EXPERIMENTAL INVESTIGATION ON REJECTION OF SODIUM SULFATE BY REVERSE OSMOSIS MEMBRANES

By

DIAN TANUWIDJAJA

UNIVERSITY OF CALIFORNIA, LOS ANGELES

2002

EXPERIMENTAL INVESTIGATION ON REJECTION OF SODIUM SULFATE BY REVERSE OSMOSIS MEMBRANES

A THESIS SUBMITTED BY

DIAN TANUWIDJAJA

IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE

OF MASTER IN SCIENCE IN CIVIL AND ENVIRONMENTAL ENGINEERING

UNIVERSITY OF CALIFORNIA IN LOS ANGELES

2002

ACKNOWLEDMENTS

The studies described in this thesis were performed at the Department of Civil and Environmental Engineering, National University of Singapore. It is my pleasure to have this opportunity to express my sincere gratitude and appreciation to those who have contributed to my thesis in one way or another.

First, I would like to thank my supervisor, Associate Professor Song Lianfa for his guidance, and patience over the past 5 months. I believe that what I have learnt from him will be infinitely profitable for the rest of my life. I am deeply grateful to my supervisor, Associate Dean Michael Stenstrom for his constant support and for giving me the opportunity to study in Singapore. Without their help, this thesis would never have been completed.

I would like to extend my appreciation to all the staff in the Environmental Engineering Laboratory for their kind assistance.

Finally, I wish to express my sincere gratitude to my parents and brother for their love and prayers for my progress.

TABLE OF CONTENTS

Chapter One: Introduction

Chapter Two: Literature Review

Chapter Three: Experimental Set-Up and Procedures

Chapter Four: Results and Discussion

Chapter Five: Conclusions and Recommendations

Appendices

ABSTRACT

Reverse osmosis (RO) membrane is an excellent barrier for most dissolved inorganic and organic species in water solution and therefore it has been extensively used for various water treatment and purification. RO process possesses many advantages over the conventional water treatment and purification processes, such as high product water quality, multi-pollutants removal, and small footprint. As the resources of drinking water further diminishes and more stringent water quality standards put into enforcement, RO process will see a even greater development in the future.

Ion transport through RO membrane is of paramount importance to the success of a RO process. Many theories or models are available in the literature for membrane transport based either on irreversible thermodynamics (IT) or on transport mechanisms. However, most of these models, although they can be used to correlate a particular set of experimental data, they generally do not have the capacity to predict. It is especially true when the theories are applied to describe the effects of feed concentration on salt rejection. The solute/salt permeability coefficients found in these models are mostly dependent on feed concentration and the values of the coefficients cannot be determined *a priori*.

This research aimed to obtain a better understanding of salt rejection by reverse osmosis membrane experimentally. The SEPA cell (Osmonics) and RO CA ST-28 membrane (Company) were used in all experiments conducted in this study. In all the experiments, the inflow rate is kept constant at 1.0 mL/min and the effect of inflow rate is not investigated. Salt rejection of the membrane and the effect of salt concentration were investigated in a wide range of transmembrane pressure. Because of time constraint, the rejection experiments were conducted only for the salt of sodium sulfate in water solution.

The results showed that the rejection of sodium sulfate by the RO membrane increased with transmembrane pressure, which is generally agreeable with previous experiments. The common theoretical explanation of this trend is the dilution effect, which assumes the salt transport is a constant while permeate flux increases with the transmembrane pressure. The experimental data also showed a weaker dependence of salt rejection on salt concentration. The salt rejection decreased with increasing salt concentration as theories predicted. Some experimental data did not follow the general trend, which was probably due to unexpected damage in the conductivity meter (it was adjusted by someone without noticing).

A strong nonlinearity was found between permeate flux and transmembrane pressure. The permeate flux did not diminish to zero when the transmembrane pressure reduced to equal to the osmotic pressure of the feed solution. On the contrary, there is a noticeable permeate flux when the transmembrane pressure is equal to or even smaller than the solution osmotic pressure. This is a rather interesting phenomenon on which further study is needed.

Rejection rates of sodium sulfate obtained in this experiment also were compared previous data for sodium chloride rejection with the same membrane. Sodium sulfate is more readily rejected by the RO membrane than sodium chloride. It may mean that the univalent ions can penetrate the RO membrane more easily than bi- or multivalent ions.

LIST OF TABLES

LIST OF FIGURES

CHAPTER ONE: INTRODUCTION

1.1 Background

The International Union of Pure and Applied Chemistry (IUPAC) defines reverse osmosis (RO) as a “pressure-driven process in which applied transmembrane pressure causes selective movement of solvent against its osmotic pressure difference” (IUPAC 1996). Reverse osmosis (RO), also called hyperfiltration, is capable of the highest filtration level possible, including separating dissolved salts and removing bacteria, pathogens and organics from water. The applications of RO include but are not limited to separation and concentration of solutes in many fields, such as chemical and biomedical industry, food and beverage processing, and water and wastewater treatment.

Reverse Osmosis can be used for seawater desalination, groundwater treatment, and for tertiary treatment to reclaim the secondary effluent for advance reuse purposes. Water Factory 21 in Fountain Valley, Orange County, California has been using RO technology for more than 20 years to treat their secondary effluent. The product water from Water Factory 21 must have a Total Dissolved Solids (TDS) content of 500 mg/L or lower. Demineralization of a third of the plant's process water is achieved in the reverse osmosis (RO) process. In addition to removing TDS, RO is very effective in reducing other minerals, ammonia, and total organic carbon (TOC). Six million gallons of secondary effluent enters RO treatment per day after leaving the multi-media filters. The membranes remove 90 percent of TDS. The concentrated brine (15 percent of the total input) is returned to the County Sanitation Districts for disposal via their ocean outfall.

Reverse Osmosis has many advantages over the conventional water and wastewater treatment operations and processes. It is able to remove many dissolved substances efficiently, yet produce good quality finished water. It does not require any addition of chemicals into the water for separation. The separation of the dissolved substances from the influent is achieved physically or physico-chemically. RO is even more attractive in land-constrained areas because it of reduced land requirement. It is anticipated that RO processes will be used more widely in water industry to replace the large conventional water treatment systems.

RO was first developed in the 1950's by the US government to provide fresh drinking water for the Navy, and since then, advances have made it much more feasible for obtaining purified water from wastewater. It is essentially a molecular squeezing process, using a semi-permeable membrane which causes water molecules to separate from the contaminants. The separated water molecules then pass thru to the inside of the membrane to a holding reservoir. The contaminants are flushed from the membrane and disposed. Recently, RO has been used in treating boiler feed water, in addition to industrial and process wastewaters. Boilers are found throughout the chemical processing industry and the primary method to treat boiler wastewater is ion-exchange. However, RO has been demonstrated to be more cost effective than this demineralization process.

Drinking water is scare and its scarcity is increasing. In certain parts of the areas, water resources are limit development, and the problem of water scarcity has become more serious. This e applies for the second largest city in America, Los Angeles. The population of Los Angeles increased from 5,728 in 1870 to 102,479 by 1900. According to the 2000 census, there are 3.7 million people living in Los Angeles. Along with inherent growth problems, the City is facing a serious water shortage. As population increases, water supplies are being reduced.

The available water is of less quality because the more quality water has been used up. Reverse Osmosis is a good way of dealing with this problem especially since water quality standards are becoming more stringent. Consumers expect cleaner water to drink. Three-quarter of Earth's surface is covered with seawater, which makes seawater desalination for drinking water become very attractive. Although previously regarded as too expensive to use on a widespread basis, water reclamation and seawater desalination with RO membranes are currently becoming an affordable and reliable water source. Coupled with the continuous improvement of membrane technologies, the application of the RO process and membranes in seawater desalination and water reclamation will continue to increase in importance.

1.2 Objectives

The objective of this study is to gain a deeper understanding into the salt rejection behavior of RO membrane under different experimental conditions.

The scope of this study includes a literature review on membrane transport through RO membranes, salt rejection experiments in a laboratory-scale RO process, and discussion on the experimental results. A SEPA cell (Osmonics) was used in the salt rejection experiments The experiments focused on sodium sulfate (Na_2SO_4) rejection. The operational conditions included six different salt solutions, ranging from 100 ppm to 5000 ppm and a wide range of operating pressure from 100 psi to 800 psi.

CHAPTER TWO: LITERATURE REVIEW

2.1 Basic Principle of Osmosis

Osmosis is a principle of physics according to which, if two saline solutions with different concentrations are separated by a semi-permeable membrane, which is permeable to water but impermeable to salt, water will spontaneously pass from the lesser concentrated solution to the other because of its low chemical potential. When pure water is in contact with both sides of an ideal semi-permeable membrane at equal pressure and temperature, there will be no net flow across the membrane because of the chemical potential is equal on both sides. According to the Second Law of Thermodynamics, if salt is added into one side of the membrane, the chemical potential of the salt is reduced, and osmotic flow will take place from pure water side across the membrane to the side with salt until the chemical potential on both side of the membrane is equalized.

If the membrane were permeable instead of semi-permeable, salt would migrate to the fresh water side until equilibrium is restored. However, the salt does not pass through the semi-permeable membrane; only fresh water can move to achieve equilibrium. The fresh water is doing all the work to reach equilibrium, so the fresh water side will eventually be depleted in an effort to reduce the relative saltiness of the salty side.

Equilibrium occurs when the hydrostatic pressure difference resulting from the volume changes, Δh, on both sides, is equal to the osmotic pressure difference, ΔΠ of the two solutions (See Figure 2.1). Osmotic pressure is a solution property proportional only to the salt concentration.

