Modeling Of Membrane Solute Mass Transfer In Ro/nf Membrane Systems

Yu Zhao
University of Central Florida

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MODELING OF MEMBRANE SOLUTE MASS TRANSFER
IN NF/RO MEMBRANE SYSTEMS

by

YU ZHAO
B.S. Tongji University, 1994
M.S. Tongji University, 1997

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ABSTRACT

Five articles describing the impact of surface characteristics, and development of mass transfer models for diffusion controlled membrane applications are published in this dissertation.

Article 1 (Chapter 3) describes the impact of membrane surface characteristics and NOM on membrane performance for varying pretreatment and membranes during a field study. Surface charge, hydrophobicity and roughness varied significantly among the four membranes used in the study. Membrane surface characteristics, NOM and SUVA measurements were used to describe mass transfer in a low pressure RO integrated membrane system. Inorganic and organic solute and water mass transfer coefficients were systematically investigated for dependence on membrane surface properties and NOM mass loading. Inorganic MTCs were accurately described by a Gaussian distribution curve. Water productivity, NOM rejection and inorganic rejection increased as membrane surface charge and NOM loading increased. Inorganic MTCs were also correlated to surface hydrophobicity and surface roughness. The permeability change of identical membranes was related to NOM loading, hydrophobicity and roughness. Organic fouling as measured by water, organic and inorganic mass transfer was less for membranes with higher hydrophilicity and roughness.

Article 2 (Chapter 4) describes the development of a diffusion controlled solute mass transfer model to assess membrane performance over time. The changing mass transfer characteristics of four low-pressure reverse osmosis (LPRO) membranes was correlated to feed stream water quality in a 2000 hour pilot study. Solute mass transfer coefficients (MTCs) were correlated to initial solute MTCs, solute charge, feed water temperature, monochloramine loading and organic loading (UV254). The model can be used to predict cleaning frequency,
permeate water quality and sensitivity of permeate water quality to variation of temperature, organic and monochloramine mass loading.

Article 3 (Chapter 5) describes a comparison of the long standing method of assessing membrane performance (ASTM D 45160 and another approach using mass transfer coefficients (MTCs) from the homogenous solution diffusion model (HSDM) using a common data set, water productivity and standardized salt passage. Both methods were shown to provide identical assessments of water productivity, however different assessments of salt passage. ASTM D 4516 salt passage is normalized for pressure and concentration and does not show the effects of flux, recovery, temperature or specific foulants on salt passage. However the MTC HSDM method is shown to consider all those effects and can be easily used to predict membrane performance at different sites and times of operation, whereas ASTM D 45160 can not. The HSDM MTC method of membrane evaluation is more versatile for assessment of membrane performance at varying sites and changing operational conditions.

Article 4 (Chapter 6) describes the development of a fully integrated membrane mass transfer model that considers concentration, recovery and osmotic pressure for prediction of permeate water quality and required feed stream pressures. Osmotic pressure is incorporated into the model using correction coefficients that are calculated from boundary conditions determined from stream osmotic pressures of the feed and concentrate streams. Comparison to homogenous solution diffusion model (HSDM) with and without consideration of osmotic pressure and verification of IOPM using independently developed data from full and pilot scale plants is presented. The numerical simulation and statistical assessment show that osmotic pressure corrected models are superior to none-osmotic pressure corrected models, and that IOPM improves model predictability.
Article 5 (Chapter 7) describes the development and comparison of a modified solution diffusion model and two newly developed artificial neural network models to existing mechanistic or empirical models that predict finished water quality for diffusion controlled membranes, which are generally restricted to specific solute MTCs that are site and stage specific. These models compensate for the effects of system flux, recovery and feed water quality on solute MTC and predict permeate water quality more accurately than existing models.
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LIST OF SYMBOLS

\( A_{m(i)} \) = Membrane surface area at small unit i \((M^2)\);
\( C_c \) = Concentrate solute concentration \((M/ L^3)\)
\( C_f \) = Feed concentration \((M/ L^3)\)
\( C_{fi} \) = Feed solute concentration at membrane inlet \((M/ L^3)\)
\( C_{NH2Cl} \) = Chloramines concentration of membrane feed stream, \((mg/L C L2)\).
\( C_p \) = Permeate stream solute concentration \((M/ L^3)\)
\( C_{turb} \) = Turbidity of membrane feed stream, \((ntu)\).
\( C_{UV254} \) = UV254 of membrane feed stream, \((1/cm)\).
\( dC \) = Increment of bulk concentration in finite membrane unit;
\( \Delta X \) = Concentration gradient \((M/ L^3)\), \((( C_f + C_c)/2 - C_p)\)
\( dR \) = Increment of recovery in finite membrane unit;
\( F_w \) = Water flux \((L^3/ L^2t)\)
\( F_wC_{NH2Cl} \) = Chloramines loading
\( F_wC_{turb} \) = Turbidity loading
\( F_wC_{UV254} \) = UV254 organic loading
\( F_wt \) = Water loading
\( K_s \) = Solute MTC \((L/t)\)
\( K_{s25} \) = \( K_s \) value at standardized temperature 25 °C
\( K_{st} \) = \( K_s \) value at temperature \( T \).
\( K_{TDS} \) = TDS osmotic pressure coefficient
\( K_w \) = Solvent MTC \((L^2t/M)\)
\( Q_c \) = Concentrate stream flow \((L^3/t)\)
\( Q_f \) = Feed stream flow \((L^3/t)\)
\( Q_p \) = Permeate flow \((L^3/t)\)
\( R \) = Recovery
\( r \) = Recycle rate=\( Q_r/ Q_f \)
\( T \) = Membrane run time, \((hr)\)
\( T \) = Temperature in °C
\( \Delta C \) = Concentration gradient \((M/ L^3)\)
\( \Delta P \) = Pressure gradient \((L)\)
\( \Delta \Pi \) = Osmotic pressure \((L)\)
\( \theta_s \) = Temperature correction factor for solute diffusivity
\( \theta_w \) = Temperature correction factor for productivity
CHAPTER 1: INTRODUCTION

1.1 Problem Statement

Diffusion controlled membrane processes (reverse osmosis (RO) and nanofiltration (NF)) have been employed in an increasing number of applications during the past two decades. NF/RO has become a competitive technology to traditional water treatment processes because of (1) highly effective in removing most inorganic and organic contents to produce ultra-pure water which complies with existing and future drinking water regulations; (2) capable to treat all fields of source waters from sea water, brackish ground water and surface water; (3) versatile for all purpose of water quality control in removing Total Dissolved Solids (TDS), heavy metals, pesticides, disinfection by-product (DBP), natural organic matter (NOM) and other Volatile Organic Chemicals (VOC).

There are different theories and models have been developed to model mass transfer describing flux of water and salt through the membrane. Researchers in recent years have paid a great deal of attention to seeking more accurate models in that modeling performance of NF/RO processes is beneficial to pre-design studies, design, operation and other facets of the advancements in water treatment. In diffusion controlled membrane process, the diffusion solution models are most widely used and were based on a few basic principles of diffusion, convection, film theory and electro-neutrality. The parameters used in diffusion solution models are actual operation conditions that can be directly monitored other than some theoretical models which have parameters that are difficult to be measured in reality.

In diffusion solution models, water and solute mass transfer coefficients (MTC) are the two most important parameters that describe permeability of water and solute through the
solvent-membrane film. Theoretically, solute MTCs can be determined by solving model equations or directly estimated by other existing theoretical approaches, but it is much more challenging to model solute MTCs in reality for the following reasons: (1). The solute MTCs are found varying with different feed water qualities, operating conditions, and intrinsically membrane physic-chemical properties, which may sensitive to changes of conditions or time. (2). Variation of the solute MTCs with different water qualities constrains the model application from one system to another. A previous study (Laisure, 1993) reported solute MTCs that determined by the Homogenous solution diffusion model (HSDM) were found both stage specific and site specific. Therefore, it limited HSDM in making accurate prediction of solute permeate concentration by using solute and solvent MTC values from one system to the other different system. (3). Solute MTCs also found dependent on the test unit scale as different operating conditions may exist in these units, consequently, it also limit the model accuracy in membrane scale-up prediction. The difference of inorganic solute MTCs between flat sheet test, single element and large scale units was reported in a previous study (Lovins, 2000), which focused on correlation and modeling of productivity and water quality between laboratory and field scale integrated membrane system.

The solute MTC has been modified to improve solution diffusion model predictability. Several factors, which have reversible or irreversible impacts on solute MTC, have been incorporated into the solution model. As for the reversible impacts, no permanent change that occur on membrane-water film interface or material. Solute MTCs may vary interactively with operating conditions such as flux, recovery, feed water qualities and temperature. The solute MTC has been modified by incorporation of flux and recovery, which significantly reduced model error and enabled a more accurate prediction of pesticide rejection in a pilot scale study
HSDM has been integrated along membrane channel with respect to recovery, which improved predictability at high recovery, (Mulford, 1999); Other alternative approach is to apply HSDM by mathematically divide membrane element into several identical sub-elements, with each sub-element has less than 1% recovery (Chellam and Taylor 2001, Chellam et al 2001). The result of the Chen’s modification was significant. The integration method more accurately represents the feed concentration distribution and was expected to improve predictability at high recovery (Mulford, 1999). The solution diffusion model can be improved as the effects of solute form, osmotic pressure, membrane surface characteristics and flux or recovery on solute mass transfer has not been considered.

Variations of the solute MTC that caused by chemical or mechanical instability is quite often irreversible with respect to changes in membrane material and membrane solvent interface. Membrane material may react with, such as, solvent by the effect of hydrolysis, oxidants by resulting in chemical degradation or bioorganic by causing biological degradation. Moreover, changes affecting solute MTC may happen on membrane and solvent interface during the operation, these changes may include but not limit to such as scaling, colloidal fouling, biological fouling, metal oxide fouling, plugging and membrane corrugation. To model these irreversible changes, most of the recent developments are focused on productivity model (Aimar 1986, Lovins 2000, Christopher 2000), and currently no solute mass transfer model have been developed to assess long term membrane performance and water quality deterioration.

In current diffusion solution models, the effect of osmotic pressure increment along the membrane channel has not been considered. Typical approach is taking linear or log mean concentration approximation to correlate osmotic pressure into net driving force. Although it is recognized when membrane feed water is concentrated continually in membrane channel, the
osmotic pressure is also increased thus reduces flux and increases permeate concentration for diffusion-controlled solutes, little has been done to incorporate this factor into current diffusion solution model.

There are no models that have been developed that incorporate the membrane surface characteristics. Membrane surface characteristics are relative to membrane performance. The membrane surface characteristics are typically modified by manufacturers to enhance the membrane performance. Increasing surface roughness will increase membrane production. Changing charge will alter solute rejection and membrane fouling. Although these effects are well recognized by the water community, few efforts if any have related membrane surface characteristics to the solution diffusion modeling. Since the membrane performance is determined by the properties of the membrane-solution interface, both the membrane surface and solution properties should be considered in modeling. The coefficients in all existing solution models are dependent on membrane surface characteristics in that the coefficients are developed for only that specific membrane, which has unique surface characteristics. On the other hand, the concentration polarization can lead to membrane fouling by causing scaling or gelation of the retained component on the membrane surface (Bhattacharya, 1997). Solutes such as natural organic matter (NOM) and surfactants adsorbed to the membrane have the complex influence on the membrane surface properties (Childress 1996, Amy 1999, Koo et al. 1999, Her et al. 1999). In summary, further development of models considering membrane surface characteristics along with solute interference such as NOM impaction is needed.

American Standard for Testing Materials (ASTM) D 4516-85, a normalization technique for RO permeate flow and salt passage, is currently the basis for all normalization programs available from the membrane manufacturers and water plant operators. ASTM D 4516-85 is
utilized to produce long-term trend of permeate flow and salt passage for evaluating RO membrane performance. ASTM D 4516-85 method has been reported in several technique papers for RO membrane long-term performance evaluation. However, little has been done with comparing the solution diffusion model to this industry-standard for long-term performance evaluation.

Current research efforts have been devoted to membrane separation mechanisms. However, it remains difficult to accurately identify the preponderant physical-chemical phenomena because of the complexity of solvent, solute and membrane characteristics as well as their interactions. Along with the conventional methods to simulate membrane separation, non-mechanism approaches such as artificial neural network models have been developed (Niemi, 1993). Neural network model is a black box type of a correlation method and it does not apply any physical laws thus overcomes the problems of previous complexity. Neural network models are easy to use, and the models typically are site specific.

1.2 Factors Affecting RO/NF Solute Mass Transfer

The objective of this section is to provide a more fundamental understanding of the factors that may affect solute mass transfer in membrane systems, their relationships to the actual physic-chemical complexity, and the resulted limitations of the realistic modeling. The factors that may possibly affect solute MTCs in pressure driven membrane systems are discussed below.

1.2.1 Membrane Physic-chemical Properties

Membrane composition and characteristic are the primary factors that affect MTC; they can be polymeric or ceramic, homogeneous or heterogeneous, and symmetric or thin-film
composite (TFC) (Mulford, Taylor, 2000). For RO/NF applications, cellulose acetate (CA) and polyamide (PA) are two major commercial organic membranes. PA membrane exhibits higher water flux and better salt rejection than CA membrane. The active layer thickness is a primary factor that affects membrane MTC. Typically, thin film composite (TFC) PA membrane has active layer thickness ranges from 0.05-0.1 µm. Active layer thickness of CA membrane is approximately 0.2 µm. The active layer thickness is hard to be measured although several techniques do exist, such as plasma etching or using X-ray photoelectron spectrometry.

Membrane material stability affects solute MTC. CA membrane is quite resistant to chemical disinfectants such as chlorine, but its application is limited to a narrow feed pH range (4-6.5) because of polymer hydrolysis, CA membrane is also susceptible to microbiological attach. On the other hand, PA membrane is sensitive to chlorine even at very low level of chlorine exposure but demonstrate good hydrolytic stability over a wide range of pH (2-11) (Sammon 1984, Parekh 1988, Glater 1994). The exact chemical structure of the film can be identified but limited to some specific chemical components and functionalities.

1.2.2 Solvent and Solute Properties

The solute MTC by the homogeneous surface diffusion theory is expressed as solute diffusivity over film thickness (Weber 1972). Consequently, any solvent (water) and solute properties that are relative to diffusivity and film thickness will affect solute MTC, such as solute form (size and charge), solute concentration, electrostatic phenomena like solute coupling effect and partitioning effect. Theoretical or empirical correlations do exist for determining solute diffusivity value for simple situations like nonelectrolytes or single ion in dilute solution; however, due to a wide spectrum of solutes in reality, solute MTC is determined by experiment
data, consequently such approaches are restricted by the specific system. Moreover, incomplete characterization of feed water composition and unavailability of methods to identify dominant ion pairs can be expected to further complicate mass transfer from multi-solute solutions (Chellam and Taylor, 2001).

1.2.3 Membrane Surface Properties

It has been shown that membrane surface morphology and structure can influence permeability, rejection and colloidal fouling behavior of RO/NF membranes (Vrijenhoek, Hong et al. 2001). The surface properties that researchers believe have the greatest effect on membrane mass transfer are surface charge, surface roughness and hydrophobicity.

The membrane is endowed with fixed surface charges thus the separation mechanism of the process is related to the electrostatic effects between the membrane and the external solutions. Membrane surface charge has a significant effect on membrane performance. Inorganic salts, organic matters and solution pH are all relative to membrane surface charge. Afonoso reported a relationship between the membrane surface charge, $C_M$, and the feed solution concentration, $C_f$, $\ln|C_M| = a + \ln C_f$ (Afonoso et al, 2001). Childress reported surface charge for RO/NF membranes were markedly influenced by adsorption of dissolved natural organic matter (Childress, 1996). pH was also found to correlate well with the zeta potential and a minimum rejection rate around the isoelectric point was observed in laboratory experiment (Childress, 1996, Hagmeyer, 2001).

Surface roughness is related to membrane effective surface area and hydrodynamics near the membrane, and directly correlates to water MTC. More emphasis in previous researches have been put in studying surface properties and their interaction with fouling mechanism, while
less effort has been put in correlating surface roughness to solute MTC. Madaeni reported membrane roughness have a significant effect on membrane solute rejection, membranes of same material, rougher surface obtained higher rejection (around 72%) while smoother surface lower rejection (15%) (Madaeni, 2001).

These works show that surface characteristics and solute form affect solute mass transfer in membrane systems. Incorporating membrane surface characteristics in a solution diffusion model may be a valid alternative for improving prediction of solute mass transfer.

1.2.4 Interface Properties

Concentration polarization effect can be the cause of a substantial reduction in the solute rejection rate and in the permeate flux, the polarization of the components leads to a decrease in the available driving force of the preferentially permeating species across the membrane and an increase for the less permeable species. This reduces the overall efficiency of separation.

A traditional integrated film theory model was developed based on assuming constant solute diffusivity within the boundary layer and non-porous membrane wall. It has been used for the past 30 years to describe concentration polarization in pressure driven membrane systems given the film layer thickness and diffusivity is known. It is questioned that solute diffusivity is also a function of film thickness, and alternatively the diffusivity in traditional film theory represents an integrated diffusivity through the boundary layer (Bhattacharya, 1997) because of the concentration in the layer over the membrane modifies the solute/solvent properties such as viscosity, density and solute molecular diffusivity. Zydney provided more rigorous mathematical work to examine the effects of concentration-dependent viscosity and diffusivity on the stagnant film, and proved the general validity of the film model with two assumptions: 1).
Product of water viscosity and solute diffusivity in the film remains approximately constant; 2). The extent of concentration polarization is not too large (Zydney, 1997). Bhattacharya and Hwang presented an expression of polarization index as the ratio of concentration near the wall and bulk concentration, it is rational thus the polarization index is only a function of flux (Bhattacharya and Hwang 1997).

In addition to the concentration polarization effect, NOM or surfactants that has been adsorbed on membrane surface will affect solute MTCs as described previously.

1.2.5 Module Geometry

Module geometry will certainly affect solute MTCs. Spiral –wound and Hollow-fiber systems are regarded as the two most advantageous membrane modules due to their large surface-to-volume ratio. A spiral-wound module configured by several flat membranes sandwiched between plastic screen supports (known as spacers) and then rolled into a “swiss roll” around a central tube. The edges of the membranes are sealed and the central tube is perforated to allow for recovery of the permeate solute. The resultant spiral-wrap module is fitted into a tubular steel pressure vessel.

Membrane channel height (spacer thickness) is an important factor of module geometry that affects membrane MTC. The small height of its rectangular cross section, when compared with the other channel dimensions of width and length results in a fully developed laminar flow, which leads to a high value of mass transfer resistance or to severe problems of concentration polarization (Geraldes, 2002). Membrane space is typically related to flow hydrodynamics and thus affects membrane MTC. A small membrane space is expected greater turbulence, reduced concentration polarization and thus higher solvent MTC and lower solute MTC. However, this
seemingly straightforward conception may be illusionary, for example, Sablani and co-workers investigated the influence of spacer thickness on membrane permeate flux and its salinity. They reported the solvent MTC decreases by up to 50% in going from a spacer thickness of 0.1168 to 0.0508 cm, for both low salinity water (0% NaCl) and high salinity (5% NaCl) solution, noticeable the results are from testing a 1-m-long pressure vessel applying same membrane but different spacer (Sablani, 2002). Typically, the initial spacer thickness is available from manufacture for new membrane.

1.2.6 Operating Condition

Membrane system flow rate, flux, recovery, feed pressure, pressure drop, transmembrane pressure drop and temperature certainly affect the hydrodynamic conditions of the system. Other operating conditions include such as different chemical dosing including pH control, antiscalant or biocide addition. Membrane systems can be maintained in similar but not possibly identical manner; solute MTCs will greatly be affected by different operating conditions.

Flow rate, flux, recovery, feed pressure, pressure drop, transmembrane pressure drop are interrelated each other and affect solute MTCs by influence on all properties as described in the previous chapter. Temperature may change solvent properties such as solvent viscosity or solute diffusivity as previously described, also it may affect the physical properties of the polymeric membrane such as the pore size and possibly the diffusivity of solvent in the membrane, in addition, the affect on solvent and membrane material may not synchronizing. Goosen reported that polymer membrane is very sensitive to changes in the feed temperature. There was up to a 60% increase in the permeate flux when the feed temperature was increased from 20 to 40°C, interestingly, a minimum flux was observed at an intermediate feed temperature implies that
complex physical changes may be occurring in the membrane as the temperature is increased. (Goosen, 2002).

In summary, a simplified solution diffusion model theoretically defines the performance of a diffusion controlled membrane in terms of two simple coefficients $K_w$ and $K_s$ as constants related to the physical and chemical characteristics of each specific membrane. However, in reality, there are many factors that can affect the MTCs. Membrane-solute-solvent interactions play an important role on the solute mass transfer, and these factors and their effects are complex and mixed.

1.3 Objectives

The work presented in this dissertation was directed toward developing new models for solute mass transfer in NF/RO membranes. The study focused on NF/RO membrane solute mass transfer models. The objectives of this research effort were to:

Model membrane surface characteristic effects on inorganic and organic solute mass transfer. Correlate surface properties to initial membrane mass transfer; correlate surface properties to long-term solute membrane mass transfer variations caused by fouling or combined chlorine degradation. Provide evidence and correlate surface properties to membrane mass transfer variations in conjunction with the effect of feed water qualities, with an emphasis on assessing the effects of natural organic matter. This information is important to delineate a clearer understanding of membrane performance in realistic; conduct a long-term parallel investigation on pilot scale tests with through membrane surface characteristics analysis including surface charge, roughness and hydrophobicity measured in laboratory.
Model membrane performance over time. Develop a solute mass transfer model that can model membrane solute mass transfer deterioration over time, a model that can be used to predict cleaning frequency, permeate water quality and sensitivity of permeate water quality to variation of temperature, organic and monochloramine mass loading.

Evaluate and justify the ASTM D 4516 productivity and salt passage standardization methods for long-term RO performance evaluation. Develop the evaluation methodology using the HSDM MTC for standardizing salt passage, which is more versatile for assessment of membrane performance at varying sites and changing operation.

Develop an integrated diffusion based mass transfer model based on the current solution diffusion models. The new model incorporates concentration, recovery and osmotic pressure in fully integrated approach. Evaluate the new integrated model by numerical simulations. Validate the newly developed model by comparison to HSDM with and without consideration of osmotic pressure using independent data sets from full and pilot scale plants.

Develop hybrid and artificial neural network models to account for the dependency of membrane MTCs on operations or site or stage specific.

Data from the CH2M Hill St. John’s River membrane pilot study as well as previous data from the USEPA ICR data bank and independent UCF laboratory and field studies were used for original model development and validation.
CHAPTER 2: LITERATURE REVIEW AND THEORY OF MEMBRANE DIFFUSION MODELS

Theoretical efforts to predict the $K_s$ value have not met much success. Direct measurements of $K_s$ value other than field measurements are difficult and results are limited by existing technologies such as optical or microelectrode measurements (Murphy et al. 1997). Other theoretical approach of extended Nernst-Plank equation only found applications in Laboratory scale (Gauwbergen, 1997; Straatsma, 2002).

Membrane MTC can be determined from the membrane transport models. In this manner, membrane MTC can be further related to membrane-solution physic-chemical characteristics. The solute MTCs were found relative to membrane feed water qualities. A model for prediction of solute MTCs has been developed using normal distribution and solute molecular weight and charge (Duranceau, 1990). Solute MTCs have been found to change via different solution composition, (Sung, 1993).

Most of these models for NF/RO membranes are developed with fundamental equations that consider a mass balance around the membrane element, pressure driven solvent and concentration gradient driven solute mass transfer, recovery and recycle rate. In fact, these basic parameters are the primary basis for development of existing models. Models have been improved by consideration of some basic principles such as film theory, concentration polarization, solute diffusion, ion coupling and electro-neutrality. A diagram of a NF/RO single element is shown in Figure 2-1. This diagram shows the flow, solute concentration and pressure of the feed, permeate and concentrate streams for a single element.
Figure 2-1 NF/RO flow diagram

\[ F_w = K_w \left( \Delta P - \Delta \Pi \right) \frac{Q_p}{A} \]  \hspace{1cm} Eqn. 2-1

\[ J_i = K_s \Delta C = \frac{Q_p C_p}{A} \]  \hspace{1cm} Eqn. 2-2

\[ R = \frac{Q_p}{Q_f} \]  \hspace{1cm} Eqn. 2-3

\[ Q_f = Q_c + Q_p \]  \hspace{1cm} Eqn. 2-4

\[ Q_f C_f = Q_c C_c + Q_p C_p \]  \hspace{1cm} Eqn. 2-5

\[ r = \frac{Q_r}{Q_f} \]  \hspace{1cm} Eqn. 2-6

Where:

- \( F_w \) = Water flux (L\(^3\)/ L\(^2\)t)
- \( J_i \) = Solute flux (M/ L\(^2\)t)
- \( K_w \) = Solvent MTC (L\(^2\)t/M)
- \( K_s \) = Solute MTC (L/t)
- \( C_f \) = Feed concentration (M/ L\(^3\))
- \( C_c \) = Concentrate concentration (M/ L\(^3\))
- \( C_p \) = Permeate concentration (M/ L\(^3\))
- \( Q_f \) = Feed stream flow (L\(^3\)/t)
- \( Q_c \) = Concentrate stream flow (L\(^3\)/t)
- \( Q_p \) = Permeate stream flow (L\(^3\)/t)
- \( R \) = Recovery
- \( \Delta P \) = Pressure gradient (L)
- \( \Delta \Pi \) = Osmotic pressure (L)
- \( \Delta C \) = Concentration gradient (M/ L\(^3\))
2.1 Size Exclusion Model (SEM)

When solute rejection is independent of flux and recovery as shown in Eqn. 2-7, the size exclusion model as shown in Eqn. 2-8 can be used to describe the solute rejection.

\[
Rej = \frac{C_f - C_p}{C_f} \quad \text{Eqn. 2-7}
\]

\[
C_p = (1-Rej) C_f = \phi C_f \quad \text{Eqn. 2-8}
\]

Permeate concentration can predicted by size exclusion constant \(\phi\).

