronics VI-470 video camera and digitized using a Flashpoint 128 framegrabber.

ATR-FTIR:
Membrane swatches were cut from the feed, middle and brine sections of the fouled Koch reverse osmosis element. Swatches were placed in plastic petri dishes and dried in a glovebox purged with compressed air passed through a Balston drier. A swatch of the unused membrane was placed in a 20 mL scintillation vial and sonicated for 30 min in 1 mM sodium chloride solution. The NaCl solution was changed after 15 min. The swatch was dried as described above. Spectra of polymer separations membranes were obtained by attenuated total reflection Fourier transform infrared (ATR/FTIR) spectrometry (Magna 550, Thermo Electron, Madison, WI). The small pieces of membrane were pressed against a 45° single reflection germanium (Ge) ThunderDome internal reflection element (IRE) (Thermo Spectra-Tech). Single beam spectra (256 scans at 4-cm⁻¹ resolution) were ratioed against a bare Ge background spectrum, converted to absorbance, ATR corrected and baseline corrected utilizing GRAMS/32 software (Version 7.02, Thermo Galactic, Salem, NH). Difference spectra were obtained by digitally subtracting a reference spectrum of the unused polyamide membrane.
Appendix 2 (Continued)

Protein/Carbohydrate Analysis:
Membrane swatches recovered from the feed, middle and brine end of the RO leaf were divided into strips of known surface area (between 6 and 9 cm$^2$). The strips from each swatch were more finely divided and placed in 22 mm scintillation vials, and 1.5 ml of 0.1% sodium pyrophosphate in mineral salts buffer added to enhance desorption of material from the membrane surface. The vials were sonicated 10 minutes to dislodge foulants, and the resulting suspension sampled for protein and carbohydrate analysis.

Protein was determined as per Lowery et. al., 1951; carbohydrate was determined by the method described by Strickland and Parsons, 1968. Mass recovered was in all cases normalized with respect to membrane surface area.

Microbial Community Profile Analysis Method:
Bacteria from 1 liter of feed water were recovered on 0.2u filters. Bacteria from 1 L of sand filter backwash were recovered by centrifugation at 12,000 RPM for 10 minutes. Bacteria on membrane samples from the feed, middle and brine ends of the leaf were recovered by cutting membrane swatches. Membrane swatches, filter material and pelleted material were extracted using a MoBio Soil DNA extraction kit to recover total DNA. Extracts were normalized to constant DNA by UV 260nm absorption. Aliquots of the normalized extracts were amplified using a fluorescent tagged “Universal” 16S rRNA PCR primer. Resultant amplicons were cut with $Dde1$ endonuclease, and the resulting fragments were separated and sized
Appendix 2 (Continued)

using capillary electrophoresis with fluorescent detection to generate electropherograms representing the total microbial population in the extracted samples.

Electropherogram patterns were compared using dendritic cluster analysis using both the number of fragments and the relative intensity of signal in each fragment (semi-quantitative representation of population density). In addition, several community diversity indices were also computed for comparison purposes.
Appendix 3: Phone Survey to Other Water Treatment Plants

Chemical Cleaning Phone Questionnaire

Interviewer Name: ____________________________
Date of Interview: __________________________

Pre-questionnaire

Do you treat seawater, brackish water, or freshwater? (Circle)

Do you have a biofouling issue? (Circle Y or N)

Only complete survey for brackish water or freshwater facilities.

Facility Information

Facility Name:
____________________________________________________________

Facility Location:
____________________________________________________________

Name of Operations Supervisor:
____________________________________________________________

Phone Number: ___________  Email: ______________________________

Flow Rate for Plant: _______________  Built Out Flow: _______________
Appendix 3 (Continued)

Membrane Information

Membrane Make: __________ Membrane Model: ________________

Membrane Dimensions: _______ Year(s) Purchased: ____________

Membrane Configuration Information

How many stages? ______________ Array setup? ________________

Number of Skids/Trains: ___ Number of Membranes per Pressure Vessel: ___

Do you rotate skids? (Circle Y or N)

If so, how often do you rotate? ____________

If so, how do you preserve the membranes?