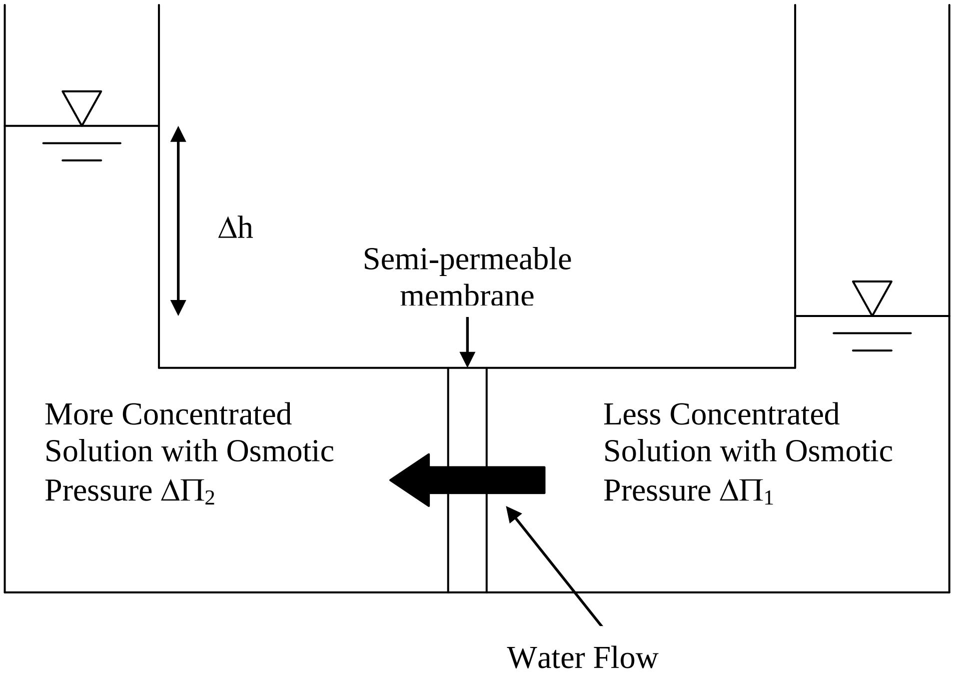


Figure 2.1: Simple Osmosis

2.2 Basic Principle of Reverse Osmosis

Reverse Osmosis is the reverse process of spontaneous osmosis. The osmosis process can be reverted by adding external pressure on the salty side so that some of the fresh water molecules on the salty side will end up on the fresh water side. The problem is that the osmotic pressure tends to force water to the more saline side, which is opposite of the desired outcome. To overcome this tendency, the osmotic pressure can be overcome by the applied pressure, forcing water from the saline side to the less saline side. Reverse osmosis is schematically presented in Figure 2.2.

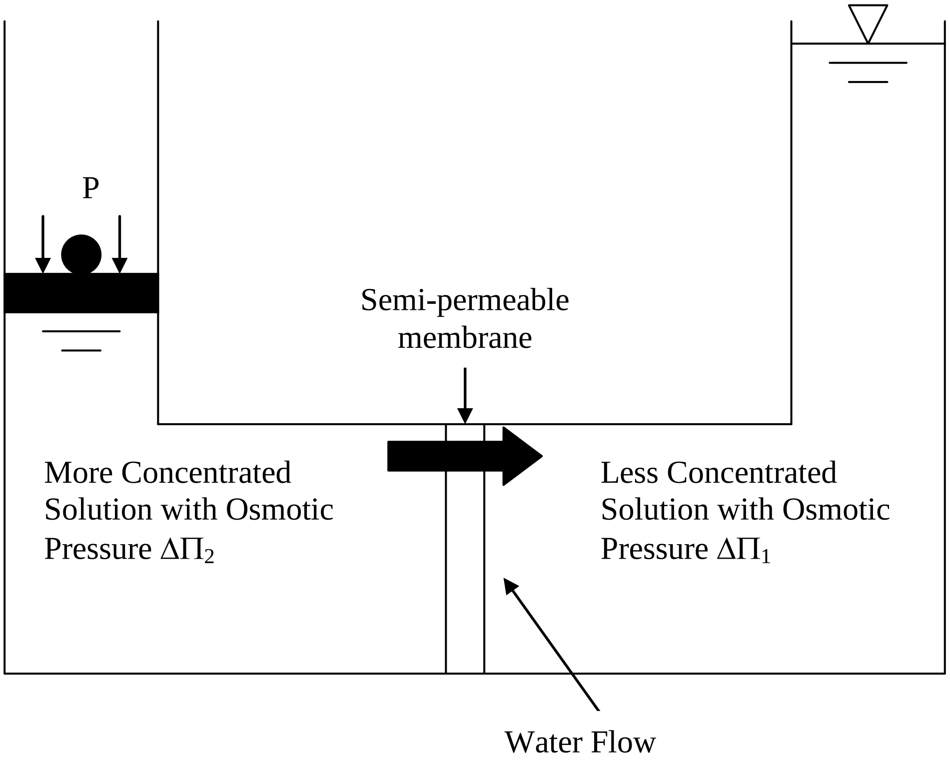


Figure 2.2: Simple Reverse Osmosis

As the pressure increases, the migration of fresh water to salty water slows down. If enough external pressure is applied, an osmotic equilibrium will be reached and the water stops going from the fresh water side to the salty side. When the external pressure becomes higher than the osmotic pressure on the salty side, fresh water from the salty side will start migrating to the fresh water side. In many industrial practices, an external pressure greater than the osmotic pressure is added to the more concentrated solution of the membrane to reverse the process, leading to the phenomenon called reverse osmosis or hyperfiltration

2.3 Salt Rejection Mechanisms in RO Membrane

In a membrane separation process, it is critical for the membranes to have a satisfactory salt rejection. Salt rejection by an RO membrane is mainly affected by the membrane properties, salt activities, and water chemistry. However, the detailed mechanisms for salt rejection are not very clear yet. There are two popular mechanisms that are often used to explain salt rejection in RO membrane. They are the Solution-diffusion model and the Donnan exclusion model.

The Solution-Diffusion Mechanism assumes that both solvent and solute dissolve in the homogeneous nonporous surface layer of the membrane. They are transported by a diffusion mechanism in an uncoupled manner (Lonsdale et al. 1965). To have a high salt rejection, it is necessary to have membranes with a completely nonporous surface layer which has higher solubility and diffusivity for the solvent as compared with those of the solute. These differences in solubility and diffusivity between the solvent and solute result in different mass transfer rates of the solvent and solute. It is this fact that the solvent and solute have different mass transfer rates through a given membrane that creates the phenomena of salt rejection. No membrane is ideal in the sense that it absolutely rejects salts. The different transport rates create an apparent rejection.

In the Donnan exclusion mechanism, there exists an important interaction between the solute and membrane, which is called the “charge effects”. RO membranes are made of polymeric materials and acquire surface charges when in contact with an aqueous medium (Shaw 1969; Jacobasch and Schurz 1988; Childress and Elimelech 1996). These acquired charges will influence the distribution of ions at the membrane-solution interface: co-ions (i.e., ions of same charge of the membrane) will be repelled while counter-ions (i.e., ions with the opposite charge) may be attracted by the charged membrane. The electrostatic repulsion of co-ions is termed as “Donnan exclusion”. Due to this phenomenon, an electrostatic force is exerted against an electrolyte solution (Tsuru *et al*. 1991a; Peeters *et al.* 1998).

In a charged membrane in contact with an electrolyte solution, the concentration of co-ions in the membrane will be lower than that in solution, while the counter-ions have a higher concentration in the membrane than in the solution. Because of this concentration difference of the ions, a potential difference is generated at the interface between the membrane and the solution to maintain electrochemical equilibrium between the solution and membrane. This potential is called ‘Donnan potential’. By Donnan potential, co-ions are repelled by the membrane while counter-ions are attracted. Due to Donnan exclusion, the transport of co-ions through the membrane can be significantly reduced. Because the solution has to maintain electro neutrality, the counter-ions cannot travel through the membrane alone.

2.4 Solute Transport Models for RO Membrane

Solute transport models can be grouped into two categories. The first category comprises models based on transport mechanisms such as the solution-diffusion mechanism and the Donnan exclusion mechanism. The second category includes models based on irreversible thermodynamics where the membrane is treated as a black box, that is, no transport mechanism is assumed. In the irreversible thermodynamics model, separation through the membrane is considered a slow process taking place near equilibrium and, therefore the rate of transport can be determined by thermodynamic principles.

The Solution-Diffusion Model was developed by Lonsdale *et al*. (1965), and it is assumed that both solvent and solute dissolve in the homogeneous nonporous surface layer of the membrane at the high pressure side and then are transported by a diffusion mechanism under the chemical potential gradient in an uncoupled manner. Solubilities and diffusivities of both the solvent and solute are important parameters in this model.

Solvent flux is governed by the magnitude of the difference between applied pressure and differential osmotic pressure between solutions. The equation describing solvent flux through a semi-permeable membrane at constant temperature is given by:

$$J_v = A(\Delta p - \Delta \Pi) \qquad (2.1)$$

where J_v is the solvent flux, A the solvent permeability coefficient (function of diffusivity of solvent), Δp the applied pressure, $\Delta\Pi$ the differential osmotic pressure.