2.2 Homogenous Solution Diffusion Model (HSDM)

HSDM or linear solution diffusion model is developed by correlation of the average feed concentration to system recovery. The HSDM assumes the solute MTC is independent of pressure. A linear approximation which averaged between the initial feed concentration and final concentration was used to described the solute on the feed side of membrane surface. The permeate concentration can be derived by solving Eqn. 2-1 to Eqn. 2-5 with homogenous feed concentration as related to recovery. The result is given in Eqn. 2-9 and was the first model developed for a high recovery system (Taylor et al. 1987, 1989).

\[
C_p = \frac{K_w C_f}{K_w(\Delta P - \Delta \Pi)\left(\frac{2 - 2R}{2 - R}\right) + K_s} \quad \text{Eqn. 2-9}
\]

\(K_w, K_s, C_p\) as defined before, where as \(C_f\) in Eqn. 2-9 represents concentration of inlet stream.

The HSDM can be utilized to predict permeate concentrations, given the solvent and solute MTC, water recovery, trans-membrane pressure and feed concentration.
The HSDM is based on the mass balance, solvent convection, solute diffusion and film theory for solute accrual on the feed side of the membrane, and also the electro-neutrality of the input and output streams.

If HSDM further consider recycle, Eqn. 2-9 becomes:

\[
C_p = \frac{K_r C_f}{K_w (\Delta P - \Delta \Pi) \left( \frac{(1 + r)(2 - 2R)}{2 + 2r - R} \right) \left( \frac{2 - 2R}{2 - R} \right) + K_s} \tag{Eqn. 2-10}
\]

The HSDM has been modified by combining the Film Theory Model (FTM). FTM consider the increase in solute concentration at the membrane surface due to solute rejection and back diffusion of the solute into the feed stream, which also called concentration polarization near membrane surface.

The HSDM has been modified by Ion Coupling Model (Sung, 1993). The solute MTCs was correlated to the difference of coupled ion free energy at membrane interface and bulk. Coupling Model explains the different performance of multivalent and mono-valence ions (Sung, 1993). Statistically significant discrepancies were reported in inorganic contaminants between theoretical predictions and observations from pilot and full-scale test, which was interpreted by solution electrostatic interactions, ion coupling and complexation (Chellam, 2002).

Integrated HSDM has been developed by integration the recovery along the membrane which simulates the actual feed concentration. HSDM and FTM are based on a linear approximation of average feed concentration, which can produce errors at high recovery (Mulford, 1998). Either the integrated and linear average HSDM or FTM models could be used for simulation of nanofiltration processes (Mulford, 1999).
In the study of pesticide rejection by RO membranes, it was found that the solute MTCs were not constant but dependent on flux and recovery (Taylor, Chen, Mulford, Norris, 2000). $K_s$ is dependent on concentration, flux and recovery for Chen’s work. Chen reported improvement of model predictability by incorporating flux and recovery into the HSDM and FTM solute MTC (Chen, 1998)

2.3 Film Theory Diffusion Model (FTM)

Concentration build up at the membrane-liquid interface is concentration polarization. At steady state, the solute flux is constant through the film and equals the solute flux through the membrane. Eqn. 2-11 considers the material balance, which demonstrated in Figure 2-2.

$$J_i = -D_s \frac{dC}{dx} + C_i F_w$$

Eqn. 2-11

Where:
$D_s$ = Diffusivity
$C_i$ = Concentration from the bulk to the membrane interface
$x$ = Path length or film thickness

Figure 2-2 Film theory diagram

Integration of Eqn. 2-12 by the film boundary conditions yields.
\[
\begin{bmatrix}
C_s - C_p \\
C_b - C_p
\end{bmatrix} = e^{\frac{F_w}{K_b}}
\]  
Eqn. 2-12

Where:
Cp = Solute concentration in the membrane permeate
Cb = Solute concentration in the membrane feed
Cs = Solute concentration at the membrane surface
Fw = Water flux through the membrane
kb = Ds/x = Diffusion coefficient from the surface to the bulk

Solute diffusivity changes with solute concentration, thus diffusivity Ds is also a function of boundary layer thickness. However, in tradition film theory model, diffusivity Ds was assumed as constant in integration. Alternatively, in tradition film theory model Ds in kb represents an integrated diffusivity through the boundary layer. Zydney mathematically proved the kb actually is constant with two assumptions: (1). Product of water viscosity and solute diffusivity in the film remains approximately constant; (2). The extent of concentration polarization is not too large (Zydney, 1997).

There are four ways to estimate the solute back-transport MTC kb as below:

(1). Theoretical expressions for kb can be developed by solving the governing mass transfer equations in the same system but with a non-porous boundary.

(2). Empirical correlations can be developed by fitting film model equation to experimental data in an actual membrane device.

(3). From sources of publication.

(4). Empirical correlations expressed in terms of Sherwood Reynolds and Schmidt numbers. The dimensionless correlations as following.
Sh = a(Sc)^b(Re)^c  \quad \text{Eqn. 2-13}

Where:
Sh = Sherwood number \( k_s h / D_s \)
Re = Reynolds number \( \nu h / \gamma \)
Sc = Schmidt number \( \gamma / D_s \)
h = channel height
\( \nu \) = cross flow velocity
\( D_s \) = solute aqueous diffusivity
\( \gamma \) = kinematic viscosity of water

Method (1) is actually evaluated for a system with no filtration, method (2) is device specific, method (3) is limited to single solute in dilute solution, while method (4) is most widely used as described below in detail. Schmidt number is related to solute MTC assuming mass balance between convective mass transfer across the membrane and solute diffusion. Generalized correlations of mass transfer suggest that the Sherwood number, Sh, is related to the Reynolds number, Re, and Schmidt number, Sc as Eqn. 2-13. The dimensionless correlation as can be determined given membrane channel height and cross flow velocity. Numerous correlations have been reported in literature, Wilke-Chang equation Sh = 0.76(Sc)^{0.50}(Re)^{0.33} assumes that the concentration layer thickness equals channel height (Weber, 1996). Further elaborate relation predicting boundary layer thickness can be found in laboratory scale (Geraldes, 2001). These theoretical efforts have been briefly discussed and do not consider any membrane properties nor the diffusivity of individual solutes in a multi-solute solution.

Thin Film Theory incorporated with the HSDM results in Eqn. 2-14:
\[ C_p = \frac{C_i K_s e^{Fw/k_b}}{K_w (\Delta P - \Delta \pi) \left(\frac{2 - 2R}{2 - R}\right) + k_s e^{Fw/k_b}} \]  

Eqn. 2-14

Similarly, by considering recycle Eqn. 2-14 becomes:

\[ C_p = \frac{C_i K_s e^{Fw/k_b}}{K_w (\Delta P - \Delta \pi) \left[\frac{(1 + r)(2 - 2R)}{2 + 2r - R}\right] + K_s e^{Fw/k_b}} \]  

Eqn. 2-15

2.4 Modified Film Theory Model (MFTM)

While applying the above HSDM and FTM in membrane pilot and plant study on pesticide removal by reverse osmosis, solute rejection was increased from the highest recovery and lowest flux to the lowest recovery and highest flux, which indicated diffusion controlled mechanism for pesticide rejection by nanofiltration. However, it was observed that the prediction error was systematically related to flux and recovery. The solute MTC was empirically modified by incorporation of flux and recovery as shown in Eqn. 2-16, which improved predictability (Chen, 1999).

\[ C_p = \frac{C_i (K_s + A \times Fw + B \times R) e^{Fw/k_b}}{K_w (\Delta P - \Delta \pi) \left(\frac{2 - 2R}{2 - R}\right) + (K_s + A \times Fw + B \times R) e^{Fw/k_b}} \]  

Eqn. 2-16
2.5 Semi-empirical Differential HSDM

Solute MTCs can be determined by membrane laboratory-scale studies using a flat-sheet test. However, flat-sheet tests are often conducted at very low feed water recoveries (e.g. 1%), whereas municipal NF/RO facilities are operated at high feed water recoveries (e.g. 85%). In order to eliminate the errors caused by the geometry and concentration distribution difference between flat-sheet test and municipal facilities, this method conceptually divides the membrane element into several identical sub-elements, so that each sub-element has less than 1% recovery (Chellam, 2002). A linear axial pressure drop as shown in Eqn. 2-17 is assumed to calculate the driving force for permeate flow from each sub-element.

\[
\Delta P(i) = \left( P(1) - (i - 0.5) \frac{P(1) - P(n + 1)}{n} \right)
\]

Eqn. 2-17

Permeate concentration from each small element is calculated by applying HSDM in each sub-element as shown in Eqn. 2-18 through Eqn. 2-20.

\[
J_w(i) = \frac{Q_p(i)}{A} = K_w \Delta P(i)
\]

Eqn. 2-18

\[
Q_j(i) = Q_j(1) - \sum_{j=1}^{i-1} P_p(j)
\]

Eqn. 2-19

\[
C_j(i) = \frac{Q_j(i)C_j(i) - Q_p(i)C_p(i)}{Q_j(i + 1)}
\]

Eqn. 2-20

\[
C_p(i) = \frac{C_t(i)k_s e^{F_w(i)/k_b}}{F_w(i)\left(\frac{2 - 2R(i)}{2 - R(i)}\right) + k_s e^{F_w(i)/k_b}}
\]

Eqn. 2-21

Once the local permeate concentration in each sub-element was determined from Eqn. 2-21, the permeate concentration was calculated using Eqn.2-22:
\[ C_p = \frac{\sum_{i=1}^{n} Q_p(i) C_p(i)}{\sum_{i=1}^{n} J_w(i) A_m(i)} \quad \text{Eqn.2-22} \]

2.6 Integrated Homogenous Solution Diffusion Model (IHSDM)

One effort to estimate membrane actual feed concentration was developed by integrating the feed concentration with respect to recovery, (Mulford, 1998), as shown in Eqn. 2-23 through Eqn. 2-26.

\[ C_{\beta} = \frac{C_{f0}}{1 - \left( \frac{RF_w}{F_w + K_s} \right)} \quad \text{Eqn. 2-23} \]

Integrating Eqn. 2-23 with respect to R

\[ C_{f_{avg}} = \frac{C_{f0}}{-RF_w} \ln \left( \frac{RF_w}{F_w + K_s} \right) = C_b \quad \text{Eqn. 2-24} \]

\[ C_p = \frac{K_sC_f}{-RF_w} \ln \left( 1 - \frac{RF_w}{F_w + K_s} \right) \quad \text{Eqn. 2-25} \]

\[ C_p = \frac{C_f(1+r-R)}{rR - \frac{F_w R(1+r)(1-R)}{K_s \ln \left( \frac{1 - \frac{RF_w}{F_w + K_s}}{F_w + K_s} \right)}} \quad \text{Eqn. 2-26} \]

2.7 Irreversible Thermodynamics Model

The Irreversible thermodynamics model is based on non-equilibrium and treats the membrane as a black box in which relatively slow processes proceed to near equilibrium. The
mechanisms of transport and the structure of the membrane are ignored. The first irreversible thermodynamics model is the model of Kedem-Katchalsky (Kedem, 1958). The working equations of the Spiegler-Kedem (Spiegler and Kedem, 1966) model were Eqn. 2-27 through Eqn. 2-29:

\[ F_w = K_w (\Delta P - \sigma \Delta \pi) \quad \text{Eqn. 2-27} \]

\[ \text{Rej} = \sigma (1 - F) / (1 - \sigma F) \quad \text{Eqn. 2-28} \]

Where:

\[ \text{Rej} = 1 - \frac{C_p}{C_f} \]

\[ F = \exp[-F_w \alpha] \]

\[ \alpha = (1 - \sigma) / K_b \]

Here \( \sigma \) is the reflection coefficient which represents the rejection capacity of a membrane, i.e., \( \sigma = 0 \) means no rejection and \( \sigma = 1 \) means 100% rejection.

Rearrange to result:

\[ \text{Rej} / (1 - \text{Rej}) = \frac{\sigma}{1 - \sigma} \left[ 1 - \exp(-F_w \alpha) \right] \exp(-F_w / K_b) \]

\[ \text{Eqn. 2-29} \]

Substitute Eqn. 2-3, Eqn. 2-4 and Eqn. 2-5 by taking feed concentration as the average of inlet and outlet concentration, the permeate concentration becomes:

\[ C_p = C_f \frac{(2 - R)}{(2 - 2R) \left[ 1 + \frac{\sigma}{1 - \sigma} \left[ 1 - e^{-F_w (1 - \sigma) / K_b} \right] e^{-F_w / K_b} \right] + R} \]

\[ \text{Eqn. 2-30} \]

Murthy (1997) reported solute MTCs can be determined accurately in laboratory by both solution diffusion model and Spiegler-Kedem model, while \( k_b \) was correlated to dimensionless
Eqn. 2-13, with the coefficients a, b and c specified by nonlinear fitting of laboratory cell test data, however, only NaCl-water systems were tested, besides, the way to determine Eqn. 2-13 is device specific which also implicates no universal correlation exists, thus hindered applying in reality.

Notice that if reflection efficient $\sigma$ value approaching 1, which means lack of water/solute coupled permeation, then by Taylor’s expression.

$$e^{-\frac{-F_w(1-\sigma)}{K_s}} \approx 1 + e^{-\frac{-F_w(1-\sigma)}{K_s}}$$

Eqn. 2-31

Eqn. 2-30 can be reduced to Eqn. 2-14.

$$C_p = \frac{C_f K_s e^{\frac{F_w}{K_s}}}{K_w \left(\Delta P - \Delta \pi \left(\frac{2 - 2R}{2 - R}\right) + K_s e^{\frac{F_w}{K_s}}\right)}$$

Eqn. 2-14

Thus ITFTM model can be simplified to FTM when the reflection efficient approaches one.
CHAPTER 3: INFLUENCE OF MEMBRANE SURFACE PROPERTIES AND FEED WATER QUALITIES ON RO/NF MASS TRANSFER

The influence of surface characteristics and natural organic matter (NOM) on membrane performance is significant but not well understood. The impact of membrane surface characteristics and NOM on membrane performance has been investigated for varying pretreatment and membranes in a field study. Surface charge, hydrophobicity and roughness varied significantly among the four membranes used in the study. The membranes were tested in parallel following two different pretreatment processes, an enhanced Zenon ultrafiltration process (ZN) and a compact CSF process (Superpulsator (SP)) prior to RO membrane treatment for a total of eight integrated membrane systems. All membrane systems were exposed to the similar temperature, recovery and flux as well as chemical dosage. The feed water qualities were identical following ZN pretreatment and SP pretreatment except for NOM concentration. Membrane surface characteristics, NOM and specific UV absorption (SUVA) measurements were used to describe mass transfer in a low pressure RO integrated membrane system. Solute and water mass transfer coefficients were systematically investigated for dependence on membrane surface properties and NOM mass loading.

Inorganic mass transfer coefficient (MTCs) were accurately described by a Gaussian distribution curve. Water productivity, NOM rejection and inorganic rejection increased as membrane surface charge and NOM loading increased. Inorganic MTCs were also correlated to surface hydrophobicity and surface roughness. The permeability change of identical membranes was related to NOM loading, hydrophobicity and roughness. Organic fouling as measured by water, organic and inorganic mass transfer was less for membranes with higher hydrophilicity and roughness.
3.1 Introduction

Characterization of membrane surface properties is of great interest to researchers since they greatly influence separation properties and fouling of membranes. Membrane permeability, flux decline ratio and solute selectivity have been related to surface properties, NOM characteristics and operation conditions (Zhang et al. 1990, Elimelech et al. 1994, Childress 1996, Elimelech et al. 1997, Hong et al. 1997, Deshmukh et al. 2001, Vrijehhoek et al. 2001); however these works have focused on fouling behavior and were mostly studied on a laboratory scale. The effects of membrane surface properties and NOM on membrane performance has not been reported using field data.

Childress et al. (1998) reported that humic substances and surfactants adsorbed to the membrane might influence membrane surface charge. Amy and Cho (1999) observed negative charge density of hydrophobic acid promoted NOM rejection for nanofiltration (NF) and ultrafiltration (UF). Her et al. (2000) also noted negative surface charge can reduce fouling due to electrostatic repulsion of negatively charged NOM components. Koo et al. (2002) specifically suggested that charge attraction has a stronger effect than hydrophobicity on fouling. Also, Her et al. (2000) found that a hydrophilic membrane can effectively reject NOM.

3.2 Pilot Study

3.2.1 Operation

The raw water was highly organic and brackish surface water taken from the St. John’s River at Lake Monroe in Sanford, Florida. Pretreatment consisted of ferric sulfate coagulation in
situ with Zenon (ZN) UF, and by Super Pulsator (SP) coagulation followed by pressurized dual media filtration.

The four models of thin-film-composite low-pressure reverse osmosis membranes used in the study were LFC1 (Hydranautics), X20 (Trisep), SG (Osmonics) and BW30 FR1 (Filmtec). Each membrane model received both pretreated waters. Eight 4"X40" single elements (2 each of each membrane) were simultaneously tested in parallel at varying water quality and temperature. Operation for all membrane systems was identical.

The Zeta potential (charge), roughness and hydrophobicity (Contact Angle) were measured on flat sheets for all membranes used in the field. The relationship between solvent (water) and solute (inorganic and organic) mass transfer coefficients, membrane surface properties and NOM mass loading was investigated.

3.2.2 Source Water Quality

Ultraviolet (UV\textsubscript{254}) adsorption at 254 nm was correlated to non-purgeable dissolved organic carbon (NPDOC) and used for general organic measurement of nominal organic material (NOM). NOM is used to describe organic solutes. Specific ultraviolet absorbance (SUVA), the ratio of UV\textsubscript{254} and dissolved organic carbon, for raw water varies with season range from 2.3 L/mg-m to 4.9 L/mg-m in the wet and dry season respectively. A summary of water quality parameters for raw water and these two pretreatment are shown in Table 3-1. A schematic plot of IMS pilot study is depicted in Figure 3-1.
Figure 3-1 Schematic diagram for pilot study configuration

SP: Super Pulsator pretreatment process; ZN: Zenon ultrafiltration pretreatment process.
Table 3-1:Summarized water qualities for raw water and SP, ZN break tank water.

<table>
<thead>
<tr>
<th></th>
<th>NPDOC</th>
<th>TDS</th>
<th>Cond. umho/cm</th>
<th>Ba$^{2+}$</th>
<th>Ca$^{2+}$</th>
<th>Mg$^{2+}$</th>
<th>Na$^+$</th>
<th>Sr$^{2+}$</th>
<th>SiO$_2$</th>
<th>Br$^-$</th>
<th>Cl$^-$</th>
<th>SO$_4^{2-}$</th>
<th>UV$_{254}$ cm$^{-1}$</th>
<th>color</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>Raw-Avg</td>
<td>21.7</td>
<td>838.2</td>
<td>1534.0</td>
<td>0.08</td>
<td>55.1</td>
<td>22.3</td>
<td>180.1</td>
<td>1.4</td>
<td>4.8</td>
<td>0.6</td>
<td>349.1</td>
<td>137.1</td>
<td>0.6</td>
<td>69.5</td>
<td>8.3</td>
</tr>
<tr>
<td>Raw-Max</td>
<td>27.9</td>
<td>1004.8</td>
<td>1849.0</td>
<td>0.14</td>
<td>146.8</td>
<td>35.6</td>
<td>255.9</td>
<td>2.0</td>
<td>7.0</td>
<td>1.3</td>
<td>430.0</td>
<td>168.0</td>
<td>1.0</td>
<td>93.0</td>
<td>9.9</td>
</tr>
<tr>
<td>Raw-Min</td>
<td>12.8</td>
<td>387.2</td>
<td>774.3</td>
<td>0.03</td>
<td>31.4</td>
<td>12.7</td>
<td>114.3</td>
<td>0.6</td>
<td>3.0</td>
<td>0.1</td>
<td>226.4</td>
<td>98.0</td>
<td>0.4</td>
<td>50.0</td>
<td>7.1</td>
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<tr>
<td>Raw-Std</td>
<td>4.2</td>
<td>146.2</td>
<td>274.5</td>
<td>0.04</td>
<td>23.1</td>
<td>4.7</td>
<td>35.3</td>
<td>0.4</td>
<td>1.2</td>
<td>0.4</td>
<td>57.7</td>
<td>16.1</td>
<td>0.1</td>
<td>15.4</td>
<td>0.8</td>
</tr>
<tr>
<td>SP-Avg</td>
<td>3.3</td>
<td>894.9</td>
<td>1702.8</td>
<td>0.07</td>
<td>56.8</td>
<td>23.1</td>
<td>209.4</td>
<td>1.4</td>
<td>4.4</td>
<td>0.6</td>
<td>324.0</td>
<td>248.1</td>
<td>0.0</td>
<td>1.8</td>
<td>6.9</td>
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<td>1138.3</td>
<td>2047.0</td>
<td>0.14</td>
<td>175.6</td>
<td>27.8</td>
<td>263.5</td>
<td>1.9</td>
<td>5.7</td>
<td>1.0</td>
<td>381.3</td>
<td>450.5</td>
<td>0.1</td>
<td>3.0</td>
<td>7.6</td>
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<td>1214.6</td>
<td>0.01</td>
<td>31.7</td>
<td>17.8</td>
<td>156.3</td>
<td>0.9</td>
<td>1.4</td>
<td>0.1</td>
<td>228.6</td>
<td>146.4</td>
<td>0.0</td>
<td>1.0</td>
<td>6.2</td>
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<td>252.1</td>
<td>0.04</td>
<td>37.4</td>
<td>3.1</td>
<td>32.9</td>
<td>0.3</td>
<td>1.8</td>
<td>0.4</td>
<td>53.0</td>
<td>71.9</td>
<td>0.0</td>
<td>0.8</td>
<td>0.4</td>
</tr>
<tr>
<td>ZN-Ave</td>
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<td>831.8</td>
<td>1617.8</td>
<td>0.06</td>
<td>46.7</td>
<td>23.2</td>
<td>193.0</td>
<td>1.5</td>
<td>4.0</td>
<td>0.7</td>
<td>331.1</td>
<td>225.6</td>
<td>0.1</td>
<td>4.3</td>
<td>6.6</td>
</tr>
<tr>
<td>ZN-Max</td>
<td>8.0</td>
<td>955.4</td>
<td>1942.2</td>
<td>0.12</td>
<td>63.7</td>
<td>26.8</td>
<td>243.3</td>
<td>1.9</td>
<td>6.0</td>
<td>1.2</td>
<td>429.1</td>
<td>272.2</td>
<td>0.2</td>
<td>5.0</td>
<td>8.0</td>
</tr>
<tr>
<td>ZN-Min</td>
<td>3.1</td>
<td>678.1</td>
<td>1129.1</td>
<td>0.02</td>
<td>33.7</td>
<td>16.8</td>
<td>152.7</td>
<td>0.9</td>
<td>1.6</td>
<td>0.1</td>
<td>230.8</td>
<td>183.8</td>
<td>0.1</td>
<td>3.0</td>
<td>5.9</td>
</tr>
<tr>
<td>ZN-Std</td>
<td>1.7</td>
<td>92.2</td>
<td>252.5</td>
<td>0.04</td>
<td>10.2</td>
<td>3.2</td>
<td>30.4</td>
<td>0.3</td>
<td>1.6</td>
<td>0.4</td>
<td>60.6</td>
<td>29.8</td>
<td>0.0</td>
<td>1.0</td>
<td>0.5</td>
</tr>
</tbody>
</table>

Water qualities are based on samples collected from April 2nd to July 12th. 23 weekly raw samples and 12 SP and ZN break tank samples. Avg: average; Max: maximum; Min: minimum; Std: standard deviation.
3.2.3 Pretreatment

The pretreatment processes removed particulate matter, NOM, and pathogens. Raw water was coagulated with ferric sulfate and discharged to a tank housing the ZN membranes, which were immersed. A vacuum was applied to interior of the hollow fiber, which sucked the pretreated water through the membrane. To reduce cake buildup on the membrane fibers, air was introduced at the bottom of the membrane feed vessel to scour the solids from the membrane surface. SP is a high rate clarification process, which utilizes an upflow solids contact clarifier and special sand to enhance coagulation and settling in one unit. Following SP clarification, the water was filtered using a pressurized dual (anthracite and sand) media filter. pH was adjusted to 6.0 using sodium hydroxide before LPRO membrane filtration. Chloramines and antiscalant were added before the membrane units for control of bio fouling and salt scaling.

3.2.4 Single Element Unit

The single element bench scale units used in this study were similar in design and configuration and are based on the units described in the “ICR Manual for Bench- and Pilot-Scale Treatments Studies” (Taylor et al 1999, 2000, 2002, Reiss, 1999). Each unit consisted of a high pressure feed pump, a 5-micron cartridge pre-filter, pressure vessel, recirculation loop with pressure gages and flow meters installed. They were operated in continuous feed mode with a recycle of concentrate flow to maintain minimum concentrate flow requirements. The flows and pressures in the unit were adjusted with the feed, recycle, concentrate and permeate valves.
3.2.5 Pilot Operation

Recovery and flux were identical for the eight single element units. Recovery was controlled by values on the input and output lines for each system. The targeted recovery and flux were 70% and 12 gsfd. Chemical dosing for all unit operations prior to LPRO was similar.

3.2.6 Pilot Monitoring

Operating variables were recorded twice daily. Pressure and temperature were measured for each feed, concentrate and permeate stream. Permeate and concentrate flows were measured directly with a 2-Liter cylinder and stopwatch to ensure the accuracy. Cumulative membrane run time was recorded by a SCADA system. Water quality including pH, conductivity, turbidity, UV254, color and mono chloramines were monitored instantaneously and recorded with operational data.

3.2.7 Water Quality

Water quality samples were regularly collected for raw, feed, permeate and concentrate streams for all eight single element units on a weekly basis. After collection, samples were immediately transported to the UCF-ESEI laboratory and stored at 4°C. Organic parameters, major anions and cations were measured in the laboratory. The measured water quality was Cl⁻, SO₄²⁻, Br⁻ and silica by DX-120 Ion Chromatography (Dionex); Na⁺, Ca²⁺, Mg²⁺, Sr²⁺, Fe³⁺, and Ba²⁺ by Unicam 969 AA Spectrometer (Unicam) and Hitachi Zeeman-AAS Z-9000 (Hitachi); Non-purgeable dissolved organic carbon (NPDOC) by a Phoenix 8000 UV-Persulfate TOC Analyzer (Dohrmann). UV254 performed by Hach 4500 spectrophotometer with 1 cm path length.
3.3 Membrane Surface Properties

3.3.1 Surface Charge

The zeta potential of the membrane surface was determined using a streaming potential analyzer (BI-EKA, Brookhaven). All measurements are performed at room temperature, approximately 22°C (72°F), with a background electrolyte solution of 0.02 M NaCl. Two separate tests are performed for each membrane, and trend lines developed using the zeta potential points at varying pH (Norberg, 2003).