_________________________________________________________________________
Appendix 3 (Continued)

**System Settings (Per Skid/Train)**

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<thead>
<tr>
<th></th>
<th>Skid 1</th>
<th>Skid 2</th>
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<tbody>
<tr>
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<td>$\Delta P$</td>
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<td>NPF (Normalized Permeate Flow)</td>
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<td>MTC (Normalized Flux)</td>
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**Pretreatment Information**

Do you use Microfiltration prior to Reverse Osmosis? (Circle Y or N)

If so, what filter size? _______ Nominal or Absolute (Circle)

<table>
<thead>
<tr>
<th>Chemical</th>
<th>Concentration in Feed</th>
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<tr>
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<tr>
<td></td>
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</tr>
</tbody>
</table>
Appendix 3 (Continued)

**Cleaning Information**

What determines when next cleaning is performed? (NPF, ΔP, etc.):
_____________________________________________________________
_____________________________________________________________
_____________________________________________________________

How often do you clean?
_____________________________________________________________

Size of Tank:
_____________________________________________________________

Protocol:

<table>
<thead>
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<th>Physical Parameters</th>
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Appendix 3 (Continued)

<table>
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<th>Chemical Parameters</th>
<th>Recirculation Duration</th>
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<th>Temp</th>
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<th>Forward Flush of Backwash After Cleaning</th>
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</tr>
</tbody>
</table>

Do you know of any other plants that I should survey?

________________________________________________________
________________________________________________________
________________________________________________________
Appendix 4: Koch TFC 9921-S Membrane Specification Sheet

Product Specification Sheet
TFC® 9921S-400 Membrane Softening

MgSO₄ REJECTION: 99%
NaCl REJECTION: 85-90%
PRODUCTIVITY: 8,000 gpd (30.3 m³/d)
MEMBRANE ACTIVE AREA: 400 ft² (37.2 m²)
SPACER THICKNESS: 31 mil (0.79 mm)

Test conditions:
1. Mixed feed with 700 mg/l TDS of which at least 45% are monovalent ions, at 80 psi (552 kPa) applied pressure, 15% recovery, 77°F (25°C) and pH 7.5. Data are collected after 30 minutes of operation. Rejection values shown are typical.
2. 1000 mg/l MgSO₄ in distilled water, at 80 psi (552 kPa) applied pressure, 15% recovery, 77°F (25°C) and pH 7.5. Data are collected after 30 minutes of operation. Rejection values shown are typical.

TFC®-S softening membrane is used in applications where softening (hardness removal) and organic reduction are the main treatment objectives.

see reverse side for important product technical and warranty information
Appendix 4 (Continued)

Technical Information

TFC® 9921S-400 Membrane Softening

1. Individual element productivity may vary ±20-15% of the nominal value shown on the front side of this document.

2. Allowable operating pH range: 4.0 to 11. Cleaning pH range: 2.5 to 11. Refer to Koch Membrane Systems Cleaning Instructions for additional information.

3. Maximum operating pressure: 350 psi (2,410 kPa). Operation at any pressure below 350 psi (2,410 kPa) is allowed provided the operation is within the hydraulic limits stated in 4 and 9 below.

4. Maximum recommended differential pressure across any element is 10 psi (69 kPa). Maximum allowable differential pressure across any length pressure vessel is 60 psi (413 kPa).

5. Allowable feedwater temperature range: 1°C to 45°C (34°F to 113°F). The effect of temperature on net operating pressure and/or permeate productivity can be calculated from Koch Membrane Systems Bulletin, TEMPERATURE EFFECT.

6. Exposure of TFC®-S membrane to free chlorine or other similar oxidizing agents is not recommended. Sodium metabisulfite is the preferred chemical reducing agent for chlorine or other similar oxidizing agents. Contact Koch Membrane Systems for additional information.

7. Elements may be cleaned with anionic or nonionic surfactants. Cationic surfactants should be avoided as irreversible fouling may occur.

8. During element installation, use only glycerin or water as a lubricant. Do not use petroleum or vegetable based oils or solvents for brine seal or O-ring lubrication as damage to the element may occur and void the warranty.

9. Maximum recommended recovery rate for any pressure tube in the system as a function of the number of elements per tube:

<table>
<thead>
<tr>
<th>Elements/tube</th>
<th>One</th>
<th>Two</th>
<th>Three</th>
<th>Four</th>
<th>Five</th>
<th>Six</th>
</tr>
</thead>
<tbody>
<tr>
<td>Maximum recovery (%)</td>
<td>17</td>
<td>29</td>
<td>38</td>
<td>44</td>
<td>49</td>
<td>53</td>
</tr>
</tbody>
</table>

10. Operation at recoveries greater than the guideline maximums stated in 9 may result in excessive boundary layer conditions or brine concentrations. Contact your distributor or Koch Membrane Systems for assistance.

