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Caustic Treatment of the Pulp: Caustic Recovery by Reverse Osmosis

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CAUSTIC TREATMENT OF THE PULP: CAUSTIC RECOVERY BY REVERSE
OSMOSIS

by

Miroslav Suchy

A Thesis
Submitted to the
Faculty of The Graduate College
in partial fulfillment of the
requirements for the
Degree of Master of Science
Department of Paper Engineering, Chemical Engineering, and Imaging

Western Michigan University
Kalamazoo, Michigan
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Miroslav Suchy

CAUSTIC TREATMENT OF THE PULP: CAUSTIC RECOVERY BY REVERSE OSMOSIS

Miroslav Suchy, M.S.

Western Michigan University, 2006

The benefit of caustic treatment on changing cellulose properties has long been known. When the treated pulp is later intended for use in personal or in health care product industries, it is important that all residual chemicals are removed and that the pure cellulose or carbohydrate portion of the pulp remains. The removal is usually facilitated by washing. Due to the low caustic concentration in the washing filtrates the removal of the excess water by standard techniques such as evaporation would not be economical.

The main objective of this investigation was to evaluate the concept of using reverse osmosis for recovery of caustic soda (NaOH) from filtrates generated by washing of the treated pulp. This was achieved by assessing membrane separation effectiveness (selectivity) and productivity (flux) measured at different levels of caustic solution concentration. In addition, initial testing of the membrane longevity in retaining both separation selectivity and productivity was evaluated.

Initial investigation demonstrated that the reverse osmosis is capable of concentrating the diluted solution of NaOH. The flux values for 1% NaOH solution at 800 psi transmembrane pressure and an average temperature of 25°C was measured at 85 l/hr.m² range with over 85% salt rejection. The membrane tested showed no deterioration in performance over the period of 50 hours of running and retained its performance characteristics after exposure to NaOH solution for period of 45 days.

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CHAPTER I

INTRODUCTION

Overall Technology Description

Cellulosic materials, such as pulp, have long been used in the personal care products industry. Manufactured from naturally abundant renewable matter, with favorable absorption properties and biodegradability, pulp is a popular material for manufacturing personal care products.

Cellulose is a complex carbohydrate compound consisting of long chains of glucose units. These units are connected via chemical bonds, called glycosidic links. The cellulose structure favors the organization of the individual chains into bundles with crystalline order held together by hydrogen bonds. These crystalline regions are interrupted by less ordered, amorphous regions.

Despite the fact that the structural unit of cellulose is glucose, which in itself is a water-soluble sugar, cellulose is insoluble in water. However, the presence of the three hydroxyl groups on each anhydroglucose residue in the chain makes cellulose very hygroscopic.

The adsorption of water and subsequent swelling occurs only in the amorphous regions of cellulose. The adsorbed moisture does not change its crystalline structure, indicating that the water molecules enter the accessible (amorphous) regions rather than the crystalline regions. The interaction of cellulose with water is an example of intercrystalline swelling - swelling that involves only the accessible portion of cellulose. However, there are many liquid solutions that can penetrate and

cause swelling in both accessible (amorphous) and crystalline regions of the cellulose. The most common example of liquid that can lead to intracrystalline swelling is aqueous solution of sodium hydroxide¹.

The benefit of caustic treatment on changing cellulose properties has long been known. As early as 1844, John Mercer discovered that treating cotton with caustic soda while under tension improved its strength, luster, dyeability and absorbency². The process was called “mercerization”. This finding and later further development of the process was fundamental for utilization of cellulose in variety of industries, such as textile, plastics, personal care products and others.

The mercerization process carried out under suitable conditions is capable of converting cellulose from its native form into a more thermodynamically stable and less crystalline form. The mercerized cellulose is less crystalline and more of an amorphous structure, thus the sorption characteristics and accessibility for further treatment with other reagents are increased.

The actual treatment, its modifications and optimal conditions are well described and documented³. The process in itself is not complicated. However, when the treated pulp is later intended for use in personal or in health care product industries, it is important that all the chemicals are removed and that only the pure cellulose or carbohydrate portion of the pulp remains.

While the majority of the caustic soda solution used in the treatment can be recovered from the pulp mechanically (i.e. presses), the removal of the residual caustic soda presents a challenge. The removal is usually facilitated by washing, and requires a large quantity of fresh water. The resulting washing filtrate contains caustic soda in the form of a dilute solution. In addition to the economical impact associated with the caustic soda losses, recent environmental concerns about effluents from pulp

mills and pulp processing mills have led to increased awareness regarding spent chemicals and strengthened the importance of mill process closure. The cost of sodium recovery and effluent treatment may present the economical bottleneck of the process. Proper and cost effective processing of the diluted caustic solution is thus necessary for the overall economical viability of the application.

Due to the low caustic concentration of the generated washing filtrates, the removal of the excess water by standard and implemented techniques such as evaporation would not be economical. Therefore, alternative methods of caustic recovery, such as membrane separation processes, must be considered.

Membrane assisted processes are well known and successfully implemented in various industries such as chemical, pulp and paper, food processing, water treatment and others. The common feature of these processes is the use of semi-permeable membranes that act as very specific filters letting water flow through, while retaining suspended solids and other substances. The main application areas of membrane processes in pulp and paper industry are mill effluent treatment and boiler feed water treatment^{4,5,6,7,8,9}.

Reverse osmosis, a representative of the membrane separation processes, is considered to be the lowest particle size filtration technology available. In recent years, reverse osmosis has been increasingly used for water and wastewater treatments^{10,11}. In theory, reverse osmosis should be capable of concentrating the solution of caustic soda (NaOH). The main challenges associated with the processing of NaOH solutions with reverse osmosis are high osmotic pressure and high pH of the solutions.

Recently developed membranes that can operate in a wide range of pH (up to pH of 14) have become commercially available. However, their industrial application

in processing solutions of NaOH has not been reported. The objective of this investigation is to evaluate the feasibility of reverse osmosis in recovery of NaOH from low concentration filtrates generated from washing of the treated pulp.

Chemical Recovery, Washing of Pulp and Mill Water Closure

Chemical recovery system in the pulp and paper mills is an integral part of overall manufacturing. A properly managed recovery reduces water and air pollution by converting the waste products to useful materials and energy. The main objective of chemical recovery is regeneration of inorganic chemicals used in pulping for reuse, while the organic matter contained in the spent pulping liquors is used for generation of heat energy by burning in recovery boilers.

In processing of lignin free pulp, the effluents of the treatment are usually cleaner compared to those of pulping or bleaching. Due to increased importance on purity of the washed pulp, the medium used for washing is usually fresh water, as opposed to the diluted recycled solutions used in washing after pulping or bleaching of the pulp. The effluents usually contain chemicals in very low concentrations, preventing their cost effective recovery. In addition, their presence in effluents requires proper processing in effluent treatment facilities, increasing the overall cost of the process.

Pulp washing is an important operation in pulp manufacturing or pulp processing. The main purpose of pulp washing is to remove and recover the maximum amount of chemicals contained in the pulp with minimum water addition. The washing of the pulp is a highly complex process involving inter-fiber mass transfer, diffusion, and adsorption mechanisms¹².

A continuing objective of the pulp and paper industry is to reduce the water

consumption in the pulp mill operations. Reduction of water consumption requires the recycle of wash water effluents. Effective washing is crucial for a successful closure of the water system in a pulp production and processing. In addition, efficient recovery of the dissolved materials is essential to minimize the make-up of reactants, lower the overall chemical consumption and decrease the effluent loading.

The development of a multistage counter-current washing sequence has improved the overall washing efficiency. The cleanest wash water is applied to the last stage where the pulp is cleanest. The filtrate is then used as a wash medium in the preceding stage. Three main mechanisms involved in pulp washing are displacement, diffusion and dilution/extraction. In displacement washing, clean water is applied to the pulp sheet on a wire/mesh. Using vacuum or pressure differential, an equal volume of dirty water is displaced.

Diffusion washing is used mainly in pulp washing after cooking. It requires relatively long period of contact between pulp and the moving wash liquor, which allow for diffusion or leaching solids from the fiber structure.

Dilution/extraction method is the oldest method of pulp washing. The pulp is first diluted with the washing liquid and then thickened.

In pulp bleaching and processing, the main objective of washing is to remove soluble organic or inorganic material from the pulp mass after either the bleaching reaction or special treatment of the bleached pulp.

Water is used by all pulp, paper, and recycling mills in significant quantity. There are a number of processes that use water and generate wastewater, however the primary uses are pulp washing following digestion and bleaching processes. A bleach plant typically uses at least half of the total water consumed in a conventional pulp mill and thus produces at least half of its effluents.

Since most water used by a pulp mill is heated prior to use, reducing water usage can very significantly reduce energy usage. High cost of energy offers an additional incentive for water usage reduction programs.

Prior to the 1970's, bleach plants used mainly warm fresh water, as there was no restriction on discharging large effluent volumes. As the energy cost increased and, due to more pronounced environmental concerns that lead to more stringent water pollution restrictions, various means for reducing water usage and effluent generation were investigated.

Several developed techniques, such as countercurrent washing systems allowed for significant reduction of fresh water usage. Water cycles closure, especially in bleach plants, can reduce the amount of fresh water required by the process. However, recycling washing filtrates can lead to accumulation of dissolved or suspended solid components (organic and inorganic), which can later cause problems¹³. These problems include impaired selectivity, increased bleach chemical consumption and scale formation¹⁴. Therefore, a partial or complete removal of some of these components from the closed system is necessary. Ideally, a recycled stream would be separated into water and concentrated chemical solution. The water could be used to lower the demand of fresh water necessary for overall material balance of the process, while the concentrated solution could be later processed (regenerated) and reused.

Membrane Separation Processes

Membrane technology has become a dignified separation technology over the past two decades. Membranes and membrane separation techniques have grown from simple laboratory tools to industrial processes with considerable technical and

commercial impact. The advantages of membrane technology are that it functions without the addition of chemicals, requires a relatively low energy usage, and is easy to use under well-arranged process conditions. Currently, membranes are used on a large scale in many important applications: to produce potable water from the sea, to generate process water from groundwater, surface water or wastewater, to clean industrial effluents and recover valuable constituents, to fractionate macromolecular solutions in food and drug industry and many more. The membrane separation technologies are now competitive with conventional separation techniques.