3.3.2 Roughness

The Digital Instruments (DI) NanoScope™ was used to analyze surface roughness for all membrane samples. The DI AFM was operated in Tapping Mode; three scans are performed for each membrane. The roughness of the membranes is reported in terms of RMS which stands for root mean squared of the average height of the membrane surface peaks, which is the standard deviation of the roughness (Norberg, 2003).

3.3.3 Contact Angle

The contact angle measurements were obtained through the captive or adhering bubble technique (Goniometer, Rame-Hart). In order to complete these measurements, each membrane sample was mounted on a flat surface with the active layer exposed. The assembly was inverted, and lowered into a quartz cell, which contained DI water, such that the active layer of the membrane was face down. A submerged syringe with a U-shaped needle attachment delivers a bubble, of pre-determined size. Once the air bubble stabilizes with the surface of the membrane,
the contact angle on each side of the bubble is measured by an automated goniometer. Six (three on each side of the bubble) contact angle measurements were made for three separate membrane samples (Norberg, 2003).

3.4 Results and Discussion

3.4.1 Water Quality

From April 2nd to July 12th, totally 23 samples were collected weekly and analyzed in the laboratory. There was no difference between pretreated ZN and SP water quality except for NOM and alkalinity. The ZN treated NOM (6.3 mg/L) was higher than the SP treated NOM (3.5 mg/L) because of different coagulation pHs. The coagulation pH of the SP system was 4.5, which could be reduced to 6 before filtration to minimize iron carry over. As the ZN system had no opportunity for pH adjustment, the coagulation pH was 6 to avoid iron carry over. The results from T tests assuming equal variance for paired data sets for SP and ZN pretreated water quality (membrane feed stream) show pretreated water quality was identical except for the NOM (NPDOC) and alkalinity, which was due to coagulation pH. The water quality shown in Table 3-1 is filtered water quality, so the difference in coagulation pH is not shown in Table 3-1.

NOM was characterized using NPDOC in this study. The average NOM between SP and ZN pretreatment process demonstrated significantly different organic loading for the membranes following two pretreatment processes. Moreover, SUVA for SP and ZN units was 1.16 L/mg-m and 1.68 L/mg-m respectively (26 observations, standard deviation 0.25 L/mg-m), see Figure 3-2. SUVA has been reported as a good indicator of humic content. Typically raw SUVA was from 4 to 5 L/mg/m, which indicates a significant humic fraction of NOM. SUVA less than 3
L/mg-m represents the non-humic fraction (Barrett, Krasner and Amy, 2000). The average raw water NOM and SUVA was 22.9 mg/L and 3.03 L/mg-m respectively. SUVA and NOM were reduced 78 and 88 %, and 44% and 62% by ZN and SP pretreatment respectively. As there was no significant difference in coagulant or dose, these results show the organic removal was improved at a lower coagulation pH (approximately 6 vs. 4.5), and that more SUVA than NOM removal was achieved at these pHs.

![Graph](image)

Figure 3-2 SUVA for SP, ZN pretreated water.

3.4.2 Operation

Pilot operation was similar for all Integrated Membranes Systems (IMSs). Pressure, recovery, and flux as well as same chemical dosage of monochloramines, anti-scalent and ferric
sulfate were essentially identical. The statistics of recovery, flux and temperature by membranes are tabulated as shown in Table 3-2. Table 3-2 shows that for operation from April 10 to August 9, 2002, the average recovery for eight single element units varied from 70.1% to 72.3% with standard deviation from 0.9% to 2.3%. Similarly, the flux for all membrane systems is shown in Table 3-2 with average flux varied from 12.3 gsfd to 12.8 gsfd with standard deviation from 0.4 to 0.9. Flux and recovery were maintained by adjusting input and output value settings as necessary. The concentrate stream temperature for all membrane systems is shown in Table 3-2. Average temperature varied from 32.1 °C to 33°C with a standard deviation from 1.7 °C to 1.8 °C for each membrane system. The data in Table 3-2 show that the recovery, flux and temperature for all membranes did not vary significantly and indicates that all membrane systems were operated similarly. Pretreatment also included of 2.7 mg/L antiscalant, 1 mg/L monochloramines and 5-micron cartridge filtration prior to LPRO membrane filtration.

The data shown in Table 3-2 clearly showed that all systems were operated in a similar manner and provided an accurate means for comparing the performance of each membrane.
3.4.3 Surface Characteristics

Membrane surface charge, roughness and hydrophobicity of the membranes used in this study are reported in Table 3-3. Each of these membranes has unique surface properties. BW30FR has a relatively neutral and hydrophilic surface with medium surface roughness; X20 has a highly negatively charge; LFC1 has a low negative charge and medium hydrophobicity, the roughness of this membrane is in the range of medium to high; SG is less roughness and more hydrophobic than the other membranes while its surface charge is in the range of low to medium. Clearly, these membranes have significantly different surface charge, roughness and hydrophobicity.

Table 3-2 Recovery, flux and temperature by system using data from Apr. 10 to Aug. 9, 2002

<table>
<thead>
<tr>
<th>Membrane</th>
<th>Num.</th>
<th>Recovery (%)</th>
<th>Flux (gsfd/psi)</th>
<th>Temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Mean</td>
<td>Std.</td>
<td>Mean</td>
<td>Std.</td>
</tr>
<tr>
<td>SP-BW30FR1</td>
<td>144</td>
<td>71.2</td>
<td>1.0</td>
<td>12.2</td>
</tr>
<tr>
<td>SP-LFC1</td>
<td>150</td>
<td>72.0</td>
<td>2.3</td>
<td>12.3</td>
</tr>
<tr>
<td>SP-SG</td>
<td>147</td>
<td>72.3</td>
<td>1.7</td>
<td>12.3</td>
</tr>
<tr>
<td>SP-X20</td>
<td>147</td>
<td>72.3</td>
<td>1.3</td>
<td>12.4</td>
</tr>
<tr>
<td>ZN-BW30FR1</td>
<td>152</td>
<td>71.3</td>
<td>1.2</td>
<td>12.3</td>
</tr>
<tr>
<td>ZN-LFC1</td>
<td>154</td>
<td>71.7</td>
<td>1.7</td>
<td>12.4</td>
</tr>
<tr>
<td>ZN-SG</td>
<td>154</td>
<td>70.1</td>
<td>0.9</td>
<td>12.8</td>
</tr>
<tr>
<td>ZN-X20</td>
<td>153</td>
<td>70.5</td>
<td>1.1</td>
<td>12.5</td>
</tr>
</tbody>
</table>

Num.: Number of observation from Apr.10 to Aug.9; Mean: Average of all observations; Std: Standard deviation of all observations. A-B: A represents pretreatment process, B represents membrane.
### Table 3-3 Summarized membrane surface characteristics by membrane

<table>
<thead>
<tr>
<th>Membrane</th>
<th>Roughness (µm)</th>
<th>Charge (mv)</th>
<th>Contact Angle (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LFC1</td>
<td>67.4</td>
<td>-3.9</td>
<td>51.8</td>
</tr>
<tr>
<td>SG</td>
<td>13.09</td>
<td>-7.0</td>
<td>60.9</td>
</tr>
<tr>
<td>X20</td>
<td>41.64</td>
<td>-13.2</td>
<td>52.3</td>
</tr>
<tr>
<td>BW30FR1</td>
<td>65.01</td>
<td>-6.7</td>
<td>43.8</td>
</tr>
</tbody>
</table>

Charge measured by Zeta Potential at pH 6.5

#### 3.4.4 Effects of Surface Characteristics on Productivity

The mathematical symbol for the water MTC is $K_w$, which will be used to describe the water MTC or productivity. The initial $K_w$ was determined by normalizing the initial $K_{ws}$ for temperature during the first hundred hours of actual operation and averaging that data set. Eqn. 3-1 was used to calculate $K_w$. The initial normalized $K_{ws}$s are shown in Table 3-4.

### Table 3-4 Summarized initial inorganic $K_s$, NOM rejection, water $K_w$ by membrane.

<table>
<thead>
<tr>
<th>Membrane</th>
<th>$K_{sCa^{2+}}$</th>
<th>$K_{sMg^{2+}}$</th>
<th>$K_{sNa^{+}}$</th>
<th>$K_{sSO_2}$</th>
<th>$K_{sCl^{-}}$</th>
<th>$K_{sSO_4^{2-}}$</th>
<th>Rej NOM</th>
<th>$K_w$</th>
</tr>
</thead>
<tbody>
<tr>
<td>SP-LFC1</td>
<td>gsfd</td>
<td>gsfd</td>
<td>gsfd</td>
<td>gsfd</td>
<td>gsfd</td>
<td>gsfd</td>
<td>96.5</td>
<td>0.21</td>
</tr>
<tr>
<td>ZN-LFC1</td>
<td>0.006</td>
<td>0.008</td>
<td>0.30</td>
<td>0.57</td>
<td>0.36</td>
<td>0.008</td>
<td>97.0</td>
<td>0.16</td>
</tr>
<tr>
<td>SP-SG</td>
<td>0.01</td>
<td>0.009</td>
<td>0.31</td>
<td>1.54</td>
<td>0.33</td>
<td>0.055</td>
<td>96.7</td>
<td>0.11</td>
</tr>
<tr>
<td>ZN-SG</td>
<td>0.007</td>
<td>0.009</td>
<td>0.16</td>
<td>1.62</td>
<td>0.20</td>
<td>0.048</td>
<td>98.7</td>
<td>0.09</td>
</tr>
<tr>
<td>SP-X20</td>
<td>0.009</td>
<td>0.01</td>
<td>0.16</td>
<td>0.79</td>
<td>0.18</td>
<td>0.046</td>
<td>94.5</td>
<td>0.14</td>
</tr>
<tr>
<td>ZN-X20</td>
<td>0.005</td>
<td>0.009</td>
<td>0.10</td>
<td>1.02</td>
<td>0.13</td>
<td>0.045</td>
<td>99.3</td>
<td>0.15</td>
</tr>
<tr>
<td>SP-BW30FR1</td>
<td>0.006</td>
<td>0.009</td>
<td>0.03</td>
<td>0.81</td>
<td>0.08</td>
<td>0.056</td>
<td>97.5</td>
<td>0.13</td>
</tr>
<tr>
<td>ZN-BW30FR1</td>
<td>0.026</td>
<td>0.009</td>
<td>0.06</td>
<td>0.87</td>
<td>0.09</td>
<td>0.012</td>
<td>98.2</td>
<td>0.11</td>
</tr>
</tbody>
</table>

A-B: A represents pretreatment process, B represents membrane.
\[ K_w = \frac{Q_p}{A \times (\Delta P - \Delta \Pi) \times 1.026^{(T-25)}} \]  

Eqn. 3-1

\( K_w \) is defined in Eqn. 3-1 and is normalized with respect to pressure and temperature. \( Q_p \) represents permeate flow; \( A \) represents membrane surface area; \( \Delta P \) and \( \Delta \Pi \) are hydraulic pressure and osmotic pressure respectively; \( T \) is temperature.

The effect of surface charge, roughness, hydrophobicity on the productivity (\( K_w \)) was investigated using linear regression. Charge was the only surface characteristic that was not significant at the 95% confidence interval. The final regression equation is shown in Eqn. 3-2. As shown in Figure 3-3, membrane productivity (\( K_w \)) increased with contact angle and roughness. The increase of \( K_w \) with roughness is consistent with the increase in surface area with roughness. However \( K_w \) typically decreases with contact angle (hydrophobicity) due to the repulsion of water. The range of roughness of the membranes was from approximately 13 to 67 microns (five-fold), whereas the range of contact angles was from approximately 44 to 66 degrees (less than two-fold). The smaller range of contact angles may have affected the trend.

\[ K_w = 0.00127 \times \text{Roughness(\( \mu \text{m} \))} + 0.00151 \times \text{Contact Angle(\( \circ \))} \]  

Eqn. 3-2
$K_w = 0.00127 \times \text{Roughness(}\mu\text{m}) + 0.00151 \times \text{Contact Angle(°)}$

Figure 3-3 Predicted and actual $K_w$ versus contact angle and roughness

3.4.4.1 Effects of NOM on Productivity

The effects of NOM on productivity was assessed by determining $\Delta K_w$ for identical membranes that received SP (3.5 mg/L NPDOC) and ZN (6.5 mg/L NPDOC) pretreated water. The SP and ZN average turbidities in the pretreated feed stream were 0.10 NTU and provided equal particle loading on the membranes. $\Delta K_w$'s for LFC1, SG, BW30FR1 and X-20 membranes were determined by subtracting the average $K_w$ for the initial 100 hours of operation of the LFC1, SG, BW30FR1 and X-20 membranes receiving ZN pretreatment from the average $K_w$ for
the initial 100 hours of operation of the LFC1, SG, BW30FR1 and X-20 membranes receiving SP pretreatment.

The results of the $\Delta K_w$ comparisons are shown in Figure 3-4. All $\Delta K_w$'s are positive, which indicates the identical membranes receiving higher NOM (ZN pretreatment) had lower $K_w$'s or productivity. Hence, productivity decreased as NOM loading increased. The productivity drop also decreased as the negative charge increased. The data in Figure 3-4 suggests that adverse effects of NOM on membrane productivity effects were offset by negative charge, and charge can be used to reduce organic fouling.

The order of $\Delta K_w$'s is X-20$<$BW30FR1$\approx$SG$<$LFC1, and is similar to the order of membrane charge (X-20$<$ SG $\approx$ BW30FR1$<$LFC1). All four membranes were negatively charged. It is feasible that a negatively charged membrane surface opposes the NOM deposition on membrane surface due to repulsion of like charges. Because the X-20 membrane has lowest (highest negative charge) surface charge, the X-20 repels NOM better than the other membranes in this study. Therefore X-20 productivity was affected the least by NOM adsorption. In contrast, the LFC1 membrane has a relatively neutral surface charge, forms a tighter NOM film and loses more productivity than the more negatively charged membranes.
3.4.5 Effects of Surface Characteristics on $K_s$

Solute MTCs for sodium, calcium, magnesium, chloride, sulfate and silica were calculated using Eqn. 3-3. Solute MTCs are represented mathematically by $K_s$, which will be used to represent solute MTCs. The organic rejection rate was calculated using Eqn. 3-4. Similar to $\Delta K_w$, $\Delta \text{Rej}$ and $\Delta K_s$ were determined for the same membrane based on pretreatment and solute. Rej and $K_s$ were determined from operational data by subtracting the average solute $K_s$ for SiO$_2$, Na$^+$, Ca$^{2+}$, Mg$^{2+}$, Cl$^-$ and SO$_4^{2-}$ for the initial 100 hours of operation of the membranes receiving ZN pretreatment from average solute SiO$_2$, Na$^+$, Ca$^{2+}$, Mg$^{2+}$, Cl$^-$ and SO$_4^{2-}$.
for the initial 100 hours of operation of the membranes receiving SP pretreatment for like membranes.

\[
K_s = \frac{Q_p \times C_p}{A \times \left(\frac{C_f + C_c}{2} - C_p\right)}
\]  \hspace{1cm} \text{Eqn. 3-3}

\[
\text{Re} = j = 1 - \frac{C_p}{C_f}
\]  \hspace{1cm} \text{Eqn. 3-4}

Eqn. 3-3 is a simplified diffusion solution model in which \(C_p\) represents permeate solute concentration, \(C_f\) and \(C_c\) represent membrane feed and concentrate streams solute concentration. Eqn. 3-4 was used to NOM calculate rejection.

The \(K_s\)'s for \(\text{Na}^+\) and \(\text{Cl}^-\), were linearly regressed against charge, roughness and contact angle similar to productivity. The regression equation is shown as Eqn. 3-5

\[
K_s = 0.0067 \times \text{Roughness(\mu m)} + 0.0311 \times \text{Contact Angle(\degree)} - 1.74
\]  \hspace{1cm} \text{Eqn. 3-5}
Figure 3-5 Predicted and actual $K_s$ versus roughness and contact angle

Roughness and contact angle were significant at the 95 % CI and had positive regression coefficients in Eqn. 3-5, which meant $\text{Na}^+$ and $\text{Cl}^-$ mass transfer ($K_s$) increased as roughness and contact angle (hydrophobicity) increased. This relationship is shown in Figure 3-5. Charge was not significant. Roughness, contact angle and charge had similar effects on water productivity ($K_w$).

3.4.5.1 Effects of NOM and Surface Characteristics on % NOM Rejection

NOM rejection has been proposed to be controlled by size exclusion, partial diffusion, electrostatic repulsion and hydrophobicity interactions between the aromatic content of NOM and the membrane surface (Jaewon et.al.1999). In this study, the average initial NOM rejection
rate for the X-20, BW30FR1, SG, and LFC1 membranes receiving ZN pretreated water was 99.3%, 98.2%, 98.7% and 97.0% respectively; X-20, BW30FR1, SG, and LFC1 membranes receiving SP pretreated water rejected less NOM (94.5%, 97.5%, 96.7% and 96.5% respectively). NOM rejection increased with decreasing surface charge. As shown in Figure 3-6, Δ%NOM rejection increased with charge and has the same trend with charge as ΔK_w. Possibly, decreasing charge reduced the NOM film on the membrane surface and the associated effects of increasing NOM loading on productivity and NOM rejection due to repulsion of negatively charged NOM solutes.

Figure 3-6 Delta NOM rejection versus charge
3.4.5.2 Solute Charge and $K_s$

A membrane specific Gaussian model was developed for the inorganic $K_s$'s as a function of solute charge using non-linear regression as shown in Eqn. 3-6 with model exponents for each membrane. The model results are shown in Figure 3-7. The correlation coefficients were greater than 0.98 for all models. The six ions were SiO$_2$, Na$^+$, Ca$^{2+}$, Mg$^{2+}$, Cl$^-$ and SO$_4^{2-}$. Model development found the inorganic $K_s$'s were not statistically different by pretreatment but were statistically different by membrane. The result is similar to a previous study (Duranceau et al. 1990) which described $K_s$ as a function of charge, and molecular weight and charge using a Gaussian distribution.

![Figure 3-7 Ks versus solute valance by membranes.](image)

Figure 3-7 $K_s$ versus solute valance by membranes.
\[ K_s = K_{s0} e^{(x_0 \times \text{Charge})} \] 

Eqn. 3-6

Where

\( x_0 = -1.50 \) for X-20, \(-2.94 \) for BW30FR1, \(-1.84 \) for SG, \(-0.70 \) for LFC1

\( K_{s0} = 0.56 \) for X-20, \(1.24 \) for BW30FR1, \(1.58 \) for SG, \(0.61 \) for LFC1

3.4.5.3 Solute Charge and \( K_s \)

The variation of contact angle and roughness by membrane and pretreatment versus \( \Delta K_s \) for Na and Cl is shown in Figure 3-8 and Figure 3-9. Although there was no statistical difference in the \( K_s \)'s, there was a statistical difference and a trend in \( \Delta K_s \)'s by membrane and pretreatment. As shown in Figure 3-8, \( \Delta K_s \) increased with increasing contact angle (hydrophobicity) and \( \Delta K_s \)'s for membranes receiving ZN pretreated water were lower than for membrane receiving SP pretreated water. NOM loading and SUVA were higher in the ZN pretreated water, which caused more organic fouling and higher \( \Delta K_s \)'s. As noted, this dynamic hydrophobic film increased with NOM loading and reduced productivity and salt passage. This phenomenon is supported by Figure 3-8.
Figure 3-8 Na\(^+\) and Cl\(^-\) delta $K_s$ versus membrane contact angle

Figure 3-9 Na\(^+\) and Cl\(^-\) delta $K_s$ versus membrane roughness
As shown in Figure 3-9, $\Delta K_s$'s for $\text{Na}^+$ and $\text{Cl}^-$ decreased as roughness increased. The increased surface area associated with increased surface roughness reduced the impact of organic fouling. Although surface charge did affect NOM rejection, surface charge did not affect inorganic mass transfer ($K_s$). NOM films on membrane surface impacted $K_s$, which was related to contact angle (hydrophobicity) and roughness. Consequently, less hydrophobic and rougher surfaces would reduce NOM fouling and maintain more constant inorganic solute mass transfer. Less hydrophobic membranes have also been shown to reduce membrane degradation, (Zhao, Taylor, and Hong 2003).

3.5 Conclusions

Negatively charged membranes had higher productivity, organic and inorganic solute rejection.

All membranes had uniquely different surface characteristics. The SG film was smoother; the X-20 film was more negatively charged; the LFC1 film had zero surface charge and was neutral and the BW30FR was more hydrophilic relative to the films of the four membranes. The surface characteristics of the films are controlled by the membrane manufacturers who apparently have manipulated different surface characteristics to control performance.

The membrane systems were operated in a similar manner and provided a basis for comparing membrane performance as affected by surface characteristics and water quality.
Productivity ($K_w$) and solute mass transfer ($K_s$) increased with surface roughness and contact angle (hydrophobicity). Hence more hydrophilic and rougher membranes are less likely to foul in integrated membrane system applications.

NOM loading affected membrane mass transfer. NOM and inorganic solute rejection ($K_s$) increased as NOM loading increased and as surface charge increased.

The initial inorganic $K_s$'s were different for each of the four membranes for similar solutes, but the $K_s$'s for each membrane were accurately described as function of charge using a Gaussian distribution model.
3.6 References


Taylor, J.S. Membrane, Chapter 11 (1999) Water Quality and Treatment, Denver, Colo.: AWWA.


CHAPTER 4: MODELING RO/NF PERFORMANCE OVER TIME

A diffusion control solute mass transfer model was developed to describe permeate water quality over time of operation. The changing mass transfer characteristics of four low-pressure reverse osmosis (LPRO) membranes was correlated to feed stream water quality in a 2000 hour pilot study. Solute mass transfer coefficients (MTCs) were correlated to initial solute MTCs, solute charge, feed water temperature, monochloramines loading and organic loading (UV254). Independent data were used to validate the model. The model can be used to predict cleaning frequency, permeate water quality and sensitivity of permeate water quality to variation of temperature, organic and monochloramine mass loading.
4.1 Introduction

Polyamide membranes are adversely affected by the continuous use of chlorine, and possibly by chloramines over time. Researchers have and are seeking a chlorine resistance diffusion controlled membrane that can be used to treat aerobic waters in combination with oxidants. However, many surface water applications incorporate chlorination and, dechlorination prior to RO or NF membrane filtration to avoid membrane destruction. A membrane has been described as chlorine resistant if exposure to 1 mg/L or more of chlorine does not cause membrane damage in several years (Singh, 1994). However, there are no current models that predict change of membrane performance due to chloramines over time. Such information would be beneficial to pre-design studies, design, operation and other facets of membrane use in the water community.

In this work, a mass loading methodology of modeling membrane performance is introduced and a mass loading model is developed. The newly developed model can be used to predict membrane productivity and permeate water quality over time of operation. The impact of significant mass loading water quality parameters can be determined from sensitivity analysis using the model.

4.2 Theoretical Development

Several models have been developed to describe solute mass transfer in diffusion controlled membranes (Chellam et al. 2001; Chen et al. 1999; Duranceau et al. 1990, 1993; Laisure et al. 1993; Mulford et al. 1999; Robert 1999; Sung 1995; Taylor et al. 1991, 1994, 1989; Lovins 2000; Thompson 1995) Specific developments include non-linear modifications of the
pressure differential and concentration differential across and through the membrane as well as integration of recovery and incorporation of film theory into models predicting permeate concentration. Although these models have incorporated fundamentally rational phenomena, they have not been shown to be superior to the homogenous solution diffusion (HSDM) model for predicting permeate concentration (Laisure et al 1993; Thompson 1995; Mulford 1999; Lovins 2000). Hence the HSDM is used in this work. The work equation of Homogeneous solution diffusion model (HSDM) is shown in Eqn. 4-1.

\[
C_p = \frac{K_w C_f}{K_w (\Delta P - \Delta \Pi) \left( \frac{2 - 2R}{2 - R} \right) + K_s} 
\]

Eqn. 4-1

Where:

- \( K_w \) = Solvent MTC
- \( \Delta P \) = Pressure gradient
- \( \Delta \Pi \) = Osmotic pressure gradient
- \( K_s \) = Solute MTC
- \( C_p \) = Permeate concentration
- \( C_f \) = Feed concentration
- \( R \) = Recovery = \( Q_p/Q_f \)

Membrane solvent mass transfer is pressure driven and is opposed by osmotic pressure \( (\Pi) \), which can be related to solute concentration by the Van’t Hoff equation, however in practice \( \Delta \Pi \), is related to solute total dissolved solids (TDS) as shown in Eqn. 4- 2.

\[
\Delta \Pi = K_{TDS} \times C_{TDS} 
\]

Eqn. 4- 2

Where:
\[ C_{TDS} = \frac{C_{L_{TDS}} + C_{C_{TDS}}}{2} \times C_p \]

\[ \Phi = TDS \text{ osmotic pressure correlation coefficient} \]

If solute mass transfer is not diffusion controlled, a size exclusion mechanism can be used to predict solute mass transfer. Size exclusion mechanisms have been proposed for natural organic matter and pathogens (Chen 1999). A size exclusion model is shown in Eqn. 4-3.

\[ C_p = \Phi C_f \]

Eqn. 4-3

Where:

\[ \Phi = \text{Size exclusion coefficient} \]

The HSDM model was modified for recycle of the concentrate stream into the feed stream as shown in Figure 4-1 and described in Eqn. 4-4. The recycle of a portion of the concentrate stream into the feed stream does not affect permeate concentration of solutes controlled by size exclusion. Such solutes are uniformly distributed in the raw water and pass a constant concentration that is independent of recovery and recycle. Single element pilot units have been used to accurately describe multi-scale pilot units and full-scale plants (Kothari et al, 1998; Lovins 2000; Mulford 1999; Taylor et al, 2000). More detailed discussions of these developments are also available (Taylor et al. 1996, 1999)
Figure 4-1 Single element flow diagram with recycle

\[
C_p = \frac{K_s C_f}{k_w (\Delta P - \Delta IT) \left( \frac{1+r}{2+2r-R} \right) + K_s} \quad \text{Eqn. 4-4}
\]

Solute mass transfer through a diffusion controlled membrane is not constant with time. Several authors have modeled the effect of solute charge and membrane surface characteristics on solute mass transfer in a membrane process (Elimilech et al, 1997; Hong et al, 1999; Jacangelo et al, Mandaeni, 2001). Meanwhile, variation of membrane productivity has been correlated to cumulative mass loading (Chellam et al. 1998; Lovins 2000). In this study, \(K_s\) is modified by mass loading during operation in a similar manner to these models reported for productivity. \(K_s\) changes due to natural film degradation, oxidation (\(\text{NH}_2\text{Cl}\)) and organic (\(\text{NPDOC}\) or \(\text{UV}-254\)) or particulate (turbidity) fouling. This model is shown in Eqn. 4-5 and correlates \(K_s\) to mass loading; however the model can accommodate other solutes affecting \(K_s\) if their concentration is known.

\[
K_s = K_{so} + \sum_{i=1}^{n} x_i \sum_{i=1}^{n} F_i \times C_i \times t_i \quad \text{Eqn. 4-5}
\]
Initial $K_{s0}$ has been related to solute charge (Duranceau, Taylor 1990), and was used here as shown in Eqn. 4-6.

$$K_{s0} = K_{s25} \times e^{(x_o \times \text{CHARGE}^2)}$$  \hspace{1cm} \text{Eqn. 4-6}

Temperature affects solute diffusivity and the viscosity of water. Consequently temperature has a significant effect on $K_s$, which is described mathematically in Eqn. 4-7. This equation is empirically developed but has the same form as the theoretically developed equation relating $K_w$ and temperature.

$$K_{sT} = K_{s25} \times \theta_s^{(T-25)}$$  \hspace{1cm} \text{Eqn. 4-7}

The general $K_s$ model incorporating temperature, solute species and membrane mass loading is shown in Eqn. 4-8.

$$K_{sT} = \theta_s^{(T-25)} \left[ K_{s25} \times e^{(x_o \times \text{CHARGE}^2)} + \sum_{i=1}^{l} \sum_{j=1}^{n} F_w \times C_i \times t_i \right]$$  \hspace{1cm} \text{Eqn. 4-8}

4.3 Pilot Study and Data

4.3.1 Operation

Highly organic and brackish surface water taken from the St. John’s River at Lake Monroe in Sanford, Florida was used as the water source. Two processes were used for advanced pretreatment, which were (1) ferric sulfate coagulation in situ with Zenon (ZN) UF, and (2) ferric sulfate coagulation using a Super Pulsate (SP) system followed by pressurized dual media filtration.
Four different thin-film-composite low-pressure reverse osmosis membranes were used in the study, which were LFC1 (Hydranautics), X20 (Trisep), SG (Osmonics) and BW30 FR1 (Filmtec) 4” X 40” membrane elements. All membrane models received both pretreated waters. Eight 4"X 40" single elements (2 each of each membrane) were simultaneously tested in parallel at varying water quality and temperature. Operation for all membrane systems was identical.