For solute flux, the chemical potential difference due to pressure is negligible and the flux is almost entirely due to concentration gradient. The equation describing solute flux through a semi-permeable membrane at constant temperature is given by:

$$J_s = B(C_o - C_p) \tag{2.2}$$

where J_s is the solute flux, B the solute permeability coefficient (function of diffusivity and solubility of solute), C_o the inflow solute concentration and C_p the permeate solute concentration.

In Irreversible Thermodynamics Theory, membrane transport is described thermodynamically and the membrane is treated as a "black box." A general description is obtained and no description of flow and separation mechanisms are needed.

In a non-ideal membrane, two fluxes J_v and J_s can be distinguishably driven by forces F_v and F_s respectively. Because the system is assumed not far from equilibrium, according to the irreversible thermodynamics principle, the fluxes are linearly related to the driving forces. The linear dependence between all fluxes and forces are given by:

$$J_v = L_{vv}F_v + L_{vs}F_s \tag{2.3}$$

$$J_s = L_{sv}F_v + L_{ss}F_s \tag{2.4}$$

where J_v is the total solvent flux, J_s the total solute flux, L_{sv} and L_{vs} the cross phenomenological coefficients, L_{ss} and L_{vv} the straight phenomenological coefficients. F_v and F_s are driving forces.

2.5 Salt Rejection

The transport of salt across a membrane is commonly expressed as salt passage or salt rejection. Salt passage is defined as the ratio of concentration of salt on the permeate side of the membrane relative to the average feed concentration. The equation describing salt passage is given by:

$$SP = C_p/C_o \times 100\% \tag{2.5}$$

where SP is the percentage salt passage, C_p the permeate salt concentration and C_o the average feed salt concentration.

The equation describing salt rejection is given by:

$$R = 100\% - SP \tag{2.6}$$

where R is the percentage salt rejection.

2.6 Limitations of Transport and Irreversible Thermodynamics Models

Though many models have been proposed in an attempt to explain transport and separation mechanisms in reverse osmosis membranes, not all aspects of membrane transport are fully understood. There exist limitations and inadequacies in these models. To prove these limitations and inadequacies, the Solution-diffusion model is examined. It will be shown that the solute flux equation does not adequately describe the dependency of solute flux on feed concentration.

In the Solution-diffusion model, if solute concentration in permeate, C_p, is negligible and then the solute flux equation $J_s = B(C_o - C_p)$ can be reduced to:

$$J_s = BC_o \tag{2.7}$$

where C_o is the feed concentration and B the solute permeability coefficient.

Salt rejection equation is given by:

$$R = 1 - C_p/C_o \tag{2.8}$$

Permeate solute concentration is given by:

$$C_p = J_s/J_v \tag{2.9}$$

By substituting equation (2.7) into equation (2.9),

$$C_p = BC_o/J_v \tag{2.10}$$

By substituting equation (2.10) into equation (2.8),

$$R = 1 - B/J_v \tag{2.11}$$

Hence, it can be implied from equation (2.11) that salt rejection, *R* is independent of inflow solute concentration, C_o and a graph of *R* against C_o will give a theoretical straight horizontal line.

However, literature references (Sourirajan, 1964) suggest that this independence is not true, and all experiments on membrane transport indicate that salt rejection is a function of inflow solute concentration. Figure (2.3) shows the effect of inflow solute concentration on solute separation characteristics of a cellulose acetate RO membrane.

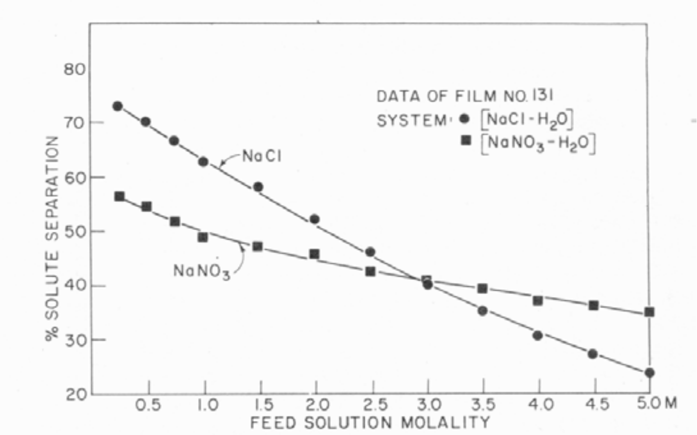


Figure 2.3: Dependence of solute separation (%) on feed concentration (molality) using a RO cellulose acetate membrane (Sourirajan 1964)

From figure (2.3), salt rejection can be related to feed concentration by a power function and equation (2.11) can be hypothetically modified to:

$$R = 1 - BC_o^{\alpha-1}/J_v$$

$$= 1 - BC_o^{\alpha}/J_vC_o \qquad (2.12)$$

$$= 1 - J_s/J_vC_o \qquad (2.13)$$

$$= 1 - C_P/C_o$$

From equation (2.12) and (2.13), it can be deduced that

$$J_s = BC_o^{\alpha} \qquad , \alpha>1 \qquad (2.14)$$

Equation (2.14) suggests that solute flux is dependent on inflow solute concentration to a certain power, α whereby $\alpha>1$. This clearly spells out the inadequacy and limitation of the solute flux equation based on the Solution-diffusion model.

Similarly, most transport and irreversible thermodynamics models have failed to address this inadequacy whereby solute flux is dependent only to the first power of inflow solute concentration.

CHAPTER THREE: EXPERIMENTAL SET-UP AND PROCEDURE

3.1 Experimental Set-Up

The major component of the experimental set-up is a bench-top laboratory test device known as a SEPA CF cell. Figure 3.1 shows the various components that make up the SEPA CF system. The SEPA CF membrane cell is designed to simulate the performance of commercially available spiral-wound and tubular membrane elements. This simulation is achieved by using the same materials of construction as the commercially available elements and by creating similar fluid dynamics. The SEPA CF cell functions in a true cross-flow or tangential flow mode, similar to commercially available filtration units.

The SEPA CF system consists of three major components: the cell body, cell holder, and feed pump. The cell body consists of a cell body bottom where a single piece of rectangular membrane is placed on it, together with a feed spacer and a cell body top that fits over the guideposts. The function of the mesh spacer in the feed channel promotes turbulence in the flow channel is to reduce the build-up of solutes near the membrane while that of the guideposts is to assure proper orientation of the cell body halves.

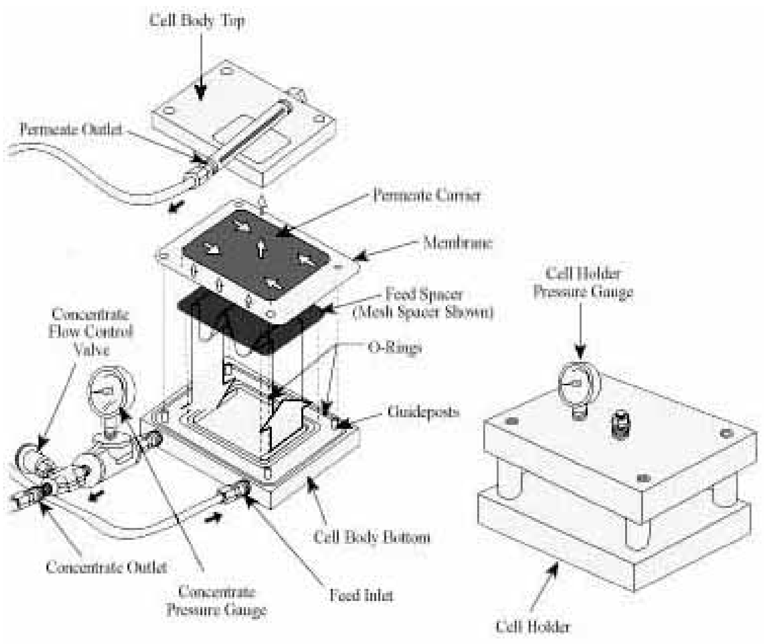


Figure 3.1: Standard Configuration of a SEPA CF system (adapted from Osmonics)

The cell body is inserted into the cell holder. Hydraulic pressure is then applied to the top of the holder. This pressure causes the piston to extend downward and compress the cell body against the cell holder base. Double O-rings in the cell body provide a leak-proof seal. The feed stream is pumped from the feed vessel to the feed inlet, which is located on the cell body bottom. Flow continues through a manifold into the membrane cavity. Once in the cavity, the solution flows tangentially across the membrane surface. Solution flow is controlled and is laminar or turbulent depending on the fluid velocity used.

A portion of the solution permeates the membrane and flows through the permeate carrier which is located in the cell body top. The permeate flows to the centre of the cell body top, is collected in a manifold, and then flows out through the permeate outlet connection. The concentrate stream, which contains the material rejected by the membrane, continues sweeping over the membrane and collects in the manifold. The concentrate then flows through the concentrate flow control valve back into the feed vessel.