Membrane processes are capable of separating or removing substances ranging in size from ionic to molecular. Membrane filtration can be used as an alternative for flocculation, sediment purification techniques, adsorption (sand filters and active carbon filters, ion exchangers), extraction and distillation.

Membrane technology includes a number of different, very characteristic separation processes. The common feature of these processes is usage of semi permeable membranes, which act as a very specific filter that allows water flow through, while retaining suspended solids and other substances.

There are two main parameters that describe the effectiveness of a membrane filtration process: selectivity and productivity. Selectivity is expressed either in solute passage (ratio between solute concentration in permeate to feed solute concentration, in %) or salt rejection. Salt rejection is calculated using the following equation:

$$R = 1 - \left(\frac{C_p}{C_f} \right)$$

where C_p is concentration of permeate stream and C_f is concentration of bulk feed solution. It can also be expressed in % (calculated as 100% minus solute passage value).

Productivity, or efficiency, is expressed as a parameter called flux. Flux describes how fast a product passes through membrane. It is reported as volume/area-time ($\text{l/m}^2\cdot\text{h}$). Selectivity and productivity are membrane-dependent.

There are various methods to enable substances to penetrate a membrane. Examples of these methods are the applications of high pressure, the concentration gradient on both sides of the membrane and the introduction of an electric potential. A list of membrane separation processes, size of material retained, their driving force and type of membrane is shown in Table 1.

Table 1: Membrane separation processes: Materials retained, driving force and type of membrane

Process	Size of materials retained	Driving force	Type of membrane
Microfiltration	0.1-10 μm microparticles	Pressure difference (0.5-2bar/7.5-29psi)	Porous
Ultrafiltration	1-100nm macromolecules	Pressure difference (1-10bar/15-145psi)	Microporous
Nanofiltration	0.5-5nm molecules	Pressure difference (10-70bar/145-1015psi)	Microporous
Reverse Osmosis	< 1nm molecules	Pressure difference (10-100bar/145-1450psi)	Nonporous
Dialysis	< 1nm molecules	Concentration difference	Nonporous or microporous
Electrodialysis	< 1nm molecules	Electrical potential difference	Nonporous or microporous
Pervaporation	< 1nm molecules	Concentration difference	Nonporous
Gas Permeation	< 1nm molecules	Partial pressure difference	Nonporous
Membrane Distillation	< 1nm molecules	Partial pressure difference	Microporous

Membrane filtration can be divided into four main groups, each determined by the size of particle which can be retained by the membrane material. These range from reverse osmosis (RO), which provides the finest level of filtration, through nanofiltration (NF) and ultrafiltration (UF) to microfiltration (MF), which uses the coarsest of membranes. UF and MF membranes are typically rated in terms of pore size, or porosity, while RO and NF membranes are rated by terms of percent salt rejection and flow. The driving force of these separation processes is pressure differential. The required fluid pressure varies depending on the size of the openings in the membrane matrices (pores). Reverse osmosis membranes have the smallest pores, thus requiring significant fluid pressure, while microfiltration membranes have the largest pores, hence require the least pressure (see Table 1).

Microfiltration and ultrafiltration are applied when membrane filtration is used for the removal of larger particles. Because of the open character of the membranes the productivity is high while the pressure differences are low.

When salts need to be removed from water, nanofiltration and reverse osmosis are applied. NF and RO membranes do not work according to the principle of pores, but separation takes place by diffusion through the membrane. The pressure that is required to perform nanofiltration and reverse osmosis is much higher than the pressure required for micro and ultra filtration, while productivity is much lower. Figure 1 shows a chart of separation from ionic to particulate range. The overlap in membrane classes indicates that the sharp distinction between the membrane types and processes is not yet available.

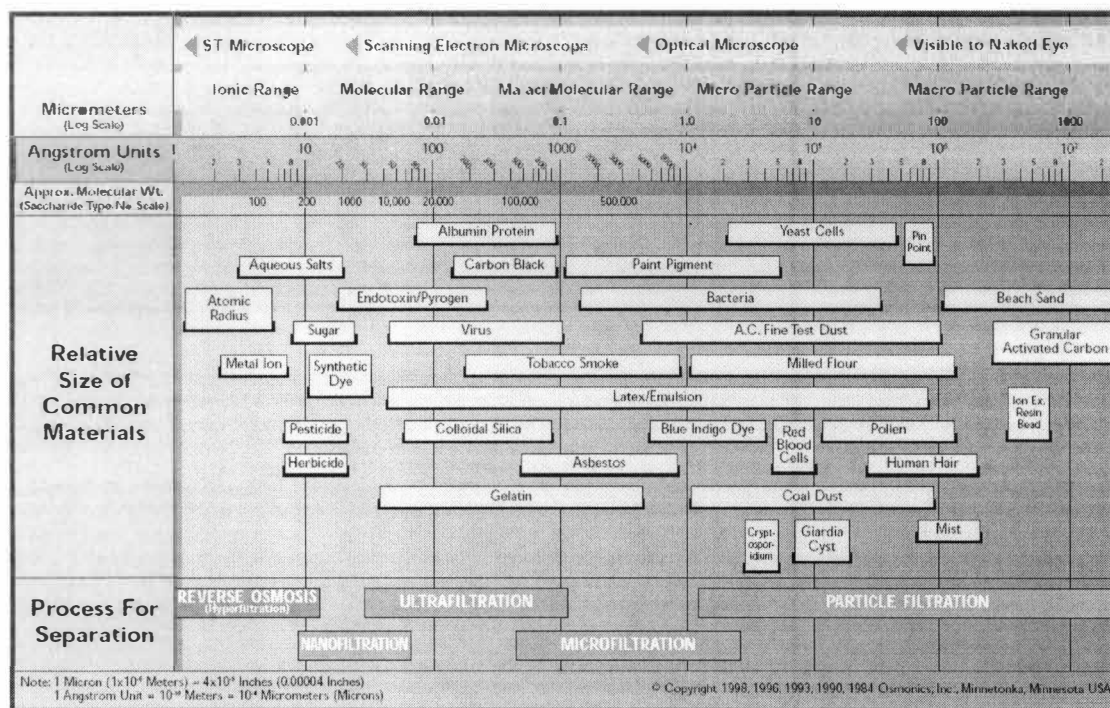


Figure 1. Overview of main membrane separation processes¹⁵

While the four membrane types have similar features, they each perform different functions in a variety of applications.

Microfiltration (MF) is a low pressure process for separating larger size solutes from aqueous solutions by means of a semi-permeable membrane. Large suspended solids are retained, while some suspended solids and all dissolved material passes through the membrane. Membrane pore size ranges from 0.1 micron to 3 micron

There are two common forms of this technique. One form is cross-flow separation, in which a fluid stream runs parallel to a membrane. The pressure differential across the membrane causes some of the fluid pass through the membrane,

while the remainder continues across the membrane, cleaning it. The other form of filtration is called dead-end filtration, or perpendicular filtration. In this process, all of the fluid passes through the membrane, and all the particles that cannot fit through the pores of the membrane are stopped. Microfiltration is usually used either as a prefiltration step or final filtration.

Ultrafiltration (UF) uses moderate hydraulic pressure to transfer water and low molecular weight species through membrane while retaining contaminants such as suspended solids, bacteria, colloids and large organic molecules. It is generally used for separations where particle sizes are larger than that of salt ions. The membrane pore sizes ranges from 0.005 to 0.1 micron.

The application is similar to microfiltration, usually in the cross-flow design. The UF membranes are frequently used in conjunction with reverse osmosis in the generation of ultra pure water and other applications.

Nanofiltration (NF) membrane technology separates solution to the molecular level. It rejects various large size organic compounds, including dyes and sugars. In addition, the nanofiltration membranes reject divalent ions and highly charged multivalent salts, while monovalent ions usually pass freely through the membrane.

Nanofiltration generally uses spiral wound membranes configures in a similar design as reverse osmosis (see later). Some of the applications include partial water softening of feed water, removal contaminants from water or alkali/acid streams, pretreatment for reverse osmosis or other high purity systems.

Reverse osmosis (RO), also known as hyperfiltration, is the finest filtration technology available. This process allows for removal of the particles as small as ions from solution. The process and its principle are described in the following section.

Reverse Osmosis

The process of reverse osmosis is based on the fact that when a solution (i.e. salt dissolved in water) and water are separated by a semi-permeable membrane, the water will move into the solution to reach concentration equilibrium. This is known as osmosis. If a mechanical force, i.e. pressure, is applied to exceed the osmotic pressure (the pressure necessary to stop the process of osmosis), the water is forced to move down the concentration gradient: from high (solution) to low (water) concentration. The openings in the membrane material (pores) are so small that a significant fluid pressure is required to drive the liquid through them. The principle of reverse osmosis is shown in Figure 2.

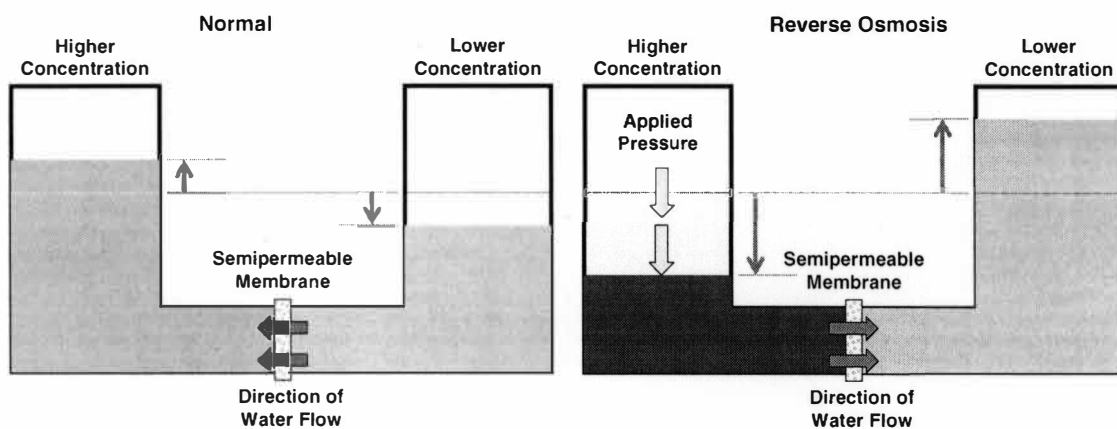


Figure 2. Principle schematics of reverse osmosis

In industrial reverse osmosis applications, the water that is being purified first passes through a filter unit to remove suspended solids, and then sent on to the reverse osmosis unit. In the unit the pressure is applied to water on one side of a semi-permeable membrane, forcing the water to diffuse through the membrane. The membranes will reject dissolved and residual suspended materials including monovalent salts. Since essentially all dissolved and suspended material, such as

minerals, salts and colloids, is rejected by the membrane, the permeate (liquid passing through the membrane) is usually pure water.