4.3.2 Source Water Quality

The raw water source for the pilot study was the St. Johns River at Lake Monroe in Sanford, FL. The TDS and organic carbon in the St. Johns varies seasonally. During the rainy season (May-September), organic carbon is high (to 40 mg/L) and TDS is low (less than 300 mg/L) due to run off. In the dry season (October-April) organic carbon decreases (less than 10 mg/L) and TDS increases (to 1500 mg/L). Ultraviolet (UV$_{254}$) adsorption at 254 nm was correlated to non-purgeable dissolved organic carbon (NPDOC) and used for general organic measurement of nominal organic material (NOM). NOM is used to describe organic solutes. A schematic plot of IMS pilot study is shown in Figure 4-2.
Figure 4-2 Schematic diagram for pilot study configuration

SP: Super Pulsator pretreatment process; ZN: Zenon ultrafiltration pretreatment process.

4.3.3 Pretreatment

The pretreatment processes removed particulate matter, NOM, and pathogens. Raw water was coagulated with ferric sulfate and discharged to a tank housing the ZN membranes, which were immersed. A vacuum was applied to the interior of the hollow fiber, which sucked the pretreated water through the membrane. To reduce cake buildup on the membrane fibers, air was introduced at the bottom of the membrane feed vessel to scour the solids from the membrane surface. SP is a high rate clarification process, which utilizes an upflow solids contact clarifier and special sand to enhance coagulation and settling in one unit. Following SP clarification, the water was filter using a pressurized dual (anthracite and sand) media filter. pH was adjusted to 6.0 using sodium hydroxide before LPRO membrane filtration. Chloramines and antiscalant were added before the membrane units for control of biological fouling and salt scaling.
4.3.4 Single Element Units

The single element bench scale units used in this study were similar in design and configuration and are based on the units described in the “ICR Manual for Bench- and Pilot-Scale Treatments Studies”. Each unit consisted of a high pressure feed pump, a 5-micron cartridge pre-filter, pressure vessel, recirculation loop with pressure gages and flow meters installed. They were operated in continuous feed mode with a recycle of concentrate flow to maintain minimum concentrate flow requirements. The flows and pressures in the unit were adjusted with the feed, recycle, concentrate and permeate valves.

4.3.5 Pilot Operation

Recovery and flux were identical for the eight single element units. Recovery was controlled by values on the input and output lines for each system. The targeted recovery and flux were 70 % and 20.4 L/hr•m² (12 gsfd). Chemical dosing for all unit operations prior to LPRO was similar.

4.3.6 Pilot Monitoring

Operating variables were recorded twice daily. Pressure and temperature were measured for each feed, concentrate and permeate stream. Permeate and concentrate flows were measured directly with a 2-Liter cylinder and stopwatch to ensure the accuracy. Cumulative membrane run time was recorded by a SCADA system. Water quality including pH, conductivity, turbidity, UV254, color and mono chloramines were monitored instantaneously and recorded with operational data.
4.3.7 Water Quality

Water quality samples were regularly collected for raw, feed, permeate and concentrate streams for all eight single element units on a weekly basis. After collection, samples were immediately transported to the UCF-ESEI laboratory and stored at 4°C. Organic parameters, major anions and cations were measured in the laboratory. Alkalinity was determined by titration. The measured water quality was Cl\textsuperscript{-}, SO\textsubscript{4}\textsuperscript{2-}, Br\textsuperscript{-}, and silica by DX-120 Ion Chromatography (Dionex); Na\textsuperscript{+}, Ca\textsuperscript{2+}, Mg\textsuperscript{2+}, Sr\textsuperscript{2+}, Fe\textsuperscript{3+}, and Ba\textsuperscript{2+} by Unicam 969 AA Spectrometer (Unicam) and Hitachi Zeeman-AAS Z-9000 (Hitachi); Non-purgeable dissolved organic carbon (NPDOC) by a Phoenix 8000 UV-Persulfate TOC Analyzer (Dohrmann). UV254 performed by Hach 4500 spectrophotometer with a 1 cm path length. Total dissolved solids (TDS) were measured by summing the concentrations of seven major inorganic ions (Ca\textsuperscript{2+}, Mg\textsuperscript{2+}, Na\textsuperscript{+}, HCO\textsubscript{3}\textsuperscript{-}, SO\textsubscript{4}\textsubscript{2-}, Cl\textsuperscript{-}, Sr\textsuperscript{2+}) and NPDOC as determined by specific solute measurements. The relationship between TDS by sum and TDS by gravimetric measurement was verified in the laboratory using known solutions. TDS measurement by sum was found to be more accurate than measuring TDS gravimetrically using blind samples of known TDS.

4.4 Model Development and Verification

Models were developed for all membranes. The model for the LFC1 membrane is discussed to illustrate model development. $K_s$s for the LFC1 membrane were determined for major ions from the initial operational data and modeled as a function of charge using Eqn. 4-6. The major ions were sodium, chloride, calcium, bicarbonate, magnesium, sulfate and silica. The major ions and NPDOC was summed to determine TDS in the membrane feed streams. The data sets following SP and ZN pretreatment were combined for model development. The predicted
and actual $K_{s\text{act}}$s are shown in Figure 4-3. The statistical parameters associated with the model are shown in Table 4-1.

![Figure 4-3 Initial $K_s$ versus charge for LFC1 membrane.](image)

X value of $\pm 2$, $\pm 1$, 0 represents different solute valance of $\text{Ca}^{2+}$, $\text{Mg}^{2+}$, $\text{Na}^+$, $\text{SiO}_2$, $\text{Cl}^-$, $\text{SO}_4^{2-}$; two independent observations for each parameter are from SP and Z pretreatment.

Table 4-1 Diffusion controlled model coefficients and statistical parameters for initial $K_s$ for LFC1 membrane

<table>
<thead>
<tr>
<th>Coefficient</th>
<th>Std. Error</th>
<th>T</th>
<th>P</th>
<th>$R^2 = 0.99$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$K_{s25}$</td>
<td>0.6081</td>
<td>0.0333</td>
<td>18.236</td>
<td>&lt;0.0001</td>
</tr>
<tr>
<td>$x_0$</td>
<td>-0.6986</td>
<td>0.0818</td>
<td>-8.5426</td>
<td>&lt;0.0001</td>
</tr>
</tbody>
</table>
Kₘs changed during operation and were modeled as a function of time using Eqn. 4-8. The independent variables used to model Kₘ as a function of time were temperature, the initial Kₘ, water loading, organic loading (UV₂₅₄), particle loading (turbidity) and chloramines loading. The loading terms represent independent variables affecting Kₘ due to mass loading on the membrane surface. The model was evaluated using the raw feed stream concentration for Cᵣ and using the weighted average of the raw and recycled concentrate streams for Cᵣ. There was no statistical difference regardless of which Cᵣ was used. Hence, Cᵣ was described by the raw water concentration. The final model was determined by non-linear regression and retained only significant terms. As shown in Table 4-2, only temperature and monochloramine loading significantly affect the change of Kₘ during operation using Eqn. 4-9.

\[
K_{\text{hydr}} = \theta s \exp \left[ \frac{\text{SS}}{T - 25} \right] + x_1 \sum_{i=1}^n F_w i \cdot t_i + x_2 \sum_{i=1}^n F_w i \cdot C_{\text{UV} 254 - 1} t_i + x_3 \sum_{i=1}^n F_w i \cdot C_{\text{turb}} - 1 t_i + x_4 \sum_{i=1}^n F_w i \cdot C_{\text{NH}_3 Cl} - 1 t_i
\]

Eqn. 4-9

Table 4-2 Temperature and mass loading diffusion controlled model coefficients for LFC1 membranes

<table>
<thead>
<tr>
<th>Coeff.</th>
<th>Std. Err.</th>
<th>T</th>
<th>P</th>
<th>R²</th>
</tr>
</thead>
<tbody>
<tr>
<td>θₘ</td>
<td>1.13</td>
<td>0.0105</td>
<td>108.5</td>
<td>&lt;0.0001</td>
</tr>
<tr>
<td>X₄</td>
<td>0.06</td>
<td>0.0177</td>
<td>3.4</td>
<td>0.001</td>
</tr>
</tbody>
</table>

Actual vs. predicted TDS, Ca²⁺, Mg²⁺, Na⁺, SO₄²⁻, Cl⁻, Sr²⁺ and NPDOC is shown in Figure 4-4. Permeate solute concentrations were predicted using Eqn. 4-4 and Eqn. 4-8. The predicted and actual TDS was determined by summing Ca²⁺, Mg²⁺, Na⁺, HCO₃⁻, SO₄²⁻, Cl⁻, Sr²⁺ and NPDOC. As shown in Figure 4-4, the model accurately predicted solute concentration in the
permeate stream. The data shown in Figure 4-4 was generated from more than 2000 hours of run time.

$K_s$ models for all inorganic solutes and all membranes are shown in Table 4-3. Monochloramine cumulative loading significantly affected $K_s$ for all membranes during time of operation. Organic loading as determined by $UV_{254}$ significantly affected $K_s$ for the SG and BW30FR1 membranes. Water or Turbidity loading did not significantly affect $K_s$ for any membrane. Note these $K_s$ models were developed for the conditions of water quality and operation for this pilot study as shown in Table 4-4. Applying these models outside of the conditions shown in Table 4-4 should be done with caution.

Table 4-3 Solute MTC model formula for LFC1, X20, SG and BW30FR1 membrane.

<table>
<thead>
<tr>
<th>Membrane</th>
<th>Model Formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>LFC1</td>
<td>$K_{sT} = 1.135 \quad (T^{-25}) \quad \left[ 0.608\exp \left( -0.699 \times \text{CHARGE}^2 \right) + 0.00558 \sum_{i=1}^{n} F_{wi} C_{NH_2Cl - t_i} \right]$</td>
</tr>
<tr>
<td>X20</td>
<td>$K_{sT} = 1.126 \quad (T^{-25}) \quad \left[ 1.069\exp \left( -2.2026\text{CHAR} \times \text{GE}^2 \right) + 0.00085 \sum_{i=1}^{n} F_{wi} C_{NH_2Cl - t_i} \right]$</td>
</tr>
<tr>
<td>SG</td>
<td>$K_{sT} = 1.055 \quad (T^{-25}) \quad \left[ 1.0473\exp \left( -1.60 \times \text{CHARGE}^2 \right) - 0.0871 \sum_{i=1}^{n} F_{wi} C_{UV_{254} - t_i} \right]$</td>
</tr>
<tr>
<td></td>
<td>$\left. + 0.0164 \sum_{i=1}^{n} F_{wi} C_{NH_2Cl - t_i} \right]$</td>
</tr>
<tr>
<td>BW30FR1</td>
<td>$K_{sT} = 1.0099 \quad (T^{-25}) \quad \left[ 0.9037\exp \left( -2.845 \times \text{CHARGE}^2 \right) - 0.0388 \sum_{i=1}^{n} F_{wi} C_{UV_{254} - t_i} \right]$</td>
</tr>
<tr>
<td></td>
<td>$\left. + 0.00563 \sum_{i=1}^{n} F_{wi} C_{NH_2Cl - t_i} \right]$</td>
</tr>
</tbody>
</table>

Where:

$F_{w,t} = \text{m}^3/\text{m}^2$
\[ F_{\text{wC}}_{\text{turb}} = \text{m}^3/\text{ntu/m}^2 \]
\[ F_{\text{wC}}_{\text{NH2CL}} = \text{g/m}^2 \]
\[ F_{\text{wC}}_{\text{uv254}} = \text{m}^3/\text{cmm}^2 \]

Table 4-4 Data range of operating and water qualities for model development

<table>
<thead>
<tr>
<th></th>
<th>Turbidity</th>
<th>NH\textsubscript{2}Cl</th>
<th>UV\textsubscript{254}</th>
<th>TDS</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>ntu</td>
<td>mg/L</td>
<td>cm\textsuperscript{1}</td>
<td>mg/L</td>
</tr>
<tr>
<td>ZN</td>
<td>Mean</td>
<td>0.103</td>
<td>0.9</td>
<td>0.11</td>
</tr>
<tr>
<td></td>
<td>Min-Max</td>
<td>0.047-0.286</td>
<td>0-2.3</td>
<td>0.034-0.201</td>
</tr>
<tr>
<td>SP</td>
<td>Mean</td>
<td>0.099</td>
<td>0.8</td>
<td>0.044</td>
</tr>
<tr>
<td></td>
<td>Min-Max</td>
<td>0.049-0.297</td>
<td>0-1.9</td>
<td>0.013-0.089</td>
</tr>
<tr>
<td>Overall</td>
<td>Mean</td>
<td>0.102</td>
<td>0.8</td>
<td>0.087</td>
</tr>
<tr>
<td></td>
<td>Min-Max</td>
<td>0.047-0.297</td>
<td>0-2.3</td>
<td>0.013-0.201</td>
</tr>
</tbody>
</table>

Figure 4-4 Predicted versus actual for LFC1 membrane
The models shown in Table 4-3 were also developed by using a weighted average of the raw water and recycled concentrate feed streams to determine mass loading on the membrane. The resulting models were statistically identical to the models shown in Table 4-3. Hence the simplest models were reported. This result was somewhat surprising but indicates the water quality of the recycled stream did not have the same impact on mass transfer as the pretreated feed stream water quality. This could possibly reflect differences in the organic solutes that did not react with the membrane surface during the first pass and the organic solutes that did, which is not unreasonable for aggregate parameters like UV\textsubscript{254}.

The initial $K_s$ for TDS can be calculated by determining a weighted charge for TDS as shown in Eqn. 4-10, where $WC$ is the weight charge, $z$ is the specific solute charge and $m$ is the moles of solute in solution. In this study, Na$^+$, Cl$^-$, Ca$^{2+}$, Mg$^{2+}$, HCO$_3^-$ and SO$_4^{2-}$ are major ions in the feed stream. The average weighted TDS charge for all observations of the feed stream was 1.203. The weighted TDS charge was used to determine the $K_s$ for TDS using Eqn. 4-7. Eqn. 4-4 was used to predict TDS.

$$WC = \frac{\sum_{i=1}^{n} z_i m_i}{\sum_{i=1}^{n} m_i} \quad \text{Eqn. 4-10}$$

The predicted permeate and actual TDS for the four membranes are shown in Figure 4-5, 6, 7 and 8. Paired T tests found no statistical difference for the predicted and actual TDS for any of the membranes. A predicted TDS plane is also shown in these figures to demonstrate the variation of permeate TDS with temperature and monochloramine loading at the average
operating conditions for this work, which were 0.8mg/L NH₂Cl as Cl₂ and 0.087 cm⁻¹ UV₂₅₄ in the feed stream, and 20.4 L/hr·m² (12 gsfd) and 72% recovery.

Noting the difference in the TDS scales in these figures, the permeate TDS variation with monochloramine loading and temperature indicates the BW30FR1 membrane was more monochloramine resistant, more temperature resistant and rejected more TDS relative to the other membranes. Generalization of the effects of temperature and chloramines on TDS transfer are not linear as shown in Figure 4-5, 6, 7 and 8. However in all cases TDS mass transfer is predicted to increase with increasing chloramine concentration and temperature. Reducing temperature and chloramine concentration is beneficial to maintenance of high TDS rejection. However, little can be done to reduce temperature in plant applications and control of biological fouling may require high chloramine loading.

Figure 4-5 Actual and predicted TDS versus monochloramine loading and temperature for LFC1 membrane

Figure 4-6 Actual and predicted TDS versus monochloramine loading and temperature for X20 membrane
Finally, these models can be used to predict membrane cleaning frequency or membrane life once pretreated water quality and maximum acceptable permeate TDS is assumed. It is mathematically possible to assume membrane feed stream water quality that would offset the negative and positive terms in each of the models shown in Table 4-3. While it is reasonable to assume some organic fouling would offset chloramine deterioration, it is unreasonable to assume there would be no change in solute mass transfer if these terms are mathematically balance using the equations in Table 4-3, just as it is unreasonable to assume that turbidity would not affect membrane performance if turbidity was significantly outside of the range shown in Table 4-4. Reasonably used, the equations shown in Table 4-3 can provide predictions of water quality, performance, cleaning frequency and membrane replacement.
4.5 Conclusion

A diffusion controlled model has been developed that considers the effects of water quality and time on solute mass transfer.

Initial solute MTCs were described mathematically using a Gaussian distribution based on solute charge and membrane. The change of solute MTCs with time was described mathematically using a mass loading model that considered the initial solute MTC and water quality, specifically temperature, water, turbidity, monochloramines and organic (UV254). Monochloramine mass loading affected all of the membranes, UV254 mass loading affected two of the four membranes used in this work. Turbidity and water mass loading had no statistically significant effect on solute rejection by any membrane for the conditions of this work.

Modeling permeate TDS indicated there was significant differences in performance among the tested membranes regarding chloramine resistance, temperature and TDS rejection.

Taking the feed water concentration ($C_f$) either as the raw water TDS or the weighted average of the raw water and recycled stream TDS resulted in no statistical between predicted TDS in the permeate stream.
4.6 References


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CHAPTER 5: ASSESSMENT OF ASTM D 4516 FOR EVALUATION OF REVERSE OSMOSIS MEMBRANE PERFORMANCE

The evaluations of reverse osmosis membrane performance using ASTM D 4516 and a modified form of the mass transfer coefficient (MTC) from the homogenous solution diffusion model (HSDM) on a common data set were different. The evaluation methodology using the HSDM MTC is developed and presented for standardizing salt passage. ASTM D 4516 is based on normalized pressure over time for a given set of data, considers temperature only for water production but not for salt passage. Normalization of the HSDM MTCs for temperature and pressure over time provides a universal assessment for the water and water quality produced by a specific diffusion controlled membrane. Assessment of water production was identical by either method. Assessment of salt passage was different. Salt Passage determined by the ASTM method is dependent on actual net driving force, while HSDM determined Salt Passage is dependent on specific flux and net driving force. Evaluation of membrane performance using the ASTM and HSDM MTC methods provide different results when flux, recovery, feed stream concentration or membrane mass transfer characteristics change. The HSDM MTC method of membrane evaluation is more versatile for assessment of membrane performance at varying sites and changing operation.
5.1 Introduction

Reverse Osmosis (RO) and nanofiltration (NF) are significant technologies for production of drinking water. RO and NF performance is typically evaluated by the change of water productivity and salt passage over time. Standardization of productivity and salt passage (membrane performance) is required to compare inter and intra site membrane performance. The American Standard for Testing Materials (ASTM) standard method, ASTM D 4516 Method - Standard Practice for Standardizing Reverse Osmosis Performance Data, provides a procedure to normalize permeate flow (Qp) and salt passage (SP) for an RO system [1] that can be used to assess membrane performance. ASTM D 4516 has been reported in several technique papers for RO membrane long-term performance evaluation [2-4].

ASTM method of assessing membrane performance requires normalization of actual operating conditions using standard operating conditions for pressure, temperature, conversion and feed concentration which changes the ASTM specified Qp and SP [1]. As stated in the ASTM method, the standardized SP can be inaccurate if a significant concentration of ions passing the membrane are independent of pressure and there is a large difference in pressure between actual and standard conditions [1]. As most ions are diffusion controlled, only low molecular weight and neutral solutes would be affected by the ASTM caveat. However, large pressure differences can be caused by changing temperature, feed stream water quality and membrane mass transfer characteristics.

Other methods have been developed for assessment of diffusion controlled membrane performance [5-9]. These methods evaluate mass transfer coefficients (MTC) for water ($K_w$, also referred to as specific flux), and solutes ($K_s$) over time. These MTCs are normalized for
pressure, temperature over time and provide a more universal method of performance assessment. This paper presents assessment of membrane performance on a common data set using both methods.

5.2 Theory

5.2.1 Homogenous Solution Diffusion Model (HSDM)

The HSDM describes water flux, $J_w$, and mass solute flux $J_s$, through diffusion controlled (RO/NF) membranes as shown in Eqn. 5-1 and Eqn. 5-2 [10, 11]. Eqn. 5-3 is the HSDM and has successfully described steady-state permeation of water and solutes through diffusion controlled membranes [12-14]. A membrane flow diagram showing influent and effluent flow, concentration and pressure of the feed, permeate and concentrate streams is presented in Figure 5-1.

![Figure 5-1 NF or RO membrane flow diagram](image)

The HSDM has been developed by mathematically relating the average feed stream concentration to system recovery in a mass balance approach [10]. The HSDM was the first model developed for a high recovery system [15]. HSDM can be utilized to predict permeate
concentrations for any RO or NF membrane application given the feed stream concentration, flux, recovery and MTCs ($K_w$, $K_s$),

\[ J_w = K_w \times (\Delta P - \Delta \pi) = \frac{Q_p}{A} \]  
Eqn. 5-1

\[ J_s = K_s \times \Delta C = J_w \times C_p \]  
Eqn. 5-2

\[ C_p = \frac{K_s C_f}{K_w (\Delta P - \Delta \pi)(\frac{2 - 2R}{2 - R}) + K_s} \]  
Eqn. 5-3

Where:
- $J_w$ = Water flux
- $K_w$ = Solvent MTC
- $\Delta P$ = Pressure gradient
- $\Delta \pi$ = Osmotic pressure gradient = $\pi_{fb} - \pi_p$
- $Q_p$ = Permeate stream flow
- $A$ = Membrane surface area
- $J_s$ = Solute flux
- $K_s$ = Solute MTC
- $\Delta C$ = Concentration gradient
- $C_p$ = Permeate concentration
- $C_f$ = Feed concentration
- $R$ = Recovery = $Q_p/Q_f$
- $Q_f$ = Feed stream flow

The osmotic pressure gradient is the difference between the feed-brine and permeate osmotic pressure, it can be estimated by the ASTM method as described previously, or by using total dissolved solids (TDS) as shown in Eqn. 5-4[11].

\[ \pi = K_{TDS} \times TDS \]  
Eqn. 5-4
Permeate flow and salt passage increase as temperature increases [16, 17]. $K_w$ can be compensated for changes in viscosity and membrane film, e.g. membrane pore radius by normalization with respect to temperature [7, 11]. Eqn. 5-5 and Eqn. 5-6 were used to normalize temperature. If Eqn. 5 is developed only from the viscosity of water, $\theta_w$ will be equal to 1.03, which is what is used in ASTM D 4516. If this equation is developed by non-linear regression of actual operating data, $\theta_w$ will be normalized for changes in the membrane film as well as the viscosity of water. $K_s$ can be normalized for temperature using a similar expression as shown in Eqn. 5-6.

\[
K_w^T = \theta_w^{(T-25)} \times K_{w25} \quad \text{Eqn. 5-5}
\]
\[
K_s^T = \theta_s^{(T-25)} \times K_{s25} \quad \text{Eqn. 5-6}
\]

Where:
$K_w^T$ = Solvent MTC at temperature T ($^\circ$C)
$K_{w25}$ = Standardized solvent MTC at 25 $^\circ$C
$\theta_w$ = $K_w$ temperature correction factor
$K_s^T$ = Solute MTC at temperature T ($^\circ$C)
$K_{s25}$ = Standardized solute MTC at 25 $^\circ$C
$\theta_s$ = $K_s$ temperature correction factor

5.2.2 ASTM Standardization Methods

ASTM D 4516 utilizes $Q_p$ and SP indices as shown in Eqn. 5-7and Eqn. 5-8. [1]. As shown in these equations, normalization of permeate flow is achieved using the standard and
actual (a) net driving forces (b) temperature correction factors and (c) permeate stream flows.