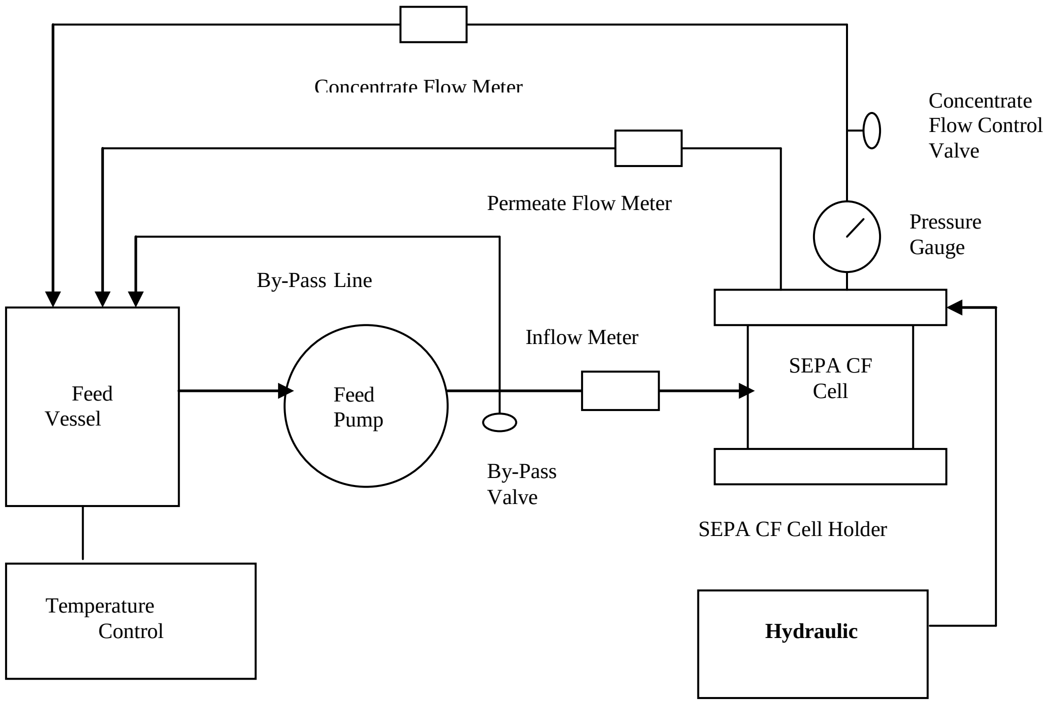


Figure 3.2: Schematic diagram of the experimental set-up

Figure 3.2 shows the schematic diagram of the whole experimental set-up. Feed solution is pumped to the inlet of the SEPA CF cell by a feed pump (T-100k Test Pump, Japan). The inflow rate is controlled and maintained at 1.0mL/min, using a by-pass valve that controls the quantity of feed solution being channeled back to the feed vessel. The feed solution enters the SEPA CF cell, after which salt rejected by the membrane exits at the concentrate outlet and the purified solvent exits at the permeate outlet of the cell. The concentrate and permeate flows are measured using a Signet flow meter (location here) and a 101 Flo-Sen, McMillan Co (location). flow meter respectively. The permeate conductivity is measured using a TDS 705 Hanna Instruments (location) conductivity meter. The concentrate flow valve controls the operating pressure which is equivalent to the trans-membrane pressure. This pressure is measured by a pressure gage located at the concentrate outlet. The experiments are carried out in a 'total recycle' mode where the concentrate and permeate are remixed so as to keep the feed concentration unchanged. The feed solution is maintained at a constant temperature of 25ºC by a re-circulating heater/chiller.

Figure 3.3 shows the overall experimental set-up. Figure 3.4 shows a close-up external view of the SEPA CF cell while Figure 3.5 shows the instrumental panel, which comprises of concentrate flux meter, permeate flux meter and permeate conductivity meter.

Figure 3.3: Overall experimental set-up

Figure 3.4: SEPA CF cell

Figure 3.5: Instrumental panel

3.2 Membrane Specifications

A SEPA membrane (RO CA ST-28, Osmonics) for reverse osmosis was used to carry out the experiments. The membrane is composed of acetate (CA). This device has an effective membrane area of 155 cm^2. The membrane has a salt rejection capability of up to 99.2 %. It is designed and manufactured to operate at a maximum operating pressure of 1000 psi and maximum temperature of 50 °C.

3.3 Preparation of Feed Solutions

Sodium sulfate is used to prepare 6 salt solutions of different concentrations. Table (3.1) shows the different feed concentrations in ppm and the respective mass of Na_2SO_4 in grams per liter of water required to prepare the individual feed solution.

Table 3.1: Preparation of feed solutions

Solution Number	Concentration (ppm)	Mass of Na_2SO_4 per liter of water (g/L)
1	100	0.1
2	300	0.3
3	500	0.5
4	1000	1.0
5	3000	3.0
6	5000	5.0

3.4 Experimental Procedure

Each of the six feed solutions is used through the entire experimental procedure, starting progressively with the lowest feed concentration of 100 ppm. With the help of the by-pass valve, the inflow rate is maintained at 1.0 mL/min. Next, the operating pressure is adjusted to the required trans-membrane pressure using the concentrate flow control valve. The experiment is initially carried out at an operating pressure of 100 psi, followed by 200 psi and at subsequent incremental pressure intervals of 100 psi until 800 psi is reached. Operating pressure as high as 800 psi will be required in the highly concentrated salt solutions in order to obtain salt rejection results, provided a steady permeate conductivity is obtainable.

In the case of the SEPA CF cell, increasing the operating pressure by closing more of the concentrate flow control valve will result in a decrease in the inflow rate. Increasing the inflow rate by closing more of the by-pass valve will also lead to an increase in operating pressure. As a result, careful and fine adjustments have to be made using the both the by-pass valve and concentrate flow control valve to obtain the inflow rate and operating pressure required. Also, checks are carried out regularly to ensure that the total permeate and concentrate flows equal to that of the feed inflow using the flow meters in the set-up.

The feed solution is maintained at a temperature of 25 ºC inside the feed tank. At each particular operating pressure, the RO system will be run continuously for 1.5 hour to achieve stabilization before the concentration of the permeate is measured.

3. 5 Calibration of Conductivity Meter

Two conductivity meters were calibrated with standard salt solution before experiments. The standard solution was made of distilled water by adding known amounts of sodium sulfate. The conductivity of the standard solution is then measured with the conductivity meters and the correlations between the salt concentration and conductivity can be determined from the measurements. One of conductivity meters is installed on line of the RO process and it automatically measured the conductivity of the permeate. This conductivity meter is referred to as "on-line" even it was taken off the line for calibration. The other conductivity meter is called the "manual" conductivity meter; this is the one that is separate from the system. Figure 3.6 and figure 3.7 shows the two conductivity meters used. Figure 3.8 will show the calibration curve in converting the NaCl reading from the conductivity meters into the Na_2SO_4 reading that we need. The conversion is 1.1365 for the manual conductivity meter, and 1.1117 for the on-line conductivity meter. Salt rejection at the particular feed concentration and operating pressure can then be calculated, based on the salt passage equation (2.5) and salt rejection equation (2.6). The whole procedure is repeated again at the next incremental operating pressure and done so for all the six different feed solutions.

Figure 3.6: "Manual" conductivity meter used in the experiment

Figure 3.7: “On-line” conductivity meter used in the experiment.

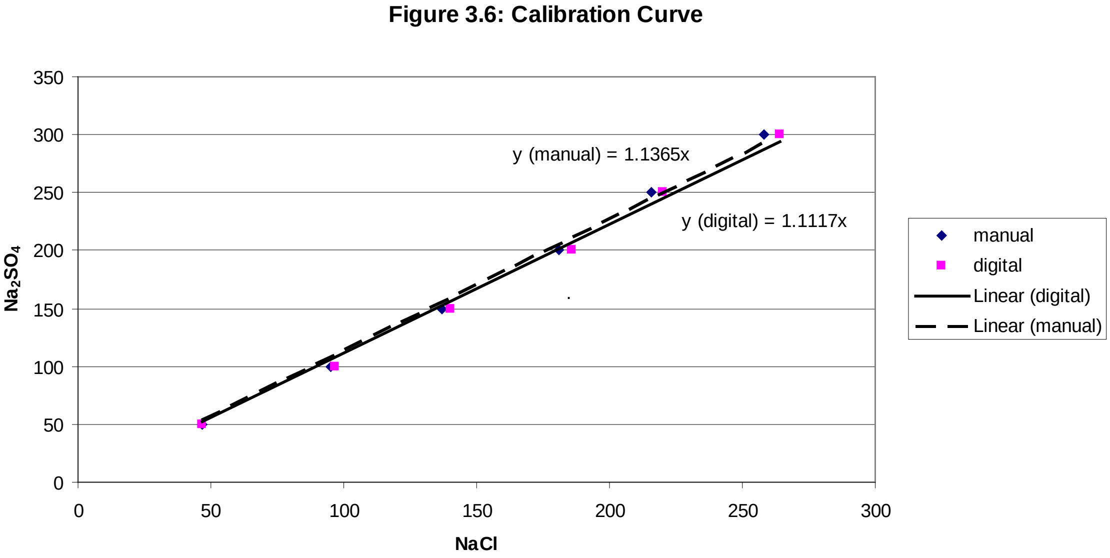


Figure 3.8: Calibration curved used to calibrate the data

CHAPTER FOUR: RESULTS AND DISCUSSION

4.1 Effect of Operating Pressure on Salt Rejection

The effect of operating pressure on salt rejection at feed concentrations of 100 ppm, 300 ppm, 500 ppm, 1000 ppm, 3000 ppm, 5000 ppm are plotted in Figures 4.1 and 4.2. The data for both figures were collected under different operating conditions.