Reverse osmosis membranes are usually designed as cross-flow separation, where a feed stream is introduced into the membrane element under pressure and passed over the membrane surface in a controlled flow path. Retained solutes, such as particulate matter and concentrated dissolved salts, leave with the flowing process stream and do not accumulate on the membrane surface. The amount of salt and other impurities is often referred to as total dissolved solids, or TDS. The higher the TDS, the more feed pressure required.

The process is efficient at wide range of temperatures (0-85°C/32-185°F). This is an advantage when a low temperature treatment of heat-sensitive matter is necessary, thus these applications are widely used in food production. Most of the energy that is required is used to pump liquids through the membrane. The total amount of energy that is used is minor, compared to alternative techniques, such as evaporation.

Membrane Processes in Pulp and Paper Industry

The evaluation of membrane separation processes for possible application in pulp and paper industry dates back to early 1970's, however the growth of their applications was slow, largely due to economic reasons. Initial investigation was focused on mill effluent processing, and the membrane processes were evaluated for mill effluent color removal and reduction of COD and BOD levels before releasing.

The treatment of effluent from the alkaline extraction stage of a conventional kraft pulp mill with ultrafiltration reduced the color by 90%, COD by 80%, and BOD by 25-50%¹⁶. Effects on total mill effluent are 65-70% color reduction, 40% COD

reduction, and 10% BOD reduction. Comparable reductions were obtained in pilot trials (reductions of 85% and 75% in effluent color and COD respectively)¹⁷.

The other applications of membrane separation in effluent treatment were investigated, such as the use of microfiltration and ultrafiltration for treatment of acidic and alkaline bleaching effluents¹⁸, removal of chlorinated organic compounds (AOX) by ultrafiltration¹⁹.

Recently, a pulp mill in New Brunswick (Canada) implemented reverse osmosis technology as an alternative to conventional secondary effluent treatment facility. Using reverse osmosis, the pollution levels were lowered, however, the costs associated with the implementation of the technology were quite significantly higher compared to the conventional treatment facility²⁰.

Water treatment is another area of application of membrane processes. In the early 1980's, reverse osmosis was implemented as an alternative or supplement to ion exchange systems in water purification before use as boiler feed water²¹. Recently it has been reported that the reverse osmosis can offer economical advantages when used for treatment of makeup water for use as a boiler feed water in some mills⁸, depending on the quality of makeup water solid contents and other parameters.

The membrane separation technology was also evaluated for application in chemical recovery. Recovery of caustic from spent alkaline pulping and bleaching effluents using membrane and electrolytic acidification has been described and patented²².

While membrane separation processes may still be costly to implement compared to conventional techniques, there are other advantages associated with their application, i.e. superior performance in color removal from the effluent, or removal of the chemicals present in the effluents which even in very small amounts can have

detrimental effect to the environment. The constant development in membrane construction and manufacturing leads towards lowering the overall cost of the process, while increasing the separation performance and extending functional durability.

CHAPTER II

PROBLEM STATEMENT

Process Schematics, Objectives and Challenges

WMU has been given a Kimberly-Clark patent, US 5,858,021, and has proposed a project on development and commercialization of the patented technology. The patent, "Treatment Process for Cellulosic Fibers" describes a method to change the cellulose fiber morphology through the use of solution of caustic soda (sodium hydroxide) on high consistency pulp. The treated pulp demonstrated increased curl, and hence the sheet bulk and absorbency.

An important aspect of the overall economical feasibility of the technology is caustic recovery. The caustic recovery study consists of identifying and evaluating methods to recover and reuse the caustic used for the fiber treatment. The proposed areas of investigation were focused on evaluation of washing efficiency - removal of residual caustic from the pulp after treatment, and assessment of alternative methods that could be used for purifying and concentrating the resulting waste liquor.

The general schematics of the process and areas of proposed investigations are shown in Figure 3.

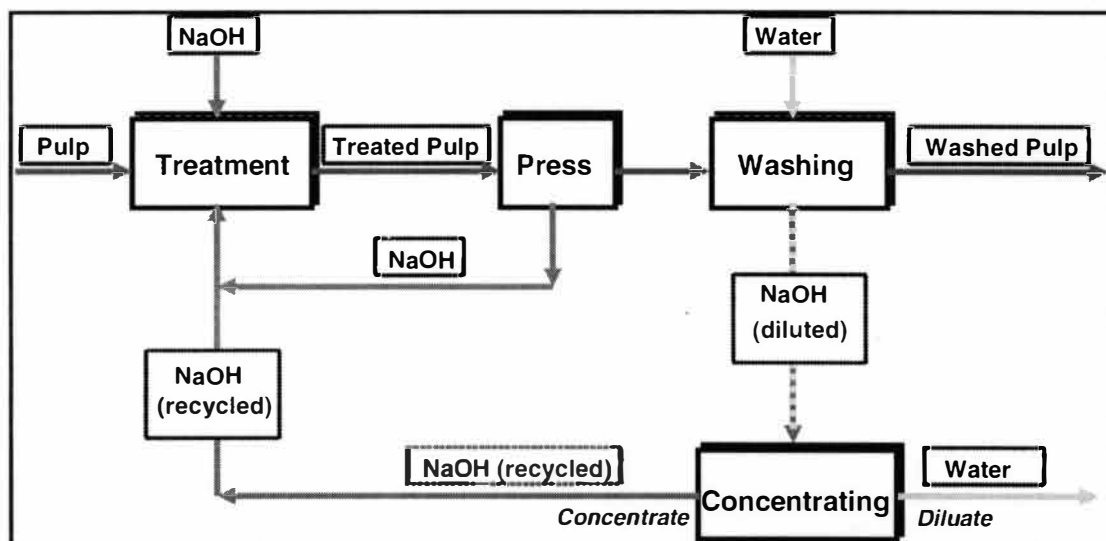


Figure 3. Overall schematics of pulp treatment with caustic

The intended uses of the treated pulp require that the pulp is of high purity (chemical free). Therefore, all of the chemicals, more specifically caustic retained in the pulp, must be removed prior to the further treatment. It is thus expected that in addition to a large quantity of fresh water that will be required to remove the caustic from the pulp, a large amount of diluted caustic will be generated. A proper processing of the diluted caustic solution is essential for overall economic viability of the process.

In order to properly design the actual caustic recovery experiment, the estimated flow rate values of generated diluted washing filtrate and its concentration are required. There are several commercially available computer programs designed to simulate pulp washing process (e.g. CADSIM). Using the computer simulation, the overall mass and sodium balances can be carried out. These simulations can provide all the necessary information, including amount of water required and a quantity of diluted caustic solution generated. This information is used for designing the

operating condition caustic recovery study.

Due to the amount of diluted caustic generated by the process, conventional techniques, such as evaporation, cannot be effectively and economically used for the caustic recovery. From several alternative techniques, membrane assisted processes appear to be most promising alternatives, and could be used for filtration and further concentration of the diluted caustic solution. Based on the nature of the generated filtrate (dissolved solids) reverse osmosis appears to be the most suitable candidate for caustic recovery after the pulp treatment.

In theory, reverse osmosis (RO), which is successfully used for processing solutions of sodium chloride (desalination) and producing pure water, should be capable of concentrating the solution of caustic soda. The RO membrane should reject all the dissolved caustic, allowing the water to penetrate through the membrane. By removing the water from the solution, the concentration of dissolved caustic soda in retentate (caustic solution) increases. However, there are differences that discriminate processing of these two chemicals. The main difference between diluted caustic solution and solution of sodium chloride is pH. Solutions of caustic soda (sodium hydroxide) are of high pH, compared to near neutral pH levels of sodium chloride. Therefore, the two main challenges associated with the processing of caustic soda (NaOH) solutions with reverse osmosis include high osmotic pressure and high pH of the solutions. The osmotic pressure, which needs to be exceeded in order to facilitate the separation, increases with the concentration of processed solution. Osmotic pressure approximation can be calculated using the following equation:

$$\pi = \frac{n}{V_m} RT$$

where n is number of mol of solute (salt), V_m is volume of pure solvent, R is

the gas law constant and T is temperature in K.

Calculated osmotic pressure estimates for the NaOH solutions of different concentrations at 20°C are shown in Figure 4.

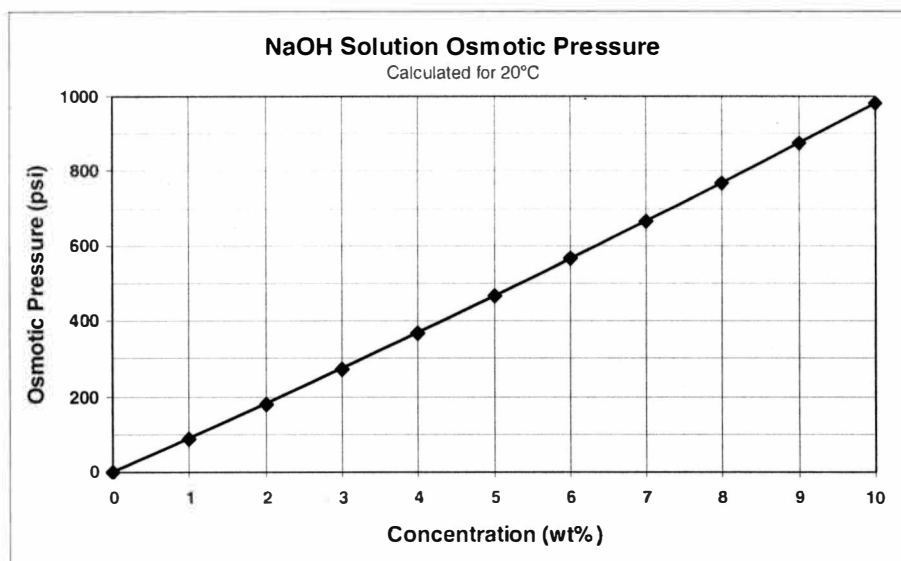


Figure 4. Osmotic pressure estimated values of NaOH solutions at 20°C

To process the solution of concentration greater than 10% (weight) would require pressure higher than 1000 psi. This would create significant cost increases due to the higher energy requirement for pressure generation and cost of equipment capable of withstanding such pressure levels. In addition, high pressure application may increase safety concerns.