Whereas SP is normalized using standard and actual (a) net driving force, (b) feed and brine (concentrate) stream concentrations and (c) SPs. Standard values of any of these variables are determined by averages of each over the data set under consideration. Consequently large variations in temperature, conversion (recovery), pressure (flux or fouling) or feed stream concentration are compensated for by averaging the associated parameters, which limits the utility of this approach. This method is recommended for both spiral-wound and hollow fine fiber membrane systems.

\[
Q_{pa} = \frac{\left( P_{fs} - \frac{\Delta P_{fbs}}{2} - P_{ps} - \pi_{fbs} + \pi_{ps} \right) \times \left( TCF_s \right)}{\left( P_{fa} - \frac{\Delta P_{fba}}{2} - P_{ps} - \pi_{fba} + \pi_{ps} \right) \times \left( TCF_a \right)} \times Q_{pa}
\]

Eqn. 5-7

\[
SP_s = \frac{\left( P_{fs} - \frac{\Delta P_{fbs}}{2} - P_{ps} - \pi_{fbs} + \pi_{ps} \right) \times \left( C_{fbs} \right) \times \left( C_{fa} \right)}{\left( P_{fa} - \frac{\Delta P_{fba}}{2} - P_{ps} - \pi_{fba} + \pi_{ps} \right) \times \left( C_{fbs} \right) \times \left( C_{fa} \right)} \times SP_a
\]

Eqn. 5-8

Where:

- \( Q_{pa} \) = actual permeate flow
- \( P_{fa} \) = actual feed pressure
- \( Q_{ps} \) = standard permeate flow
- \( P_{fs} \) = standard feed pressure
- \( P_{pa} \) = actual permeate pressure
- \( SP_s \) = standard salt passage
- \( \pi_{fba} \) = actual feed-brine osmotic pressure
- \( \pi_{fa} \) = actual permeate osmotic pressure
- \( \Delta P_{fbs}/2 \) = standard one half device pressure drop
- \( \Delta P_{fba}/2 \) = actual average device pressure drop
- \( \pi_{fbs} \) = standard feed-brine osmotic pressure
- \( \pi_{ps} \) = standard permeate osmotic pressure
- \( TCF_s \) = standard temperature correction factor
- \( C_{fbs} \) = standard linear or log mean of feed-brine concentration, mg/L NaCl
- \( C_{fa} \) = actual feed concentration, mg/L NaCl
- \( C_{fba} \) = actual linear or log mean of feed-brine concentration, mg/L NaCl
- \( C_{fs} \) = standard feed concentration, mg/L NaCl

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Osmotic pressure is related to temperature and concentration as NaCl (in mg/L) using Eqn. 5-9.

\[
\pi = 0.2654 \times C \times (T + 273.15) / (1000 - C / 1000)
\]

Eqn. 5-9

Where:

\[\pi\] = osmotic pressure in kilopascals
\[C\] = NaCl equivalent concentration in mg/L
\[T\] = temperature in °C

5.3 Methods

A large scale pilot study was conducted from July 16, 2002 to April 2, 2003 during which the Filmtec BW30FR, Filmtec BW30LE, Trisep X20 and Osmonics SG were tested simultaneously. These four membranes were low pressure reverse osmosis membranes. A flow diagram for the pilot study is shown in Figure 5-2. The raw water was highly organic and brackish surface water from St, Johns River in Florida, U.S.A. The surface water was pretreated by ferric sulfate coagulation using Super Pulsator and Actiflo technologies and dual-media filtration. Sulfuric acid was used for pH adjustment. Chloramine addition and 5-micron cartridge filtration also preceded membrane filtration. As shown in Figure 5-2, a single stage membrane system consisting of a single pressure vessel containing three 4 inch spiral wound modules.

The permeate flux and system recovery were maintained at 22 L·hr\(^{-1}\)·m\(^{-2}\) (13 gsfd) and 30%. Flow was controlled by changing valve position on the feed stream, thus feed stream
pressure increased during operation. Pressure, flow and temperature were typically recorded twice daily during daylight hours for the feed, concentrate and permeate streams. pH, conductivity, turbidity, UV$_{254}$ and chloramine residual were recorded when operational data was recorded. Additional water quality was measured weekly and included chloride, bromide, sulfate, silica, sodium, calcium, barium, strontium, total iron and NPDOC. The data shown in this paper is for X20 membrane. The membrane was replaced after 2370 hours of cumulative run time on the membrane.

![Diagram](image)

**Figure 5-2** Integrated membrane system showing super pulsator (SuP) and actiflow (AF) pretreatment

### 5.4 Theoretical interpretations

The ASTM method of standardizing permeate flow is based on Eqn. 5-7 and can be developed from the equations used to develop the HSDM. However ASTM method of standardizing salt passage (SP) as shown in Eqn. 5-8 can not be developed from the solute mass
transfer equations used to develop the HSDM and is different. The actual and standardized permeate flows are shown in Eqn. 5-10 and Eqn. 5-11 using the fundamental flux definition, membrane area, K_w, net driving force and temperature normalization. Solving these two equations for Q_{ps} produces Eqn. 5-12 and demonstrates evaluations of water productivity from a RO or NF process using either the ASTM or HSDM methods are identical.

\[
Q_{pa} = J_{wa} \times A = K_{w25} \times (\Delta P_a - \Delta \pi_a) \times A \times \theta_w^{(T_{a-25})} \quad \text{Eqn. 5-10}
\]

\[
Q_{ps} = J_{ws} \times A = K_{w25} \times (\Delta P_s - \Delta \pi_s) \times A \times \theta_w^{(T_{s-25})} \quad \text{Eqn. 5-11}
\]

\[
Q_{ps} = \frac{(\Delta P_s - \Delta \pi_s) \times \theta_w^{(T_{s-25})}}{(\Delta P_a - \Delta \pi_a) \times \theta_w^{(T_{a-25})}} \times Q_{pa} \quad \text{Eqn. 5-12}
\]

The ratio of the permeate concentration to the bulk concentration is shown in Eqn. 5-13. The HSDM can be developed from Eqn. 5-13 keeping the bulk feed concentration constant and incorporating recovery as shown in Eqn. 5-13. If the permeate concentration is dropped from the concentration gradient, a similar ratio of permeate concentration to the average bulk concentration can be developed as shown in Eqn. 5-13. A 1.5 % concentration gradient error was produced in this work by dropping C_p, however the error would increase as C_f or K_w (nanofiltration) increased. However, ASTM D 4516 is only meant for standardization of SP and Q_p from RO membranes, which have relatively low K_w's and K_a's.

The left hand side of Eqn. 5-13 is developed by assuming the permeate to average bulk ratio is simply the ratio of the solute mass transfer coefficient and water flux. The equation for SP calculation in shown in Eqn. 5-14 and is a simple ratio of diffusion controlled solute flux divided by solvent flux. Note HSDM solute flux is the product of the average concentration gradient and solute mass transfer coefficient. This is a reasonable approach initially but errors in that recovery and permeate solute concentration is not considered. Consequently a recovery term
and solute MTC \( (K_s) \) appear in the denominator of Eqn. 5-3 and are absent from Eqn. 5-8. Consequently, the ratio of permeate and feed stream concentration or SP using the ASTM approach considers SP to be the ratio of diffusion controlled solute transport and flux mechanistically but did not develop SP fully using mass balances.

\[
\frac{C_p}{C_{fb}} = \frac{C_p}{\Delta C} = \frac{K_s}{K_w \times (\Delta P - \Delta \pi)} \quad \text{Eqn. 5-13}
\]

\[
SP = \frac{C_p}{C_f} = \frac{K_s \times C_{fb}}{K_w \times (\Delta P - \Delta \pi) \times C_f} \quad \text{Eqn. 5-14}
\]

The ASTM approach does not rely on any MTCs and does not provide a means of predicting the impact of different membranes or operating conditions on SP. It does provide a means of comparing permeate production and SP for any set of operating conditions and any environments. The membrane permeate production and SP would be normalized for comparison to any other membrane permeate and production in any environment. However, the actual SP for any given condition of temperature, flux, recovery or feed stream concentration in a different environment could not be predicted unless the standard values specified in Eqn. 5-7 and Eqn. 5-8 were known. The HSDM considers five different independent variables, is derived from a fundamental diffusion controlled mass transfer approach and offers a easy method of considering the impact of different membranes or operating conditions on SP. The ASTM approach for evaluation of SP was likely postulated from rational thinking but not derived.

Temperature is not considered in ASTM D 4516 for SP, but it is considered for \( Q_p \). The assumption is that temperature does not affect solute diffusion. However, solute diffusion
increases at a higher rate with respect to temperature than the viscosity of water decreases with respect to temperature. Consequently, salt rejection will increase as temperature decreases.

Temperature, normal use (water loading), organic loading (UV \(_{254}\)), turbidity loading, and monochloramine loading are independent variables that could potentially affect productivity and solute mass transfer. Eqn. 5-15 and Eqn. 5-16 are direct mass loading expressions that consider the impact of temperature and feed water quality on water and solute mass transfer. \( K_w \) and \( K_s \) are empirically related to the change in membrane mass transfer by specific consideration of degradation (by water), oxidation (by NH\(_2\)Cl) and organic (by NPDOC or UV-254) or particulate (by turbidity) fouling. \( \theta_w \) and \( \theta_s \) as well as all of the water quality coefficients (\( x_i \)) are determined by non-linear regression. These equations much like the ASTM SP equation are postulated rational equations for prediction of the impact of several variables on RO membrane mass transfer. But unlike the ASTM Eqn. 5-7 and Eqn. 5-8, these equations when combined with Eqn. 5-3 provide a means of predicting productivity and SP or permeate concentration at any time, temperature, flux, recovery, feed concentration or fouling conditions.

\[
K_w = \theta_w^{(T-.25)} \left[ K_{w25} + x_{water} \sum_{i=1}^{n} J_w t_i + x_{UV} \sum_{i=1}^{n} J_w C_{UV254-1} t_i 
+ x_{turb} \sum_{i=1}^{n} J_w C_{turb} - t_i + x_{NH2Cl} \sum_{i=1}^{n} J_w C_{NH2Cl} - t_i \right]
\]  
Eqn. 5-15

\[
K_s = \theta_s^{(T-.25)} \left[ K_{s25} + x_{water} \sum_{i=1}^{n} J_w t_i + x_{UV} \sum_{i=1}^{n} J_w C_{UV254-1} t_i 
+ x_{turb} \sum_{i=1}^{n} J_w C_{turb} - t_i + x_{NH2Cl} \sum_{i=1}^{n} J_w C_{NH2Cl} - t_i \right]
\]  
Eqn. 5-16

Where:
5.5 Results and Discussion

5.5.1 Mass Loading Model Development

The standard conditions for normalization are shown in Table 5-1 and were set to the average actual conditions as specified in ASTM D 4516. Since the X20 membrane was replaced at 2370 hours, the average conditions were determined before and after 2370 hours as shown in Table 5-1. The feed water quality, recovery, flow and flux are similar but the feed pressure and device pressure drop were different for each period. These standard conditions are averaged from more than 2000 hours of operation of each membrane.
Table 5-1 Standard conditions for normalization of SP for LR2 system

<table>
<thead>
<tr>
<th>Standard condition</th>
<th>1st Membrane</th>
<th>2nd Membrane</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaCl feed mg/L</td>
<td>350</td>
<td>350</td>
</tr>
<tr>
<td>Pressure drop device kPa (psi)</td>
<td>303 (44)</td>
<td>152 (22)</td>
</tr>
<tr>
<td>Pressure feed kPa (psi)</td>
<td>1020 (148)</td>
<td>1344 (195)</td>
</tr>
<tr>
<td>Pressure permeate kPa (psi)</td>
<td>138 (20)</td>
<td>138 (20)</td>
</tr>
<tr>
<td>Recovery</td>
<td>0.3</td>
<td>0.3</td>
</tr>
<tr>
<td>Flow feed m³·d⁻¹ (gpm)</td>
<td>42.0 (7.7)</td>
<td>39.8 (7.3)</td>
</tr>
<tr>
<td>Flux L·m⁻²·hr⁻¹ (gsfd)</td>
<td>23.3 (13.7)</td>
<td>22.1 (13.0)</td>
</tr>
<tr>
<td>Temperature °C</td>
<td>25.0</td>
<td>25.0</td>
</tr>
</tbody>
</table>

1 kPa = 0.145 psi; 1 m³·d⁻¹ = 0.183 gpm; 1 L·m⁻²·hr⁻¹ = 0.589 gsfd.

The effects of temperature and water quality on mass transfer were assessed by regressing $K_w$ and $K_s$ over time using Eqn. 5-15 and Eqn. 5-16 and the water quality data set corresponding to periods one and two. Initially, all independent variables shown in Eqn. 5-15 and Eqn. 5-16 were regressed in the mass loading models to determine significance. The most insignificant variable as determined by the highest p or $\alpha$ values over 0.05 was dropped and the regression was repeated. This continued until there were no insignificant terms remaining. Both $\theta_w$ and $\theta_s$ were significant and are shown in Table 5-2. The model coefficients indicate $K_w$ is more influenced by temperature than $K_s$.

Table 5-2 Nonlinear regression coefficients of $K_w$, $K_s$ mass loading model.

<table>
<thead>
<tr>
<th>System</th>
<th>$K_{w25}, K_{s25}$</th>
<th>$X_{water}$³</th>
<th>$X_{UV}$</th>
<th>$X_{turb}$</th>
<th>$X_{NH2Cl}$</th>
<th>$\theta_w$, $\theta_s$</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$K_w$</td>
<td>0.68 (L·d⁻¹·m⁻²·kPa⁻¹)¹</td>
<td>-3.90E-07</td>
<td></td>
<td></td>
<td></td>
<td>1.041</td>
<td>0.78</td>
</tr>
<tr>
<td>$K_s$</td>
<td>0.214 (L·hr⁻¹·m⁻²)²</td>
<td>3.60E-06</td>
<td></td>
<td></td>
<td></td>
<td>1.006</td>
<td>0.29</td>
</tr>
</tbody>
</table>

¹ 1 L·m⁻²·hr⁻¹ = 0.589 gsfd; ² 1 L·d⁻¹·m⁻²·kPa⁻¹ = 0.169 gsfd/psi; ³ Cumulative water flux in m³/m².
5.5.2 Standardized ASTM Qp and HSDM \( K_w \)

The normalized \( K_w \) and ASTM standardized \( Q_p \) versus membrane run time for the X20 membrane are shown in Figure 5-3. ASTM standardized \( Q_p \) was calculated from Eqn. 5-7 and the normalized \( K_w \) was calculated from Eqn. 5-4 and Eqn. 5-5. The X20 membrane used in period one is described as the first membrane. The X20 membrane used in period two is described as the second membrane. Clearly, both the ASTM PF and normalized \( K_w \) decreased with time. The ASTM PF and \( K_w \) changed proportionally over time. There is no difference in the normalized HSDM \( K_w \) and ASTM \( Q_p \) as shown in Figure 5-3 and as predicted by the previous theoretical discussion. Therefore, both methods provided equivalent assessments of membrane productivity over time of operation.

![Figure 5-3 ASTM standardized PF and normalized \( K_w \) versus membrane run time, X20 membrane.](image)

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The actual and predicted $K_w$s are shown in Figure 5-4. $K_w$ was predicted using Eqn. 5-15 and as shown in Figure 5-4 is accurately predicted. The model coefficients for Eqn. 5-15 are listed in Table 5-2. The variation of $K_w$ over time was caused by membrane fouling and deterioration and represents actual not normalized mass transfer of water.

Figure 5-4 Actual $K_w$ and HSDM predicted $K_w$ versus membrane run time for the X20 membrane.

5.5.3 ASTM and HSDM standardized SP

The predicted TDS permeate concentration and predicted SP versus time are shown in Figure 5-5. The HSDM as shown in Eqn. 5-3 with incorporation of Eqn. 5-13 for $K_w$ and $K_s$ was
used to predict $C_p$ and calculate predicted SP. As shown in Figure 5-5, the HSDM accurately predicts permeate TDS and salt passage. There is significantly more variation in $C_p$ than SP, which is due to Figure 5-5 scale differences. ASTM SP is not shown in Figure 5-5 because ASTM predicted SP methodology is not defined in ASTM D 4516 and is probably not developed.

![Figure 5-5 Actual and HSDM predicted TDS and SP versus membrane run time, X20membrane.](image)

Membrane replacement can be determined by SP and membrane life can be determined by predicting SP. Simple linear regression equations relating standardized SP to time are shown in Figure 5-6 for each period of operation for the X20 membrane. SP was standardized in order to compare the ASTM D 4517 and HSDM SP over time on an equivalent basis. The conditions for standardization are given in Table 5-1. Simple trend lines are shown in Figure 5-6 for ASTM
and HSDM SP with time for period 1 and period 2. The slope of the ASTM trend line was greater than the slope of the HSDM trend line in period one, both slopes were positive in period one. The inference of increasing SP with time is that the membrane will have to be replaced at some time due to excess SP. In period two, the slope of the SP trend line was negative whereas the slope of the HSMD trend line was positive. A negative slope indicates the membrane can be used indefinitely to reject salt. The results of the two methods are different. Normalization is essential to see what is happening to SP during time, however the lack of consideration of temperature in ASTM D 4516 standardization of SP likely caused the negative trend of SP with time in period two. SP can decrease with time, but it is noted that actual SP did not decrease with time as shown in Figure 5-6.

![Figure 5-6 ASTM standardized SP and HSDM SP normalized for temperature versus run time.](image)

Figure 5-6 ASTM standardized SP and HSDM SP normalized for temperature versus run time.
5.5.4 Temperature Effects on HSDM and ASTM SP

ASTM SP standardization is essentially based on actual and standard net driving forces and actual and standard feed and bulk stream salt concentrations. Only osmotic pressure is corrected for temperature in the ASTM model; however temperature impacts solute more than water transport because of the relative changes in ion diffusivity and the viscosity of water. SP increases as temperature increases because ion diffusivity increases more rapidly than the viscosity of water decreases with increasing temperature. Although water flux increases as temperature increases, the diffusion of ions increases more rapidly and SP increases as temperature increases. Al-bastaki and Al-Qahtani also noted that SP increases with temperature due to an increase in pore size with temperature [16]. As noted previously, feed stream pressure was varied in order to maintain constant flux.

In order to calculate osmotic pressure using Eqn. 5-8, a specific correlation between conductivity and standardized NaCl concentration was established. Lab water quality data from April 2002 to March 2003 were analyzed in UCF ESI LAB that included all major cation and anion in feed water. Salt in NaCl was calculated using summation of molarities of Ba$^{2+}$, Ca$^{2+}$, Mg$^{2+}$, Na$^{+}$, SiO$_2$, Br$^-$, Cl$^-$, SO$_4^{2-}$ and Alkalinity in the feed water. On the other hand, field measured feed water conductivity and field measured feed water temperature were recorded twice every day. Finally, the correlation between field measured conductivity (in ms/m) and NaCl in mg/L was developed and is shown as Eqn. 5-17.

\[ \text{NaCl} = 4.16 \times \mu \]  
\[ \text{Eqn. 5-17} \]

Where:
NaCl  = mg/L NaCl
µ  = conductivity in ms/m @ 25 °C

The effect of temperature on SP is shown in Table 5-3 for the HSDM, ASTM D 4516 and Rosa program distributed by Dow for Filmtec membranes. The same membrane and operating conditions are represented in all cases. Eqn. 5-17 and Eqn. 5-9 were used to determine the effect of temperature on ASTM D 4516 SP, which essentially did not vary with temperature and was affected the least of the three methods. ROSA predicted SP was affected the most and varied from 0.55 % at 5 °C to 1.33 % at 40 °C. However, the data in Table 5-3 clearly shows that ASTM D 4516 normalization removes any significant impact of temperature on SP.

Table 5-3 Comparison of ASTM and HSMD SP at varying temperature

<table>
<thead>
<tr>
<th>Temperature</th>
<th>HSDM-SP</th>
<th>ASTM-SP</th>
<th>ROSA-SP</th>
</tr>
</thead>
<tbody>
<tr>
<td>°C</td>
<td>%</td>
<td>%</td>
<td>%</td>
</tr>
<tr>
<td>5</td>
<td>1.50</td>
<td>1.442</td>
<td>0.55</td>
</tr>
<tr>
<td>10</td>
<td>1.55</td>
<td>1.443</td>
<td>0.63</td>
</tr>
<tr>
<td>20</td>
<td>1.64</td>
<td>1.454</td>
<td>0.83</td>
</tr>
<tr>
<td>25</td>
<td>1.69</td>
<td>1.455</td>
<td>0.93</td>
</tr>
<tr>
<td>30</td>
<td>1.74</td>
<td>1.456</td>
<td>1.05</td>
</tr>
<tr>
<td>35</td>
<td>1.79</td>
<td>1.456</td>
<td>1.18</td>
</tr>
<tr>
<td>40</td>
<td>1.84</td>
<td>1.457</td>
<td>1.33</td>
</tr>
</tbody>
</table>

ROSA-SP: Prediction using design software ROSA 4.3 for a BW30-4040 membrane, 3_vessels_single_stage.

5.5.5 SP Comparison at Varying Flux and Recovery

The predicted ASTM D 4516 SP and HSDM predicted SP at different Ks of 0.5, 0.85 and 1.7 L·m⁻²·hr⁻¹ are shown in Figure 5-7. Predicted SP using the HSDM model was calculated
for 400 mg/L TDS concentration in the feed stream TDS at 25 °C. Flux and recovery were varied from 8.5 to 51 L·m⁻²·hr⁻¹ (5 to 30 gsfd) and from 5 to 90 % respectively. \(K_w\) was assumed to be constant at 0.59 L·d⁻¹·m⁻²·kPa⁻¹ (0.1 gsfd/psi), SP was calculated using HSDM predicted \(C_p\) which accounted mass balance without neglecting the permeate concentration, the required pressure and concentration terms for ASTM D 4516 were calculated from mass balances and water fluxes assuming the same \(K_w\) as for the HSDM. Neglecting the permeate concentration at higher recovery and lower flux introduces significant error in ASTM SP standardization.

As shown in Figure 5-8, the predicted SP using ASTM D 4516 does not change for varying flux and recovery, however the predicted SP using the HSDM does change with flux and recovery. The essential point of ASTM D 4516 is illustrated by the lack of variation of SP with flux and recovery. This method of standardization removes nearly all effects of feed concentration, flux and recovery on SP, and can be used to compare SP in different environments and for different RO membranes. ASTM D 4516 can be used accurately for determining standardized SP on RO membranes, which are membranes with \(K_w\)s less than 0.59 L/d-m² (0.1 gsfd/psi) and \(K_s\)s less than 0.51 L·d⁻¹·m⁻²·kPa⁻¹ (0.3 gsfd), which represent the upper end of water and solute mass transfer coefficients for RO membranes. If ASTM were used to standardize SP of a NF membrane the resulting plane would not be flat as shown in Figure 5-7. Note, the plane generated by the lowest \(K_w\) and \(K_s\) is relative flat, but more plane curvature is generated in Figure 5-7 by higher lowest \(K_w\) and \(K_s\). Hence, the effects of flux and recovery on SP using a NF membrane would not be removed using this method and SP standardization would not be achieved. Moreover, if the predicted SP plane is not flat, the SP does not meet the ASTM D 4516 criteria for standardization. Consequently, NF SP using different membrane in different environments could not be accurately compared. Additionally ASTM D 4516 can not be easily
used if at all used to predict actual SP. The HDSM is more flexible than ASTM D 4516 and can be used to predict SP for varying concentration, flux, recovery and temperature for any membrane once the solute and water MTCs are known [16, 17].

Figure 5-7 ASTM standardized SP and HSMD SP versus flux and recovery for varying $K_s$

Plane1: $K_s = 0.5 \text{L·hr}^{-1} \cdot \text{m}^{-2}$; Plane2: $K_s = 0.85 \text{L·hr}^{-1} \cdot \text{m}^{-2}$
Plane3: $K_s = 1.7 \text{L·hr}^{-1} \cdot \text{m}^{-2}$; $K_w = 0.00103 \text{L·d}^{-1} \cdot \text{m}^{-2} \cdot \text{d}^{-1}$
In summary ASTM D 4516 provides a method of evaluating membrane productivity and salt passage for any environment and any set of operating conditions by normalization. Production ($Q_p$) is normalized to temperature, pressure and permeate flow. Salt passage is normalized to pressure, salt concentration and salt passage. Hence, normalized production and salt passage can be compared for any environment and any set of operating conditions. ASTM D
4516 is not meant to be used and can not be easily used to predict actual production for different feed stream concentrations, flux, recovery or temperature. ASTM D 4516 assessment of water production was verified by derivation from basic mass transfer equations, but the assessment of salt passage was probably developed by rational postulation. Prediction of productivity and salt passage for varying temperature, foulants, feed concentrations, flux and recovery for different membranes is easily done using the HSDM.

5.6 Conclusion

5.6.1 General Conclusions

ASTM D 4516 and HSDM methods of assessing membrane productivity and solute mass transfer are different. The HSDM method considers water quality mass solute and water MTCs, fluxes, recoveries, foulants and temperatures which are directly transferable to any other water quality environments. ASTM D 4516 is based on a ratio of operating results to average operating conditions and does not consider major factors that influence mass transfer. However the ASTM D 4516 does provide standardized measures of production and salt passage that can be directly used to assess membrane performance among any environments and operating conditions. ASTM D 4516 just can not be easily used to predict actual performance.

5.6.2 Specific Conclusions

ASTM D 4516 should be modified to reflect a mass transfer approach and develop solute and water MTCs that can be modified to accommodate changes in feed water quality, foulants and temperature during operation and easily predict actual membrane performance.
ASTM D 4516-85 consideration of temperature significantly limits comparison of RO processes in cold and warm weather environments.

There was no difference in comparison of X20 productivity using ASTM D 4516-85 or HSDM predicted permeate flow.