The general trend shown in both Figure 4.1 and Figure 4.2 for all feed concentrations indicates that the salt rejection increases with operating pressure until it approaches a limiting value. The rate of increase of salt rejection is the highest when the operating pressure is increased within the ranges of 0 psi to 200 psi. Figure 4.1 shows that the increase in salt rejection rate is higher for feed solutions with low salt concentrations that for feed solutions with high salt concentrations, which can be found in figure 4.2. For the high concentrated salt solution in figure 4.2, the rate of increase of salt rejection with operating pressure is relatively constant and the graph flattens out instead of plateaus to a limiting value as compared to the one found in figure 4.1. Both figures also show that the curve with higher salt concentration generally has lower rejection rate for the same pressure except for very low pressure.

Table 4.1: Rejection rates for given feed concentration and operating pressure.

	Pressure (psi)							
Feed Concentration (ppm)	100	200	300	400	500	600	700	800
100	0.81	0.94	0.96	0.96	0.98	0.98	0.98	0.99
300	0.91	0.94	0.94	0.96	0.97	0.97	0.98	0.98
500	0.94	0.95	0.96	0.96	0.97			
1000	0.93	0.96	0.98	0.98	0.99	0.99	0.99	0.99
3000	0.94	0.98	0.98	0.98	0.98	0.99	0.99	0.99
5000	0.93	0.97	0.98	0.98	0.98	0.99	0.99	0.99

The concentration effect was not significant for the two figures because the experiments for both were conducted under different operating conditions. The conductivity meters were recalibrated and adjusted in the middle of the experiments therefore it yielded different results. This interruption was out the control of the experimenter, therefore two sets of data are observed instead of only one.

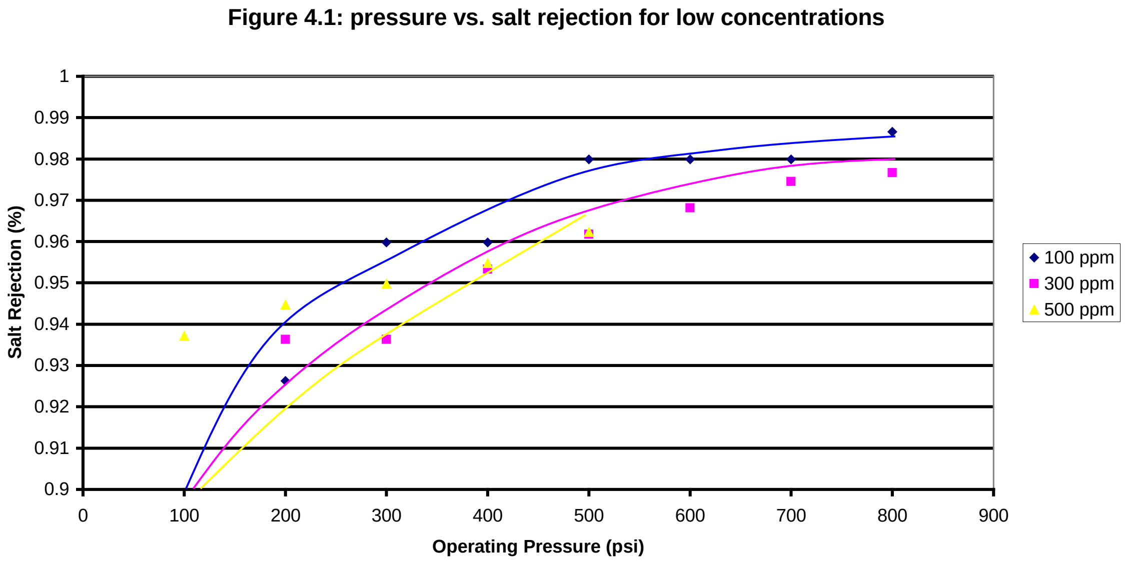


Figure 4.1: Effect of operating pressure (psi) on salt rejection (%) at different feed concentration for low concentrated salt.

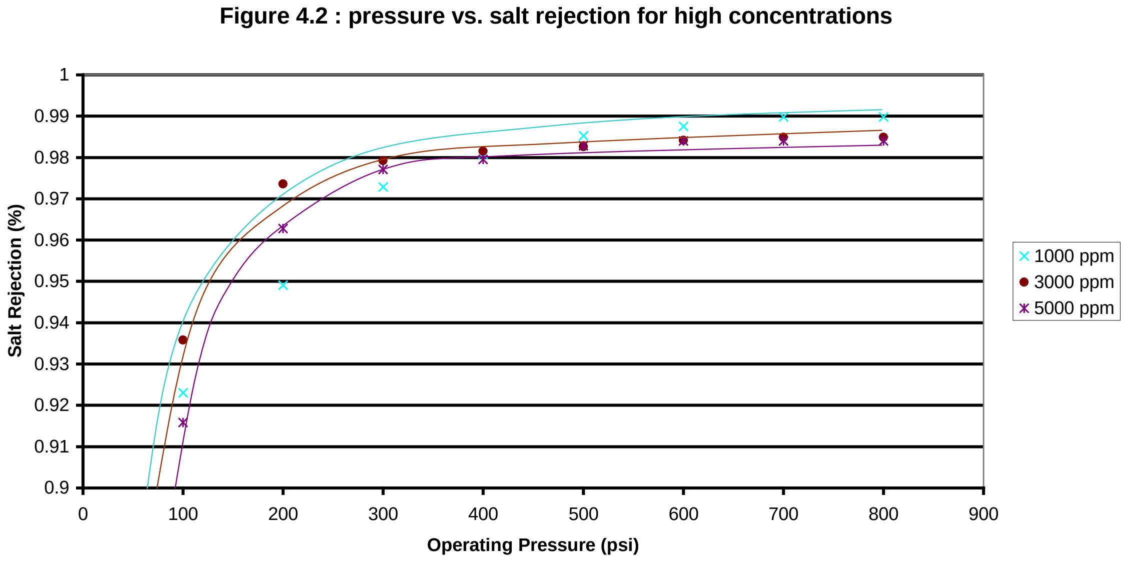


Figure 4.2: Effect of operating pressure (psi) on salt rejection (%) at different feed concentration for high- concentrated salt.

4.2 Effect of Permeate Flux on Salt Rejection

The effect of permeate flux on salt rejection at different feed concentration of 100 ppm, 300 ppm, 500 ppm, 1000 ppm, 3000 ppm, 5000 ppm are plotted in Figure 4.3.

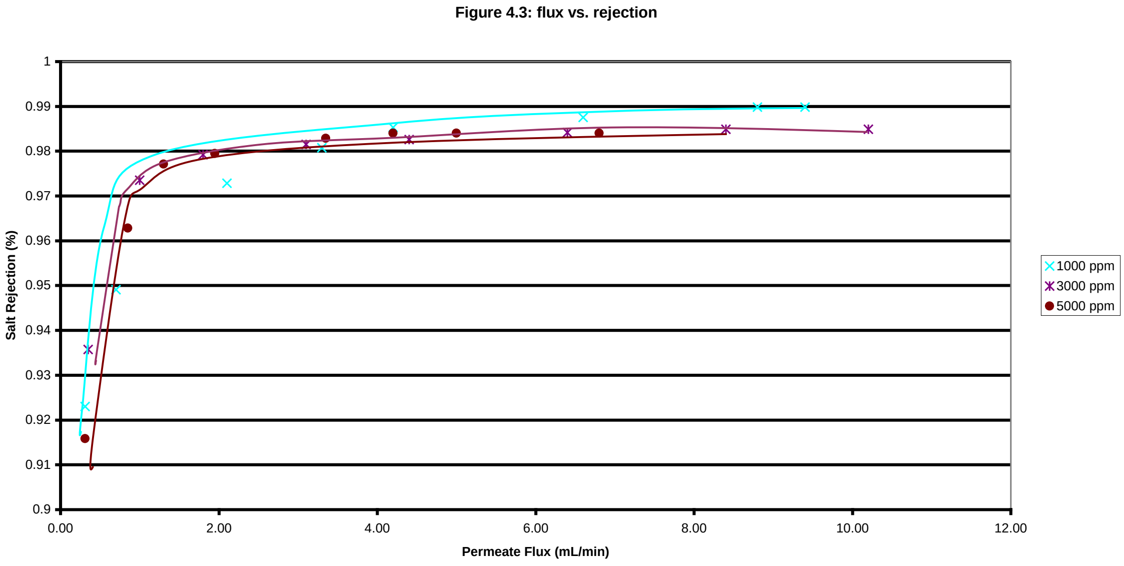


Figure 4.3: Salt rejection as a function of permeate flux at different feed concentrations.

Permeate flux is closely related to operating pressure (it is actually proportional to the net driving pressure that is the difference between the transmembrane pressure and the osmotic pressure), so similar trends are observed from Figures 4.3 which indicate that for all feed concentrations, an increase in permeate flux results in increasing salt rejection until it approaches a limiting value. Again, salt rejection increases faster between the ranges of 0 psi to 200 psi. The rate of increase of salt rejection with permeate flux between 200 psi to 800 psi is relatively constant and the graph flattens out at higher flux. Figure 4.3 also show that the curve with higher concentration of salt generally has lower rejection rate. Compare to Figure 4.1 and Figure 4.2, we can see that the rejection rate increases faster in Figure 4.3.

4.3 Effect of Pressure on Permeate Flux

The effect of pressure on permeate flux at different feed concentrations of 100 ppm, 300 ppm, 500 ppm, 1000 ppm, 3000 ppm, 5000 ppm is shown in Figure 4.4. Figure 4.4 shows that permeate flux increases as pressure increases. From the data collected, there is a non-linear relationship between the flux increase and the pressure increase for all different feed concentrations. When pressure is lower, permeate flux increases slowly with pressure. As pressure becomes higher, the flux increases faster.