The high pH of the NaOH solution is another possible hindrance of a successful application. The pH values of all the solutions used in this experiment are shown in Figure 5.

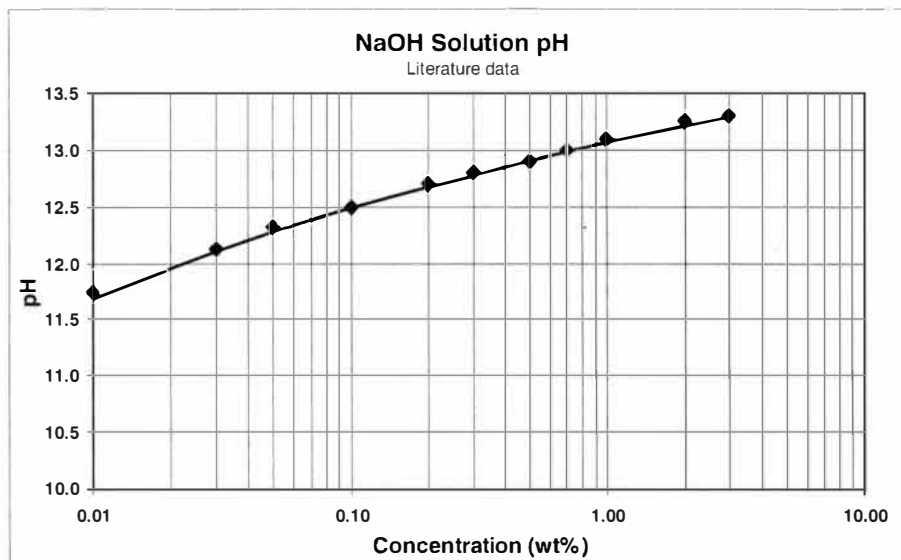


Figure 5. Correlation between pH and concentration for NaOH solutions²³

At a concentration as low as 0.02% the solution has a pH value higher than 12, which is higher than the recommended operating range of most commercial membranes.

Recently developed membranes that can operate in a wide range of pH (up to pH of 14) are commercially available. However, their industrial application in processing solutions of sodium hydroxide has not yet been reported.

After an extensive search of the available commercial membranes, AFC99 membrane (by PCI Membrane Systems) was selected as the most suitable candidate for the experiment. The AFC99 reverse osmosis membrane is designed for a variety of applications. Despite the relatively wide operating pH range (1.5-12), the application of this membrane for NaOH concentration has not yet been reported. The effect of continuous exposure of high strength caustic solution on membrane

performance is not known; however a solution of NaOH is commonly used for cleaning the membrane. In dairy applications, the membrane is cleaned on a daily basis with 0.2% NaOH solution concentration for approximately 40 minutes. Therefore, the membrane should be able to withstand exposure to the caustic for an extended period of time, making this membrane suitable for this trial.

While membrane can operate at high pH, it can be expected that the ability of selective separation may deteriorate with time. The longevity of the membrane will have a significant impact on overall economical balance of the process.

In order to assess the feasibility of reverse osmosis application in caustic solution recovery, there are several parameters which need to be evaluated. The concentration of the diluted caustic will determine the pressure levels needed for separation. The value of osmotic pressure of the solution is concentration dependent. Thus the maximum pressure that can be generated by the available laboratory equipment will determine the highest possible concentration that can be reached after separation.

The main objective of this investigation is to evaluate the concept of using reverse osmosis for recovery of caustic from filtrates generated by washing of the caustic treated pulp. This will be achieved by assessing membrane separation effectiveness (selectivity) and productivity (flux) measured at different levels of caustic solution concentration. Both the parameters are membrane specific. In addition, initial testing of the membrane longevity in retaining both separation selectivity and productivity will be evaluated.

CHAPTER III

EXPERIMENTAL DESIGN AND METHODOLOGY

Computer Simulations

Using computer simulation software (CADSIM Plus Dynamic Process Simulator by Aurel Systems Inc), proper overall material balances of important components involved in the process were established. The main information retrieved from this simulation included quantity and concentration of generated diluted sodium hydroxide during the effective removal of sodium hydroxide by washing.

Membrane Processes in Pulp and Paper Industry

The test solutions were prepared by dissolving calculated amounts of NaOH pellets in deionized water. For each experiment, 50 liters (l) of solution were prepared and used.

The Reverse Osmosis unit consisted of an 100 l plastic feed tank, a recirculation pump capable of generating desirable flow and fluid pressure, a pressure control valve and a Micro 240 stainless steel module housing a membrane. AFC99 thin film polyamide composite membranes provided by PCI Membrane Systems were used in the experiments. This membrane is normally used in the pH range 1.5 to 12 at operating pressures up to 940 psi, with reported rejection of NaCl higher than 99%. The picture of reverse osmosis unit set up is shown in Figure 6.

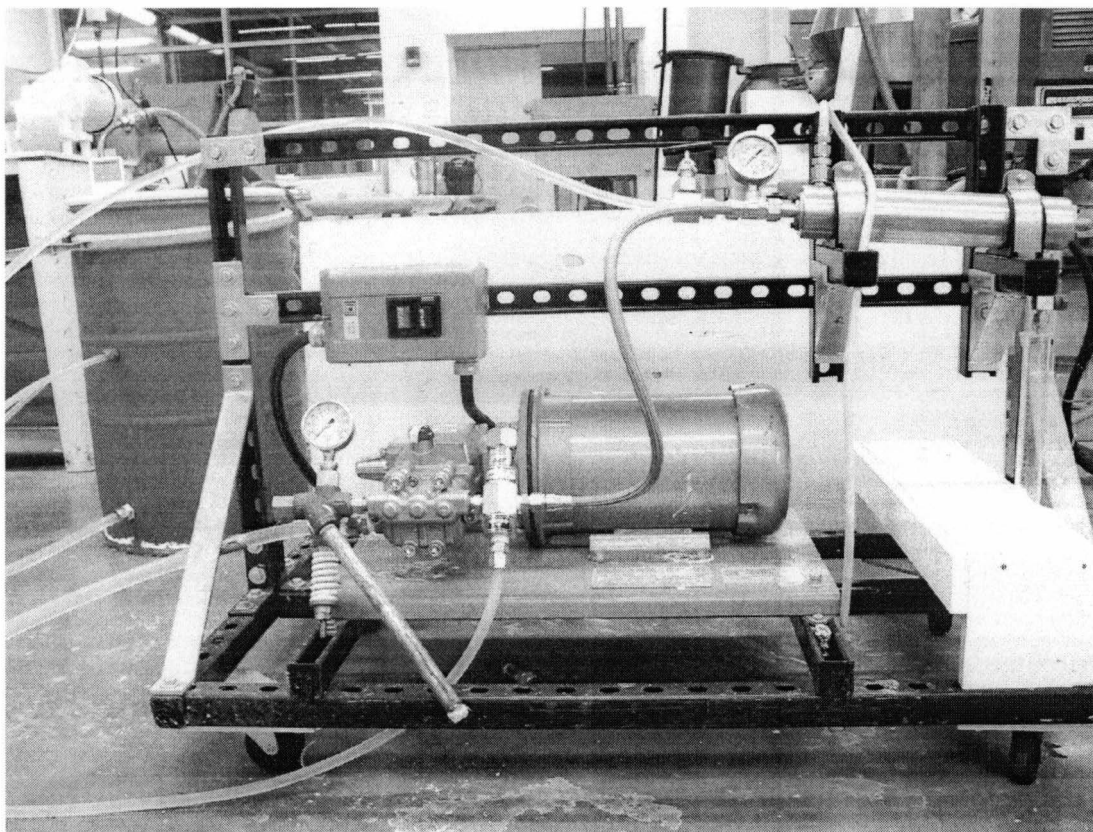


Figure 6. Reverse osmosis unit set up

The initial testing runs were carried out at constant 800 psi pressure. Transmembrane pressure was controlled by the pressure control valve located just after the membrane housing. The concentrate flow was kept constant at 19 l/min (5gpm). At the start of each experiment, the valve was fully opened and the deionized water was circulated throughout the RO system for additional membrane conditioning. After 20 minutes, a concentrated solution of NaOH was added to the feed tank in amount to reach the desired concentration of the feed solution. Using the valve after the membrane housing, the pressure was adjusted to 800 psi. The temperature of the feed solution was controlled by a coiled copper tube with circulating cold water placed in the feed tank.

There were two configurations of the RO unit implemented in this testing. When the effect of concentration on membrane performance was studied, the permeate (filtrate) was discarded after analysis. For the membrane performance over time study, both permeate and concentrate were circulated back to the feed tank and mixed. Once the operating pressure was stabilized, the samples of permeate were collected and flow rate and feed temperature were recorded. The samples were collected at 30 or 60 minutes intervals and the pH and NaOH concentrations were measured. The NaOH concentration was analyzed by an acid-base titration method with 0.1/0.01N HCl standard solution with phenolphthalein as indicator. The concentration and pH of feed solution was measured periodically.

After completing and evaluating the measured data of the initial testing, a second round of testing was carried out. Due to the significant impact of temperature on membrane performance, a better temperature control of the feed solution was incorporated. This was achieved by installing an inline thermometer which provided continuous actual temperature reading, allowing for faster response to temperature increase by adjusting cooling water flow and thus keeping the constant temperature. The second round of testing was carried out at constant temperature of 24°C, and two different transmembrane pressure levels (600 and 800 psi).

Another modification to the process was gradual increase of the feed solution concentration. After stabilizing the system at given feed solution concentration, multiple flow rate and concentration measurements were carried out. Then the concentration of the feed solution was increased by addition of calculated volume of concentrated NaOH solution to the feed tank. After additional stabilizing period (30-40 minutes) the flow rate and NaOH concentration measurements (feed and permeate) were carried out.

CHAPTER IV

RESULTS AND DISCUSSION

Initial Computer Simulation

The data from the study of actual caustic treatment of the pulp and its optimization were used for computer simulation in order to estimate concentration of diluted caustic soda solution after washing of the treated pulp. The simulation was carried out for treatment of 100 tons per day. The treatment conditions of 15% consistency and using 15% of NaOH on o.d. fiber were used in the simulation. The estimated concentration of NaOH in washing filtrate was 0.94%. The results of initial simulation are shown in Table 2. Detailed process simulation is shown in Appendix.