The trend of salt passage over time of production using ASTM D 4516 was negative and the HSDM trend of salt passage over time was positive. Negative trends of salt passage over time indicate acceptable membrane performance indefinitely, positive trends infer membrane replacement sometime.
5.7 References


CHAPTER 6: INCORPORATION OF OSMOTIC PRESSURE IN AN INTEGRATED INCREMENTAL MODEL FOR PREDICTING RO OR NF PERMEATE CONCENTRATION

Consideration of concentration, recovery and osmotic pressure has been incorporated in a fully integrated diffusion based mass transfer model identified as integrated osmotic pressure model (IOPM). Osmotic pressure is incorporated into the model using correction coefficients that are calculated from boundary conditions determined from stream osmotic pressures of the feed and concentrate streams. Comparison to homogenous solution diffusion model (HSDM) with and without consideration of osmotic pressure and verification of IOPM using independently developed data from full and pilot scale plants is presented. The numerical simulation and statistical assessment show that osmotic pressure corrected models are superior to non-osmotic pressure corrected models, and that IOPM improves model predictability.
6.1 Introduction

Reverse Osmosis (RO), low-pressure reverse osmosis (LPRO) and nanofiltration (NF) are diffusion controlled, pressure-driven membrane processes. Model modifications included non-linear modification of pressure and concentration differentials across and through the membrane as well as integration of recovery and incorporation of film theory into membrane mass transfer models that predict permeate concentration (Sung 1993, Taylor 1999, Mulford 1999, Chellam, Taylor 2001). Pressure and osmotic pressures in the feed and permeate streams were averaged for model development. Membrane bulk osmotic pressure was described in the initial homogenous diffusion models using a TDS-osmotic pressure analogue that correlated TDS to osmotic pressure (Weber 1972). Linear approximation of a non-linear concentration profile of the membrane feed stream incorporates a known error that can bias model predictions in current diffusion models. While the linear model is still useful, there is no doubt that describing actual mass transfer conditions as accurately as possible will improve model application. Obstacles to incorporating osmotic pressure are describing the solute concentration profile accurately and solving a differential equation that incorporates non-linear variations of osmotic pressure along the membrane feed stream channel. The development of a fully integration model incorporating increments of osmotic pressure described as a integrated osmotic pressure model (IOPM) is presented in this work. IOPM consists of a simple equation that utilizes osmosis pressure correction coefficients, which are determined from the feed and concentrate stream TDS.

Development and verification of the model was done using data from two full scale plants as documented in the USEPA Information Collection Rule database and a large scale
membrane pilot study. Verification was done using independently derived data that was not used for model development.

6.2 Model Development

The Homogeneous solution diffusion model (HSDM) is developed from the five basic equations shown in Eqn. 6-1 to Eqn. 6-5, The HSDM equation is shown in Eqn. 6-6 and was the first model developed for a high recovery system (Taylor, Mulford, Duranceau, Barrett, 1989). The HSDM has been developed by mathematically relating the average feed stream concentration to system recovery in a mass balance approach (Taylor, 1999). HSDM can be utilized to predict permeate concentrations for any RO or NF membrane application given the feed stream concentration, flux, recovery and MTCs (Kw, Ks).

A single element flow diagram showing input and output stream flow, concentration and pressure of the feed, permeate and concentrate streams is shown in Figure 6-1.

\[ F_w = K_w (\Delta P - \Delta \Pi) = \frac{Q_p}{A} \quad \text{Eqn. 6-1} \]
\[ J_i = K_i \Delta C = \frac{Q_p C_p}{A} \quad \text{Eqn. 6-2} \]
Membrane solvent mass transfer is pressure driven and is opposed by osmotic pressure, \( \Pi \), which can be related to solute concentration by the Van’t Hoff equation, however in practice \( \Pi \) is related to solute total dissolved solid TDS as shown in Eqn. 6-6, 7. \( \Delta C \) is defined as the difference of the average feed and concentrate stream concentration and the permeate stream concentration.

\[
C_p = \frac{K_s C_f}{k_w \left( \Delta P - \Delta I \right) \left( \frac{2 - 2R}{2 - R} \right) + K_s}
\]

Eqn. 6-6

\[
\Pi = k_{TDS} \times C_{TDS}
\]

Eqn. 6-7

An integrated solution diffusion model has been developed based on the diffusion model. The concentration increment along the membrane channel is illustrated by finite units with respect to \( R \) (recovery) as shown in Eqn. 6-8 (See Appendix A). Schematic representation of the model geometry is shown in Figure 6-2.
Figure 6-2 Schematic representation of the model geometry

\[
\frac{dC}{C} = \frac{F_w dR}{(F_w + K_s)(1 - R)} \quad \text{Eqn. 6-8}
\]

\(F_w\) and \(K_s\) are water flux and solute mass transfer coefficient (MTC) respectively. Water is driven through the membrane by pressure (convection), where as mass transfer of most inorganic and some organic solutes are diffusion controlled. Consequently, a simplification using the average bulk pressure of inlet and outlet pressure was made for model development as data was taken from spiral wound membrane full or pilot scale plants. The osmotic pressure in membrane permeate stream can be neglected since TDS in the permeate stream contributes very little to osmotic pressure for nanofiltration or RO. The ratio of solutes in membrane bulk solution was assumed as fixed. Therefore, the water flux can be expressed as shown in Eqn. 6-9, where \(C\) is concentration of one specific component (e.g. sodium), \(k_1\) is the corresponding factor that relates \(C\) to osmotic pressure and \(k_1C\) represent the osmotic pressure at the feed side.

\[
F_w = K_w (\Delta P - \Delta \Pi) = K_w (\Delta P - k_1C) \quad \text{Eqn. 6-9}
\]

Combining Eqn. 6-8 with Eqn. 6-9 gives Eqn. 6-10.
\[
\int_{C_{f_0}}^{C_c} \frac{dC}{C} = \int_0^R \frac{[K_w(\Delta P - k_1C)]dR}{[[K_w(\Delta P - k_1C)] + K_s](1 - R)} \quad \text{Eqn. 6-10}
\]

Integration under the boundary condition of C from inlet \(C_{f_0}\) to \(C_c\) as recovery increases from inlet 0 to outlet R, results in Eqn. 6-11.

\[
\left(\frac{C_c}{C_{f_0}}\right)^{\frac{1 - k_1}{K_{s,\Delta P}}} \left(\frac{\Delta P - k_1C_{f_0}}{\Delta P - k_1C_c}\right)^{\frac{K_s}{K_{s,\Delta P}}} = \frac{1}{1 - R} \quad \text{Eqn. 6-11}
\]

A solute mass balance of the membrane system is shown in Eqn. 6-12.

\[
C_c = \frac{C_{f_0} - RC_p}{1 - R} \quad \text{Eqn. 6-12}
\]

Incorporation of Eqn. 6-12 into Eqn. 6-11 results in Eqn. 6-13, which is rearranged into the final model or Eqn. 6-14, where \(\Delta \Pi_{in}\) is bulk osmotic pressure at membrane inlet, \(\Delta \Pi_{out}\) is bulk osmotic pressure at membrane outlet and \(k_2\) is the osmotic pressure correcting coefficient.

\[
\left[\frac{C_{f_0} - RC_p}{C_{f_0}(1 - R)}\right]^{\frac{1 - k_1}{K_{s,\Delta P}}} \left[\frac{\Delta P - k_1C_{f_0}}{\Delta P - k_1C_c}\right]^{\frac{K_s}{K_{s,\Delta P}}} = \frac{1}{1 - R} \quad \text{Eqn. 6-13}
\]

\[
C_p = \frac{C_f}{R} \left\{1 - \left[k_2(1 - R)\right]^{\frac{K_s}{K_{s,\Delta P} + K_s}}\right\} \quad \text{Eqn. 6-14}
\]

Where:

\[
k_2 = \left(\frac{\Delta P - k_1C_c}{\Delta P - k_1C_{f_0}}\right) = \left(\frac{\Delta P - \Delta \Pi_{out}}{\Delta P - \Delta \Pi_{in}}\right) \quad \text{Eqn. 6-15}
\]

Note that \(k_1C_f\) is osmotic pressure as approximated by the TDS correlation to osmotic pressure. Eqn. 6-14 and Eqn. 6-15 showed the model, which incorporated a general osmotic pressure correction factor that can be estimated using a specific TDS or conductivity relationship with osmotic pressure. The final model is shown in Eqn. 6-16 and uniquely predict permeate
stream concentration of diffusion controlled solutes using a continuous correction for osmotic pressure.

\[
C_p = \frac{C_f}{R} \left[ 1 - \frac{\Delta P - k_{TDS} \times TDS}{\Delta P - k_{TDS} \times TDS_f} \left( 1 - R \right) \right]^{\frac{k_s}{k_s - \Delta P - k_{TDS}}} 
\]

Eqn. 6-16

Where:

\[
k_{TDS} = 69 \text{ Pa/(mg/L TDS)} \text{ or } 0.01 \text{ psi/(mg/L TDS)} \text{ or determined specifically.}
\]

6.3 Numerical Simulation

In the previous model development, static pressure drop along the membrane channel was assumed negligible compared to the overall static pressure (pressure in concentrate stream minus pressure in permeate stream), pressure change in membrane channel was determined as the linear average of the membrane inlet and outlet pressures. Therefore, the use of constant cross-membrane pressure may lead to an inaccurate estimation of the MTC. One way to avoid this is to check this assumption by numerical simulation.

As a basic diffusion model in the finite membrane unit, the concentration near membrane surface at the permeate side given by Eqn. 6-17.

\[
C_p = C_B \frac{K_s}{F_w + K_s} 
\]

Eqn. 6-17

Rearrange Eqn. 6-17 gives

\[
C_B - C_p = C_B \frac{F_w}{F_w + K_s} = C \frac{F_w}{F_w + K_s} 
\]

Eqn. 6-18
The difference between concentration near membrane concentrate side and permeate side is related to the osmotic pressure by Eqn. 6-6. Actual pressure drop incorporating osmotic pressure therefore can be related to water MTC as Eqn. 6-19 and Eqn. 6-20.

\[ F_w = K_w \left[ P_B - P_p - K_{TDS}(C_B - C_p) \right] \]  

Eqn. 6-19

Where:

\[ P_B = P_{IN} - (P_{IN} - P_{OUT}) \frac{2R - R^2}{2R_0 - R_0^2} \]  

Eqn. 6-20

Eqn. 6-20 describes the static pressure at membrane concentrate side \( (P_B) \) as a function of recovery with \( P_B = P_{in} \) at \( R=0 \) and \( P_B = P_{out} \) at \( R = R_0 \). Notice that \( P_B \) is assumed constant or determined by a linearly averaged pressure in HSDM or IOPM. Eqn. 6-20 is derived by assuming laminar flow in the membrane channel where friction loss is proportional to flow velocity (See Appendix B). Substitution of Eqn. 6-18, Eqn. 6-19 and Eqn. 6-20 into Eqn. 6-7 resulted in Eqn. 6-21, which is the final differential equation including all variables.

\[ \frac{dC}{dR} = \frac{F_w C}{(F_w + K_s)(1-R)} = f(C_F, R_0, K_w, K_s, P_{IN}, P_{OUT}, P_p, K_{TDS}, C, R) \]  

Eqn. 6-21

The integration of Eqn. 6-21 is not easy; the results are not explicit and far too complicated to apply. Consequently, another MATLAB tool of ODE solver (function ODE45) was utilized to numerically simulate the bulk and permeate concentration (See Appendix C). The ODE solver is a numerical simulation function to solve the differential equation written in a formula like \( dy/dx = f(x, y) \) with given boundary conditions. Once concentrate concentration in membrane channel is determined, permeate concentration then can be calculated by solute mass balance. The differential equations for ODE solver are from Eqn. 6-17 to Eqn. 6-21.
6.4 Results and Discussion

6.4.1 Numerical Simulation

Figure 6-3 depicts predicted concentrate and permeate stream concentration profiles for the HSDM, the HSDM without osmotic pressure correction (HSDMNO), IOPM and numerical simulation results (IOPM ODE). The concentrations profiles are shown for varying recovery at normal operating conditions for RO, LPRO and NF, which are shown as Case 1, Case 2 and Case 3 in Table 6-1. Lower MTCs and higher feed stream pressures are required for tighter membranes, hence the MTCs increase in the order of NF>LPRO>RO membranes, whereas the order of feed pressures is RO>LPRO>NF. A constant feed stream TDS of 5000 mg/L was assumed for all cases, which provided enough osmotic pressure to demonstrate differences among these applications.

Table 6-1: Summarized operating conditions and MTCs

<table>
<thead>
<tr>
<th>Case</th>
<th>$K_w$ L·d⁻¹·m⁻²·kPa⁻¹</th>
<th>$K_s$ L·hr⁻¹·m⁻²</th>
<th>Recovery</th>
<th>Pin (kPa)</th>
<th>Pout (kPa)</th>
<th>Pp (kPa)</th>
<th>$C_{TDS}$ (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Case 1</td>
<td>0.591</td>
<td>0.170</td>
<td>0-75%</td>
<td>2068.4</td>
<td>1792.6</td>
<td>68.9</td>
<td>5000</td>
</tr>
<tr>
<td>Case 2</td>
<td>0.886</td>
<td>0.849</td>
<td>0-65%</td>
<td>1379.0</td>
<td>1103.2</td>
<td>68.9</td>
<td>5000</td>
</tr>
<tr>
<td>Case 3</td>
<td>0.886</td>
<td>2.546</td>
<td>0-60%</td>
<td>1379.0</td>
<td>1103.2</td>
<td>68.9</td>
<td>5000</td>
</tr>
</tbody>
</table>

1 kPa = 0.145 psi; 1 L·hr⁻¹·m⁻² = 0.589 gsfd; 1 L·d⁻¹·m⁻²·kPa⁻¹ = 0.169 gsfd/psi

The first purpose of numerical analysis is to evaluate the newly developed IOPM for constant static pressure drop, therefore 276 kPa (40 psi) of membrane static pressure loss is assumed for each Case. Secondly, model predictions are dependent on system recovery, hence these models are assessed over a range of recovery. The maximum recovery in Table 6-1 is
determined such that osmotic pressure equals static pressures at maximum recovery. Finally, the HSDMNO is considered to demonstrate the impact of osmotic pressure on concentrate and permeate stream concentration.

Figure 6-3 1a, 1b depicts the permeate and concentrate stream concentration profiles for a relative tight RO membrane (Case 1). The inlet and outlet pressures are 2068 kPa (300 psi) and 1792 kPa (260 psi). The water and TDS MTCs ($K_w$ and $K_s$) are $0.59 \text{ L d}^{-1} \text{ m}^{-2} \text{ kPa}^{-1}$ (0.1 gsfd/psi) and $17 \text{ L hr}^{-1} \text{ m}^{-2}$ (0.1 gsfd). As shown in Figure 6-3 1a and 3 1b, the different models predict different concentration and permeate stream concentration profiles for Case 1. HSDMOS shown as dashed line in Figure 6-3 1a is biased towards predicting a lower permeate concentration by neglecting osmotic pressure, the degree of biasness increases with recovery because osmotic pressure increases with recovery but is neglected only in the HSDMOS. In Figure 6-3 1a, the IOPM prediction (dash-dot line) is close to IOPMODE numerical simulation (solid line) over entire recovery range from 1% to 75%, and shows averaging the static pressure is feasible approximation. The IOPM and HSDM overlapped when recovery is less than 40% but increasingly differ past 40% recovery. For example, the predicted TDS concentration in the permeate stream at 74% recovery is 85mg/L using the HMSD and 62 mg/L using IOPM. As shown in Figure 6-3 1b, all models predicted nearly the same TDS concentration in the concentrate stream, which is reasonable since $K_s$ is small for RO applications and very little TDS relative to the feed stream concentration passes the membrane.
Figure 6-3 Predicted permeate (a) and concentrate (b) stream TDS profiles for RO (1a,1b), LPRO (2a, 2b) and NF (3a,3b) membrane applications
The permeate and concentrate stream profiles for a LPRO membrane (Case 2) are shown in Figure 6-3 2a and 3 2b. The water and solute MTCs for illustration of LPRO, application are $0.89 \text{L}\cdot\text{d}^{-1}\cdot\text{m}^{-2}\cdot\text{kPa}^{-1}$ (0.15 gsfd/psi) and $0.85 \text{L}\cdot\text{hr}^{-1}\cdot\text{m}^{-2}$ (0.5 gsfd). From Figure 6-3 2a, at 65% recovery, the predicted permeate concentration for HSDM, IOPM, IOPMODE and HSDMNO are 401, 375, 366 and 182 mg/L respectively. Still the IOPM prediction is close to numerical simulation and IOPM predicted 35 mg/L less than HSDM at 65% recovery. Notice HSDMNO predicted 30% to 55% less permeate stream TDS than did the HSDM. Consequently, the HSDMNO predicted higher concentrate stream TDS as shown in Figure 6-3 2b.

NF TDS rejection is illustrated in Figure 6-3 3a and 3b. As shown previously, IOPM and HSDM predicted significantly lower permeate stream TDS than did the IOPM ODE. Although the NF has a lower feed pressure, the NF MTCs are higher and permit a higher transfer of water and TDS, which limits the impact of osmotic pressure.

6.4.2 Numerical Simulation

Model fitting and comparison was performed using data from two full-scale membrane plants taken from the USEPA Information Collection Rule Treatment Study Database. These two plants were two-stage high recovery systems, and provided daily operating and total dissolved solid (TDS) data for more than 8000 hours of continuous operation on ground water sources. Pressure, water quality, normalized flux and recovery were monitored for the feed, concentrate and permeate streams. Additional information on membrane operation, monitoring, raw water quality and pretreatment, chemical cleaning as well as raw experimental data is available in the ICR database. The general operation conditions for these two full-scale
membrane plants are summarized in Table 6-2. Each plant had two stages, which provided four data sets for model development and verification.

Table 6-2 General information of verification data source

<table>
<thead>
<tr>
<th></th>
<th>Plant-1</th>
<th>Plant-2</th>
<th>Pilot Study</th>
</tr>
</thead>
<tbody>
<tr>
<td>Membrane Plant</td>
<td>Palm Beach City of Boynton</td>
<td>City of Sanford</td>
<td></td>
</tr>
<tr>
<td>Scale</td>
<td>Full-scale Full-scale Pilot-Scale</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Run Time (hr)</td>
<td>8500 8000 2000</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Capacity</td>
<td>9.3MGD 4MGD 0.2MGD</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Manufacturer</td>
<td>Koch Film Tec Film Tec</td>
<td></td>
<td></td>
</tr>
<tr>
<td>M.W.C (^1)</td>
<td>200 200 200</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Construction</td>
<td>Stage 2 Stage 2</td>
<td>TFC</td>
<td>TFC</td>
</tr>
<tr>
<td>Static P (kPa) (^3)</td>
<td>732.2 560.5 718.4</td>
<td>565.4 710.8</td>
<td></td>
</tr>
<tr>
<td>Osmotic P (kPa) (^4)</td>
<td>73.8 152.4 73.8</td>
<td>153.8 196.5</td>
<td></td>
</tr>
<tr>
<td>Recovery (%)</td>
<td>55.2 66.5 63.5</td>
<td>58.5 71.3</td>
<td></td>
</tr>
</tbody>
</table>

\(^1\) TFC=thin film composite; \(^2\) M.W.C=molecular weight cutoff (Dayton); \(^3\) Average static pressure at inlet; \(^4\) Average osmotic pressure for concentrate stream.

The model comparison was done as follows: Feed stream TDS, permeate stream TDS and concentrate stream TDS as determined by a mass balance for Stage 1 and Stage 2 and simultaneous operating data in the ICR database were used for modeling. The data from Plant 1 and Plant 2 used in modeling are shown in Figure 6-4. Continuous data were reported for the two membrane plants in the ICR database. However, for plant 2, permeate TDS jumped at 2058 and 6647 hours of run time for Stage 1 and Stage 2. The plants were maintained at constant flux and recovery, however the information for these changes are not reported. Therefore, data from 0 to 8856 hours for Plant 1 and from 2058 to 8316 hours in Stage 1 data and 2058 to 6647 hours
in Stage 2 from Plant 2 were used for model comparison as shown in Figure 6-4. $K_s$ values were estimated by nonlinear regression for IOPM using Eqn. 16 and HSDM using Eqn. 6

Figure 6-4 Data scope for statistical analysis model assessment showing permeate TDS for stage 1 (S1) and stage 2 (S2) for plant 1 (P1) and plant 2 (P2) versus time of operation

Additional data from an integrated membrane system pilot study was utilized to verify IOPM in comparison with HSDM. The experimental procedures are as follows: The raw water for this pilot study was highly organic and brackish surface water taken from the St. John’s River at Lake Monroe in Sanford, Florida. The membrane feed streams were pretreated by coagulation and filtration by a Super Pulsator and a Zenon ultrafiltration systems that were in parallel prior to low pressure RO filtration by a BW30 membrane. The BW30 FR (Filmtect) membranes received both pretreated waters and were simultaneously tested in parallel. Operation for the two membrane systems was identical. The single element bench scale units used in this study were
similar in design and configuration and are based on the units described in the “ICR Manual for
quality samples were regularly collected for raw, feed, permeate and concentrate streams for all
units on a weekly basis. The measured water quality was Cl−, SO4^{2−}, Br− and silica by DX-120
Ion Chromatography (Dionex); Na^{+}, Ca^{2+} and Mg^{2+} by Unicam 969 AA Spectrometer (Unicam)
and Hitachi Zeeman-AAS Z-9000 (Hitachi); Non-purgeable dissolved organic carbon (NPDOC)
by a Phoenix 8000 UV-Persulfate TOC Analyzer (Dohrmann).

Akaike's (1973, 1974) information criterion (AIC) and Schwarz's (1978) Bayesian
information criterion (BIC) have been widely used as criteria for evaluating models estimated by
the maximum likelihood method. The AIC and BIC equations are shown in Eqn. 22 and Eqn.
23. A smaller AIC or BIC number indicates a better model. Both AIC and BIC compare the
predicted and actual sum of residual squares (RSS) and penalize models for increasing
observations and independent variables.

AIC= n+n\log_2\pi+n\log(RSS/n)+2(p+1) \quad \text{Eqn. 6-22}

BIC=n+n\log_2\pi+n\log(RSS/n)+(\log n)(p+1) \quad \text{Eqn. 6-23}

Where:
n = number of observation
p = number of independent variables
RSS = residual of sum of square between actual and predicted value

The statistical analysis for comparing model fitted and actual TDS permeate
concentration for the two full-scale plants were done. RSS, AIC and BIC are calculated for
HSDMNO, HSDM and IOPM and results of are shown in Table 6-3. The ICR database provided
352 observations of TDS for Plant 1 and 229 and 181 observations for Plant 2.
IOPM has all least RSS for both Stage 1 and Stage 2 of Plant 1 and Plant 2, notice the RSS values between IOPM and HSDM are close while HSDMNO has much high RSS showing IOPM and HSDM are significantly better than HSDMNO. Although HSDM has 7 dependent variables and IOPM has 8, IOPM RSS was less that HSDM RSS as shown in Table 6-3. The IOPM AIC and BIC were smaller that the HSDM AIC and BIC for Plant 1 but this was reversed for plant 2. The membranes used in Plant 2 are looser than the ones used in Plant 1, the effects of osmotic pressure are less in Plant 2 than in Plant 1 and there is little difference between the two models. IOPM is not much superior to HSDM in nanofiltration. Hence the results are expected that IOPM describes better for a tighter membrane.

Notice Table 6-3 showed that $K_s$ determined by IOPM and HSDM are different, at given conditions, IOPM $K_s >$ HSDM $K_s$ and the difference increase with system recovery. This may be important in scale-up prediction. A significant different prediction will result when apply IOPM and HSDM using $K_s$ determined by laboratory low-recovery flat-sheet unit. Note also $K_s$ is significantly different in stage I and II for Plant 2. Hence, $K_s$ needs to be modified by some other factor that represents additional phenomena that occurs during membrane filtration.
Table 6-3 Statistic test results of TDS, Na⁺, Cl⁻, and NPDOC for Plant 1, 2 and Pilot study

<table>
<thead>
<tr>
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<th>HSDM-NO</th>
<th>HSDM</th>
<th>IOPM</th>
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<tbody>
<tr>
<td><strong>TDS-P1-S1</strong></td>
<td>2.39</td>
<td>2.39</td>
<td>2.63</td>
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<td></td>
<td>352</td>
<td>352</td>
<td>352</td>
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<tr>
<td><strong>RSS</strong></td>
<td>29717.5</td>
<td>27994.4</td>
<td>27232.8</td>
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<tr>
<td><strong>AIC</strong></td>
<td>1325.1</td>
<td>1317.9</td>
<td>1315.7</td>
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<td><strong>BIC</strong></td>
<td>1328.9</td>
<td>1322.3</td>
<td>1320.7</td>
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<table>
<thead>
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<th>IOPM</th>
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<tr>
<td><strong>TDS-P1-S2</strong></td>
<td>2.09</td>
<td>2.09</td>
<td>2.63</td>
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<td></td>
<td>352</td>
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<td><strong>RSS</strong></td>
<td>116818</td>
<td>26495.3</td>
<td>25424.7</td>
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<tr>
<td><strong>AIC</strong></td>
<td>1534.3</td>
<td>1309.5</td>
<td>1305.2</td>
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<tr>
<td><strong>BIC</strong></td>
<td>1538.1</td>
<td>1313.9</td>
<td>1310.1</td>
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<table>
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<th>HSDM</th>
<th>IOPM</th>
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<tbody>
<tr>
<td><strong>TDS-P2-S1</strong></td>
<td>7.27</td>
<td>7.61</td>
<td>8.84</td>
</tr>
<tr>
<td></td>
<td>229</td>
<td>229</td>
<td>229</td>
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<tr>
<td><strong>RSS</strong></td>
<td>46328.2</td>
<td>20615</td>
<td>20366</td>
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<tr>
<td><strong>AIC</strong></td>
<td>953.9</td>
<td>875.3</td>
<td>876.1</td>
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<tr>
<td><strong>BIC</strong></td>
<td>956.4</td>
<td>878.2</td>
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<table>
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<th>IOPM</th>
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<td><strong>TDS-P2-S2</strong></td>
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<td>3.11</td>
<td>3.29</td>
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<td>465715</td>
<td>46831.1</td>
<td>44642.5</td>
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<tr>
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<td>956.8</td>
<td>780.3</td>
<td>776.4</td>
</tr>
<tr>
<td><strong>BIC</strong></td>
<td>958.6</td>
<td>778.2</td>
<td>778.8</td>
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<table>
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<th>HSDM</th>
<th>IOPM</th>
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<tr>
<td><strong>Na⁺</strong></td>
<td>0.073</td>
<td>0.073</td>
<td>0.075</td>
</tr>
<tr>
<td></td>
<td>21</td>
<td>21</td>
<td>21</td>
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<tr>
<td><strong>RSS</strong></td>
<td>82.97</td>
<td>63.27</td>
<td>58.21</td>
</tr>
<tr>
<td><strong>AIC</strong></td>
<td>64.29</td>
<td>63.82</td>
<td>64.29</td>
</tr>
<tr>
<td><strong>BIC</strong></td>
<td>59.54</td>
<td>58.40</td>
<td>59.55</td>
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<td><strong>Cl⁻</strong></td>
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<td>0.076</td>
<td>0.078</td>
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<td>21</td>
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<td><strong>RSS</strong></td>
<td>100.45</td>
<td>40.63</td>
<td>32.46</td>
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<td><strong>AIC</strong></td>
<td>66.04</td>
<td>59.73</td>
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<td>61.29</td>
<td>53.63</td>
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<th>HSDM</th>
<th>IOPM</th>
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<td><strong>Alkalinity</strong></td>
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<td>1.07</td>
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</tr>
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<td></td>
<td>21</td>
<td>21</td>
<td>21</td>
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<tr>
<td><strong>RSS</strong></td>
<td>70.84</td>
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<td>50.69</td>
</tr>
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<td>62.85</td>
<td>61.62</td>
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<td>58.11</td>
<td>56.19</td>
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<th>HSDM</th>
<th>IOPM</th>
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<tbody>
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<td><strong>NPDOC</strong></td>
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<td>0.30</td>
<td>0.31</td>
</tr>
<tr>
<td></td>
<td>17</td>
<td>17</td>
<td>17</td>
</tr>
<tr>
<td><strong>RSS</strong></td>
<td>0.782</td>
<td>0.681</td>
<td>0.671</td>
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<td>21.83</td>
<td>22.82</td>
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<td><strong>BIC</strong></td>
<td>16.45</td>
<td>16.66</td>
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<th>HSDM-NO</th>
<th>HSDM</th>
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<td>0.018</td>
<td>0.018</td>
<td>0.018</td>
</tr>
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<td><strong>RSS</strong></td>
<td>0.740</td>
<td>0.686</td>
<td>0.687</td>
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<td>22.57</td>
<td>24.57</td>
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<tr>
<td><strong>BIC</strong></td>
<td>16.50</td>
<td>17.15</td>
<td>18.47</td>
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<table>
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<tbody>
<tr>
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<td>0.01</td>
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</tr>
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<tr>
<td><strong>RSS</strong></td>
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<td>0.022</td>
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<td><strong>BIC</strong></td>
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<td>-14.12</td>
<td>-12.88</td>
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<th>HSDM-NO</th>
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<th>IOPM</th>
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<tr>
<td><strong>SO₄²⁻</strong></td>
<td>0.009</td>
<td>0.009</td>
<td>0.009</td>
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<tr>
<td></td>
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<td>21</td>
<td>21</td>
</tr>
<tr>
<td><strong>RSS</strong></td>
<td>4.29</td>
<td>3.83</td>
<td>3.82</td>
</tr>
<tr>
<td><strong>AIC</strong></td>
<td>34.13</td>
<td>38.25</td>
<td>40.22</td>
</tr>
<tr>
<td><strong>BIC</strong></td>
<td>32.53</td>
<td>32.83</td>
<td>34.13</td>
</tr>
</tbody>
</table>

1 L/hr-1•m-2 = 0.589 gsfd; P1-S1 = Plant 1 Stage 1.
The model fitting and verification from the independent pilot study is shown in Figure 6-5. In Figure 6-5 a shows model fitting and verification by IOPM while Figure 6-5 b shows HSDM fitting and verification. As previously described, SP data were used for model fitting while ZN data were used independently for validation. The predicted and actual TDS, Na⁺, Cl⁻, Alkalinity, Ca²⁺, Mg²⁺, SO₄²⁻ and NPDOC data showed both IOPM and HSDM is centered close to the 45° ideal line. While both IOPM and HSDM are applicable, the similar statistical analysis based on RSS, AIC and BIC are done, and the results are shown in Table 6-3.