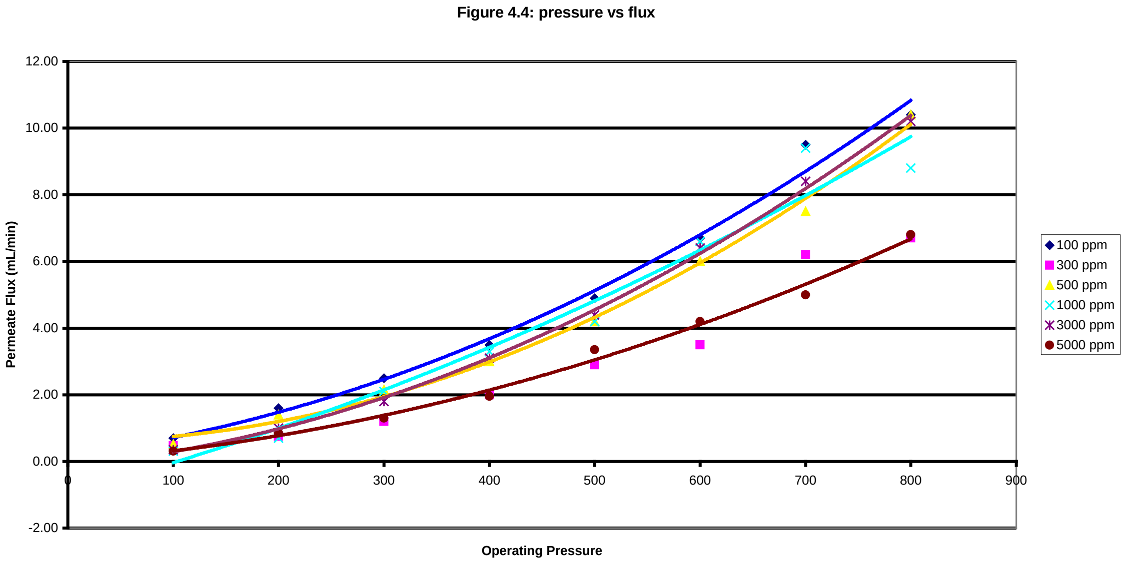


Figure 4.4: Permeate flux as a function of pressure at different feed concentrations

These upward bending flux curves in Figure 4.4 are contradictory to linear relationship between flux and pressure as predicted by classic membrane transport theory, equation (2.1). Similar behavior of permeate fluxes was observed before in this laboratory with different salt solutions. The experimental results show that the current membrane transport theory is inadequate to accurately describe the flux in a RO process, especially when it is operated at a relative low pressure. Advanced theoretical work is needed to further our knowledge on this aspect.

4.4 Comparison of Na_2SO_4 with NaCl

The difference in salt rejection affected by operating pressure for Na_2SO_4 and NaCl at different feed concentration of 100 ppm, 500 ppm, 1000 ppm, and 5000 ppm are plotted in Figure 4.5 a, b, c, and d. The data collected for Na_2SO_4 and NaCl were collected under different operating condition but with the same RO device.

Figure 4.5 shows that Na_2SO_4 is rejected more strongl than NaCl at all feed concentrations under the same operating pressure. The difference in salt rejections increases with increasing salt concentration. This observation indicates that the membrane has high rejection for sodium sulfate regardless the salt concentration. In general, membranes has a relatively low salt rejection and at that level the rejection can be significantly affected by salt concentration.

The obvious difference in rejection rate to sodium chloride and sodium sulfate may imply that the electrical charge of ions would have a substantial impact on ion transport through RO membranes. The divalent ions are more difficult to pass through the membrane than the univalent ions. (easier to reject)

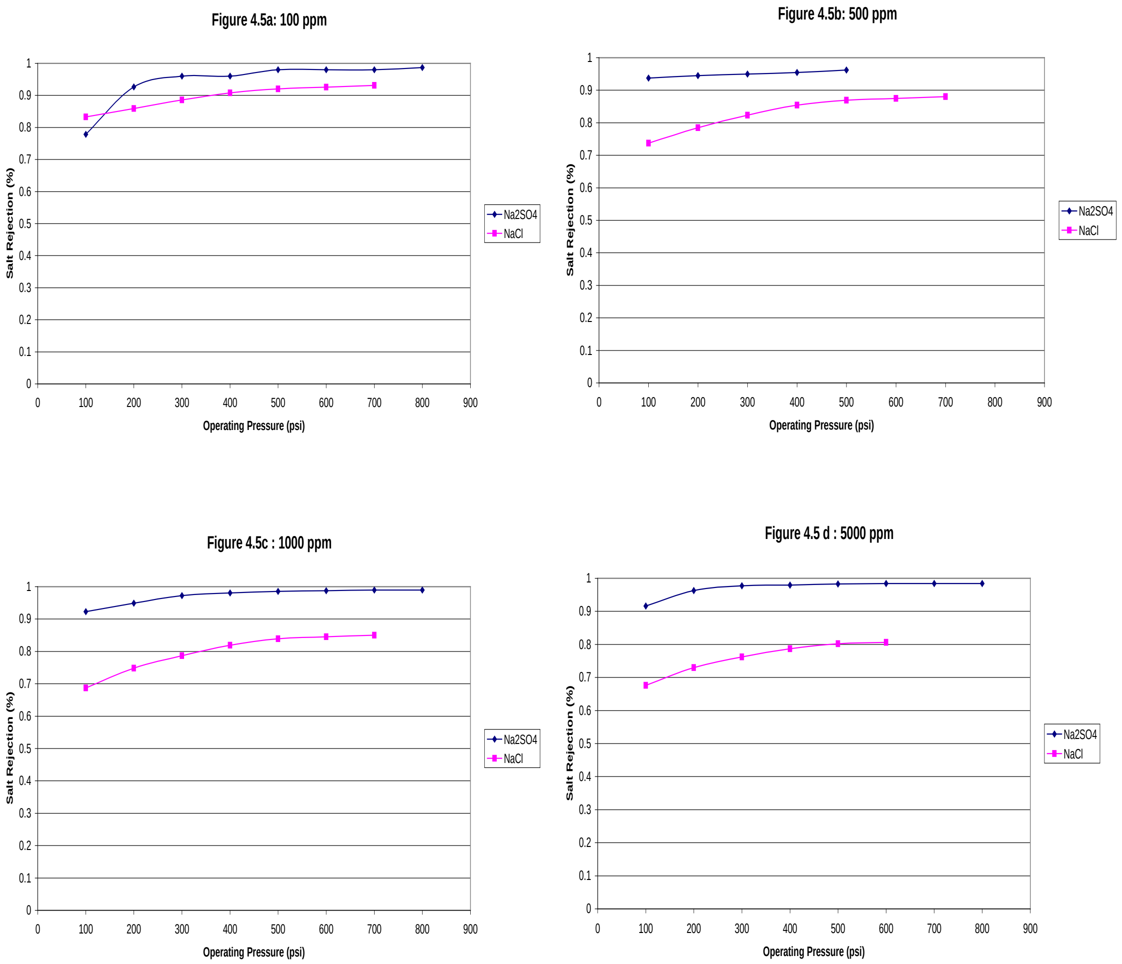


Figure 4.5: Comparison of Operating Pressure vs. Salt Rejection for Na_2SO_4 and NaCl at feed concentrations of (a) 100 ppm, (b) 500 ppm, (c) 1000 ppm, and (d) 5000 ppm.

CHAPTER FIVE: CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

Conclusions are drawn based on literature review and experimental investigation conducted in this study, with respect to the objectives defined in section (1.2).

Experimental Results obtained are in good agreement with results from past experiments. Similar salt rejection trends under different experimental parameters such as feed concentrations and operating pressures are observed. Salt rejection increases with increasing operating pressure. Salt rejection decreases with increasing feed concentrations.

Divalent salts (sodium sulfate) are more easily rejected by RO membranes than univalent ions (sodium chloride) for all salt concentration and transmembrane pressure. The rejection of divalent salt is less affected by salt concentration. In fact, the effect of concentration on salt rejection is difficult to measure in the experiments conducted in this study. The higher rejection of the membrane to divalent salt may be attributed to higher electrical charge of the ions.

A non-linear relationship was found to exist between permeate flux and transmembrane pressure. The permeate flux increases with an increasing rate as the transmembrane pressure increases. This behavior cannot be reasonably explained with the classic membrane transport theory. This indicates there is a need for fundamental research to develop advanced theory for membrane transport.

Understanding salt rejection is important for more efficient and effective application of RO membrane technology in water and wastewater treatment. As water supplies become less available, RO membrane technology will offer a resourceful alternative to meet the demands for reliable potable water.

5.2 Project Limitation

Project Limitations affect the accuracy of the experimental results obtained. These limitations occur mainly from the experimental set-up.

1. At a high operating pressure of 700 and 800 psi, the pressure pump heats up dramatically. This in turn heats up all the fluid running in the whole experimental set-up and as a result, the chiller was not able to maintain the feed solution at a constant room temperature of 25°C. Conductivity increases with temperature and consequently, the conductivity meter will give an over-estimate of the permeate concentration. Therefore, salt rejection at high operating pressure of 700 psi and 800 psi may not be accurate.