Table 2. Results of initial process simulation

Stream Variable	Unit	Simulated Values	
		Feed	Washing Filtrate
WATER	kg/s	1.042	35.944
FIBER	kg/s	1.042	0.000
NaOH	kg/s	0.000	0.344
VOLUMETRIC_FLOW	l/s	1.735	36.537
AIR_DRY_TONNAGE	t/d	100.000	0.035
DISS_SOL_CONC	%	0.000	0.950

The simulation of the alkaline treatment of the pulp using CADSIM software showed that adequate washing of the treated pulp will generate the washing filtrate of approximately 1% (weight) NaOH concentration. For treatment of 100 t/day of pulp,

the estimated flow rate of generated filtrate is 131,500 l/h (36.5 l/s). Therefore the 1% caustic concentration was used in the first round of experiments.

First Round of Reverse Osmosis Testing

Effect of Concentration on Membrane Performance

The concentration of the feed solutions increases as the portion of water passes through the RO membrane while dissolved matter remains in the feed solution. It has been previously reported that during the regeneration of diluted dairy caustic washing solutions, a fraction of the dissolved NaOH passed through the RO membrane²⁴. The first round of experiment was carried out to determine the ability of the membrane to concentrate the solution of NaOH and determine the separation efficiency of the tested membrane.

The pressure at which the experiments were carried out was selected to be 800 psi. This pressure level is higher than the osmotic pressure of 1% NaOH solution, which is around 180 psi, but lower than the upper limit of the pump and the RO unit (~900 psi). It is well documented that the pressure has a significant impact of membrane performance. In this study, in order to evaluate the effect of other parameters on the membrane characteristic, the pressure was kept constant for all experiments described in this paper.

For this evaluation, 50 liters of 1% solution of NaOH were used. The feed flow rate was 19 l/min. Once the membrane was conditioned and the system stabilized, the samples of permeate were collected. Initially, every 30 minutes a sample of permeate was collected and the flow rate of the permeate was measured. The permeate was collected in separate container and discarded after analysis. By removing the permeate, the overall volume of the feed solution slightly decreased.

Total run time of this experiment was 13 hours. The pH levels of filtrates collected were between 12.7 and 13.2. This indicated that a portion of dissolved NaOH passed through the membrane. This was confirmed by the NaOH concentration measurement. The permeate concentration increased from 0.15% to 0.32%. The second experiment was designed to simulate secondary RO treatment of permeate from initial separation, thus the feed solution concentration was 0.22%. Run time was 7 hours. Finally, in order to generate a proper permeate to feed concentration ratio, a third experiment was carried out with feed starting concentration of 0.8%. For each experiment, a new set of membranes was used. The summary of the experiments is shown in Table 3.

Table 3. Measured initial and final pH and concentration values

Run time [hrs]	Concentration [wt%]		pH	
	Feed	Permeate	Feed	Permeate
0.5	1.00	0.148	13.6	12.7
13	1.58	0.320	13.7	13.2
0.5	0.77	0.092	13.6	12.6
9	1.15	0.160	13.8	13.1
0.5	0.22	0.012	12.8	11.2
7	0.31	0.017	13.1	11.5

All pH values measured for feed and permeate solutions are shown in Figure 7. Literature correlation is included for reference.

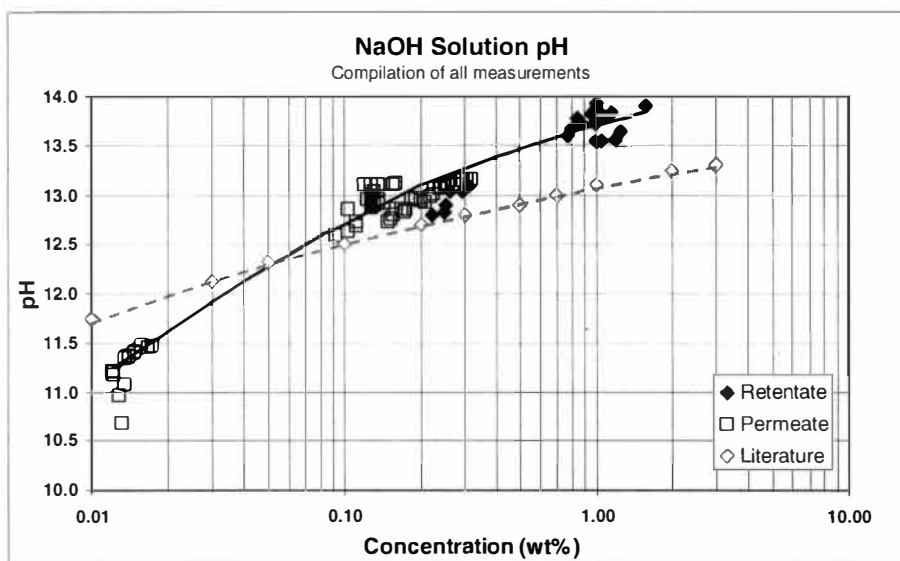


Figure 7. Correlation between measured pH and concentration values

Compared to the literature data²³, the measured values showed lower pH values at very low concentration levels; however a more pronounced increase in pH values with concentration was observed. This could be due to the fact that after passing through the membrane the water did not have any buffering capacity for the caustic present.

All measured concentration values and generated correlation between feed and permeate concentrations are shown in Figure 8.

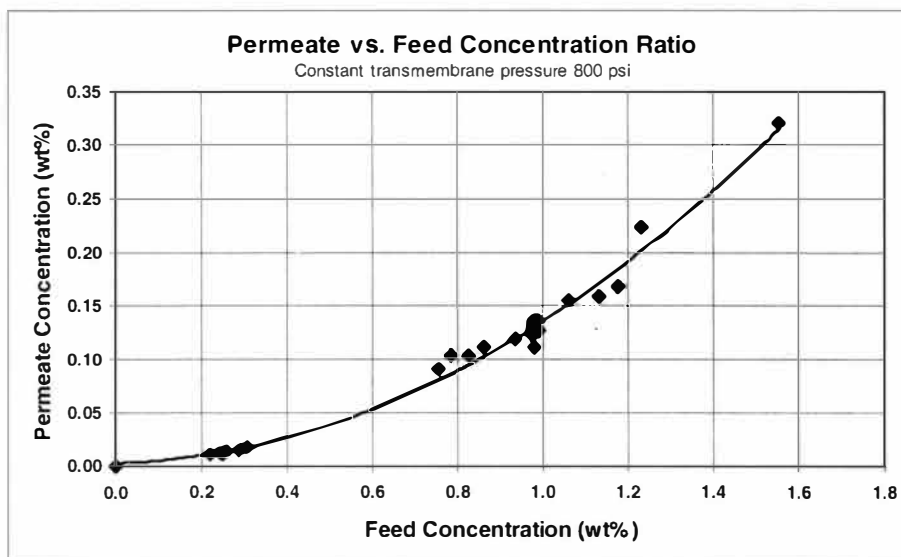


Figure 8. Correlation between feed and permeate concentrations

The values from all three experiments correlated well. The correlation shows increased permeability of dissolved NaOH with increased feed concentration. This increase is more pronounced at higher feed concentrations. At 0.2% feed concentration, the solute passage (ratio between solute concentration in permeate to feed solute concentration) is approximately 5%, while at 1.5% feed solution concentration this value increases to 19%.

In membrane separation processes, salt rejection (calculated as 100% minus solute passage value) is a standard parameter describing membrane separation characteristics based on permeability of the solute through the membrane at different feed concentrations. The correlation between salt rejection and feed concentration is shown in Figure 9.

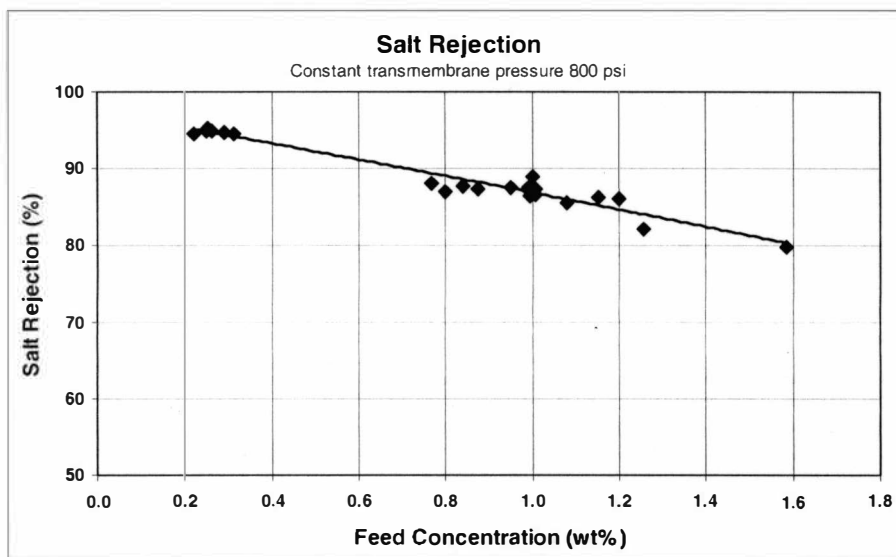


Figure 9. Correlation between salt rejection and feed concentration

The correlation clearly demonstrates the decrease of membrane separation efficiency with increasing feed solution concentration. At 0.2% feed solution concentration the salt rejection is greater than 95%. With increasing feed concentration this values decreases significantly, and at 1.6% feed concentration the salt rejection is only 80%.

In addition to the higher concentration of the feed, the increase in permeate concentration is caused by the increase in the feed osmotic pressure. As a result, the water flux through the membrane decreases, and thus concentration in the permeate increases²⁵.

The salt rejection is a parameter describing the separation efficiency of the membrane for specific salt and conditions. The most common and important parameter describing the overall performance of the membrane is flux. In general, the flux describes the flow of liquid through the membrane per unit area. The flux depends on several parameters, including transmembrane pressure differential, salt

concentration and, consequently, the osmotic pressure of the solution, and temperature. This parameter is important for designing the membrane separation unit so that it can handle the required amounts of solutions to be processed.

Because of the variables affecting the membrane flux, in this study the initial values of the membrane flux for the range of concentration tested were intended to be measured at constant pressure and temperature. However, due to inconsistency in cooling water temperature between the days of testing, the temperature of the feed solution varied between 25°C and 30°C. Since the flux is influenced by the temperature, the measured values were sorted by the temperature at which they were measured. The values were divided into two groups representing the temperature intervals of 25 to 27°C and 27 to 30°C. The membrane flux values measured for different feed concentrations at 800 psi pressure are shown in Figure 10.