For those water quality parameters Na⁺, Cl⁻ and TDS with permeate concentration sufficiently high and above the minimum detective level, IOPM has smaller RSS for Na⁺, Cl⁻ and TDS, and IOPM was found slightly less AIC and BIC than HSDM for Na⁺ and Cl⁻, however, TDS is reversed. Interestingly, IOPM is found not superior for alkalinity, NPDOC and low concentration ions of Ca²⁺, Mg²⁺, and SO₄⁻. A possibly explanation for alkalinity is it may also affected by pH where SP and ZN were operated at different pH, NPDOC is known as partly size exclusion and partly diffusion controlled therefore the result is as expected. For Ca²⁺, Mg²⁺, SO₄⁻, these ions in permeate stream are extremely low, therefore, although both IOPM and HSDM determined low MTC values, it can not be accurately captured due to the instrument detection level.
6.5 Model Application

The significance of consideration of integrated instead of linearly averaged concentration is illustrated in the following examples. The illustration requires development of equations for average concentration and flux using IOPM. Beginning this development, rearranging Eqn. 6-11 for the concentrate stream concentration gives Eqn. 6-24.

\[
Cc = C_{F0} \times \left( 1 - R \right)^{-\frac{Kw\Delta P}{Ks+Kw\Delta P}} \times \left( \frac{\Delta P - k_{TDS} \times TDS_f}{\Delta P - k_{TDS} \times TDS_c} \right)^{-\frac{Ks}{k+Kw\Delta P_s}} \tag{Eqn. 6-24}
\]

Then the average overall \( F_w \) can be expressed as Eqn. 6-25

\[
F_w = \frac{\int_0^R K_w \times (\Delta P - k_{TDS} \times Cc) dR}{R} \tag{Eqn. 6-25}
\]

Substituting Eqn. 6-24 into Eqn. 6-25 and integrating results Eqn. 6-26. Eqn. 6-26 is the IOPM average flux equation. The overall average flux is the function of \( K_w, K_s, C_f, \) and static
pressure drop $\Delta P$. Concentrate stream TDS can be estimated by using trial and error by using Eqn. 16 and mass balance.

$$K_w \times k_{TDS} \times C_{F0} \times \left( \frac{\Delta P - k_{TDS} \times TDS_f}{\Delta P - k_{TDS} \times TDS_c} \right)^{-K_s \over K_s + K_w \Delta P_s} \times \left( K_s + K_w \times \Delta P \right) \times \left( 1 - (1 - R) \frac{K_s}{K_s + K_w \Delta P_s} \right) \over K_s$$

$$F_w = K_w \times \Delta P - \frac{R}{R}$$

Eqn. 6-26

The average bulk concentration is developed as follows. Average concentration can be integrated with respect to recovery as expressed in Eqn. 6-27, which yields Eqn. 6-28 and is the IOPM average concentration stream concentration. Eqn. 6-28 can be more conveniently be expressed as Eqn. 6-29.

$$C_{avg} = \frac{C_{F0}}{R} \times \frac{\int_0^R C \times dR}{R} = \frac{\int_0^R C_{F0} \times \left( 1 - R \right) \frac{-K_w \Delta P}{K_s + K_w \Delta P_s} \times \left( \frac{\Delta P - k_{TDS} \times TDS_f}{\Delta P - k_{TDS} \times TDS_c} \right)^{-K_s \over K_s + K_w \Delta P_s} \times dR}{R}$$

Eqn. 6-27

$$C_{avg} = \frac{C_{F0}}{R} \times \left( \frac{\Delta P}{\Delta P} k_{TDS} \times TDS_f \right)^{ks \over K_s + K_w \Delta P_s} \times \left( \frac{K_s + K_w \times \Delta P}{K_s} \right) \times \left( 1 - (1 - R) \frac{K_s}{K_s + K_w \Delta P_s} \right) \over K_s$$

Eqn. 6-28

$$C_{avg} = \frac{(K_w \Delta P - F_w)}{(K_w \times k_{TDS})}$$

Eqn. 6-29
A case application is illustrated as follows: the RO membrane plant has membrane MTCs and feed water quality as shown in Table 6-4. The pressure loses across the membrane are 345 kPa (50 psi) (DP) and the permeate pressure (Pp) is 209 kPa (30 psi). The membrane plant is designated at productivity 25.5 L·d⁻¹·m⁻²·Kpa⁻¹ (15 gsfd).

Table 6-4 Membrane plant design parameters

<table>
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<tr>
<th>FW</th>
<th>Kw</th>
<th>Ks</th>
<th>Pp</th>
<th>CTDS</th>
<th>DP</th>
</tr>
</thead>
<tbody>
<tr>
<td>L·d⁻¹·m⁻²</td>
<td>L·d⁻¹·m⁻²·Kpa⁻¹</td>
<td>L·hr⁻¹·m⁻²</td>
<td>kPa</td>
<td>mg/L</td>
<td>kPa</td>
</tr>
<tr>
<td>25.5</td>
<td>0.30</td>
<td>0.17</td>
<td>206.84</td>
<td>5000</td>
<td>344.7</td>
</tr>
</tbody>
</table>

1 kPa = 0.145 psi; 1·m³·d⁻¹ = 0.183 gpm; 1 L·m⁻²·hr⁻¹ = 0.589 gsfd.

The feed stream pressures using the HSDM, HSDMNO and IOPM are shown in Table 6-5. Water production and flux are constant, hence feed stream pressure is constant for HSDMNO, but increases for the HSDM and IOPM with recovery due to increasing osmotic pressure associated with increasing concentrate stream TDS. Osmotic pressure increases more with recovery for the HSDM than IOPM because of a linear average is greater than an integrated average for an exponentially increasing curve. The predictions of permeate concentrations have a similar relationship with models. The IOPM predicts the lowest C_p because the integrated average C_f is lower than the linearly C_f, which results in a lower driving force and lower C_p. There is no difference in C_p for the HSMDNO and HSMD because the average flux is the same for both, although the feed pressure is higher for the HSMD due to the consideration of osmotic pressure. Clearly, consideration of integrated averages provides a more accurate prediction for actual feed stream pressures and concentrations than do linear averages. Notably, the cost of
energy is actually less and the quality is better using the more accurate IOPM, which results in an approximate power savings of $0.06/Kgal at 85 % recovery as shown in Table 6-5 relative to the HSDM and assuming $0.075/KWH.

Table 6-5 Membrane Feed pressure and permeate water quality by HSDM,HSDMNO and IOPM

<table>
<thead>
<tr>
<th>Recovery %</th>
<th>P&lt;sub&gt;HSDM&lt;/sub&gt;</th>
<th>P&lt;sub&gt;IOPM&lt;/sub&gt;</th>
<th>P&lt;sub&gt;HSDMNO&lt;/sub&gt;</th>
<th>C&lt;sub&gt;HSDM&lt;/sub&gt;</th>
<th>C&lt;sub&gt;IOPM&lt;/sub&gt;</th>
<th>C&lt;sub&gt;HSDMNO&lt;/sub&gt;</th>
<th>C&lt;sub&gt;HSDM&lt;/sub&gt;</th>
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<td>10%</td>
<td>2448</td>
<td>2811</td>
<td>2811</td>
<td>34.9</td>
<td>34.9</td>
<td>34.9</td>
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</tr>
<tr>
<td>20%</td>
<td>2448</td>
<td>2832</td>
<td>2835</td>
<td>37.2</td>
<td>37.0</td>
<td>37.2</td>
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</tr>
<tr>
<td>30%</td>
<td>2448</td>
<td>2857</td>
<td>2866</td>
<td>40.2</td>
<td>39.4</td>
<td>40.2</td>
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<tr>
<td>40%</td>
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<td>2887</td>
<td>2906</td>
<td>44.1</td>
<td>42.5</td>
<td>44.1</td>
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<tr>
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<td>2448</td>
<td>2924</td>
<td>2963</td>
<td>49.5</td>
<td>46.3</td>
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<tr>
<td>60%</td>
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<tr>
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<td>98.0</td>
<td>75.4</td>
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<tr>
<td>85%</td>
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<td>3745</td>
<td>124.6</td>
<td>95.5</td>
<td>124.6</td>
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</tr>
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</table>

1 kPa = 0.145 psi;

6.6 Conclusions

A model was developed for prediction of diffusion-controlled solutes for nanofiltration or reverse osmosis membrane filtration that continuously corrects for increases in osmotic pressure as recovery increases.

IOPM was verified using independent data from the USEPA ICR database by comparison of predicted and actual inorganic solutes concentration in the permeate stream, IOPM was statistically more accurate than the HSDM and is a more accurate model for predicting feed stream pressures and permeate concentrations. Future verification is recommended for IOPM in desalination systems to fully illustrate the actual advantages of IOPM.
Comparison of stage I and II $K_s$’s shows that either model is stage and site specific and additional modification is necessary to compensate for phenomena that occurs during increasing recovery and RO or NF membrane filtration.

A further numerical simulation was conducted by Matlab ODE solver, which considered hydraulic pressure decrease along membrane channel. The result revealed operating condition and mass transfer coefficient scopes in which IOPM is superior to HSDM.
6.7 References


Taylor, J.S., 1999, Membrane, Chapter 11 of Water Quality and Treatment, A Handbook of Community Water Supplies. Denver, Colo.: AWWA.

USEPA, 2000, ICR Treatment Study Database, Office of Ground Water and Drinking Water, Cincinnati, OH.

Membrane solute mass transfer is affected by physico-chemical properties of membrane films, solvent (water) and solutes. Existing mechanistic or empirical models that predict finished water quality from a diffusion controlled membrane can be significantly improved. Modeling membrane solute mass transfer by diffusion solution model is generally restricted to developing specific solute mass transfer coefficient (MTCs) that are site and stage specific. A modified solution diffusion model and two artificial neural network models have been developed for modeling diffusion controlled membrane mass transfer using stage specific solute MTCs. These models compensate for the effects of system flux, recovery and feed water quality on solute MTC and predict more accurately than existing models.
7.1 Introduction

Utilization of reverse osmosis (RO) and nanofiltration (NF) is increasing exponentially in drinking water treatment. Modeling of RO and NF performance is beneficial to pre-design studies, design and operation of membrane plants. The diffusion solution models are widely used to predict RO and NF performance. Solute mass transfer coefficients (MTCs or $K_s$) are typically assumed to be constant in solution diffusion models, but are known to vary with influent water quality, operating conditions and intrinsically physico-chemical membrane properties which also vary with operation, quality and time. Solute specific $K_s$s vary by site and stage and limit modeling of membrane mass transfer.

Recent model developments include a non-linear description of the pressure differential and concentration differential across and through the membrane as well as the mathematical integration of recovery into linear and film theory models (Taylor 1999, Mulford, Taylor 1999, Chellam, Taylor 2001). However since the effects of solute-solvent, solute-solute and solute-film interactions on solute mass transfer are essentially unknown, no mechanistic models have been developed that can compensate for these interactions. It is rational to assume that $K_s$ varies with membrane flux. The flux, normalized MTC for water ($K_w$) and $K_s$ are almost always larger for stage1 than for stage 2. Typically the stage 1 driving force exceeds the stage 2 driving force because of energy losses associated with osmotic pressure and hydraulics. Recovery can also be related to energy losses associated with osmotic pressure and hydraulics.

Artificial Neural Network (ANN) models have been used to improve modeling mass transfer in RO or NF membrane processes. Most of ANN applications have modeled fouling (Delgrange et al. 1998, Teodosiu et al. 2000, Cabassud et al. 2002, Shetty and Chellam 2003).
Fewer ANN models have been developed for modeling membrane water quality. Historically the mass transfer of water has been described much more accurately than solute mass transfer in RO and NF processes. Niemi and Palosaari (1994) reported prediction of solute water quality using an ANN model was nearly the same as that obtained by using a diffusion controlled model for the separation of aqueous ethanol and acetic acid in a laboratory investigation. Bowen et al. (2000) established an ANN model that accurately predicted salt rejection from salt solutions using nanofiltration in laboratory tests. Recently, Shetty and Chellam (2003) reported development of a more universal membrane-specific ANN model using data from the Information Collection Rule (ICR) database for different source waters and operating conditions using data from laboratory, pilot scale and full scale processes. This work significantly expanded the use of neural networks from laboratory treatment of a controlled solution to practical applications. Disadvantages of ANN models are the lack of information the model provides on mechanisms of mass transfer, the need for extensive data (limits the feasibility for general application), and all present ANN applications only use the Multi-layer perceptron (MLP) model.

This paper compares actual and predicted permeate stream TDS using a conventional, modified conventional and two ANN models. The conventional and modified conventional models are the solution diffusion models and a modified solution diffusion based model (Hybrid Model) that modifies $K_s$ using flux, recovery and net-driving-force (NDF). One ANN model uses MPL perceptron and the other ANN model uses a normal radial basis function for model development.
7.2 Theory

7.2.1 Solution Diffusion Model

The first model developed for a high recovery system was the linear homogenous solution diffusion model (HSDM), which was developed by correlation of the average feed concentration to system recovery (Taylor et al., 1989). The HSDM is shown in Eqn. 7-1.

\[
C_p = \frac{C_f K_s}{K_w (\Delta P - \Delta \Pi) \left(\frac{2 - 2R}{2 - R}\right) + K_s}
\]

Eqn. 7-1

Where:
- \(K_w\) = Solvent MTC (L^2/t/M)
- \(K_s\) = Solute MTC (L/t)
- \(C_f\) = Feed concentration (M/L^3)
- \(C_p\) = Permeate concentration (M/L^3)
- \(R\) = Recovery (fraction)
- \(\Delta P\) = Pressure gradient (L)
- \(\Delta \Pi\) = Osmotic pressure (L)

Specific developments of mass transfer models have included non-linear modification of pressure and concentration differentials across and through the membrane as well as integration of recovery and incorporation of film theory into models predicting permeate concentration (Sung 1993, Taylor 1999, Mulford 1999, Chellam, Taylor 2001).

The film theory model utilizes mass transfer based on two film theory to incorporate concentration polarization into a predictive model for diffusion control membrane mass transfer. Constant solute flux is assumed. The HSDM as modified by film theory (HSDM-FT) is shown in Eqn. 7-2.
\[
C_p = \frac{C_f K_s e^{F_w/K_s}}{K_w (\Delta P - \Delta \pi) \left(\frac{2 - 2R}{2 - R}\right) + K_s e^{F_w/K_s}}
\]

Eqn. 7-2

Where:
\(F_w = \) Water flux through the membrane
\(D_s = \) Diffusivity
\(K_b = D_s/x = \) Diffusion coefficient from the surface to the bulk

The linear approximation of the non-linear concentration profile of the membrane feed stream incorporated a known error into the HSDM and HSMD. Mulford (1999) developed an integrated HSDM (IHSDM) by developing, integrating and incorporating a differential equation relating instantaneous feed stream concentration into the HSDM and HSDM-FT The IHSDM and IHSDM-FM are as shown in as presented in Eqn. 7-3 and Eqn. 7-4.

\[
C_p = \frac{K_s C_f}{-RF_w} \ln \left(1 - \frac{RF_w}{F_w + K_s}\right)
\]

Eqn. 7-3

\[
C_p = \frac{K_s C_f}{-RF_w e^{(F_w/K_s)}} \ln \left(1 - \frac{RF_w}{F_w + K_s e^{(F_w/K_s)}}\right)
\]

Eqn. 7-4

The HSDM and IHSDM do not compensate for any variations in pressure, osmotic pressure or flux through the membrane elements or arrays. The recently developed incremental diffusion model (IDM), and integrated osmotic pressure model (IOPM) model do consider changes in flux, pressure and osmotic pressure through the membrane elements and arrays. Those models without and with incorporation of film theory are shown in Eqn. 7-5 through 7-8. The IDM and IOPM are shown in Eqn. 7-5 and Eqn. 7-6. The IDM-FT and IOPM-FT are shown in Eqn. 7-7 and Eqn. 7-8.
\[ C_p = \frac{C_{f0}}{R} \left[ 1 - (1 - R) \frac{K_s}{F_w + K_s} \right] \]  
Eqn. 7-5

\[ C_p = \frac{C_f}{R} \left\{ 1 - \left[ \frac{(\Delta P - \Delta \Pi)_{\text{out}}}{\Delta P - \Delta \Pi_{\text{in}}} \right] (1 - R) \right\}^{\frac{K_s}{K_w \Delta P + K_s}} \]  
Eqn. 7-6

\[ C_p = \frac{C_{f0}}{R} \left[ 1 - (1 - R) \left( \frac{F_w \left( 1 - e^{-\frac{F_w}{-K_s}} \right) + K_s}{F_w + K_s} \right) \right] \]  
Eqn. 7-7

\[ C_p = \frac{C_f}{R} \left\{ 1 - \left( \frac{\Delta P - \Delta \Pi_{\text{out}}}{\Delta P - \Delta \Pi_{\text{in}}} \right) \right\}^{\frac{K_s}{K_s + K_s \Delta P}} \times (1 - R) \left\{ 1 - \frac{e^{F_w/K_w \Delta P} \times K_s \Delta P}{K_s + K_s \Delta P} \right\} \]  
Eqn. 7-8

Where:
\[ \Delta \Pi_{\text{in}} = \text{bulk osmotic pressure at membrane inlet} \]
\[ \Delta \Pi_{\text{out}} = \text{bulk osmotic pressure at membrane outlet} \]

7.2.2 Modified Solution Diffusion Model

NF and RO membranes were shown to remove pesticides in a field study supported by AWWARF and Kiwa (Chen, Taylor, 1999). Pesticide concentration in the permeate stream was diffusion controlled but the error for pesticide prediction using the HDSM model was systematically related to flux and recovery. Prediction of pesticides in the permeate stream were improved by modifying \( K_s \) which is a hybrid model where \( K_s \) was modified by incorporation of flux and recovery. This hybrid model is a solution diffusion based model that incorporated factors that impacted \( K_s \). There are numerous model equations can be developed in this manner.

A good hybrid model must meet specific requirements even though it may be partly or totally empirical. A good hybrid model should be sensitive to factors that change \( K_s \) such as flux and recovery. A good hybrid model should have physical meaning for ranges of independent
variables that are not uncommon to normal operation, but may be beyond the range of the original data. Mathematically correct models converge at all mathematically feasible operational environments. The close-to-linear nonlinear model was used to ensure model convergence for screening model equations (Ratkowsky, 1990). The new hybrid model equations are based on solution diffusion model and compensate for flux, recovery and net driving force parameters that are common to membrane plant operation.

A hybrid model for $K_s$ is shown in Eqn. 7-9. The $K_s$ model was developed from the IDM by trial and error, and emphasizes the effect of flux more than recovery on $K_s$. This model is diffusion based and has only one unknown model coefficient and one unknown model exponent. Eqn. 7-9 can be substituted in any model that utilizes a solute mass transfer coefficient to predict permeate stream solute concentration in a diffusion controlled membrane process. To avoid unreasonable model predictions, model validation also was checked at extended boundaries, such as $K_s >0$ at 0 and 90 % recovery and flux > 0.

$$K_s = \frac{F_w^A \ln(1 - B \times R)}{\ln(1 - R) - \ln(1 - B \times R)}$$ \hspace{1cm} \text{Eqn. 7-9}

Where: $A>0$, $B<1$

7.2.3 ANN Models

Neural networks can predict any continuous relationship between inputs and the target. Similar to linear or non-linear regression, artificial neural networks develop a gain term that allows prediction of target variables for a given set of input variables. Physical-chemical
relationships between input variables and target variables may or may not be built into the association of target and input variables.

Two types of ANN models for \( K_s \) are described in this work. The models use the same input parameters as the theoretical solution diffusion models and the hybrid model. \( K_s \)'s developed by regression and ANN can be compared, or can be inserted in existing solute mass transfer models and accuracy of the predicted permeate solute concentrations can be easily compared.

7.2.3.1 Multilayer Perceptron Model

Multilayer Perceptron (MLP) is the most common type of neural network used for supervised prediction. Most of the previous literature describing membrane models used MLPs. A MLP is a feed-forward neural network that uses a sigmoid activation function, i.e. the hyperbolic tangent. The following is a simple MLP model with 1 hidden layer containing two hidden neurons. The general form of a feed-forward neural network expresses a transformation of the expected target (here \( C_p \)) as a linear combination of nonlinear functions of linear combinations of the inputs (here feed water quality \( C_f \), system flux \( F_w \) and recovery \( R \)).

\[
g_0^{-1}(E(C_p))=w_0+w_1H_1+w_2H_2
\]

\[
H_1 = \tanh(w_{01} + w_{11} \times C_f + w_{21} \times F_w + w_{31} \times R)
\]

\[
H_2 = \tanh(w_{02} + w_{12} \times C_f + w_{22} \times F_w + w_{32} \times R)
\]

\[
\tanh(x) = \frac{e^x - e^{-x}}{e^x + e^{-x}}
\]

Where: \( g_0^{-1}(E(C_p)) \) is the transformation of the expected target as the inverse of output activation function, and equals combination functions (here linear combinations) for the
arguments of activation functions. $w_1$, $w_{11}$, $w_{12}$ represents weights and $w_0$, $w_{01}$, $w_{02}$ are bias which are estimated by fitting model to data.

### 7.2.3.2 NRBFEQ Model

A normalized radial basis function (NRBF) network is a feed forward network with a single hidden layer using the softmax activation function, which is applied to a radial combination of inputs. In contrast to MLP, each basis function is the ratio of a bell-shaped Gaussian surface to sum of Gaussian surfaces. The following is a NRBF model containing 2 hidden neurons. The transformation of the expected target ($C_p$) is a linear combination of softmax functions of nonlinear combinations of the inputs ($C_f$, $F_w$ and $R$).

$$g_0^{-1}(E(C_p))=w_1H_1+w_2H_2$$

$$H_1 = \frac{e_1}{e_1 + e_2}, H_2 = \frac{e_2}{e_1 + e_2}$$

$$e_i = \exp(f \times \ln(a_i) + w_{0i2}((C_f-w_{1i})^2+(F_w-w_{2i})^2+(R-w_{3i})^2)$$

For the model NRBF given equal width and height (NRBFEQ), $a_i=1$, the combination function becomes:

$$e_i = \exp(w_{0i}^2((C_f-w_{1i})^2+(F_w-w_{2i})^2+(R-w_{3i})^2)$$

Where:

$w_{0i}$, $w_{1i}$, $w_{2i}$ represents weights which are estimated by fitting model to data.
7.3. Data

Data from USEPA Information Collection Rule (ICR) database was used for this study that was collected from a 9 MGD two-stage nanofiltration plant located in Palm Beach County in Florida. Using data from a full scale membrane plant for model development and verification benefits future model utilization by the water community. The general information for this full-scale membrane plant is summarized in Table 7-1.