2. The SEPA CF cell is made of stainless steel and highly corrosive-resistant, but the high pressure pump is less resistant. When the highly concentrated feed solution of 5000 ppm is used, the feed solution in the feed vessel, where the permeate and concentrate are recycled, turned orangey-brown after a day’s run. Brown particles were observed and mild corrosion may have taken place internally in the pressure pump at high feed concentrations.
3. At a low operating pressure of 100 psi, permeate fluxes for solutions with high salt concentrations are extremely low. The conductivity meter used in the experimental set-up was not able to detect any permeate conductivity at such low permeate fluxes.
4. At a high operating pressure of 700 psi and 800 psi, a steady permeate conductivity was difficult to obtain. Even after three hours period of waiting, the permeate conductivity was still changing.

5.3 Recommendations

1. Increase stabilization time for each experimental run to half a day and to a full day for lower operating pressures. This will allow the system to be fully stabilized and the effects of feed concentration on salt rejection to be assessed in a longer time frame.
2. In measuring permeate flux for higher operating pressures, it’s best to measure the permeate flux 5 minutes after starting up the system. This way, the temperature

has not increased too far from 25ºC, and the 5 minutes will give the system some time to stabilize

3. In ultra low pressure RO, it is recommended to operate RO not too far below 200 psi, because below 200 psi, the rejection rate drops rapidly.
4. It is not necessary to operate the system above 300 psi because the rejection rate is constant after 300 psi; if there is an increase in rejection rate, it is not a big increase. Operating the system below 300 psi will conserve energy and give almost the same result.
5. Use at least 30 liters of solution to run the system. If less than 30 liters used, turbulence will occur, and this turbulence will cause the pressure to become unstable.

REFERENCES

Andrij Yaroshchuk, Eberhard Staude, “Charged Membranes for Low Pressure Reverse Osmosis Properties and Applications”, *Desalination*, 86, 1992, pp.115-134

Andrij E. Yaroshchuk, “Solution-diffusion-imperfection Model Revised”, *Journal of Membrane Science*, 101, 1995, pp.83-87.

Jonsson G., “Overview of Theories for Water and Solute Transport in UF/RO Membranes”, *Desalination*, 35,1980, pp.21-38.

Levenstein R., D. Hasson, R. Semiat, “Utilization of the Donnan Effect for Improving Electrolyte Separation with Nanofiltration Membranes”, *Journal of Membrane Science*, 116, 1996, pp.77-92.

Peeters J.M.M., Boom J.P., Mulder M.H.V., Strathmann H., “Retention Measurements of Nanofiltration Membranes with Electrolyte Solutions”, *Journal of Membrane Science*, 116, 1996, pp. 77-92.

Richard Bowen W, Hilmi Mukhtar, “Characterisation and Prediction of Separation Performance of Nanofiltration Membranes”, *Journal of Membrane Science*, 112, 1996, pp.263-274.

Soltanieh. M. and Gill W. N., “Review of Reverse Osmosis Membranes and Transport Models”, *Chem. Eng. Commun.*, 12, 1981, pp.279-363.

Song LianFa, “Thermodynamic Modelling of Solute Transport Through Reverse Osmosis Membrane”, *Chem. Eng. Comm.*, 180, 2000, pp.145-167.

Sourirajan, S., “Reverse Osmosis”, *Academic Press*, 1970.

Van Gauwbergen D., J. Baeyens, “Modelling Reverse Osmosis by Irreversible Thermodynamics”, *Separation and Purification Technology*, 13, 1998, pp.117-128.

APPENDIX A.1

Data and graphs on effects of operating pressure on salt rejection:

100 ppm feed concentration

Operating Pressure (psi)	100	200	300	400	500	600	700	800
Salt Rejection (%)	0.81	0.94	0.96	0.96	0.98	0.98	0.98	0.99

300 ppm feed concentration

Operating Pressure (psi)	100	200	300	400	500	600	700	800
Salt Rejection (%)	0.91	0.94	0.94	0.96	0.97	0.97	0.98	0.98

500 ppm feed concentration

Operating Pressure (psi)	100	200	300	400	500	600	700	800
Salt Rejection (%)	0.94	0.95	0.96	0.96	0.97			

1000 ppm feed concentration

Operating Pressure (psi)	100	200	300	400	500	600	700	800
Salt Rejection (%)	0.93	0.96	0.98	0.98	0.99	0.99	0.99	0.99

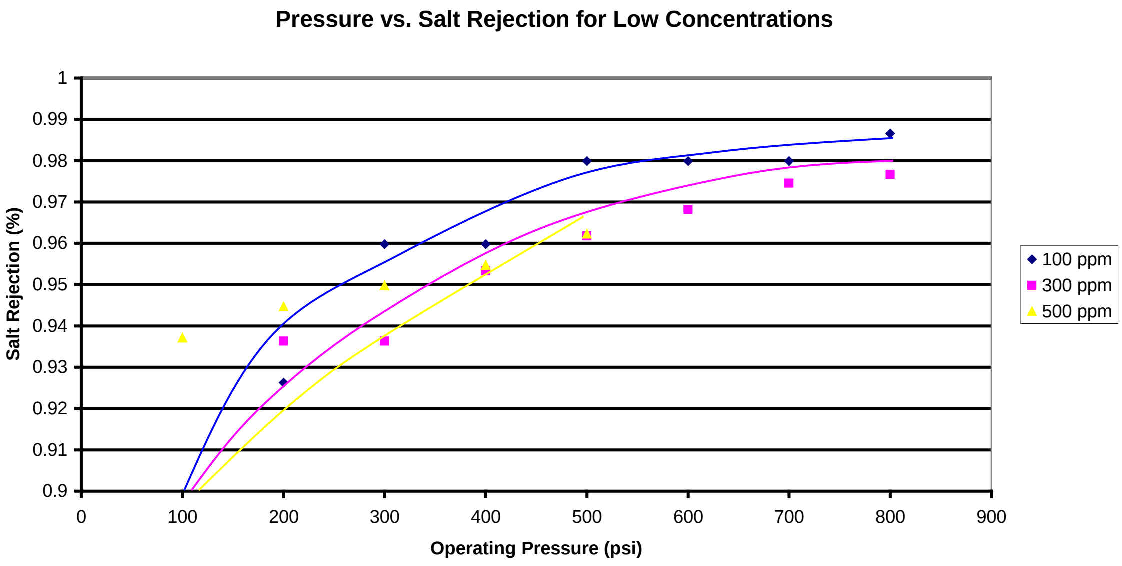
3000 ppm feed concentration

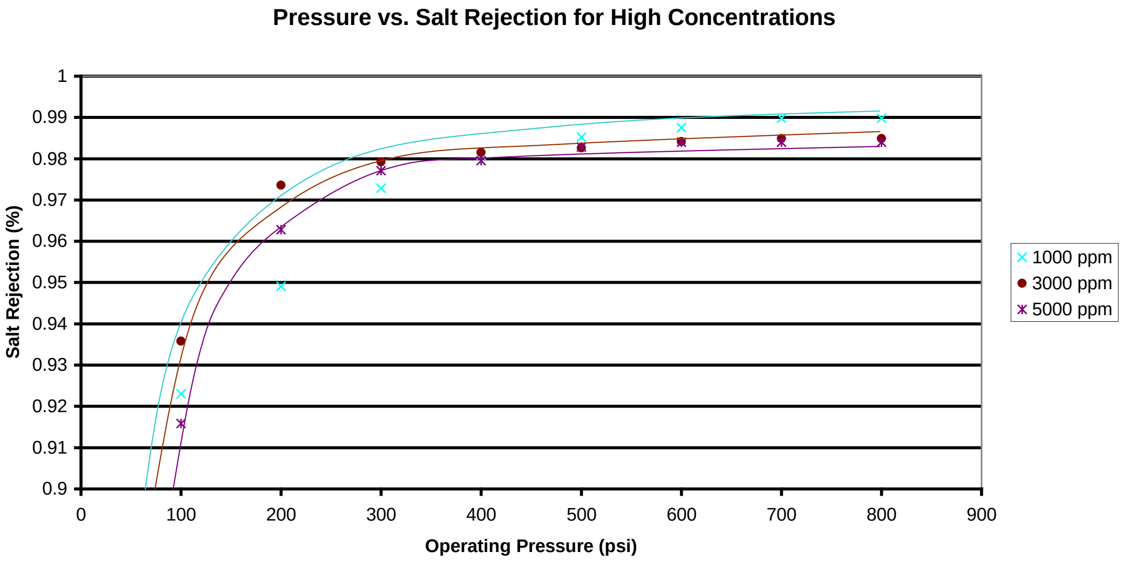
Operating Pressure (psi)	100	200	300	400	500	600	700	800
Salt Rejection (%)	0.94	0.98	0.98	0.98	0.98	0.99	0.99	0.99

5000 ppm feed concentration

Operating Pressure (psi)	100	200	300	400	500	600	700	800
Salt Rejection (%)	0.93	0.97	0.98	0.98	0.98	0.99	0.99	0.99

Graphs of Salt Rejection (%) against Operating Pressure (psi)





APPENDIX A.2

Data and graph on effects of solvent flux on salt rejection:

Effective membrane area = 155 cm^2

100 ppm feed concentration

Solvent flux x 10^{-6} (m/s)	0.75	1.72	2.69	3.76	5.27	7.20	10.22	11.18
Salt Rejection (%)	0.78	0.93	0.96	0.96	0.98	0.98	0.98	0.99

300 ppm feed concentration

Solvent flux x 10^{-6} (m/s)	0.51	0.81	1.29	2.15	3.12	3.76	6.67	7.20
Salt Rejection (%)	0.89	0.94	0.94	0.95	0.96	0.97	0.97	0.98