11. Elements are provided with a feed channel spacer thickness of 31-mil nominal.

Koch Membrane Systems

revision 1, 2002
Appendix 5: Pre and Post Tests for All FSM Cleanings

This appendix contains graphs that illustrate the conditions during the pre and post tests for cleanings on the FSM. The first graph shows the difference between temperature corrected specific flux and raw specific flux over time. The second graph shows the difference between temperature corrected percent rejection and raw percent rejection over time. The third graph illustrates how temperature changes over time.
Figure 29: Pre Cleaning Data for 2/19/07 (15 min, NaOH, Ambient Temp)
Figure 30: Post Cleaning Data for 2/19/07 (15 min, NaOH, Ambient Temp)
Figure 31: Pre Cleaning Data for 3/26/07 (15min, NaOH, Ambient Temp)
Appendix 5 (Continued)

Figure 32: Post Cleaning Data for 3/26/07 (15min, NaOH, Elevated Temp)
Appendix 5 (Continued)

Figure 33: Pre Cleaning Data for 2/19/07 (30 min, NaOH, Ambient Temp)
Figure 34: Post Cleaning Data for 2/19/07 (30 min, NaOH, Ambient Temp)
Figure 35: Pre Cleaning Data for 3/26/07 (30 min, NaOH, Ambient Temp)
Figure 36: Post Cleaning Data for 3/26/07 (30 min, NaOH, Ambient Temp)
Appendix 5 (Continued)

Figure 37: Pre Cleaning Data for 5/02/07 (45 min, NaOH, Ambient Temp)
Figure 38: Post Cleaning Data for 5/02/07 (45 min, NaOH, Ambient Temp)
Figure 39: Pre Cleaning Data for 5/02/07 (45 min, NaOH, Ambient Temp)
Figure 40: Post Cleaning Data for 5/02/07 (45 min, NaOH, Ambient Temp)
Appendix 5 (Continued)

Figure 41: Pre Cleaning Data for 3/25/07 (60 min, NaOH, Ambient Temp)
Figure 42: Post Cleaning Data for 3/25/07 (60 min, NaOH, Ambient Temp)
Figure 43: Pre Cleaning Data for 5/4/07 (60 min, NaOH, Ambient Temp)
Appendix 5 (Continued)

Figure 44: Post Cleaning Data for 5/4/07 (60 min, NaOH, Ambient Temp)
Appendix 5 (Continued)

Figure 45: Pre Cleaning Data for 2/18/07 (15 min, NaOH, Elevated Temp)
Appendix 5 (Continued)

Figure 46: Post Cleaning Data for 2/18/07 (15 min, NaOH, Elevated Temp)
Figure 47: Pre Cleaning Data for 3/20/07 (15 min, NaOH, Elevated Temp)
Figure 48: Post Cleaning Data for 3/20/07 (15 min, NaOH, Elevated Temp)
Appendix 5 (Continued)

Figure 49: Pre Cleaning Data for 2/18/07 (30 min, NaOH, Elevated Temp)
Appendix 5 (Continued)

Figure 50: Post Cleaning Data for 2/18/07 (30 min, NaOH, Elevated Temp)
Figure 51: Pre Cleaning Data for 3/13/07 (30 min, NaOH, Elevated Temp)
Figure 52: Post Cleaning Data for 3/13/07 (30 min, NaOH, Elevated Temp)
Figure 53: Pre Cleaning Data for 2/23/07 (45 min, NaOH, Elevated Temp)
Appendix 5 (Continued)

Figure 54: Post Cleaning Data for 2/23/07 (45 min, NaOH, Elevated Temp)
Appendix 5 (Continued)

**Figure 55: Pre Cleaning Data for 5/06/07 (45 min, NaOH, Elevated Temp)**

[Graphs showing specific flux, percent rejection, and temperature over time]
Appendix 5 (Continued)