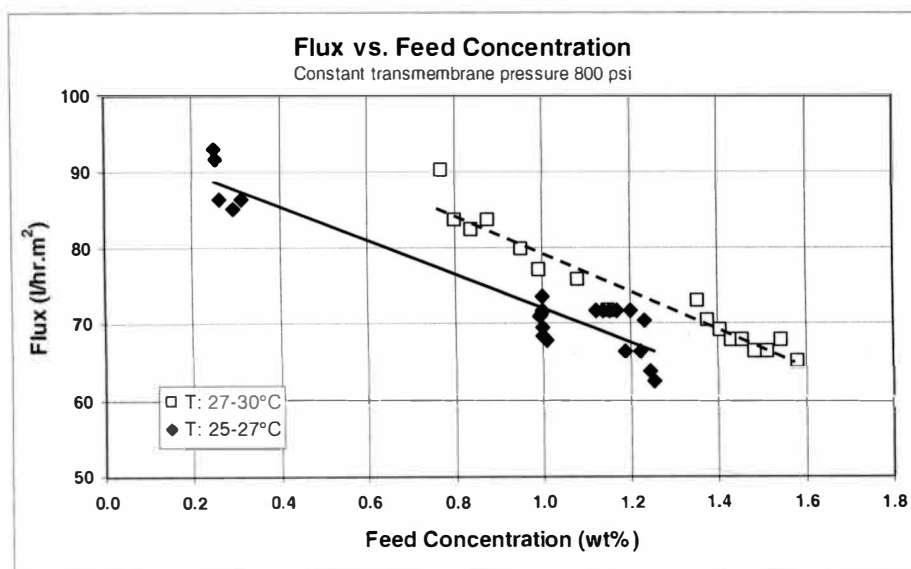


Figure 10. Correlation between membrane flux and feed concentration

Despite the variation in the measured values due to temperature variation and limited amount of measurements covering the whole investigated range, the correlation clearly demonstrates the effect of concentration on overall membrane performance. Since the osmotic pressure is a function of concentration of salt, as salt concentration increases, so does the osmotic pressure. Osmotic pressure increases from 35 psi at 0.2% concentration to 214 psi at 1.2%. Because the feed pressure is constant, the pressure differential, which is a driving force of the separation, decreases with the feed concentration increase. The flux decreased from 90 l/hr.m^2 at 0.2% feed consistency to approximately 70 l/hr.m^2 at 1% feed concentration. By separating the measured values by the feed temperature at the time of measurement, the effect of the temperature can be clearly observed. On average, a temperature increase of 2°C can increase the flux by close to 10 l/hr.m^2 .

Effect of Temperature on Membrane Performance and Membrane Longevity Testing

The longevity of the membrane will have a significant impact on overall economical balance of the process. The membrane performance is affected by various factors. In order to investigate performance of the membrane over time, all the conditions had to be constant. In this experiment, the RO unit was closed. After the separation, the permeate was circulated back to the feed tank and mixed to guarantee the constant feed concentration. In addition, to minimize the concentration change, the total volume of feed solution was increased to 80 liters. The feed concentration was 1% NaOH. The pressure was kept constant at 800 psi.

Due to the above mentioned issues with cooling of the feed solution, the effect of temperature on membrane performance was investigated. At the beginning of the trial, a new membrane was installed. The membrane was operated for several hours

for conditioning and for the unit to stabilize. Then the temperature of the feed solution was lowered to approximately 23.5°C by increasing flow in the cooling coil. Once the temperature was stabilized, several flow rate measurements were carried out. Then the cooling water flow was reduced, and the procedure was repeated for other temperature levels. The temperature range of 23.5°C to 33°C was investigated and the correlation is shown in Figure 11.

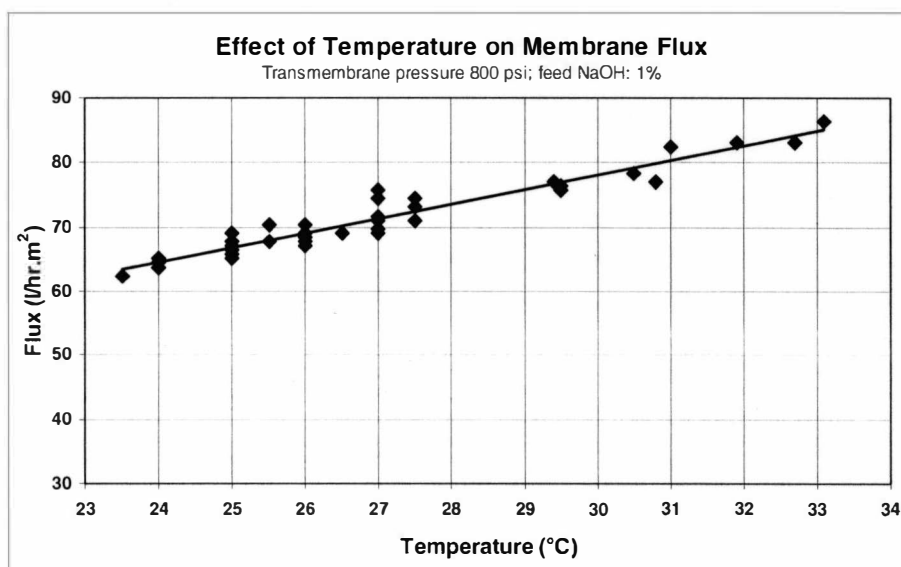


Figure 11. Effect of temperature on membrane flux

As expected, the effect of temperature on membrane performance is significant. In the covered range, the flux increased from 60 l/hr.m² at 23°C to 85 l/hr.m² at 33°C. This correlation was used in flux calculations to compensate for temperature variation in the membrane longevity study.

The investigation of membrane performance over time was carried out in the same manner as the testing of the temperature effect on the membrane performance. The permeate was circulated back to the feed tank; the volume of feed solution was

80 liters. The feed concentration was 1% NaOH and pressure 800 psi. The temperature was kept in the 25-27°C range. The testing was carried out in increments of 9, 8, 8, 8, 11, and 8 hours for a total of 52 hours of running over a period of 7 days. Every hour a flow rate and concentration of the permeate were measured. The concentration of feed solution was checked at the beginning, in the middle, and at the end of testing for every day of the running. The measured flux values are shown in Figure 12.

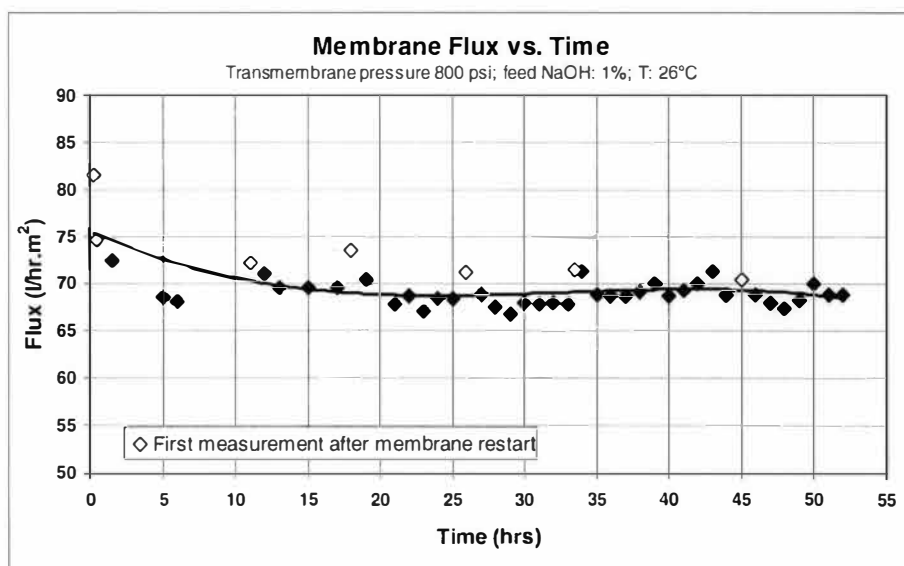


Figure 12. Membrane performance - flux - over the running period of 52 hours

After an initial high flux, the flux stabilized at around 67 l/hr.m² after 3 hours of running. An increase in the membrane flux was observed every time the unit was restarted, despite reconditioning (RO unit running without pressure and then pressurized for at least 10 and 30 minutes respectively) of the membrane before sampling. The values measured after the membrane restarts are shown in the Figure 7 as white points.

Overall, it can be concluded that for the period of 52 hours of running, the membrane retained its performance. In addition to the running time, the membrane was exposed to a solution of NaOH for a total of over 7 days without affecting its performance. The separation ability of the membrane was monitored during the testing, and the separation efficiency of the membrane expressed as salt rejection values are shown in Figure 13.

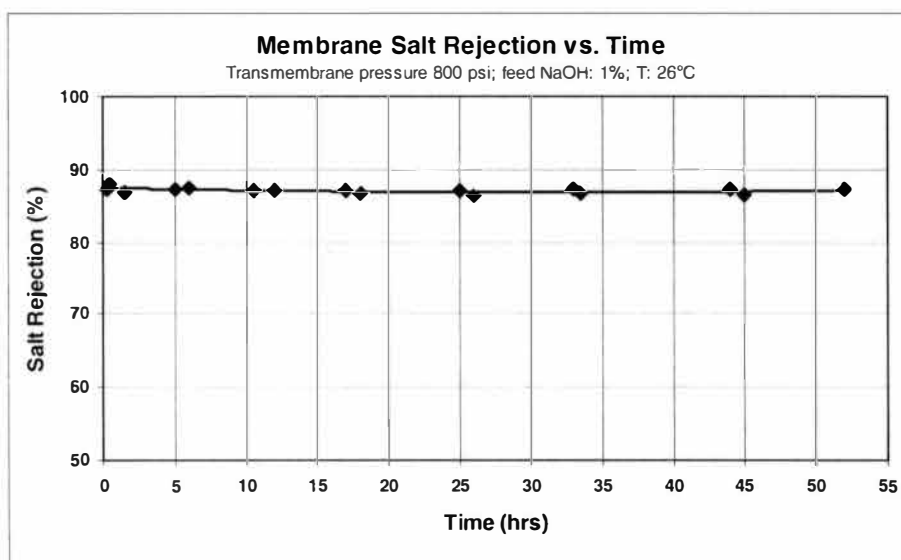


Figure 13. Salt rejection values measured over the period of 52 hours running

After 52 hours of running time and total of over 7 days of constant exposure to the NaOH solution, the membrane retained its separation efficiency. The flux variation observed after the restarts of the membrane had no effect on membrane salt rejection.