Table 7-1 General information of verification data source

<table>
<thead>
<tr>
<th>Membrane Plant</th>
<th>Palm Beach County</th>
</tr>
</thead>
<tbody>
<tr>
<td>Scale</td>
<td>Full-scale</td>
</tr>
<tr>
<td>Array</td>
<td>2-stage Array</td>
</tr>
<tr>
<td>Source</td>
<td>Ground Water</td>
</tr>
<tr>
<td>Run Time (hr)</td>
<td>0-8856</td>
</tr>
<tr>
<td>Capacity</td>
<td>9.32MGD</td>
</tr>
<tr>
<td>Manufacturer</td>
<td>Koch</td>
</tr>
<tr>
<td>M.W.C$^1$</td>
<td>200</td>
</tr>
<tr>
<td>Material</td>
<td>Polyamide</td>
</tr>
<tr>
<td>Construction</td>
<td>TFC$^2$</td>
</tr>
</tbody>
</table>

$^1$: M.W.C molecular weight cutoff (Dayton); $^2$: TFC thin film composite.

Experimental data from 3/12/1998 to 3/16/1999 provided more than 8800 hours observations of run time and 706 observations for Stage1 (354 observations) and Stage2 (352 observations) TDS. A summary of statistical operating data for flux, recovery, net driving force, feed and permeate stream TDS is shown in Table 7-2. The range and variation of flux, recovery and NDF as shown in Table 7-2 are typical of a nanofiltration plant operating at steady state on a groundwater source.
Table 7-2 Summary of water quality and operating condition

<table>
<thead>
<tr>
<th></th>
<th>Feed TDS</th>
<th>Permeate TDS</th>
<th>Flux</th>
<th>recovery</th>
<th>NDF</th>
</tr>
</thead>
<tbody>
<tr>
<td>Stage1-Mean</td>
<td>341.5</td>
<td>50.4</td>
<td>13.6</td>
<td>55.2%</td>
<td>81.3</td>
</tr>
<tr>
<td>Stage1-Std.</td>
<td>15.2</td>
<td>6.9</td>
<td>0.4</td>
<td>0.1%</td>
<td>1.3</td>
</tr>
<tr>
<td>Stage1-Min</td>
<td>301.3</td>
<td>42.0</td>
<td>12.5</td>
<td>54.0%</td>
<td>72.4</td>
</tr>
<tr>
<td>Stage1-Max</td>
<td>587.0</td>
<td>71.0</td>
<td>14.9</td>
<td>56.5%</td>
<td>84.8</td>
</tr>
<tr>
<td>Stage2-Mean</td>
<td>720.2</td>
<td>115.0</td>
<td>13.2</td>
<td>66.5%</td>
<td>46.1</td>
</tr>
<tr>
<td>Stage2-Std.</td>
<td>9.7</td>
<td>7.1</td>
<td>0.4</td>
<td>0.3%</td>
<td>1.2</td>
</tr>
<tr>
<td>Stage2-Min</td>
<td>690.0</td>
<td>104.0</td>
<td>12.1</td>
<td>65.2%</td>
<td>42.7</td>
</tr>
<tr>
<td>Stage2-Max</td>
<td>747.0</td>
<td>164.0</td>
<td>14.4</td>
<td>69.9%</td>
<td>49.0</td>
</tr>
</tbody>
</table>

7.4. Model Procedure

The following procedure was used for model development.

Seventy percent of the Stage 1 and Stage 2 data were randomly selected for model development. The remaining thirty percent of the data were used for model verification. $K_s$ values and other unknown parameters for the HSDM, IHSDM, IDM, IOPM and film theory models were determined by nonlinear regression of the development data set using Eqn. 7-1 through Eqn. 7-8.

Outliers for target variables $K_s$ and Flux, Recovery and NDF detected and discarded by the Cook Distance or Cove Ratio procedures.

The model fitting statistics included $t$ statistics for significant model parameters coefficients, $t$-Tests of paired samples demonstrate the significance between model predicted and actual values and Pearson numbers for model fit of actual and predicted data.

Validation statistics: Similar to the model fitting statistics but uses data that were not used for model development.
Model extrapolation: Check model predictions in the expanded range of recovery and flux.

Neural network models are evaluated in the same manner as regression models. The same data and parameter testing is used for experimental and expanded data ranges.

The neural network model developed in this paper was based on software SAS Enterprise Miner.

7.5. Results and Discussion

7.5.1 Solution Diffusion Model

The mass transfer coefficients that were developed by nonlinear regression for the HSDM, IHSDM, IDM and IOPM with and without film theory are shown in Table 7-3. The data set containing seventy percent of the total data was used for nonlinear regression and model development.

The large $k_b$ values in Table 7-3 mean the concentration polarization effect represented by $k_b$ in the film theory models is not significant. The large exponents reduce the film theory concentration factor to one and the film theory models become identical to the solution diffusion models that did not incorporate film theory.
Table 7-3 Solution diffusion model results

<table>
<thead>
<tr>
<th>Model</th>
<th>$K_a$ (gsfd)</th>
<th>$k_b$ (gsfd)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HSDM</td>
<td>1.249</td>
<td></td>
</tr>
<tr>
<td>IHSDM</td>
<td>1.520</td>
<td></td>
</tr>
<tr>
<td>IDM</td>
<td>1.483</td>
<td></td>
</tr>
<tr>
<td>IOPM</td>
<td>1.548</td>
<td></td>
</tr>
<tr>
<td>HSDM-FT</td>
<td>1.249</td>
<td>$9.99 \times 10^{10}$</td>
</tr>
<tr>
<td>IHSDM-FT</td>
<td>1.520</td>
<td>$6.87 \times 10^{7}$</td>
</tr>
<tr>
<td>IDM-FT</td>
<td>1.483</td>
<td>$1.76 \times 10^{10}$</td>
</tr>
<tr>
<td>IOPM-FT</td>
<td>1.548</td>
<td>$1.15 \times 10^{9}$</td>
</tr>
</tbody>
</table>

The actual versus predicted permeate stream TDS is shown in Figure 7-1 by stage for the HSDM, IHSDM, IDM and IOPM models using the independent verification dataset. The 45° line in Figure 7-1 is the line that represents a plot of actual versus predicted TDS if there were no error. The predicted versus actual TDS is clustered into Stage 1 and Stage 2 groups. Although $R^2$ based on a combined Stage 1 and 2 data sets was greater than 0.9, $R$ values based on individual stage data were negative and are shown in Figure 7-1. No significant difference was found for the predicted and actual TDS for any of these models using a paired t test. The high $R^2$ indicates these models can be used effectively for prediction, but the negative Rs for each stage indicate the models could be improved. The models over predicted the actual TDS for low TDS observations and under predicted actual TDS for high TDS observations, which is a common fault of predictive models for solute mass transfer in RO or NF membranes. Certainly, these models can be used but clearly they can be improved.
7.5.2 Hybrid and ANN Model Development

Estimates of the unknown parameters for the Hybrid model shown in Eqn. 7-9 were determined using nonlinear regression and are presented in Table 7-4. Model verification was determined by conducting a paired t test on the predicted and actual TDS in the independent data set. As shown by the paired t tests and Figure 7-2, there was no difference between predicted and actual TDS for the Hybrid or ANN models. The correlation coefficient for each stage data
set is positive and indicates significantly improved model predictability. \( R^2 \) for the combined stage 1 and 2 data set was 0.98.

Table 7-4 Hybrid model results

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Estimate</th>
<th>Std. Error</th>
<th>Lower 95% CI</th>
<th>Upper 95% CI</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>2.59</td>
<td>0.149</td>
<td>2.30</td>
<td>2.88</td>
</tr>
<tr>
<td>B</td>
<td>0.0026</td>
<td>0.00099</td>
<td>0.00061</td>
<td>0.0045</td>
</tr>
</tbody>
</table>

A comparative study between the ANN models which set target variable \( C_p \) directly (\( C_p \) model) against the ANN models using \( K_s \) as target variable (\( K_s \) model) in conjunction with HSDM model was done. The predicted versus actual permeate concentration by these two procedures showed the ANN \( C_p \) model is superior than the ANN \( K_s \) model. Table 7-5 summarizes the correlations for stage1 and stage2 and \( R^2 \) value for combined stages between model predicted and actual \( C_p \). Clearly, although the \( R^2 \) are all very high (0.99), the direct \( C_p \) model had better \( R \) values than the \( K_s \) model. The ANN MLP and NRBSEQ model results are shown in Table 7-6. Development of the ANN models was done by processing paired TDS permeate stream concentrations, flux, recovery and TDS feed stream concentrations using SAS Enterprise Miner to develop the results shown in Table 7-5 for development of the MLP and NRBSEQ models. The ANN MLP and NRBSEQ models describe \( C_p \) as a function of flux, recovery and feed stream TDS. These models could be utilized manually by calculating \( H_1 \) and \( H_2 \), then using \( H_1 \) and \( H_2 \) to determine the \( C_p \) inverse activation function, which allows direct calculation of \( C_p \). However, practical application of these models would be best achieved by
simply inputting the values shown in Table 7-5 in one of several computer programs, which are capable of processing ANN models such as SAS or Matlab.

Table 7-5 Summarized $K_s$ statistics for ANN $C_p$ model and ANN $K_s$ model.

<table>
<thead>
<tr>
<th></th>
<th>Overall $R^2$</th>
<th>Stage1 $R$</th>
<th>Stage2 $R$</th>
</tr>
</thead>
<tbody>
<tr>
<td>MLP-$C_p$</td>
<td>0.99</td>
<td>0.83</td>
<td>0.77</td>
</tr>
<tr>
<td>NRBSEQ-$C_p$</td>
<td>0.99</td>
<td>0.8</td>
<td>0.85</td>
</tr>
<tr>
<td>MLP-$K_s$</td>
<td>0.99</td>
<td>0.77</td>
<td>0.78</td>
</tr>
<tr>
<td>NRBSEQ-$K_s$</td>
<td>0.99</td>
<td>0.76</td>
<td>0.79</td>
</tr>
</tbody>
</table>

Where:
MLP-$C_p$ represents direct $C_p$ MLP model, and MLP-$K_s$ represents direct $K_s$ ANN model and so on.

Table 7-6 MLP and NRBSEQ model results

<table>
<thead>
<tr>
<th>MLP Weighted Variables</th>
<th>Weight</th>
<th>NRBSEQ Weighted Variables</th>
<th>Var1</th>
<th>Weight</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_f_{H11}$</td>
<td>$W_{11}$</td>
<td>$C_f_{H11}$</td>
<td>$W_{11}$</td>
<td>-0.11333</td>
</tr>
<tr>
<td>$FLUX_{H11}$</td>
<td>$W_{21}$</td>
<td>$FLUX_{H11}$</td>
<td>$W_{21}$</td>
<td>-0.0767</td>
</tr>
<tr>
<td>RECOVERY</td>
<td>$W_{31}$</td>
<td>RECOVERY</td>
<td>$W_{31}$</td>
<td>-0.25441</td>
</tr>
<tr>
<td>$C_f_{H12}$</td>
<td>$W_{12}$</td>
<td>$C_f_{H12}$</td>
<td>$W_{12}$</td>
<td>-0.14478</td>
</tr>
<tr>
<td>$FLUX_{H12}$</td>
<td>$W_{22}$</td>
<td>$FLUX_{H12}$</td>
<td>$W_{22}$</td>
<td>0.025737</td>
</tr>
<tr>
<td>RECOVERY</td>
<td>$W_{32}$</td>
<td>RECOVERY</td>
<td>$W_{32}$</td>
<td>0.27545</td>
</tr>
<tr>
<td>$BIAS_{H11}$</td>
<td>$W_{01}$</td>
<td>$BIAS_{H11}$</td>
<td>$W_{01,W_{02}}$</td>
<td>1.1203</td>
</tr>
<tr>
<td>$BIAS_{H12}$</td>
<td>$W_{02}$</td>
<td>$H_{11_C_p}$</td>
<td>$W_{1}$</td>
<td>20.534</td>
</tr>
<tr>
<td>$H_{11_C_p}$</td>
<td>$W_{1}$</td>
<td>$H_{12_C_p}$</td>
<td>$W_{2}$</td>
<td>146.76</td>
</tr>
<tr>
<td>$H_{12_C_p}$</td>
<td>$W_{2}$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$BIAS_{C_p}$</td>
<td>$W_{0}$</td>
<td></td>
<td></td>
<td>89.155</td>
</tr>
</tbody>
</table>

Actual and predicted TDS from the Hybrid, MLP and NRBSEQ model verification is shown in Figure 7-2. Immediately obvious is the improved grouping for the actual and predicted
TDS using the Hybrid, MLQ and NORFEQ models. All correlation coefficients were positive. The NORFEQ model had the highest $R^2$. Again, paired sample T-Tests showed no significant differences between the predicted and actual permeate concentrations using any of the models, and hence all models were verified using the independent data set.

Figure 7-2 Actual versus predicted TDS using data not used for model development for the HHSDM (a), MLP (b) and NRBSEQ (c) models
Prediction of $C_p$ versus flux and recovery is shown in Figure 7-3 assuming 1000 mg/L TDS in the feed stream for the Hybrid, MLP and NRBFEQ models. The $C_p$ predicted plane using the Hybrid model is very smooth and has no striking $C_p$ change for varying flux and recovery. However, the Hybrid model provided the least accurate prediction of $C_p$. The MLP and NRBFEQ are neural network models and produced predicted $C_p$s that changed dramatically at selected fluxes and recoveries. The MLP model predictions for $C_p$ almost appear like a step function at 60 % recovery and 2 gsfd going from 50 to 100 mg/L. This trend can be clearly seen in Figure 7-3 (b). Another similar change is seen in the back section of the predicted $C_p$ plane in Figure 7-3 (b). The NRBFEQ model predicted a $C_p$ dramatically but smoother changing $C_p$ than the MLP model. NRBFEQ predicted $C_p$s increased from 50 mg/L at 80 % recovery to 130 mg/L at 90 % recovery. It is likely that the ANN models would change if actual data from the extended independent variable ranges were used in model development.
Figure 7-3 Permeate TDS predicted by Hybrid (a), MLP (b) and NRBFEQ (c) Models

The shaded area represents the variation scope of original data.

Prediction of $C_p$ at various feed TDS concentration is shown in Figure 7-4 for the MLP and NRBFEQ models. The three layers from top to bottom in Figure 7-4 (a) and (b) represent prediction at feed TDS 300 mg/L, 500 mg/L and 1000mg/L. Clearly, when feed concentration is
within the intermediate range of actual feed concentration (300 mg/L to 800 mg/L, e.g. 500 mg/L), MLP and NRBFEQ model predict in similar manner; however, the prediction diverge at 300 and 1000 mg/L feed concentration, MLP is a model weighed more on $C_f$, while NRBFEQ is more weighted on operating conditions.

![Graphs showing predicted Permeate TDS for different feed concentrations.](a) MLP model predictions. (b) NRBFEQ model predictions.)

Figure 7-4 Permeate TDS predicted MLP (a) and NRBFEQ (b) Models at feed TDS 300 mg/L, 500 mg/L and 1000 mg/L.

### 7.6. Conclusions

Several diffusion based, Hybrid and two ANN models were developed for predicting permeate TDS using an ICR data base from a full-scale nanofiltration plant.

All concentration polarization or film theory terms were insignificant.

All diffusion based models that did not consider concentration polarization, Hybrid and ANN models were verified by comparing actual and predicted data using a t test.
The diffusion based models over predicted TDS at low TDS concentrations and under predicted TDS at high TDS concentrations, which is typical of diffusion based models.

The Hybrid and ANN models predicted permeate TDS more accurately than any of the diffusion based models, and did not over or under predict permeate TDS at low and high permeate TDS.

Although ANN models are not mechanistically based, these models did predict dramatic changes in permeate TDS for certain combinations of flux and recovery. Such phenomena can be investigated at extended ranges of flux and recovery and could give new insight into mechanisms affecting membrane mass transfer.

Numerous Hybrid and ANN models can be developed and could significantly improve prediction of membrane performance.
7.7 References


J.S. Taylor (1999) Membrane, Chapter 11, Water Quality and Treatment, Denver, Colo.: AWWA

L. Sung (1993) Film Theory and Ion Coupling Models for a Diffusion Controlled Membrane Process. PH.D. Dissertation, University of Central Florida


USEPA, ICR Treatment Study Database (2000) Office of Ground Water and Drinking Water, Cincinnati, OH.


APPENDIX A

DERIVATION FOR EQUATION 6-8
Consider a membrane finite unit as depicted in Figure 6-2, the finite membrane unit produced permeate flow \( dQ_p \), and bulk concentration in this finite unit increased along the membrane channel as \( C \) to \( C + dC \) respectively. The symbols used here are same as shown in Figure 6-2 unless otherwise specified.

Recall Eqn. 6-4 and Eqn. 6-5 and solve these equations for the membrane finite unit as shown in Eqn. A-1.

\[
C + dC = C - \frac{dQ_p}{Q_F} C_p (1 - \frac{dQ_p}{Q_F}) 
\]

Eqn. A-1

\( Q_F \) for a small unit at any location of recovery is shown in Eqn. A-2 and is incorporated into Eqn. A-1 and shown in Eqn. A-3.

\[
Q_F = (1-R)Q_{f0} 
\]

Eqn. A-2

\[
C + dC = \frac{C - \frac{dQ_p}{(1-R)Q_{f0}} C_p}{(1 - \frac{dQ_p}{(1-R)Q_{f0}})} 
\]

Eqn. A-3

Homogeneity is assumed in the finite membrane unit. The average feed solution concentration of a finite unit is the average of inlet concentration \( C \) and outlet concentration \( C + dC \), which allows the development of Eqn. A-4.

\[
C_p = \frac{C_f k_s}{F_w \left( \frac{2 - 2dR}{2 - dR} \right) + k_s} 
\]

Eqn. A-4

When \( dR \rightarrow 0 \), Eqn. A-4 simplifies to Eqn. A-5
\[ C_p = \frac{CK_s}{F_w + K_s} \quad \text{Eqn. A-5} \]

Substituting Eqn. A-5 into Eqn. A-3 yields:

\[
C + dC = \frac{dQ_p}{(1-R)Q_f0} \left[ C - \frac{C}{F_w + K_s} \right] \quad \text{Eqn. A-6}
\]

\[
1 - \frac{dQ_p}{(1-R)Q_f0}
\]

Rearranging Eqn. A-6:

\[
\frac{dC}{C} = \frac{F_w \frac{dQ_p}{Q_f0}}{(F_w + K_s)(1-R) - (F_w + K_s) \frac{dQ_p}{Q_f0}} \quad \text{Eqn. A-7}
\]

When \( dQ_p \rightarrow 0 \)

\[
\frac{dC}{C} = \frac{F_w \frac{dQ_p}{Q_f0}}{(F_w + K_s)(1-R)} = \frac{F_w dR}{(F_w + K_s)(1-R)} \quad \text{Eqn. A-8} \]
APPENDIX B

DERIVATION FOR EQUATION 6-20
In laminar flow region, friction loss is proportional to first order of flow velocity.

\[ R = \frac{Q_P}{Q_0} \]

Since \[ R = \frac{Q_P}{Q_0} \] \text{ Eqn. B-1 }

Therefore flow at recovery \( R \) is,

\[ Q = Q_0 - Q_P = Q_0(1-R) \] \text{ Eqn. B-2 }

Channel cross area = \( A \)

Velocity at recovery \( R \) in channel is,

\[ V = \frac{Q_0(1-R)}{A} = k(1-R) \] \text{ Eqn. B-3 }

Friction loss at over recovery range 0 to \( R \) therefore equals,

\[ P_f = \int \left[ k(1-R) \right] dR = k \left( R_0 - \frac{R_0^2}{2} \right) \] \text{ Eqn. B-4 }

Given the boundary condition

\[ P_f \bigg|_{R=0} = P_{in} - P_{out} \] \text{ Eqn. B-5 }

Eqn. B-4 and Eqn. B-5 results,

\[ k = \frac{2P_{in} - 2P_{out}}{2R_0 - R_0^2} \] \text{ Eqn. B-6 }

Pressure in membrane channel is,

\[ P_B = P_{in} - P_{f} = P_{in} - (P_{in} - P_{out}) \left( \frac{2R - R^2}{2R_0 - R_0^2} \right) \] \text{ Eqn. B-7 }
Function: MAIN.M

clear;
close;

%CREATE VICTOR STORE RESULT1*100
RHSDMR=repmat(0,[100 1]);
RHSDMCP=repmat(0,[100 1]);
RHSDMCC=repmat(0,[100 1]);
RHSDMNOCP=repmat(0,[100 1]);
RHSDMNOCC=repmat(0,[100 1]);
RIOPMCP=repmat(0,[100 1]);
RIOPMCC=repmat(0,[100 1]);
RIOPMODECP=repmat(0,[100 1]);
RIOPMODECC=repmat(0,[100 1]);

%initialcond;

%RO
KS=0.1;PIN=300;POUT=260;PP=10;K1=0.01;CF=5000;KW=0.1;
%LRRO KS=0.5;PIN=200;POUT=160;PP=10;K1=0.01;CF=5000;KW=0.15;
%NF KS=1.5;PIN=200;POUT=160;PP=10;K1=0.01;CF=5000;KW=0.15;
CFTDS=5000;
DP=(PIN+POUT)./2-PP;
RMAX=1-K1.*CFTDS./DP;RMAX=RMAX-0.05;

%HSDM
```matlab
i=1;
for RMAX0=0.01:0.01:RMAX
R=(0.001:0.001:RMAX0);
FW=KW.*((POUT+PIN)./2-PP-K1.*(CFTDS.*(2-R)./(2-2*R)));
CP=HSDMCP(CF,R,KS,FW);
CC=CPTOCC(CF,CP,R);
COUNT=RMAX0/0.001;
RHSDMCP(i,1)=CP(COUNT);
RHSDMR(i,1)=RMAX0;
RHSDMCC(i,1)=CC(COUNT);
i=i+1;
end;

%HSDMNO
i=1;
for RMAX0=0.01:0.01:RMAX
R=(0.001:0.001:RMAX0);
FW=KW.*((POUT+PIN)./2-PP);
CP=HSDMCP(CF,R,KS,FW);
CC=CPTOCC(CF,CP,R);
COUNT=RMAX0/0.001;
RHSDMNOCP(i,1)=CP(COUNT);
RHSDMNOR(i,1)=RMAX0;
```

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RHSDMNOCC(i,1)=CC(COUNT);

i=i+1;

end;

%IOPM

i=1;

for RMAX0=0.01:0.01:RMAX

R=(0.001:0.001:RMAX0);

CP=IOPMCP(CF,CFTDS,R,KS,KW,PIN,POUT,PP,K1);

CC=CPTOCC(CF,CP,R);

COUNT=RMAX0/0.001;

RIOPMCP(i,1)=CP(COUNT);

RIOPMOR(i,1)=RMAX0;

RIOPMCC(i,1)=CC(COUNT);

i=i+1;

end;

%IOPMODE

i=1;

for RMAX0=0.01:0.01:RMAX

R=(0.001:0.001:RMAX0);

zz=FIOPM(CF,CFTDS,RMAX0,KS,KW,PIN,POUT,PP,K1);

tt=inline(vectorize(zz),'x','y');
options=odeset('AbsTol',1e-8,'RelTol',1e-8);

[R CC]=ode45(tt,[0:0.001:RMAX0],CF);

CP=CCTOCP(CF,CC,R);

COUNT=RMAX0/0.001;

RIOPMODECP(i,1)=CP(COUNT);

RIOPMODEOR(i,1)=RMAX0;

RIOPMODECC(i,1)=CC(COUNT);

i=i+1;

eend;

HSDM
Filename: HSDMCp.M

function Cp=HSDMCp(Cf,R,Ks,Fw)

%where:Cc--concentrate mg/L;

%Cf--membrane feed(inlet) concentration mg/L;

%R--recovery (0-1);

%Fw--flux (gsfd);

%Ks--specific MTC (gsfd);

function Cp=HSDMCp(Cf,R,Ks,Fw);

Cp=Cf.*Ks./(Fw.*(2-2*R)./(2-R)+Ks);

IOPM
Filename: IOPMCP.M
function Cp=IOPMCp(Cf,CfTDS,R,Ks,Kw,Pin,Pout,Pp, K1);

DP=(Pin+Pout)./2-Pp;

Cp=(Cf./R).*(1-(((DP-K1.*CfTDS)./(DP-K1.*CfTDS./(1-R))).^(-Ks./(Kw.*DP)).*(1-
R)).^(Ks./(Kw.*DP+Ks)));

IOPMODE

Filename: FIOPM.M

function z=FIOPM(CF,CFTDS,RMAX,KS,KW,PIN,POUT,PP,K1);

syms x y;

%define x y as out variable

PB=PIN-(PIN-POUT)./(2*RMAX-RMAX.^2)*(2.*x-x.^2);

%Estimate PB at x (recovery) given Pin,Pout,Rmax , PB is a vector

z=KW.*(PB-PP-K1.*((((KS/KW-PIN+(PIN-POUT)./RMAX.*x+K1.*y).^2+4*((PIN-(PIN-
POUT)./RMAX.*x).*KS)./KW)^0.5+PIN-(PIN-POUT)./RMAX.*x-K1.*y-
KS./KW).*KW./2/((((KS/KW-PIN+(PIN-POUT)./RMAX.*x+K1.*y).^2+4*((PIN-(PIN-
POUT)./RMAX.*x).*KS)./KW)^0.5+PIN-(PIN-POUT)./RMAX.*x-K1.*y-
KS./KW).*KW./2+KS).*y)).*y./(KW.*(PB-PP-K1.*((((KS/KW-PIN+(PIN-
POUT)./RMAX.*x+K1.*y).^2+4*((PIN-(PIN-POUT)./RMAX.*x).*KS)./KW)^0.5+PIN-(PIN-
POUT)./RMAX.*x-K1.*y-KS./KW).*KW./2/((((KS/KW-PIN+(PIN-
POUT)./RMAX.*x+K1.*y).^2+4*((PIN-(PIN-POUT)./RMAX.*x).*KS)./KW)^0.5+PIN-(PIN-
POUT)./RMAX.*x-K1.*y-KS./KW).*KW./2+KS).*y)))+KS).*(1-x));

Converting Module Function
Function: CcTOCp.M

function Cp=CcTOCp(Cf,Cc,R);
Cp=Cc+(Cf-Cc)./R;

Function: CpTOCc.M

function Cc=CpTOCc(Cf,Cp,R);
Cc=(Cp-Cf./R)./(1-1./R);
REFERENCES