500 ppm feed concentration

Solvent flux x 10^{-6} (m/s)	0.56	1.51	2.31	3.23	4.52	6.45	8.06	11.18
Salt Rejection (%)	0.94	0.94	0.95	0.95	0.96			

1000 ppm feed concentration

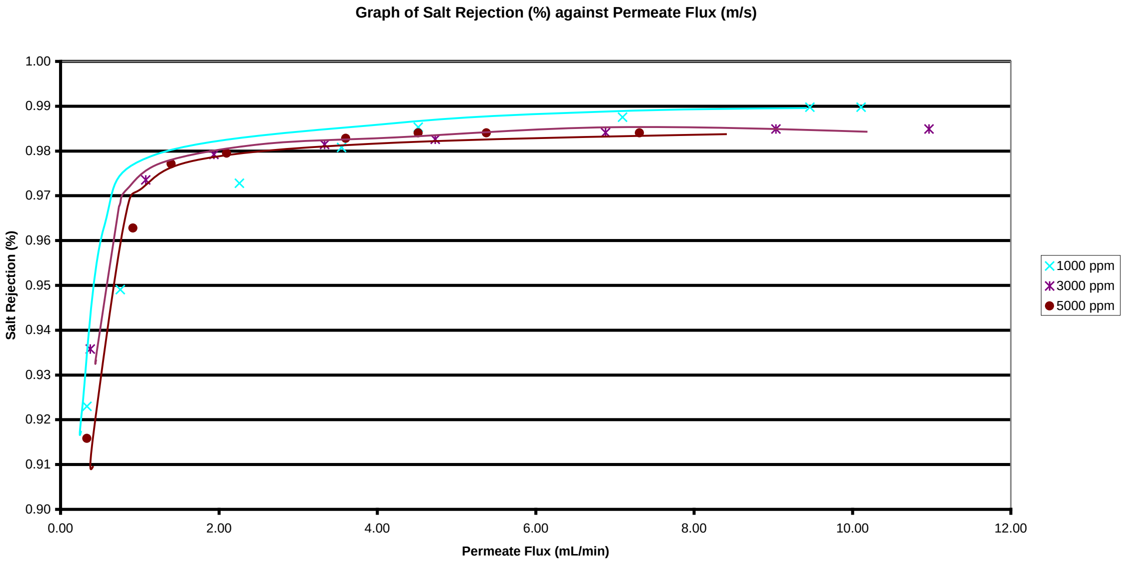
Solvent flux x 10^{-6} (m/s)	0.33	0.75	2.26	3.55	4.52	7.10	10.11	9.46
Salt Rejection (%)	0.92	0.95	0.97	0.98	0.99	0.99	0.99	0.99

3000 ppm feed concentration

Solvent flux x 10^{-6} (m/s)	0.38	1.08	1.94	3.33	4.73	6.88	9.03	10.97
Salt Rejection (%)	0.94	0.97	0.98	0.98	0.98	0.98	0.98	0.98

5000 ppm feed concentration

Solvent flux x 10^{-6} (m/s)	0.33	0.91	1.40	2.10	3.60	4.52	5.38	7.31
Salt Rejection (%)	0.92	0.96	0.98	0.98	0.98	0.98	0.98	0.98



APPENDIX B

Data on effects of feed concentration on salt rejection:

100 psi operating pressure

Feed Concentration (ppm)	100	300	500	1000	3000	5000
Salt Rejection (%)	80.5	90.7	94.5	93.2	94.3	92.5

200 psi operating pressure

Feed Concentration (ppm)	100	300	500	1000	3000	5000
Salt Rejection (%)	93.5	94.4	95.1	95.5	97.7	96.7

300 psi operating pressure

Feed Concentration (ppm)	100	300	500	1000	3000	5000
Salt Rejection (%)	96.5	94.4	95.6	97.6	98.2	98.0

400 psi operating pressure

Feed Concentration (ppm)	100	300	500	1000	3000	5000
Salt Rejection (%)	96.5	95.9	96.0	98.3	98.4	98.2

500 psi operating pressure

Feed Concentration (ppm)	100	300	500	1000	3000	5000
Salt Rejection (%)	98.2	96.6	96.7	98.7	98.5	98.4

600 psi operating pressure

Feed Concentration (ppm)	100	300	500	1000	3000	5000
Salt Rejection (%)	98.2	97.2		98.9	98.6	98.6

700 psi operating pressure

Feed Concentration (ppm)	100	300	500	1000	3000	5000
Salt Rejection (%)	98.2	97.8		99.1	98.7	98.6

800 psi operating pressure

Feed Concentration (ppm)	100	300	500	1000	3000	5000
Salt Rejection (%)	98.8	97.9		99.1	98.7	98.6

APPENDIX C

Data and graph on effects of operating pressure on permeate flux:

100 ppm feed concentration

Operating Pressure (psi)	100	200	300	400	500	600	700	800
Permeate Flux (mL/min)	0.70	1.60	2.50	3.50	4.90	6.70	9.50	10.40

300 ppm feed concentration

Operating Pressure (psi)	100	200	300	400	500	600	700	800
Permeate Flux (mL/min)	0.47	0.75	1.20	2.00	2.90	3.50	6.20	6.70

500 ppm feed concentration

Operating Pressure (psi)	100	200	300	400	500	600	700	800
Permeate Flux (mL/min)	0.52	1.40	2.15	3.00	4.20	6.00	7.50	10.40

1000 ppm feed concentration

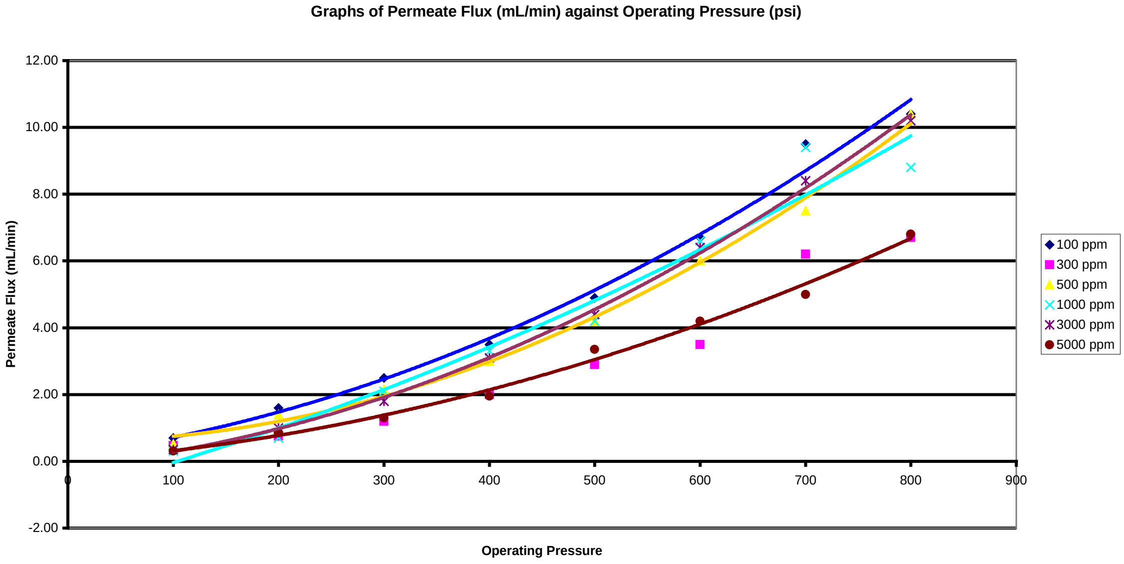
Operating Pressure (psi)	100	200	300	400	500	600	700	800
Permeate Flux (mL/min)	0.31	0.70	2.10	3.30	4.20	6.60	9.40	8.80

3000 ppm feed concentration

Operating Pressure (psi)	100	200	300	400	500	600	700	800
Permeate Flux (mL/min)	0.35	1.00	1.80	3.10	4.40	6.40	8.40	10.20

5000 ppm feed concentration

Operating Pressure (psi)	100	200	300	400	500	600	700	800
Permeate Flux (mL/min)	0.31	0.85	1.30	1.95	3.35	4.20	5.00	6.80



APPENDIX D

Data on effects of operating pressure on salt rejection for NaCl:

100 ppm feed concentration

Operating Pressure (psi)	50	100	200	300	400	500	600	700	800
Salt Rejection (%)	67.3	76.9	83.3	85.9	88.6	90.8	92.0	92.6	93.1

500 ppm feed concentration

Operating Pressure (psi)	50	100	200	300	400	500	600	700	800
Salt Rejection (%)	49.3	61.0	73.7	78.5	82.3	85.4	86.9	87.5	88.0

1000 ppm feed concentration

Operating Pressure (psi)	50	100	200	300	400	500	600	700	800
Salt Rejection (%)	40.5	54.0	68.7	74.8	78.7	81.9	83.9	84.5	85.0

5000 ppm feed concentration

Operating Pressure (psi)	100	200	300	400	500	600	700	800
Salt Rejection (%)	35.5	59.2	67.6	73.0	76.2	78.7	80.2	80.6

10000 ppm feed concentration

Operating Pressure (psi)	100	200	300	400	500	600	700
Salt Rejection (%)	28.6	51.8	62.8	66.5	68.9	72.8	74.1

30000 ppm feed concentration

Operating Pressure (psi)	100	200	300	400	500	600	700
Salt Rejection (%)	18.0	29.6	37.5	45.7	52.9	60.0	62.6