Second of Reverse Osmosis Testing

Effect of Transmembrane Pressure on Overall Membrane Performance

The initial round of experiments clearly demonstrated the effect of temperature on the membrane functioning. In order to properly evaluate the membrane performance characteristics, a better temperature control was necessary. That was achieved by installing an inline thermometer which provided continuous actual temperature reading, allowing for faster response to temperature increase by adjusting cooling water flow and thus keeping the constant temperature. The second round of testing was carried out at constant temperature of 24°C.

In order to shorten the data collection time between different concentration levels, another modification to the experiment was implemented. The concentration of feed solution was gradually increased by addition of concentrated NaOH solution to the feed tank as opposed to increasing the concentration by permeate removal only. After each concentration increase the system was allowed to stabilize and then multiple flow rate and concentration measurements were carried out. The measurements were carried out at 600 psi and 800 psi pressure levels. The permeate vs. feed concentration correlations for both pressure levels is shown in Figure 14.

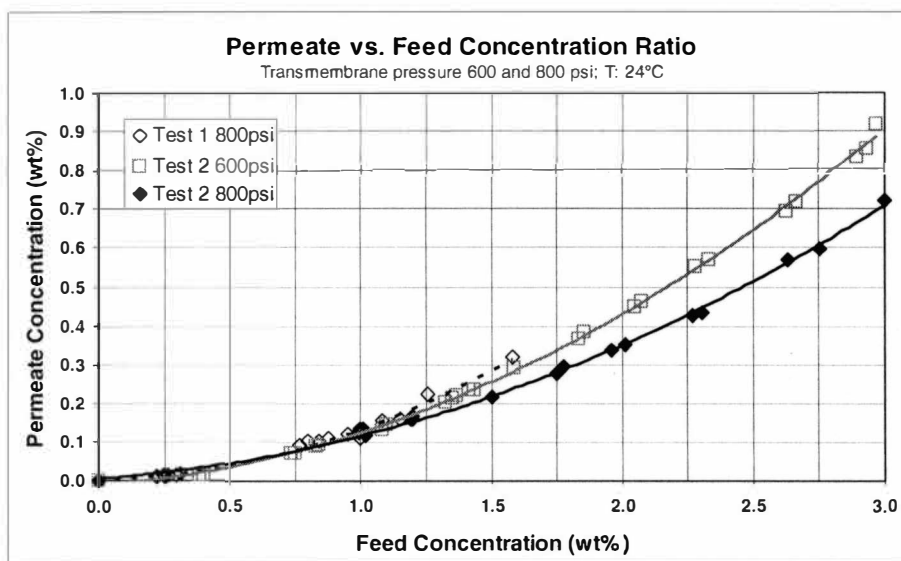


Figure 14. Feed and permeate concentrations correlation for different pressures

The values generated in this testing correlated well with the data obtained in first trial. At lower concentration levels the difference in transmembrane pressure does not have an effect on membrane separation performance. The concentration correlations were identical up to 1.2% feed concentration. At higher feed concentration the membrane separation efficiency starts to differ, and appears to be better for the higher transmembrane pressure applied. At 3% feed concentration, the permeate concentration was 0.9% at 600 psi pressure testing, while at 800 psi testing this value was 0.7%.

The comparison between first and second testing showed that for the concentration interval tested the correlation generated in the initial experiment at 800 psi agreed with the correlation generated for 600 psi pressure in the second trial. However, due to the differences in experimental design, there were only two available data points measured above 1.2% feed concentration for the initial testing correlation.

The comparison of membrane salt rejection for both pressure levels tested at

different feed concentration is shown in Figure 15.

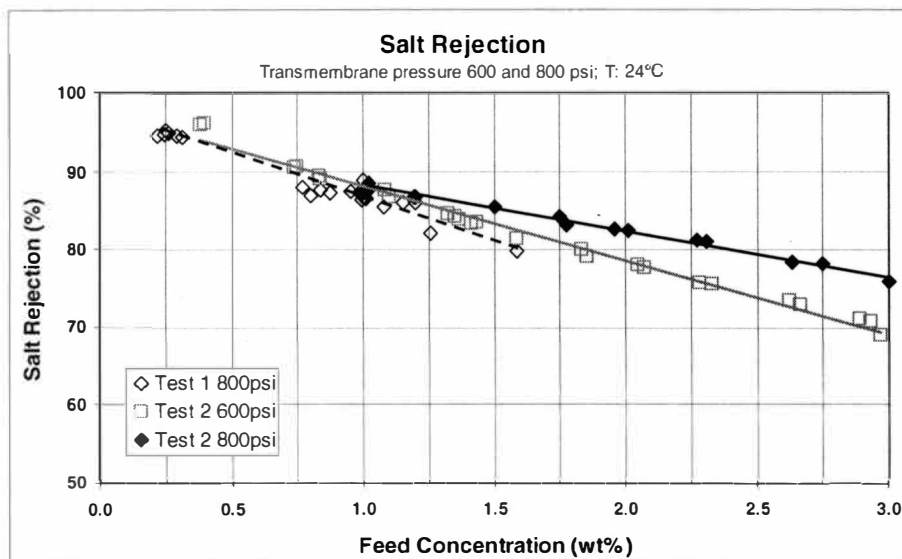


Figure 15. Salt rejection vs. feed concentration for different transmembrane pressure

The comparison confirmed that at higher feed concentrations the separation efficiency increases with the increasing transmembrane pressure. This is due to greater increase in solvent (water) passage through the membrane compared to the solute (NaOH) transfer by diffusion¹⁵.

The membrane performance - flux - is directly proportional to pressure differential between solution osmotic pressure and applied transmembrane pressure. The comparison of flux measured at 600 and 800 psi transmembrane pressure at different feed concentrations is shown in Figure 16.

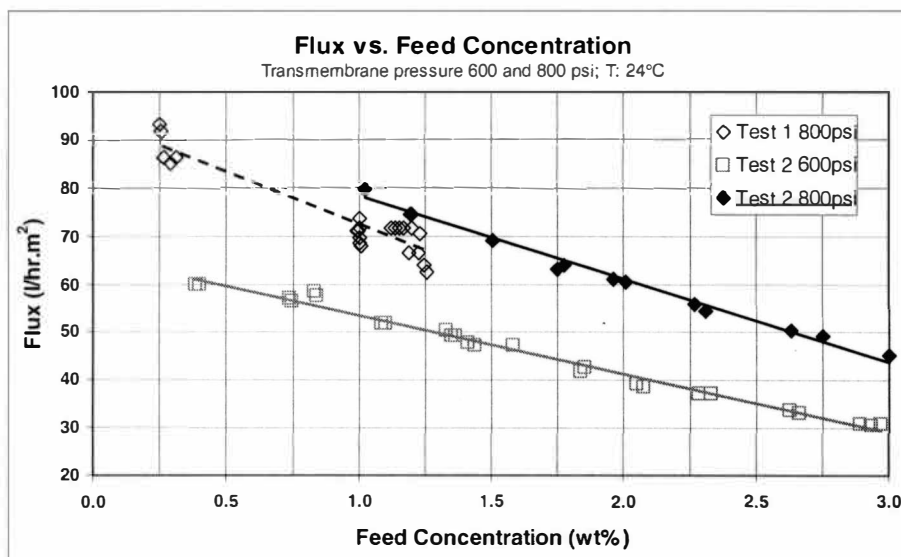


Figure 16. Measured flux at different feed concentration and different pressure

As expected, the higher transmembrane pressure resulted in higher flux. At 1% feed concentration, the difference was 25 l/hr.m² (80 vs. 55 l/hr.m²). This difference decreases with the increasing feed concentration, and at 3% feed concentration the difference was 15 l/hr.m² (45 vs. 30 l/hr.m²). The flux values measured in the first trial were slightly lower compared to values measured in the second trial at the same pressure (~8 l/hr/m² at 1% feed concentration).

Overall, the flux of the membrane decreases by approximately 45% in 1% - 3% feed concentration range (80 to 45 l/hr.m² at 800 psi and 55 to 30 l/hr.m² at 600 psi).

The decrease in membrane flux is caused mainly by decrease in pressure differential, which is the driving force of the separation. At constant applied pressure, increasing feed concentration and resulting higher osmotic pressure lowers the pressure differential. Pressure differential (PD) is calculated using following equation:

$$PD = (\Delta P - \Delta \pi) = (P_1 - P_2) - (\pi_1 - \pi_2)$$

where P is hydrostatic pressure applied on feed (P_1) and permeate (P_2), and π is osmotic pressure of feed π_1 and permeate π_2 . The flux value for both pressure levels were plotted against calculated pressure differential. The pressure differential values were calculated using osmotic pressure estimates (both feed and permeate) calculated from the correlation shown in Figure 4. The correlation is shown in Figure 17.

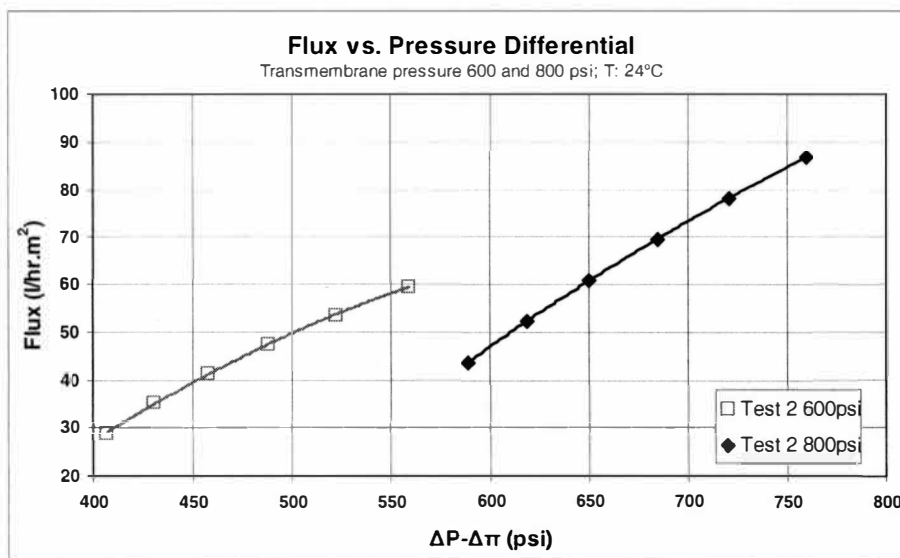


Figure 17. Flux vs. pressure differential for and different transmembrane pressure

The comparison of measured flux vs. pressure difference correlations showed that the values flux measured at different applied pressures did not correlate well, indicating that there might be other factors affecting the membrane flux in addition to pressure difference.