Figure 56: Post Cleaning Data for 5/06/07 (45 min, NaOH, Elevated Temp)
Figure 57: Pre Cleaning Data for 3/13/07 (60 min, NaOH, Elevated Temp)
Figure 58: Post Cleaning Data for 3/13/07 (60 min, NaOH, Elevated Temp)
Appendix 5 (Continued)

Figure 59: Pre Cleaning Data for 5/6/07 (60 min, NaOH, Elevated Temp)
Appendix 5 (Continued)

Figure 60: Post Cleaning Data for 5/6/07 (60 min, NaOH, Elevated Temp)
Figure 61: Pre Cleaning Data for 3/30/07 (15 min, Citric Acid, Elevated Temp)
Appendix 5 (Continued)

Figure 62: Post Cleaning Data for 3/30/07 (15 min, Citric Acid, Elevated Temp)
Figure 63: Pre Cleaning Data for 5/8/07 (15 min, Citric Acid, Elevated Temp)
Appendix 5 (Continued)

Figure 64: Post Cleaning Data for 5/8/07 (15 min, Citric Acid, Elevated Temp)
Figure 65: Pre Cleaning Data for 2/13/07 (30 min, Citric Acid, Elevated Temp)
Figure 66: Post Cleaning Data for 2/13/07 (30 min, Citric Acid, Elevated Temp)
Appendix 5 (Continued)

Figure 67: Pre Cleaning Data for 3/30/07 (30 min, Citric Acid, Elevated Temp)
Figure 68: Post Cleaning Data for 3/30/07 (30 min, Citric Acid, Elevated Temp)
Appendix 5 (Continued)

Figure 69: Pre Cleaning Data for 5/10/07 (45 min, Fisher Detergent, Elevated Temp)
Figure 70: Post Cleaning Data for 5/10/07 (45 min, Fisher Detergent, Elevated Temp)
Appendix 5 (Continued)

Figure 71: Pre Cleaning Data for 5/10/07 (45 min, Fisher Detergent, Elevated Temp)
Figure 72: Post Cleaning Data for 5/10/07 (45 min, Fisher Detergent, Elevated Temp)
Figure 73: Pre Cleaning Data for 2/26/07 (45 min, KochKleen, Ambient Temp)
Appendix 5 (Continued)

Figure 74: Post Cleaning Data for 2/26/07 (45 min, KochKleen, Ambient Temp)
Figure 75: Pre Cleaning Data for 5/4/07 (45 min, KochKleen, Ambient Temp)
Figure 76: Post Cleaning Data for 5/4/07 (45 min, KochKleen, Ambient Temp)
Figure 77: Pre Cleaning Data for 3/2/07 (45 min, KochKleen, Elevated Temp)
Figure 78: Post Cleaning Data for 3/2/07 (45 min, KochKleen, Elevated Temp)
Appendix 5 (Continued)

**Figure 79: Pre Cleaning Data for 3/6/07 (45 min, KochKleen, Elevated Temp)**
Figure 80: Post Cleaning Data for 3/6/07 (45 min, KochKleen, Elevated Temp)
Figure 81: Pre Cleaning Data for 3/27/07 (15 min, Permeate, Ambient Temp)
Figure 82: Post Cleaning Data for 3/27/07 (15 min, Permeate, Ambient Temp)
Figure 83: Pre Cleaning Data for 5/8/07 (15 min, Permeate, Ambient Temp)
Figure 84: Post Cleaning Data for 5/8/07 (15 min, Permeate, Ambient Temp)
Figure 85: Pre Cleaning Data for 3/9/07 (30 min, Permeate, Ambient Temp)
Appendix 5 (Continued)

Figure 86: Post Cleaning Data for 3/9/07 (30 min, Permeate, Ambient Temp)
Figure 87: Pre Cleaning Data for 3/9/07 (30 min, Permeate, Ambient Temp)
Figure 88: Post Cleaning Data for 3/9/07 (30 min, Permeate, Ambient Temp)
Appendix 5 (Continued)

Figure 89: Pre Cleaning Data for 2/23/07 (45 min, Permeate, Ambient Temp)
Figure 90: Post Cleaning Data for 2/23/07 (45 min, Permeate, Ambient Temp)
Figure 91: Pre Cleaning Data for 5/8/07 (45 min, Permeate, Ambient Temp)
Figure 92: Post Cleaning Data for 5/8/07 (45 min, Permeate, Ambient Temp)