Effect of Temperature on Membrane Performance

The temperature has a pronounced effect on membrane performance. After

initial testing of the effect of temperature on membrane flux, additional testing was included in the second trial. Because of better temperature control and more precise measurement, a wider range of temperatures was covered. The results of the testing are shown in Figure 18.

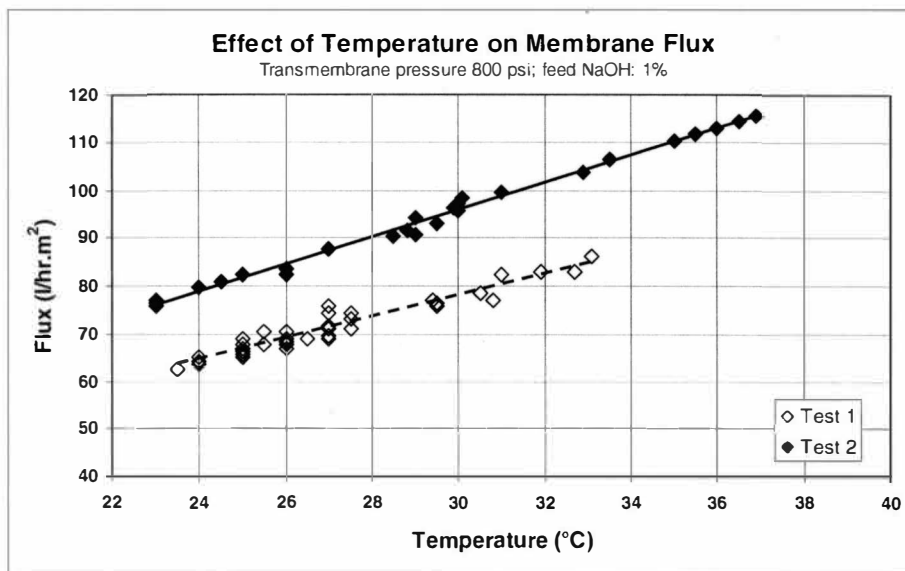


Figure 18. Effect of temperature on membrane flux

The measurement confirmed the difference in flux observed between initial testing and this evaluation. The flux measured was higher by 15 - 20 l/hr.m² in the temperature interval tested. In both cases the effect of temperature on membrane flux was evident. The flux increased from 75 l/hr.m² at 23°C to 115 l/hr.m² at 38°C. The flux increase with temperature is a result of decrease of solvent viscosity¹⁵.

The temperature has a positive effect on membrane flux; however this increase may be compromised by the decrease in membrane separation efficiency and thus lower product quality¹⁵. The efficiency of membrane separation was assessed by measuring the NaOH concentration in permeates collected for test runs at different

feed temperatures. The results are shown in Figure 19.

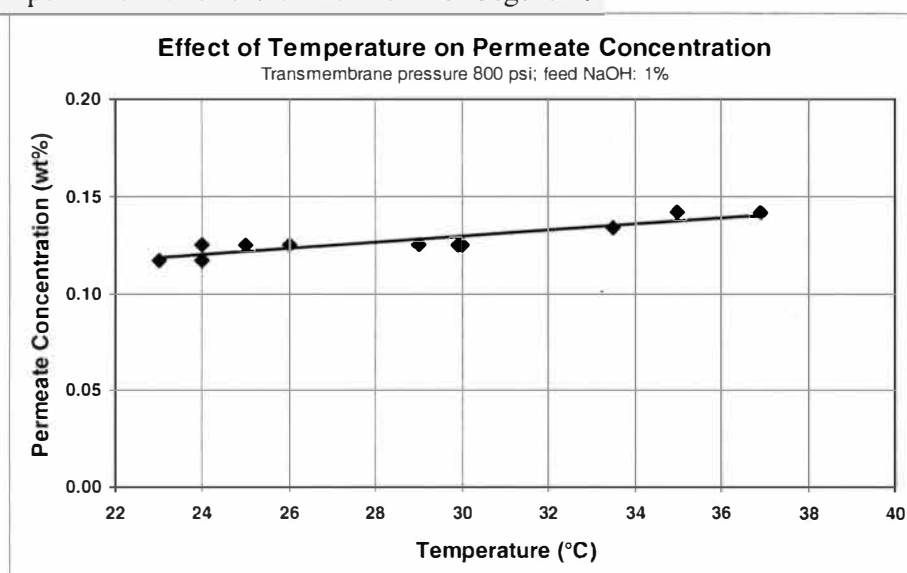


Figure 19. Effect of temperature on membrane separation efficiency

In the temperature range testing the concentration of NaOH in the permeate increased from 0.12% at 23°C to 0.14% at 38°C.

Membrane Longevity Testing

The final part of this evaluation included a performance comparison of new membranes to the performance of the membranes run and being exposed to the solution of NaOH for extended periods of time. In the initial evaluation, the membrane retained its performance characteristics during the period of 52 hours of running and total of 7 day of continuous exposure to NaOH solution. In this testing, a new membrane were installed and run for 12 hours. Then the unit was shut down (with membrane casing filled with the solution of NaOH to prevent membrane drying) for period of 45 days. After this period the unit was started, flushed with freshly prepared solutions of NaOH. After the stabilizing of the system, the membrane

separation efficiency (salt rejection) testing was carried out. The measured values were compared with data obtained previously.

The performance comparison of new and NaOH exposed membranes is shown in Figure 20.

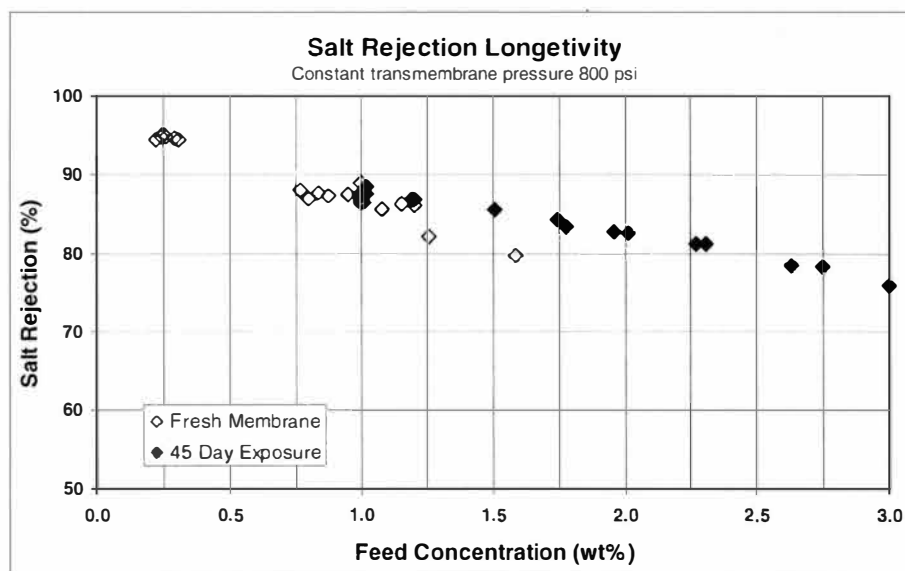


Figure 20. Salt rejection comparison of new and exposed membranes

The comparison showed that after 12 hours running and 45 days exposure to the NaOH solution, the membrane separation efficiency was not affected. The salt rejection values in the 1.0-1.2% range were similar. Except for the two data points measured for new membranes (1.2% and 1.7% feed concentration), all the other the salt rejection values compared well.

CHAPTER V

CONCLUSIONS

Initial investigation of reverse osmosis for caustic recovery demonstrated that the process is capable of concentrating the diluted solution of NaOH. The membrane tested showed no deterioration in performance over the period of testing - in excess of 50 hours of running.

The membrane retained its separation and performance characteristics after continuous exposure to NaOH solution for period of 45 days.

The flux values measured for 1% solution of NaOH at 800 psi transmembrane pressure and an average temperature of 26°C is around 70 l/hr.m², with over 85% salt rejection. In the second round of testing at similar conditions the flux was measured at 80 l/hr.m².

The effect of temperature and feed solution concentration on membrane performance and separation characteristics were clearly demonstrated.

The testing at different pressure levels (600 and 800 psi) showed that at lower concentration levels the difference in transmembrane pressure does not have an effect on membrane separation performance. The concentration correlations were identical up to 1.2% feed concentration. At higher feed concentration the membrane separation efficiency starts to differ, and appears to be better for the higher transmembrane pressure applied. At 3% feed concentration, the permeate concentration was 0.9% at 600 psi pressure testing, while at 800psi testing this value was 0.7%.

The comparison of salt rejection measured for both transmembrane pressure levels confirmed that at higher feed concentrations the separation efficiency increases

with the increasing transmembrane pressure.

The higher transmembrane pressure had a positive effect on membrane flux. At 1% feed concentration, the difference between 800 and 600 psi pressure was 25 l/hr.m² (80 and 55 l/hr.m² respectively). This difference decreases with the increasing feed concentration, and at 3% feed concentration the difference was 15 l/hr.m² (45 vs. 30 l/hr.m²). The flux values measured in the first trial were slightly lower compared to values measured in the second trial at the same pressure (~8 l/hr/m² at 1% feed concentration).

Overall, the flux of the membrane decreases by approximately 45% in 1% - 3% feed concentration range (80 to 45 l/hr.m² at 800 psi and 55 to 30 l/hr.m² at 600 psi).

This testing was designed to obtain initial values for better understanding of the process and to investigate the feasibility of reverse osmosis application for diluted NaOH solution processing. Subsequent investigations should include optimizing the reverse osmosis separation process in order to find the optimal combination of pressure and temperature to achieve maximum membrane performance without compromising its separation characteristics. The longevity limit of the membrane is another important parameter which has to be determined. This is necessary for overall economical balance of the separation process. Once all the optimal parameters are determined, process modeling and comparison with the other concentrating/recovery processes can be carried out and overall economical feasibility can be determined.

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APPENDIX

Results of initial process simulation

